AP - 011

STAGE 1 & 2 REPORTS

DATE: Nov. 10, 2003

Southern U.S. Business Unit
Domestic Production

Marathon Oil Company

P.O. Box 552
Midland, TX 79702-0552
Telephone 915/682-1626

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NOV 14 2003

Oil Conservation Division
Environmental Bureau

November 10, 2003

Mr. William C. Olson
Hydrologist
Environmental Bureau
Oil Conservation Division
1220 South St, Francis Drive
Santa Fe, New Mexico 87505

RE: OCD Reference Material Request by letter dated October 22, 2003
State 2 Abatement Plan
Bertha Barber Tank Battery
Ground Water Abatement Plan (AP-11)

Dear Mr. Olson,

Please find enclosed copies of reference materials you requested. As you pointed out in the above referenced letter 3 of the 10 reference materials were submitted to you in August, 2003. The remaining 7 reference materials are attached with this letter.

Please call me at (432) 687-8138 if you need additional information.

Sincerely,

Vijay Kurki

Vijay K. Kurki, P.E.
Advanced HES Professional

Attachments

cc: Mr. Chris Williams, OCD Hobbs District Supervisor w/attachments
Mr. Joe Sologub Jr, w/o attachments

NM-BBTB-E700-001-4

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Ref #6

H I L G A R D I A

A Journal of Agricultural Science Published by the California Agricultural Experiment Station

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PHYTOTOXICITY OF HYDROCARBONS[1]

H. B. CURRIER and S. A. PEOPLES[2]

INTRODUCTION

HYDROCARBON OILS are employed in the control of weeds, where the aim is complete elimination. They are used not only as toxicants, but also as carriers and cosolvents for other herbicides. On the other hand, oils find various horticultural applications—as carriers of insecticides and fungicides, for example—where it is important to minimize injury to the plant while providing adequate control of pests. To better accomplish these aims it is important to study the physiological effects of pure hydrocarbons on various plant functions, especially those processes involved in injury and death.

There is no agreement as to the mechanism of oil injury to plants. Literature reviews may be found in several publications (Crafts and Reiber, 1948; Minshall and Helson, 1949; Havis, 1950; Currier, 1951; Dallyn and Sweet, 1951).

There is evidence that hydrocarbons exert a solvent action on the external plasma membrane, the ectoplast, with resulting disorganization, increase of permeability, and leakage of cell sap into the intercellular spaces. This view was supported after studying the response of plants exposed to hydrocarbon vapors (Currier, 1951). That the plasma membrane is the critical structure in susceptibility and tolerance to oils is also the view of Dallyn and Sweet (1951), who arrived at this conclusion by use of quite different methods. The idea of "protoplasmic resistance" as a basis of selectivity of oils, as suggested by Crafts and Reiber (1948), has in general been substantiated by the more recent studies. However, it seems to be true that after oil is found within a cell severe injury or death invariably results (Dallyn and Sweet, 1951). This further stresses the importance of the protoplasmic surface.

Emphasis has been placed by some investigators on interference with normal progress of photosynthesis, respiration, and transpiration. Minshall and Helson (1949), on the basis of a careful series of measurements, concluded that petroleum naphtha caused a decrease in the rate of photosynthesis and transpiration, and changes in respiratory rate as well. There is

[1] Received for publication March 20, 1953.

[2] Mr. Currier is Associate Professor of Botany and Associate Botanist in the Experiment Station, Davis; Mr. Peoples is Professor of Comparative Pharmacology and Pharmacologist in the Experiment Station, Davis.

no doubt but that such effects are associated with oil phytotoxicity, but it would seem that they aid in explaining slow-developing chronic injury more than rapid-acting acute injury. Spray oil injury to citrus, clearly chronic in nature, has been shown to be correlated with decreased photosynthetic and respiratory rates (Wedding, *et al.*, 1952).

The retarding effect on respiratory activity of bean leaves by oxidized spray oils was studied by Johnson and Hoskins (1952). They found that acids and peroxides produced by laboratory oxidation at high temperature markedly increased the toxicity of highly refined spray oils containing almost entirely saturated aliphatic and naphthenic compounds. The lethal action of the oxidized oil was rapid and of the acute type. Tucker (1936) had previously associated chronic injury of spray oils with their acid content.

TABLE 1

CERTAIN PHYSICAL PROPERTIES OF HYDROCARBONS TESTED

Hydrocarbon	Molecular weight	Density, $\frac{20°}{4}$	Boiling point, °C†	Vapor pressure, mm Hg at 25°C		Water solubility, mols/l solution, 25°C (observed)
				Calculated	Observed	
Benzene	78.11	0.8794	80.1	94.6*	94.5	0.0237
Cyclohexene	82.14	.8102	83.2	.....	87.0	.0031
Cyclohexane	84.16	.7791	80.8	98.9‡	98.8	.0013
Hexene-1	84.16	.6732	63.5	.....	183.0	.00092
n-Hexane	86.17	0.6603	69.0	149.5*	151.0	0.00069

* From Handbook of Chemistry and Physics (1950).
† From Timmermans (1950).
‡ From Phillips Petroleum Co. (1949).

It may be pointed out here that in future work a clear distinction should be made between acute and chronic injury, and that pure compounds or oils of known composition must be employed, if interpretation of data is to have significance.

In an earlier study, the phytotoxicity of the series benzene, toluene, xylene, trimethylbenzenes was investigated by exposing plants to the hydrocarbon vapors dispersed in air (Currier, 1951[3]). These experiments permitted the conclusions: (1) that the type of injury produced is in each instance of the acute type rather than chronic; (2) that the hydrocarbons act more in a biophysical than in a biochemical manner; (3) that the plasma membrane is the critical structure affected; and (4) that the concentration range is very narrow, and partition phenomena determine concentration at point of action.

While the behavior of the four benzenes referred to suggests that they act nonspecifically in a more or less biophysical way, additional studies with respect to different types of hydrocarbons will help to establish relations between structure, physical properties, and phytotoxicity. This paper is the report of such a study.

[3] In this paper, concentrations in air of the hydrocarbons were erroneously reported too low by a factor of ten.

Five hydrocarbons were chosen: *n*-hexane, hexene-1, cyclohexane, cyclohexene, and benzene.[4] They were selected because all are 6-carbon compounds with similar molecular weights and exhibiting vapor pressures that are not too dissimilar (table 1), yet each represents a different type of hydrocarbon.

The investigations reported in this paper were in general of three kinds: (1) treatment of plants with hydrocarbon vapors diluted with air, (2) treatment with aqueous solutions of the hydrocarbons, and (3) determination of solubility and distribution phenomena, involving the phases air, water, and various oils.

TREATMENT WITH VAPORS

Procedure

For test plants, barley and carrot were used. Grown in cans in the greenhouse, barley was treated 2 weeks after planting, when the plants were in the two-leaf stage; carrots were 63 to 95 days from seed when treated. In certain tests designed to determine the effect of age on susceptibility, plants that varied more widely than the above were used.

The plants were treated in a simple gas chamber, described earlier (Currier, 1951). An air stream controlled by a flowmeter was passed through a vaporizing bottle containing the hydrocarbon, the level of which was kept constant by continuous addition through a burette. The concentration of vapor in the air stream was changed by varying the temperature of the water bath surrounding the vaporizing bottle. The operation was conducted in diffuse light in the greenhouse.

The variables in these experiments, in addition to species and age of test plants, were the following: (1) initially, with treatment time constant at 15 minutes, the concentration of hydrocarbon was varied; (2) with concentration constant, treatment time was varied from 30 minutes to 2 hours; (3) with concentration constant at a level not toxic in 2 hours, treatment time was extended to 8 hours; (4) finally, enough tests were run to establish the minimum concentration of each hydrocarbon giving 90 to 100 per cent injury in a 1-hour exposure.

Notes describing plant responses were recorded immediately after treatment, and after 24 hours, and 1, 2, and 4 weeks.

In the assessment of injury, assignment of values is based on the percentage of total leaf area killed. This is an approximation, but with carefully grown plants and with one individual making the judgments, consistent results can be obtained.

Results

Symptoms. The symptoms were those of acute injury, and have been described (deOng, Knight, and Chamberlin, 1927; Currier, 1951). No chronic injury (slow developing, systemic, long lasting) has been observed as an effect of any of the five hydrocarbons investigated.

[4] The *n*-hexane and hexene-1 were supplied by the Phillips Petroleum Co., the cyclohexane by the Shell Development Co.; the cyclohexene was Eastman #1043, and the benzene Baker's CP.

First noticeable is the escape of foliage odor. This is definite, and it indicates an increase of permeability, at least with respect to these volatiles. Plants can release such odors and still fail to exhibit serious injury. As further evidence that an increase in permeability has occurred, very slight pressure on the leaf will darken it, owing to cell sap filling the intercellular

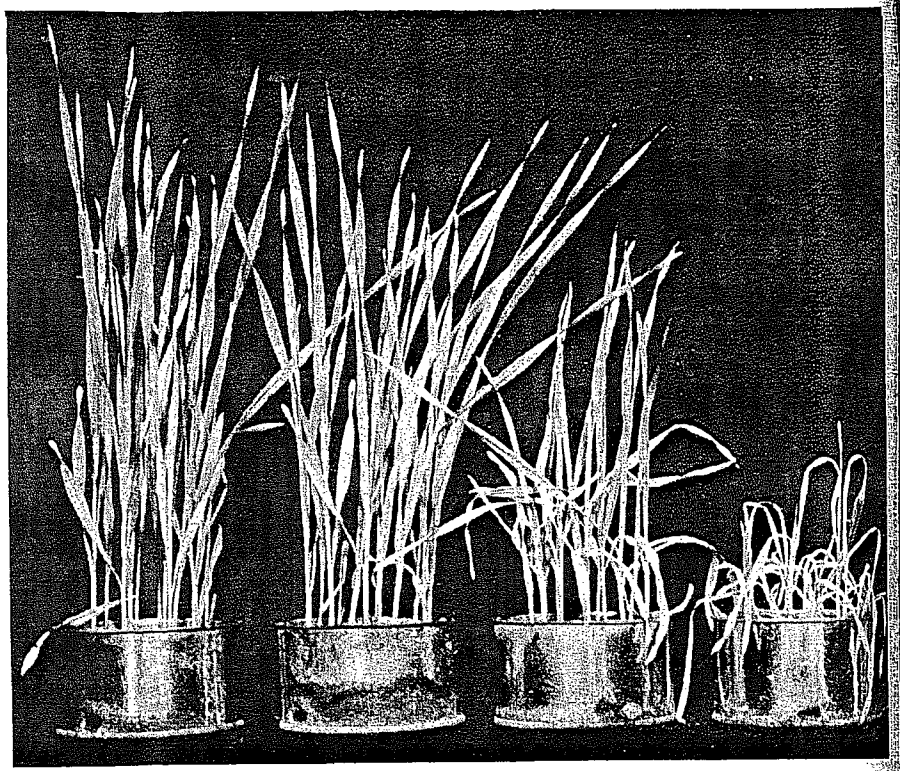

Fig. 1. Treatment of barley with hexene vapor, 15 minutes in each instance. Concentration from left to right: 0, 4.3, 7.1, and 10.0 mM/l of air. Original injury 0, 0, 25, and 95 per cent respectively. Photographed 10 days after treatment. Plants third from left are recovering.

spaces of the leaf. Considerably more pressure is required to produce the same effect on untreated leaves.

Next, dark areas appear in the leaves, followed by loss of turgor, complete wilting, and death.

Similarity of Action. The type of plant response to hexane, hexene, cyclohexane, cyclohexene, and benzene was the same in all treatments as far as visual judgment can be a basis. This is also the same response produced by vapors of toluene, xylene and mesitylene.

Barley and Carrot Compared. Aside from the selectivity noted below, the two plants exhibited qualitatively identical injury symptoms, except that when leaves are killed, carrot almost invariably recovers by the development

of new leaves from the crown; barley does not. Exceptions are that very young carrot plants did not resprout, and that young (5 day) barley sometimes continued to grow after all aerial growth had been killed. The latter response is apparently due to the protection provided the barley apical meristem at this stage of growth.

Selectivity. Carrots were more resistant than barley to all five hydrocarbons, under the conditions of the experiments (table 3). This indicates rather clearly that selective action is associated with the low-boiling hydrocarbons in weed-killing oils. It is known that the differential phytotoxicity, grasses *versus* carrots, is demonstrated in the field in connection with the acute type of injury (Crafts, Currier, and Leonard, 1951).

Age of Plants. As carrots grow older under greenhouse conditions they become somewhat more resistant to hydrocarbon vapors, as shown by tests with cyclohexane and cyclohexene. The degree of decreasing injury to 28, 63, 72, and 126-day old plants was in the order of 95, 85, 75, and 70 per cent, respectively, where injury was judged 24 hours after treatment. Similar tests on 5, 7, 12, and 26-day-old plants of barley indicated that age within these limits is not an important factor, since the amount of injury was the same in all.

Order of Toxicity. A 15-minute treatment was found to be insufficient for equilibrium distribution of the hydrocarbon between the air and the plant; hence these data are not included in the tables. However, even with this brief exposure, all of the hydrocarbon vapors were definitely toxic. Figure 1 represents the response of barley to hexene vapors.

In all exposures the toxicity, on a molar basis, increased for both barley and carrot in the order hexene, hexane, cyclohexane, cyclohexene, benzene (tables 2, 3). Toxicity is considered to bear a reciprocal relation to minimum lethal concentration. The two straight-chain hydrocarbons were considerably less toxic than the three cyclic compounds. There was little difference between hexene and hexane, but vapors of the latter were slightly more toxic. For example, 7.6 mM/l of hexene and 6.3 mM/l of hexane both produced 60 per cent injury in barley as a result of 15-minute treatments and 90 to 100 per cent after 60 minutes.

When sprayed on plants, the toxicity of pure hydrocarbons has been found to increase in the order straight-chain paraffins, olefins, naphthenes or cycloparaffins, aromatics (Crafts and Reiber, 1948; Havis, 1950; Leonard and Harris, 1952). In tests on carrots, Crafts and Reiber reported that cyclohexene and benzene were equally toxic, and that these were somewhat more so than cyclohexane; *n*-hexane was much less toxic. The studies reported in this paper indicate a similar order of toxicity when hydrocarbon vapors are used instead of liquids. Employing a larger assortment of hydrocarbons, Ivens (1952) noted that some, not toxic in the vapor phase, were extremely toxic as liquids. Lack of toxicity was explained by a low vapor pressure.

Time and Concentration. There is no simple time-concentration relation in acute hydrocarbon toxicity. The behavior of plants treated for 15 minutes indicated that the reaction is quite rapid when the concentration is at a lethal level. While there was usually increased injury when the treatment

TABLE 2

PER CENT INJURY TO BARLEY AND CARROT PLANTS FOLLOWING ONE-HALF TO TWO-HOUR TREATMENT WITH HYDROCARBONS

Hydrocarbon	Concentration, mM/l air mixture	Plant	Days after treatment	Per cent injury with: ½-hour treatment	1-hour treatment	2-hour treatment
Hexane	4.5	Barley	1	0	5	5
			14	0	5	5
			28	0	0	0
	4.5	Carrot	1	0	0	0
			14	0	0	0
			28	0	0	0
Hexene	4.6	Barley	1	0	5	5
			14	0	5	5
			28	0	0	0
	4.6	Carrot	1	0	0	0
			14	0	0	0
			28	0	0	0
Cyclohexane	2.8	Barley	1	10	15	25
			14	95	98	85
			28	100	100	85
	4.2	Carrot	1	10	15	25
			14	25	25	30
			28	25	25	35
Cyclohexene	2.8	Barley	1	95	95	95
			14	100	100	100
			28	100	100	100
	4.2	Carrot	1	90	95	95
			14	60	85	80
			28	25	30	25
Benzene	2.7	Barley	1	85	90	95
			14	95	100	100
			28	95	100	100
	2.7	Carrot	1	0	0	0
			14	0	0	0
			28	0	0	0
	3.0	Carrot	1	10	10	10

time was extended from ½ hour to 1 and 2 hours, the differences were not great, and beyond 2 hours, time seems an even smaller factor. As further evidence, when an 8-hour exposure to a concentration just below that which is lethal in 1 hour was given, there was either no injury or it was slight (table 4). For experimental purposes 1 hour is a convenient and satisfactory treatment period.

TREATMENT WITH AQUEOUS SOLUTIONS OF HYDROCARBONS

Toxicity studies have shown that for many plant tissues visual judgment of vitality based on apparent necrosis is not a satisfactory criterion. Plasmolysis is generally infallible (Currier, 1949), but this method is tedious.

TABLE 3

CONCENTRATION IN AIR OF HYDROCARBON FOUND TO PRODUCE 90–100% INJURY IN A ONE-HOUR TREATMENT

Judgments made 24 hours later

Hydrocarbon	Concentration in air, mM/l: With barley	With carrot
Benzene	2.6	3.9
Cyclohexene	2.7	4.2
Cyclohexane	3.9	5.4
Hexane	6.3	7.6
Hexene	7.6	9.7

TABLE 4

INJURY TO BARLEY AND CARROT WITH LONGER EXPOSURES TO HYDROCARBON VAPORS

Plant	Hydrocarbon	Concentration, mM/l of air mixture	Time after treatment	Per cent injury with: 2-hour treatment	4-hour treatment	8-hour treatment
Barley	Benzene	1.2	1 day	0	0	Trace
			2 weeks	0	0	Trace
			4 weeks	0	0	Trace
Barley	Cyclohexane	2.3	1 day	0	5	10
			2 weeks	0	0	0
			4 weeks	0	0	0
Carrot	Cyclohexene	1.7	1 day	0	0	0
			2 weeks	0	0	0
			4 weeks	0	0	0
Barley	Cyclohexene	1.7	1 day	10	20	30

Application of the tetrazolium reaction to biological problems (cf. Smith, 1951) is a distinct contribution. Living tissues absorb and reduce the colorless dye to a red formazan. Dehydrogenases are believed responsible for the reduction (Jensen, Sacks, and Baldauski, 1951).

Comparative tests (unpublished) of the tetrazolium reaction and plasmolysis, using *Anacharis* as test material, indicate good agreement between the two methods of distinguishing living from dead cells. In applying the method to *Anacharis*, and to the leaf and root segments tested, a 0.05 per cent solution of 2,3,5 triphenyltetrazolium chloride in local tap water (pH 7.8) was

employed. There was adequate color development after 16 to 24 hours in the dark at 25° C, and the toxicity was low enough to permit cells to remain alive after this period. Cells of both control and treated plants containing considerable formazan deposits remained plasmolyzable.

Tests on Anacharis

Anacharis canadensis (elodea) material was available from greenhouse culture tanks, where the plants grow in tap water the year round. A submerged aquatic, it is suitable for studies with aqueous solutions. Shoot seg-

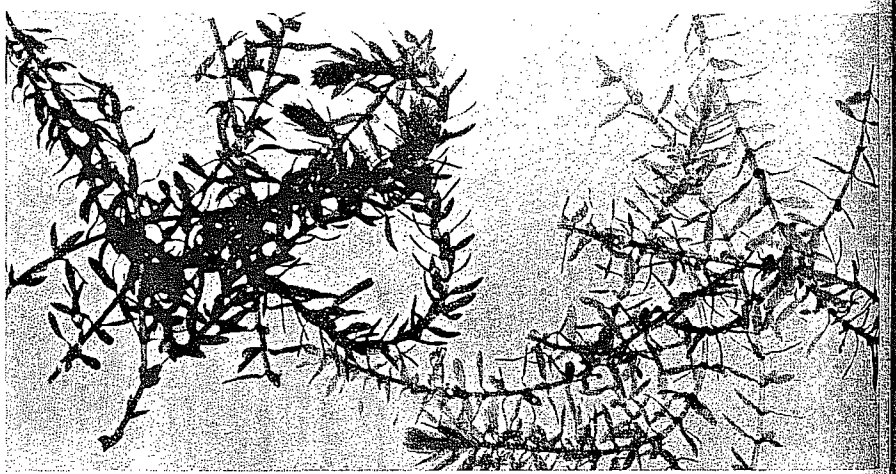

Fig. 2. The tetrazolium reaction in *Anacharis* shoots. Left, treated with tetrazolium (red in color); right, untreated (normal green).

ments 2½ inches long, in replicates of four, were treated for 1 hour with aqueous solutions of the hydrocarbons in capped Mason jars mounted on a rocking-type agitator. The temperature was controlled at 25° C and light intensity at 200 foot-candles.

Saturated solutions were prepared by gently agitating tap water in contact with an excess of hydrocarbon liquid, at 25° C. Dilutions were subsequently made by addition of tap water, and concentrations were calculated from the saturation value.

After treatment with the hydrocarbons in aqueous solution the shoots were placed in 0.05 per cent tetrazolium chloride solution. After 24 hours in the dark, living shoots were red, dead shoots normal green. The difference between the concentration which permitted the tissues to remain alive (as judged by their red color) and that which killed was surprisingly small. Figure 2 compares treated and untreated shoots of *Anacharis*.

In a preliminary experiment, saturated solutions of all the hydrocarbons except hexane killed quickly, at least within 1 hour. Hexane-treated shoots showed no significant injury after 20 hours of exposure to the solution.

Next half-saturated solutions were used, with the result that benzene and cyclohexene killed in 1 hour, hexene and cyclohexane did not. Subsequent

trials of graded solutions in steps of 0.05 per cent saturation gave the results shown in table 5. These minimum lethal concentrations were confirmed by another procedure in which fresh solution constantly flowed into the treatment vessel.

On a per cent saturation basis, the increasing toxicity series is hexane, hexene, cyclohexane, cyclohexene, benzene. However, on a concentration basis the order is just the reverse. This matter is considered further in a later section.

Tests on Leaves and Roots

Greenhouse-grown barley and carrot plants were employed. One-inch segments were cut from the second leaf of 14-day-old barley plants, using the

TABLE 5

AMOUNTS OF HYDROCARBON KILLING *ANACHARIS* IN ONE HOUR AT 25° C

Expressed as relative saturation (complete saturation = 1.0) and millimols per liter of water

Hydrocarbon	Relative saturation	mM per l
Benzene	0.40	9.48
Cyclohexene	0.45	1.53
Cyclohexane	0.80	1.07
Hexene	0.90	0.83
Hexane	1.0 not lethal	>0.69

middle two thirds of the leaf. Duplicates were treated in capped Mason jars with aqueous solutions of the various hydrocarbons, varying in steps of 0.1 of saturation at 25° C, or sometimes in steps of 0.05. Terminal 1½-inch segments of main barley roots, carrot leaflets, and thin (500 micron) sections of ½-inch diameter carrot roots were also treated. The leaf segments were weighted to keep them from collecting at the top; the root sections did not require this.

After 8 hours at 25° C and 200 foot-candles of light, the sections were transferred directly to 0.05 per cent tetrazolium chloride solutions. The leaf segments gave a rather poor response to the dye, but loss of turgor and darkening were additional criteria of death. Carrot root slices gave quite positive results, but barley-root behavior was difficult to interpret. Plasmolysis tests aided in establishing minimum lethal concentrations. The tetrazolium reaction in barley root was most pronounced in the stele, but was also observed in cortical parenchyma and in the apical meristem, the cells of which seemed to be the most resistant of all in the root to the hydrocarbons. A solution was considered lethal if it killed all cells except possibly these meristematic cells.

The minimum lethal concentrations determined for the five hydrocarbons, under the conditions of the experiment, are shown in table 6. Barley leaf behaved very much as did *Anacharis*. Carrot leaf was considerably more resistant. It is of interest that with benzene the root segments remained alive in concentrations that were lethal for leaves. Several supplementary

tests of benzene solutions on radish, turnip, parsnip, and celery, indicated that the first two were the more susceptible, and that roots in each instance were more resistant than leaves. However, this relation was not shown in the effect of the other four hydrocarbons on barley and carrot (table 6).

TABLE 6

MINIMUM AMOUNTS OF HYDROCARBONS IN AQUEOUS SOLUTION LETHAL TO BARLEY AND CARROT LEAF AND ROOT SECTIONS IN AN 8-HOUR EXPOSURE AT 25° C

Expressed as concentration in millimols per liter and as relative saturation (100 per cent = 1)

Hydrocarbon	Concentration, mM/l				Relative saturation			
	With barley leaf	With carrot leaf	With barley root	With carrot root	With barley leaf	With carrot leaf	With barley root	With carrot root
Benzene	8.3	14.2	11.9	21.3	0.35	0.60	0.50	0.90
Cyclohexene	1.4	2.4	1.4	2.4	0.40	0.70	0.40	0.70
Cyclohexane	0.91	....*	0.91	....*	0.70	>1.0*	0.70	>1.0*
Hexene	0.73	....*	0.73	....*	0.80	>1.0*	0.80	>1.0*
Hexane	....*	....*	0.69	....*	>1.0*	>1.0*	1.0	>1.0*

* Not lethal in saturated solution.

TABLE 7

DISTRIBUTION COEFFICIENTS AT 25° C

Hydrocarbon	Water / Air		Oil* / Air		Oil* / Water	
	mols/l	K	mols/l	K	mols/l	K
Benzene	$\frac{0.0237}{0.0051}$	4.65	$\frac{4.88}{0.0051}$	960	$\frac{4.88}{0.0237}$	206
Cyclohexene	$\frac{0.0034}{0.0047}$	0.72	$\frac{4.26}{0.0047}$	911	$\frac{4.26}{0.0034}$	1,270
Cyclohexane	$\frac{0.0013}{0.0053}$	0.25	$\frac{2.97}{0.0053}$	560	$\frac{2.97}{0.0013}$	2,210
Hexene	$\frac{0.00092}{0.0099}$	0.093	$\frac{2.80}{0.0099}$	283	$\frac{2.80}{0.00092}$	3,040
Hexane	$\frac{0.00069}{0.0082}$	0.085	$\frac{2.49}{0.0082}$	305	$\frac{2.49}{0.00069}$	3,590

* Cottonseed oil.

Greater resistance of roots to hydrocarbons than of leaves would be in agreement with the idea that the root is adapted to absorption of polar substances, the leaf to nonpolar substances (Crafts, 1948). Perhaps it could be said that the root is simply more polar than the leaf, and it is not improbable that the plasma membranes of root cells are more hydrophilic than those of leaf cells, and consequently absorb relatively less hydrocarbon.

Further importance in these results may be noted in the fact that isolated sections of carrot root and leaf appear to show the same relative resistance to hydocarbons as do intact plants. Thus the individual cell is probably the important entity in this type of toxicity and selectivity, rather than whole plants or organs.

DETERMINATION OF PHYSICAL CONSTANTS

Solubility phenomena are considered the most important physical properties of the hydrocarbons in this investigation. In addition to solubility in air, water, and oil, interesting relations are shown by equilibrium distribution of hydrocarbon between the systems water-air, oil-air, and oil-water. All may be calculated on the basis of vapor-pressure measurements using a Van Slyke manometric blood gas apparatus. The method in general is an adaptation of that outlined by Van Slyke (1939). Improvements and details of technique will appear elsewhere.[5]

Concentration of hydrocarbon in air is a direct function of its partial pressure, according to Dalton's Law. Knowing volume of flask, volume of liquid, and concentration of hydrocarbon in liquid, Henry's Law may be employed to calculate the water/air distribution ratio at any concentration. This law may be stated:

$$m = Pk_w$$

where P = partial pressure of hydrocarbon vapor in equilibrium with hydrocarbon dissolved in the liquid, k_w = Henry's Law constant, m = mols of hydrocarbon per liter of water. Mols per liter of air $= \frac{n}{V} = \frac{P}{RT}$, where n = number of mols of hydrocarbon vapor, V = volume in liters, R = gas constant in the relation $PV = nRT$, and T is absolute temperature.

The water/air distribution coefficient then is equal to:

$$K_{w/a} = \frac{\text{mols per liter in water}}{\text{mols per liter in air}} = \frac{Pk_w}{P/RT} = k_w RT.$$

Oil/air distribution constants may be similarly calculated:

$m = Pk_o$, where k_o = Henry's Law constant for oil.

$$K_{o/a} = \frac{\text{mols per liter in oil}}{\text{mols per liter in air}} = \frac{Pk_o}{P/RT} = k_o RT.$$

Finally, oil/water distribution coefficients may be obtained:

$$K_{o/w} = \frac{K_{o/a}}{K_{w/a}} = \frac{k_o RT}{k_w RT} = \frac{k_o}{k_w}$$

The above calculations and measurements assume ideal behavior of solutions of hydrocarbons. This is believed to be a valid assumption for nonpolar substances of low water solubility.

Values obtained by these procedures are shown in table 7, where cottonseed oil (Wesson oil) served as the model. The use of corn oil (Mazola) led to quite similar values, but paraffin oil (Standard No. 3 White) gave values which were not of the same order (table 8).

[5] Peoples, S. A. Unpublished data, 1953.

DISCUSSION AND CONCLUSIONS

Mechanism of Toxicity

Low-boiling hydrocarbons such as benzene are narcotic substances, characterized by their ability to depress certain cellular functions. Used in sufficient amount, they become markedly toxic and act as cytolytics to disrupt cellular organization. When they are employed as herbicides this disruption apparently occurs first at the ectoplast, the external protoplast surface, resulting in a pathological and irreversible increase in permeability.

The protoplast surface may be viewed as a lipid–hydrated protein complex a few molecules thick (see, for example, Davson and Danielli, 1952), the structure of which must be maintained by a continuous expenditure of energy. The lipids may be predominantly phospholipids. In the most elementary view, a hydrocarbon such as benzene becomes adsorbed on or dissolved in the lipid phase and disrupts the supposedly intimate bonds between the protein and fatty components of the surface membrane. As the concentration of hydrocarbon increases, there is a point where the membrane becomes so permeable that the cell contents leak out.

TABLE 8

DISTRIBUTION COEFFICIENTS WHERE CORN AND PARAFFIN OILS WERE USED AS MODELS

Hydrocarbon	Corn oil		Paraffin oil	
	Oil/air	Oil/water	Oil/air	Oil/water
Benzene	850	183	607	131
Cyclohexene	736	1,020	780	1,080
Cyclohexane	542	2,170	853	3,410
Hexene	286	3,080	350	3,760
Hexane	272	2,930	368	3,960

It is of course illogical to consider that a substance acts wholly in a physical or wholly in a chemical way, because ultimately the same forces are involved. This is especially true with reference to the plasma membrane, a living structure that is maintained by chemical reactivity. But without any strict distinction, it is advantageous to separate certain toxicants which may be considered nonspecific, or indifferent, remaining unchanged in the process, from other substances which are toxic because they enter directly into biochemical reactions (Ferguson, 1939; Albert, 1951; Danielli, 1950).

The herbicidal activity of hydrocarbons, at least the low-boiling type dealt with in the present report, must depend on the same mechanism and factors as those operating in the Overton-Meyer lipid solubility theory of narcosis (Overton, 1901), which was later amplified and extended by Meyer and Hemmi (1935). Overton showed the strength of certain indifferent substances to lie in the same order as their oil/water partition coefficients. The employment of this theory in studying herbicidal mechanisms may help to solve some of the problems associated with the penetration of many different kinds of substances, herbicides and others, into leaves and roots. While the same principles may be operating as in animals, the reaction in plants is different in some respects. Lack of a specialized nervous system permits focusing of attention more on the individual cell. Presence of intercellular air spaces makes possible the detection of leakage from cells.

The idea that cell lipids constitute the critical phase in which hydrocarbons and other indifferent substances exert their action agrees well with experimental facts (Meyer and Hemmi, 1935). Under the present circumstances the critical lipid structure seems to be that of the protoplasmic surface. This is based on the observation that darkening of the leaf is the first visible response in the gas chamber, and that sublethal concentrations do not seem to cause injury. Chloroplasts are high in lipid, yet it seems that they do not suffer injury while the plasma membrane remains intact.

The structure of the plasma membrane is unknown, but there are many theories concerning it. The lipid phase may be homogeneous or nonhomogeneous; it may consist of orientated apolar chains of proteins as well as phospholipids. Use of a seed oil as a model assumes that the lipid of the membrane may have similar solvent properties toward hydrocarbons. The present data suggest that this might be true. One would think that the assumed definite orientation of lipid molecules in the membrane would result in different solvent power as compared with random arrangement in bulk. The first stage of accumulation of hydrocarbon at the protoplast exterior is doubtless an adsorption process, but from this initial point to the lethal concentration it is not known whether adsorptive forces bringing about accumulation at surfaces can be distinguished from solution forces. Distribution coefficient values were calculated on the basis of solution equilibria, and it is simpler at this stage of knowledge to consider that hydrocarbon "dissolves" in the lipid portion of the membrane.

As many have pointed out, a positive correlation between narcotic strength and lipid solubility does not constitute a mechanism, but only suggests that a lipid phase in the cell may be the site of action. While the evidence points to increased permeability as the toxic mechanism, underlying this change must be submicroscopic changes in membrane structure. As to these, some rather specific suggestions have been made, a discussion of which may be found in a review by Butler (1950).

Van Overbeek and Blondeau (1953) have developed the most complete picture of hydrocarbon phytotoxicity at the molecular level yet proposed. Solubilization, the incorporation of foreign molecules in the colloidal micelles of surface-active substances, plays an important role. Hydrocarbon molecules are considered to solubilize in the lipid portions of the plasma membrane and thus "open up" this surface, which results in leakage of cell contents and death. These workers suggest that chronic oil injury, in addition to acute injury, is explainable as a solubilization phenomenon, except that in chronic injury a different time factor is involved.

Any disruption of energy supply would affect permeability, and this could be due to the presence of the foreign molecules themselves at the surface, or to their accumulation in regions of the interior protoplasm that are intimately associated with energy metabolism. More definite conclusions as to what is precisely happening at the surface will come with better understanding of its structure and function.

There is a lack of information as to the extent to which higher plants can metabolize hydrocarbons, with the production of acids and peroxides. But while enzymatic or other oxidation occurring within the plant may be an important aspect of chronic oil injury, it is less likely that this is true of acute injury, and particularly with reference to the compounds dealt with here. Further investigations are desirable to determine to what extent permeability factors are involved in chronic toxicity, and also in the quite rapid killing by highly acidic oils (Johnson and Hoskins, 1952).

Relation of Various Physical Factors to Toxicity

Molecular Structure. From studies made to correlate toxicity of narcotic-like hydrocarbons with molecular structure, one concludes that structure is important only as it determines certain physical properties (Ferguson, 1939; Albert, 1951; Danielli, 1950). Ivens (1952), determining toxicity of eighteen kinds of hydrocarbon vapors, concluded that it is impossible to say that one class of compounds is more toxic than another. The present data conform to this view. Some attention has been given to the herbicidal effect of inserting a double bond into a paraffin molecule. Havis (1950), working with a large group of pure hydrocarbons of various kinds, concluded that this increased toxicity only slightly. On the other hand, Leonard and Harris (1952) found that, with the exception of the pair hexene-1 and *n*-hexane, the olefins were considerably more toxic than the paraffins when applied as spray to cotton hypocotyls. Why hexene and hexane should behave differently is not clear at present. Changes in physical properties due to the double bond doubtless have more influence on toxicity than any increased chemical reactivity. The toxicity of olefins is known to increase upon storage in the light, and this could be a factor, especially in chronic injury resulting from treatment with higher-boiling compounds.

The demonstrated injury resulting from reaction products of olefins and ozone (Haagen-Smit *et al.*, 1952) has to do with a somewhat different problem. It is quite evident that rather small quantities of these ozonides can be toxic, but under the conditions of the present experiments it is not likely that they were present in sufficient amount to have contributed to acute injury.

Water Solubility. In homologous series of hydrocarbons it has been shown (Richet, 1893) that, within limits, toxicity is inversely correlated with water solubility, and this is demonstrated in the series benzene, toluene, xylene, mesitylene. That this relation fails however, when different types of hydrocarbon vapors are considered is indicated in the present work, where there is a positive correlation between these quantities, provided toxicity is considered as the reciprocal of minimum lethal concentration. As a further complication, in aqueous solution there is an inverse correlation of toxicity and solubility. This is why Ferguson (1939) concluded that toxicity ratings based on concentration can be misleading. It is clear that in comparing toxicities the diluent must be specified.

Oil Solubility. Oil solubility of hydrocarbons (see table 7) seems generally correlated in a direct way with toxicity, especially when vegetable oils are used as solvents.

Distribution Coefficients. Of the distribution coefficients the oil/air values seem to agree better with the order of toxicity in the vapor tests than the water/air or the oil/water values (table 7). This conforms to the idea that it is really the air-lipid distribution that determines the equilibrium toxic concentration in the ectoplast. When plants are treated with aqueous solutions the oil/water values are important.

Activity versus Concentration

It was mentioned above that on a concentration basis the toxicity of the series benzene, cyclohexene, cyclohexane, hexane, hexene, decreases when applied as vapor diluted with air, but increases when water is the diluent. On this basis, in air hexene is about one third as toxic as benzene, but in water it is about eleven times as toxic. A similar situation reported by Fühner (1923) is that on an equimolar basis chloroform in the gaseous phase is more toxic than carbontetrachloride, while the reverse is true in water. Meyer and Hemmi (1935) interpret this as due to differing solubility relations and distribution constants, and this will also explain the benzene-hexene situation.

Ivens (1952) found that in a homologous series of hydrocarbons, as the vapor pressure decreased a point was reached where the vapors became non-toxic. This he termed the "cut-off" point in the series. In our terminology, this result is due to a low value of the $\frac{\text{cell lipid}}{\text{air}}$ distribution of hydrocarbon.

Ferguson (1939) suggested that the effectiveness of toxicants which act essentially in a biophysical manner is best compared by the value of the chemical potential in the external phase, because by thermodynamic consideration it is known that the potential in the cellular phase involved (point of action) will be the same. The activity function of G. N. Lewis is used as an expression of chemical potential. The hypothesis seems generally to be supported by the work of several investigators (Hurst, 1943; Burtt, 1945; Gavaudan, Dodé, and Poussel, 1946; Brink and Posternak, 1948; Webb, 1949; Ivens, 1952). Much of this work has dealt with the effect of toxic vapors on insects. The principal also finds support in certain of the present data.

In the gaseous state, the degree of saturation (relative saturation) is equal to the thermodynamic activity of the toxic vapor. Ferguson and Pirie (1948) found that whereas the relative saturation of the physically acting toxicants lay between 0.1 and 1.0 for grain weevils, concentrations varied within wide limits. For example, at equal thermodynamic activity, ethyl chloride is shown to be about 200 times as concentrated as *s*-tetra-chloroethane.

Dalton's law of partial pressure implies that a gas will diffuse into a space already occupied by another gas as if the second gas were not there. Consequently the air saturation values at 25° C can be calculated from the relation $n = \frac{PV}{RT}$. And from the minimum lethal amount of hydrocarbon vapor known to be present (table 3) the relative saturation of air can be determined (table 9). There is a general increase in saturation with increase in minimum lethal concentration—this in contrast to the benzene, toluene,

xylene, mesitylene series (Ferguson and Pirie, 1948; Currier, 1951), where the relative saturation increases as the minimum lethal concentration *decreases*. The explanation for these differences probably lies in a decreasing lipid solubility for the series benzene, cyclohexene, cyclohexane, hexane

TABLE 9

RELATIVE SATURATION IN AIR AND IN WATER OF HYDROCARBONS AT MINIMUM LETHAL CONCENTRATION

Based on data in tables 3 and 6

Hydrocarbon	Relative saturation in air		Relative saturation in aqueous solution	
	With barley leaves	With carrot leaves	With barley leaves	With carrot leaves
Benzene	0.51	0.77	0.35	0.60
Cyclohexene	.58	0.90	0.41	0.71
Cyclohexane	.73	1.0	0.70	>1.0
Hexene	.77	0.98	0.79	>1.0
Hexane	0.78	0.96	>1.0	>1.0

TABLE 10

THEORETICAL CONCENTRATION, IN MOLES PER LITER, OF HYDROCARBON IN CELL LIPID, WHERE EXTERNAL CONCENTRATION IS LETHAL MINIMUM

Calculated by use of oil/air and oil/water distribution constants, with oil models as indicated

Hydrocarbon as vapor

Hydrocarbon	Cottonseed oil		Corn oil		Paraffin oil	
	Barley	Carrot	Barley	Carrot	Barley	Carrot
Benzene	2.5	3.7	2.2	3.3	1.6	2.4
Cyclohexene	2.5	3.8	2.0	3.1	2.1	3.3
Cyclohexane	2.2	3.0	2.1	2.9	3.3	4.6
Hexane	1.9	2.4	1.7	2.1	2.3	2.9
Hexene	2.2	2.7	2.2	2.8	2.7	3.4

Aqueous solutions*

Hydrocarbon	Elodea	Barley leaf	Barley root	Carrot leaf	Carrot root
Benzene	1.9	1.7	2.4	2.9	4.4
Cyclohexene	1.9	1.7	1.7	3.0	2.2
Cyclohexane	2.4	2.0	2.0	>2.5	>2.5
Hexane	>2.5	>2.5	2.5	>2.5	>2.5
Hexene	2.5	2.2	2.2	>2.5	>2.5

* Cottonseed-oil values employed.

hexene, and a markedly decreasing vapor pressure for the series benzene, toluene, xylene, mesitylene.

Ferguson's Principle predicts that substances which act in a physical manner, when present at the same degree of saturation in a diluent, have

the same degree of toxicity. In addition to hydrocarbon vapors, there is supporting evidence where the diluent is water. For example, in table 5 it can be seen that benzene and cyclohexene will kill *Anacharis* at about the same relative saturation, whereas the concentration of the first is roughly six times that of the second. From a practical viewpoint—for example in water-weed control—it should be of interest to seek toxic compounds of low solubility, but where the minimum lethal concentration is below 100 per cent saturation. That there is a limit as to how low the solubility can be is evidenced by the fact that saturated hexane-in-water solutions are essentially nonlethal, judging from the results of experiments reported in a previous section.

Relative saturation values in water at lethal minimum concentrations are included in table 9. Comparative values are somewhat less for benzene and cyclohexene than in air; otherwise there is fair agreement.

Theoretical Concentration in Cell Lipid

Using cottonseed and corn oils as models, the theoretical concentration of hydrocarbon in cell lipid can be calculated by means of distribution coefficients. The values obtained with respect to hydrocarbon vapor and oil/air coefficients suggest rather constant values of about 2 molar for barley and 3 molar for carrot tissue (table 10, upper section), indicating that there is no great difference in the absolute toxicity of the five species of hydrocarbons. That is, apparent differences in toxicity are due to physical factors involved in movement of the molecules to the site of action and their retention there. Such calculations were made by Meyer and Hemmi (1935) for a series of animal narcotics and they also arrived at rather constant values.

Where the hydrocarbons are dissolved in water, and where oil/water coefficients are used in similar calculations, one obtains similar values (table 10, lower section).

The data reveal that differences among plants must be more important than differences in structure of hydrocarbons. Some unique variation in the nature of the carrot ectoplast may explain the relative resistance of this plant and its relatives to weed oils, as compared with other plants. What this difference might be is the subject for continuing study.

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Evaluation of Limiting Constituents Suggested for Land Disposal of Exploration and Production Wastes

Health and Environmental Sciences Department
and
Exploration and Production Department

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TABLE OF CONTENTS

SECTION 1

INTRODUCTION AND EXECUTIVE SUMMARY

Onshore exploration and production (E&P) activities generate a limited variety of wastes. Ninety-eight percent of E&P waste (by volume) is composed of produced water, most of which is disposed of via Class II injection wells. The remaining 2% is composed of drilling wastes (drilling muds and wellbore cuttings that yield pit solids and liquids) and associated wastes which include production solids, tank bottoms, oily emulsions, and so forth. E&P wastes that are not recycled or managed at off-site facilities are commonly disposed of on site in pits or landspread over larger areas.

The objective of this study was to develop salinity and petroleum hydrocarbon threshold values for one-time landspreading, on-site burial, or road spreading of these E&P wastes. Definition, technical justification and guidance for the application of these threshold values is provided. Measurable parameters which serve as indices for proper management of salinity and petroleum hydrocarbons include: electrical conductivity (EC), sodium adsorption ratio (SAR), and exchangeable sodium percentage (ESP) for salinity; and oil and grease (O&G) for petroleum hydrocarbons.

The threshold guidance values generally recommended for land-applied waste:soil mixtures are EC <4 millimho per centimeter (mmho/cm), SAR <12, ESP <15%, and O&G <1%. The parameter

thresholds have been developed to be generally applicable for any waste containing salts or petroleum hydrocarbons including E&P wastes under ordinary conditions. Previous studies cited within this document provide supporting technical justification for selection of the threshold values.

In general, waste:soil mixtures that test below the threshold values are shown to have minimal impact to soil and vegetation for one-time applications. Yield reductions for many crops is less than 15% in the first year after application. Under certain restrictive conditions, the guidance threshold values have to be adjusted or crops temporarily changed to more tolerant species. Depending on drainage, crop cover, and soil amendments (gypsum and fertilizer), a soil with a loading no greater than that recommended should recover over a few seasons. **The operator must determine whether the guidance values apply over the short- or long-term, or whether site-specific conditions warrant more or less restrictive values.**

In general, the references cited within this report provide support for the recommended guidance values to avoid potential groundwater contamination. In addition, API is developing a contaminant fate and transport model to verify the appropriateness of the threshold values for a range of hydrogeologic environments found at E&P sites.

SECTION 2

TECHNICAL JUSTIFICATION AND LITERATURE REVIEW

2.1 Limiting Constituents

Salts and hydrocarbons have been identified as the principal limiting constituents of concern relative to onshore E&P operations because they may induce a phytotoxicity or, in the case of sodium salts, may deteriorate soil structure interrupting normal soil-plant-water relationships and causing excessive erosion (Miller and Honarvar, 1975; Ferrante, 1981; Freeman and Deuel, 1984; Nelson et al., 1984). Salts and hydrocarbons associated with E&P wastes may pose a significant threat to surface and groundwater resources when not properly managed (Henderson, 1982; Murphy and Kehew, 1984).

2.2 Salinity

Salinity is a general term reflecting the levels of available cations and anions in aqueous solution. Major ions include sodium (Na), calcium (Ca), magnesium (Mg), potassium (K), chloride (Cl), sulfate (SO_4), bicarbonate (HCO_3), carbonate (CO_3) and hydroxide (OH). EC reflects the ionic strength or total level of these constituents, while SAR and ESP consider the influence that specific ions may have under particular circumstances.

2.2.1 Definitions

Charged particles in solution will conduct an electric current to an extent determined primarily by the concentration and type of ionic species present, hence the term electrical conductivity. EC is measured directly in reciprocal units of resistance and conveniently reported in mmho/cm. Since dissolved solids are predominately dissolved salts in the form of dissociated charged particles, EC may be used as an indirect, approximate measure of total dissolved solids (TDS).

TDS is defined in chemical terms as the unfilterable residue associated with aqueous fluids resulting from the evaporation of a known quantity of water, and is reported in terms of mass per unit volume (mg/liter). This residue is predominately composed of salts, but may include organic materials (humic substances or anthropogenic compounds) or mineral colloids passing through the filter.

An exact relationship exists between concentration of a specific salt in pure water and electrical conductance of that solution (Barrow, 1966). However, this relationship is inaccurate at high-salt concentration, solutions of mixed salt species, or presence of nonionic dissolved species. Of more immediate use have been empirical correlations between TDS and EC for various aqueous solutions:

$$TDS = (A) \times (EC)$$

with the regression constant "A" (slope), being used as a conversion factor. Values of "A" have been found to range naturally from 540 to 960 cm.mg/mmho.liter (Hem, 1985). For naturally occurring saline/sodic soils a constant of 640 may be assumed (U.S. Salinity Laboratory Staff, 1954). Using the above equation, one calculates a TDS of 2560 mg/liter at a corresponding EC of 4 mmho/cm, and "A" of 640 cm.mg/mmho.liter. A recent analytical review of E&P wastes by the EPA (1987), and parallel review by the API (1987), suggested that an "A" value of 613 more accurately estimates TDS in E&P wastes when calculated from EC. This value is used in subsequent TDS calculations within this document.

TDS is generally not an accurate measure of salinity for many E&P wastes, due to errors associated with hydrocarbons and fine clay passing the filtration step. If one wants the perspective of salinity on a mass basis, it is best estimated from EC. EC has long been the parameter of choice in defining salinity hazards associated with production agriculture.

2.2.2 Concerns

2.2.2.1 Plants and Soil

Although some elements, such as boron, are toxic to plants, generally the ill effects of salinity are caused by increased osmotic pressure of soil solution in contact with plant roots (Haywood and Wadleigh, 1949; U.S. Salinity Laboratory Staff, 1954). Osmosis is a process that controls the movement of water between solutions and depends upon the number of dissolved molecules or ions (salinity). Water flows from lower to higher

osmotic pressure. Plants have an osmotic pressure associated with their cell solution which varies greatly between plant species and to some degree between cultivars within species. If the osmotic pressure in soil solution outside the plant exceeds that inside, the plants wilts. The point of permanent wilting is reached when the plant can not recover even when exposed to less saline water. There is a direct relationship between osmotic pressure and EC:

Osmotic Pressure (OP), atm. = 0.36 X EC, mmho/cm

Salts also affect plants by disrupting normal nutrient uptake and utilization (Kramer, 1969). The mechanism is one of simple antagonism, whereby a given salt specie in excess inhibits the plant intake of required elements. The effect is usually manifested as a deficiency resulting in lowered yield expectations or overall crop quality.

There is no one critical or threshold salinity level where all plants fail to grow or maintain acceptable yields (Maas and Hoffman, 1977). General crop response to soil salinity is shown in Table 1 (U.S. Salinity Laboratory Staff, 1954). The sensitivities of various agricultural crops to salt are shown in Figures 1 through 3 generated from equations and data in Maas (1986). For example: At an EC of 4 mmho/cm, barley, cotton, and bermuda grass are not affected by salt, whereas yields are expected to decrease for rice and corn (0-15%), alfalfa and sugarcane (15-30%) and beans (30-50%). Yield response intervals shown in Figures 1 through 3 were developed from agricultural

Table 1. General Crop Response as a Function of EC.

(After U.S. Salinity Laboratory Staff, 1954)

EC (mmho/cm)	Effect on Crop Yield
0 - 2	None
2 - 4	Slight to none
4 - 8	Many crops affected
8 - 16	Only tolerant crops yield well
> 16	Only very tolerant crops yield well

systems receiving salt-containing irrigation over the long term and may overestimate the anticipated response for a one-time land disposal of E&P wastes. Based on Lunin (1967), the authors believe that salinity guidelines for continual use systems can reasonably be doubled for a one-time application; the rationale being that salt accumulated outside the bulk soil mass (in pores and on ped surfaces) is more easily displaced than that penetrated into and reacted with the bulk soil mass.

If the salinity is initially too high for a given crop after land applications of waste, soils will generally recover following rainfall or irrigation containing less salt because excess salts are leached when adequate drainage is present. Growth of more salt tolerant plants may be desirable during the interim

Fiber, Grain, and Special Crops

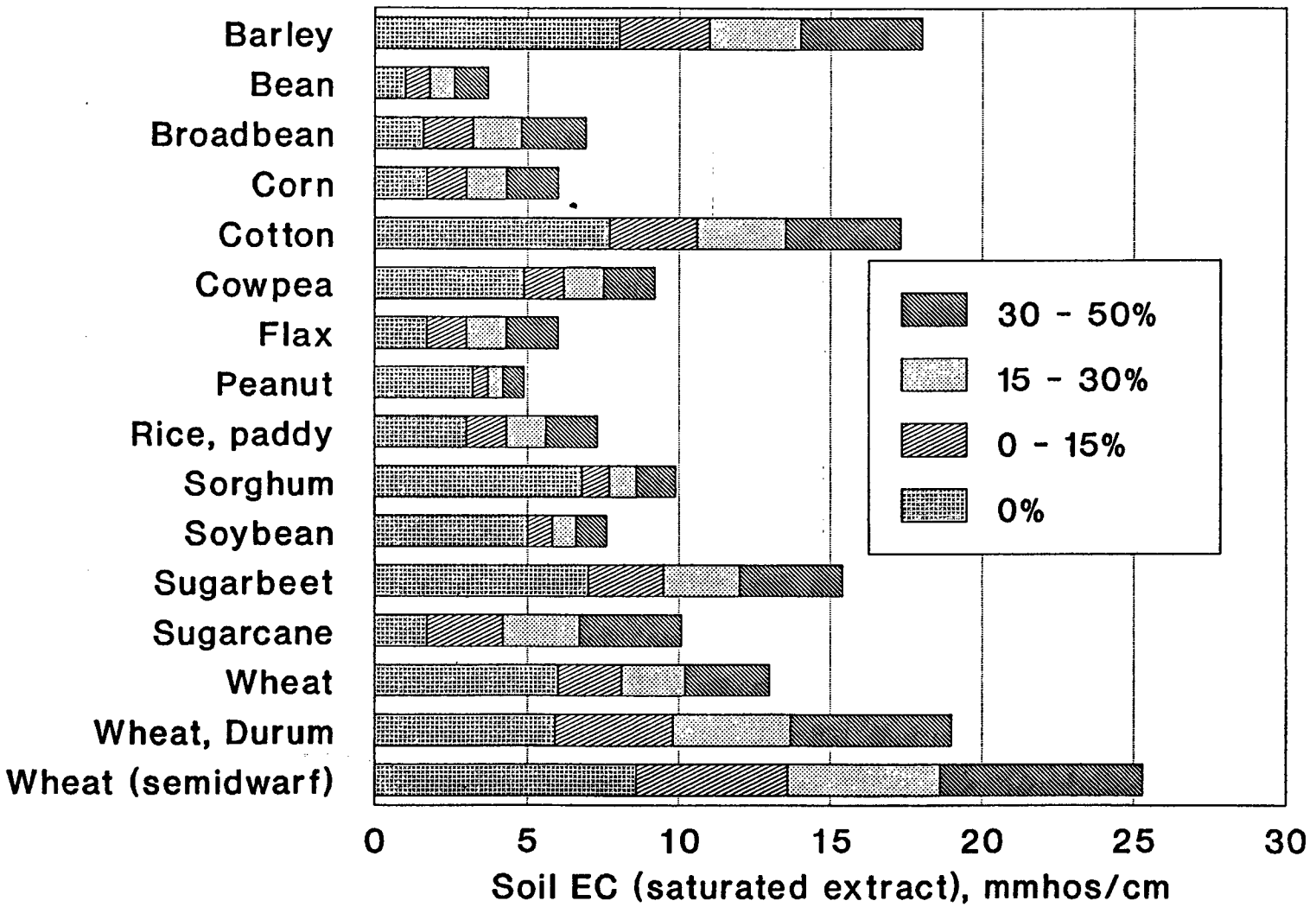


Figure 1. Yield decrease due to soil salinity (Maas, 1986)

Grasses and Forage Crops

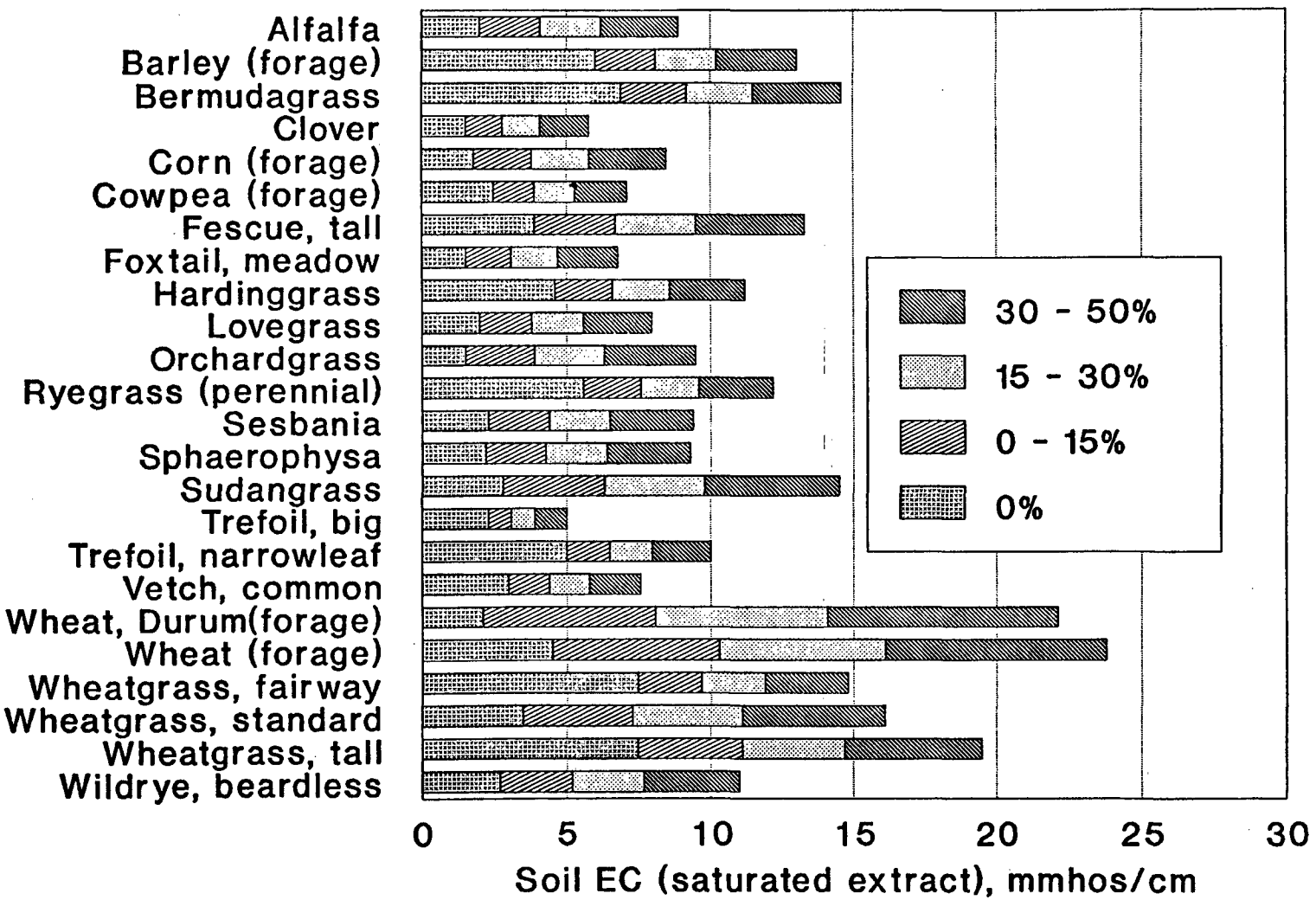


Figure 2. Yield decrease due to soil salinity (Maas, 1986)

Vegetable and Fruit Crops

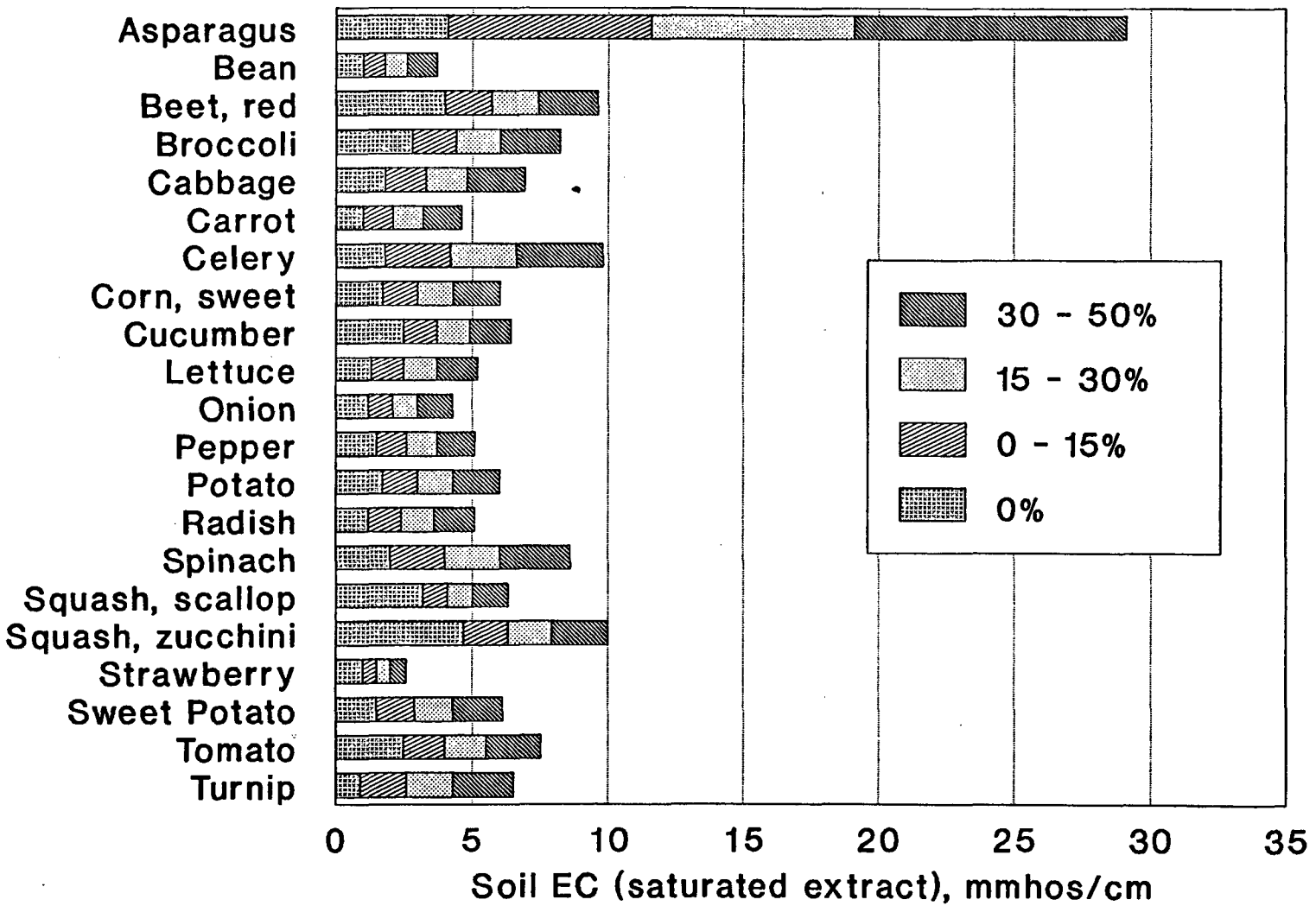


Figure 3. Yield decrease due to soil salinity (Maas, 1986)

between application and recovery (Foth and Turk, 1972). Reclamation of salt-containing soils may be hastened through the application of calcium sulfate (gypsum) which results in the replacement of exchangeable sodium by calcium (Oster and Rhoades, 1984). Plants grown on gypsiferous soils will tolerate an EC approximately 2 mmho/cm higher than those shown in Figures 1 through 3 (Mass, 1986). This is because gypsum is dissolved at moisture equivalents used in preparing saturated soil extracts for analysis but not at moisture equivalents normal to field conditions.

USDA Handbook 60 (U.S. Salinity Laboratory Staff,1954) classifies water with EC values above 2.25 mmho/cm as unfit for agricultural purposes except under very special circumstances. Soils with salinity.levels > 4 mmho/cm are considered saline. The recommended criteria of 4 mmho/cm is too high for the more salt sensitive crops (Table 1), and some adjustments may have to be made relative to intended land use. Miller and Pesaran (1980) found that high concentrations of soluble salts in mud-treated soil hindered plant growth in a 1:1 mud:soil mixture. Extracting their data where EC of the mud:soil mixture was < 8 mmho/cm, yield decreases averaged only 7% for green beans and 13% for sweet corn. Nelson et al. (1984) measured average yield decreases of 20% and 38% for swiss chard and rye-grass, where EC ranged from 6.3 to 18.6 mmho/cm. In these studies EC was above the recommended criteria of < 4 mmho/cm. Tucker (1985) reported adding drilling mud with resulting EC values from 1.3 to 5.3

mmho/cm with no adverse effect on bermudagrass and at 1.7 mmho/cm with no adverse effect on alfalfa. He also reported a significant decrease in EC with time following application, reflecting the leaching of salts out of the root zone.

The expected yield decrease associated with a one-time EC application guideline of 4 mmho/cm is <15% for most crops. In those cases where precipitation, drainage, or crop type places special restrictions on waste management, some adjustments may have to be made relative to waste addition levels or intended land use while the soil recovers.

2.2.2.2 Water Resources

In areas of net infiltration, the soluble salts are transported from the surface to lower soil zones. Murphy and Kehew (1984) found that soluble salts from a pit containing saturated brine drilling fluids (EC > 200 mmho/cm) posed a threat to localized groundwater resources. However, the EC of 200 mmho/cm greatly exceeds the recommended threshold of 4 mmho/cm. Bates (1988), working with a freshwater drilling fluid, demonstrated that Cl was not retained in the zone of incorporation when mixed with surface soil.

The criteria of 4 mmho/cm (2452 mg/liter TDS for "A" = 613) can be expected to have no measurable impact on groundwater even in the most sensitive hydrological settings. Water and associated dissolved constituents do not move through soils as an isolated unit (plug flow), instead there is a natural redistribution controlled by water potentials, pore dynamics, dispersion, and

diffusion (i.e., chromatographic effect). Recent field research studies conducted by Owens et al. (1985) and Bruce et al. (1985) perhaps best illustrate this principal in that they were conducted at concentrations comparable in magnitude to the 4 mmho/cm threshold. Both studies observed the redistribution of surface-applied bromide (Br) by rainfall infiltration and percolation.

The Owens group demonstrated better than a 7-fold decrease in Br after passing through only 2.4 m of well-drained silt loam and fractured shale due to attenuation processes mentioned above. Under conditions similar to their study, a surface loading of NaCl equivalent to 4 mmho/cm (2452 mg/liter TDS) would result in an EC <0.6 mmho/cm and corresponding Cl of < 213 mg/liter at a depth of 2.4 m. Bruce et al. (1985) showed Br redistribution from as great as 1800 mg/liter at the surface to <20 mg/liter below a depth of 3 m after nearly 4 years and 4.7 m of rainfall. The Br level was 100 mg/liter at a depth of 1.5 after 4 years with none detected below 3.8 m. If one substitutes Cl for the Br salts used in these studies it becomes apparent that percolating water will be at or below the EPA secondary drinking water quality standard of 250 mg/liter Cl (40 CFR, Part 143, Sec. 143.3) within a few feet of the source at controlled land applications (EC < 4 mmho/cm).

2.2.3 Criteria

In summary, the EC criteria of 4 mmho/cm based on a one-time application serves to protect vegetation, land and groundwater resources at most drilling and production locations, including

those located in sensitive regions, if amenable to a temporary adjustment in plant species. The criteria may be adjusted to meet special requirements.

2.3 Sodicity (ESP and SAR)

2.3.1 Definitions

2.3.1.1 Exchangeable Sodium Percentage (ESP)

The capacity of a soil to adsorb positively charged ions (cations) is called the cation exchange capacity (CEC) and may be expressed in meq/100 g.

It follows that the exchangeable cations in a soil are those positively charged ions held on the surface exchange sites and in equilibrium with the soil solution. The major cations calcium (Ca), magnesium (Mg), sodium (Na), and K (potassium) are called basic cations, and the percentage of the CEC occupied by these cations is called the base saturation. Fertile soils have a base saturation greater than 80% with the cations distributed mainly as Ca and Mg.

ESP is a measure of the degree to which the soil exchange sites are saturated with sodium and is calculated as follows:

$$ESP,\% = (NaX / CEC) \times 100$$

where NaX (exchangeable Na) and CEC are expressed in meq/100g.

2.3.1.2 Sodium Adsorption Ratio (SAR)

Ca and Mg are generally needed in relatively large amounts to maintain good soil structure (physical status relative to tilth and permeability) and fertility, but they form salts of low solubility in soils. Na salts are much more soluble and readily dominate soil solutions, often with a detrimental impact.

SAR is an empirical mathematical expression developed by the USDA Salinity Laboratory as an index to detrimental sodium effects in soils (U.S. Salinity Laboratory Staff, 1954). SAR is computed as follows:

$$SAR = Na / \sqrt{(Ca + Mg)/2}$$

where concentrations are expressed in meq/liter. Concentrations are determined by direct chemical analysis of pit liquids or aqueous extracts of waste solids or soils. An empirical equilibrium expression developed by the USDA Salinity Laboratory relating the ESP of the solid phase to the SAR of irrigation water or soil solution is given below:

$$ESP = 100\ (-.0126 + .01475\ SAR) / 1 + (-.0126 + .01475\ SAR)$$

2.3.2 Concerns

High Na levels (SAR >12) in soil solution cause Ca and Mg deficiencies in plants by both antagonistic reactions and shifting of solubilities by common ion effect (Kramer, 1969; U.S. Salinity Laboratory Staff, 1954).

Soils reacted with solutions of high SAR are at risk of becoming sodic. A soil is termed sodic when the ESP exceeds 15% of the CEC (U.S. Salinity Laboratory Staff, 1954). The most distinguishing feature of sodic soils is their lack of structure and tendency to disperse in water. A dispersed soil condition has a devastating impact on plants by limiting the free exchange of air and infiltration of water (Reeve and Fireman, 1967; Bresler et al., 1983).

Research conducted by Tucker (1985) involving land disposal of waste drilling fluids indicated that SAR < 10 and ESP < 15% are required for maintaining good soil structure and normal plant growth. Miller and Pesaran (1980) measured ESP for 1:1 and 1:4 mud:soil mixtures and found average yield decreases of 12% for green beans and 20% for sweet corn at an average ESP of 11.5%. These results are from samples with ESP ranging from 0.6-19.7% and EC < 8 mmho/cm.

SAR is somewhat less critical in that it represents the more easily altered solution phase. Deuel and Brown (1980) showed that the detrimental effect for water with an EC of 2.6 mmho/cm and SAR of 16.1 was directed proportionate to the solid-phase Ca in receiving soil. The occurrence of appreciable amounts of gypsum in the soil, either naturally or by amendment, may permit the disposal of highly sodic E&P wastes, particularly if the ionic strength of total salt is relatively low. Freeman and Deuel (1984) reported the successful pit closure in terms of the soil and plant environment (SAR < 15, ESP < 15%) by land disposal of E&P waste solids with SARs > 200 and ESP > 90, when salinities were < 4 mmho/cm. Treatment consisted

of blending waste solids with native soils at chemically defined mix ratios in conjunction with gypsum and fertilizer amendments.

2.3.3 Criteria

Therefore, the API Environmental Guidance Document recommends a SAR of <12 and ESP of <15% for a single application land disposal of E&P wastes. These values are widely accepted thresholds recommended by the USDA for preventing soil sodicity (U.S. Salinity Laboratory, 1954). Field and laboratory studies with drilling muds have also shown them to be reasonable values.

It is important to note that guidance values pertain to final disposition or closure status: These values do not limit the composition of the wastes that can be land disposed. However, operators must be prepared to provide necessary management inputs for wastes applied to land in exceedance of recommended values.

2.4 Hydrocarbons

2.4.1 Composition and Analysis

Crude oil and diesel are the principal hydrocarbons associated with E&P wastes (Miller et al., 1980; Thoresen and Hinds, 1983; Whitfill and Boyd, 1987). They are sometimes added to water base drill systems to lubricate the drill bit and pipe string. O&G levels in freshwater drilling wastes are generally < 4% (Freeman and Deuel, 1986). Other E&P waste such as tank bottoms, emulsions, and oil-contaminated soil may have higher concentrations of O&G.

Crude oil and diesel fractions are comprised of a complex array of saturate and aromatic hydrocarbons (Thoresen and Hinds, 1983, Oudot et al., 1989). Both fractions are readily partitioned from water by solvent using a separatory funnel or extracted from solid mineral components using a Soxhlet apparatus (Brown et al.,1983). Hydrocarbons extracted are assayed gravimetrically and reported collectively as oil and grease (O&G). Methylene chloride is the solvent of choice owing to its efficiency for extracting petroleum hydrocarbons without co-extracting significant quantities of naturally occurring organic matter (Brown and Deuel, 1983).

2.4.2. Concerns

2.4.2.1 Plants and Soils

A considerable amount of research has been carried out on the detrimental effects of crude oil and gas on plants and soils (Baldwin, 1922; Murphy, 1929; Schollenberger, 1930; Harper, 1939; Plice, 1948; Schwendinger, 1968; Garner, 1971; Odu, 1972). The most phytotoxic compounds are lower molecular weight aromatic hydrocarbons present initially or formed as metabolites of the various degradation processes (Baker, 1970; Patrick, 1971). Several studies (Murphy, 1929; Plice, 1948; Honarvar, 1975; Udo and Fayemi, 1975) reported marked inhibition of germination and corresponding yield reduction for row crops planted to soils receiving crude or waste oil applications in excess of 2% by weight. Pal and Overcash (1978) reported that the growth of vegetables and row crops were affected at an

oil application of 1% by weight. Yields were generally 50% of control at 2% oil by weight. Bulman and Scroggins (1988) showed that plant growth was good on field plots with oil content of 3.5% or less but poor on plots with oil content of over 5%. At another site they found reduced crop growth in the first season after applying 1% and 2% oil in the soil. However, areas that received levels of 0.5% oil showed enhanced crop growth.

Frankenberger and Johanson (1982) reported certain crude oil components and refined petroleum products added to soil at 20% to 60% disrupt the oxidative and soil microflora activity requisite for biological assimilation following oil spillage events with oxidation being slowest for heavier molecules.

Miller et al. (1980) found that a 1% soil loading with diesel fuel resulted in decreased yields of 49% and 69% for beans and corn, respectively. Replanting after 4 months resulted in near normal growth. Younkin and Johnson (1980) grew reed canarygrass in soil initially containing 0.45% diesel fuel and found an initial germination decrease of 69%, a first harvest yield decrease of 79% and no yield decrease with a second harvest (75 days after diesel addition). Overcash and Pal (1979) determined an oil level of about 1% of soil weight as the threshold for reduced yields, and with 1.5 - 2% causing yield reductions greater than 50%. These effects occur immediately after application before hydrocarbon is assimilated by the various loss mechanisms. Table 2 lists the oil tolerance for selected crops (Overcash and Pal, 1979). Crop investigations as early as 1919 suggested that oil damage in soil was due to poor aeration-water interac-

tions rather than direct toxicity (Carr, 1919). Work by Ellis and Adams (1961) suggested that iron and manganese released under anaerobic conditions contribute to the phytotoxic response to soil contamination by petroleum hydrocarbons. Phytotoxic response was lowered after assimilation of the hydrocarbon by the soil.

Table 2. Oil Tolerance for Selected Crops

Crop Type	Single Oil Application
yams, carrots, rape, lawngrasses, sugar beets	< 0.5% of soil weight
ryegrass, oat, barley, corn, wheat, beans, soybeans, tomato	< 1.5% of soil weight
red clover, peas, cotton. potato, sorghum	< 3.0% of soil weight
perennial grasses, coastal bermuda grass, trees, plantain	> 3.0% of soil weight

These studies indicate that under hydrocarbon loadings >1%, E&P wastes may be detrimental toward plant growth. However, at 1% or less of mixed hydrocarbons, little or no yield reduction is expected based on existing information. This is the rationale for the selection of the 1% limit. Also, recovery of the site is expected after a few months to one growing season, following a one-time application.

2.4.2.2 Water Resources

Several general observations of oil mobility in soil bear directly on any assessment of potential groundwater contamination. Plice (1948) observed that when oil enters the soil as a liquid, there is a natural segregation whereby the higher molecular weight, more viscous compounds are held near the surface while the lighter fractions penetrate deeper. Also, while the overall concentrations tend to decrease with depth, the composition toward the lighter end aromatic fraction tends to increase (Duffy et al., 1977; Weldon, 1978).

The recent review by EPA (1987) of E&P wastes showed only produced waters contained significant levels of the notably more mobile hydrocarbons including benzene, toluene, ethyl benzene, and xylenes (Roy and Griffin, 1985). These compounds were present in diesel oil-base drilling fluids but at concentrations that would be readily attenuated in subsurface strata by an adsorptive mechanism (El-Dib et al., 1978). Mobilities are also restricted by the chromatographic effect of liquids moving through a porous media (Waarden, Groenewoud, and Bridie, 1977). Oil floats, and its movement through soils is restricted to those

pores of passable diameter, not saturated with water. Movement is further retarded by the "Jamin effect" or obstruction of a non-wetting fluid in a porous media (Schiegg, 1980).

At low levels of hydrocarbon addition to surface soils, leaching has not been found to be a problem. Watts et al. (1982) found no migration at a 30- to 45-cm depth after applying 14% industrial waste oil to the top 15 cm. Raymond et al. (1976) added about 2% oil to the top 15 cm and determined that 99% remained within the top 20 cm after 1 year. With loading rates of 3 and 13% of soil weight per year, Streebin et al. (1985) found no significant oil migration below the zone of incorporation. Oudot et al. (1989) found the potential for leaching of unmodified hydrocarbons toward the groundwater was slight at a loading of 2% oil in soil. The one-time 1% level recommended for production waste additions to soil is therefore not expected to create any leaching problems.

2.4.3 Biodegradation

It has been demonstrated that soils have an adequately diverse microbial population and capacity to degrade E&P waste hydrocarbons (Raymond et al., 1967; Atlas and Bartha, 1972; Jobson et al., 1972; Kincannon, 1972; Westlake et al., 1974; Horowitz et al., 1975; Sveinung et al., 1986). Saturates and light-end aromatics are degraded first, with kinetics or rate of degradation controlled by concentration and composition of hydrocarbons, nutritive status, aeration, moisture and temperature (Schwendinger, 1968; Francke and Clark, 1974; Huddleston and

Meyers, 1978; Dibble and Bartha, 1979; Brown et al., 1983; Flowers et al., 1984; Bleckmann et al., 1989). Mechanisms and pathways of biodegradation of petroleum hydrocarbons are quite complex and are beyond the scope of this paper. Suffice it to say that the narrower the carbon:nitrogen ratio (60-100 C:N) and the nearer the moisture and temperature are to optimum levels (60-80% of the moisture retained in soil at 0.33 bar pressure and 35-38°C, respectively), the greater the rate of degradation.

Watts et al. (1982) measured a 2-year half life for a 14% by volume loading of oil to soil. Streebin et al. (1985) also found a half life of about 2 years for API separator sludge at a similar loading rate. At a loading rate of 2% in the field, 94% of hydrocarbons were removed after 3.5 years (Oudot et al, 1989). Lynch and Genes (1987) determined a half life of 77 days on a field plot containing up to 1% polyaromatic hydrocarbons in soil with 5% benzene extractable hydrocarbons.

It has been demonstrated that degradative processes attenuate the more mobile, light-end aromatic and water-soluble petroleum hydrocarbons when applied to the surface with little potential for contaminant migration (Raymond, 1975; Brown et al., 1983; Brown and Deuel, 1983; Whitfill and Boyd, 1987; Bleckmann et al., 1989). Whitfill and Boyd (1987) reported that soils may be treated with up to 5% oil by weight with no adverse environment impact. Several studies have shown that controlled oil applications actually improve soil physical conditions and fertility status (Plice, 1948; Mackin, 1950; Ellis and Adams, 1961; Baker, 1970; Giddens, 1976).

2.4.4 Criteria

The API Environmental Guidance Document recommends a 1% oil and grease threshold for land disposal of E&P wastes based on attenuation and degradation processes that will occur under landspreading conditions. This value is predicated on the concept of minimum management, whereby an operator may load a soil (add hydrocarbon) at an appropriate mix ratio (E&P waste:soil) not to exceed 1% oil and grease. Available information demonstrates that 1% hydrocarbon by weight was a reasonable threshold initiating only temporary plant yield reductions.

2.5 Summary This information supports the guidance values that have been developed for the land disposal of exploration and production wastes. For a one-time application the guidance values are EC < 4 mmho/cm, SAR < 12, ESP < 15%, and O&G <1%. These guidance values have been developed to be generally applicable for any waste containing salts or petroleum hydrocarbons including E&P wastes. They are designed to protect the environment under conditions most likely to be found at E&P locations. <u>While being generally applicable, it is up to the operator to determine whether they apply to his particular site.</u>

SECTION 3

PIT OPERATIONS AND LAND DISPOSAL

3.1 Pit Operations

3.1.1 Sealing Process

One factor that limits the potential of contaminant migration from waste drilling fluids managed in earthen pits and buried on site is the effective sealing offered by dispersed particulates (Rowsell et al., 1985).

Many drilling muds are primarily clay-water suspensions that function to clean any cuttings from beneath the drill bit and carry them to the surface, seal and stabilize the bore hole, and lubricate the drill string and bit. A significant portion of this mud is circulated to the reserve pit as waste drilling fluid along with the drill cuttings. Clay and fine silt particles associated with mud and cuttings penetrate the natural earthen surface defining the pit walls and bottom. This seals the pit forming a natural liner system. The more clay and the smaller the pore diameter of the native soil the quicker the seal.

It has been observed by the author of this paper that pits constructed in coarser textured soils, and loamy or clayey soils in an aridic soil moisture regime, are penetrated deeper by waste drilling fluids and require more fine particulates to develop a natural liner condition than in moist loamy or clayey soils. The soil layer composing this "natural" liner not only serves as a physical barrier, but also has chemisorptive properties further

reducing the potential for pollutant migration.

Prewetting the surface of pits constructed in coarse textured soils or loamy and clayey soils exhibiting vertical cracks may reduce the depth of penetration and the amount of fine particulates needed to effect a natural liner seal.

3.1.2 Pit Liquids

3.1.2.1 Operative Criteria

Pit liquid is defined as the aqueous phase above settled solids. The API Environmental Guidance Document recommends an operative criteria of 4 mmho/cm (2452 mg/liter TDS for "A" = 613). See Section 2.2.1 for parameter definitions and comparative discussion. EC serves as an index parameter for decision-making purposes relative to pit liquid disposal options. Pit liquid analyses do not necessarily reflect what is in the pit solids, separate analyses are required to obtain a complete understanding of pit contents.

3.1.2.2 Sampling and Analysis

Numerous grab samples at various depths improve statistical probability of obtaining a representative sample. Containers that can be opened below the surface at a selected depth interval are a must when sampling multiphase liquids (oil layer over water).

Expensive sampling equipment is usually not necessary and more often than not fails under field trials. Scrupulous cleaning of sampling hardware is requisite in preventing cross

contamination between sample locations.

The specific analytical protocol is given in the Appendix.

3.1.2.3 Pit Liquid Disposal

The EC criteria may be relaxed (subject to state and local regulations) where the native soil or freshwater wetlands are of poorer quality than the wastes themselves.

Pit liquids approaching the threshold criteria should not be applied to agricultural soils except as a one-time application, and with careful management of potentially damaging levels of sodium. Careful management should include, at a minimum, a laboratory bench scale equilibrium study to define an acceptable loading rate and/or a contingency plan for saline-sodic soil reclamation.

3.1.3 Pit Solids

3.1.3.1 Operative Criteria

EC, SAR, ESP and O&G must be measured for pit solids in order to provide sufficient information to properly land dispose according to guidance values (4 mmho/cm, 12, 15% and 1%, respectively). Land disposal may include such techniques as burial or landfill, and landspreading. Roadspreading is not recommended for pit solids.

EC and O&G are operative parameters for materials buried or landfilled. EC, O&G, SAR and ESP are used for managing waste disposal by landspreading.

3.1.3.2 Sampling and Analysis

Sampling of pit solids can be achieved by simply pushing a hollow tube, open at both ends, into the solids across all layers such that the composition of the sample is representative of the entire matrix. Earthen pits are sampled to consolidated native soil. A lined pit is sampled to the top of the liner. An end cap or other suitable plugging device usually will allow a back suction to form keeping the sample in the core barrel on retrieval.

Experience has shown that the best approach to sampling a large pit is to divide it into sections with an area of approximately 5000 ft^2. A minimum of 10 cores are then taken in each section and composited to form a section sample. Section samples may be analyzed separately and averaged as representative of pit solids, or composited by weight or volume prior to analysis.

E&P waste:soil mixtures are sampled after closure to verify correct landspreading procedures. Multiple corings are made for preparing composites representative of the zone of incorporation.

Analytical protocols specific for each parameter are detailed in the attached Appendix.

3.1.3.3 Pit Solids Disposal

The most limiting constituent for managing E&P wastes by landspreading is salt (NaCl). Sodicity (SAR for pore liquids and ESP for solids) is a major concern but easily managed by calcium amendment (i.e., gypsum) if the total salt is kept in check. Petroleum hydrocarbons, as O&G, are best managed in the

natural environment by the landspreading technique.

In practice, E&P waste solids are added to the receiving soil then disked to an appropriate depth such that the final waste:soil mixture meets the constituent threshold criteria.

Landspreading is best suited in the more humid and warmer sectors of the country (precipitation > 25 in/year). Higher rainfall affords a greater margin for error. E&P waste solids are very difficult to manage from a standpoint of spreading and mixing. This generally results in what may be termed as "hot spots." Organics will degrade, but salts require leaching by rainfall to move them out of the intended root zone. Also amendments to alter sodic soil conditions require significant soil moisture for cation exchange to occur and displace desorbed Na.

Burial or landfill is best suited to a semi-arid (rainfall < 20 in/year) or drier climate with no potential for leaching to the subsurface. The recommended criteria could be relaxed in semi-arid regions after evaluation of the site for any potential environmental impact.

3.2 Summary of Guideline Thresholds and Application

A summary of guideline thresholds and application relative to waste type, method of disposal, and criteria is given in Table 3. E&P waste type is differentiated between liquid and solid phases. Pit solids may have utility as construction fill in arid and semi-arid regions, but generally do not constitute a suitable weight-bearing and driving surface. Therefore, roadspreading is not recommended as a method of disposing pit solids. Road-

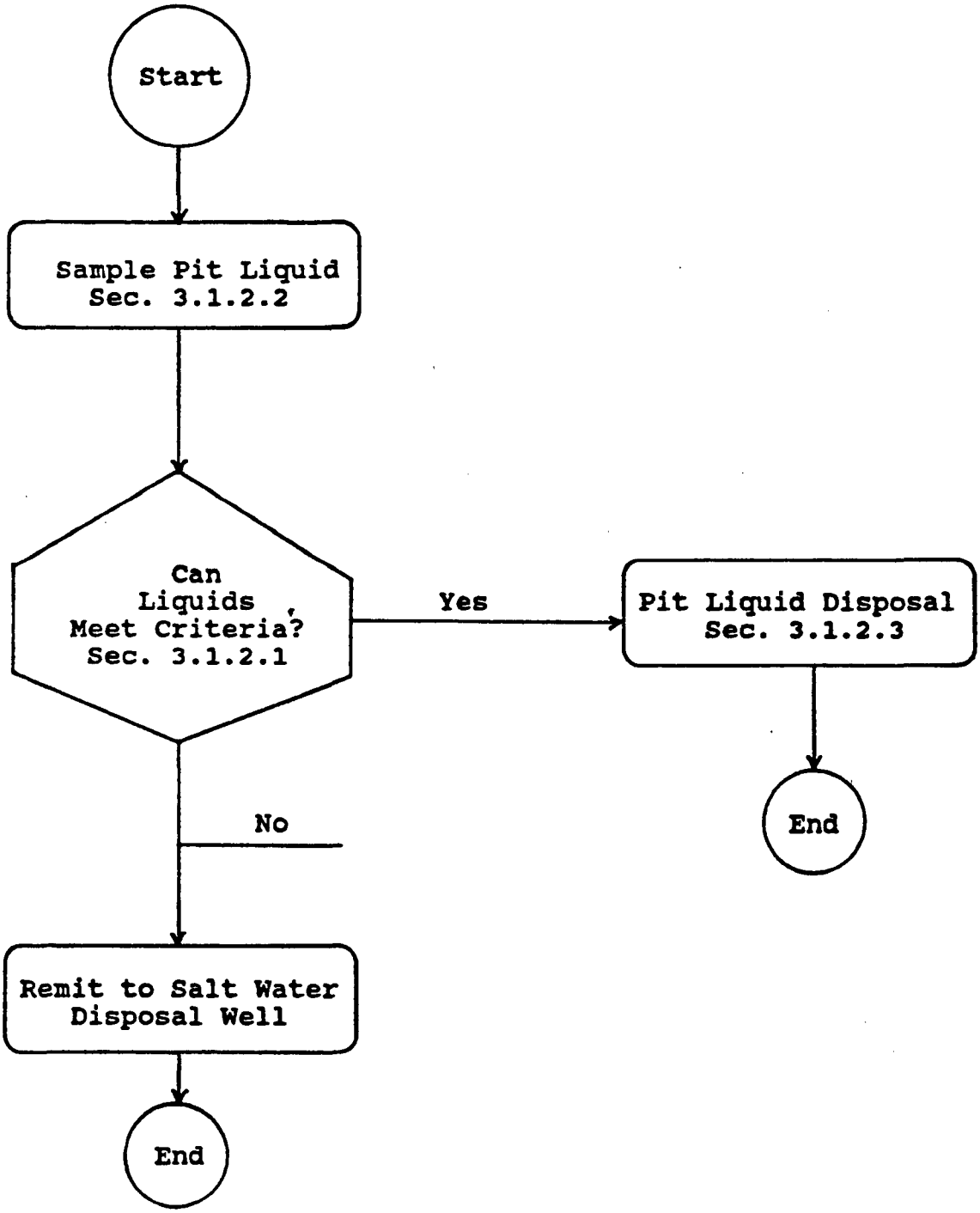
spreading applications are defined in the API Environmental Guidance Document.

Table 3. Summary of E&P Waste, Disposal Technique, and Operative Criteria

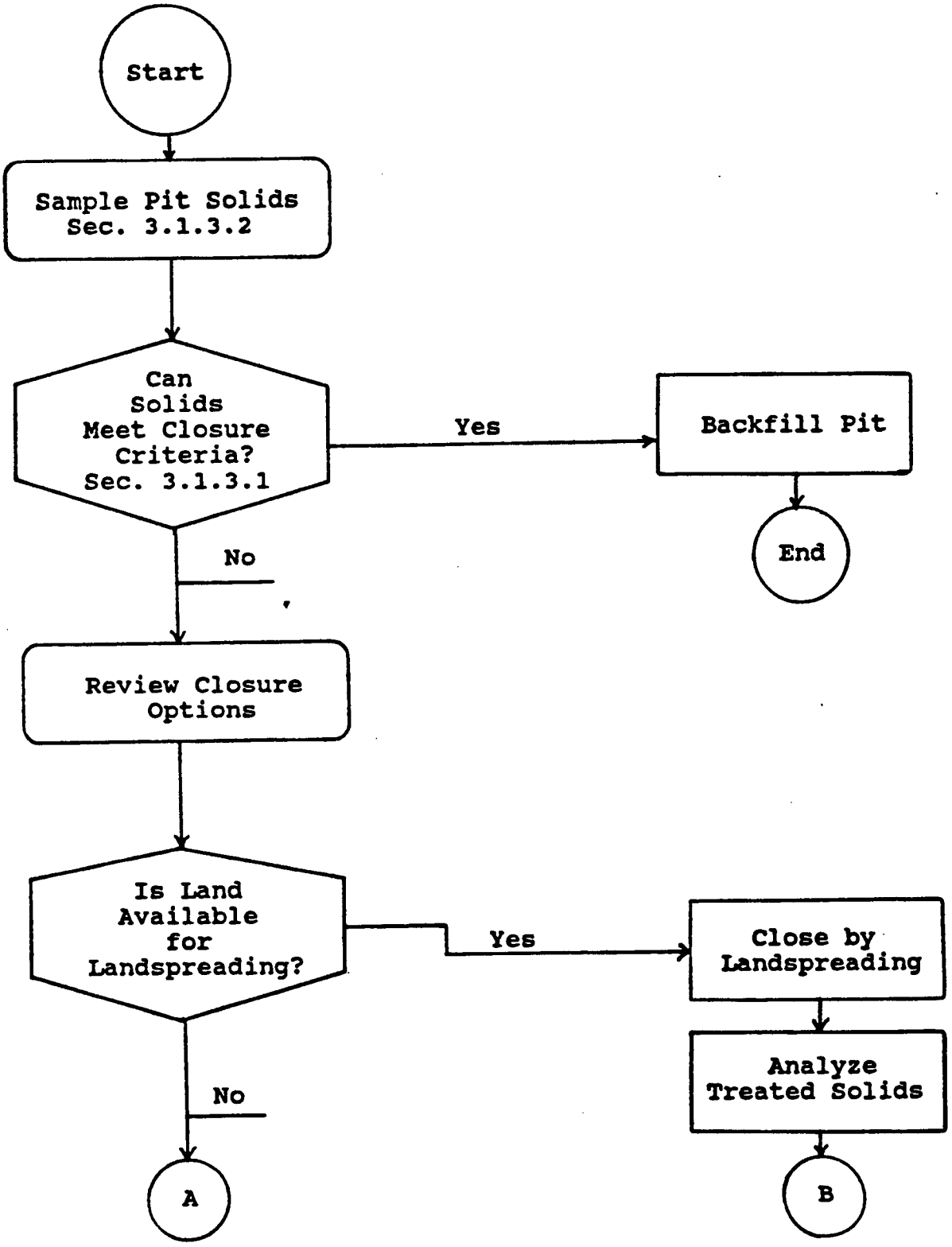
E&P Waste	Disposal Technique	Criteria EC	SAR	ESP	O&G
		mmho/cm	ratio	%	%
Liquid	roadspreading	4	NA*	NA	NA
	landspreading	4	12	15	1
Solids	landspreading	4	12	15	1
	burial or landfill	4	NA	NA	1

NA* - not applicable

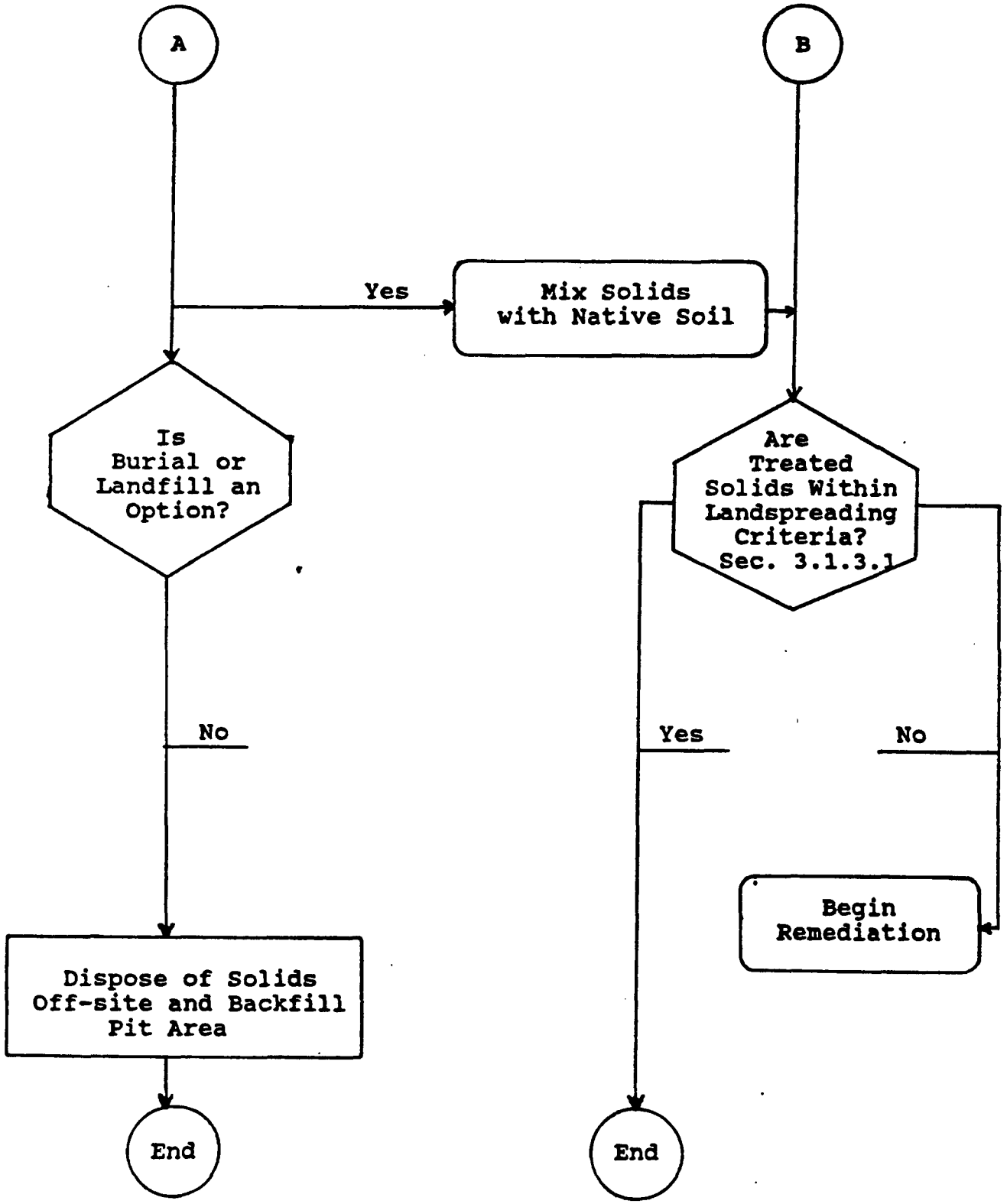
3.3 Flow Diagram for Pit Liquid Disposal



3.4 Flow Diagram for Pit Solids



3.4 Flow Diagram for Pit Solids (Continued)



3.5 Parameters and Example Calculations for Management of Pit Wastes by Land Treatment

3.5.1 Pit Material and Native Soil Characteristics

Parameter[+]	Pit[++] Liquid	Pit[*] Solids	Native[*] Soil	Threshold[#] Level
Moisture, %	NA	243	NA	NA
TDS, mg/liter	1,410	24,830	272	NA
EC, mmho/cm	2.3	40.5	0.4	4
SAR, ratio	4	25	<1	12
Na, meq/liter	9.3	260	0.4	NA
Ca, meq/liter	10.9	199	2.5	NA
Mg, meq/liter	1.7	16	0.9	NA
CEC, meq/100 g	NA	13.5	39.6	NA
Na, meq/100 g	NA	2.8	0.3	NA
Ca, meq/100 g	NA	18.5	24.8	NA
Mg, meq/100 g	NA	0.3	7.5	NA
ESP, %	NA	20.7	<0.1	15
O&G, %	0.2	10.1	<0.1	1
Volume, bbl	12,938	21,897	NA	NA

[+]Parameters are reported on a dry weight basis unless noted otherwise.

[++]NA means the parameter meets the guidance threshold or is not applicable for that matrix.

[*]Soluble constituents were determined for saturated paste extracts of pit solids and native soil.

[#]An ESP of 12% is recommended in establishing land requirements for Na management.

3.5.2 Determination of Limiting Constituent(s)

3.5.2.1 Pit Liquid Management

a) Comparison of pit liquid analyses and threshold values show no chemical limitation for land application.

b) Native soil loading capacity for Na using an ESP of 12%, and materials distribution depth of 6 in/acre.

Given: 1 acre-6 in = 2,000,000 lb

1 mg/kg = 1 lb/1,000,000 lb

Na, mg/kg = CEC meq/100g X (ESP/100) X 23 mg/meq X 10

= 39.6 X 0.12 X 23 X 10

= 1093

Na, lb/acre-6 in = 1093 mg Na/kg soil X 2

= 2186

c) Total Na mass of pit liquid.

Na,lb = (9.3 meq/l X 23 mg/meq X 3.8 l/gal X 42 gal/bbl X 12,938 bbl/pit) / (1000 mg/g X 454 g/lb)

= 973

d) Land requirement on Na mass basis, assuming a materials distribution to a depth of 6 in

Acres = (973 lb Na) / (2186 lb Na/acre-6 in)

= 0.45

e) Liquid management limitation.

Pit liquid, acre-in = (12,938 bbl X 42 gal/bbl) / (27,152 gal/acre-in)

= 20

f) Native soil has an infiltration rate of 1.12 in/hr but drops to less than 0.1 in/hr within 10 min. A dry surface can receive about 1.3 in without producing runoff.

g) Acreage needed for a one-time application so as not to generate runoff.

Land needed, acre = 20 acre-in/1.3 in application

= 15.4

h) Construction of temporary levees for containment during infiltration reduces land requirement.

3.5.2.2 Pit Solids Management.

a) Comparison of pit solid analyses and recommended thresholds show EC, SAR, ESP and O&G as potential limiting constituents.

b) Given the fact that the exchangeable Ca is high in both waste solids and the receiving soil, one would not consider SAR limiting.

c) Pit solids contained 243% moisture (M) on a dry weight basis. The equivalent percent water on a wet weight basis is 70.85%.

Dry wt, g = (100 g wet wt X 100) / (100 + 243% M)

= 29.15 g

solids, % = (29.15 g / 100 g) X 100

= 29.15%

d) Volume of dry solids used to calculate land requirement.

Dry solids, bbl = 21,897 bbl wet X .2915

= 6383

e) TDS land requirement (based on relationship from Section 2.2.1).

2452 mg/l = (6383 bbl)(24,830 mg/l) + (X bbl)(272 mg/l) / (6383 bbl + X bbl)

X bbl = 65522

acre-6 in = (65522 bbl) / (3875 bbl/acre-6 in)

= 16.9

f) EC land requirement.

4 mmho/cm = (6383 bbl)(40.5 mmho/cm) + (X bbl)(0.4 mmho/cm) / (6383 bbl + X bbl)

X bbl = 64717

acre-6 in = (64717 bbl) / (3875 bbl/acre-6 in)

= 16.7

g) ESP land requirement.

12% = (6383 bbl)(20.7%) + (X bbl)(0.1%) / (6383 bbl + X bbl)

X bbl = 4667

acre-6 in = (4667 bbl) / (3875 bbl/acre-6 in)

= 1.2

h) O&G land requirement.

1 % = (6383 bbl)(10.1%) + (X bbl)(0.1%) / (6383 bbl + X bbl)

X bbl = 64539

acre-6 in = (64539 bbl) / (3875 bbl/acre-6 in)

= 16.7

i) The land-limiting constituent is EC, requiring 64717 bbl of native soil to effect management (EC <4 mmho/cm). The land requirement is met by spreading waste solids over 16.7 acres then mixing it to a depth of 6 inches.

j) Wet solids are spread over the receiving soil at a depth of 2 in, allowed to dry, then mixed with soil to a depth of 6 in by a disk operation.

Depth wet solids, in = (21,897 bbl/16.7 acre) /(647 bbl/acre-in)

= 2.03

k) A salt-sensitive crop such as strawberries would require 68 acres to effect management (EC <1 mmho/cm).

1) Nitrogen (N) is added to the receiving soil in the form of ammonium sulfate or urea at rates to provide an O&G:N ratio of 150:1. Phosphorus (P) and potassium (K) are added to provide a N:P:K ratio of 4:1:1.

O&G, lb/acre = (O&G, 1%) X (10,000 ppm/%) X (2 ppm/lb/acre

= 20,000

N requirement, lb/acre = (20,000 lb O&G/acre) / 150

= 133

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APPENDIX

E&P SAMPLE PREPARATION

1.0 Scope and Application

1.1 This method is used to prepare samples for analysis by the protocols listed below:

1.1.1 Sodium Adsorption Ratio

1.1.2 Exchangeable Sodium Percentage

1.2.3 Cation Exchange Capacity

2.0 Summary of Method

2.1 The sample is homogenized, dried at 105C and ground prior to the individual analyses.

3.0 Apparatus and Materials

3.1 Oven capable to 105C (+/- 2C)

3.2 Grinding apparatus

3.3 Drying pans

3.4 Balance

4.0 Procedure

4.1 Homogenize the sample thoroughly.

4.2 Weigh a pan to the nearest 0.1 g that is large enough to hold 250-g sample.

4.3 Weigh 100- to 200-g homogenized sample to pan, and place pan in oven at 105C until a constant weight is achieved. Record weights to calculate moisture content.

4.4 Grind the material so that it will pass a 2-mm sieve. Sample is now ready for analysis.

5.0 Procedure for Hydrophobic Material

5.1 Tests for hydrophobicity

5.1.1 Visible blobs of oil or grease

5.1.2 The sample presses into a single, damp-looking mass when crushed with mortar and pestle and will not hydrate with water.

5.1.3 Sample leaves an oily mark when pressed between two pieces of filter paper.

5.1.4 Sample feels damp when pinched between fingers.

5.2 Place sample in muffle furnace and heat to 250C for 1hr.

5.3. Increase temperature to 350C at 50C intervals allowing smoke to dissipate between adjustments. Do not allow sample to catch fire or exceed 390C.

5.4 Cool the sample and grind it to pass 2-mm sieve. The sample is now ready for the appropriate analyses.

6.0 Calculation

6.1 Moisture Content

$$\text{Moisture},\% = (W - D)/(D - P) \times 100$$

where: W = wet weight of sample + pan, g

D = dry weight of sample + pan, g

P = weight of pan, g

SATURATED PASTE EXTRACT

1.0 Scope and Applications

1.1 Saturation percentage is a condition of soil related to field moisture and associated plant response. It is reproducible and approximately equivalent to twice the percentage moisture at field capacity (0.3 bar) and four times the percentage moisture at permanent wilting (15 bar). This method is used to obtain a saturation extract for the following analyses:

1.1.1 TDS

1.1.2 EC

1.1.3 SAR

2.0 Summary of Method

2.1 Water is added to a known amount of sample until the point where no more water can be added without forming free water layer.

3.0 Interferences,

3.1 Excessive stirring puddles the sample and reconstitute the dispersed condition of most E&P waste solids. Puddled soils represent a gross overestimation of the saturation percentage.

4.0 Apparatus

4.1 Container of 250-ml capacity.

4.2 Buchner funnel, filter paper, vacuum source, and collection vessel.

5.0 Procedure

5.1 Weigh 100-g, dried, ground and sieved solids into 250-ml container.

5.2 Add distilled water to fill pores, stirring gently as needed to achieve saturation. The solid:water mixture is consolidated occasionally by tapping container on workbench.

5.3 At saturation the mixture glistens as it reflects light and flows slightly when the container is tipped.

5.4 Allow paste mixture to stand 1 hr and check for conditions of paste. Mixture should not stiffen nor should free water form at the surface.

5.5 Add solid sample material if free water forms or more distilled water if mixture stiffens.

5.6 Record the weight of water used to achieve saturation and transfer to the vacuum filter apparatus. Vacuum extraction should be terminated when air begins to pass through the filter.

5.7 Extract is used to measure TDS, EC and SAR

6.0 Calculation

Saturation Percentage (SP),% = (W - D)/(D - C) X 100

where:

W = wet weight of sample + container

D = dry weight of sample + container

C = weight of container

7.0 References

U. S. Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkali soils. Agriculture Handbook 60.

TDS

1.0 Scope and Application

1.1 This can be applied to E&P aqueous phase samples including produced water, pit liquids and saturated paste extracts.

2.0 Summary of Method

2.1 Total dissolved solid is mineral matter passing a standard glass filter, which remains after drying at 180C to constant weight.

3.0 Interferences

3.1 The principle interference is from fine clay fractions and organic colloids passing the filter and stablizing at 180C.

4.0 Apparatus and Materials

4.1 Evaporating dishes

4.2 Filtration equipment

4.3 0.45-um filters

4.4 Drying oven, for operation to 180C (+/- 2C)

4.5 Analytical balance, capable to 0.1 mg

5.0 Procedure

5.1 Assemble filtration equipment and insert 0.45-um filter.

5.2 Apply vacuum and wash disk with three, 20-ml volumes of distilled water. Discard washings.

5.3 Filter measured volume of homogenized sample through filter, wash with three, 10-ml volumes of distilled water, allowing complete drainage between washings.

5.4 Transfer filtrate to weighed evaporation dish previously cleaned by ignition to 550C for 1 hr.

5.5 Evaporate water at 180C to a constant weight. Evaporation dish is cooled in desiccator prior to weighing.

6.0 Calculation

TDS, mg/liter = (A - B) X 1000/sample volume, ml

where: A = weight of residue + dish, mg

B = weight of dish, mg

7.0 References

7.1 Standard Methods for the Examination of Water and Wastewater. 1985. 16th Edition. APHA. AWWA. WPCF. Method 209 B. Total Dissolved Solids Dried at 180C.

EC

1.0 Scope and Application

1.1 Electrical conductivity is an indicator of the quantity of soluble salts in an aqueous sample. This method applies to pit liquids and saturated paste extracts.

2.0 Summary of Method

2.1 EC is measured direct with the reading corrected to specific conductance at 25C.

3.0 Apparatus and Materials

3.1 Temperature-compensating conductivity meter

3.2 Conductivity cell

3.3 Reagents

3.3.1 ASTM Type II water

3.3.2 0.01 N potassium chloride

4.0 Procedure

4.1 Rinse conductivity cell and fill with calibration standard. Read and record conductivity.

4.2 Rinse conductivity cell and fill with sample. Read and record conductivity.

5.0 Calculations

5.1 Cell Constant, C

$$C = (1.413 \text{ mmho/cm}) / (EC_{KCL} \text{ mmho/cm})$$

where:

EC_{KCL} = measured conductance, mmho/cm

5.2 Specific Conductance of Sample

$$EC = (EC_m)(C)$$

where:

EC_m = measured conductance of sample, mmho/cm

C = cell constant

6.0 References

6.1 Rhoades, J.D. 1982. Soluble Salts. p. 172-173. In A.L Page (ed.) Methods of Soil Analysis. Part 2 - Chemical and Microbiological Properties. 2nd Edition. (Ed.) ASA Agronomy Monograph 9.

SAR

1.0 Scope and Application

1.1 This method is applicable to most E&P wastes including pit liquids and water extracts of pit solids or waste solid:soil mixtures.

2.0 Summary of Method

2.1 Soluble cations are determined by atomic absorption spectrophotometry or other suitable instrumentation for pit liquids or water extracts of solid-phase samples. The sodium adsorption ratio (SAR) is calculated from the cationic distributions.

3.0 Procedure

3.1 Calibrate instrumentation using standards of known concentration.

3.2 Read concentrations of Na, K, Mg and Ca direct for pit liquid samples and aqueous extracts including saturated pastes.

4.0 Calculations

4.1 Conversion to meq/liter

Na, meq/liter = (Na mg/liter) / (23 mg/meq)

K, meq/liter = (K mg/liter) / (39 mg/meq)

Ca, meq/liter = (Ca mg/liter) / (20 mg/meq)

Mg, meq/liter = (Mg mg/liter) / (12 mg/meq)

4.2 SAR

$$SAR = (Na, meq/l) / \sqrt{(Ca, meq/l + Mg, meq/l)/2}$$

5.0 References

5.1 Rhoades, J.D. 1982. Soluble Salts. p. 173-174 A.L Page (ed.) Methods of Soil Analysis. Part 2 - Chemical and Microbiological Properties. 2nd. Edition. ASA Agro. Monograph 9.

EXCHANGEABLE CATIONS

1.0 Scope and Application

1.1 This method is applicable to most soils and E&P waste solids and is used to determine the distribution of cations adsorbed on the solid phase.

2.0 Summary of Method

2.1 The sample is saturated with an excess of ammonium acetate resulting in an exchange of adsorbed cations. The cations released into solution are then quantified as extractable cations and when adjusted for soluble cations are reported as exchangeable cations.

3.0 Interferences

3.1 Sparingly soluble salts may give erroneously high cation distribution values.

4.0 Apparatus and Materials

4.1 Centrifuge and centrifuge tubes

4.2 Mechanical shaker

4.3 Atomic absorption or other suitable instrumentation

5.0 Procedure

5.1 Weigh 5 g of sample to a 50-ml centrifuge tube.

5.2 Add 30-ml 1.0N ammonium acetate reagent to the tube, stopper, shake for 5 min and centrifuge to yield a clear, supernatant liquid.

5.3 Decant the supernatant as completely as possible into a 100-ml volumetric flask. Repeat step 5.2 two more times combining extracts.

5.4 Dilute to volume, mix, and determine the amounts of the various extracted cations using AAS or other suitable instrumentation.

5.5 Soluble cations must be determined for an aqueous extract of the same sample if not determined previously.

6.0 Calculations

6.1 Extractable Cations

extractable cation, meq/100g = (cation concentration of extract in meq/liter X 10) / (sample wt in g)

6.2 Soluble Cations

soluble cation, meq/100g = (cation concentration of saturation extract in meq/liter) X (saturation percentage) / 1000

6.3 Exchangeable Cations

exchangeable cation, meq/100g = (extractable cation in meq/100g) - (soluble cation in meq/100g)

7.0 References

7.1 Thomas, G.W. 1982. Exchangeable Cations. p. 159-161. In A.L. Page (ed.) Methods of Soil Analysis. Part 2 - Chemical and Microbiological Properties. 2nd. Edition. ASA Agron. Monograph 9.

CATION EXCHANGE CAPACITY

1.0 Scope and Application

1.1 This method is applicable to most soils and E&P waste, including calcareous and non-calcareous samples.

2.0 Summary of Method

2.1 The sample is saturated with an excess of sodium acetate solution, resulting in an exchange of other cations by sodium. Subsequently, excess sodium is rinsed from the sample followed by quantitative desorption of sodium by ammonium. The concentration of displaced sodium is then determined by atomic absorption, emission spectroscopy, or an equivalent means as available and approved by EPA.

3.0 Interferences

3.1 Soluble salts and gypsum will interfere with the CEC determination if they are present in sufficient quantities. These may be overcome by washing the solids with water before saturating with sodium, or employ a more exhaustive saturation procedure.

4.0 Apparatus and Materials

4.1 Centrifuge and centrifuge tubes

4.2 Mechanical shaker

4.3 Volumetric flask: 100 ml

4.4 Atomic absorption or equivalent instrumentation

5.0 Reagents

5.1 Sodium acetate 1.0 N buffered to pH 8.2

5.2 Ammonium acetate 1.0 N buffered to pH 7.0

5.3 Isopropyl alcohol: 99%

5.4 Sodium standards in 1.0 N sodium acetate

6.0 Sample Preparation

6.1 See E&P Sample Preparation

7.0 Procedure

7.1 Weigh 5-g sample into a 50-ml centrifuge tube.

7.2 Add 30 ml of 1.0 N sodium acetate, stopper and shake for 5 min, then centrifuge to clear supernatant.

7.3 Decant and discard supernatant, and repeat step 7.2 three more times to effect sodium saturation.

7.4 Add 30 ml of 99% isopropyl alcohol, stopper and shake for 5 min, then centrifuge to clear supernatant.

7.5 Decant alcohol and discard supernatant, and repeat step 7.4 three more times to effect washing of solids.

7.6 Add 30 ml of ammonium acetate, stopper and shake 5 min, then centrifuge to clear supernatant liquid. Decant supernatant into a 100-ml volumetric flask.

7.8 Repeat step 7.6 two more times decanting into the same volumetric flask.

7.9 Dilute the volumetric to mark with ammonium acetate,and determine sodium concentration by atomic absorption or other instrumentation

8.0 Calculations

8.1 CEC

CEC, meq/100 g = (sodium, meq/liter X 10) / (sample wt, g)

8.2 ESP

ESP, % = (Exchangeable Sodium, meq/100g) / (CEC, meq/100g) X 100

9.0 References

9.1 Chapman, H.D. 1965. Cation Exchange Capacity. p. 891-900. In C. A. Black (ed.) Methods of Soil Analysis. Part 2-Chemical and Microbiological Properties. ASA Agron. Monograph 9.

OIL & GREASE

1.0 Scope and Applications

1.1 This method is used to recover O&G by chemically drying wet E&P waste solids and then extracting by Soxhlet apparatus.

2.0 Summary of Method

2.1 Anhydrous sodium sulfate is used to combine with water and enhance recovery of petroleum hydrocarbon. After drying, the O&G is extracted with methylene chloride using the Soxhlet apparatus.

3.0 Apparatus and Materials

3.1 Soxhlet extraction apparatus

3.2 Analytical balance

3.3 Extraction thimble

3.4 Grease-free glass wool

3.5 Vacuum distilling apparatus

3.6 Desiccator

4.0 Reagents

4.1 Concentrated hydrochloric acid

4.2 Anhydrous sodium sulfate

4.2 Nanograde methylene chloride

5.0 Procedure

5.1 Weigh 25 g (+/- 0.5g) of wet E&P waste solid of soil into 150-ml beaker.

5.2 Acidify to pH 2 with concentrated hydrochloric acid.

5.3 Add anhydrous sodium acetate as necessary to dry solids.

5.4 Transfer sample to extraction thimble, covering sample

with glass wool, then place in Soxhlet apparatus.

5.5 Add methylene chloride and commence extraction at 20 cycles/hr for a minimum of 6 hr.

5.6 Using grease-free glass wool filter extract into a pre-weighed boiling flask, previously rinsed with solvent.

5.7 Connect boiling flask to vacuum distillation head and evaporate solvent.

5.8 Place boiling flask in a dessicator to cool and remove trace water on glass.

5.9 Weigh boiling flask and record weight gain.

6.0 Calculations

6.1 O&G

O&G,% = (weight gain in flask, g) / (sample wt, g) X 100

where:

sample wt, g = (wet weight X 100) / (100 + % moisture)

7.0 References

7.1 Test Methods for Evaluating Solid Waste. 1986. Method 3540. Soxhlet Extraction. EPA SW-846. USEPA Washington D.C.

Ref #17

The Effect of Oil Pollution of Soil on Germination, Growth and Nutrient Uptake of Corn[1]

E. J. Udo and A. A. A. Fayemi[2]

ABSTRACT

The effect of crude oil pollution of soil on the growth of plants and uptake of nutrients was investigated by growing corn (*Zea mays* L.) on a soil polluted by crude petroleum. The levels of the crude oil application varied from 0 to 10.6% by weight of soil. Three corn crops were raised in succession, each for a period of 6 weeks, in the same soil. The yields and plant contents of N, P, K, Ca, Fe, and Mn were determined. The soil was analyzed for organic C, total and available N, extractable P, and exchangeable K, Ca, Fe, and Mn after each cropping. Germination and yields were drastically reduced as the level of pollution increased. At 4.2% crude oil pollution level, the average reductions were 50% and 92% in germination and yield, respectively. The amount of organic C, total N, and exchangeable K, Fe, and Mn increased in the soil with level of crude oil addition, while extractable P, NO_3-N, and exchangeable Ca were reduced. The poor growth was attributed to suffocation of the plants caused by exclusion of air by the oil or exhaustion of oxygen by increased microbial activity, interference with plant-soil-water relationships, and toxicity from sulfides and excess available Mn produced during the decomposition of the hydrocarbons.

Additional Index Words: carbon-nitrogen ratio, crude petroleum, hydrocarbons in soil, manganese toxicity, nitrate immobilization, nitrogen fixation, reducing conditions.

Oil pollution of the environment is a common occurrence in the oil industry. When this pollution occurs in soils, the physical and chemical properties of the soil undergo major changes which affect the growth of plants.

A number of workers have observed significant changes in the soil properties as a result of oil or gas contamination. Schollenberger (1930) and Adams and Ellis (1960) showed that gas pollution brought about reducing conditions in the soil resulting in the accumulation of manganous (Mn) and ferrous (Fe), ions which may reach a toxic level for plants. Baldwin (1922) and Murphy (1929) reported a reduction in nitrates in oil-polluted soils. After an oil blowout in the River State of Nigeria, Odu (1972) observed increases in C/N ratios and microbial counts in the contaminated soils when compared to the surrounding normal soils. Loss of structure and an increase in the water holding capacity were observed in "gassed" soil by Schollenberger (1930), and Adams and Ellis (1960), respectively.

Growth of plants in the contaminated soils has been observed to be inhibited or enhanced depending on the changes taking place in the soil. Schollenberger (1930) observed some injury to oats (*Avena sativa* L.) after 2 weeks of pollution with gas. Harper (1939) indicated no growth of Bermudagrass (*Cynodon dactylon* L.) and wheat (*Triticum aestivum* L.) above gas leaks. Similar observations of injurious effects were made by Murphy (1929), Baldwin (1922), Schwendinger (1968), and Odu (1972). Garner (1971) attributed the deterioration and death of trees and ornamentals to toxicity by sulfides and excess Mn brought about by the anaerobic soil atmosphere created by the leaking natural gas displacing the soil air.

Although the damaging effect has been more widely reported, some workers have observed improvement in the growth of crops as a result of soil contamination with crude oil or natural gas. Plice (1948) found that the soil contaminated with crude oil to a depth of 121.9 cm (4 feet) remained boggy and barren for several years, but after 7 years one of the oil-soaked soils appeared more productive than the surrounding normal soil. Carr (1919), Schollenberger (1930), and Harper (1939) also reported some enhancement of growth of crops in the gas- or oil-contaminated soil.

The explanation of these rather conflicting reports is that when a soil is contaminated with natural gas or crude oil, plant growth is adversely affected for a time. After the hydrocarbons have been decomposed and changed into the normal soil organic matter, the growth of plants is improved because of the increase in organic matter, addition of plant nutrients present in the oil or gas, and the subsequent improvement of the soil physical conditions.

A number of blowouts from oil wells recently occurred in Nigeria causing serious crude oil pollution of some soils. The purpose of this investigation was to determine the effect of crude oil pollution of the soil on the germination, growth, and nutrient uptake of corn (*Zea mays* L.) soon after the pollution.

MATERIALS AND METHOD

The soil used came from the rubber plantation plot of the University of Ibadan Teaching and Research Farm. It is classified as ferruginous tropical soil. The surface soil was collected, air-dried, and passed through a 2-mm sieve.

Four-kilogram samples were put in plastic buckets and each were given a basal dressing of NPK at the rate of 90, 67, and 45 kg/ha, respectively. Seven levels of crude oil application were used by adding 0, 50, 100, 200, 300, 400, and 500 ml of oil to different pots. These corresponded to approximately 0.0, 1.1, 2.1, 4.2, 6.4, 8.5, and 10.6% levels of crude oil pollution of the soil by weight. (The density of the oil was found to be 0.875 g/cm^3.) The soil was well-mixed with the oil. The treatments were replicated three times.

Four maize grains were planted in each pot and after germination, the seedlings were thinned down to two per pot. The plants were watered daily to about field capacity throughout the growing period. The plants were harvested 6 weeks after planting and three crops were raised in succession in the same soil.

After each harvest, the soils were analyzed for total N by the macro-Kjeldahl method (Jackson, 1958). Exchangeable Ca, K, Fe, and Mn were extracted with normal ammonium acetate (Jackson, 1958) and Ca and K were determined by flame photometer, while Fe and Mn were determined by atomic absorption spectrophotometer; organic C by the method of Walkley and Black (1934); extractable P by Bray's P_1 method (Bray and Kurtz, 1945); and ammonium and nitrate nitrogen by the method of Greweling and Peech (1968).

[1]Contribution from the Dep. of Agronomy, University of Ibadan, Nigeria. The work was supported in part by Shell B. P. and Safrap Oil Companies of Nigeria. Received 8 April 1974.

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The plant samples were ground and analyzed for nutrient content. Total nitrogen was determined by the micro-Kjeldahl method (Jackson, 1958). After wet-digesting, P was determined in the extract by the vanadomolybdate method (Kitson and Mellon, 1944), Ca and K by flame photometer, and Fe and Mn by atomic absorption spectrophotometer.

The crude oil was analyzed for N content by the micro-Kjeldahl method (Jackson, 1958). For the determination of Mn, Fe, Ca, K, and P, the crude oil was digested with concentrated H_2SO_4 and after burning off the carbonaceous material, the residue was dissolved in dilute HCl. Manganese, Fe, Ca, and K were determined as previously described and P by the method of Murphy and Riley (1962). Oxidizable organic C was determined by the chromic acid method (Walkley and Black, 1934).

RESULTS AND DISCUSSION

Effect on Germination

Maize germination was affected adversely by the pollution of the soil, the effect being proportional to the level of crude oil pollution. In high pollution levels, germination was not only delayed, but the percentage of germination was greatly reduced. At the 10.6% level of crude oil addition, there was no germination at all. The effect on the viability of maize grains is shown in Fig. 1. At the 6.8% level of crude oil application only 44% of the grains germinated. When dug up, the ungerminated grains were found to be swollen and shiny indicating much oil absorption. These observations agree with the findings of Murphy (1929) and Plice (1948). Murphy noted that the small amounts of oil would delay germination and larger amounts might even stop germination entirely. Plice noticed that volatile fractions of oil had a high wetting capacity and penetrating power. If in contact with a seed, the oil would enter the seed coat and readily kill the embryo.

Effect on Growth

The performance of the maize plants after germination was seriously affected by oil pollution. Growth was generally poor in the polluted soil samples. The higher the level of pollution, the poorer the performance of the maize seedlings. The affected plants showed general chlorosis of the leaves and with high levels of crude oil application, the plants tended to dehydrate indicating water deficiency. Growth was stunted and there was an eventual death of the growing point.

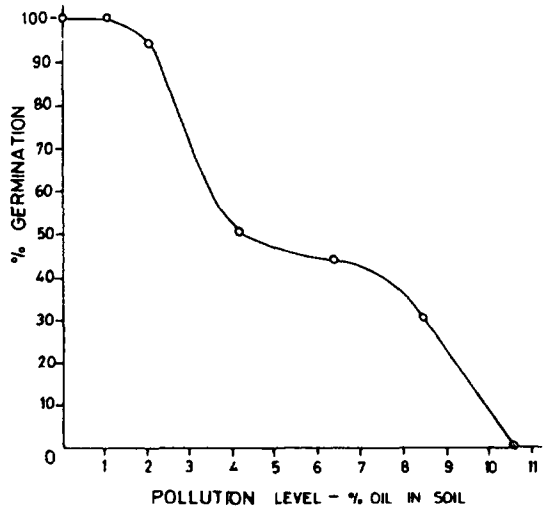

Fig. 1—Effect of the level of crude oil addition to the soil on the germination of maize grains.

Table 1—Dry matter yield of corn as influenced by oil pollution of the soil

Oil in soil	Yield				Reduction in yield*
	1st crop	2nd crop	3rd crop	Mean	
%	g/pot				%
0.0	36.3	20.6	21.5	26.1	0
1.1	21.0	16.9	17.4	18.4	30
2.1	14.8	13.4	8.3	12.2	53
4.2	1.6	2.3	2.4	2.1	92
6.4	1.6	1.8	1.4	1.6	94
8.5	1.4	1.2	1.4	1.3	95
10.6	0.0	0.0	0.0	0.0	100

* Based on the mean values with control taken as the maximum yield.

Effect on Yield

The effect of polluting the soil with crude petroleum on yield of corn is shown in Table 1. The yield was expressed as the weight of dry matter. Dry matter yield was generally reduced by oil pollution of the soil when compared with the yield in the unpolluted soil. The yield reduction increased with the increasing level of the crude oil addition varying from 30% dry matter yield reduction at 1.1% crude oil pollution to 100% at 10.6% level of contamination.

After studying the damaging effect of oil on plants, Schwendinger (1968) reported that plants could tolerate up to 3% oil pollution of the soil. The present investigation shows that a reduction in growth occurred even when the level of crude oil pollution was as low as 1%. It is, however, possible that at levels lower than 1% the injurious effect may not be noticeable.

Some stimulation of growth has been reported at the low levels of oil in the soil. Carr (1919) observed improved growth and root nodule development of soybeans (*Glycine max* L. Merr.) at 0.75% of crude oil in the soil. A further investigation is, therefore, necessary to establish the critical level of pollution that will affect the different plant species especially in the tropical soils.

Effect on Nutrient Uptake

The data in Tables 2 and 3 show the analysis of the nutrients in plant tissues expressed in percent dry matter and as total content, respectively. The concentration of N and P showed no variation with the level of pollution, but the percentage of K, Ca, Fe, and Mn content of the plant appeared to increase with the level of pollution. This may suggest that pollution of soil with crude oil could result in enhanced uptake or accumulation of these nutrients by the plants. However, it was observed that at a level of pollution above 2.1%, the plants suffered serious injuries as a result of the pollution, and the dry matter production was greatly reduced. An increased concentration of this nature may, therefore, be expected since the plants had stopped growing normally. The fact that no accumulation of nutrients occurred is confirmed in Table

Table 2—Effect of oil addition to the soil on the nutrient uptake of corn

Oil in soil	Nutrient content in plant tissue					
	N	P	K	Ca	Fe	Mn
%	%				ppm	
0.0	0.68	0.17	0.75	0.32	138	137
1.1	0.63	0.11	0.82	0.43	133	1,233
2.1	0.70	0.11	1.82	0.50	201	1,500
4.2	0.68	0.12	2.90	0.60	224	1,266
6.4	0.97	0.16	2.89	0.77	292	1,925
8.5	0.68	0.15	3.20	0.67	259	1,290

Table 3—Total nutrient content of plant tissue as affected by the level of crude oil addition to the soil

Oil in soil	N	P	K	Ca	Fe	Mn
%	g					
0	0.177	0.044	0.196	0.084	0.0036	0.0036
1.1	0.116	0.020	0.151	0.079	0.0024	0.0227
2.1	0.084	0.013	0.222	0.061	0.0024	0.0183
4.2	0.014	0.003	0.061	0.013	0.0004	0.0026
6.4	0.016	0.003	0.046	0.012	0.005	0.0031
8.5	0.009	0.002	0.042	0.009	0.003	0.0017

3 which shows no increase in total uptake as the level of pollution increased. With the exception of K and Mn which showed some increase over the control up to 2.1% level of oil, the total nutrient content of maize plants tended to decrease with increase in the level of oil application. However, for Mn it was obvious that the uptake was enhanced by the oil addition and the concentration in the plant tissues could be regarded as reaching a toxic level. According to Labanauskas (1966) a concentration of Mn in plant tissues on a dry weight basis up to 1,000 ppm will be toxic to plants. Morris (1948) in his study of the content of Mn in sweetclover (*Melilotus indica*) and lespedeza (*Lespedeza* sp.) found that plants having a level of 400 to 500 ppm Mn in the tissues showed obvious signs of Mn toxicity. Garner (1971) also partly attributed the death of woody ornamentals to excess available Mn resulting from the contamination of soil with natural gas. The data in Table 2 strongly indicate that one of the causes of the poor performance of corn plants was toxicity caused by excess Mn.

Effect on Soil Properties

The analysis of the crude oil revealed a content of 0.16% of N and 49.92% of oxidizable C. The other elements—Ca, K, Fe, Mn, and P were not detected and, therefore, could be regarded negligible if present. The addition of the crude oil to the soil would, therefore, raise the level of total N in the soil by 0.0018% at 1.1% crude oil addition and up to 10 times this value at 10.6% pollution level. The corresponding increase in organic carbon would be 0.55% and 5.3% at 1.1% and 10.6% crude oil pollution, respectively.

After harvesting the crop, the soil was analyzed for organic C, total N, NH_4-N, NO_3-N, extractable P, and exchangeable K, Ca, Fe, and Mn. The results are shown in Tables 4 and 5. The organic C increased from about 1% in the unpolluted sample to over 6% in the sample containing 10.6% crude oil. The corresponding range of total N

Table 4—Effect of crude oil addition to the soil on organic carbon, total N, NO_3-N, extractable P, and pH of the soil

Oil in soil	Organic carbon	Total nitrogen	Percent NO_3-N	NH-N	C/N	Extractable P	pH
	%		ppm			ppm	
0.0	1.00	0.078	4.1	20.3	12.8	17.9	6.00
1.1	1.41	0.089	5.4	18.8	15.8	14.7	6.20
2.1	1.85	0.095	10.2	18.9	19.5	17.4	6.20
4.2	2.84	0.101	1.9	28.0	28.1	16.2	6.25
6.4	4.07	0.115	1.3	19.7	35.4	9.3	6.30
8.5	5.05	0.117	1.1	22.7	43.2	5.8	6.33
10.6	6.71	0.126	1.1	24.4	53.2	3.0	6.38

was from 0.078 to 0.126%. At 10.6% pollution level, the percent increase attributable to N content of the oil would be 23 whereas what was found in the soil amounted to about 62% increase of total N. The excess of total N over the amount attributed to the added crude oil may be due to the fixation of atmospheric N by the microorganisms which assimilated the hydrocarbons as suggested by Schwendinger (1968).

The increase in organic C at 10.6% pollution was 470%. This was more than 5 times greater than the corresponding increase in total N. Obviously, these increases were attributable to the carbon from the crude oil. The greater increase in the organic C resulted in high C/N ratios especially with high levels of crude oil addition to the soil. The ratios varied from 12.8 in the control to 53.3 in the treatment with 10.6% crude oil. The soil content of NO_3-N was reduced by the oil additions, but NH_4-N remained approximately constant in all the treatments. The high C/N ratios leading to immobilization of the soil nitrates, coupled with the reducing environments brought about by the oil pollution, accounted for the low level of NO_3-N in the oil-treated samples.

The amount of extractable P decreased when the level of oil addition to the soil was higher than 4.2%. This agrees with the preliminary investigation in this laboratory on the effect of oil pollution on soil properties (Udo, 1973). This is contrary to the findings of Adams and Ellis (1960) who found that available P increased in the gas-polluted soil. In the latter report, the pH of the soil was brought to around 7 by the gas pollution, a situation that would favour high availability of P. In the present investigation the pH of the soil was not appreciably affected and still remained in the acidic range. The reduction in the extractable P was probably due to the high C/P ratio resulting from the crude oil addition. Since the oil contained a negligible amount of P, the microorgan-

Table 5—Effect of crude oil addition on the exchangeable cations in the soil

Oil in soil	Exchangeable cations in soil				
	Ca	K	Fe	Mn	Fe/Mn
%	ppm				
0.0	4,080	32.4	9.5	14.0	0.68
1.1	3,000	28.5	12.6	33.0	0.38
2.1	3,020	39.4	22.0	50.0	0.44
4.2	3,020	101.8	32.3	89.0	0.36
6.4	2,280	124.0	32.7	85.0	0.38
8.5	2,580	109.2	23.9	99.0	0.24
10.6	1,980	83.5	21.9	75.0	0.29

isms which attack the hydrocarbons would immobilize the inorganic P in the soil thus bringing about a reduction in the extractable P.

The addition of the oil to the soil caused an increase in the level of exchangeable Fe and Mn; the increase with increasing pollution levels being more pronounced in the case of Mn. The ratio of exchangeable Fe to Mn (Fe/Mn) was low, the values decreasing with the increasing level of crude oil. With regard to the effect of these ions on plant growth, Somers, Gilbert, and Shive (1942) consider the ratio of Fe/Mn, for maximum growth of plants in the soil, should be between 1.5:1 and 2.5:1. Since the values obtained were below this range in all the samples, one would expect Mn toxicity of the plants, the effect increasing with the level of oil addition. In absolute values, Black (1968) and Morris and Pierre (1949) indicated that the levels of exchangeable Mn between 1 and 15 ppm and above would be injurious to the growth of plants. The data in Table 3 showed that the values varied from 14 in the control to 99 ppm at 8.5% level of oil addition. Intensification of Mn toxicity would, therefore, be expected in the oil-polluted samples since the control already contains exchangeable Mn in an amount that is within the toxic range.

CONCLUSION

The results of these investigations suggest damage to plants growing in oil-polluted soils as a result of several changes taking place in the soil.

The damage to plants may be due to anaerobic and hydrostatic conditions that interfere with soil-plant-water relationships. It may also be attributed to the toxic effect of sulfides and excess of available Mn and Fe which are produced during the decomposition of the hydrocarbons. Adams and Ellis (1960) attributed the decrease in plant stands in a "gassed" soil to a hydrostatic relationship in the soil whereby plants were unable to ramify the soil with their roots. Grummer (1965) also thought that the reduction in yield as a result of oil pollution was due to interference with the water and nutrient supply of the crop and that this, rather than any direct toxic effect, caused the damaging effect. In his summary on the effect of oil pollution on plant growth, Schwendinger (1968) concluded that symtoms of oil pollution of soil were typical of extreme nutrient deficiency of plants, and since symptoms are directly proportional to water uptake, plant damage is most likely due to a disturbance of the plant-water relationships of the roots in the soil. In our investigations, all available data indicated that the toxic effect of excess available Mn, and the immobilization of P and N in the soil added to the unfavourable conditions observed by previous workers, and contributed significantly to the poor plant growth. Suffocation of plant roots would also occur as a result of the exclusion of air by oil or exhaustion of oxygen by increased microbial activity.

The unfavourable conditions will persist as long as the hydrocarbons exist undecomposed in the soil. When, however, most of them have been decomposed and changed into the normal soil organic matter, the increased organic matter will improve the structure of the soil. There will also be an increased fertility largely through the addition of nutrients from the decomposed crude oil and possibly through the fixation of atmospheric N by microorganisms which utilize the hydrocarbons. Plants growing later in the treated soil may tend to do better than those in uncontaminated soil. According to Schwendinger (1968) rapid reclamation of crude oil-polluted soils can be achieved by ploughing the soil, adding N fertilizers, or by use of seeders, organisms which utilize hydrocarbons, or more effectively, by a combination of the above operations.

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140,523

THE EFFECTS OF OILS ON PLANTS

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ABSTRACT

Oils vary in their toxicity according to the content of low-boiling compounds, unsaturated compounds, aromatics, and acids. The higher the concentration of these constituents, the more toxic the oil. After penetrating into a plant, the oil may travel in the intercellular spaces and possibly also in the vascular system. Cell membranes are damaged by penetration of hydrocarbon molecules, leading to leakage of cell contents, and oil may enter the cells. Oils reduce transpiration rate, probably by blocking stomata and intercellular spaces. This may also be the reason for the reduction of photosynthesis which occurs, though there are other possible explanations of this—such as disruption of chloroplast membranes and inhibition caused by accumulation of end-products. The effects of oils on respiration are variable, but an increase of respiration rate often occurs, possibly due to mitochondrial damage resulting in an 'uncoupling' effect. Oils inhibit translocation probably by physical interference. The severity of the above effects depends on the constituents and amount of the oil, on the environmental conditions, and on the species of plant involved.

INTRODUCTION

Oil pollution effects may vary according to the type and amount of oil involved, the degree of its weathering, the time of year, and the species and age of the plant or plants concerned. The effects that have been observed include the oil-trapping ability of vegetation, the yellowing and death of oiled leaves, a great reduction of seedlings and of annual species, differing susceptibilities and recovery rates of perennials, a competitive advantage to some species, and growth stimulation. Chronic pollution may completely eliminate vegation. Literature on oils and their

Environ. Pollut. (1) (1970) pp. 27–44—

effects on plants has been searched for information that could be basic to the understanding of these effects.

Information about oil has been gained from standard works on organic chemistry. Petrol (gasoline), kerosene, diesel oil, fuel oil, and specially formulated oils, are used as herbicides, fungicides, and other pesticides, and many papers concerning the effects of these substances on weeds and crop plants have been published. In addition, some workers have applied pure hydrocarbons experimentally to crop plants.

Further information has resulted from work on water pollution and from observations following oil spillages.

COMPOUNDS PRESENT IN CRUDE OIL AND REFINERY PRODUCTS

Crude petroleum is a complex mixture of hydrocarbons, together with organic compounds of sulphur, nitrogen, and oxygen. The three main hydrocarbon classes are:

Alkanes (paraffins). Saturated chain compounds, *e.g.* hexane.

Cycloalkanes (naphthenes). Saturated cyclic compounds, *e.g.* cyclohexane.

Aromatics. Compounds whose structure contains the benzene ring. Further aromatics are produced by refining processes.

The following are present in much smaller amounts:

Alkenes (olefins). Unsaturated chain compounds. Not usually present in crude oil but are produced by refining processes.

Naphthenic acids. Alicyclic compounds with carboxylic acid groups.

Sulphur. Present as free sulphur, hydrogen sulphide, and various organic sulphur compounds such as thioalcohols (mercaptans).

Nitrogen and Oxygen Compounds. A minor constituent present in basic compounds.

In addition there are traces of metals, particularly vanadium (British Petroleum Company, 1966).

Different crude oils vary in such properties as the proportion of paraffinic to naphthenic hydrocarbons, the sulphur and vanadium contents, and viscosity. A table comparing seven crude oils is given by Dean (1968).

During refining, crude oil is first separated into 'cuts' of different boiling ranges,

which vary according to the nature of the crude oil but are approximately as follows (Bezzant, 1967):

Cut	*Approximate boiling range*	*Approximate molecular size*
Refinery gases	up to 25°C	C_3–C_4
Gasoline*	40–150°C	C_4–C_{10}
Naphtha	150–200°C	C_{10}–C_{12}
Kerosene	200–300°C	C_{12}–C_{16}
Gas oils	300–400°C	C_{16}–C_{25}
Residual oil	above 400°C	above C_{25}

* Gasoline here refers to a basic cut of crude oil. The name is also used as a synonym of petrol and in that case refers to the basic cut after further treatment.

Basic cuts are further refined. Products relevant to this review are:

Petrol. Contains straight- and branched-chain alkanes and aromatics. Sulphur and alkenes are removed.

Kerosene. Sulphur and aromatics are removed.

Diesel fuel. May be a refined high-boiling kerosene or refined low-boiling gas oil.

Fuel oil. May be a residual oil or a distillate or a blend of these.

Alkenes and aromatics. Produced by cracking and refining processes.

Pesticidal and fungicidal spray oils. Usually contain a high proportion of saturated hydrocarbons owing to the smaller risk of toxicity to green plants than when unsaturated compounds are employed.

Herbicidal oils. Contain phytotoxic compounds such as aromatics.

TOXICITIES

Different Classes of Compounds Compared

The distinction between rapid or acute injury caused by light oils, and slow or chronic injury resulting from heavy oils, first made by deOng *et al.* (1927), was elaborated by Crafts & Reiber (1948), who classified injury into four categories:

Acute injury from volatile unsaturates.
Acute injury from volatile acidic compounds formed in low-boiling unsaturates.
Chronic injury from high-boiling unsaturates.
Chronic injury from non-volatile acidic compounds formed in high-boiling distillates upon exposure to light and air.

Unsaturated hydrocarbons, naphthenic acids, and other compounds containing aromatic groups, sulphur, and nitrogen, are removed during refining by treatment with sulphuric acid (Green, 1936). These compounds include many that are toxic, and Gray & deOng (1926) discovered that the phytotoxicity of spray oils can be measured quantitatively by the percentage reduction in volume after the sulphuric acid treatment.

There is agreement that toxicity increases along the series: paraffins—naphthenes and olefins—aromatics (Crafts & Reiber, 1948; Havis, 1950; Leonard & Harris, 1952). Within each series of hydrocarbons the smaller molecules are more toxic than the larger; octane and decane are very toxic, while dodecane and higher paraffins are nearly non-toxic. However, 12-carbon atom olefins are quite toxic, and 12-carbon atom aromatics are more so (van Overbeek & Blondeau, 1954).

Currier & Peoples (1954) tested barley and carrot with hydrocarbon vapours and found that toxicity increases along the series: hexane—hexene—cyclohexane—cyclohexene—benzene. Currier (1951) had reported an increase in toxicity along the series: benzene—toluene—xylene—trimethylbenzene, and had concluded that the increase in number of the methyl groups promoted penetration. It seemed that toxicity could be inversely correlated with water solubility—an idea first put forward by Richet (1893).

Aromatics

Due to the high toxicity of aromatic compounds, the herbicidal activity of oils increases with increasing aromatic content (Havis *et al.*, 1950). Shaw & Timmons (1949) demonstrated the effectiveness of light aromatic compounds in controlling submerged water-weeds in irrigation ditches. The effective concentration of emulsified hydrocarbons was 300 ppm. Currier & Peoples (1954) found that some aromatic hydrocarbons rapidly killed aquatic plants at a concentration of 1%. Cuille & Blanchet (1958) found that the growth of maize plants was seriously affected by an oil containing 10% of aromatics, while an aromatic content of 33% reduced growth by 31%. Bruns *et al.* (1955) found that aromatic solvents with a boiling range of 117–216°C and an aromatic content of not less than 85% were the most effective for the control of aquatic weeds.

Currier (1951) reported that benzene, toluene, and xylene, all cause acute rather than chronic injury. However, polycyclic aromatics cause chronic injury as they penetrate much more slowly into the plasma membrane (van Overbeek & Blondeau, 1954).

Acids and Peroxides

Tucker (1936) suggested that the portion of the oil removed by sulphuric acid treatment is less important than the acidic substances to which it gives rise during exposure to light and air either before or after application to the plant. He attributed toxic effects to the oil-soluble asphaltogenic acids of high molecular weight (this

would come into category four of the classification of Crafts & Reiber. Van Overbeek & Blondeau (1954) found that purified oils increase in toxicity when exposed to light, due to the formation of acids. Some oils increase in toxicity with storage, due to acid formation (Johnson & Hoskins, 1952). Naphthenic acids found in crude oil are known to be toxic to many animals (Cairns & Scheier, 1962), and high concentrations (10%) are toxic to salt-marsh grasses (Baker, 1969).

Galtsoff (1936) refers to Russian investigations with Baku petroleum which showed that its toxic action on fish and invertebrates was due to hexahydrobenzoic acid. He found that a heavy layer of oil on the surface of culture flasks inhibited the growth of the marine diatom *Nitzschia closterium*, and concluded that crude oil discharged into the sea yields water-soluble substances that are toxic.

In addition to acids, peroxides may be formed in oils exposed to light and these may cause acute plant injury (Crafts & Reiber, 1948).

EFFECTS OF PHYSICAL PROPERTIES OF OILS ON TOXICITY

In general, the smaller the hydrocarbon molecule, the more toxic the oil is to plants (van Overbeek & Blondeau, 1954). Molecule size affects boiling range and viscosity. Havis (1950) found that boiling range influences toxicity independently of the hydrocarbon series. High-boiling materials may have molecules too large to penetrate plant tissues and volatile oils may evaporate before they have any effect on the plant. Low-boiling range herbicidal oils are selective, high-boiling range oils are non-selective (Havis *et al.*, 1950). In general, hydrocarbons within the boiling range of 150–275°C, *i.e.* the naphtha and kerosene fractions, are most toxic to plants. Cowell (1969) found that weathered crude oil is less toxic to salt-marsh vegetation than fresh oil which contains low-boiling compounds. Baker (1969) found that fresh crude oil was more toxic to *Puccinellia maritima* than was residual crude oil.

Viscosity and surface tension influence the rate at which an oil will spread over and penetrate into a plant. The viscosity of a petroleum oil determines to a limited extent its toxicity to plants. Ginsberg (1931) studied the penetration of refined petroleum oils into the tissues of plants and noted high penetration of low-viscosity oils and low penetration of emulsified oils. Aqueous solutions do not penetrate stomata (van Overbeek & Blondeau, 1954).

EFFECTS OF ENVIRONMENTAL CONDITIONS ON TOXICITY

Cuille & Blanchet (1958) used 84 different oils in tests on maize plants. They concluded that there are three distinct factors related to phytotoxicity of oils, namely

the properties of the oils, the quantity applied, and the environmental conditions. If an emulsion of light oil is sprayed on young plants in the light when the stomata are open, the plants are killed. If the same emulsion is applied during the night when the stomata are closed, the plants are not harmed. During very sunny or hot weather the risk of phytotoxicity is greater than at other times. Bruns *et al.* (1955) investigated the control of aquatic weeds using aromatic solvents and found that results were best if the solvents were applied at a water temperature of 21°C. In apple trees, Kelly (1930) states that a high humidity favours oil damage, but Young (1930) found that the greatest damage from oil occurred when trees are suffering from drought. A high humidity could mean that stomata are open, which would aid oil penetration. Drought conditions probably favour the formation of toxic acids in the oil.

In the case of oils which penetrate easily, environmental conditions may not have any effect: for example the entry of n-decane into certain plants is at different conditions of humidity, time of day, or the water relations of the plant is always rapid (Boyles, 1967).

PENETRATION OF OIL FROM THE PLANT SURFACE

Plant surfaces are readily wetted by petroleum oils, which spread as a thin film. The retention of the oil is affected by pubescence, leaf-angle, and the presence of surfactants (Ennis *et al.*, 1952). Penetration from the surface into the leaf tissue continues only so long as there is free oil on the surface (Rohrbaugh, 1941). The rate and extent of penetration depend upon the oil type, the part of the plant oiled (leaves or roots), the thickness of cuticle, and the frequency of stomata. The surface tension and viscosity of the oil are important in determining the rate of penetration (Knight *et al.*, 1929; Minshall & Helson, 1949). For example, the former authors found that leaves of *Erodium* immersed in kerosene showed complete penetration in 40–60 min, but a saturated petroleum oil of 110 sec viscosity required 300–360 min for penetration. Dallyn (1953) reports that non-toxic oils enter through stomata whereas highly toxic oils enter indiscriminately from the point of contact.

The roots of barley and carrot are more resistant than the leaves to benzene (Currier & Peoples, 1954), which agrees with the theory that roots are adapted for the absorption of polar compounds and leaves for the absorption of non-polar compounds.

Penetration through stomata has been demonstrated in *Citrus* leaves (Knight *et al.*, 1929; Turrell, 1947). Plants with heavy cuticles and few stomata permit little penetration of oils, *e.g.* the xerophyte *Sedum* is resistant and shows no penetration by kerosene after 8 hours' exposure (Knight *et al.*, 1929; Minshall & Helson, 1949). Land plants seemed more readily affected by 'Torrey Canyon' oil than algae which are probably protected by their mucilaginous outer layers (Nelson-Smith, 1968).

Oils creep into and penetrate the crowns of grasses where the growing tissues are located (Crafts & Robbins, 1962, p. 357; van Overbeek & Blondeau, 1954).

MOVEMENT OF OIL IN THE PLANT

After penetrating the surface of a leaf, the oil moves into the intercellular spaces (Knight *et al.*, 1929; Rohrbaugh, 1934; Young, 1935; Minshall & Helson, 1949; Laville, 1963), and may then travel within the plant. Knight *et al.* (1929) found that the leaves of young beans and peas which were grown in oil-treated sand showed a higher oil content than plants which were grown in normal soil. Oil absorbed by the roots must have moved upwards. Oil applied to cut roots can move up into the leaves, and oil applied to leaves can move down into the roots (Klingman, 1961, p. 217). Boyles (1967) found that C^{14}-labelled n-decane moved from leaves to stems of sunflower and carrot plants. In a large turgid dandelion root, oil moved at a rate of 4–5 cm per hour in the intercellular spaces (Minshall & Helson, 1949).

Most workers believe that the oil travels primarily in the intercellular spaces, with little or no movement through the vascular system (Rohrbaugh, 1934; Young, 1935; Minshall & Helson, 1949). However, Knight *et al.* (1929) claim that there is some translocation in the vascular system, and deOng (1948) describes the passage of the lighter oils through the tracheids as small globules in the water system, the tracheids becoming clogged only by more viscous oils. He concludes that oils are distributed through the vascular system and parenchyma, and that viscous oils penetrate tissues more slowly and less uniformly than the lighter ones. Young (1935) found that oils spread more in the intercellular spaces than in the vascular system of potato, onion, and cucumber stems.

PENETRATION OF OILS INTO CELLS

Knight *et al.* (1929) found spray oil in *Citrus* cells and Young (1935) found it in apple, onion, and potato cells. Minshall & Helson (1949) observed penetration of spray oils into living cells and Havis (1950) states that oil can only enter cells after they are injured.

If oils are to enter plant cells, they must pass through the cell-walls and the cell-membranes. According to Lewis (1945), the outer walls of the mesophyll cells are lipophyllic, but cell-walls are normally saturated with water which would impede the passage of oil (Young, 1935). Young suggests that gravitational force and wind movements of tissues push oil against and through cell-walls.

The oil-mass theory of Young (1935) postulates an oil 'chain', from intercellular oil through oil in the cell-wall, and an oil-miscible plasma membrane to intracellular

oil. Along this chain oil can flow, aided by external forces such as gravity and wind movements of tissues.

The plasma membrane is the critical structure. Van Overbeck & Blondeau (1954) have suggested how hydrocarbons dissolve in the plasma membrane and open it up by displacing fatty molecules. Boyles (1967) has shown disruption of cytoplasmic membranes in onion epidermis by n-decane. Damage to the plasma membrane increases permeability, and cell-sap leaks into the intercellular spaces. Materials may move into petroleum oils from the cells. Young (1935) reported unidentified materials moving from apple cells into stained oil, where they precipitated the stain. Knight *et al.* (1929) found that intercellular oils were made green by extracted chlorophyll. Leakage of cell-sap into intercellular spaces containing oils causes darkening of the leaf, loss of turgor, and an odour of macerated tissue (Currier, 1951).

TRANSPIRATION

Oils have been consistently shown to reduce transpiration rates (*cf.* Table 1). Knight *et al.* (1929), and Bartholomew (1936), found that with spray oils on *Citrus* this effect was temporary, and Riehl *et al.* (1958) concluded that reduction in transpiration is due to physical interference by the spray oil on or in the leaf tissue,

TABLE 1

THE EFFECTS OF OILS ON TRANSPIRATION

Plant	*Oil*	*Effect*	*Source of information*
Citrus	Highly refined white oil	Transpiration reduced	Knight *et al.* (1929)
Citrus	Kerosene	Transpiration reduced	Knight *et al.* (1929)
Citrus	Light lubricating oils	Transpiration reduced	Knight *et al.* (1929)
Citrus	Insecticidal spray oils	Transpiration reduced	Knight & Cleveland (1934)
Citrus	Insecticidal spray oils	Transpiration reduced	Bartholomew (1936)
Citrus	Insecticidal spray oils	Transpiration reduced	Riehl *et al.* (1958)
Citrus	Insecticidal spray oils	Transpiration reduced	Riehl & Wedding (1959*a*)
Apple	Insecticidal spray oils	Transpiration reduced	Kelly (1930)
Parsnip	Petroleum naphtha	Transpiration reduced	Minshall & Helson (1943)
Mustard	Petroleum naphtha	Transpiration reduced	Minshall & Helson (1943)

so that recovery of transpiration occurs with dissipation of oil from the leaves. The rate of recovery depends on the oil type, the amount of oil and the plant species. Recovery is faster in the case of kerosene and light lubricating oils than with saturated high-viscosity oils (Knight *et al.*, 1929). Riehl & Wedding (1959*a*) found that recovery from naphthenic oil was faster than that from paraffinic oil. Even a small percentage of unsaturates in an oil postpones recovery (Knight *et al.*, 1929).

Where oil is applied in small amounts, *e.g.* as an emulsion, recovery is faster than where it is painted on in large amounts (Knight *et al.*, 1929). Minshall & Helson (1949) treated parsnip and mustard leaves with petroleum naphtha. The transpiration rate of the parsnip leaves dropped to 20% of normal, but five hours after application it had returned to 50% of normal. There was no recovery of the mustard leaves.

RESPIRATION

The conflicting results shown in Table 2 may be due to the following reasons:

(a) Different oils. The very toxic oxidised oils and aromatics such as p-cymene reduce or stop respiration and cause widespread injury and death; non-herbicidal oils generally increase respiration rates.

(b) Different plants. The same oil may have different effects upon different plants; for example, petroleum naphtha increases the respiration rate of parsnip and decreases that of mustard (Nozzolillo & Helson, 1959). The fact that the paraffin n-dodecane, a constituent of petroleum naphtha, reduces the respiration rate of mustard and finally kills the plant (*ibid*), indicates that the paraffin fraction as well as the aromatic fraction of petroleum naphtha has a toxic effect on susceptible species.

(c) Early workers used leaves with a content of respirable materials which varied with previous exposure to light.

TABLE 2

THE EFFECTS OF OILS ON RESPIRATION

Plant	*Oil*	*Effect*	*Source of information*
Citrus	Highly refined white oil	Respiration increased	Knight *et al.* (1929)
Bean	Poorly refined oil	Respiration increased	Green & Johnson (1931)
Bean	Highly refined oil	Respiration increased	Green (1936)
Dandelion	Kerosene	Respiration increased	Rasmussen (1947)
Parsnip	Non-herbicidal	Respiration increased	Nozzolillo & Helson (1959)
Mustard	Non-herbicidal	Respiration increased	Helson & Minshall (1956)
Parsnip	Petroleum naphtha	Respiration increased	Helson & Minshall (1956)
Parsnip	n-dodecane	Respiration increased	Helson & Minshall (1956)
Sunflower	n-decane	Respiration increased	Boyles (1968)
Bean	Highly refined oil	Respiration reduced	Green & Johnson (1931)
Deciduous fruit trees	Dormant spray oil	Respiration reduced	Oberle *et al.* (1944)
Mustard	Herbicidal oil	Respiration reduced	Minshall & Helson (1949)
Citrus	Insecticidal oil	Respiration reduced	Wedding *et al.* (1952)
Bean	Oxidised (acidic) oils	Respiration reduced	Johnson & Hoskins (1952)
Mustard	Petroleum naphtha	Respiration reduced	Helson & Minshall (1956)
Mustard	n-dodecane	Respiration reduced	Helson & Minshall (1956)
Mustard	p-cymene (an aromatic)	Respiration ceased	Nozzolillo & Helson (1959)
Parsnip	p-cymene (an aromatic)	Respiration ceased	Nozzolillo & Helson (1959)
Parsnip	Herbicidal oil	No change	Minshall & Helson (1949)

(d) Oil, by plugging stomata to different degrees, may interfere in different ways with gaseous exchange. The results of Green (1936) do not support this supposition, as he found that small amounts of oil caused about the same change in respiration rate as large amounts, but in contrast to this a number of workers have considered that oil acts as a physical barrier in inhibiting transpiration and respiration.

Rasmussen (1947) found that kerosene applied as a herbicide to dandelion caused increased digestion and respiration of reserve carbohydrates. The accelerated hydrolysis of carbohydrates was shown by an increase in reducing-sugar content in the roots. Johnson & Hoskins (1952) found that oxidised oils prevented the synthesis of sucrose from glucose infiltrated into bean leaves, and explained this result as stemming from the respiration decrease and consequent decrease of available energy. The oxidised oils did not inhibit the hydrolysis of infiltrated sucrose.

Helson & Minshall (1956) found that under anaerobic conditions a paraffin oil had no effect on the respiration rate of parsnip leaves, while petroleum naphtha caused an increase. This indicates that the paraffin oil stimulated the aerobic oxidation processes while the petroleum naphtha stimulated both the aerobic and glycolytic processes of respiration.

There has been little speculation on the mechanism of oil effects on respiration, and when considering this it is necessary to remember that four distinct processes are involved—namely gaseous exchange, glycolysis, the tricarboxylic acid cycle, and oxidative phosphorylation—each of which may be affected in a different way. Enzymes involved in the tricarboxylic acid cycle and in oxidative phosphorylation are located in mitochondria, which are membranous organelles. Glycolytic enzymes are not contained within any organelle but may be bound to the endoplasmic reticulum. When mitochondria are broken up, for example by immersion in a hypotonic solution, ability to respire aerobically is lost. In contrast, the glycolytic enzymes operate in extracted juice in the same way as they do in the cell. The tricarboxylic acid cycle and oxidative phosphorylation are oxygen-requiring processes, whereas glycolysis can take place in anaerobic conditions.

Ways in which oils could possibly affect these processes are as follows:

(a) Oils may interfere with gaseous exchange by blocking stomata and intercellular spaces. Evidence on this point, discussed earlier, is conflicting, but Brown & Reid (1951) have shown that gaseous diffusion can occur readily through oil films.

(b) Dinitrophenol (DNP) increases oxygen uptake by 'uncoupling' electron transport from phosphorylation (Beevers, 1953). The rate of electron transport is increased, but the energy release is lost as heat. It is possible that uncoupling occurs if certain spatial relationships at the catalytic surfaces within mitochondria are not maintained (Street, 1963, p. 190). Oil could possibly penetrate mitochondria and cause uncoupling without disrupting

the mitochondria completely. Nozzolillo & Helson (1959) have compared the DNP effect with oil-induced increases in oxygen uptake.

(c) If oils disrupt membranes, as described by van Overbeek & Blondeau (1954), then mitochondrial membranes could be broken up sufficiently to inhibit the TCA cycle and oxidative phosphorylation. Glycolysis could well continue, and under these conditions the Pasteur effect would operate, *i.e.* there would be a large consumption of sugars and production of large amounts of carbon dioxide (*cf.* Rasmussen, 1947) without oxygen uptake. This is because, when oxidative phosphorylation is not taking place, the supply of phosphate ions and ADP (adenosine diphosphate) to the phosphoglyceraldehyde oxidation (a pacemaker reaction in glycolysis) is increased (Street, 1963, p. 191).

PHOTOSYNTHESIS

Oils consistently reduce the rate of photosynthesis (*see* Table 3). The amount of reduction varies with the type and amount of oil and with the species of plant. Boiler fuel is more toxic than diesel oil to the kelp *Macrocystis* (Clendenning &

TABLE 3

THE EFFECTS OF OILS ON PHOTOSYNTHESIS

Plant	*Oil*	*Effect*	*Source of information*
Citrus	Highly refined white oil	Photosynthesis reduced	Knight *et al.* (1929)
Apple	Summer spray oil	Photosynthesis reduced	Hoffman (1935)
Parsnip	Petroleum naphtha	Photosynthesis reduced	Minshall & Helson (1949)
Mustard	Petroleum naphtha	Photosynthesis reduced	Minshall & Helson (1949)
Citrus	Naphthenic oils	Photosynthesis reduced	Riehl & Wedding (1959*b*)
Citrus	Paraffinic oils	Photosynthesis reduced	Riehl & Wedding (1959*b*)
Kelp	Cresols	Photosynthesis reduced	Clendenning (1960)
Kelp	Phenol	Photosynthesis reduced	Clendenning (1960)
Kelp	Boiler fuel oil	Photosynthesis reduced	Clendenning (1959)
Kelp	Diesel oil	Photosynthesis reduced	North *et al.* (1965)
Banana	Fungicidal oil	Photosynthesis reduced	Riedhart (1961)
Banana	Fungicidal oil	Photosynthesis reduced	Corke & Jordan (1963)

North, 1960). Recovery of photosynthesis in *Citrus* treated with naphthenic oils is faster than it is from treatment with paraffinic oils (Riehl & Wedding, 1959*b*). Green algae oiled with 'Torrey Canyon' oil and not treated with emulsifier remained green, and bubbles trapped in the partial oil film indicated that they were photosynthesising (Nelson-Smith, 1968). Green algae treated with fresh crude oil died (Baker, 1968). Though no quantitative results are available, it would seem that the weathered oil has no, or anyway a reduced, inhibiting effect.

Riehl & Wedding (1959) found a definite relationship between inhibition of photosynthesis and increasing oil deposit in the deposit range 300–600 μg oil/sq cm

of leaf surface. Photosynthesis in parsnip recovered from treatment with petroleum naphtha, but in mustard stopped completely (Minshall & Helson, 1949).

The principal effect of oil on photosynthesis occurs in that tissue of the leaf which is characterised by the dark discoloration known as oil soaking. Tests with the tetrazolium reaction (Smith, 1951) showed that the cells of the discoloured tissue are not killed (Riehl & Wedding, 1959).

Considering the methods by which oil inhibits photosynthesis, several workers argue that oil acts primarily as a physical barrier that interferes with gaseous exchange. The basis for this viewpoint is as follows:

(a) As the CO_2 content is increased around the oil-treated leaf, the inhibition of photosynthesis disappears (Riedhart, 1961).
(b) The duration of the photosynthesis inhibition correlates with the dissipation time of the oil (Riehl & Wedding, 1959; Riedhart, 1961, 1964, 1964*a*; McMillan & Riedhart, 1964).

Oil may also act physically by absorbing light wave lengths that are essential for photosynthesis.

Oil may inhibit photosynthesis through cell injury. Thus Wedding *et al.* (1952) suggest that photosynthesis may be affected directly through altering of the cell membranes. Van Overbeek & Blondeau (1954) suggest that oil affects photosynthesis and starch formation because hydrocarbons will tend to accumulate in the chloroplasts where there is a higher lipoid content than in the rest of the cytoplasm. Minshall & Helson (1949), using a sensitive infra-red absorption apparatus, found that when a solvent oil was applied to plants, photosynthesis ceased abruptly, whereas respiration was not initially affected. As the submicroscopic structure of the grana must be maintained for normal synthesis, van Overbeek & Blondeau (1954) suggest that the hydrocarbons or other constituents of the oil dissolve in the lipoid phase of the grana, thereby causing an increase in distance between individual chlorophyll molecules and other disruptions of sub-microscopic structures required for photosynthesis. Dallyn (1953) observes that chlorophyll destruction is one of the most obvious symptoms of oil injury.

A further possibility is that there may be an indirect effect on photosynthesis caused by accumulation of end-products brought about by inhibition of outward translocation from the leaf. For example, Knight *et al.* (1929) noted a great increase in starch accumulation in *Citrus* leaves which had been treated with a heavy oil deposit. They attributed this increase to an inhibition of the outward movement of carbohydrates from treated leaves.

Conclusive evidence has been presented to show that the application of oil sprays to *Citrus* trees results in a reduction in the total percentage of soluble solids in the fruitjuice. This decrease was first noted by Yothers & McBride (1929). Bartholomew (1936), Sinclair *et al.* (1941), and Stofberg & Anderssen (1949), have extended these results and have shown that the use of oil spray in the usual commercial dosage

causes a decrease of as much as 15% in the total soluble solids in the juice. Wedding *et al.* (1952) suggest that at least part of this decrease may be due to inhibition of photosynthesis.

Leaf drop and twig dieback in oil-sprayed *Citrus* have been reported by Ebeling (1950, p.170) and Riehl (1951).

TRANSLOCATION

Applications of insecticidal oil (Wedding & Riehl, 1958) have been shown to inhibit the translocation of radioactive phosphate to the leaves of small rooted lemon cuttings. The percentage inhibition of the translocation is proportional to the logarithm of the amount of oil deposited per unit area of leaf. Deposits in the range of 350–400 $\mu g/cm^2$ remain as effective 30 days after application as they were initially. Other experiments showed a decrease in the total ash content of oil-treated *Citrus* leaves relative to untreated leaves, which indicates that the inhibitory effects of oil on translocation are probably general and non-specific. Knight *et al.* (1929) attributed starch accumulation in oil-treated leaves to inhibition of outward translocation.

As oil is known to penetrate the phloem and xylem vessels of *Citrus* leaves (Knight *et al.*, 1929) it is probable that the effect on translocation comes about through a physical interference with the transport mechanism. This might be due to obstruction of the vessels with oil, but it seems more likely that the presence of oil partially dislocates translocation either by altering interfacial tensions within the protoplasm or by changing the structure and molecular orientation of transport pathways within the protoplasm by dissolving in its lipoid phases (Wedding & Riehl, 1958).

GERMINATION AND GROWTH

On a Milford Haven saltmarsh which had been polluted by fresh Kuwait crude oil in February 1967, the June 1967 frequencies of *Salicornia* spp. and *Suaeda maritima* were much reduced from the June 1966 values (Cowell, 1969; Cowell & Baker, 1969). As germination does not take place until March and April, inhibition of germination must have occurred. This could be due to oil entering the seed and killing the embryo, or to oil coating the seed and preventing the oxygen and water uptake essential for germination.

As regards general growth, Carr (1919) found that 0·75% of crude oil in soil improved the growth and root-nodule development of soybeans. Galtsoff *et al.* (1935) found that the water-soluble extract from the equivalent of 12% crude oil stimulated the growth of cultures of *Nitzschia closterium*. Mackin (1950, 1950*a*,

1950*b*) found that crude oil rapidly caused the death of saltgrass and saltwort but that later the plants completely repopulated the area and fertilisation, possibly from decomposition products, resulted in lush growth. Baker (1969) found that Kuwait residue the highest boiling 'cut' of Kuwait crude oil stimulated the growth of the saltmarsh grasses *Festuca rubra* and *Puccinellia maritima*, the lengths of shoots from oiled turves being significantly longer than those from control turves. Possible reasons for this growth-stimulation are release of nutrients from the oil, release of nutrients from oil-killed vegetation, or hormonal influence. These ideas are being investigated experimentally.

A number of Russian workers have claimed that 'petroleum auxin', identified as naphthenic acids, improves yields of a wide variety of crops, stimulates photosynthesis, and increases protein nitrogen. This agrees with the observation of Ginsberg, quoted by Nelson-Smith (1961), that the chlorophyll content of fruit-tree foliage may be greatly increased by oil spraying. The Russian literature is reviewed by the British Petroleum Company (1967). Experimental procedure is usually poorly described, and results are conflicting and not subjected to statistical analysis.

Baker (1969) has found that fresh Kuwait crude oil, sprayed on saltmarsh vegetation in early summer, prevents flowering in a number of species. This may be due to oil penetrating the flower primordia or young buds, or to oil killing the leaves during the photoinductive period. Further investigation is in progress.

RESISTANCE TO DISEASE

Saturated oil sprays are used for controlling a major fungus disease—leaf-spot of bananas—and a number of minor diseases. The literature is reviewed by Calpouzos (1966), who concludes that the action of the oil is on the host physiology rather than directly on the pathogen. Banana plants that are grown in full sunlight are susceptible to the disease, whereas shaded or oil-sprayed plants are resistant. It seems likely that susceptibility is connected with high sugar concentrations in the host, and oils may thus act by inhibiting photosynthesis and reducing the host's sugar content. Horsfall & Dimond (1957) noted that with diseases such as powdery mildews and rusts, susceptibility is associated with high sugar content in the host.

Oils have also been used to control aphid-transmitted virus disease.

RESISTANCE TO OIL AND SELECTIVE EFFECTS

It is clear that some species are more resistant to oil than others; for example, members of the Umbelliferae and conifers are resistant to injury by the lighter oils, which are therefore used as weedkillers on crops such as carrots or conifer seedlings (Lachman, 1944).

The resistance may be epidermal, as in the case of *Sedum* and other xerophytes (Knight *et al.*, 1929; Minshall & Helson, 1949), or at a cellular level. Van Overbeek & Blondeau (1954) found that the plasma membranes of leaf and root cells of Umbelliferae are inherently resistant to oils, including paraffins and olefins. Minshall (1961), using uptake of neutral red and plasmolysis in $CaCl_2$ as measures of cell integrity, treated parenchyma with 10% tetralin in a paraffin oil and recorded the time of death of 50% of the cells. Times for mustard, beet, carrot, and parsnip, were 35, 40, 65, and 85 min, respectively; thus Umbelliferae show tolerance at the cellular level. Increase in temperature heightened the resistance of beet cells but not those of parsnip. Growth in field conditions increased the resistance of parsnip but not beet. Minshall suggests that possibly more than one cell component may be involved in resistance.

McCauley (1966), studying the biological effects of oil pollution in a river, found that oil was toxic to many of the planktonic organisms but that several genera of freshwater algae were tolerant even when the oil pollution was at a maximum. The oil eliminated some planktonic organisms that were sensitive to it, but the more tolerant forms remained.

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Ref # 19

deOng, ER, Knight, H and Chamberlin, J.C.
"A Preliminary Study of Petroleum Oil as an Insecticide for Citrus trees".
Hilgardia, 2, 353-384 (1927)

COMPOSITION OF PETROLEUM OILS AND THEIR INJURY TO PLANTS

Nature of Injury to Trees by Petroleum Oils.—Volck(3) has shown that injury is most pronounced when the application of oil is made to the under side of the orange leaf where all the stomata of this plant are situated. This is owing to the fact that oil penetration into the leaf is much facilitated by any sort of opening, abrasion, or pore. According to the work of Magness and Burroughs(4) an oil film on the surface of stored apples may have a distinct effect on the gaseous exchange. The evolution of carbon dioxide from Winesap apples held at 65° F was reduced only 12 per cent by a coating of Oronite Crystal or other petroleum oil, but analyses of the air in the intercellular spaces showed a composition of 2.6 per cent oxygen and 25.3 per cent carbon dioxide, while check apples had 5.7 per cent oxygen and 18.3 per cent carbon dioxide. Burroughs(5) has noted a reduction in the amount of starch produced in apple leaves that seem to have been arrested in their growth by the application of an oil spray.

Gray and deOng(2) found a correlation between the specific gravity of the oil and resulting foliage injury. This correlation

[5a] A commercial emulsion of highly refined petroleum oil was being made by W. H. Volck when this later investigation by the California Experiment Station was begun in 1924.

applies only in a comparison of kerosenes with the heavier or lubricating oils. The former have a much lower boiling point and volatilize before penetration occurs; or even if penetration does take place, the oil may still volatilize before injury results. Injury may be possible, however, with certain fractions of a still lower boiling point than kerosene, especially if they contain a high percentage of unsaturated hydrocarbons. A study of lubricating oils having a much higher range of boiling points than kerosenes shows that their effect on plants and insects is more nearly related to viscosity than to specific gravity.

Injury to the foliage of citrus trees from petroleum oils is of two distinct types, acute and chronic. The former is caused by light (low-boiling-point) oils, the latter by heavy (high-boiling-point) oils. In the acute type of injury two distinct phases are noticeable. First, the leaf tissue may be killed within 48 hours after the application; and secondly, this may be followed by the leaves dropping after three or four days, although such leaves do not lose their color to any marked degree. Injury to the fruit or wood seldom occurs except with oils having a high percentage of unsaturated hydrocarbons, such as is commonly found in untreated oils, or those slightly refined. Contact of these oils with the roots may cause the death of the tree within a relatively short time.

Chronic injury is associated in varying degrees with oils of a high boiling point, which leave an oil film on the leaf and twig surface for a period of days or weeks. The foliage becomes yellow and defoliation begins within a few days and may last for weeks. The twigs and even the larger limbs are stunted or killed as shown in figure 1. The orange tree in the figure was photographed one year after a portion of it had been sprayed with lubricating distillate untreated with sulfuric acid.

The damage occurred only on the sprayed portion. The normal growth in the background, which shows no sign of injury, was unsprayed. Stunted twigs often put out a few small, weak leaves, and frequently the tree sprouts freely just below the injured parts.

Fully mature leaves, especially if senile, are more susceptible to injury from neutral oils than younger ones which are still in the growing stage. On the other hand, very young leaves are much more susceptible to injury from unrefined oils than the mature, but not senile, leaves, although this varies a great deal according to the degree of refinement of the oil used.

Commercial Refining of Oils as a Means of Reducing Injury to Plants.—Petroleum distillates are not usually in a marketable condition without chemical treatment to remove such ingredients as sulfur, resinous matter and the unsaturated and aromatic hydrocarbons. The common refinery practice is to treat the raw distillates, resulting from the heating of crude oil, with sulfuric acid. The quantity of acid

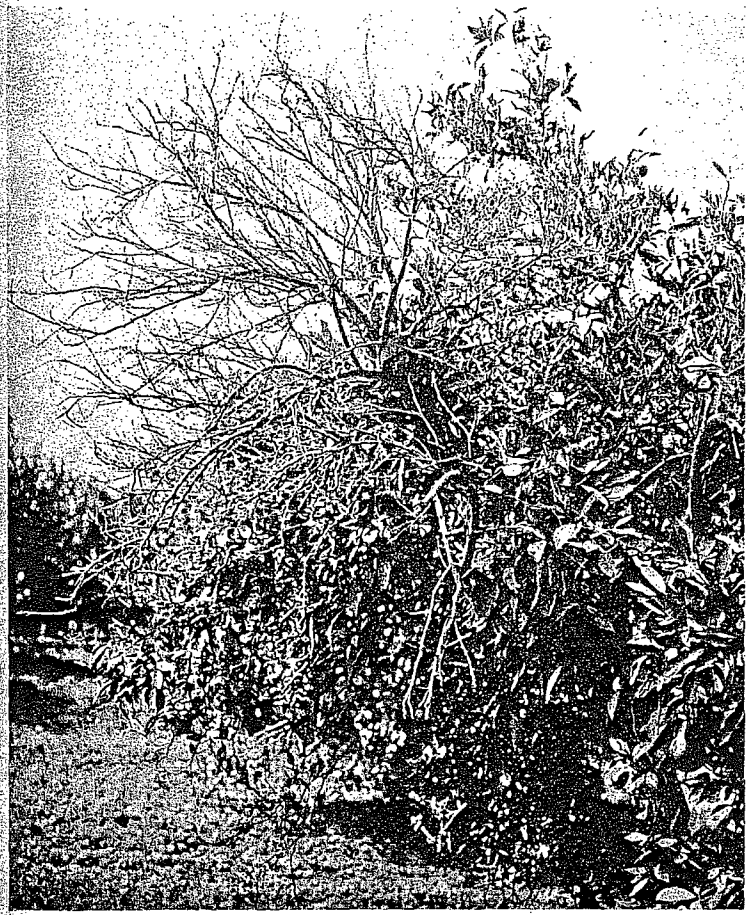

Fig. 1. Orange tree showing dead wood where the tree was sprayed with unrefined oil distillate.

required and the length of time during which treatment is continued depend on the grade of product desired and on the purity of the distillate used.

After treatment with acid, the oils are washed with a solution of caustic soda in order to remove the unchanged petroleum acids and phenols and to neutralize and remove the sulfo-acids and the sulfuric

acid remaining in the oil. The expense of refining operations is high, especially for the highly refined white oils, since the acid sludge resulting from the treatment is largely a waste product. In addition to the cost of the acid there is the loss of distillate which may amount to more than 50 per cent of the original volume treated.

In order to avoid the losses resulting from the chemical treatment, it is advisable to substitute a method of extraction more nearly of a physical type. This has been accomplished by Edeleanu(6) who found that if petroleum oil was treated with liquid sulfur dioxide the olefins are dissolved but the saturated hydrocarbons remain unaffected. Experimental work is now in progress with oils refined by this method in the hope that a satisfactory degree of refinement may be obtained at a lower cost than is possible from the sulfuric acid treatment.

Tests of Petroleum Oils in Relation to Plant Injury.—Differences in the insecticidal effects of, and plant tolerance for, various petroleum distillates have long been recognized, but until recently the only specifications commonly used for distinguishing between them were specific gravity and, perhaps, the flash point. We now know that these are inadequate criteria. The boiling point of different kerosenes, for example, has been shown by Moore(7) to be important in distinguishing between the toxicity of petroleum fractions as it relates both to insects and to plants.

Since some progress has been made in determining the relation between the unsaturated hydrocarbon content of oils and their toxicity to plants, our first attempt at selection was based on the degree of refinement, the assumption being that the oil fractions containing the least amount of sulfonatable oil would be the safest.

A series of lubricating and kerosene oils was obtained from the Standard Oil Company. These ranged from the raw untreated distillate resulting from the distillation of crude oil, up through the different degrees of refinement effected by the use of acid and filtration. Their physical and chemical specifications are shown in table 1.

These oils, with the exception of the one finally selected for study, are referred to by number throughout this paper, instead of by their trade names. Oils 1 to 6, inclusive (tables 1 and 2), are lubricating oils, oil 1 being the raw distillate, and oil 5 the end of the refined series as based on the sulfonation test. Oil 5 (Oronite Crystal) is a very bland and "neutral" oil; it is colorless, odorless and tasteless. Oils 1a to 4a are kerosenes arranged in the same way, oil 1a being the raw distillate and 4a the highly refined end product. The sulfonation test (table 2) shows the amount of unsaturated hydrocarbons present in the various samples. These oils were emulsified with

TABLE 1

PROPERTIES[a] OF OILS TESTED

No.	Gravity[b] (degrees A. P. I.)	Flash point[c] °F	Fire point °F	Viscosity[d] in seconds at 100° F	Color	Sulfur (per cent)	Unsulfonated residue of oil	Acidity in mg. of KOH per gm. of oil
1	19.2	305	.....	105	.....	.7	51	1.5
2	21.3	310	350	99	.....	.65	52	1.0
3	22.5	310	350	96	6[e]	.6	56	.6
4	22.7	320	360	107	2.5—	.6	60	.4
4x	22.7	320	360	100–110	1.5	.6	62	.03
5[h]	29.8	320	360	106	+25[f]	.006	98	.0
5x[h]	28–31	280+	.....	70–80	+25[f]	.015	98	.0
6	.....	360+	.....	330–340	3.	.6	58	.2
KEROSENES								
1a	35.9	124CT[g]	.....	375	.....	.....	81	.....
2a	41	83CT	125	320	+25[f]	.016	82	.....
3a	41.3	113CT	135	345	+25[f]	.010	93	.....
4a	43.3	143CT	175	400	+25[f]	.006	98	.....

[a] The pour point on all oils used was below zero Fahrenheit.

[b] The A.P.I. gravity table is so similar to the Baumé gravity table that for all practical purposes they may be considered identical for lubricating oils.

[c] Cleveland open cup.

[d] Viscosity of lubricating oils determined by the Saybolt Universal viscosimeter. Viscosity of kerosene fractions measured by the Saybolt "Thermoviscosimeter," which bears no relation to the lubricating-oil viscosimeter.

[e] A.S.T.M. standards.

[f] A.S.T.M. standard for kerosene by Saybolt colorimeter; the color number + 25 is an arbitrary value given to the most highly refined kerosenes.

[g] Closed Tagliabue Tester.

[h] No. 5 is Oronite Crystal oil, No. 5x, Oronite Cosmetic oil, trade names used by the Standard Oil Company of California to designate oils of the above specifications. Other numbers used in the table also refer to commercial brands of oil as sold by the Standard Oil Company. Note the gravity of Oronite Crystal oil (No. 5). This increase (from about 22.5° A.P.I. to 29.8°) is the result of the excessive treatment with acid. It follows that gravity alone is no criterion since this property of finished white oil is practically identical with that of some raw distillates such as gas oil, though obviously viscosity and flash (and molecular weight) are much higher. As a general rule the saturated hydrocarbons are much lighter in gravity than either olefins or aromatics, e.g., heptane (N), gravity 75° and toluene, gravity 32° A.P.I.

sodium oleate and applied to the trees with a hand sprayer at an oil concentration of 6 per cent. Field tests on orange and lemon trees were made during the season of 1924 at Riverside, California, where the typical high temperatures and low humidities of southern interior California occur; at Lindsay as typical of the upper San Joaquin Valley; and also at Santa Paula, which has the lower temperature characteristic of coastal conditions. The maximum temperature at the last point usually ranges 10° to 15° F lower than at Riverside. The latter experiments were made possible by the coöperation of Mr. C. T. Dodds of the Santa Paula Citrus Fruit Association. The results are clearly brought out in table 2.

TABLE 2

EFFECT OF PETROLEUM OILS OF DIFFERENT VISCOSITIES AND SULFONATION VALUES ON ORANGE TREES AT VARYING TEMPERATURES.*

OIL CONCENTRATION IN FISH-OIL SOAP EMULSION SIX PER CENT†

Oil No.	Viscosity in seconds at 100° F	Sulfonation value,‡ per cent	Riverside				Santa Paula Series I	
			Series I		Series II			
			Max. temp. range 85–100° F Applied 6/29		Max. temp. range 87–104° F Applied 8/21	Max. temp. range 61–96° F Applied 10/31	Max. temp. range 80–90° F Applied 6/16	
			Observations made 7/9	Observations made 8/2	Observations made 8/30	Observations made 11/9	Observations made 6/23	Observations made 7/21
1	105	51	Severe defoliation and burn.	70% twigs dead, 20% defoliated but sprouting.			12% defoliation, 40% fruit scarred.	10% fruit scarred, 25% leaf burn.
2	99	52	Severe defoliation and burn on twigs and fruit.	60% twigs dead, 20% defoliated but sprouting.			8% defoliation	40% fruit scarred, 20% leaf burn.
3	96	56	Slight defoliation, no burn.	8% twigs dead, 10% defoliation.			2% defoliation	20% fruit scarred, 15% leaf burn.
4	107	60	Heavy defoliation, no burn.	10% twigs and fruit dead, sprouting next injured area.	15% defoliation, no twig or fruit injury.		12% defoliation, 30% fruit scarred.	No fruit scarred, 8% leaf burn.
4x	105	62	Same as No. 4	Same as No. 4	12% defoliation, no twig or fruit injury.		15% defoliation, 40% fruit scarred.	15% leaf burn, 20% fruit scarred.
5	106	98	Slight defoliation, but showing growth.	Normal	2% defoliation		1% defoliation	Normal.
5x	75	98	Slight defoliation and twig burn, no fruit injury, new growth normal.		5% defoliation		3% defoliation	Almost normal.
6	330	58	Severe defoliation and burn, no new growth.	35% twigs dead, defoliated area sprouting.	12% defoliation	Normal	5% defoliation, 10% fruit scarred.	10% fruit scarred, 12% leaf burn.
1x	373	81	Normal	3% defoliation			Normal	Normal.
2x	320	82	Normal	Normal			Normal	Normal.
3x	400	93	Normal	Normal			Normal	Normal.
4x	400	98	Normal	Normal			Normal	Normal.

On the basis of these experiments it was possible to eliminate all those lubricating oils which did not show a high degree of refinement. The data in table 2 show that the first four oils used were dangerous to fruit and foliage and even to the tree itself. As expected, the degree of injury corresponded very closely to the amount of sulfonatable oil present. Filtration through Fuller's earth seemed to have no effect whatever in reducing injury. For example, oil 4x is a filtered oil of the type of oil 4 and, although variation in the degree of injury resulting from the use of these two oils is sometimes seen, a comparison of the effects produced in all field work thus far shows that no distinction can be drawn between them. Oils 5 and 5x are very similar from the sulfonation standpoint, but the latter is less viscous and has a lower boiling point. It "evaporates" or rather disappears from the foliage more quickly than the former and for that reason is possibly the safer. This disappearance of an oil film from foliage is not a simple phenomenon. It seems probable that it is due primarily to absorption followed by oxidation rather than to simple volatility. This point requires much further investigation before any safe generalization can be drawn. Oil 6 has a high viscosity and boiling point and is not very highly refined, and thus caused serious injury, especially at high temperatures.

These data show that only the most highly refined lubricating oils (such as 5 and 5x) are safe enough to justify experimentation on citrus trees at summer temperatures.

Under summer conditions at Riverside, the leaf drop may begin from a week to ten days after spraying. Under coastal conditions (i.e., at Santa Paula) it may be delayed six weeks or more. Under winter temperatures with maxima of 50° to 70° F, oils of lower refinement and higher boiling point are safe to use. As a result of these tests our succeeding work involved primarily a close study of oil 5, known commercially as Oronite Crystal oil.

The kerosene type of oil shows a reaction similar to the lubricating oil, in that the raw distillate 1a was more injurious than any of the three oils 2a to 4a, having various degrees of refinement. It will be noticed that 2a is less injurious than 3a, probably owing to its greater volatility. These kerosenes are all very much safer to use than the lubricating oils, but on account of their low boiling point they evaporate relatively quickly and hence are not satisfactory scalecides except possibly for the very youngest stages of scale insects.

In general, these tests indicate that a petroleum lubricating oil, to be safely used on citrus foliage in summer, must be of a very high degree of refinement and neutrality. The "white" lubricating

oils such as Oronite Crystal and Oronite Cosmetic most nearly meet this requirement. It is also evident that most kerosenes are safe under ordinary conditions but these oils must be eliminated because their volatility limits their insecticidal value. Their lack of injury to foliage is also in large part to be ascribed to their volatility.

PHYSIOLOGICAL EFFECT OF NEUTRAL WHITE OILS ON CITRUS TREES

While the neutral white oils such as Oronite Crystal have been spoken of as non-toxic, nevertheless, their presence upon a citrus tree sometimes induces certain characteristic effects which are more or less deleterious. These effects have not been studied enough to be at all adequately understood, and hence the following statement is mainly descriptive.

The most characteristic effect is a more or less heavy leaf drop, principally of senile or semi-senile leaves. For the most part this seems to be an acceleration of a normal process. It occurs on both oranges and lemons.

The next most characteristic effect consists of fruit "injury," particularly to lemons. The most common effect is the dropping of tree-ripe fruits, which is analogous to the dropping of senile leaves. A second and more important kind of fruit injury is a more or less marked delay in the coloring of green lemons subjected to the ethylene gas treatment. In some instances this delay is almost or quite permanent. This has not yet been satisfactorily explained, but it is apparently correlated with a morphological change in the oil cells in the rind of the fruit. The effect seems to consist in a withdrawal of the essential oil contained in the oil cells and may be due to its extraction by the spray oil. As shown by Fawcett(8) in 1916 the application of its own essential oil to the rind of a growing lemon inhibits or entirely prevents normal coloration.

In certain coastal areas, notably in Orange County, it is now well known that a drop of green Valencia oranges may follow application of the Oronite Crystal oil, particularly during humid weather conditions. Furthermore, ripening may be considerably retarded.

Various other pathological phenomena are continually being ascribed to the use of this oil on citrus trees, in addition to the well established ones given above. These include claims of such effects as reduction in set of fruit, actual twig, leaf, and fruit burn, dropping of newly set fruit (analogous to ordinary heat-induced "June drop") and so on, but the data available at present are too contradictory to be evaluated without further study.

THEORY OF OIL EMULSIONS

Petroleum oil is an insecticide of great value, but on account of its inherent danger to the plant, when used in effective amounts, it has been found necessary to dilute it with a material which acts as a carrier. Water lends itself readily to this purpose, but since these two liquids are immiscible it is necessary to employ some chemical or mechanical means of dispersing the oil in droplets uniformly throughout the water.

There are two types of oil emulsions. In the first, the "oil-in-water" type, the oil is dispersed as small globules throughout the water. In the second, the "water-in-oil" type, the reverse system is found. The prevailing type of oil emulsion used in insecticidal work is of the first or "oil-in-water" type, the invert form having been studied only very recently.

The nature of the emulsion, whether of the ordinary or invert type, is determined by the kind of emulsifier as has been shown by Tinkle, Draper, and Hildebrand(9) and Bhatnagar(10). Soaps of monovalent cations form the typical oil-in-water emulsion, while soaps of divalent cations, such as calcium oleate, make the invert form of emulsion with oil as the external phase.

Parsons and Wilson(11) have shown the possibility of inversion of an emulsion by mixing solutions of sodium oleate in water with magnesium oleate in oil. The addition of di- and trivalent salts such as magnesium sulfate and ferric chloride inverted the oil-in-water emulsion, for instance. Our own experiments with calcium casein mixture[6] as the emulsifier have also shown the possibility of changing the type of emulsion by varying the proportions of oil to emulsifier.

Theoretically an emulsion with oil as the external phase would be more effective than one with water as the external phase, since then the active insecticide would come immediately into direct contact with the insect. Since, however, such emulsions cannot be diluted with water and are usually of such a tough, gummy nature that they cannot be broken up readily, they do not lend themselves to orchard practice.

Quick-Breaking Oil Emulsions.—The disadvantages of the oil-in-water emulsion have been overcome to a large extent by the

[6] The commercial mixture of powdered casein and hydrated lime used as an emulsifier is, in solution form, commonly spoken of as "calcium caseinate." This term will be used henceforth in this paper. The proportions of casein and lime are approximately 1 to 4.

development of a "quick-breaking" type of emulsion, which allows the water to separate out immediately on contact and run off, leaving a film of pure oil on the leaf surface. This brings the active insecticide, oil, instead of water or a hydrated colloidal solution, into direct contact with the insect. Neither water nor a hydrated colloidal solution has any practical insecticidal value. The "quick-breaking" emulsion thus increases the insecticidal action to such an extent that the almost prohibitive cost for an effective stable emulsion made from such highly refined lubricating oils as Oronite Crystal, is reduced to a point where these oils are economically practicable for orchard spraying.

The type of oil emulsion generally used in insecticidal work is that in which the oil is broken up into the smallest possible globules and distributed uniformly throughout the water. When this is accomplished, and the oil remains thus dispersed for an indefinite period of time without separation, the resulting mixture is known as a "stable" emulsion. If there is a tendency in the course of a short period of time for the oil to separate from the mixture, the emulsion is known as "unstable." Within certain limits this instability varies inversely as the percentage of the emulsifying agent.

In practice it appears that the strength of the interfacial membrane which separates the two phases of an emulsion varies a great deal, according to the emulsifier used. Some, such as are formed by "sodium-fatty-acid" soaps, are apparently very elastic and tough; others, such as are formed by typical colloids, as, for example, starch or colloidal copper, and also by calcium caseinate, are relatively very weak and easily disrupted.

In accordance with the general principle that the stronger the interfacial membrane the more stable the emulsion, it follows that the emulsifying agent which produces the weakest possible interfacial membrane is the best from the insecticidal standpoint. On this basis casein is better than soap and a metallic colloid is better than casein.

Some emulsifiers, such as lime or kaolin and other earths, are capable of absorbing considerable amounts of oil, as well as emulsifying them. This is particularly pronounced and important when the emulsifier or spreader is used in large quantities. All such absorbed oil is unavailable for liberation as a free liquid and constitutes, therefore, a permanent loss—assuming, of course, that free oil is the effective agent. Hence, from a theoretical standpoint, the use of the emulsifier which has the least possible oil-absorptive capacity is advisable (other things being equal). Colloidal copper is an almost ideal substance in all these respects, and much superior to typical

soaps, calcium caseinate, and lime. While we regard colloidal copper as a theoretically better emulsifier than calcium caseinate, the former in a pure state requires such care in its preparation and is so difficult to buy that it is impracticable for any but laboratory work. Calcium caseinate, however, is a widely distributed commercial preparation, and hence was chosen as the emulsifier for our experimental work.

In a stable emulsion of oil in water, the oil itself cannot come into contact with the object sprayed until separation of the two phases takes place, which in a highly stable emulsion may not occur except as the water disappears by evaporation. This obviously means a greater or lesser delay before the insecticidal (particularly wax-solvent) activities of the oil can begin. Secondly, it means a large loss of oil contained in the unavoidable "drip" or "run-off" from the sprayed surface. Thirdly, it appears reasonable to suppose that the interfacial film of emulsifier will be deposited as a more or less definite layer of inert substance between the oil and the leaf or fruit surface in such a way as to delay, even where it is not sufficient to prevent, the insecticidal action of the oil. This type of action would be especially important with typical "sodium-fatty-acid" soaps.

Lime, by its absorptive capacity, tends to prevent the oil from coming into direct contact with the object sprayed, and hence serves as an inhibiting factor. If we assume, therefore, that pure oil is the effective agent, it follows that the more "stable" the emulsion or the greater the absorptive capacity of the emulsifier the less value it possesses as an insecticide. This point was brought out early in 1925 by deOng and Knight(12) in a preliminary note based upon this project.

Most of the emulsions now on the market use various "sodium-fatty-acid" soaps as the emulsifying agent. While soap itself, owing to its fatty-acid content, is a weak insecticide, and may be fairly effective against soft-bodied insects like aphis and young scale insects, it is almost certain that when used as an emulsifier it is probably never in concentration sufficiently strong to be independently effective. This was demonstrated in our laboratory work when very strong solutions of many different soaps applied as sprays failed to affect a satisfactory kill of red scale, which is an armored species.

LABORATORY EXPERIMENTS WITH OIL EMULSIONS

For the purpose of routine insecticidal tests in the laboratory, the red scale, *Chrysomphalus aurantii* (Maskell), of the strain which has developed a resistance to HCN fumigation under orchard conditions, was chosen. So far as known, this is the most difficult of all citrus scales to kill by spraying, and it was assumed that if a spray could be developed which would kill this species, it would be effective against any of the others. A spray which apparently fulfills this requirement has been developed. From data thus far obtained it seems to be equally effective against the black and purple scales. This spray, however, has not yet had wide enough testing in the field to justify recommendation by this station for general use. Furthermore, as has been shown, certain peculiar effects are often produced upon the tree, which are not yet sufficiently well understood. For this spray a "neutral" white lubricating oil (Oronite Crystal oil, specific gravity 88, viscosity 106) was taken as the insecticidal agent, calcium caseinate (see p. 361) being selected as the emulsifier.

Lemons heavily infested with scale were used in the laboratory tests. Spraying was done by means of a small atomizer, and counts for determination of scale kill were made from ten days to two weeks after the application of the spray. The scale-infested lemons were hung in the laboratory during the interim.

The inhibiting effect, previously noted, of excess emulsifier was particularly well shown in an experiment wherein the amount of oil was maintained constant at 2 per cent, while the emulsifier was progressively reduced from 2 per cent to .0078 per cent (or from equal parts of oil and emulsifier to a ratio of 100 parts of oil to 0.39 parts of emulsifier). The killing efficiency was markedly accentuated as the amount of emulsifier was decreased. This is shown in table 3.

The natural mortality on checks kept under the same conditions was 49.7 per cent, or practically the same as lot 2 in table 3. The mortality was somewhat higher in lot 1 because one of the lemons had dried out. Desiccation has of itself a marked effect on the mortality of scale insects.

In the first three lots there were many live young present after treatment. Some were crawling about over the fruit while many others had just settled. Not until an oil film was formed over the surface of the fruit, was there any marked rise in the mortality. When this did occur the kill quickly rose to 100 per cent. It would seem, therefore, that the insecticidal agent is the free oil.

It is customary to use a spreader (generally calcium caseinate or glue) with many oil sprays for citrus trees. But a spreader is also an emulsifier, and tends further to inhibit the action of the oil through increased stabilization of the emulsion. Also, as in the case of certain emulsifiers such as lime or calcium caseinate, a spreader may accentuate the loss of oil through its additional oil-absorptive capacity.

TABLE 3

RELATION OF SCALE MORTALITY TO CONCENTRATION OF EMULSIFIER IN A TWO-PER-CENT EMULSION OF ORONITE CRYSTAL OIL

No.	Concentration of calcium caseinate *Per cent*	Scale surviving at end of test* *Per cent*	Remarks
1	2	32.3	Many young alive. Oil absorbed by surplus emulsifier.
2	1	49.5	Many young alive. Oil absorbed by surplus emulsifier.
3	.5	38.3	Many young alive. Oil absorbed by surplus emulsifier.
4	.25	7.5	Sprayed surface slightly greasy. No young alive.
5	.125†	0.0	Oil film just visible on sprayed surface.
6	.0625	0.0	Oil film distinct on sprayed surface.
7	.031	0.0	Well developed oil film present.
8	.015	0.0	Well developed oil film present.
9	.0078	0.0	Well developed oil film present.

* The usual natural mortality, about 40 to 50 per cent, is necessarily included in the counts.
† This corresponds to 1 pound of calcium caseinate to 100 gallons of spray.

Nothing in common use will spread better than oil. Hence in a quick-breaking emulsion a spreader is not needed. The spreading of any liquid is facilitated by reduction in its surface tension. To make oil spread better would therefore require the introduction of an oil-soluble constituent which would reduce the surface tension of the oil itself. Casein and all other such substances customarily used as spreaders are water-soluble, being practically insoluble in oil. Hence any "spreading effect" which results concerns the water alone and not the oil. This confusion has arisen from the mistake of considering an oil emulsion as a "solution" instead of as a mixture of two independent liquids.

The use of mechanical mixtures would evidently overcome this inhibiting effect of emulsifying agents. The method is not used because reliance cannot be placed upon the mechanical agitators at present in common use. But by very slightly emulsifying the oil, ordinary spray tank agitation is capable of overcoming the natural

buoyancy of the separated oil droplets and of maintaining a fairly uniform suspension of oil throughout the body of the liquid. The emulsifying agent is used in quantities just sufficient to separate the oil into relatively large droplets. The interfacial membrane is consequently weak and easily broken, thus liberating the enclosed oil. There is no danger that the stability of the system will be sufficient to withstand rupture upon impact with the leaf or fruit surface, and the maximum amount of oil is consequently freed and made available. On the other hand, the oil in the tank is maintained in the form of isolated droplets, there being no continuous sheet of oil to be broken up as would be the case with a mechanical mixture.

It has been found by observation that the individual globules of oil in the type of emulsion just described vary from about 0.1 mm. to 2.5 mm. in diameter, the smaller sizes largely predominating. The presence of oil droplets of the size indicated makes possible a very quick liberation of oil from the emulsion stage, while separation is very much slower in the stable type of emulsion made of extremely minute droplets. If the drops were uniformly 1 mm. in diameter, then in a 2-per-cent emulsion, 1 cc. would contain about 40 of these globules. Now, if 1 cc. be sprayed on a flat surface at a distance of 3 feet with an ordinary atomizer it will cover a circular area about 15 inches in diameter and the oil droplets will strike at widely separated spots, resulting in a typical "shotgun pattern." To form a film of oil over a given area, enough of the emulsion must be applied so that the droplets of oil will coalesce and form a film. In other words, the time spent while spraying becomes an important factor in application, for it is possible to increase the amount of oil on a surface by long or repeated sprayings. This factor varies with pressure, size of nozzle opening, and rate of discharge.

It has been found in practice that a 2-per-cent emulsion works very well in the field. If less than 2 per cent of oil is used, complete coverage will not be obtained without the use of excessive time in spraying. If more than 2 per cent is used there may be an undue accumulation of oil on the tree. In these sprays, raising the percentage of oil results merely in the liberation of more oil in the same period of time. The chief need in sprays of this type is the formation of a film of oil over the entire surface of the plant and the insect.

In the following test the emulsifier was varied from 5.0 to 0.0078 per cent while the oil remained constant. The emulsion was sprayed on a glass surface, the "run-off" collected and a quantitative determination of the oil present made.

Thus, as shown in table 4, the quantity of oil in the "run-off" from highly stable emulsions distinctly increased over that of the

original concentration, so that the recovered drip was actually richer in oil than the original spray. It is only with quick-breaking emulsions that the oil percentage in the drip falls markedly below the original concentration. In the best of these, which corresponds to the one adopted for our general work, the drip even then contains 0.34 per cent of oil or about one-sixth of the original amount.

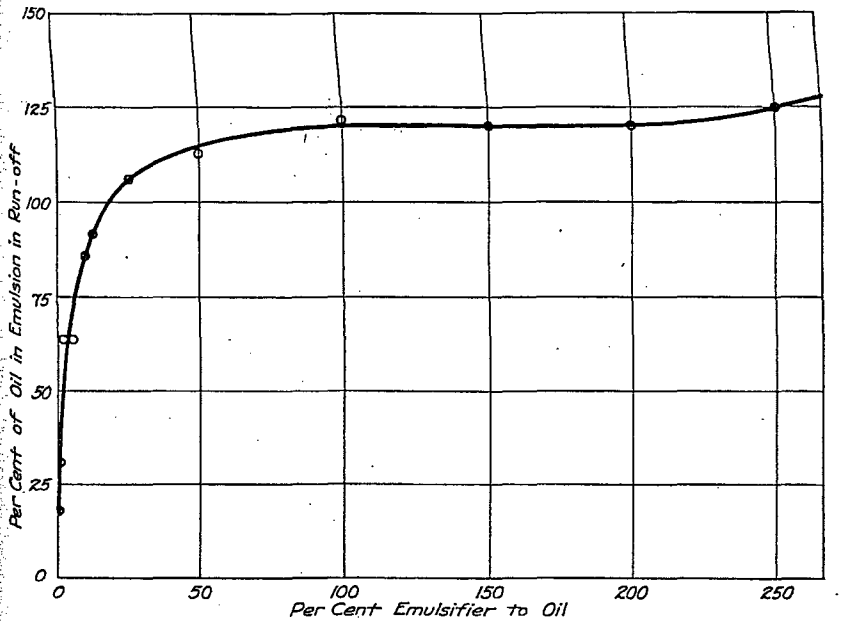

Fig. 2. Relation between amount of emulsifier used and the concentration of oil in the run-off from two-per-cent emulsions.

In experiments to obtain further evidence on the conditions of stability, emulsions were made as usual with Oronite Crystal oil. The standard emulsifier used was a mixture of powdered casein, selected for high solubility, and hydrated lime, the proportions being 1 to 4. Soap used in varying proportions as the emulsifier gave essentially similar results and hence these additional detailed data are not given.

A brief study brought out the following points in this connection. A stable emulsion containing 2 grams of oil to 98 grams of water was produced, (1) when 0.4 to 0.6 per cent of the 1 to 4 mixture of casein and hydrated lime was used; (2) when casein, dissolved in an amount of sodium hydroxide giving a hydroxyl concentration equal to that of the hydrated lime used in (1), amounted to 0.1 per cent, which corresponds approximately to 0.4 per cent of the 4 to 1 calcium casein mixture; and (3) when hydrated lime without casein was present in

TABLE 4

AMOUNT OF OIL IN RUN-OFF FROM A TWO-PER-CENT EMULSION MADE WITH VARYING AMOUNTS OF EMULSIFIER

Formula number	Calcium casein mixture *Per cent*	Ratio of emulsifier to oil *Per cent*	Ratio of concentration of oil in run-off to concentration in emulsion *Per cent*	Oil in run-off *Per cent*
1	5.0000	250.00	125.0	2.50
2	4.0000	200.00	120.0	2.45
3	3.0000	150.00	120.0	2.40
4	2.0000	100.00	122.0	2.44
5	1.0000	50.00	112.0	2.30
6	0.5000	25.00	106.0	2.20
7	0.2500	12.50	92.0	1.82
8	0.2000	10.00	86.0	1.70
9	0.1000	5.00	63.0	1.32
10	0.0500	2.50	63.0	1.24
11	0.0310	1.50	31.0	0.64
12	0.0078	0.39	17.0	0.34

the proportion of 0.6 to 0.8 per cent. The casein was found to be the more active emulsifying agent but the lime increased the general resulting stability. The principal value of the lime is in forming an alkaline solution, since casein dissolves in an acid or alkaline medium but not in a neutral one. A slight excess of lime also aids in neutralizing some of the soluble salts found in water which might hinder emulsification. Ordinary soap is now seldom used in spray practice for making emulsions, because the sodium base reacts with the calcium and magnesium salts in solution in many waters, forming insoluble soaps such as calcium oleate, thus causing the emulsion to break prematurely.

It was found, as the result of laboratory spray tests, that Oronite Crystal oil could be used effectively in emulsions of the quick-breaking type at two-per-cent concentration.

The following formula was finally developed as a standard for both laboratory and field use. The percentage values are obviously only approximate:

Oronite Crystal oil 2 per cent (2 gallons)
Calcium caseinate 0.0078 per cent (28.3 grams or 1 ounce, approximately)*
Water 98 per cent (98 gallons)

* As a result of field experience during the two years since this manuscript was originally prepared for publication it has been found that owing to the very general inefficiency of the average spray tank agitator, it is best and safest to use two to three times this quantity of emulsifier. This is not sufficient to noticeably affect insecticidal results, at least in the field.

In this formula the calcium caseinate is present in the proportion of 1 part to 200 parts of oil. In the laboratory the calcium caseinate is first dissolved in the water, then the oil is added and the whole violently shaken in order to produce emulsification. In the field a slightly different procedure is necessary. The calcium caseinate is first completely dissolved in about a quart of water. It is then added to from twenty-five to fifty gallons of water in the spray tank. The oil is next added and the agitator is started at the same time. The tank is then filled with water while the agitator is running. The emulsion is then ready to apply.

There is one point peculiar to this type of spray which is of considerable practical importance. The oil droplets are large and highly buoyant, and therefore quickly float to the surface of the water and form a definite layer or sheet of oil, which is, however, still emulsified. Vigorous agitation is, therefore, required to keep the spray of uniform consistency throughout. Only spray rigs which possess the most efficient type of agitator should be used to apply oil emulsions as quick-breaking as the one described above.

This spray has given 100 per cent kill of resistant red scale *in the laboratory*, where every scale insect was actually treated. In the field, owing to the impossibility of complete coverage and the possible effects of other factors this efficiency has never been attained.

FIELD TESTS OF A QUICK-BREAKING EMULSION

The quick-breaking Oronite Crystal oil emulsion previously described has been tested in the field. The formula found most satistory in the laboratory tests was used. As previously indicated, the resulting kills have never been as efficient(as might be expected) as those attained in the laboratory work. The results are shown in table 5.

These kills resulted from very careful application. The percentage surviving from average commercial spraying with the same material would no doubt often be above these figures. The results given are based on counts made on the fruit. Less satisfactory results occur on the twigs, possibly because of their greater oil-absorptive capacity, thus resulting in a less permanent oil film.

The criterion of effective application is complete coverage resulting in the presence of a visible film of oil over the entire surface of the plant, after the water carrier has evaporated.

TABLE 5

MORTALITY OF RED SCALE IN FIELD TESTS OF A QUICK-BREAKING TWO-PER-CENT EMULSION OF ORONITE CRYSTAL OIL

Place	Per cent of scale† surviving on fruit at end of test
Riverside, Calif.	5.05 and 2.94 (2 plots)
Whittier, Calif.*	7.95
La Habra, Calif.*	2.96
Santa Ana, Calif.*	2.13 (On purple scale, *Lepidosaphes beckii* (Newman), 2.00)
Tustin, Calif.*	3.43
Santa Barbara, Calif.	5.86 and 3.90 (2 plots)
Lindsay, Calif.	7.8 and 0.0 (2 plots) (on the citricola scale *Coccus pseudomagnoliarum* Kuwana)
Average	4.0

* Resistant-scale areas.

† The red scale *Chrysomphalus aurantii* (Mask.) is meant except as otherwise noted.

EXPERIMENTS RELATING TO THE NATURE OF THE INSECTICIDAL ACTION OF NEUTRAL OILS

The following test illustrates the essential blandness and "neutrality" characteristic of these white, highly refined petroleum oils, a fact which finds further confirmation in that it is this type of oil which is utilized in human medicine. Coleman's mealybug (*Phenacoccus colemani* Ehr.) were continuously immersed in Oronite Crystal oil and examined twice a day until all had died. Death was assumed to take place concurrently with cessation of all bodily movements, as determined by absence of response to stimulation by a needle.

Table 6 includes the combined results of two distinct tests. The same data are shown graphically in figure 3.

Some supplementary data on other insects were obtained which check very well with the results recorded above.

Thus with cabbage aphis (*Aphis brassicae* Linn.), out of eight individuals which were tested two were still alive after 18 hours' immersion in the oil. There is little doubt that aphids on the whole are more susceptible than mealybugs.

Larvae of the orange tortrix (*Tortrix citrana* Fern.) likewise survive a considerable period of immersion in this oil. In one test involving two individuals, one specimen was dead at the end of the 72nd hour and the other at the end of the 96th. In this case cessation of the pulsation of the dorsal vessel was taken as indicative of death.

In the case of ladybird beetles (*Hippodamia convergens Guerin*) visible movements cease in from 3 to 7 minutes.

TABLE 6

SURVIVAL OF COLEMAN'S MEALYBUG IMMERSED IN ORONITE CRYSTAL OIL

Hours elapsed since beginning of test	Insects dead	Insects still living
0	0	40
68	1	39
72	6	33
77	4	29
96	1	28
114	4	25
120	5	20
144	2	18
148	1	17
160	1	16
166	1	15
184	4	11
240	3	8
264	1	7
288	2	5
294	2	3
312	1	2
336	1	1
384	1	0
Totals (end of test)	40	0

Average time of lethal immersion, $\frac{6524}{40}$ = 163 hours, or nearly 7 days.

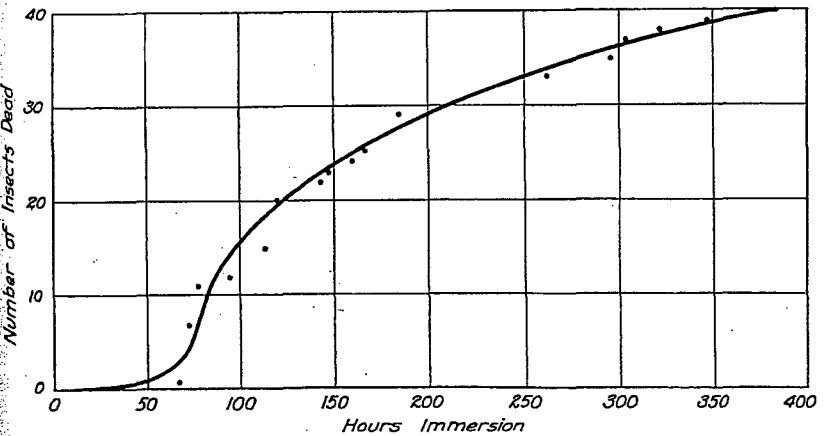

Fig. 3. Lethal curve of Coleman's mealybug, *Phenacoccus colemani* Ehrhorn, immersed in Oronite Crystal Oil.

The contrast between the long period of immersion required for mealybug and the shorter one for beetles was puzzling. As a check, beetles were immersed in tap water, and the apparent anomaly was then explained. Furthermore, there were obtained some data confirming our belief that the lethal effects of these highly refined oils could be explained almost solely upon the basis of suffocation.

Beetles were floated to the top of a water-filled, inverted test tube, and it was found that all visible movements ceased within practically the same length of time as in the oil. That cessation of movement in this instance was not indicative of death was clearly shown when beetles that had been immersed in water for several hours revived very rapidly upon being warmed and dried. This indicates that with these insects at least, cessation of movement is not a definite criterion of death.

There is little doubt that oil-immersed beetles would likewise revive rapidly and completely if the adhering oil could be dissipated as completely and rapidly as the water. The fact that they do not do so indicates that enough oil adheres permanently to the body and completely covers the spiracles so that the insect cannot be removed from its oil bath.

Mealybugs were likewise treated with water as a lethal agent. Four insects so immersed for four hours and apparently dead, all movement having ceased, revived completely. In a succeeding check test ten mealybugs were kept under water for a period of five hours. Of these only two revived. These results indicate a very much lower average lethal immersion limit for water than for oil. Movement ceases much sooner in water than in oil.

As a final test of the "oxygen-deprivation hypothesis" eighteen mealybugs were placed in an atmosphere of pure hydrogen, which is essentially inactive so far as living organisms are concerned. Impurities due to the processes of generation were doubtless present in some degree, but on the whole the results check very well with those previously given. Of the eighteen specimens treated eleven were dead at the end of 24 hours; four more at the end of 48 hours and the remainder (thirteen) at the end of 72 hours. This is an average lethal immersion period of 64 hours, approximately two and one-half days.

In view of the foregoing data, it may be stated that death of scale insects through the action of white neutral oils may be ascribed almost entirely to suffocation. At least, this one factor offers a satisfactory explanation for all the known facts.

After the completion of the original draft of the manuscript of this paper it was found that we had overlooked two important articles bearing upon this same subject, written by George D. Schafer (13, 14) in 1911 and 1915 respectively. It is unnecessary to review his conclusions relative to our work, which was done entirely independently, but it is worth while to note that our results bear practically the same implications and are confirmatory of his conclusions on the subject of oxygen deprivation.

TABLE 7

RELATION OF VISCOSITY OF OIL TO ITS EFFECT ON RED SCALE

No. of test	Oil description	Viscosity	Percentage of oil in emulsion	Per cent scale surviving test*	Remarks
1	Castor oil	1840	2	48.0	No more than natural mortality.
2	No. 6, a heavy lubricating oil	364	2	0.0	
3	Oronite Crystal oil	100	2	0.0	
4	A special light lubricating oil (specifications not given)	38	2	2.0	This oil was just below the lethal viscosity limit.
5	No. 4a, a refined kerosene	21+	20†	19.0	

* The basis for scale counts ranged from 200 to 600 insects.

† In spite of the high percentage here used only a very poor kill was obtained; at 2 per cent only the natural mortality would have been found.

In laboratory tests, oils within a rather wide range of high viscosity, other things being equal, gave complete control. Below the minimum of this range, the lighter an oil the less certain will be the kill. On the other hand, extremely high viscosities are likewise ineffective. These facts are illustrated in table 7, which is based upon laboratory tests.

Under the heading "viscosity" are given a series of values which are approximate only. Oronite Crystal oil was arbitrarily taken as a standard and assigned a value of 100. The values were determined by measuring the time of flow of 50 cc. of the oil from a small burette at a constant temperature.

These tests were made with the resistant red scale (*Chrysomphalus aurantii*). All emulsions were of the quick-breaking type.

These oils (excepting castor oil) are all almost entirely non-toxic and castor oil even with its toxicity fails to kill. Evidently castor oil and oil 4a are ineffective for different reasons. In the case of castor oil the cause is probably mechanical, as this oil is apparently too viscous to spread evenly and form a continuous film. In the case of oil 4a, on the other hand, the oil evaporates so quickly that a film is not maintained long enough to kill the more resistant individuals. The minimum viscosity[7] limit for complete killing evidently lies somewhere between Oronite Crystal oil and the "special light lubricating oil" used in this test.

Dilution tests (table 8) were then made and found to conform in general to the conclusion just stated. Kerosene distillate was used in making these viscosity reductions. These tests are not conclusive and must later be greatly extended, particularly toward the lower limits.

TABLE 8

EFFECTS OF DILUTING HEAVY OILS WITH KEROSENE DISTILLATE

Oil	Viscosity	Percentage of oil in emulsion	Percentage scale surviving test
Castor oil plus kerosene distillate	74±	2	0.0
Oronite Crystal oil plus kerosene distillate	45±	2	0.0
Oil 6 plus kerosene distillate	100	2	0.0

Kerosene distillate is of itself ineffective, but when its viscosity is increased by the addition of castor oil (or vice versa) a kill is immediately obtained. Toxicity is of paramount importance in assigning practical limits to degrees of volatility (viscosity) permissible in a given oil. For instance, an oil which might be volatile enough to disappear completely in one hour, if also sufficiently toxic to penetrate and kill the most resistant individual scales treated in thirty minutes, would obviously be entirely effective as a spray material. On the other hand a non-toxic oil which would volatilize completely in ten days would not suffice to kill red scale. The importance of these two factors lies not so much in their *absolute* as in their *relative* values.

[7] The terms 'low viscosity' and 'high volatility' cannot be used interchangeably in all cases. Oils from a similar source, distilled at the same range of temperature will be quite uniform in viscosity, but in the process of refining, the viscosity changes enormously, while volatility may remain constant. The blending of oils of different viscosities may also destroy the correlation between viscosity and volatility.

PRELIMINARY TESTS OF TOXICITY OF INSECTICIDAL MATERIALS

Table 9 gives data relating to the toxicity of a series of oils and other substances. These values should be self-explanatory in view of the preceding discussion. The tests were not all made in the same way and on the whole can be relied upon to give an idea of relative toxicity, but not of the minimum lethal limit, which is ultimately the most important factor. Five mealybugs, *Phenacoccus Colemani* (Ehrhorn), were used in making each of the determinations. Substances are listed according to toxicity, the more toxic ones coming first.

The possibility of imparting toxicity to otherwise neutral oils through the addition of toxic constituents (fatty acids or unsaturated hydrocarbons, for instance) and hence permitting higher volatility and shortening the time of insect kill may be of great importance in future work. This raising of the volatility is also of considerable significance in decreasing plant injury. Long persisting oils may tend to upset the metabolic processes of the plant even where no immediate effect is noticeable.

TRACHEAL PENETRATION OF INSECTICIDES AND SIGNIFICANCE OF SOLUBILITY OF WAX IN OILS

A study was made of the penetration of different fractions of petroleum oils, some of the vegetable oils and other spray materials, into the tracheal system of the red scale. This work was somewhat similar to that of Moore(7) on tracheal penetration.

For this purpose specimens were chosen that had passed through the second moult but had not yet reached maturity. At this stage of development the insect is free from the scale covering and can be lifted out intact. The detached insect is placed on a slide, ventral side up, and when it is immersed in liquid the tracheal system becomes plainly visible. The low refractive index of the air-filled trachea causes them to show as black lines under the microscope. If penetration of the liquid occurs, it causes an increase in the refractive index of the liquid-filled portion with a consequent lowered visibility, and the degree of penetration becomes plainly visible.

Figure 4 is a photomicrograph showing the main branches of the tracheal system of the red scale. It will be noted that the spiracles

TABLE 9

RELATIVE TOXICITY OF INSECTICIDAL SUBSTANCES TO MEALYBUGS AS INDICATED BY PERIOD OF LETHAL IMMERSION

Rank	Substance	Time of lethal immersion	Remarks
1	Benzol	3 seconds	Chemically pure
2	Ether	10 seconds	Chemically pure
3	Grain alcohol	90 seconds	95 per cent pure
4	"Zero" rosin oil	3 minutes	Georgia Rosin Products Co.
5	Double Run Zero rosin oil.	3 minutes	Georgia Rosin Products Co.
6	Triple Zero rosin oil	3 minutes	Georgia Rosin Products Co.
7	Turpentine	3.5 minutes	Commercial
8	Double-distilled coconut fatty acid.	6 minutes (average)	Armour & Co.
9	London rosin oil	7 minutes	Georgia Rosin Products Co.
10	Oleic acid	7–12 minutes	Commercial
11	Shale oil	12 minutes (maximum)	California distilled
12	Petroleum oil 1†	17 minutes (maximum)	Standard Oil Co. of Calif. (lubricating-oil distillate)
13	Furfural	10–13 minutes	Insects only partially immersed, vapors evidently toxic.
14	Special "X" rosin oil	20 minutes (average)	Georgia Rosin Products Co.
15	Liquid asphalt	30 minutes*	Standard Oil Co. of Calif.
16	Unsaturated hydrocarbons removed from kerosene	43 minutes (average)	Standard Oil Co. of Calif.
17	Vaseline plus water white distillate.	60 minutes*	Vaseline 1 part, kerosene 5 parts.
18	Petroleum oil 3†	60–360 minutes	Standard Oil Co. of Calif. (lubricating-oil distillate)
19	Petroleum oil 1a†	60–1200 minutes*	Standard Oil Co. of Calif. (kerosene distillate)
20	Petroleum oil 3a†	108 minutes (average)	Standard Oil Co. of Calif. (kerosene)
21	Petroleum oil 2a†	120 minutes*	Standard Oil Co. of Calif. (kerosene)
22	Petroleum oil 4a†	120 minutes*	Standard Oil Co. of Calif. (the least toxic of the kerosenes)
23	Whale oil	210 minutes*	Crude. Highly toxic.
24	Petroleum oil 2†	240–720 minutes	Standard Oil Co. of Calif. (lubricating-oil distillate)
25	Cottonseed oil	13–1400 minutes	Crude
26	Linseed oil	30–1300 minutes	Commercial
27	Petroleum oil 4†	240–1400 minutes	Standard Oil Co. of Calif. (lubricating oil)
28	Castor oil	1400 minutes*	Refined
29	Fish oil	1400 minutes*	Commercial
30	Petroleum oil 4x†	1400 minutes*	Standard Oil Co. of Calif. (lubricating oil)
31	Olive oil	2500 minutes*	Refined
32	Petroleum oil 6†	2500 minutes*	Standard Oil Co. of Calif. (lubricating oil)
33	Petroleum oil 5x†	2500 minutes*	Standard Oil Co. of Calif. (lubricating oil)
34	Petroleum oil 7†	1200–5760 minutes	Standard Oil Co. of Calif. (lubricating oil)
35	Petroleum oil 5† (Oronite Crystal oil)	9780 minutes (average)	Standard Oil Co. of Calif. (lubricating oil)

* The definite meaning (whether average, maximum or approximate survival limit) of the value given is unknown.

† See table 1 for further specifications.

are connected with each other by four large tracheal trunks. In addition a large number of smaller branching tubes ramify to all parts of the body. For purposes of comparison the spiracle-connecting trunks of the tracheal system are divided into three areas designated as A, B and C.

That portion of the trunk extending from the opening of the spiracle to the point where the trachea first branches is designated A. About one-third of the distance between the spiracles along the main tracheal trunk is designated B, and the entire distance C. In figure 4, these distances are shown from one spiracle only. When the oil penetrates far enough to fill the four trunks it has usually, at the same time, completely filled the smaller branches.

Table 10 shows that neither lime-sulfur solution (in ordinary dilution) nor Bordeaux 5–5–50 showed any penetration at all. When lime-sulfur and a proprietary miscible oil were combined there was a fair degree of penetration. All emulsions of the lubricating-oil type, as well as the lubricating oils themselves, gave good penetration, filling the entire tracheal system. The kerosenes, on the other hand, were very erratic in behavior. Initial penetration (2–8 minutes) was in nearly all cases very rapid but in a considerable number of instances this gradually ceased, and movement of the liquid was reversed so

that the tube emptied itself. Apparently the insects have the power of expelling these light oils from the tracheae. Furthermore, they are then able to keep these oils from penetrating for more than 30 to 40 minutes. This ability of the insect, particularly when taken

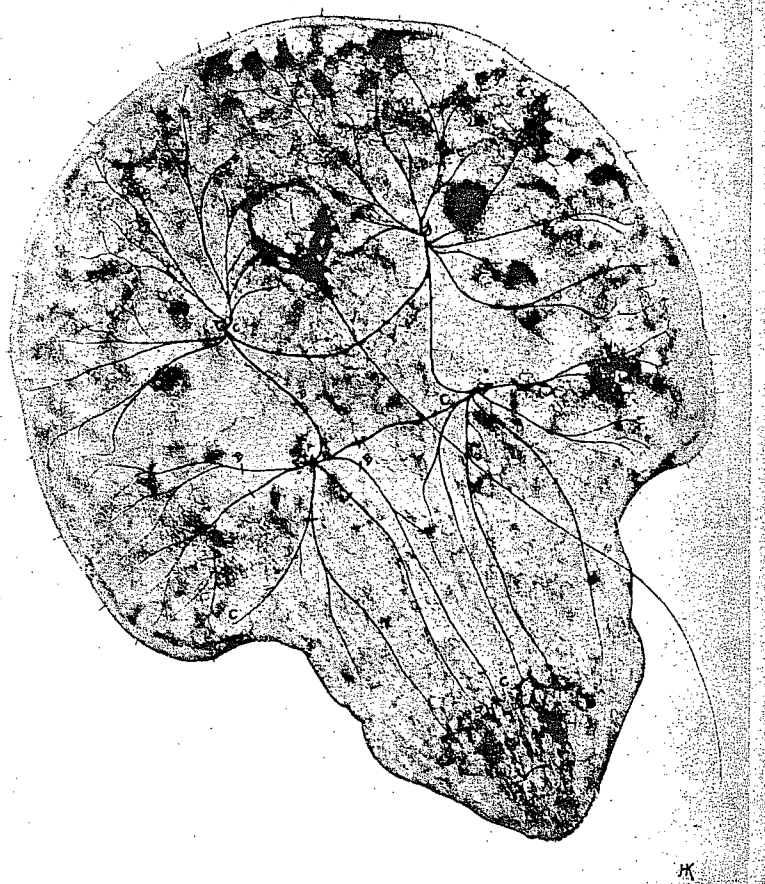

Fig. 4. Ventral aspect of the red scale, *Chrysomphalus aurantii* (Maskell), showing the tracheal system.

in connection with the high volatility of the oils, excludes the kerosenes from the class of satisfactory scalecides even though their toxicity is relatively high compared with that of neutral lubricating oils.

In these tests it was found that soaps, oils, stable emulsions and water-glue solutions were capable of penetrating into the tracheae

of these detached insects. In some cases, as in highly stable oil emulsions and lime-sulfur oil mixture, the penetration seemed to be that of the emulsion itself. This seems to raise a question, considering the emphasis previously laid upon the necessity of oil liberation. It is obvious that anything, whether a pure oil or an emulsion, which would completely clog the spiracles would ultimately suffocate the insect.

TABLE 10

TRACHEAL PENETRATION OF RED SCALE BY INSECTICIDAL SUBSTANCES

Material	Tracheal penetration
Sprays:	
Lime sulfur, 2 per cent	None
Lime sulfur, 10 per cent	None
Lime sulfur, 20 per cent	A
Lime sulfur, undiluted	A
Bordeaux, 5–5–50	None
Miscible oil, 2 per cent and lime sulfur, 1 per cent	B
Commercial oil emulsion, 5 per cent (standard type)	C
Fish-oil soap and Oronite Crystal oil emulsion, 6 per cent	C
Fish-oil soap and No. 6 petroleum oil emulsion, 6 per cent.	C
Fish-oil soap and kerosene distillate (Oil No. 1a) emulsion, 6 per cent.	Erratic, initially rapid
Fish-oil soap and kerosene oil No. 2a emulsion, 6 per cent.	Erratic, initially rapid
Bordeaux and Oronite Crystal oil emulsion, 6 per cent	C
Ferrous sulfate and Oronite Crystal oil emulsion, 6 per cent	C
Oils (pure):	
Oronite Crystal oil (No. 5)	C
Petroleum oil No. 6	C
Kerosene, No. 2a	C
Kerosene distillate, No. 1a	C
Cottonseed oil (Crude)	C
Oleic acid	B
Turpentine	B
Linseed oil	C
Miscellaneous:	
Tap water	None
Sodium silicate (water glass)	A
Xylol stained with Sudan III	Erratic, ultimately complete
Xylol (pure)	C

The paradox is explicable, however, when we consider the penetration of the trachea of an insect *in situ*. Here the armored scale (red scale), which was the subject of discussion in connection with the liberation of oil from quick-breaking emulsions, is completely protected by both a dorsal and a ventral waxy scale covering. For the insecticide to come into actual contact with the spiracles necessitates first of all penetration of this scale covering. Water is not a wax solvent and is hence completely excluded from penetrating this covering. The same consideration applies to any water mixture, including stable emulsions wherein water is the continuous phase and where little or no oil liberation takes place. Free oils on the other hand are not only capable of tracheal penetration but are wax solvents as well and hence capable of penetrating the scale covering. In a stable emulsion the oil is kept largely locked up and hence can exert no independent effect upon the wax.

This explanation is borne out by the fact that miscible oils (as is found in current practice in the field) may be fairly effective against the unarmored black scale (*Saissetia oleae* Bernard), where the spray is able to gain unobstructed access to the tracheal opening, while they fail in large degree in the case of red and other armored scales.

VEGETABLE OILS

In addition to the petroleum oils, certain vegetable oils were tested as spray materials. These include cottonseed, linseed, castor, and rosin oils. These are all much more toxic to insects (as indicated in table 9) than neutral white oils, no doubt on account of their fatty-acid content. These fatty acids seem in general to correspond to the unsaturated hydrocarbons of the petroleum oils. Like the latter, they are toxic to plants as well as to insects, although in many instances at least, to a less degree.

The most promising of the vegetable oils tested was cottonseed oil. In the field this gave an excellent kill of scale, but defoliation was considerably more severe than was the case with Oronite Crystal oil. There is a great field for future investigation of vegetable oils in connection with insecticidal spray work.

COCONUT FATTY ACID

In view of the widespread interest in the recent development of the use of coconut-oil fatty acids by Siegler and Popenoe(15), it is well to call attention to the fact that while they undoubtedly have marked insecticidal properties, they are also exceedingly toxic to plant tissue when used in concentrations even remotely approximating those necessary to kill armored scale insects of citrus. The following test shows this conclusively.

An emulsion was made with equal parts of fatty acid and gasoline, as recommended in the reference quoted, but the amount of glue was reduced so as to make an emulsion of the quick-breaking type. This mixture was diluted with water until the emulsion contained 2 per cent of the fatty acid. A potted citrus plant was sprayed with this emulsion with disastrous effect. It was completely defoliated and both the leaves and the twigs were badly burned and spotted.

Lemons infested with red scale were sprayed with the same emulsion. The fruit was burned and shriveled, but only 97 per cent of the scale was killed. Furthermore, at the time the examination was made (ten days after spraying) young were hatching and settling on the fruit. In this instance, although severe injury resulted to the plant and fruit, the scales were not all killed. This failure is probably due in large part to lack of wax solubility, with consequent inability to penetrate the scale covering. This material would probably be much more effective against the unarmored black scale (*Saissetia oleae*).

On diluting the emulsion one-half, so that it contained 1 per cent of fatty acid, a mortality of only 83.4 per cent was found and the fruit was again shriveled.

The test was repeated without the gasoline in order to get the full effect of the undiluted fatty acid. An application of a two-per-cent emulsion left only 0.66 per cent of the scale alive but severely injured both the fruit and plant.

Finally a stock emulsion was applied, made according to the formula recommended, with its full complement of glue (giving a stable emulsion) and containing 2 per cent of fatty acid (or 80 times as strong as recommended for aphids). No injury to the plant resulted from this application. When the determination of insect mortality was made, there could be found no indication that an insecticide had been applied, the count showing mortality of 43.6

per cent, which is equivalent to natural mortality only. The spray had proved totally ineffective. Young scale were found crawling *freely about within two days after the application.*

These tests again confirm the conclusions previously reached regarding the necessity of a quick-breaking emulsion in order to liberate the insecticidal agent for effective use.

SUMMARY

1. Petroleum oils of the kerosene and "stove-distillate" type (28°–32° A.P.I.) have been occasionally used as insecticides over a period of many years in citrus orchards, with varying results as to insecticidal effects and injury to the tree and fruits.

2. Non-viscous oils of a low boiling point, such as the kerosenes, are safer to use on the tree than those of high boiling points, but are unsatisfactory as scalecides because of relatively low toxicity combined with high volatility.

3. Highly refined, white lubricating oils are probably the most advisable for use on citrus trees, especially at summer temperatures. Oils of a low viscosity are apparently safer to use on trees than those of high viscosity. This is due to the more rapid disappearance of the former.

4. Severe injury to the citrus trees from the use of lubricating oil is associated with the presence of a high percentage of unsaturated hydrocarbons. Refining petroleum oil with sulfuric acid removes the following injurious constituents: aromatics, olefins, resins, and sulfur.

5. The filtration of petroleum oils through Fuller's earth has not shown itself effective in reducing the amount of injurious constituents present.

6. Gross symptoms of injury to citrus trees from the use of unrefined petroleum oils, include defoliation, fruit spotting and dropping and the killing of twigs and branches. In addition to these injuries, there is an apparent interference with the normal plant functions of transpiration and respiration.

7. A quick-breaking emulsion utilizes to the maximum degree the insecticidal agent. Two per cent non-volatile lubricating oil with 98 per cent of water as a carrier has, when applied as a quick-breaking emulsion in the laboratory, produced a complete kill of red scale on lemons. Stable oil emulsions using the same ingredients are ineffective against this scale at strengths of from 4 to 8 per cent actual oil.

8. The "quick-breaking" action in an emulsion is greatest when the average size of the dispersed oil globules is greatest, and that size is greatest when the proportion of emulsifier to oil is least.

9. The concentration of oil in the run-off from sprays containing 2-per-cent concentration of oil varied from 2.5 per cent for the stable type of emulsion to 0.39 per cent for the quick-breaking type in laboratory tests on glass plates.

10. The insecticidal action of unrefined lubricating oils seems to be the result of two principal lethal factors. These are suffocation and toxic action, or poisoning. The former results chiefly from non-volatility (film permanence), the latter chiefly from the action of unsaturated hydrocarbons in the case of unrefined petroleum oils, or that of free fatty acids in the case of vegetable oils.

11. The wax solubility of oils is one of the important factors determining the insecticidal effectiveness of lubricating oils against the red scale. In the quick-breaking emulsions the free oil dissolves the waxy scale covering and enables the oil to penetrate to the spiracles; stable emulsions, with which the liberation of free oil does not readily occur, lack this feature to a great extent and are therefore not so effective.

12. The lethal immersion period varies from a few seconds for the most toxic substance tested to sixteen days for the least toxic.

13. Volatility limits of oil range from a few minutes or hours to several weeks.

14. Various physiological disturbances, which are highly characteristic and little understood, are induced in citrus trees by the use of "neutral" white oils in quick-breaking emulsions. These disturbances are evidenced by special types of leaf and fruit drop but not by actual burning or spotting (except possibly in rare instances).

15. Free fatty acids—while highly effective as insecticides for aphids—are not suitable for use in quick-breaking emulsions at the high concentration required for the control of scale insects, because of the injurious effects on plant tissue of such concentrations of the acids.

16. The present paper is published as a progress report on a special investigation, the results of which, while highly suggestive and important, should not be construed as constituting a recommendation for practical orchardists.

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Phytotoxicity and Plant Uptake of Fuel Oil Hydrocarbons

C. H. Chaîneau, J. L. Morel,* and J. Oudot*

ABSTRACT

The phytotoxicity and phytoavailability of hydrocarbons (HC) were studied in soils artificially contaminated with fuel oil. The presence of HC in the soil inhibited seed germination and reduced plant growth. The germination and development of cultivated plants varied with the chemical structure of HC, the HC concentration in soil, and the plant species. The LC_{50} values for germination after 8 d in the presence of a fuel oil varied from 0.3 to 4% (oil/soil, w/w) for lettuce (*Lactuca sativa* L.), barley (*Hordeum vulgare* L.), clover (*Trifolium repens* L.), and maize (*Zea mays* L.) and from 4 to 9% for bean (*Phaseolus vulgaris* L.), wheat (*Triticum aestivum* L.), and sunflower (*Helianthus annuus* L.). Light aromatics and naphtas were the most phytotoxic HC. The inhibition of plant growth increased with HC concentration but was not linearly proportional to the loading rate. Reduction in aerial biomass was >80% for wheat and bean at a concentration of 0.3% and <30% for maize at 1.2%. No saturated nor aromatic fuel oil HC was detected by gas-chromatography in the stems and leaves of maize grown during 110 d on 1.2% oil-contaminated soil, indicating that no uptake of HC from soils occurred.

Hydrocarbons (HC) may enter the soil ecosystem as a result of accidental spillage or in the case of deliberate spreading of oily wastes like in landfarming operations. Whatever the origin of the contamination, an impact is observed on the vegetation that can be totally eliminated in the case of high loading rates (Kinako, 1981; Racine, 1994; Terje, 1984). Hydrocarbons have been proved phytotoxic (Currier, 1954; Havis, 1949; Amakiri and Onofeghara, 1983, 1984). Management of oil-contaminated soils requires often revegetation by plants. It has already been shown in an extensive landfarming experiment that crops could be successfully cultivated after the spreading of low rates of fuel oil (Chaîneau et al., 1996). However, the impact and fate of HC in plants received relatively little attention. The knowledge of sensitivity and resistance of common cultivated plants may be useful from the perspective of revegetating oil-contaminated soils. The possible transfer of HC from the soil to the aerial parts of plants also needed detailed studies, considering that the crops may eventually enter the food chain.

This work was undertaken to determine the phytotoxicity of fuel oil HC under controlled conditions. The effect of HC on inhibition of germination and growth of selected plants was assessed and the presence of HC in aerial parts of plants grown on HC contaminated soils was monitored.

MATERIALS AND METHODS

Soil Samples

The Ap horizon of an elluviated brown soil (Mollic Eutrochrept) was sampled, air-dried, and sieved (2-mm diam. openings). The main soil characteristics are given in Table 1.

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Fuel Oil Hydrocarbons

Two fuels were used: (i) a fuel oil (FO) composed of 60% saturated hydrocarbons (nC9–nC25), 30% aromatics, and 10% resins (Chaîneau et al., 1995); and (ii) a partially dearomatized fuel (DF) composed of 80% saturated hydrocarbons (nC9–nC25), 5% aromatics, and 15% resins. To determine the most phytotoxic compounds in FO, the fuel was distilled for 24 h at 90°C. The light fraction of FO contained the naphtas, i.e., n- and branched alkanes in the nC9–nC14 range, alkyl benzenes, and C1–C2 alkyl naphthalenes, whereas the residual heavy fraction contained the compounds above nC15. Gas chromatographic analyses of FO hydrocarbons are given in Fig. 1.

Plant Species

Seven plant species were used: sunflower (*Helianthus annuus* L.) var. Naindor, maize (*Zea mays* L.) var. DEA, wheat (*Triticum aestivum* L.) var. Fidel, barley (*Hordeum vulgare* L.) var. Plaisant, bean (*Phaseolus vulgaris* L.) var. Fetiche, lettuce (*Lactuca sativa* L.) var. Reine de Mai, and clover (*Trifolium repens* L.) var. Titan.

Phytotoxicity Tests

The phytotoxicity of FO hydrocarbons was assessed with two standardized methods. The AFNOR NF X31-201 (1982) method allowed for the determination of the toxicity of HC on germination of seeds and the AFNOR NF X31-202 (1986) was used to determine the influence of HC on plant growth.

In the germination tests, increasing amounts of the two fuels (FO, DF) were mixed with sand previously sieved (2 mm) and treated with hydrochloric acid, then rinsed with demineralized water. Resulting concentrations were in the 0.1 to 20% range (oil/sand, w/w). For each concentration, 250 g of contaminated sand was placed in a glass Petri dish (300 mL) and 80 mL of distilled water was added. For each plant species, 100 seeds were placed on each of the FO–sand mixture. The toxicity of the light and heavy fractions of FO was evaluated only on maize. For the light fraction of FO, the Petri dishes were sealed with a Teflon tape to avoid volatilization of the naphtas. The Petri dishes were incubated for 8 d at 22°C. The effects of oils and fractions on germination were determined by counting the seeds that germinated at the end of the incubation period and by computing LC_{50} values.

On the basis of the germination results, the effects of oil on plant growth were evaluated by growing resistant (bean and wheat) and fairly sensitive (maize) plants in the agricultural soil artificially contaminated with FO. A series (76) of 700-mL glass beakers was prepared, each containing 250 g of soil. Fuel oil concentrations in soil were: 0, 0.6% (6000 mg kg^{-1}), and 1.2% (12 000 mg kg^{-1}) for maize (48 beakers) and bean (12 beakers); and 0, 0.3, 0.6, and 1% for wheat (16 beakers). A concentration of 1% corresponded to a loading rate of 26 Mg HC ha^{-1} (0–20 cm layer, soil density 1.3), i.e., all concentrations were lower than those used in landfarming operations where rates are usually higher than 50 Mg HC ha^{-1} (Chaîneau et al., 1996). Each treatment was replicated four times for statistical treatment of the results by analysis of variance (ANOVA, *F* test). The soils were fertilized with 100 mL of a nutrient solution bringing 54 mg N kg^{-1} soil (NH_4NO_3), 54 mg P kg^{-1} soil (Na_2HPO_4 and KH_2PO_4,) and 54 mg K kg^{-1}

Abbreviations: HC, hydrocarbons; FO, fuel oil; DF, dearomatized fuel; GC, gas chromatography.

Table 1. Composition of the soil used in this study.

pH	7.7
Silt, %	74
Clay, %	20
Sand, %	6
Organic matter, %	2.3
Total N, ‰	1.3
C/N	10.1
P_2O_5, ‰ (Olsen)	0.15
Total Ca, %	0.4

soil (KH_2PO_4), a fertilization similar to that used in agricultural practices for maize (Chaîneau et al., 1996). Three seeds were sown per pot. Seven days after germination, one plant per pot was selected. Plants were cultivated under controlled conditions in growth chambers with a photoperiod of 16 h (darkness, 8 h at 18°C; light, 16 h at 22°C; hygrometry, 65%). Maize, wheat, and bean were cultivated for 110, 45, and 60 d, respectively. Periodic additions of sterile distilled water maintained soil moisture to 65% of the water-holding capacity. Plant height was regularly measured. At Days 40, 80, and 110 (maize); 45 (wheat); and 60 (bean) the dry biomass of aerial parts of the plants was measured and the percentage of inhibition was calculated as

$$(1 - DMc/DMh) \times 100$$

where DMc = dry matter of the control, and DMh = dry matter of plants on HC amended soil.

Analyses of Hydrocarbons in Plant Tissues

Hydrocarbons were analyzed in the aerial parts of the four maize plants cultivated on the HC-contaminated and control soils. A complementary experiment dealing with high HC concentration was conducted. Maize plants were first grown for 15 d in Knopp liquid medium without HC, then transplanted in wet sand saturated with FO (20%, w/w). The plants died within a few hours and aerial parts were analyzed for HC.

The leaves and stems were analyzed separately. They were dried for 12 h at 60°C and samples were Soxhlet-extracted with chloroform during 8 h. The extract was purified by percolating on a 60- to 100-mesh Florisil column, which retained most of the polar biogenic lipids, and was evaporated in a preweighed dish. The residue was weighed and separated in saturated, aromatic, and polar fractions by successive elution with 60 mL each of hexane, benzene, and methanol on a 15 by 1 cm chromatographic column filled with 100- to 200-mesh activated (110°C, 12 h) silica gel. Saturated and aromatic HC were analyzed by computerized gas-chromatography (GC) with a Delsi DI 200 chromatograph equipped with a direct injection port and a FID detector both set at 340°C; carrier gas was He_2 under 0.08 MPa; column was a CP Sil 5 CB (Chrompack) capillary column (50 m by 0.32 mm, film thickness 0.25 μm); temperature programing was 100 to 320°C, 3°C min^{-1}. Acquisition and numerical treatments of data were performed using custom-made computer programs. The analytical protocol has been validated in previous studies (Chaîneau et al., 1995, 1996).

RESULTS AND DISCUSSION

Effects of Fuel Oil on Seed Germination

Germination of seeds was adversely affected by the presence of HC (Fig. 2). Significant dose-dependent reductions in the germination rate were observed in all plant species. The different plants responded in different ways. Dearomatised fuel appeared less phytotoxic than FO for the most resistant plants; i.e., sunflower.

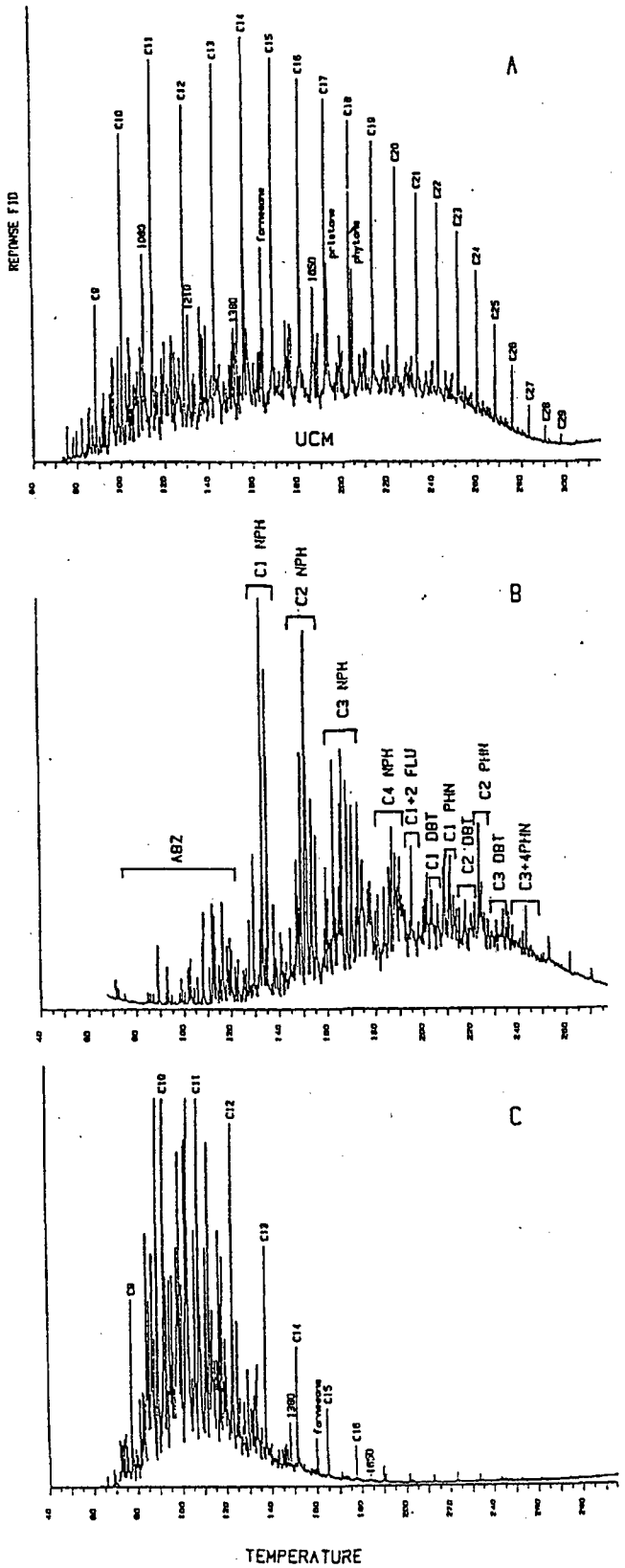

Fig. 1. Gas chromatographic analyses of (*A*) total fuel oil (FO); (*B*) aromatic fraction of FO; and (*C*) light fraction of FO. The C-numbers represent the carbon numbers of n-alkanes. 1080, 1210, 1380, 1650, isoprenoid alkanes; UCM, unresolved complex mixture; ABZ, alkylbenzenes; NPH, naphthalenes; FLU, fluorenes; PHN, phenantrenes; DBT, dibenzothiophenes; C1–C4, number of alkyl substitutions in aromatic molecular types.

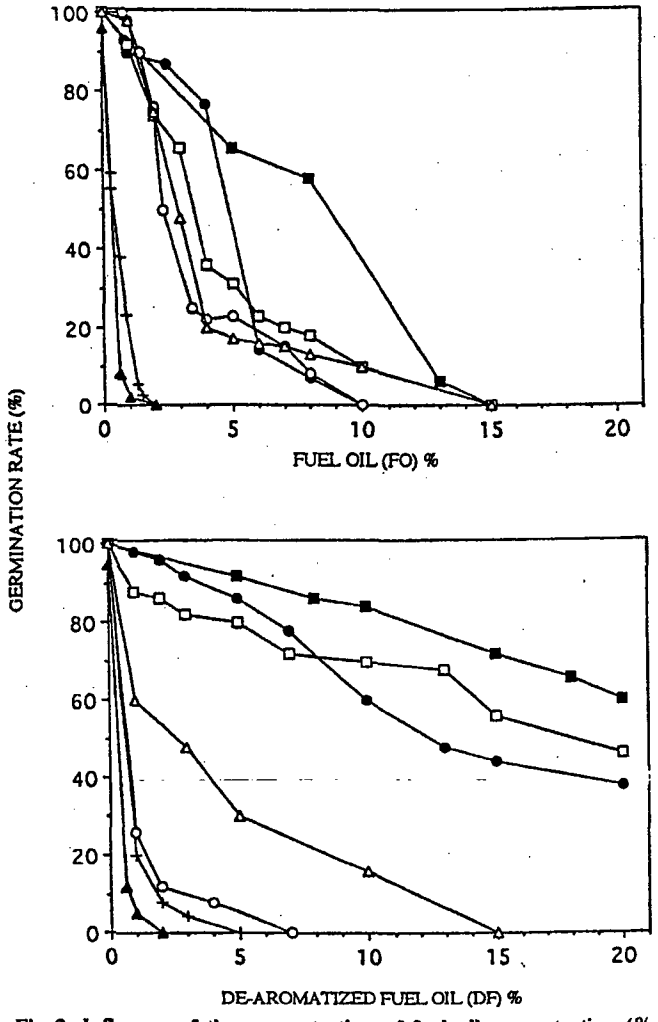

Fig. 2. Influence of the concentration of fuel oil concentration (% w/w) in the sand on germination of seeds. (●) bean, (■) sunflower, (+) barley, (○) maize, (□) wheat, (△) clover, (▲) lettuce.

wheat, and bean. For the other plants, there was no statistically significant difference between the two fuels. The resistance of seeds to oil contamination followed the decreasing order: sunflower > bean > wheat > clover > maize > barley > lettuce (Table 2). The LC_{50} values varied from 0.3% for lettuce to more than 20% for sunflower on FD. When germination occurred at concentrations higher than the LC_{50} value, the root system and the aerial parts were reduced in size. Also the incidence of fungal infection increased with HC concentrations. The effects of the fractions of FO on maize germination are presented Fig. 3. The light fraction of FO induced the most significant reduction in seed germination. Above a 1% concentration, no seed germination

Table 2. The LC_{50} values (8 d, % fuel in sand w/w) for the germination of plants in the presence of the different fuels.

Plant	Fuel oil	Dearomatized fuel
Sunflower	7	>20
Bean	5.5	12
Wheat	4	18
Clover	3	4
Maize	2.5	1.5
Barley	0.6	0.4
Lettuce	0.3	0.3

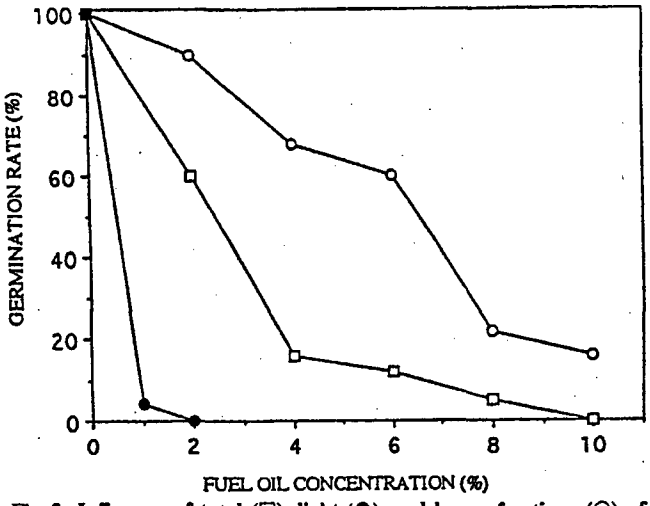

Fig. 3. Influence of total (□), light (●), and heavy fractions (○) of fuel oil (FO) on the germination of maize.

occurred. Conversely, the heavy fraction of the fuel was less phytotoxic than the complete fuel. The LC_{50} values were 2.4% for total FO, 0.3% for the light fraction, and 6% for the heavy fraction, indicating that the naphtas were 20 times more toxic than the heavy fraction of FO.

Oil can enter the seeds and alter the metabolic reactions and/or kill the embryo by direct acute toxicity (Udo and Fayemi, 1975). There is also strong evidence that the inhibition of germination is correlated with hydrophobic properties of oils that prevent and/or reduce exchange of water and gases (Amakiri and Onofeghara, 1984; Amadi et al., 1992; Udo and Fayemi, 1975). The resistance of seeds to phytotoxic properties of oils is mainly attributed to the structures of cell walls (Terje, 1984). The high phytotoxicity of naphta and light aromatics is confirmed here. Light aromatic structures are known to be potent contact herbicides (Currier, 1954; Havis, 1949). The partially DF was effectively less toxic than the complete FO and the highly toxic light fraction of FO was rich in alkylated benzenes and naphthalenes. Highly refined oils of low aromatic content are of low toxicity when sprayed onto plants (Baker, 1970; Ivens, 1952). Havis (1949) compared the toxic properties of pure hydrocarbons and showed that the toxicity decreased in the order aromatics, naphtenes, olefins, and straight chain paraffins. Polycyclic aromatic HC (PAH) also cause chronic injury to plants although they penetrate much more slowly into the plasma membranes (Baker, 1970; Bossert and Bartha, 1985, Simonich and Hites, 1994).

Effects of Fuel Oil on Plant Growth

Plant growth was significantly reduced by the presence of fuel oil (Table 3). Reduction in the dry biomass of aerial parts was higher than 80% for wheat and bean. Growth inhibition increased with HC concentration but was not linearly proportional to the loading rates. The vegetative development of these two plants was altered. After 45 d of cultivation, the average number of leaves and tillers per wheat plant were: 18.5 leaves and 4 tillers for the control; 9.6 leaves and 2 tillers for 0.3% contaminated soil; and 7 leaves and 1 tiller for 0.6 and 1.2% contaminated soils. During cultivation, bean and wheat

Table 3. Influence of fuel oil concentration on plant development.

Plant:	Maize						Wheat			Bean	
Days of cultivation:	40		80		110		45			60	
Fuel oil conc., %	0.6	1.2	0.6	1.2	0.6	1.2	0.3	0.6	1	0.6	1.2
Height, cm	86 ± 6	81 ± 4	89 ± 4	85 ± 8	99 ± 11	93 ± 8	31 ± 4	27 ± 4	25 ± 4	12 ± 3	11 ± 1
Height reduction, %	20 ± 6	25 ± 5	3 ± 3	18 ± 8	5 ± 2	17 ± 8	29 ± 2	38 ± 4	43 ± 5	81 ± 8	89 ± 7
Leaves, dry wt. reduction, %	56 ± 8	78 ± 3	28 ± 12	44 ± 11	4 ± 5	28 ± 12	85 ± 8	90 ± 6	92 ± 7	76 ± 5	85 ± 10
Stems, dry wt. reduction, %	44 ± 6	67 ± 2	27 ± 6	35 ± 8	4 ± 4	25 ± 9	81 ± 4	86 ± 5	89 ± 2	70 ± 1	75 ± 6
Fruits, dry wt. reduction, %	–	–	–	–	–	–	85 ± 6	90 ± 8	92 ± 10	20 ± 3	43 ± 11

leaves showed symptoms of chlorosis. The height and shoot biomass of maize also decreased with increasing HC loading rates (Table 3). The percentage of inhibition decreased with time, indicating that the toxicity of HC reduced after evaporation of the naphtas or that the plants recovered from the initial stress. A slowing down of the control due to limitation in cultivation conditions was also observed. After 110 d, a 30% growth inhibition was recorded on the most contaminated soil, but there was no statistical difference between the control and the 0.6% contaminated soil. No symptom of chlorosis was observed with maize.

At concentration below 1%, emergence of maize, wheat, and bean seedlings was not affected. However, plant development was reduced. Maize was reported to tolerate up to 1% oil pollution in the soil (Amakiri and Onofeghara, 1983; Udo and Fayemi, 1975; Giddens, 1976). The present investigation showed that drastic reductions in dry matter yields occurred with HC concentrations <0.6%. Wheat and bean were less tolerant to oil contamination than maize, which appeared fairly resistant. Petrogenic HC were shown to reduce growth development and yield of crops even at low concentrations (Chaîneau et al., 1996). Germination and plant growth tests gave different but complementary results since wheat and bean germinated better but grew less than maize on oil-contaminated soil.

The inhibition of plant growth may be attributed to the inherent toxicity of hydrocarbons, which results in the reduction in dry matter yields (Bossert and Bartha, 1985; Chaîneau et al., 1996). The wettability of oil-treated soil is reduced due to hydrophobic properties of crude oil bringing about perturbations in the roots development (Amakiri and Onofeghara, 1983; Udo and Fayemi, 1975) and reduction of the water and nutrients availability to the crop (Baker, 1970; Bossert and Bartha, 1985; Terje, 1984). In this way, chlorosis of wheat and bean leaves may be attributed to the inherent toxicity of HC but also to nutrient deficiencies. However, when HC are degraded in the rhizosphere by the indigenous soil microorganisms, the toxicity of the residual oil is reduced and plants develop normally even if non-biodegradable HC persist in the soil (Bossert and Bartha, 1985; Chaîneau et al., 1996; Hund and Traunspurger, 1994).

Uptake of Hydrocarbons by Maize

Identification and quantification of HC were made on maize plants collected from the growth experiment. From 40 to 110 d of cultivation, the concentration of the chloroform extractable organic matter of the shoots was about 12 000 mg kg^{-1} dry wt.: 80% were recovered from the leaves and 20% from the stems. The extracts were fractionated in saturated, aromatic, and polar fractions. In the leaves, 9% saturated, 40% aromatics, and 51% polars were recovered and in the stems values were 15% saturated, 25% aromatics, and 60% polars. These ratios were not affected by the presence of HC in soil. At each time of cultivation, the chromatograms of the saturated and aromatic fractions were identical in the leaves and in the stems, and no difference was observed between plants cultivated on unpolluted and oil-contaminated soils (Fig. 4). The saturated fraction (150–530 mg kg^{-1} in stems and leaves) was mainly composed of odd n-alkanes in the nC25 to nC33 range. Odd long chain n-alkanes are typical of biogenic HC produced by plants and are constantly isolated from soils (Chaîneau

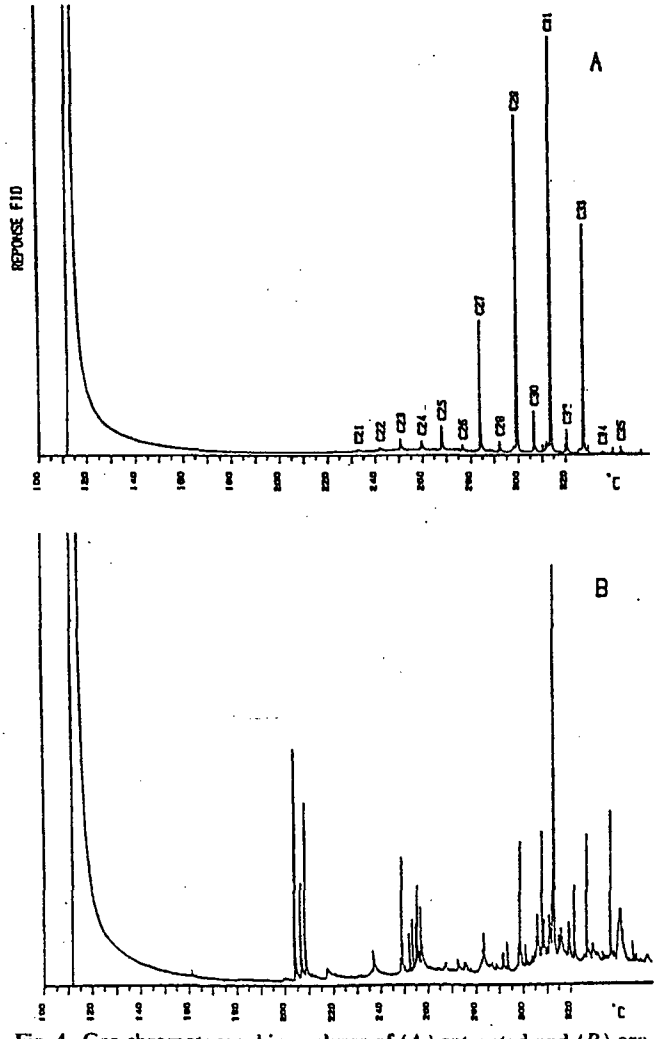

Fig. 4. Gas chromatographic analyses of (*A*) saturated and (*B*) aromatic fractions of the lipid extract of leaves of maize showing the absence of petrogenic HC. The numbers represent the carbon numbers of biogenic n-alkanes produced by the plant.

et al., 1996; Oudot et al., 1989). The *aromatic* fraction (300–900 mg kg^{-1} in the stems and 2000–3500 mg kg^{-1} in the leaves) contained numerous GC-resolved compounds that were not petrogenic aromatic HC but biogenic products. Comparison with the chromatograms of the initial fuel (Fig. 1) showed that no fuel oil hydrocarbon was detectable in the saturated or aromatic fractions of the shoots of plants grown on contaminated soils. The sensitivity of GC analyses could have allowed the detection of individual petrogenic HC at concentrations lower than 1 mg kg^{-1}, even in the presence of a high biogenic background. Earlier work showed that the seeds of maize, wheat, and pea (*Pisum sativum* L.) grown on an lightly contaminated agricultural soil did not contain any petrogenic HC (Chaîneau et al., 1996). Thus, at fuel concentrations compatible with plant growth, no uptake of petrogenic HC was observed. On the other hand, GC analyses showed that the maize plants cultivated in uncontaminated liquid medium then placed in heavily contaminated soils absorbed rapidly the fuel oil, which was detected at high concentration in the stems and leaves and presented a chromatographic spectrum exactly similar to FO. Therefore, in the case of a heavy pollution, the plants in place on the soil are not able to prevent the absorption of HC and die.

Some works have demonstrated that HC are taken up by plant leaves through air deposition in a polluted urban air (Simonich and Hites, 1994; Berteigne et al., 1989; Keymeulen et al., 1993; Calamari et al., 1994; Hauk et al., 1994; Tolls and Mclachlan, 1994). Very few studies have been undertaken to quantify the possibility of transfer of hydrocarbons from soil to aerials parts through the root system. Plants grown in sewage sludge–amended soil contained the PAH of the sludge only in the root peels, no trace of PAH was detectable in the foliage (Wild et al., 1992; Wild and Jones, 1992; Kirchman and Tengsved, 1991; Hülster et al., 1994). It has been demonstrated that the intensity of the transfer of organic compounds in the plants from soil or solutions was mainly correlated with the K_{ow} of the molecules, and hydrophilic organics may be translocated in the entire plant (Topp et al., 1994; Trapp et al., 1990, Hülster et al., 1994; Simonich and Hites, 1995). The present work showed that the phytoavailability of complex mixtures of low K_{ow} HC is negligible, even when the soil pollution is as high as 1%. Our analyses allowed only the identification and quantification of unmodified HC. It is not known, however, whether polar metabolic by-products resulting from microbial biodegradation of HC in the soil enter and are transported into the plants.

The phytotoxicity of petrogenic HC is confirmed in this work. It was highest for low molecular weight and aromatic HC and varied greatly with HC concentration in the soil and plant species. At concentrations compatible with plant growth, no uptake of petrogenic HC from the soil was observed in the aerial parts of the terrestrial plants under study, although they produce biogenic hydrocarbons.

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Fate of Summertime Airborne Organophosphate Pesticide Residues in the Sierra Nevada Mountains

Linda S. Aston and James N. Seiber*

ABSTRACT

This study examines the processes of dilution, degradation, and sorption to plant foliage of organophosphate (OP) pesticides during the summertime in an air corridor originating in the southern Central Valley of California and moving into the nearby Sierra Nevada mountains. Residues of chlorpyrifos, methidathion, and their oxons were examined in air and pine needles at three sites in the southern Sierra to delineate the role these processes play in the atmospheric fate of these residues. At the site closest to the Central Valley, we found relatively high levels of parent OPs and oxons in needle and air samples. At higher elevations needles contained lesser amounts of OP residues and at lower frequency, while air primarily contained the oxon form. With increasing elevation the ratio of thion to oxon form of chlorpyrifos in air decreased from 1.85 to 0.46 indicating that atmospheric oxidation was occuring. Based on the amounts of foliar deposition found, we estimate that during summer months nearly 16 kg of chlorpyrifos and its oxon may enter Sequoia National Park plant foliage. We deduce that for airborne OP insecticides, foliar deposition is a significant summertime fate process, along with atmospheric degradation and dilution.

California's Central Valley extends approximately 650 km from north to south and 160 km from east to west. It's eastern border is made up primarily by the Sierra Nevada mountain range. The valley itself is one of the most productive agricultural regions in the world, generating millions of dollars worth of crops that are distributed world wide. The productivity and quality of the crops are in part due to the use of pesticides. During 1994 nearly 91 million kg of pesticides were applied in California. Of this amount, nearly 6.1 million kg were OP pesticides (Cal EPA, 1994). Many of these chemicals are mobilized environmentally by volatilization and airborne transport. For example, most of the insecticide diazinon, used as dormant spray in California's Central Valley, volatilizes within a few weeks of application (Glotfelty et al., 1990). Once in the air, pesticides may remain in the gaseous state, partition onto particulate matter, be scavenged by water droplets, undergo degradation reactions, or redeposit onto soil, plant and water surfaces. The degree to which each of these processes occur is largely unknown, nor is it known what the impact is on the ecosystems in which the residues are ultimately deposited.

Dominant wind patterns bring polluted air originating in the Central Valley into the Sierra Nevada mountains. Locally, during the daytime the sun heats the slopes of the foothills of the Sierra. This causes the air mass over the slopes to rise and move up-slope from the valley. At night the processes reverse and wind movement is down-slope. In the southern Central Valley a regional nocturnal jet carries pollutants from the metropolitan areas of the northern valley to the south. A pattern of southerly wind, termed the Fresno Eddy, flows northward from the southern-most part of the Central Valley (Cahill et al., 1995). The up-slope/down-slope pattern, as well as the two regional wind patterns, combine to move air masses laden with ozone, aerosols and agricultural chemicals into the Sierra causing deteriorated air quality in the foothills and mountains (Cahill, 1989).

Environmental impacts on the Sierra ecosystems have been documented. Suspended particulate matter in Yosemite and Sequoia National Parks has severely limited visibility. Widespread ozone damage has occurred to both Jeffrey and ponderosa pines throughout the Sierra (Duriscoe, 1987). There is little information, however, about the fate or impact of airborne agrochemicals in Sierra ecosystems. The presence of OP pesticide residues in wet and dry deposition samples has been confirmed in wintertime samples from Sequoia National Park (Zabik and Seiber, 1993). There is also concern that agrochemicals, especially ones that exhibit estrogenic effects, may in part be responsible for the decline in the numbers of native amphibians in the Sierra Nevada (Boyer and Grue, 1995). It has been reported that in some areas there are no frogs to be found where only

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Abbreviations: OP, organophosphate.

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Canada-Wide Standards for Petroleum Hydrocarbons (PHCs) in Soil: Scientific Rationale

Supporting Technical Document

December 2000

TABLE OF CONTENTS:

List of Figures:

List of Tables:

Executive Summary

1.1 Synopsis

The Canada-Wide Standard for Petroleum Hydrocarbons in Soil (PHC CWS) was developed by the Canadian Council of Ministers of the Environment (CCME) under the Harmonization Sub-Agreement on Standards. The PHC CWS is a 3-tiered remedial standard for soil and subsoil protective of human and environmental health under four generic land uses – agriculture, residential/parkland, commercial and industrial. The purpose of this document is to provide an overview of the land use-based framework for the PHC CWS and the detailed scientific rationale in support of the derivation of the Tier 1 values. These values form the numerical basis of the PHC CWS and reflect the risk management and environmental quality goals of the standard as determined by CCME in consideration of scientific, technical and socio-economic factors and the substantive input of stakeholders.

1.2 Background

Petroleum hydrocarbons (PHC) describe a mixture of organic compounds found in or derived from geological substances such as oil, bitumen and coal. Petroleum products released to the environment, such as gasoline, crude oil and jet fuel, typically contain hundreds to thousands of compounds in varying proportions.

PHCs in the environment are a concern for a number of reasons. First, their reduced nature and volatility pose a fire/explosion hazard. Second, most PHC constituents are toxic to some degree. Third, lighter hydrocarbons are mobile and can be a problem at considerable distances from their point of release due to transport in ground, water or air. Fourth, larger and branched chain hydrocarbons are persistent in the environment. Fifth, PHCs may create aesthetic problems such as offensive odour, taste or appearance in environmental media. Finally, under some conditions PHCs can degrade soil quality by interfering with water retention and transmission, and with nutrient supplies.

Because PHC composition at a release site is a function of the source (e.g., gasoline vs. crude oil), site factors (e.g., soil texture, climate), time since release, and management, the effects noted above occur to varying degrees. Knowledge of the distribution and abundance of PHC types is necessary for accurate assessment and management response. However, most Canadian regulatory approaches and guidelines in the late 1990s did not consistently address this assessment requirement and also differed widely in other important ways, including the analytical methods required or accepted, scientific basis for assessment, and risk management objectives. This meant that PHC contaminated sites were not consistently evaluated and managed and that results were reported in a widely differing array of parameters and formats.

This condition is unsatisfactory and made more serious by the scope of the PHC problem. Throughout Canada, many tens of thousands of PHC release sites exist, and environmental liabilities have been estimated in the 10 billion $Can. range. Consistent, science-based assessment tools are needed to protect the environment and control costs. The PHC CWS was developed to address this need.

1.3 Framework for PHC CWS

The PHC CWS framework is based on a synthesis of the ASTM (1995) and CCME (1996) frameworks for the assessment and management of contaminated sites, and incorporates at successive tiers: (1) the application of generic (national) Tier 1 levels that are protective of human health and the environment, (2) site-specific adjustments to the Tier 1 levels to calculate Tier 2 levels that accommodate unique site characteristics, and (3) Tier 3 levels that are developed from a site-specific ecological or human health risk assessment, when assumptions inherent in the Tier 1 values are not appropriate for a site. The level of protection afforded, and the associated underlying guiding principles, are preserved throughout this tiered process. The tiered approach essentially represents increasing levels of precision in a site assessment through consideration of more specific site characteristics. Details on the phased acquisition of site information to support a sound PHC management decision are presented in a separate User Guidance document.

1.4 Approach to Development of Tier 1 Levels

The PHC CWS Tier 1 levels were developed using risk assessment and risk management techniques. In this approach, the primary environmental and human health values to be protected are identified, an analysis of how these values could be affected by PHC contamination is undertaken, and benchmark concentrations or levels of PHC in soil are calculated to provide an environmentally acceptable endpoint. The primary task is to develop an exposure scenario for each land use that adequately captures the receptors of concern and the pathways by which these can be exposed by PHC contamination in soil or subsoil. A summary of the receptor/pathway combinations addressed under each land use in the PHC CWS is presented in Table E1. Each combination is discussed further in the appropriate section of this Technical Supplement.

Tabular Tier 1 levels (see Chapter 5) are calculated for pathway/receptor combinations wherever the pathway is deemed applicable and sufficient data are available to support the derivation.

Table E1: Land-uses, key receptors and exposure pathways.

Exposure Pathway	Agriculture	Residential/ Parkland	Commercial	Industrial
Soil Contact	Nutrient cycling Soil invertebrates Crops (plants) Human (child)	Nutrient cycling Invertebrates Plants Human (child)	Nutrient cycling Invertebrates Plants Human (child)	Nutrient cycling Invertebrates Plants Human (adult)
Soil Ingestion	Herbivores Human (child)	(wildlife)* Human (child)	(wildlife)* Human (child)	(wildlife)* Human (adult)
Groundwater/ Surface Water	Aquatic Life/ Livestock Watering Human (child)	Aquatic Life Human (child)	Aquatic Life Human (child)	Aquatic Life Human (adult)
Vapour Inhalation (humans only)	Child, indoor**	Child, indoor	Child, indoor	Adult, indoor
Produce, meat and milk produced on site (humans only)	Child	Child (produce only)		
Off-site migration of Soil/Dust				Human/Eco

* wildlife dermal contact and ingestion data may be particularly important for PHCs (e.g., oiling of feathers, etc., although this should be addressed with an initial assessment of the presence of non-aqueous phase liquids - NAPL), but there are unlikely to be sufficient data to develop guidelines that address this exposure pathway

** a 30m horizontal offset is assumed between the farm residence and the PHC contamination, consistent with oil and gas development practices. Contamination nearer a farm residence triggers a residential assessment.

To address the diversity of PHC contamination types, including various crudes and product admixtures, PHCs are considered in four broad physico-chemical fractions synthesized from the sub-fractions defined by the US Total Petroleum Hydrocarbons Criteria Working Group. The fractions are defined in equivalent carbon numbers as follows:

F1: C6 to C10
F2: >C10 to C16
F3: >C16 to C34
F4: C34+

Aliphatic and aromatic sub-fractions are handled separately in the human health assessment.

Whereas the primary focus in PHC CWS standard development is prevention of toxic effects from F1-F4 on the receptors listed in Table E1, in certain situations these pathways may be of little immediate concern and PHC management is governed by other factors including:

- ignition hazard
- odour and appearance
- effects on buried infrastructure

- formation of non-aqueous phase liquids (NAPL)
- socio-economics and technological capabilities

Such factors are considered at the Tier 1 level in the integration phase, described below.

1.5 Human Health Protection

Inadvertent ingestion of soil can be a significant pathway of human exposure to contaminated soil. Studies indicate that children ingest much greater amounts of soil and dust each day than adults, primarily due to greater hand-to-mouth activity and a greater time spent playing outdoors and on the floor. In the PHC CWS children were assumed to ingest four times the amount of soil as an adult. Tier 1 levels were calculated using an algorithm common to both CCME (1996) and Atlantic PIRI (1999).

Dermal absorption of soil-borne PHC is addressed through the algorithm presented in Atlantic PIRI (1999). In no case was this pathway found to govern remedial response at the Tier 1 level.

Ingestion of cross-contaminated groundwater is addressed through use of a simple leaching/dilution model common to CCME (1996) and Atlantic PIRI (1999). It is conservatively assumed that the PHC contamination is underlain by an unconfined aquifer and that a potable well is located at the downgradient boundary of the site. At the Tier 1 level, this pathway, where applicable, would govern remedial response for F1 and F2 on sites with fine-textured soils, and F2 only on coarse-textured soils.

Migration of soil PHC vapours through cracks and imperfections in building foundations can lead to human inhalation exposure. This pathway is assessed through application of the vapour intrusion model of Johnson and Ettinger (1991), restricting transport to diffusion only in fine-textured soils and including advection in coarse soils. The vapour inhalation pathway governs remedial response at the Tier 1 level for F1 on coarse-textured sites.

1.6 Ecological Health Protection

Tier 1 levels are derived to protect key ecological receptors that sustain normal activities on the four previously defined land use categories: agricultural, residential/parkland, commercial and industrial. The derivation of Tier I levels for ecological receptors focuses on the effects of PHCs on the biotic component of a terrestrial ecosystem. Specifically, it evaluates the potential for adverse effects to occur from exposures to soil-based PHCs at point-of-contact or by indirect means (e.g., soil to groundwater pathways, food chain transfer).

Chronic, sub-chronic, acute and lethal responses of plants and invertebrates relevant to the sustainable functioning of soil under the four land uses are used to derive Tier 1 levels. A "weight of evidence" approach is used to arbitrate among the

various data sources. The direct soil contact pathway governs remedial response at the Tier 1 level for F3 and F4 under all land uses.

Concentrations of PHC in soil that would not be expected to pose a threat to aquatic life in nearby streams, rivers and lakes is estimated by modeling transport from soil through groundwater to a default discharge point 10 m downgradient from the PHC contaminated site. A dynamic, advective-dispersive model incorporating first-order biodegradation in the saturated zone (Domenico and Robbins 1984 as adapted by BC Environment) is used for this purpose. Remedial response for F2 at the Tier 1 level is governed by the Aquatic Life Protection pathway on coarse-textured sites when the surface water body is immediately adjacent to the PHC contamination. The lateral distance may be varied in Tier 2 up to a maximum of 500 m.

1.7 Integration of Human Health and Ecological Levels

A summary of the risk-based values developed for each pathway/receptor combination in the individual land use categories is presented in Chapter 5. In addition, rationale is provided for certain risk management decisions made in the final integration of human health and ecotoxicological inputs.

The principal features added to the PHC CWS at the integration stage were:

- Adjustment of eco-contact levels with respect to soil texture; and
- Addition of generic levels for subsoils – defined as earthy materials below 1.5 m depth.

In the process of developing these features the Development Committee considered several factors that are not easily accommodated in explicit, quantitative exposure and risk estimates. These factors included:

- Capabilities of current and emerging remediation technologies;
- Likelihood of subsoil disturbance and excavation under different scenarios;
- Potential effects of PHC on buried infrastructure;
- Aesthetics;
- Role of subsoil in terrestrial ecology;
- Costs of risk reduction measures; and
- Property values and environmental stewardship.

The objective of the integration is development of environmentally protective Tier 1 levels that are practical and attainable with proven remedial technologies. Remediation and conservation of PHC-affected soils is preferred over disposal.

1.8 Analytical Method

A benchmark method for determination of PHC in soil is presented that addresses major sources of variability and uncertainty related to the extraction, purification,

quantification and reporting. F1 PHC are isolated though purge and trap procedures followed by gas chromatography with a flame ionization detector (GC-FID). F2 – F4 PHC up to C50 are extracted by a Soxhlet procedure, "cleaned up" on silica gel and determined by GC-FID. C50+ PHC, if present, may be determined gravimetrically or through extended chromatography. Specific chromatographic calibration standards are required.

The analytical method has been tested in round-robin trials and found to drastically reduce variability in results over previous round robins where analytical procedures were not controlled. Performance-based alternatives to the benchmark procedures are permitted.

1.9 Recommendations for Future Research and Development

A number of important gaps in understanding were identified through the development of the PHC CWS and these are summarized in Chapter 7. Scientific review of the PHC CWS is planned for 2003, such that the standard may be revised in 2005. Key opportunities for research in the immediate future include:

- Toxicity testing of PHC fractions on aquatic receptors;
- Biodegradation rates of volatile PHC in the vadose zone;
- Toxicity assessment of gamma-diketone forming F1 aliphatics;
- Effects of soil PHC on buried infrastructure; and
- Aqueous and vapour-phase partitioning of F1, F2 PHC in the presence of residual F3, F4 PHC.

Acknowledgements

The Canada-Wide Standard for Petroleum Hydrocarbons in Soil came to be as a result of the cooperative efforts of a great many people. While it is not possible to acknowledge all participants, the contributions of some key individuals and groups must be noted.

George Murphy was the Alberta champion for the PHC CWS and kept the Development Committee on track and communicating effectively with the CCME parent committee. The Development Committee was co-chaired by Ted Nason and David Thornton, both of whom provided frequent after hours service to the project. The Development Committee was advised and supported by the Technical Advisory Groups. The Development Committee is deeply appreciative of the dedication and skill of the TAG chairs in facilitating discussions with stakeholders, providing sound technical advice, and vetting the ideas of the Development Committee. Doug Bright (Royal Roads University) chaired the Ecological Technical Advisory Group, Warren Kindzierski (University of Alberta) chaired the Human Health Fate and Transport Technical Advisory Group (HHFT TAG), Richard Turle (Environment Canada) chaired the Analytical Methods Technical Advisory Group, and Doug Younie (Alberta Environment) chaired the Socio-Economic Analysis Technical Advisory Group. The complete memberships of the Development Committee and Technical Advisory Groups are provided in Appendix A.

In addition to chairing the HHFT TAG through two separate phases, Warren Kindzierski also chaired the Protocol Improvement Working Group, which carried out an intensive nine-month review and development of the human health basis of the PHC CWS. Lin Callow (Gulf Canada Resources), Claude Chamberland (Shell Canada), Sharon Vervaet (NS Environment) and Ted Nason/Mike Zemanek (Alberta Environment) provided insights, data and substantial sweat equity.

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Glossary

absorption: The uptake of a chemical by a cell or an organism across biological membranes and including any transport to other tissues.

adsorption: The physical process of attracting and holding molecules of other substances or particles to the surfaces of solid bodies with which the former are in contact with.

advective flow: A process that transports a chemical from one location to another by virtue of the fact that the chemical is a component of a moving physical system (e.g. wind, flowing water, sediment transport).

aliphatic compounds: Organic compounds in which the carbon atoms exist as either straight or branched chains. Examples include pentane, n-hexane (not cyclohexane), and octane. The alkane group of aliphatics have maximum hydrogen content (saturated hydrocarbons), whereas alkenes have one or more double bond between adjacent carbon atoms. Alkynes have at least one triple bond between adjacent carbon atoms. Alkenes and alkynes are termed "unsaturated" hydrocarbons..

aromatic compounds: Contain ring structures formed from closed loops of carbon chains (most often containing six C atoms) where carbons in the ring have resonant double bonds. Aromatic compounds include compounds such as benzene, toluene, ethylbenzene, and xylene (*BTEX*), as well as polyaromatic compounds such as naphthalene. Because of the double bonding between carbon atoms, the molecules are not saturated with hydrogen atoms (un-saturated hydrocarbons).

asphaltene: Generally defined by the solution properties of petroleum residuum in various solvents. Asphaltenes are, broadly speaking, n-heptane insoluble and aromatic soluble. Structurally, asphaltenes are condensed polynuclear aromatic ring systems bearing mainly alkyl sidechains. The number of rings in oil asphaltenes can vary from 6 to 15. Tars or asphaltenes occur in many crude oils as colloidally suspended solid particles. Precipitation takes place when the crude loses it ability to keep those particles dispersed.

assessment endpoint: The characteristic of the ecological system that is the focus of the risk assessment. Formal expressions of the actual environmental value to be protected (e.g., fishable, swimmable water)

benefits: Positive changes resulting from an activity or project (e.g., increased income or productivity, reduced health risks, increased recreational opportunities).

bioaccumulation: The process by which chemical compounds are taken up by terrestrial and aquatic organisms directly from the surrounding environmental medium and/or through consuming contaminated food.

bioavailability: The amount of chemical available for uptake from environmental media to the target tissues of a receptor following exposure.

biodegradation: A microbiologically mediated process (e.g., due to the action of bacteria, yeasts, and fungi) that chemically alters the structure of a chemical,

the common result being the breakup of the chemical into smaller components (ultimately CO_2 and H_2O for aerobic biodegradation of hydrocarbons).

BTEX: Abbreviation for benzene, toluene, ethylbenzene and xylenes. These compounds are somewhat soluble, volatile and mobile in the subsurface environment and are useful indicators of contaminant migration.

Canada-wide standard (CWS): National standards that can include qualitative or quantitative standards, guidelines, objectives and criteria for the protection of the environment and human health. Included in the CWSs are numeric limits (e.g. ambient, discharge, or product standards), a commitment and timetable for attainment, a list of preliminary actions required to attain the standard and a framework for reporting to the public.

carbon-fractions: Petroleum hydrocarbons are categorized by fractions (F1 to F4) according to the equivalent normal straight-chain hydrocarbon (nC) boiling point ranges (Fraction #1: nC6 to nC10; Fraction #2: >nC10 to nC16; Fraction #3: >nC16 to nC34; and, Fraction #4: nC35+). In general, each carbon fraction contains all extractable hydrocarbon constituents which, on a DB1 *gas chromatographic column*, elute between and thus have a boiling point between the lower and higher indicated normal straight chain hydrocarbon.

clay: Soil components of equivalent diameter <0.002 mm usually consisting of clay minerals but commonly including amorphous free iron oxides, humic materials and trace quantities of primary minerals.

coarse-grained soils: Soil which contains greater than 50% by mass particles greater than 75 µm mean diameter (D_{50} > 75 µm).

conservative exposure scenario: A site conceptual model that includes receptors and pathways characteristic of a sensitive but plausible use of the land and water resources.

consumers: Organisms which require energy in the form of organic material from external food sources (heterotrophs).

costs: Negative changes resulting from an activity or project (e.g., capital and annual costs of a project, land removed from agricultural production, increased health risk, reduction of wildlife habitat).

critical receptor: The taxon, cohort, and developmental stage believed to be the most biologically sensitive among a larger target group that is potentially exposed to a contaminant (e.g. for humans, toddlers 6 months to 4 years old are often critical receptors for non-cancer causing substances).

critical threshold: The dose/concentration below which no adverse effect is expected to occur.

crude oil: Complex mixture of thousands of *petroleum hydrocarbon* and non-hydrocarbon compounds, extracted from natural deposits and prior to any distillation or other substantive refinement. Hydrocarbons comprise more than 75% of crude and refined oils, however heavy crude oils can contain more than 50% nonhydrocarbons (molecules containing oxygen, sulfur, nitrogen, or metals in addition to carbon and hydrogen). Crude oil

classification depends on specific gravity (light, medium or heavy) which can be further separated into fractions based on their boiling point.

decomposers: Organisms which derive their energy from breaking down organic matter from other deceased organisms (detritus).

downstream industry: *Petroleum hydrocarbon* industry sectors which are responsible for the marketing, sales, and re-distribution of a wide variety of end products and intermediates derived from refining crude oil. (e.g. petroleum retailers, refuelling stations such as airports, shipping ports, etc.). The downstream industry and its customers (including individuals, government and private sector entities) constitute a potential source for soil contamination of *PHCs* (e.g. leaky underground storage tanks, overflow spills, etc.).

ecological receptors: A non-human organism potentially experiencing adverse effects from exposure to contaminated media either directly (contact) or indirectly (food chain transfer). In the context of the PHC CWS, ecological receptors are the range of non-human organisms that might be found at a *PHC* release site and thus exposed to PHCs in the environment.

effects concentration low (ECL): A level of protection determined for commercial and industrial lands above a threshold effect concentration. It is derived from the distribution of effects data (*LOEC*, EC_{50} , LC_{50}) only and is preferably calculated using the weight of evidence approach, or alternatively by obtaining the geometric mean of available *LOEC* data. (see also Appendix D)

environmental quality benchmarks: Risk-based numerical values for the protection of sensitive ecological receptors from potentially toxic substances. Any value below which environmental risks to humans or ecological receptors are deemed to be unlikely, based on an evaluation of the existing scientific knowledge, in concert with policy decisions concerning biological effects levels above which environmental quality might be compromised.

equivalent carbon number (ECN): ECN is empirically related to the boiling point of a chemical normalized to the boiling point of the n-alkanes (straight-chain alkanes), or its retention time in a boiling point gas chromatographic column. It allows for the determination of an equivalent number of carbon atoms for chemicals where only the boiling point is known. The ratio of the number of C atoms to ECN for compounds with an ECN < ~12 is very similar to 1:1. See *carbon-fractions* for ECN ranges for individual PHC fractions.

estimated daily intake: Total "background" exposure to a chemical experienced by most Canadians. Estimated daily intake arises from the low levels of contamination commonly found in air, water, food, soil, and consumer products (e.g. tobacco, paints, and medicines). Estimated daily intake of a chemical is determined through a multimedia exposure assessment.

exposure pathway: The means by which organisms are exposed to contaminants. The possible categories of exposure pathways for humans or terrestrial ecological receptors include (i) direct transfer from the surrounding medium of contaminants (from air, water soil or sediment – by dermal uptake or absorption across external epithelial solution, (ii) ingestion of contaminated

soil or sediment, (iii) ingestion of contaminated water, (iv) inhalation of contaminated vapours or particulates, and (v) ingestion in food substances (including trophic transfer). The exposure pathway may also refer to the media from which an organism is exposed (air, water, soil, sediment, or combination thereof) and route of contaminant transport from source to receptor.

fine-grained soils: Soil which contains greater than 50% by mass particles less than 75 μm mean diameter (D_{50} < 75 μm).

gas chromatography: An analytical technique used in the quantification of PHC compounds. A sample is vaporized and injected into a carrier gas (e.g. helium or nitrogen) which passes through a solid-state elution column (a 100% polydimethylsiloxane column is used for PHCs). The sample is thereby separated into its component compounds according to the unique affinity of each compound for the stationary phase. The components appear separately at the effluent end of the column where they can be quantified using a flame ionization detector (for *PHC*s). The signal peak for each separated component compound is proportional to the quantity of the compound injected, making it possible to provide a quantitative analysis by calibration with known standards.

geo-environment: The *vadose* and saturated zones of the earth –excluding surface water bodies – participating in or communicating with the biosphere.

groundwater recharge: Process which occurs when the water content of the unsaturated zone becomes high enough to cause excess water to percolate downward to the water table, usually as a result of the infiltration of snow melt or rainwater into surface soils. Using a water balance approach, recharge is equal to the total amount of precipitation less the amount of surface runoff and evapotranspiration.

groundwater: Subsurface water beneath the water table in fully saturated geologic formations.

Hazard Quotient: An indication of potential risk from non-carcinogenic contaminants. It is estimated by dividing the expected exposure level by the associated *reference dose* for that contaminant. A value of <1 is presumed to be protective of the human population.

Heinz bodies: Molecules that accumulate at the red-blood-cell membrane, where they can damage or destroy red blood cells.

Henry's Law constant: A partition coefficient defined as the ratio of a chemical's concentration in air to its concentration in water at steady state. The dimensionless Henry's Law constant is obtained by dividing the Henry's Law constant by the gas constant, R.

hydraulic conductivity (*K*): The proportionality factor between hydraulic gradient and flux in Darcy's Law. It is a measure of the ease with which water is conducted through porous material and is primarily dependent on the characteristics of the porous material and to a minor extent, changes in viscosity of water.

lipophilicity: From lipophilic: literally – lipid-loving. The degree to which a substance will dissolve in organic, non-polar solvents. Lipophilic substances have very low water solubility.

LOEC (*Lowest Observed Effect Concentration*): The lowest concentration of a chemical used in a toxicity test that has a statistically significant adverse effect on test organisms relative to a control.

measurement endpoint: An effect on an ecological component that can be measured and described in some quantitative fashion (e.g., EC_{50}).

mogas: A commonly used refinery blend of motor gasoline. A special additive-free formulation of mogas was used to determine the toxicity of the F1 fraction (nC6 to nC10). Mogas contains approximately 30% aromatic and 70% total aliphatic compounds by weight.

monetizable benefits: Benefits to which a dollar value can be attached.

Monte Carlo simulation: An iterative process involving the random sampling of stochastic model parameter values from specified frequency distributions, simulation of the system, and output of predicted values. The distribution of the output values can be used to determine the probability of occurrence of any particular value.

multimedia exposure assessment: The simultaneous assessment of potential contaminant exposure from several environmental media (e.g. air, water, soil, etc.) by applicable exposure pathways (i.e., inhalation, dermal contact, ingestion).

NOEC (*No Observed Effect Concentration*): The highest concentration of a contaminant used in a toxicity test that has no statistically significant adverse effect on the exposed population of test organisms.

non-specific narcosis-type effects: General, reversible mode of toxic action to most biota from organic chemicals which disrupt normal cellular functions, presumably through either indiscriminate protein binding or disruption of the fluid mosaic architecture of cell membranes, resulting in impaired ion transport and polarization across cell membranes.

petroleum hydrocarbon (PHC): A hydrocarbon is a molecule consisting solely of carbon and hydrogen. Hydrocarbon groups present in *petroleum* products include: alkanes, alkenes, alkynes, aromatics, polynuclear aromatics, and complex hydrocarbon compounds containing oxygen, nitrogen, and sulfur. PHC compounds are found in or derived from geological sources such as oil, coal and bitumen.

petroleum: Products which consist of crude oils and a wide variety of refined-oil products.

porewater: The water occupying the space between particles of sediment or soil.

producers: Organisms which undergo photosynthesis to convert CO_2 and H_2O into sugars (autotrophs).

Qsoil: The advective flow of gas through soil.

reference concentration (RfC): An estimate (with *uncertainty* spanning perhaps an order of magnitude) of continuous inhalation exposure to the human population, including sensitive subgroups, that is likely to be without

appreciable risk of deleterious effects during a lifetime. RfC is used to evaluate potentially noncarcinogenic effects only.

reference dose (RfD): An estimate (with *uncertainty* spanning perhaps an order of magnitude) of daily exposure to the human population, including sensitive subgroups, that is likely to be without appreciable risk of deleterious effects during a lifetime. RfD is used to evaluate potentially noncarcinogenic effects only.

sand: A soil particle between 0.075 and 2 mm in diameter

silt: A soil particle between 0.002 and 0.075 mm in equivalent diameter.

slab-on-grade: Building foundation built as a concrete slab directly on the ground surface with no basement.

socio-economic factors: Includes benefits, costs, and technological considerations.

soil allocation factor (SAF): The relative proportion which soil constitutes in the total exposure from various environmental pathways (air, soil, food, water, consumer products).

soil organic matter: The organic fraction of the *soil*; includes plant and animal residues at various stages of decomposition, cells and tissues of soil organisms, and substances synthesized by the soil population. It is usually determined on soils that have been sieved through a 2.0 mm sieve.

soil: Normally defined as the unconsolidated material on the immediate surface of the earth that serves as a natural medium for terrestrial plant growth. Here limited to unconsolidated, surficial, mineral materials.

solubility: The maximum concentration of a chemical that can be dissolved in water when that water is both in contact and at equilibrium with the pure chemical.

standard deviation: A measure of the dispersion of samples in a data set from the mean value. The standard deviation is equal to the square root of the sum of squares (sum of differences between individual values and the mean) divided by the degrees of freedom (sample size minus one). A small standard deviation indicates that the values are clustered close to the mean, while a large standard deviation indicates a wide range in values in the data set.

statistical significance: In hypothesis testing a sample is said to be significantly different from a hypothetical population if the observed test statistic differs from the associated critical value at a specified probability level ($P \leq \alpha$; where α is a probability error of rejecting a true null hypothesis). Generally, α-levels > 0.05 are not considered to be statistically significant.

stomatal functioning: Stomata (sing. stoma) are minute pores or openings in the epidermis of leaves and herbaceous stems. They are flanked by two guard cells which open and close to regulate the rate of gas exchange and transpiration in the plant.

subsoil: Unconsolidated regolith material above the water table not subject to *soil* forming processes. Nominally includes *vadose zone* materials below 1.5 m depth.

surrogate: A representative compound used to assess the toxicity of the individual *CWS PHC* fractions.

texture: A categorical description of the proportions of sand, silt, and clay present in a soil.

threshold effects concentration (TEC): The concentration of a chemical below which no adverse effect is expected to occur. Ideally, it is derived from the distribution of the no-effects and effects data (i.e. *NOEC*, *LOEC*, LC_{50}, EC_{50}).

Tier 1 levels: Numerical values (soil concentrations) which form the basis of the *CWS* for *PHC*s and reflect the risk management and environmental quality goals of the standard as determined by CCME. This level represents the first of a three-tiered approach recommended for the assessment and remediation of petroleum contaminated sites.

Tier 2 levels: Numerical values calculated from Tier 1 levels in consideration of site-specific factors.

tolerable daily intake (TDI): The level/rate of chemical exposure to which a person may be exposed with no expected adverse effects. A tolerable daily intake can only be determined for chemicals with threshold effects (i.e., non-carcinogens).

transmissivity (*T*): The rate of water movement (m^2/sec) within a specified thickness of an aquifer. *T* is equal to the product of the *hydraulic conductivity* and the height of the modeled aquifer boundary.

trophic levels: Position in the food chain determined by the number of energy transfer steps to that level. Primary producers such as plants occupy the first trophic level, herbivores occupy the second trophic level, animals that prey on herbivores occupy a third trophic level, and so on.

uncertainty factor: A unitless numerical value applied to a reference toxicological value (e.g., EC_{50}) to account for the uncertainty in the estimate of a final soil quality guideline. Uncertainty factors may be applied, for example, when there is a need for extrapolation to long-term values from short-term data, extrapolation from laboratory to field conditions, or to account for inter- or intra-specific variation between individual test organisms and species.

uncertainty: The relative confidence in a scientific result owing to (1) variability in identified, contributing parameters and (2) ignorance regarding certain processes and phenomena. Uncertainty related to (1) can be reduced through data acquisition whereas uncertainty related to (2) cannot.

unconfined aquifer: A region of saturated ground material unbound by an impermeable or low-permeability layer such as clay. These systems allow for the draining of soil *porewater* and the subsequent movement of air (or water) to fill the spaces vacated by the moving water.

upstream industry: Petroleum hydrocarbon industry sectors which are responsible for the exploration and extraction of crude oil from subterranean reservoirs and oil sands, transfer to refineries, and the refining. As such, upstream industries pose a potential source for soil contamination of *PHCs* (e.g. leaks or spills occurring during the extraction procedure or by pipeline delivery, etc.).

vadose zone: Refers to the upper portion of the unsaturated zone in the subsurface environment, where both air and water are present between mineral grains.

volatilization: The chemical process by which chemicals spontaneously convert from a liquid or solid state into a gas and then disperse into the air above contaminated soil.

weathering: As applied to PHC, the change in composition and bioavailability with time as related to natural processes including volatilization, differential mobility, biodegradation and stabilization.

weight-of-evidence approach: Procedures that combine multiple, often disparate, toxicological data sources to develop an *environmental quality benchmark*. As applied in the *PHC CWS*, uses a percentile of the effects data set to estimate a concentration in the soil expected to cause no adverse biological effects.

whole Federated crude oil: Un-fractionated *crude oil* obtained from the Federated pipeline in west central Alberta.

Acronyms

ACH: air changes per hour
AEHS: Associates for the Environmental Health of Soils
AENV: Alberta Environment
AEP: Alberta Environmental Protection
AM TAG: Analytical Methods Technical Advisory Group
ASHRAE: American Society of Heating, Refrigerating and Air-Conditioning Engineers
ASTM: American Society for Testing and Materials
ATSDR: Agency for Toxic Substances and Disease Registry
BCMELP: British Columbia Ministry of Environment, Lands and Parks
BTEX: benzene, toluene, ethylbenzene, xylene
CAPP: Canadian Association of Petroleum Producers
CCME: Canadian Council of Ministers of the Environment
CFLRI: Canada Fitness and Lifestyle Research Institute
CMHC: Canada Mortgage and Housing Corporation
CPPI: Canadian Petroleum Products Institute
CSST: Contaminated Sites Soil Taskgroup of British Columbia
CWS: Canada-Wide Standards
DRO: diesel range organics
EC-L: effects concentration - low
ECN: equivalent carbon number
EcoTag: Ecological Task Advisory Group
ECx: effective concentration for x percentage of the test population
EDI: estimated daily intake
GC-FID: gas chromatography - flame ionization detector
GC-MS: gas chromatography - mass spectrometry
GRO: gasoline range organics
HC: Health Canada
HEPH: heavy extractable petroleum hydrocarbons
HHFT TAG: Human Health, Fate and Transport Technical Advisory Group
K_d: distribution coefficient
K_{OC}: organic carbon - water partition coefficient
K_{OW}: octanol - water partition coefficient
LCx: lethal concentration for x percentage of the test population
LEPH: light extractable petroleum hydrocarbons
LF: leaching factor
LO(A)EL: lowest observed (adverse) effects level
LOEC: lowest observed effect concentration
MADEP: Massachusetts Department of Environmental Protection
MEFQ: Ministère de L'Environnement et de la Faune Québec
MOEE or OMEE: Ontario Ministry of Environment and Energy

MOG: mineral oil and grease
NAPL: non-aqueous phase liquids
NHW: National Health and Welfare
NO(A)EL: no observed (adverse) effects level
NOEC: no observed effect concentration
OAEI: O'Connor Associates Environmental Inc.
OMEE: Ontario Ministry of Environment and Energy
PAHs: polycyclic aromatic hydrocarbons
PHC CWS: Canada-Wide Standard for Petroleum Hydrocarbons in Soil
PHC: petroleum hydrocarbon
PIRI: Partners in *RBCA* Implementation
PIWG: Protocol Improvement Working Group
PST: petroleum storage tank
PTAC: Petroleum Technology Alliance Canada
QA/QC: quality assurance/quality control
RAFs: relative absorption factors
RBC: red blood cells
RBCA: Risk - Based Corrective Action
RBSLs: Risk - Based Screening Levels
RfC: reference concentration
RfD: reference dose
RRfC: residual reference concentration
RTDI: residual tolerable daily intake
SAF: soil allocation factor
SQG: soil quality guideline
TDI: tolerable daily intake
TEC: threshold effect concentration
TED_{LDW}: daily threshold effect dose for livestock drinking water
TPHCWG: Total Petroleum Hydrocarbon Criteria Working Group
TRPH: total recoverable petroleum hydrocarbon
UF: uncertainty factor
US EPA: United States Environmental Protection Agency
VF: volatilization factor
VPH: volatile petroleum hydrocarbons
WIR: water ingestion rate

1. Introduction

The Canada-Wide Standard for Petroleum Hydrocarbons in Soil (PHC CWS) was developed by the Canadian Council of Ministers of the Environment (CCME) under the Harmonization Sub-Agreement on Standards. Alberta championed the PHC CWS and co-chaired the national Development Committee with Canada. The Development Committee was assisted immeasurably by the participation of key stakeholders from the oil and gas and environmental consulting industries, environmental non-governmental organizations and universities. An overview of the consultative processes used to develop the PHC CWS is provided in Appendix A.

The purpose of this document is to provide an overview of the land use-based framework for the PHC CWS and the detailed technical scientific rationale in support of the derivation of the Tier 1 values. The Tier 1 values are also presented in brief in the 'approved in principle' PHC CWS and Technical Supplement (www.ccme.ca). These values form the numerical basis of the PHC CWS and reflect the risk management and environmental quality goals of the standard as determined by CCME in consideration of scientific, technical and socio-economic factors and the substantive input of stakeholders.

This document outlines the goals and principles used in developing the standard (Chapter 1), the risk management and environmental quality objectives within the land use-based framework (Chapter 2), and details the approach adopted for the derivation of the human health (Chapter 3) and ecological Tier 1 values (Chapter 4). Chapter 5 includes the tabulated Tier 1 values for surface soils and generic values for sub-surface soils. This chapter discusses the integration of the ecological and human health values, and the role of risk management in the derivation process. Chapter 6 discusses the critical role of the recommended analytical method in defining the standard and supporting its consistent use. Chapter 7 (Summary and Recommendations) summarizes the features and benefits of the PHC CWS, indicates gaps in the current understanding of PHC as related to standard development and provides recommendations for future priority research.

This document is not intended as guidance to users on implementation of the PHC CWS. Technical options available to jurisdictions in implementing the PHC CWS are being developed in a separate volume (CCME 200X).

1.1 Background

Petroleum hydrocarbons (PHC) describe a mixture of organic compounds found in or derived from geological substances such as oil, bitumen and coal. Petroleum products released to the environment, such as gasoline, crude oil and jet fuel,

typically contain hundreds to thousands of compounds in varying proportions, composed predominantly of carbon and hydrogen, with minor amounts of nitrogen, sulphur and oxygen. PHC contamination in soils varies with the petroleum source, soil type, the composition, degree of processing (crude, blended or refined) and the extent of weathering caused by exposure to the environment. Such factors have complicated the assessment of the human and environmental health risks associated with PHC contamination in soils.

PHCs in the environment are a concern for a number of reasons. First, their reduced nature and volatility pose a fire/explosion hazard. Second, most PHC constituents are toxic to some degree. Third, lighter hydrocarbons are mobile and can be a problem at considerable distances from their point of release due to transport in ground, water or air. Fourth, larger and branched chain hydrocarbons are persistent in the environment. Fifth, PHCs may create aesthetic problems such as offensive odour, taste or appearance in environmental media. Finally, under some conditions PHCs can degrade soil quality by interfering with water retention and transmission, and with nutrient supplies.

Canadian regulatory agencies have responded to these problems with assessment and remediation requirements applicable where PHCs are released to soils and groundwater. A blend of generic guidelines and site-specific, risk-based approaches has emerged across Canada, but there is very little consistency across jurisdictions in the rationale for guidelines, numerical values provided, or application to land uses. Moreover, a vast array of analytical options exist for quantifying hydrocarbons in soil. Various methods have been developed to quantify all or part of the hydrocarbons present in a sample based on different extraction, purification, detection and data treatment approaches. Lack of standardization in sampling, storage and analytical procedures has led to high variability in results and confusion for users of the data.

This condition is unsatisfactory and made more serious by the scope of the PHC problem. When both production ("upstream") and marketing ("downstream") sectors are considered, over a quarter million actual or potential PHC release sites exist in Canada. Liabilities are estimated in the billion dollar plus range (Komex 2000). It is important that guidelines and other assessment tools be as accurate and reproducible as possible to protect the environment and control costs. The costs of failing to control risks are very high; for example, losses of community water supplies have occurred as a result of PHC releases.

The PHC CWS was developed in recognition of the above factors.

1.2 Goals and Principles

The overall goal of the PHC CWS is to provide a sound Canadian framework and scientific toolkit for the assessment and management of PHCs in soil and subsoil consistent with the principles of the Harmonization Accord and Sub-Agreement on Environmental Standards.

While all principles of these two enabling agreements apply, the following are especially significant to the PHC CWS:

- Performance-based, results oriented and science-based;
- Openness, transparency, accountability and effective participation of stakeholders in decision making;
- Allow for flexible implementation required to reflect variations in ecosystems and local, regional, provincial and territorial conditions;
- Consensus-based and driven by the commitment to attain the highest level of environmental quality within the context of sustainable development;
- Pollution prevention is the preferred approach to environmental protection.

More specific goals and principles were identified by stakeholders at the two national workshops and captured in the workshop reports posted on the CCME website (www.ccme.ca). Key stakeholders recommendations included:

- Protection of ecological and human health;
- A risk-based, 3-tiered framework for assessment of PHC contamination consistent with CCME and ASTM approaches;
- Tier 1 standards based on four boiling point range fractions to meaningfully group fate, behaviour and toxicological properties;
- Incorporation of socio-economic factors to ensure that Tier 1 standards are practical and appropriate for many sites – while not compromising human and ecological health;
- Provision for a flexible Tier 2 process that responds to influential site factors while maintaining symmetry and consistency with Tier 1 standards;
- Risk management should include consideration of aesthetics and physical-chemical effects on soil;

- Development of a standard analytical method based on gas chromatography;
- Inclusion of a means to review and update standards in response to new data and insights.

1.3 Overview of PHC CWS Features

The PHC CWS is based in the science of environmental risk assessment and management. This approach defines acceptable environmental quality in terms of receptors (living things and other valued ecosystem components), their susceptibility to contaminants, and the pathways along which exposure to contamination may occur. The objective is to ensure that exposures are kept below levels at which adverse effects are expected.

Meeting these risk management objectives for complex and variable mixtures such as PHCs requires a systematic approach and a number of simplifying assumptions. The PHC CWS considers PHCs in four fractions that provide broad groupings with respect to environmental fate, behaviour and effects. These fractions are defined with respect to analytical procedures (boiling point range – Chapter 2) but correlate roughly with gasoline, diesel, lubricant and heavy lubricant ranges. The PHC CWS in soils presents for these four fractions a three-tiered, risk-based remedial standard developed for four generic land uses - agriculture, residential/parkland, commercial and industrial (Figure 1.1). Tier 1 levels for each land use are derived through a systematic evaluation of all pathways of exposure that apply to the receptors of concern identified under the land use. Tier 2 levels may be generated and used when site conditions exist that significantly modify the exposure and risk scenarios. At Tier 3, a site-specific ecological and/or human health risk assessment is conducted. The objective of the standard is to improve the protection of human health and the environment and to provide consistency and accuracy in the management of PHC contaminated soils.

An appropriate remediation decision can be identified through consideration of site characterization data, site and surrounding land use factors, technical factors, and benefits and costs attached to options at Tiers 1, 2 and 3. General risk management objectives do not change among the Tiers, however, the means of minimizing or eliminating exposure can vary. This provides good flexibility in responding to PHC contamination of soils and subsoils. Details can be found in CCME (200X).

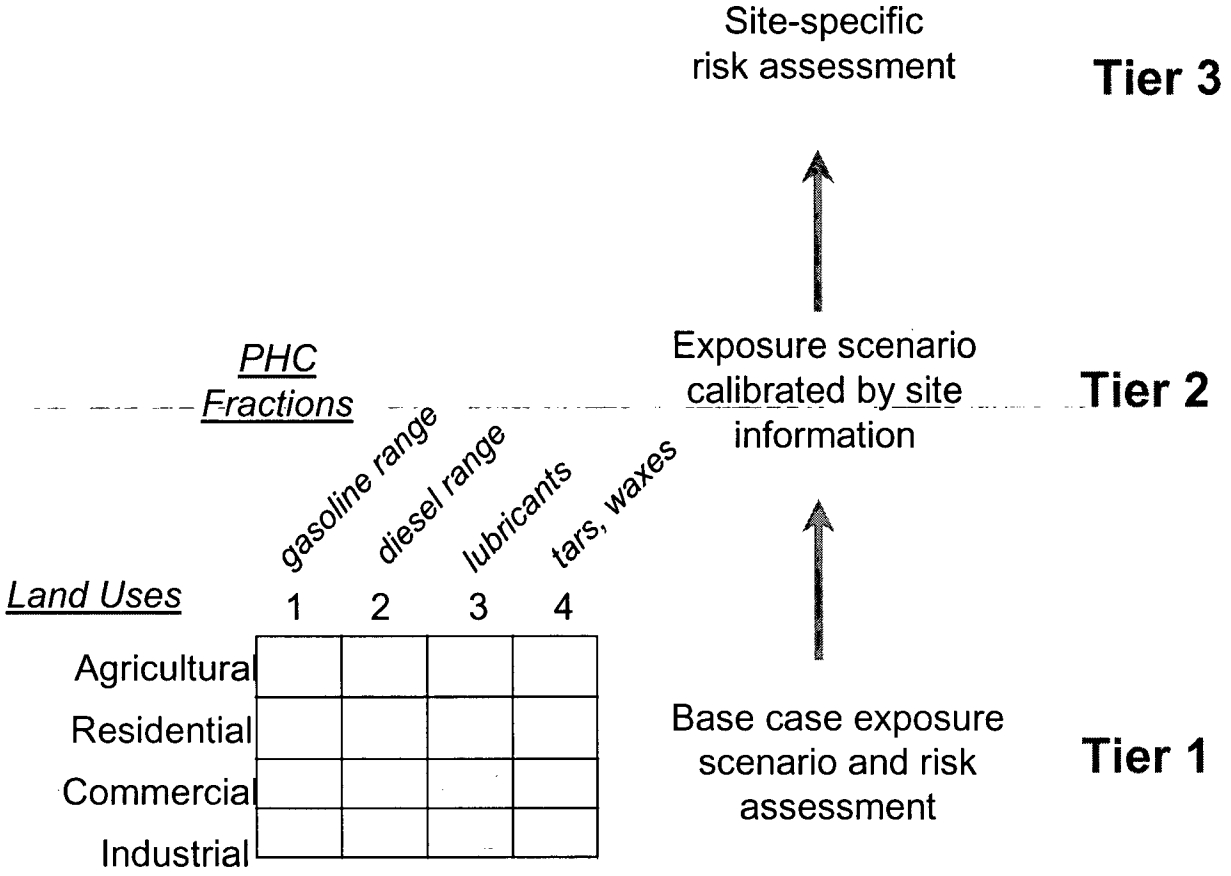


Figure 1.1: Tiered risk-based approach to managing PHC-contaminated soils.

2. Development of Tier 1 Generic Soil Quality Levels

2.1 Sources of Information

The PHC CWS is founded on documented and scientifically defensible risk-based methodology. The chief sources were:

1. 1996 *CCME Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines*;
2. American Society for Testing & Materials (ASTM) *Risk-based Corrective Action (RBCA) Standard Guide 1739-95* - and additions/improvements thereon, including the Atlantic *Partners in RBCA Implementation (Atlantic PIRI 1999);*
3. US TPH Criteria Working Group Series Vols. 1-5 (1997-1999);
4. British Columbia Environment Matrix Standards for VPH, LEPH and HEPH (1998).

Consequently, the derivation of the Tier 1 levels of the CWS involves explicitly listed receptors - both human and ecological, and the levels of protection accorded. It also involves defined exposure scenarios, and documented underlying assumptions and equations as outlined in more detail in Sections 3 and 4 of this document.

Very important additional concepts and features were adopted or adapted from numerous other sources including Alberta Environment's Petroleum Storage Tank Guidelines (AEP 1994) and Ontario Ministry of Environment's Guideline for Use at Contaminated Sites in Ontario (OMEE 1996).

A discussion of risk-based approaches adopted in North America for the assessment and management of PHC contaminated soils is presented in Appendix B. In summary, several primary initiatives have been established for the assessment of PHC contaminated soils. These include the Massachusetts Department of Environmental Protection (MADEP 1994, 1996, 1997); the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG; Weisman 1998; Potter and Simmons 1998; Gustafson et al. 1997; Edwards et al. 1997); the B.C. Ministry of Environment (Golder Assoc. 1995); CanTox Inc. (1997); and the Atlantic provinces (Atlantic PIRI 1999).

The development of human health-protective Tier 1 values is based predominantly on the work of the TPHCWG. This resulted from a review of the available information concerning the various approaches to risk-based assessment/management of PHCs, and following discussions with members of the PHC Development Committee, the Eco TAG, the AM TAG, and the HHFT TAG (Appendix A). Based on a consideration of both physical-chemical properties and

toxicological RfDs for the TPHCWG fractions, 4 carbon-fractions (F1, F2, F3, F4) have been identified and described in more detail below.

The PHC CWS is unique in the development of risk-based values that are protective of ecological health. A paucity of scientifically-defensible toxicological data on the ecological responses to PHCs rendered it necessary to generate ecotoxicological data on a carbon fraction-specific basis for the development of the standard. Data for F2 and F3, and mogas (motor gasoline) toxicity (as an approximation of F1 toxicity) and fresh Federated whole crude oil were conducted with support from CAPP/PTAC/AENV and CPPI/Crestech. Additional testing was facilitated through support from Environment Canada, Alberta Environment, Quebec Ministry of Environment, Ontario Ministry of Environment, and B.C. Ministry of Environment, Lands and Parks.

Collectively, the well-founded risk-based methodology for human and ecological receptors, generation of ecotoxicology data and the standard analytical methodology (Chapter 6) form the scientific basis of the PHC CWS. In addition, the science-based component of the PHC CWS is complemented by a consideration of socio-economic and policy based factors as illustrated in Figure 2.1. The contributions of these latter factors are further discussed in Chapter 5.

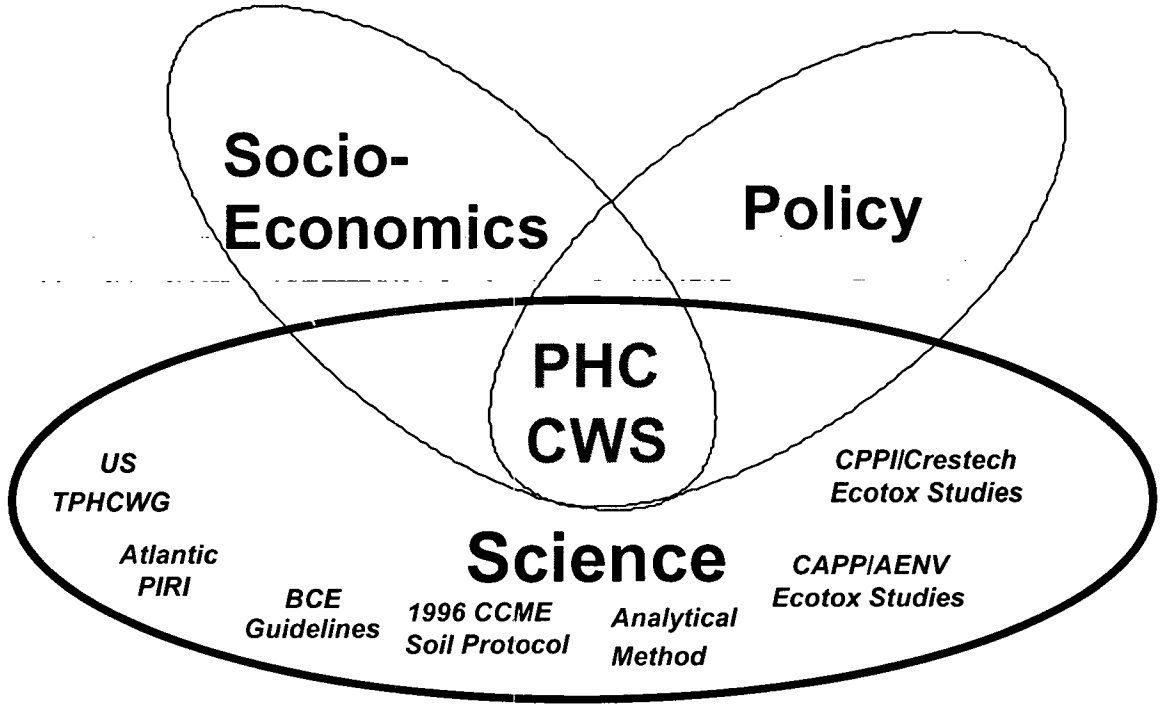


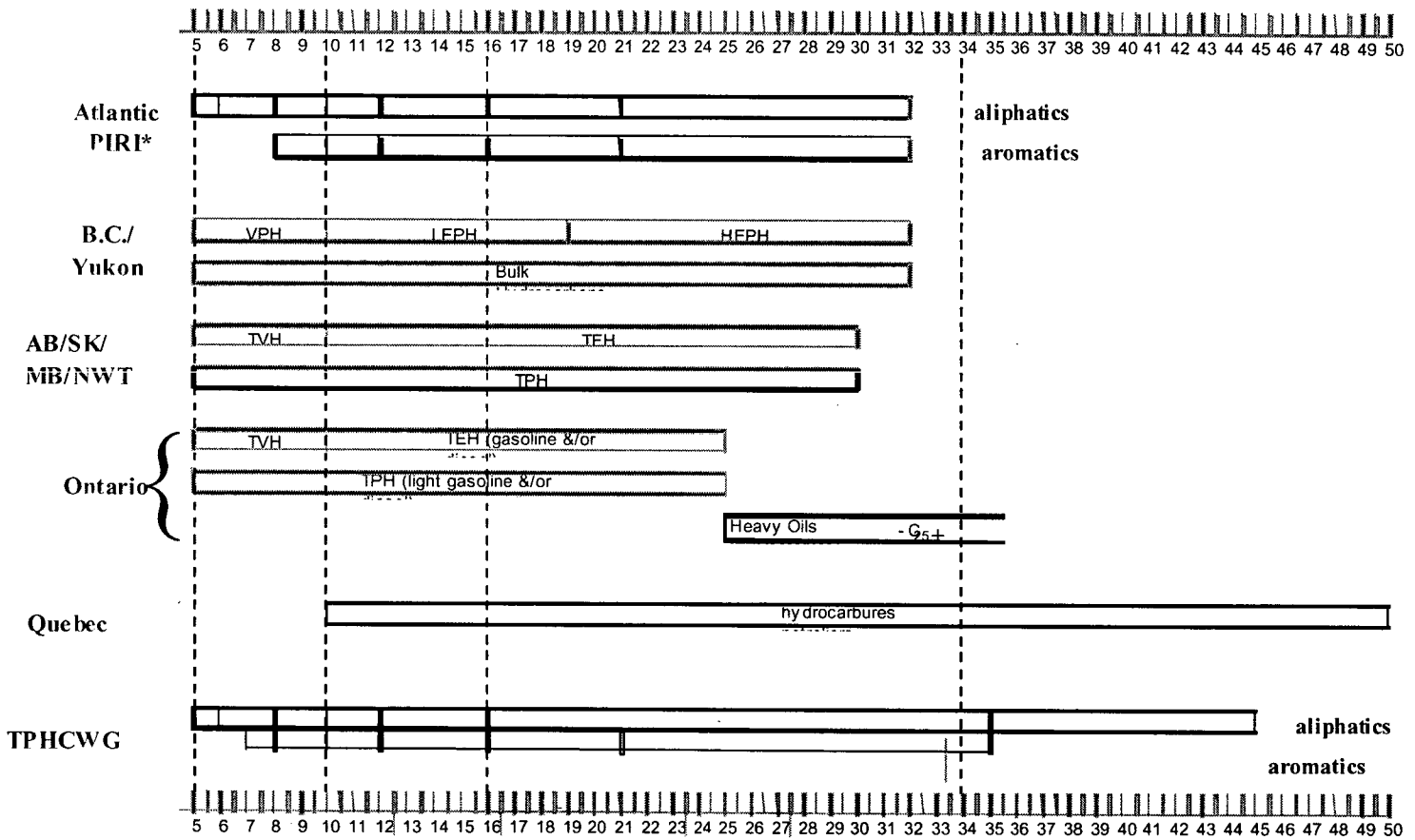
Figure 2.1. Scientific, socio-economic and policy based components of the PHC CWS.

2.2 Functional Definition of PHC Fractions

For purposes of the PHC CWS, petroleum hydrocarbons are sub-divided into fractions according to specified ranges of equivalent carbon number (ECN). Each fraction is, in turn, made of subfractions as previously defined by the TPHCWG. These subfractions that form the four CWS fractions have been described according to their relevant physical-chemical properties (e.g., solubility, Henry's Law constant, etc.) and toxicological characteristics (i.e., RfD and/or RfC) which permitted the prediction of chemical fate, exposure and potential risk. Within the CWS fractions, the balance between aromatic and aliphatic constituents is assumed to be 20/80 based on an analysis presented by TPHCWG and the petroleum industry (CAPP, CPPI) of some representative hydrocarbon products. The breakpoints defined for the 4 fractions that form the basis of Tier 1 levels were selected in consideration of analytical factors, the fit with TPHCWG subfractions and expected relevance to biological response in soils. These are described below (Figure 2.2).

I. Fraction 1 encompasses the range of ECN from C_6 to C_{10}
   - A. This fraction is composed of the following TPHCWG sub-fractions:
     1. aromatics $C_{>7}$-C_8, $C_{>8}$-C_{10}
     2. aliphatics C_6-C_8, $C_{>8}$-C_{10}
   - B. Physical-chemical properties are well defined for TPHCWG sub-fractions within this range;
   - C. Unique RfDs and RfCs are defined for each aromatic or aliphatic subfraction in the range;
   - D. BTEX should be analyzed separately and their concentrations subtracted from aromatics in this fraction;
   - E. Aliphatics in this range are represented by two RfD and RfCs; for C6-C8, and for C>8-C10;
   - F. Non-BTEX aromatics are represented by two RfD and RfCs; for C>7-C8 and C>8-C10.

II. Fraction 2 encompasses $C_{>10}$ to C_{16}
   - A. This fraction is composed of the following TPHCWG sub-fractions:
     1. aromatics $C_{>10}$-C_{12}, $C_{>12}$-C_{16}
     2. aliphatics $C_{>10}$-C_{12}, $C_{>12}$-C_{16}
   - B. Physical-chemical properties are well defined for TPHCWG sub-fractions within this range;
   - C. Aliphatics in this range are represented by a single RfD and RfC;
   - D. Aromatics are represented by a single RfD and RfC.



* PIRI guidelines presented for gasoline, diesel and heating oil.

Figure 2.2: CWSPHC carbon-fractions in relation to the TPHCWG subfractions.

III. Fraction 3 encompasses the range of ECN from $C_{>16}$ to C_{34}
   A. This fraction is composed of the following TPHCWG sub-fractions:
      1. aromatics $C_{>16}$-C_{21}, $C_{>21}$-C_{34}
      2. aliphatics $C_{>16}$-C_{21}, $C_{>21}$-C_{34}
   B. Physical-chemical properties are well defined for TPHCWG sub-fractions within this range;
   C. Aliphatics in this range are represented by a single RfD;
   D. Aromatics are represented by a single RfD.

IV. Fraction 4 encompasses the range of ECN from $C_{>34}$ to C_{50}
   A. This fraction is composed of the following TPHCWG sub-fractions:
      1. aromatics $C_{>34}$
      2. aliphatics $C_{>34}$
   B. This fraction can represent a substantial and significant proportion of environmental PHC contamination, and of petroleum products and crude oils;
   C. Although the physical-chemical properties are less well defined in this fraction, the material is not volatile and is expected to have minimal environmental migration;
   D. A study of mixtures provides the basis for an RfD for aliphatics in this range;
   E. There are no data available to derive an RfD for aromatic PHCs in this range, specifically. However, the toxicity of aromatics can be conservatively assumed to be equivalent to that of pyrene, as is currently done for all aromatics with an ECN $C_{>16}$ under the TPHCWG scheme.

2.2.1 Relative Proportion of Aromatics to Aliphatics in Each PHC Fraction

The carbon number ranges encompassed by each PHC fraction may be further classified or subdivided in terms of aliphatics and aromatics. The composition of each PHC "fraction" to be used for deriving Canada Wide Standards for PHCs in soil is summarized in Table 3.11. Also included in Table 3.11 is the recommended composition of petroleum products to be employed to derive Tier 2 soil quality guidelines for such products, in a manner that would be consistent with the Tier 1 Canada Wide Standards for PHC fractions. The recommended ratio of aliphatic to aromatic hydrocarbons in each PHC fraction is 80:20, based on a review of data presented by the TPHCWG, and on data provided by CAPP and CPPI. This requires that the content/concentrations of benzene, toluene, ethylbenzene and xylenes (BTEX) are subtracted from the content of total PHCs at the contaminated site, thus requiring that BTEX be analyzed, assessed and managed separately from PHCs.

2.3 Representing PHC Fractions: Whole Fraction Properties vs. Surrogates

TPHCWG Vol. 4 describes whole product- and surrogate-based approaches to evaluating the toxicity of mixtures such as PHC. The pros and cons of each approach are discussed and a case made that the surrogate method is best suited to deal with PHC source variability and environmental modifications related to differential mobility and dissipation. All agencies proposing risk-based approaches to PHCs have defined or selected surrogates to represent the environmental mobility (physico-chemical properties) and toxicity (RfDs, RfCs) of individual PHC fractions. Most efforts prior to the TPHCWG have focused on individual compounds within the carbon number range of specified PHC fractions. Generally, the most toxic known constituent of a given fraction was selected to represent the toxicity of the entire fraction. The physico-chemical properties of this toxic constituent were also generally employed for purposes of predicting environmental fate of each fraction.

For the purposes of developing human health Tier 1 values under the CWS for PHCs, the physicochemical properties and RfDs/RfCs described by the TPHCWG were adopted rather than selected *de novo* surrogates for defining the environmental mobility or toxicity of the four designated PHC fractions. The relevant variables are applied to each of the TPHCWG sub-fractions and these sub-fractions are added or 'rolled-up' into the four 'super' fractions defined herein. The addition of TPHCWG sub-fractions is undertaken on the basis of the weight percent of each sub-fraction within the CCME PHC fractions.

Rather than relying on a strict, surrogate approach for the derivation of ecological Tier 1 values, a *weight of evidence* approach was used that combined whole product, whole fraction and compound surrogate information. Responses to whole Federated crude oil (drawn from the Federated pipeline in west central Alberta), distillate cuts prepared from that crude, and chemical surrogates were used. Surrogate compounds were identified to represent the aromatic and aliphatic portions of each fraction as follows: F2- napthalene and decane, F3- pyrene and eicosane. In addition, a critical body residue approach was taken in the assessment of F1 and F2 effects on aquatic receptors through potential movement of PHC through groundwater. Details of how these toxicity information sources were combined are presented in Chapter 4.

2.4 Land Use Definitions

The PHC CWS in soils has been developed for four generic land uses - agriculture, residential/parkland, commercial and industrial. A generic land use scenario has been envisioned for each category based on the 'normal' activities on these lands (Figure 2.3). The risk-based nature of the PHC CWS means that, for each land use, all values to be protected (life-forms or receptors, ecosystem properties) are

explicitly documented as well as the contaminants considered within PHCs and the pathways by which PHCs can affect these values. This approach provides great flexibility; it allows assessment and management of different variations within a land use and even extension of the standard to other land use categories (e.g., wildlands). The vision, or exposure scenario, attached to each land use is the heart of the PHC CWS. The four land uses are defined as follows:

Agricultural lands: where the primary land use is growing crops or tending livestock. This also includes agricultural lands that provide habitat for resident and transitory wildlife and native flora. The portion of a farm that houses people is considered a residential land use.

Residential/Parkland: where the primary activity is residential or recreational activity. The ecologically-based approach assumes parkland is used as a buffer between areas of residency, but this does not include wild lands such as national or provincial parks, other than campground areas.

Commercial: where the primary activity is commercial (e.g., shopping mall) and there is free access to all members of the public, including children. The use may include, for example, commercial day-care centres. It does not include operations where food is grown.

Industrial: where the primary activity involves the production, manufacture or construction of goods. Public access is restricted and children are not permitted continuous access or occupancy.

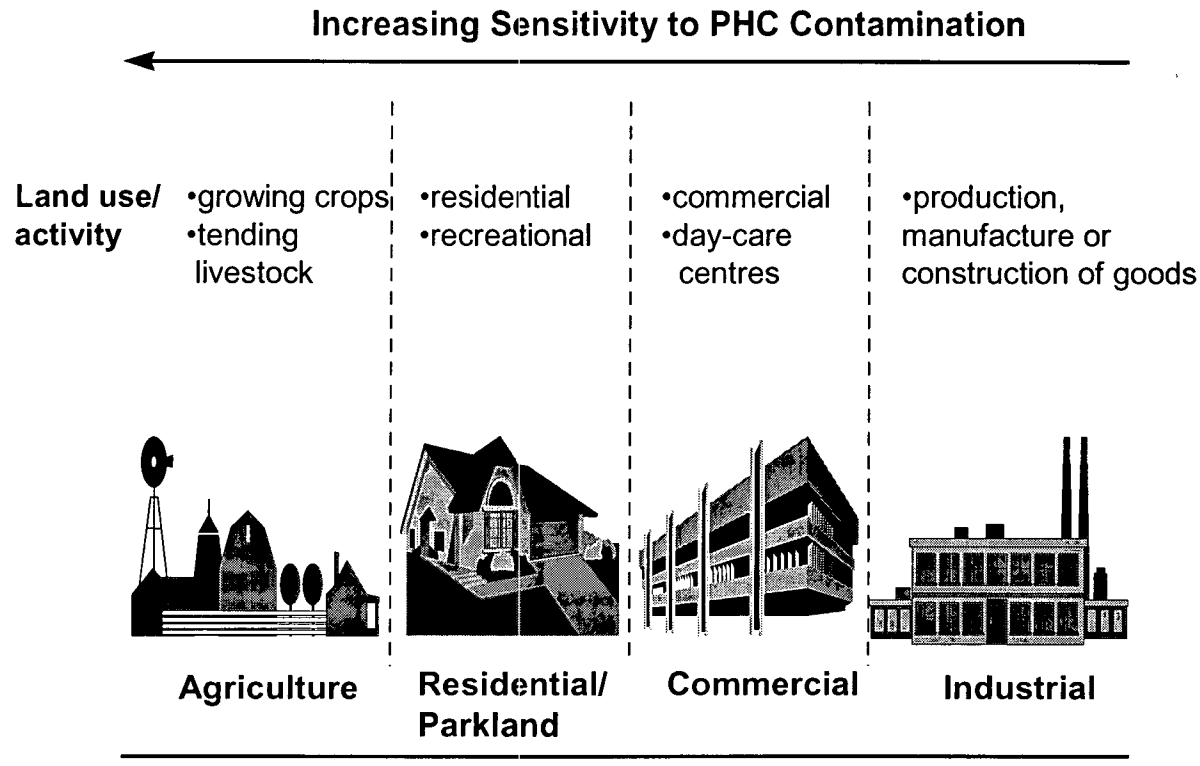


Figure 2.3: Generic land-use scenarios and their associated activities.

2.5 Receptors and Pathways

Tier 1 levels for each land use are derived through a systematic evaluation of all pathways of exposure that apply to the receptors of concern, including human health and ecological, identified under that land use. A summary of the receptor/pathway combinations addressed under each land use in the PHC CWS is presented in Table 2.1. Each combination is discussed further in the appropriate section of this document.

Tier 1 levels in the PHC CWS are presented as a summary of the above pathway/receptor combinations where data were sufficient to support the derivation procedure. In application, users will gather information on relevant pathways and will frequently require information on secondary pathways. Decisions are made in relation to the governing pathway(s) applicable at individual sites. Procedures supporting this decision-making process are presented in the user guidance (CCME 200X).

Table 2.1: Land-uses, key receptors and exposure pathways.

Exposure Pathway	Agriculture	Residential/ Parkland	Commercial	Industrial
Soil Contact	Nutrient cycling Soil invertebrates Crops (plants) Human (child)	Nutrient cycling Invertebrates Plants Human (child)	Nutrient cycling Invertebrates Plants Human (child)	Nutrient cycling Invertebrates Plants Human (adult)
Soil Ingestion	Herbivores Human (child)	(wildlife)* Human (child)	(wildlife)* Human (child)	(wildlife)* Human (adult)
Groundwater/ Surface Water	Aquatic Life/ Livestock Watering Human (child)	Aquatic Life Human (child)	Aquatic Life Human (child)	Aquatic Life Human (adult)
Vapour Inhalation (humans only)	Child, indoor**	Child, indoor	Child, indoor	Adult, indoor
Produce, meat and milk produced on site (humans only)	Child	Child (produce only)		
Off-site migration of Soil/Dust				Human/Eco

* wildlife dermal contact and ingestion data may be particularly important for PHCs (e.g., oiling of feathers, etc., although this should be addressed with an initial assessment of the presence of non-aqueous phase liquids - NAPL), but there are unlikely to be sufficient data to develop guidelines that address this exposure pathway

** a 30m horizontal offset is assumed between the farm residence and the PHC contamination, consistent with oil and gas development practices. Contamination nearer a farm residence triggers a residential assessment.

Jurisdictional approaches to implementation of the CCME land use categories differ somewhat but frequently make use of land zoning systems to capture "compliant" and "non-compliant" uses. A scientific basis for decisions on how specific site uses connect with the CCME categories lies in an examination of the specific receptors and exposure pathways.

In addition to the toxic risks addressed by the receptor/pathway analyses, certain other management considerations apply. Chief among these are:

- ignition hazard
- odour and appearance
- formation of non-aqueous phase liquids (NAPL)

Whereas the primary focus in PHC CWS standard development is prevention of toxic effects to the receptors in Table 2.1, in certain situations these pathways may be of little immediate concern and PHC management is driven by consideration of policy factors. Aesthetics and avoidance of free product considerations have been incorporated as policy factors in the development of the Tier 1 levels as indicated in Fig. 2.1.

2.5.1 Treatment of Soil-to-Groundwater Exposure Pathways

Soils are hydrologically linked to groundwater systems. A major concern with soil contamination is that it can and does lead to groundwater contamination, which may be technically, economically, or otherwise difficult or currently impossible to remediate. Tier 1 levels for the PHC CWS are designed to prevent unacceptable transfers of contaminants to groundwater systems.

Procedures are undertaken to assess and manage the soil-to-groundwater pathway with respect to three uses of groundwater (Table 2.1):

- Human consumption (potable water);
- Aquatic life;
- Livestock watering.

In order to address these pathways at Tier 1, soil contamination is considered to exist in a reasonably sensitive hydrogeological setting. It is assumed that the site is underlain by an unconfined aquifer and that soil contamination extends to the water table (this assumption can be adjusted in relation to site data at Tier 2). Petroleum hydrocarbons in F1 and F2 partition between soil organic matter, soil water and soil air. Petroleum hydrocarbons dissolved in soil water move with recharge water to the water table and are diluted with the groundwater flow. At some distance downgradient groundwater is either withdrawn for the specified use - typically through a well - or discharged to a natural or engineered surface water body.

The precise treatment of these soil-to-groundwater pathways at Tier 1 differs somewhat depending on the groundwater protection goal. In the case of potable groundwater, it is assumed that use or potential use occurs on the PHC-contaminated site. For the other two groundwater uses, it is assumed that a minimum lateral distance of 10 m exists between the contamination source in soil and the point of discharge or withdrawal. These different assumptions necessitate different technical approaches.

Details on the technical description of movement and attenuation of PHCs in groundwater for potable use and aquatic life/livestock watering are provided in Chapters 3 and 4 respectively. In overview, potable groundwater protection at Tier 1 involves use of a simple, steady state mixing-dilution model that assumes a well exists at the downgradient boundary of a site uniformly contaminated to the Tier 1 soil standard. This model has been used previously in CCME (1996), US EPA (1997) and Atlantic PIRI (1999). Under this model description, on-site groundwater quality is assured because PHC concentrations increase with site length; concentrations are maximal at the downgradient boundary. A vertical mixing depth must be specified and a nominal 2 m value is used here in consideration of practical factors cited in CCME (1996).

A simple mixing-dilution model is inappropriate for supporting aquatic life and livestock watering uses of groundwater because it is assumed that a minimum

separation of 10 lateral meters exists between the PHC contaminated soil and the point of groundwater use/discharge. A dynamic advective-dispersive model is needed to describe such an arrangement. Tier 1 values in PHC CWS were calculated using solutions to the advective-dispersive flow equation published by Domenico and Robbins (1984). Under this mathematical description attenuation of PHC includes:

- retardation by organic matter in the aquifer;
- a conservative, anaerobic biodegradation process;
- a vertical mixing zone calculated from a dispersive relationship that depends on lateral distance travelled.

The method of determining the vertical mixing zone differs from that used for on-site potable groundwater and generally gives values less than 2 meters over practical lateral separation distances. While different vertical mixing results are obtained by the two methods each is considered appropriate in the circumstances. In the potable water case, vertical mixing is assured through depth averaging related to well construction and operation details (see CCME 1996). In contrast, it is difficult to assume any particular mixing pattern related to withdrawal or discharge for the other groundwater uses. In such applications groundwater may be discharging to a dugout or natural standing water body where mixing prior to or during exposure is very uncertain. Thus, for aquatic life and livestock watering uses of groundwater, the vertical mixing zone is determined using a dispersive algorithm described in Chapter 4.

Throughout the PHC CWS, a distinction is made between fine-textured and coarse textured soils. While "texture" is used in the normal connotation for soil (e.g., see Soil Classification Working Group 1998) the terms fine-textured and coarse textured are based solely on the geo-technically accepted size cutoff between sand and silt (75 µm; ASTM 2000). Specifically, fine textured soils are defined as having greater than 50% by mass particles less than 75 µm mean diameter (D_{50} < 75 µm). Coarse textured soils are defined as having greater than 50% by mass particles greater than 75 µm mean diameter (D_{50} > 75 µm). Simply put, coarse soils are defined as having more than 50% sand by mass and fine soils are defined as having less than 50% sand by mass.

2.6 Approach for PHCs

This section summarizes the approaches adopted for deriving Tier 1 human health and ecological levels. A more detailed description of each approach and the toxicological basis and methods to calculate the Tier 1 values are presented in the appropriate sections (Chapters 3, 4).

Human Health Summary

Petroleum hydrocarbons are grouped by physico-chemical properties into 4 carbon chain length fractions. Group toxicological and physico-chemical properties are used to estimate concentrations of PHC in soil that would not lead to an exposure exceeding a hazard quotient of 1 along 4 pathways – inhalation of vapours, dermal contact, incidental ingestion of soil and ingestion of cross-contaminated groundwater. The same pathways and same exposure equations are used for all land uses, however, exposure duration and frequency vary between land uses and only an adult's exposure is considered for the industrial land use. Average values for most parameters and characteristics are used which, when combined, gives a conservative but practical result. There are insufficient data to evaluate PHC exposure through the food chain. The few data available suggest that plant uptake of PHC and subsequent exposure at higher trophic levels is not a concern (see discussion in Section 4.1).

Ecological Health Summary

Tier 1 levels are derived to protect key ecological receptors that sustain normal activities on the four previously defined land use categories: agricultural, residential/parkland, commercial and industrial. The derivation of Tier I levels for ecological receptors focuses on the effects of PHCs on the biotic component of a terrestrial ecosystem. Specifically, it evaluates the potential for adverse effects to occur from exposures to soil-based PHCs at point-of-contact or by indirect means (e.g., soil to groundwater pathways, food chain transfer).

The approach adopted for the derivation of Tier 1 levels of PHCs in soils for the protection of ecological receptors is based on a 'weight of evidence' method as outlined in the CCME 1996 Protocol with some modifications. This approach facilitates the incorporation of disparate types of high quality information on the risks of PHCs to ecological receptors by calculating a percentile of the effects data set to estimate a concentration in soil expected to cause no adverse biological effects.

2.7 Incorporating Scientific Uncertainty and Socio-Economic Considerations

Estimates of exposure and risk to receptors related to environmental contamination are subject to many uncertainties and these considerations apply in standards development as well. Indeed, in developing generic standards it is generally necessary to make a number of conservative assumptions concerning uncertain exposure and toxicity factors such that the conservative exposure scenario does not lead to adverse environmental and health effects. Examples of sources of uncertainty include toxic response in humans in relation to test animals, contact rates of biota with contamination (reasonably certain for soil organisms, less certain for humans), construction details affecting entry rates of vapours into enclosed spaces, hydrological factors affecting the rate of contaminant movement between soil and groundwater, soil and groundwater conditions affecting the rate of biodegradation, and variability in primary scientific measurements during toxicity testing. Generally, conservative assumptions are made regarding these uncertainties such that a standard is protective. Many conservative assumptions were made in the development of the PHC CWS.

However, conservatism must be balanced with practical considerations in order to achieve an attainable, yet environmentally protective standard. Provided decisions concerning receptors, pathways, and exposure remain within the scientific uncertainty associated with a conservatively chosen exposure scenario, we can be confident that a protective standard will result. Chapters 3 and 4 include information on the uncertainties considered and the assumptions made in developing the PHC CWS.

2.7.1 Socio-Economic Analyses

Socio-economic analyses were undertaken at two stages in the development of the PHC CWS. A largely qualitative scoping analysis was undertaken at the outset to identify major release scenarios, affected parties, remedial technologies and benefits of their application (ChemInfo Services 1998). This was useful in showing the extreme diversity of PHC releases and the corresponding need for a *general* approach to PHC assessment and management. Such information was influential in pointing the way to a fraction-based approach and a flexible, tiered framework.

In a second stage, a quantitative screening analysis was carried out under the guidance of a multistakeholder advisory committee (Komex 2000). Eleven scenarios were developed to represent the more common and important PHC releases to the geo-environment. Typical volumes of contaminated soil for each scenario were estimated based on exceedance of "seed values" – screening estimates of risk-based Tier 1 guidelines available from the Development Committee in 1999 – and 5-fold adjustments of the seed values up (less stringent case: LS) and down (more stringent case: MS). Site remediation to Tier 1 levels was considered to occur via excavation/landfill for more contaminated material and biotreatment for less contaminated material. For screening purposes, other

technologies were not investigated and no Tier 2 or Tier 3 remediations were considered. Estimated costs of remediation were compared to monetizable benefits including recovery of property value, avoidance of property "blight", and avoidance of agricultural crop damage. Human health and ecological benefits were not monetized.

Under the assumptions and constraints described above, projected costs were roughly 2.5 to 3 times the monetizable benefits. While this outcome appears disjunct from societal experience with PHCs in the geo-environment, it is largely explained by the incomplete monetization of benefits and conservative description of remedial response. Nevertheless, the study describes well the distribution of releases by sector and region and provides useful screening estimates of liabilities under varying standard stringency. Very broadly, the study shows that costs of Tier 1 remediation are in the 10 billion dollar range. Even the LS standard, which includes values exceeding the most liberal guidelines presently in use in Canada, leads to estimated Tier 1 remediation costs of about $5 billion Cdn. Thus, *any* generic remediation standard (for example, merely removing free product) will generate liability estimates in excess of a billion dollars.

Because of the large upstream oil and gas industry in Western Canada (many sites) and the fact that benefits, as monetized in the screening study, are greater in populous areas, about 70% of costs are centred in Western Canada while about 70% of the benefits are in Eastern Canada.

The PHC CWS Development Committee duly considered these screening socio-economic studies in rendering its final risk management recommendations. These recommendations included:

- A tiered framework that encourages acquisition and application of site information useful in refining estimates of exposure and risk;
- Provision for flexible risk management within the framework;
- Inclusion of soil texture and depth within the generic standards;
- Careful selection of receptor and exposure pathways as appropriate to each land use;
- Careful consideration of the model and parameter uncertainty in the major exposure pathways.

Details on how these responses to socio-economic considerations were implemented appear in subsequent chapters.

2.8 Generic Subsoil Levels

One important way in which socio-economic considerations were applied in the PHC CWS is in the development of exposure scenarios and generic levels for subsoils. The rationale for, and details of the development of these generic subsoil levels are presented in Chapter 5. The approach is based on the reduced exposure and hence, risk, posed by contamination at depth. However, it is recognized that a stratified approach to PHC remediation does pose certain potential limitations on use within a land use category. For this reason, the subsoil levels are not considered Tier 1 levels, where remediation to specified levels is consistent with full site use flexibility within a land use category and thus no need for administrative notifications or controls.

3. Human Health Soil Quality Levels

Tier 1 levels for PHCs have been developed for four general land uses (agricultural, residential/parkland, commercial, industrial) and two soil textures (coarse-grained and fine-grained). Surface and sub-surface levels are also developed to account for the location of the contaminant in the soil stratum, recognizing the influence of contaminated soil accessibility and availability on human exposure and health risk.

3.1 Land Uses

The frequency, duration and intensity with which people contact pollutants at a contaminated site are proportional to the nature of the land use. Also, the critical receptor in any land category is dependent on the ease of public access and the activities inherent to that land use. CCME has defined four general land uses for developing PHC soil quality levels: agricultural, residential/parkland, commercial, industrial.

3.1.1 Agricultural

Agricultural land encompasses a wide range of activities including dairy, livestock and/or crop production. Most farms include a homestead so that the land immediately surrounding and beneath the home is assumed to be a residential property to which the assumptions and guidelines for residential land use apply (see below). Agricultural lands are generally accessible by the farmer and his/her family members, including children, which represent the more sensitive human receptor category. Therefore, the critical human receptor in the agricultural land use category is assumed to be a toddler who receives 100% of his/her daily intake of soil and drinking water (groundwater) from the property. For exposure to PHC vapours, it is assumed that agricultural land is at least 30 m from the residential building and that volatile PHCs must migrate a minimum of 30 m through clean soil before reaching and penetrating the building foundation.

3.1.2 Residential/Parkland

The generic residential property assumed for PHC Tier 1 derivation is a typical detached, single family home with a backyard where children, particularly toddlers, play. The critical receptor assumed on a residential property is a toddler who receives 100% of his/her daily intake of soil, drinking water (groundwater), and air (indoors) from the property. Separate Tier 1 levels have been developed for two house foundation construction styles - 1) below-grade concrete foundation wall and floor slab (basement); and 2) concrete slab-on-grade foundation. The two foundation construction styles only affect the indoor infiltration pathway by which volatile PHCs penetrate the building envelope via foundation cracks and gaps.

Parks may serve as areas for children's play and other family activities and are therefore also included in the residential land use category.

3.1.3 Commercial

Commercial properties span a wide variety of uses with varying degrees of public access. For purposes of deriving PHC Tier 1 levels, the generic commercial property is assumed to contain a daycare facility, a sensitive commercial property use that is permitted in many municipal jurisdictions in Canada. It is assumed that the critical receptor (toddler) spends a substantial portion of the weekdays at a daycare. In particular, it is assumed that the toddler spends 10 hours per day, 5 days per week for 48 weeks per year at the daycare. The toddler thereby receives an amount of his/her daily intake of soil, drinking water (groundwater), and air (indoors) from the commercial property proportional to the number of hours per day, days per week and weeks per year spent at the facility. Most commercial buildings are constructed with concrete slab-on-grade foundations. Therefore, PHC Tier 1 levels for commercial properties only consider slab-on-grade foundation construction, which influences the indoor infiltration pathway by which volatile PHCs penetrate the building envelope via foundation cracks and gaps.

3.1.4 Industrial

Industrial properties span a wide variety of uses but generally do not permit direct public access and therefore, children are not likely or frequently present. For purposes of deriving PHC Tier 1 levels, the generic industrial property is assumed to be a site with a building frequented by an adult worker who spends 10 hours per day, 5 days per week for 48 weeks per year on the property. The adult receptor thereby receives an amount of his/her daily intake of soil, drinking water (groundwater), and air (indoors) from the industrial property proportional to the number of hours per day, days per week and weeks per year spent at the facility. Most industrial buildings are constructed with concrete slab-on-grade foundations. Therefore, PHC Tier 1 levels for industrial properties only consider slab-on-grade foundation construction, which influences the indoor infiltration pathway by which volatile PHCs penetrate the building envelope via foundation cracks and gaps.

3.2 Soil Texture

Tier 1 levels for PHCs in soil have been derived herein for both coarse-grained and fine-grained soils. Soil texture is defined herein according to ASTM (2000). Fine textured soils are defined as having greater than 50% by mass particles less than 75 µm mean diameter (D_{50} < 75 µm). Coarse textured soils are defined as having greater than 50% by mass particles greater than 75 µm mean diameter (D_{50} > 75 µm). Simply put, coarse soils are defined as having more than 50% sand by mass and fine soils are defined as having less than 50% sand by mass.

3.3 Exposure Pathways

As discussed in Chapter 2, exposure to PHCs from contaminated soil may occur by a variety of pathways. However, not all of these pathways are relevant for each and every land use. Also, not all pathways are well understood or their parameters adequately quantified for PHC Tier 1 levels derivation. For purposes of deriving Tier 1 levels for PHCs, the following pathways were considered (see Figure 3.1):

(a) inadvertent ingestion of PHC contaminated soil;
(b) dermal absorption of PHCs from contaminated soil deposited on the skin;
(c) inhalation of volatile PHCs emanating from the soil following their infiltration to the indoor environment; and/or
(d) ingestion of soluble PHCs which have infiltrated to, and contaminated, local groundwater used as a source of drinking water.

Following the policies and procedures set out in the CCME Protocol (CCME 1996), the recommended human health-based soil quality level is based on the single pathway that results in the greatest exposure, thereby providing the lowest overall protective numerical Tier 1 value.

3.4 Models and Assumptions

For the purpose of PHC Tier 1 level, human exposure to PHC contamination in soil is assumed to occur primarily via the four pathways described in Section 3.3. Numerous models exist with which to assess these exposures. In selecting models to support Tier ½ objectives, CCME has sought a balance among scientific rigour, complexity, ease of use, transparency and history of use in regulatory decision-making. Appendix C presents the equations developed to derive risk-based Tier 1 levels that ensure that the residual soil contamination will not result in human exposure in excess of prescribed tolerable daily intakes (TDIs) or reference air concentrations (RfCs; applicable to volatile PHCs only).

Calculations performed for vapour intrusion and water ingestion pathways involve partitioning of PHC constituents among dissolved, sorbed and vapour phases. Tier

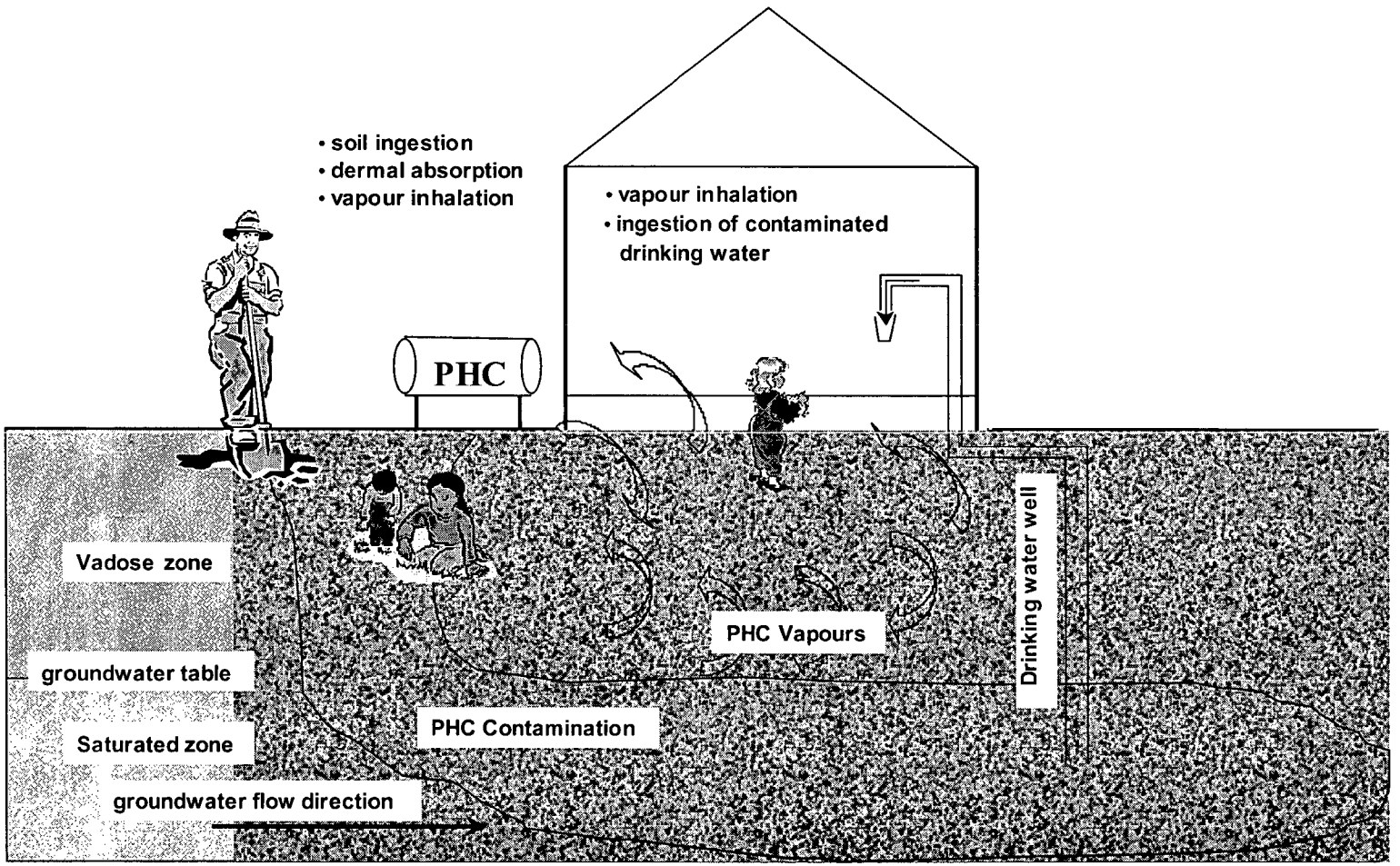


Figure 3.1. Human health exposure pathways to PHC contaminated soil.

1 levels calculated for these pathways are based on the *total* (three phase) soil concentration as would be observed through the analytical method.

3.4.1 Ingestion of PHC-contaminated soil

Inadvertent ingestion of soil can be a significant pathway of human exposure to contaminated soil. Studies indicate that children ingest much greater amounts of soil and dust each day than adults, primarily due to greater hand-to-mouth activity and a greater time spent playing outdoors and on the floor. The equation to estimate risk-based Tier 1 levels that prevent unacceptable exposure via inadvertant direct ingestion of PHC-contaminated soil is presented in Appendix C. This equation is identical to that employed within the Atlantic PIRI tool kit and by CCME (1996).

Assumptions concerning rates of daily soil ingestion by the various critical receptors (toddlers in agricultural, residential and commercial land uses and adults in industrial land uses) are included in Table 3.1.

Table 3.1: Receptor characteristics.

	Toddler [1]	Adult [2]
Body Weight (BW) (kg)	16.5	70.7
Exposure Time (ET) (agricultural)	1	1
Exposure Time (ET) (residential) [3]	1	1
Exposure Time (ET) (commercial) [3]	(10/24)*(5/7)*(48/52)	(10/24)*(5/7)*(48/52)
Exposure Time (ET) (industrial) [3]	(10/24)*(5/7)*(48/52)	(10/24)*(5/7)*(48/52)
Soil Ingestion Rate (SIR) (g/d) [3]	0.08	0.02
Surface Area - hands (SA_{HANDS})(m2)	0.043	0.089
Surface Area - other (SA_{OTHER}) (m2)	0.258	0.250
Dermal Loading to Skin (mg/m2-event) [4]		
Hands (DL_{HANDS})	1000	1000
Surfaces other than hands (DL_{OTHER})	100	100
Exposure Frequency (EF) (events/d)	1	1
Inhalation Rate (IR) (m3/d)	9.3	16.2
Water Ingestion Rate (IR_W) (L/d)	0.6	1.5

(after Richardson, 1997, unless otherwise noted)

1 Toddlers are the critical receptors for residential and commercial (day care) land uses.
2 Adults are the critical receptors for industrial land uses.
3 Source: CCME (1996)
4 Source: Kissel et al. (1996, 1998)

3.4.2 Dermal Absorption of Soil-borne PHCs

In most cases, human skin provides a relatively good barrier to passage of substances into the human body. However, depending on their chemical properties, absorption of some contaminants through the skin is potentially an important route of human exposure. To be absorbed through the skin, the invading substance must pass through the epidermis or through appendages on the skin such as sweat glands or hair follicles. Dermal absorption of organic compounds is primarily limited to substances that are very lipid (fat)-soluble. The equation to estimate risk-based Tier 1 levels that prevent unacceptable exposure via dermal absorption of PHC from contaminated soil deposited to the skin is presented in Appendix C. This equation is identical to that employed within the Atlantic PIRI tool kit. Assumptions concerning exposed skin surface area and soil loading to skin are included in Table 3.1.

3.4.3 Migration To, and Contamination of Groundwater

Protection of potable groundwater was considered in the derivation of the Tier 1 objective for the PHC Tier 1 level for hydrocarbon fractions F1 and F2. The Tier 1 levels for F1 and F2 are intended to provide acceptable drinking water quality on the down-gradient boundary of a site underlain by an unconfined aquifer, as described in Section 2.5.1. Whereas the primary focus in PHC CWS standard development is the prevention of toxic effects to potential receptors, in some cases it is possible that PHC groundwater contamination by fractions F1 and F2 may create taste or odor concerns at concentrations lower than the Tier 1 level concentrations derived to prevent health effects. Unfortunately guidelines for aesthetic factors, such as taste and odor, do not currently exist for broad PHC fractions as defined herein; guidelines for such aesthetic qualities may require future development.

Guidelines for potable groundwater protection for fractions F3 and F4 were not necessary due to their inherent low solubilities and high affinity for adsorption on soil organic carbon which significantly reduces their potential for movement into groundwater.

As shown in Figure 3.1, soil contamination is assumed to extend to the water table, though this assumption can be adjusted in a Tier 2 case if supported by relevant site-specific data. Concentration of PHCs distributed between the adsorbed, dissolved and vapour phases in soil were estimated using the linear partitioning methods described in TPHCWG Vol. 2 (1997). This method assumes there is no free hydrocarbon phase present. PHC partitioned to soil water is assumed to leach to groundwater at a rate determined by groundwater recharge. The PHC-contaminated groundwater recharge is diluted by the lateral groundwater flow as described by the relationship provided in Appendix D of CCME (1996). A Tier I soil objective that protects groundwater quality for human health consumption for PHC fractions F1 and F2 is determined by:

- Back-calculating from the applicable drinking water quality guideline derived from the residual tolerable daily intake for each TPHCWG sub-fraction within the F1

and F2 categories. In this back-calculation, the water quality guideline is multiplied by a dilution factor representing groundwater recharge and lateral flow to estimate the soil porewater concentration at the soil source. Linear partitioning constants are then applied to the porewater concentration to determine the equilibrium soil concentration as shown in Appendix C, and

- Using the algorithm provided for summing TPHCWG sub-fractions provided at the beginning of Appendix C to determine the value for the entire PHC CWS fraction.

Partitioning Relationship

Physico-chemical parameters (including log Koc) for TPHCWG sub-fractions are provided in Table B.1. Based on a review of organic C content of Canadian subsoils conducted for the PHC CWS, Foc was set at 0.5% for both coarse and fine-textured soil.

Dilution Expression

The vertical mixing zone was set at 2 m as described in Section 2.5.1. Other parameters needed for the dilution expression are listed in Table 3.2.

Table 3.2: Additional assumptions required for the migration to groundwater pathway and the indoor infiltration pathway.

Migration to Groundwater

Assumption	Value
Effective Mixing Depth (B) (m)	2
Hydraulic Gradient (*i*) (unitless)	0.05
Site Length (L) (m)	10

Indoor Infiltration

Assumption	Value
Vapour viscosity (μ) (g/cm-s)	1.73 E-04
Gas Constant (R) (atm-m^3/mol-K)	8.20 E-05
Soil temperature (T) (degrees K)	294
Vapour migration path length (L_t) (m)	
Agricultural	30
Residential, commercial, industrial	0.3

The following rationales apply:

- Recharge values were derived from Atlantic PIRI (1999) to reflect high precipitation conditions in the western and eastern coastal regions of Canada. Most other areas in Canada will have lower recharge rates and lower sensitivity to soil-to-groundwater cross contamination;

- A 10 m site length was selected to be representative of upper lateral dimensions at typical small release sites such as oil and gas wellsites and fuel stations. *Note that this value cannot be assumed to be protective at large release sites such as pipeline breaks and refineries. A Tier 2 or 3 approach should be applied in such cases.*

- Hydraulic conductivities were selected to represent a good-yielding aquifer in the coarse textured case and, for the fine textured case, a lower end yield consistent with a threshold transmissivity of 10^{-4} cm/s to support consumptive use for a small family.

Toxicological Benchmark

Toxicological endpoints and reference doses for TPHCWG sub-fractions are given in Table 3.8. A soil allocation factor of 1.0, was used for derivation of Tier 1 soil quality levels protective of potable groundwater, as described in Section 3.8.

3.4.4 Indoor infiltration of Volatile PHCs

The receptor characteristics developed to derive PHC Tier 1 levels to protect against risks posed by the indoor infiltration of PHC vapours from fine-grained soils and coarse-grained soils are presented in Table 3.1. Soil parameters and other site-specific variables assumed for these models are presented in Table 3.3 while assumptions concerning buildings into which the vapours might infiltrate are presented in Table 3.4. Table 3.5 presents assumptions for chemical-specific variables. These models are taken from the work of Johnson and Ettinger (1991).

Table 3.3: Assumed soil characteristics required for the Tier 1 indoor infiltration of vapours pathway.

	Coarse-Grained	Fine-Grained
Retention of grains on a 75 μm screen (D50) (%)	> 50	≤ 50
Saturated Hydraulic Conductivity (K) (m/y)	320	32
Recharge (R) (m/y)	0.28	0.20
Organic Carbon Fraction (f_{OC}) (g/g)	0.005	0.005
Water Content (= Mw/Ms) (θ_m)	0.07	0.12
Soil Bulk Density (ρ_B) (g/cm3)	1.7	1.4
Total Soil Porosity (θ_T)	0.4	0.3
Vapour-Filled Porosity (θ_a)	0.281	0.132
Moisture-Filled Porosity (θ_w)	0.119	0.168
Soil Vapour Permeability to Vapour Flow (K_v) (cm2)	10^{-8}	10^{-9} *
Median particle diameter, D_{50}	> 75 um	< 75 um
Distance from contamination to foundation slab, Lt (cm)**	30 (soil, and subsoil basement scenario) 139 (subsoil, slab-on-grade)	30 139

* not required for Tier 1 calculations.

**a general 30 cm separation between contamination and building slab is assumed, except for subsoil values in slab-on-grade scenarios, where a separation of roughly 139 cm is created by the distance from the bottom of the slab to the defined 150 cm+ depth of subsoil.

Table 3.4: Building characteristics assumed for indoor infiltration pathway.

	Residential Scenario (with basement)	Residential Scenario (slab-on-grade)	Commercial Scenario (slab-on-grade)
Building Length (L_B) (cm)	1225	1225	2000
Building Width (W_B) (cm)	1225	1225	1500
Building Area (A_B) (cm2)	1.50E+06	1.50E+06	3.00E+06
Building Height, including Basement (H_B) (cm)	488	488	300
Thickness of Building Foundation (cm) - L_{crack}	11.25	11.25	11.25
Area of Cracks (cm2) - A_{crack}	994.5	994.5	1846
Radius of Idealized Cylinder (cm) - r_{crack}	A_{crack} / X_{crack}	A_{crack} / X_{crack}	A_{crack} / X_{crack}
Length of Idealized Cylinder (cm) - X_{crack}	4900	4900	7000
Distance below grade to Idealized Cylinder (cm) - Z_{crack}	244	11.25	11.25
Air Exchanges per Hour (ACH) (h^{-1})	1	1	2
Pressure Differential (ΔP) (g/cm-s2)	40	40	20
Diffusivity in cracks, D^{crack}, (cm2/sec)	4.5E-04	4.5E-04	4.5E-04

Table 3.5: Chemical-specific assumptions required for the indoor infiltration of vapours pathway and/or the migration to groundwater pathway.

AROMATICS	$C_{>7}$ - C_8	$C_{>8}$ - C_{10}	$C_{>10}$ - C_{12}	$C_{>12}$ - C_{16}	$C_{>16}$ - C_{21}	$C_{>21}$ - C_{34}	$C_{>34}$ - C_{50}
Tolerable Daily Intake (TDI) (mg/kg/d) [a]	0.2	0.04	0.04	0.04	0.03	0.03	0.03
Estimated Daily Intake (EDI) (mg/kg/d) [b]	0.00477	0.00938	0	0	0	0	0
Reference Concentration (RfC) (mg/m3) [a]	0.4	0.2	0.2	0.2	NA	NA	NA
Background Indoor/Outdoor Air Conc'n (C_a) (mg/m3) [b]	0.01776	0.03745	0	0	0	0	0
Henry's Law Constant (H) (atm-m3/mol) [a]	6.49E-03	1.20E-02	3.40E-03	1.30E-03	3.10E-04	1.61E-05	4.40E-07
Organic Carbon Partition Coefficient (K_{OC}) (mL/g) [a]	$10^{2.4}$	$10^{3.2}$	$10^{3.4}$	$10^{3.7}$	$10^{4.2}$	$10^{5.1}$	$10^{6.25}$
Diffusion Coefficient in Air (D_a) (cm2/s) [c]	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Diffusion Coefficient in Water (D_w) (cm2/s) [d]	n/c	n/c	n/c	n/c	n/c	n/c	n/c
Absorption Factor for Gastrointestinal Tract (AF_G) (unitless) [e]	1	1	1	1	1	1	1
Absorption Factor for Skin (AF_D) (unitless) [e]	0.2	0.2	0.2	0.2	0.2	0.2	0.2

ALIPHATICS	$C_{>6}$ - C_8	$C_{>8}$ - C_{10}	$C_{>10}$ - C_{12}	$C_{>12}$ - C_{16}	$C_{>16}$ - C_{21}	$C_{>21}$ - C_{34}	$C_{>34}$ - C_{50}
Tolerable Daily Intake (TDI) (mg/kg/d) [a]	5	0.1	0.1	0.1	2	2	20
Estimated Daily Intake (EDI) (mg/kg/d) [b]	0.02334	0.0103	0	0	0	0	0
Reference Concentration (RfC) (mg/m3) [a]	18.4	1	1	1	NA	NA	NA
Background Indoor/Outdoor Air Conc'n (C_a) (mg/m3) [b]	0.09111	0.03881	0	0	0	0	0
Henry's Law Constant (H) (atm-m3/mol) [a]	1.2	1.9	2.9	12.5	118	13500	2.90E+06
Organic Carbon Partition Coefficient (K_{OC}) (mL/g) [a]	$10^{3.6}$	$10^{4.5}$	$10^{5.4}$	$10^{6.7}$	$10^{8.8}$	10^{13}	$10^{18.2}$
Diffusion Coefficient in Air (D_a) (cm2/s) [c]	0.05	0.05	0.05	0.05	0.05	0.05	0.05

Diffusion Coefficient in Water (D_w) (cm2/s) [d]	n/c	n/c	n/c	n/c	n/c	n/c	n/c
Absorption Factor for Gastrointestinal Tract (AF_G) (unitless) [e]	1	1	1	1	1	1	1
Absorption Factor for Skin (AF_D) (unitless) [e]	0.2	0.2	0.2	0.2	0.2	0.2	0.2

Footnotes to Table 3.5

a - based on TPHCWG

b - incorporated where data permit; estimated by OAEI

c - recommended by PIWG

d - not considered (n/c) as the contribution due to diffusion through the soil moisture will be insignificant in comparison with vapour-phase diffusion

e - assumed

NA - not available

Johnson and Ettinger (1991) provided one of the first screening level models to assess potential risks posed by the indoor infiltration of volatile contaminants emanating from soil and/or groundwater, and it has become a widely accepted work in this area. A risk assessment modelling tool based on Johnson and Ettinger (1991) has been published by the U.S.EPA (1997), and a modified version of the Johnson and Ettinger model has been adopted within ASTM Standard 1739-95 (RBCA) (ASTM 1995) and subsequently by the Atlantic Provinces PIRI initiative. Such models are routinely used in Canada and elsewhere for assessment of soil-borne volatile contaminants, particularly petroleum hydrocarbons.

Johnson and Ettinger (1991) demonstrated the mathematical rigour of their model by solving for a number of hypothetical, limiting situations. This work demonstrated that the solutions to these limiting cases agreed with what was anticipated theoretically. As yet there are insufficient data from field trials or controlled experimentation on full scale buildings to 'field validate' the model. However, laboratory research has demonstrated the validity of various components, at least at bench scale.

3.4.4.1 Mass Transfer Phenomena Controlling Vapour Migration Through Soil. A modified version of the Johnson and Ettinger model has been adopted within ASTM Standard 1739-95 (RBCA) (ASTM 1995). The primary modification within RBCA is the omission of advective (also termed convective) vapour transport through cracks and spaces in the building envelope at Tier 1. Although all the Johnson and Ettinger equations (and quantification of the necessary variables) are provided within RBCA, the RBCA Tool Kit assigns the critical variable for advective flow (Q_{soil}) a value of zero for the default case. This effectively restricts the model to diffusion-driven infiltration only. No explanation is provided within the RBCA documentation to rationalize or justify this modification. However, Nazaroff et al. (1985, 1987) report Q_{soil} values ranging from 280 cm^3/s to 2800 cm^3/s for indoor to outdoor barometric pressure differentials of 5 to 30 Pa (lower pressure indoors). Given that such pressure differentials are routinely observed in the range up to 12 Pa, depending on construction details (CMHC 1997), then the default assumption of $Q_{soil} = 0$ is inappropriate in all default cases.

Numerous authors indicate that advective (pressure-driven) flow, which moves volatile contaminants from the soil-foundation interface into the living space of the building under a net negative barometric pressure differential (possibly due to wind effects, temperature differentials, appliance fans, stack effect, etc.) must be considered when quantifying the indoor infiltration and potential health risks of soil-borne volatile hydrocarbons (Johnson and Ettinger 1991; CMHC 1997; Williams et al. 1996; U.S.EPA 1997; Hers and Zapf-Gilje 1999; Little et al. 1992; and references therein). Coarse-grained soils such as sand lack significant resistance to air flow in the soil matrix. Therefore, advective flow must be considered for coarse-textured soils and building characteristics and site features that influence advective flow must be defined.

For fine-grained soils, however, the 'tightness' of these soils and their consequently lower air space, diffusivity and permeability characteristics are anticipated to inhibit air flow through the soil matrix. As a result, only diffusion of volatile components of PHCs are considered for fine-textured soils.

Careful consideration of soil properties influencing diffusive and advective flow was undertaken in the preparation of the Tier 1 levels. Under conditions differing from those specified for Tier 1 levels (i.e., at Tier 2) it will be necessary to consider the potential contributions of both mechanisms of vapour movement.

3.4.4.2 Site Characteristics Required for Indoor Infiltration Modelling. Indoor to outdoor pressure differential (ΔP):

Recommended values are:

- Residential buildings: 4.0 Pa
- Commercial buildings: 2.0 Pa
- Industrial buildings: 2.0 Pa

One of the over-riding factors contributing to advective flow of volatile contaminants to the indoor environment is a net negative pressure differential in indoor environments, relative to outdoor environments. Indoor to outdoor barometric pressure differences have been investigated by a variety of researchers (reviewed by U.S.EPA 1997; CMHC 1997; Johnson and Ettinger 1991). In general, a net negative pressure difference on the order of 1 to 12 Pa has been observed, with this pressure difference being observed primarily during the heating season, and being influenced by factors such as house height, presence/absence of chimney, presence/absence of appliance fans, below grade versus slab on grade construction (CMHC 1997). CMHC (1997) indicates that pressure differentials between the indoor and outdoor environment during the winter heating season for 1 or 2 storey dwellings span from 2 Pa (no chimney, mild winter) to 12 Pa (severe winter, chimney, no fresh air intake for combustion air supply, frequently used exhaust fan and/or fireplace). The expected modal or average condition during winter would be a 7 Pa negative pressure differential. Assuming that the heating season lasts 6 months, and that a zero pressure difference exists for the remainder of the year, then the annual average or typical pressure differential would be 4 Pa (rounded to one significant digit from a value of 3.5 Pa). Application of an annual average pressure differential is appropriate in the derivation of Tier 1 levels for PHCs because chronic exposures ($\geq$ 365 days) are being considered and chronic reference doses and reference air concentrations are being applied to prevent potential health effects.

For commercial and industrial buildings, a lower default negative pressure differential of 2 Pa was selected. Commercial and industrial buildings are expected to maintain a lower overall pressure differential, compared to residential buildings, because of forced, calibrated air exchange designed into heating systems, and due

to the more regular and routine movement of building occupants into and out of the structure.

3.5 Air exchange rates

- Residential buildings: 1.0 ach
- Commercial buildings: 2.0 ach
- Industrial buildings: 2.0 ach

Information on air exchange rate (or air changes per hour; ACH) is required to estimate the degree of dilution of infiltrating PHC vapours in fresh (uncontaminated) indoor air. A large variety of studies have been published documenting measurements of ACH in homes. Most of those studies suggest an average ACH of between 0.3 and 0.5 for homes in Canada or homes from northern regions of the United States. However, these ACH measurements are routinely collected with conditions that simulate Canadian winter conditions: all windows and doors tightly closed. Also, these measurements are often taken in unoccupied homes. As a result, average ACH values from reported data generally do not reflect typical 'lived-in' house conditions, nor do they reflect annual average conditions. Pandian et al. (1993) reported data collected on air change rates for more than 4000 U.S. homes. Their data include measurements collected during all four seasons. Average summer measurements were between 2.8 times greater, 13.5 times greater, and 10.8 times greater than measurements collected in spring, fall and winter, respectively. The fact that ACH increases significantly with open doors and/or windows is corroborated by Otson et al. (1998) and Lamb et al. (1985).

CMHC (1997) indicates that more recently built residences have lower ACH than older homes. CMHC suggests that ACH values for homes built pre-1960 may range from 2 to 10 times greater than recently constructed 'airtight' homes. This is generally supported by data from Pandian et al. (1993), Grimsrud et al. (1983), Gerry et al. (1986) and King et al. (1986) and likely reflects building practices which increase energy efficiency in more recent construction. Based on data presented by Grimsrud et al. (1983) the geometric mean ACH for homes built prior to 1970 was 0.69, whereas homes built during or after 1970 had a geometric mean ACH of 0.46. This difference was statistically significant.

ACH values for multi-level homes tend to be greater than ACH values for single storey residences. Pandian et al. (1993) report ACH values of 0.6 and 2.8 for one-level and two-level homes, respectively. Data from Grimsrud et al. (1983) indicate geometric mean ACH values of 0.47 and 0.52 for one-level and two-level homes, respectively. Again, these latter values are statistically significantly different.

Data comparing natural air exchange rates in commercial properties are limited compared to residential homes. Greater door traffic is anticipated to result in greater natural air exchange in commercial versus residential buildings. Data

reported by Kailing (1984) on natural air exchange rates indicate ACH values ranging from 0.09 to 1.54 for commercial structures compared to 0.01 to 0.85 for residences. Many commercial properties (especially malls and other large facilities) will have mechanical ventilation systems to maintain adequate ventilation to ensure indoor air quality (see ASHRAE Standard 62-1989, for example). Sherman and Dickerhoff (1994) and Weschler et al. (1996) report ACH values of 1.5 to 1.8 ACH for small commercial buildings under mechanical ventilation.

Diffusional path length for volatile PHCs

For residential, commercial and industrial properties, it has been assumed that the soil-borne PHC contamination is a minimum of 30 cm (L_t = 0.3 m) from the building foundation. The PHC vapours must migrate through this 0.3 m of clean fill before reaching and penetrating the building foundation. When L_t is less than 0.3 m, a Tier 2/3 analysis is required because the performance of the vapour intrusion model is uncertain in this parameter range. Soil gas to indoor air dilution factors for a range of values of $L_T \geq 0.3$ m, for both fine-grained and coarse-grained soils are presented in Table 3.6.

Table 3.6: Soil gas to indoor air dilution factor (DF) as a function of depth/distance from building to contamination (L_t).

Dilution Factors for Indoor Infiltration (DF)						
L_T (cm)	Residential, with basment		Residential, slab-on-grade		Commercial/Industrial, slab-on-grade	
	f/g	c/g	f/g	c/g	f/g	c/g
30	512931	23142	512931	14350	678631	44825
100	527516	25231	527516	16439	696563	47394
200	548351	28216	548351	19424	722181	51063
300	569187	31201	569187	22409	747799	54733
500	610859	37170	610859	28378	799034	62073
1000	715038	52094	715038	43302	927123	80422
2000	923396	81942	923396	73150	1183301	117120
3000	1131754	111790	1131754	102998	1439479	153818

For agricultural land uses, the homestead site is considered residential land use and PHC contamination located on the homestead site is subject to the 0.3 m path length applicable to the derivation of residential Tier 1 levels for volatile PHCs. However, where PHC contamination is located in agricultural fields, it is assumed that PHC vapours must migrate 30 m through clean soil before reaching and penetrating the residential structure (farm homestead). This separation distance was selected to be consistent with minimum setbacks required for oil and gas development in Canada.

3.6 Receptor Characteristics

The critical human receptor, that may experience the hypothetical (modeled) exposure to PHCs, is dependent on the prescribed land use. For residential land use, the critical receptor is assumed to be a toddler, that has the greatest exposure (on a dose per unit body weight basis) of any age group. Likewise for commercial properties, the toddler was selected as the critical receptor due to the possible operation of day care facilities, which are permitted by all provincial and municipal zoning bylaws in Canada. For industrial properties, an adult was identified as the critical receptor due to the (generally) restricted public access to such sites.

The receptor characteristics relevant to developing Tier 1 human health-based soil quality values for PHCs include body weight, inhalation rate, water ingestion rate, soil ingestion rate, skin surface area, exposure duration, soil loading to skin. Receptor characteristics assumed for purposes of deriving soil quality quidelines for PHCs under the Canada Wide Standard are summarized in Table 3.1.

Available Canadian studies on exposure factors were identified and analysed by Richardson (1997). The purpose was to thoroughly and critically evaluate Canadian data, in a fashion similar to that undertaken by the U.S.EPA in their *Exposure Factors Handbook*. Additionally, through extensive biostatistical analyses, Richardson (1997) proposed statistically-derived probability density functions to facilitate defensible probabilistic risk assessments. Therefore, where Canadian data exist, receptor characteristics required to derive soil quality levels have been defined from the data presented by Richardson (1997). In cases where empirical Canadian data do not exist for receptor characteristics (soil ingestion rate, for example), alternate sources for assumptions have been used. These included, in order of preference:

- *A Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines* (CCME 1996);
- *Human Health Risk Assessment for Priority Substances* (HC 1994); and
- Relevant published scientific literature.

3.6.1 Body weight

Recommended values:

- Adult: 70.7 kg
- Toddler: 16.5 kg

Recommended body weights represent arithmetic average values from empirical Canadian data as presented by Richardson (1997). These data were derived from three Canadian surveys conducted in 1970-72, 1981 and 1988 (Demirjian 1980, CFLRI 1981, CFLRI 1988). Toddler body weight was based on data from Demirjian (1980), but adjusted for evident weight increases in the Canadian population observed between 1970 and 1988. Adult body weight was based on CFLRI (1988).

These values are based on the most recent, publicly available data in Canada; the same data upon which Health Canada (1994) recommended deterministic assumptions for risk assessments. These body weight values have also been adopted for use by the Atlantic provinces within the PIRI Tool Kit and are now widely employed throughout Canada for contaminated site risk assessments.

3.6.2 Inhalation rate

Recommended values:

- Adult: 16.2 m^3/24 hours
- Toddler: 9.3 m^3/24 hours

Recommended inhalation rates were taken from Richardson (1997) and Allan and Richardson (1998). These inhalation rates were based on a Monte Carlo simulation incorporating quantitative time-activity data with minute volume data for various levels of physical activity for each age group considered. The methods for derivation of these inhalation rates have been published in the peer-reviewed scientific literature (Allan and Richardson 1998). The recommended values are slightly conservative (higher) compared to those based on metabolic studies (see Layton 1993). These inhalation rate values have been adopted by Atlantic provinces for the PIRI Tool Kit and are now widely used in contaminated site risk assessments in Canada.

3.6.3 Water ingestion rate

Recommended values:

- Adult: 1.5 L/day
- Toddler: 0.6 L/day

Recommended water ingestion rates were taken from Richardson (1997). Adult water intake rate was based on NHW (1981). The toddler rate was based on data presented by Ershow & Cantor (1989), as the data in NHW (1981) did not adequately represent younger age groups. For adult intake, the original raw data from NHW (1981) have been lost. Therefore, Monte Carlo analysis of water ingestion rate frequencies derived from the original survey data were undertaken to simulate the original data and to generate standard deviations for these age groups.

For toddlers, Canadian data do not exist. Therefore, a mean rate was derived by calculating a weighted mean for sub-groups reported by Ershow & Cantor (1989) within the desired age range. Mean rates reported by Ershow & Cantor (1989) for adults and teens were within 0.1 L/day of mean rates reported by NHW (1981). Therefore, data for younger age groups from Ershow & Cantor were assumed to be representative of Canadians in the same age groups. The recommended assumptions concerning drinking water intake have been adopted by the Atlantic

provinces within the PIRI Tool Kit and are now widely employed throughout Canada for contaminated site risk assessments.

3.6.4 Soil ingestion rate

Recommended values:

- Adult: 20 mg/day
- Toddler: 80 mg/day

Unintentional ingestion of soil occurs in all age groups of the population (Sedman and Mahmood 1994). This results from the mouthing of unwashed hands and other surfaces, from transfer from unwashed hands to food, and from the ingestion of inhaled dirt particles deposited in the mouth and upper respiratory tract which are transferred to the esophagus by ciliary action, etc. Quantitative data concerning the inadvertent ingestion of soil by Canadians are not available. Available data on soil ingestion are limited and extremely uncertain (U.S.EPA 1997). Recent studies by Stanek and Calabrese (and co-workers) (Stanek et al. 1998, 1999, Stanek and Calabrese 1994a,b, 1995, among others) have employed tracer techniques whereby 6 to 8 inorganic tracer elements are quantified in soil, diet and human faeces in order to determine the net content in faeces that might originate from soil. However, the different tracers provide inconsistent estimates, with some occasionally suggesting negative ingestion rates.

As a result of the lack of Canadian data, and the uncertainty in existing soil ingestion data, assumptions regarding this variable are still considered "best professional judgement". Therefore, for consistency with previous methods and assumptions regarding soil ingestion by different age groups of the Canadian population, the assumptions presented within the CCME *Protocol* (CCME, 1996) have been adopted for derivation of Canada Wide Standards for PHCs.

3.6.5 Skin surface area

Recommended values:

- Adult:
  - hands: 890 cm^2
  - Other (upper and lower arms): 2500 cm^2
- Toddler:
  - hands: 430 cm^2
  - other (upper and lower arms + upper and lower legs): 2580 cm^2

Recommended skin surface areas were taken from Richardson (1997). These values are based on equations developed by U.S.EPA for estimating skin surface area from measurements of weight and height; Canadian weight and height data were then employed for calculations of skin surface areas of various body parts.

Assumptions proposed by Richardson (1997) on skin surface area have been adopted within PIRI Tool Kit by the Atlantic provinces, and are now routinely employed for site-specific risk assessments across Canada.

3.6.6 Soil to Skin Adherence

Recommended values:

- adult and toddler:
  - hands: 0.1 mg/cm^2
  - other: 0.01 mg/cm^2

Recent research on soil loading to skin, from both field and controlled trials, has been published by Kissel et al. (1996, 1998). Loadings are consistently greatest on the hands, with lower loadings to face, forearms and lower legs. Loadings are generally greater for activities involving direct contact with soil (gardening, pipe laying, for example). Duration of activity has little or no significant influence on total loading to the hands. Loadings of moist soil are about an order of magnitude greater than loadings of dry soil. Loadings on children and adults engaged in similar activities are not markedly different.

From these studies, loadings to hands for typical activities anticipated on residential and commercial properties ranged from 0.019 to 0.19 mg/cm^2 with an arithmetic average value of 0.075 mg/cm^2. Loadings to leg and arm surfaces for these same activities ranged from 0.0008 mg/cm^2 to 0.023 with an arithmetic average of 0.0077 mg/cm^2. Based on these data, an assumption of 0.1 mg/cm^2 for hands, and 0.01 mg/cm^2 for exposed surfaces of other body parts (arms, legs, face), are appropriate.

3.6.7 Exposure frequency

Recommended values are:

- Agricultural land use: 365 days/year
- Residential land use: 365 days/year
- Commercial land use: 100 days/year
  - 10 hr/d x 5 d/wk x 48 wk/yr
- Industrial land use: 100 days/year
  - 10 hr/d x 5 d/wk x 48 wk/yr

Recommendations concerning exposure frequency, for derivation of Canada Wide Standards for PHCs, were adopted from CCME (1996) to maintain consistency with previous methods and assumptions regarding exposure frequency for soil quality guidelines derivation and site-specific risk assessment in Canada.

3.6.8 Exposure duration

For purposes of deriving Canada Wide Standards for PHCs, shorter-than-lifetime exposures were not amortized (averaged) over a lifetime (70 years). Therefore,

explicit definition of a default exposure duration is not required for derivation of Tier 1 soil quality levels.

3.6.9 Route-specific absorption rates

3.6.9.1 Ingestion. Tolerable daily intakes (reference doses) for environmental contaminants are normally derived based on delivered dose, rather than the absorbed dose. Therefore, it has been assumed that the relative gastrointestinal absorption rate for all PHCs is 100%.

3.6.9.2 Inhalation. Tolerable air concentrations (TCs) (RfCs) for volatile environmental contaminants are normally derived based on the exposure concentration in test subjects or animals, rather than the absorbed dose. For those PHCs lacking TCs (RfCs), little or no data exist to accurately quantify respiratory absorption. However, such absorption does approach 100% for various individual hydrocarbon compounds. Therefore, it has been assumed that the relative respiratory absorption rate for all PHCs is 100%.

3.6.9.3 Dermal. There are two basic approaches used to quantify absorption following dermal exposure: 1) a total absorption factor; and 2) to define absorption rate as a function of the duration of dermal contact (Ryan et al. 1987). A total absorption factor, typically as a percent relative to ingestion exposure, is routinely employed for the derivation of generic soil quality guidelines (MADEP 1991, OMEE 1997). However, for site-specific risk assessment, the flux of contaminant penetrating the skin (mg/cm^2-hour) may be combined with information on duration of exposure to provide a more (theoretically) accurate estimate of dermal absorption (Ryan et al. 1987, U.S.EPA 1992a).

For the purpose of prescribing soil quality levels for the CWS PHC initiative, it is recommended that a total absorption factor approach be employed. This recommendation is based on the following:

- the nature of the generic Tier 1 derivation process prevents an accurate quantification of the duration of dermal loading;

- the uncertainties introduced by the total absorption factor approach are not anticipated to significantly increase the overall uncertainty in Tier 1 derivation, given the numerous uncertainties inherent in other assumptions made in the process.

The dermal absorption of aromatic and aliphatic petroleum fractions has been reviewed by the Agency for Toxic Substances and Disease Registry (ATSDR 1999a), but studies on the total applied dose absorbed or on skin penetration rates have not been published for the vast majority of hydrocarbon compounds. The

dermal absorption of benzene, toluene, ethylbenzene and xylenes has been summarized by the ATSDR (1995a, 1997, 1998,1999b). Generally less than 1% of a dermally-applied dose of benzene was absorbed following single dermal applications in both humans and animals (ATSDR 1997). Dermal absorption of a single dermal application of ethybenzene resulted in 3.4% absorption (ATSDR 1995b). Research indicates that absorption of a single dermal application of PAHs in an organic solvent may amount to between 50 and 80% of applied dose, but declines to less than 20% when the PAHs were applied in a soil matrix (ATSDR 1995b).

Tsuruta (1982) determined that the skin penetration rate (nMoles/cm^2-min) of volatile hydrocarbons decreased in the following order:

> benzene > toluene > styrene > ethylbenzene > o-xylene > n-pentane > 2-methylpentane > n-hexane > n-heptane > n-octane

This research indicated that, for volatile aliphatic and aromatic hydrocarbons at least, the skin penetration rate is generally proportional to water solubility (with more soluble compounds penetrating the skin at a greater rate) and that aromatic compounds are absorbed at a greater rate than aliphatic compounds of similar carbon number.

It has also been noted that dermal absorption from a soil matrix is less than dermal absorption from an aqueous solution and of the pure compound (U.S.EPA 1992a; see also ATSDR 1995b). This seems particularly true for chlorinated organics such as dioxins and may be a function of compound interactions with organic carbon (U.S.EPA 1992a).

Relative absorption factors (RAFs) have been proposed by the Ontario Ministry of Environment and Energy to quantify dermal absorption for the purpose of deriving generic soil quality guidelines (OMEE 1997). The RAF values defined by OMEE for hydrocarbon compounds are presented in Table 3.7. These values were adopted from the Massachusetts Department of Environmental Protection (MADEP 1989, 1991). OMEE RAF values for hydrocarbon compounds range from 8% (benzene) to 26% (phenol, 2,4-dimethylphenol) with the majority of hydrocarbon RAF values being 20%.

Based on the foregoing discussion, it is recommended that an absorption factor of 20% be applied to the derivation of soil quality levels for all aromatic and aliphatic PHC fractions. Although it is anticipated that dermal absorption will decrease with increasing carbon number (decreasing solubility), data are insufficient to prescribe a rigorous and defensible regression analysis with which to derive separate dermal RAF values for each TPHCWG PHC sub-fraction.

Table 3.7: Ontario Ministry of Environment and Energy relative absorption factors for dermal exposure.

CHEMICALS	OMEE RAF
Acenaphthene	0.2
Acenaphthylene	0.18
Anthracene	0.29
Benzene	0.08
Benzo(a)anthracene	0.2
Benzo(a)pyrene	0.2
Benzo(b)fluoranthene	0.2
Benzo(g,h,i)perylene	0.18
Benzo(k)fluoranthene	0.2
Chrysene	0.2
Dibenzo(a,h)anthracene	0.09
Dimethylphenol, 2,4-	0.26
Ethylbenzene	0.2
Fluoranthene	0.2
Fluorene	0.2
Indeno(1,2,3-cd)pyrene	0.2
Methylnapthalene	0.1
Naphthalene	0.1
Phenanthrene	0.18
Phenol	0.26
Pyrene	0.2
Styrene	0.2
Toluene	0.12
Xylenes (Mixed Isomers)	0.12

(from OMEE 1997)

3.7 Tolerable Daily Intakes and Reference Concentrations for TPHCWG Sub-fractions

3.7.1 Application of RfCs Versus TDIs

Soil quality levels for PHCs were derived for non-carcinogenic PHCs only. Soil quality levels for carcinogenic PHCs (benzene, PAHs) have been published elsewhere (CCME 1997). These carcinogenic components, as well as toluene, ethylbenzene and xylenes should be directly quantified and subtracted from total PHC contamination prior to application of these PHC Tier 1 levels (see Chapter 6 for analytical methods and methods for quantification of PHC concentrations).

The Development Committee for Canada Wide Standards for PHCs has opted to employ route-specific reference exposure levels for the derivation of soil quality levels for those PHCs. Route-specific reference levels are considered most appropriate for Tier 1 derivation. This eliminates necessary adjustment for relative absorption efficiencies when TDIs are applied to inhalation exposures, for example, and also eliminates the necessary assumption that the toxic effect(s) are independent of exposure route. Therefore, RfCs were applied for derivation of Tier 1 levels for PHC fractions that are volatile (F1 and F2) and for those pathways involving indoor or outdoor inhalation of vapours (penetration of the building envelope with indoor inhalation (agricultural - 30 m offset, residential, commercial, industrial). For PHC fractions considered non-volatile (F3 and F4) or for those pathways involving exposure routes other than inhalation (direct soil ingestion, ingestion of contaminated groundwater, dermal absorption), tolerable daily intakes (TDIs, also known as reference doses (RfDs)) were applied.

RfCs are defined by the U.S. Environmental Protection Agency (U.S.EPA 2000) as an estimate (with uncertainty spanning perhaps an order of magnitude) of a continuous inhalation exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime. RfCs are analogous to TDIs. As with TDIs, RfCs are derived with the application of uncertainty factors to address, among other considerations, potential human receptors with greater sensitivity to effects, compared to the norm. One such potential sensitive receptor group is toddlers, young children being potentially more sensitive to effects than adults. Given the application of an uncertainty factor for potentially-sensitive receptors, the Development Committee considers RfCs to provide adequate human health protection for all age groups.

RfCs were derived by the TPHCWG, following methods delineated by the U.S. EPA (1994a), for aromatic and aliphatic sub-fractions spanning C_6 to C_{16} (Edwards et al. 1997).

3.7.2 Toxicology of PHCs

An extensive review of the toxicity of components and fractions of PHCs has been presented by Edwards et al. (1997), along with the derivation of tolerable daily

intakes (TDIs) and reference air concentrations (RfCs) for the petroleum hydrocarbon sub-fractions defined by the TPHCWG. Edwards et al. (1997) reviewed available toxicological studies for individual compounds falling within the prescribed TPHCWG sub-fractions and also reviewed available toxicological investigations of a variety of petroleum hydrocarbon mixtures. As a result of that review, the TDIs and RfCs outlined in Table 3.8 were established. Those reference exposure values were based on studies investigating the indicated toxicological endpoints (hazards) and it is anticipated, based on current knowledge and on current reference level derivation methods, that they should prevent such hazards from arising in the vast majority of the population throughout lifelong exposure. It should be noted that reference values were generally derived from exposure levels that were free of observable effects (i.e., no-observed-adverse-effect-levels; NOAELs) in exposed animals.

3.7.2.1 Aromatics. For aromatics in the $C_{>7}$ to C_8 range, styrene is the only compound for which toxicological data are available once benzene, toluene, ethylbenzene and xylenes (BTEX) are deducted. The U.S.EPA (2000) has published a TDI for styrene of 0.2 mg/kg-d. This is based on a sub-chronic oral study in beagle dogs in which increased numbers of Heinz bodies in the red blood cells (RBC), decreased packed cell volume, and sporadic decreases in hemoglobin and RBC counts were observed at the higher dose levels. In addition, increased iron deposits and elevated numbers of Heinz bodies were found in the livers. The TDI was derived from the NOAEL of 200 mg/kg-day and an uncertainty factor of 1000 (10 for intraspecies variability, 10 for interspecies variability, and 10 for extrapolation of subchronic effects to chronic effects).

The U.S.EPA (2000) has also established an RfC of 1.0 mg/m3 based on a NOAEL from human occupational studies investigating effects on the central nervous system. However, the published RfC for toluene is lower, at 0.4 mg/m3. Despite toluene being excluded from PHCs in this range (as they are analyzed separately and deducted from total PHCs), the TPHCWG opted to apply the lower RfC for toluene to the remaining PHCs in the $C_{>7}$ to C_8 range.

In the $C_{>8}$ to C_{16} range, eight aromatic hydrocarbon compounds (isopropylbenzene, naphthalene, acenaphthene, biphenyl, fluorene, anthracene, fluoranthene, pyrene) exist for which TDIs and/or RfCs were published by the U.S.EPA. In addition, unpublished data on the effects of oral exposure of rats to a mixture of naphthalene/methylnaphtalenes were available to the TPHCWG, along with a variety of published studies on the effects of inhalation exposure to C_9 aromatics in rats and mice, from which TDIs or RfCs could be derived (following EPA methodology). Published or derived TDIs ranged from 0.03 mg/kg-d to 0.3 mg/kg-d for the various compounds and mixtures. Only two published RfCs existed (isopropylbenzene = 0.09 mg/m^3; naphthalene = 0.0013 mg/m^3), while the RfC

Table 3.8: Toxicological endpoints for tolerable daily intakes (reference doses) and reference concentrations developed by the Total Petroleum Hydrocarbon Criteria Working Group.

TPH Sub-fraction	TDI	RfC	Critical Effect
Aliphatics			
C_6-C_8	5.0	18.4	Neurotoxicity
$C_{>8}$-C_{10}	0.1	1.0	Hepatic and hematolotical changes
$C_{>10}$-C_{12}	0.1	1.0	Hepatic and hematolotical changes
$C_{>12}$-C_{16}	0.1	1.0	Hepatic and hematolotical changes
$C_{>16}$-C_{21}	2.0	N/A [1]	Hepatic granuloma
$C_{>21}$-C_{34}	2.0	N/A	Hepatic granuloma
$C_{>34}$	20.0	N/A	Hepatic granuloma
Aromatics			
$C_{>7}$-C_8	0.2	0.4	Hepatotoxicity, neurotoxicity
$C_{>8}$-C_{10}	0.04	0.2	Decreased body weight
$C_{>10}$-C_{12}	0.04	0.2	Decreased body weight
$C_{>12}$-C_{16}	0.04	0.2	Decreased body weight
$C_{>16}$-C_{21}	0.03	N/A	Nephrotoxicity
$C_{>21}$-C_{34}	0.03	N/A	Nephrotoxicity
$C_{>34}$	0.03	N/A	Nephrotoxicity

(from Edwards et al. 1997)

[1] N/A = not applicable; sub-fraction of PHCs is not sufficiently volatile to present air-borne exposure.

derived for C_9 aromatics was 0.2 mg/m^3. In consideration of the range of TDI values, and emphasizing studies of mixtures (for RfC determination), the TPHCWG selected a TDI of 0.04 mg/kg-d and an RfC of 0.2 mg/m^3 for aromatic petroleum hydrocarbon sub-fractions in the $C_{>8}$ to C_{16} range.

For aromatic PHCs in the $C_{>16}$ range, there are no published TDIs or RfCs, nor available data, for surrogates or mixtures in this range. Therefore, the TDI for pyrene (C_{16}) was selected to be applied to aromatic sub-fractions in the $C_{>16}$ range. No RfC was defined, as PHCs with $C_{>16}$ are insufficiently volatile to pose an inhalation risk.

3.7.2.2 Aliphatics. Within the aliphatic sub-fraction C_6 to C_8, n-hexane is the only compound for which the U.S.EPA has established a TDI, that value being 0.06 mg/kg-d. However, toxicity data for a variety of other hydrocarbons exists, which has been reviewed by Edwards et al. (1997). These hydrocarbons include cyclohexane, methylpentanes and methylcyclohexane. Also, data exist on commercial hexanes, and mixture containing 53% or less n-hexane. An analysis of petroleum products (Edwards et al. 1997) indicated that the n-hexane content of the $C_{>5}$ to C_8 sub-fraction of petroleum products and crude oils was generally less than 20%, while the n-hexane content of commercial hexane was 53%. Therefore, it is inappropriate to apply the TDI for n-hexane to the entire C_6 to C_{10} aliphatic sub-fraction. Toxicological investigations indicate that commercial hexane is some 80 times less toxic than n-hexane (TDIs are 5 mg/kg-d and 0.06 mg/kg-d for commercial hexane and n-hexane, respectively), suggesting a strong inhibitory/antagonistic effect on n-hexane toxicity in the commercial hexane mixture. As a result, a TDI of 5.0 mg/kg-d, based on the toxicity of commercial hexane, has been selected as the most appropriate toxicological benchmark for the C_6 to C_8 aliphatic sub-fraction, reflecting the preferred emphasis on data for mixtures to establish TDIs for mixtures of PHC. The RfC for commercial hexane was determined to be 18.4 mg/m^3 (Edwards et al. 1997).

Ten investigations of the toxicity of PHC mixtures including or spanning $C_{>8}$ to C_{16} have been conducted; these were reviewed by Edwards et al. (1997). Based on these studies of PHC mixtures, the TPHCWG determined a suitable TDI of 0.1 mg/kg-d and an RfC of 1.0 mg/m^3. These values have been adopted for the derivation of human health-based soil quality levels under the CCME Canada Wide Standard for PHCs in soil.

Studies of the toxicity of white mineral oils have been selected as the basis for a TDI for aliphatics in the range of $C_{>16}$ to C_{34}. Seven mineral oils, containing PHCs spanning C_{15} to C_{45} aliphatic hydrocarbons, had been toxicologically investigated in rats (Smith et al., 1995, 1996). Based on no-observed-effects-levels in these studies, the TPHCWG derived a TDI for C_{16} to C_{34} aliphatic hydrocarbons of 2 mg/kg-d, and derived a TDI for $C_{>34}$ aliphatics of 20 mg/kg-d. Due to the low potential volatility of C_{16} to C_{50} aliphatics, no RfC has been determined for aliphatic PHCs in this range.

3.7.3 Background Exposures, Residual TDIs and Residual RfCs

Excluding PAHs, no reports of generalized background contamination of air, water, food or soil (unrelated to contaminated sites) were located for component PHCs in fractions 2, 3 and 4 (i.e., $C_{>10}$). This likely stems from their generally low or negligible solubility and volatility. PAHs are evaluated separately from PHCs for purposes of risk assessment of contaminated sites and, therefore, they are not considered within the various PHC fractions being evaluated here.

Due to the lack of evidence for, and low probability of, ubiquitous environmental contamination with PHCs in fractions 2, 3 and 4, the estimated daily intakes (EDI) of PHCs in fractions 2, 3 and 4 from background sources are considered to be zero.

PHCs in fraction 1 (C_6 to C_{10}) are relatively volatile and soluble. As a result, aliphatic and aromatic compounds in this carbon range have been reported in drinking water, outdoor air, ambient air and some foods. These reports and available data have been summarized previously. With regard to drinking water monitoring in Canada, no provincial authority was identified that routinely monitors drinking water for non-BTEX PHCs. Therefore, it was concluded that the occurrence of these PHCs in drinking water is rare and likely related only to site-specific contamination problems.

Based on an examination of available data, contamination of foods with hydrocarbons in the C_6 to C_{10} range is sporadic and limited, and appears either to be site-specific or to be a function of food preparation (as has also been observed for PAHs in grilled and barbecued foods, for example).

Based on the available data and above-noted considerations, only inhalation exposure to PHCs in the C_6 to C_{10} range is anticipated to contribute significantly to typical background exposures (excluding BTEX and PAHs).

The estimated daily intakes (EDI) and estimated background air concentrations for TPHCWG sub-fractions within fraction 1 were calculated and these values were subtracted from their respective TDIs and RfCs in order to derive the residual TDI (RTDI) and residual reference air concentration (RRfC) for each TPHCWG sub-fraction within Fraction 1. These RTDIs and RRfCs are presented in Table 3.9.

3.8 Soil Allocation Factors to be Employed for Tier 1 Levels

People can receive exposure to contamination from five different media – vis. air, water, soil, food and consumer products. In addition, within soil there are a number of pathways by which a person can be exposed (ingestion, inhalation, dermal contact). A major objective in standards development is to ensure that total exposure does not exceed the applicable reference dose. Confidence that human health is protected by environmental quality guidelines for threshold substances can be increased by taking a *multimedia* approach. This approach, which takes account of known background exposures and "allows room" for other uncharacterized exposures from other media, was first developed and applied in the *Protocol for the Derivation of Human Health and Environmental Soil Quality Guidelines* (CCME 1996).

Table 3.9: EDIs and residual TDIs and RfCs for TPHCWG sub-fractions in PHC fraction 1.

TPHCWG Sub-fraction	Outdoor Air Concen-tration [1]	Estimated Indoor Air Concen-tration [1]	Estimated Daily Intake (EDI)			TPHCWG RFC	RESIDUAL RFC [5]	TPHCWG TDI	RESIDUAL TDI [6]
			Outdoor [2]	Indoor [3]	Total [4]				
	mg/m^3	mg/m^3	mg/kg-d	mg/kg-d	mg/kg-d	mg/m^3	mg/m^3	mg/kg-d	mg/kg-d
Aromatics, C7-C8	0.43	17.33	0.02	4.75	4.77	400	382.24	200	195.23
Aromatics, C9-C10	3.98	33.47	0.22	9.16	9.38	200	162.55	40	30.62
Aliphatics, C5-C6	23.41	161.37	1.28	44.18	45.46	18400	18215.22	5000	4954.53
Aliphatics, C7-C8	7.33	83.78	0.4	22.94	23.34	18400	18308.89	5000	4976.66
Aliphatics, C9-C10	1.49	37.32	0.08	10.22	10.3	1000	961.19	100	89.7

[1] Data provided by the Ontario Ministry of Environment.
[2] Based on outdoor air concentration and assuming 4 hour/day outdoors, 23 m^3/day inhalation rate, and 70 kg body weight.
[3] Based on indoor air concentration and assuming 20 hour/day outdoors, 23 m^3/day inhalation rate, and 70 kg body weight.
[4] Total = outdoor exposure + indoor exposure.
[5] Calculated as RFC - (Outdoor air concentration + indoor air concentration)
[6] Calculated as TDI - Total exposure.

The *Protocol* describes management of exposure within a tolerable daily intake (TDI) or reference dose (RfD) by first subtracting estimated daily (background) intake (EDI) from the TDI to generate a residual tolerable daily intake (RTDI). Subsequently, a portion of the RTDI is allocated to each of five possible media (air, water, soil, food and consumer products). Allocation to all five media is undertaken for two reasons. First, background exposure may be occurring from non-soil media that is not reported or observed – i.e., the EDI may be underestimated. Second, by reserving an allocation for each medium, room is provided for the development of guidelines for other media.

In the most general case discussed in the *Protocol*, a substance is considered to have the potential to be present in all media and therefore, on a default basis, an allocation of 20% of the RTDI is assigned to each of the 5 media. However, for specific substances, in this case PHCs, there may be properties that preclude the presence or limit the concentration in various media. When this is the case, both

the issues of uncharacterized exposure and the potential creation of a new guideline are negated or mitigated. In such cases a greater proportion of the RTDI can be allocated to critical media, such as soil.

Recommended soil allocation factors (SAF) for PHC are presented in Table 3.10 with corresponding rationale based on properties, occurrence in various media, and likelihood that guidelines for other media could be developed. These SAFs have been applied to soil ingestion, dermal contact and inhalation pathways only. The water ingestion pathway uses a SAF of 1, as consistent with the development of many Canadian Drinking Water Guidelines.

It should be noted that in using the SAF to account from each of the contaminated soil pathways, the Development Committee has assumed that there is an imbalance in exposure form the different pathways. If exposure from each of two pathways was expected to be equal and the toxic endpoint for each was the same, then it would be appropriate to assign a SAF of 0.5 to each pathway. However, based on physico-chemical properties and partitioning among media, balanced exposure is rarely expected.

3.9 Derivation of Human Health Tier 1 Soil Quality Levels

Presented in Appendix C is a sample calculation of Tier 1 values for PHC Fraction 1, for residential properties with a below-grade basement and a toddler as the critical receptor. All equations are presented in Table 3.1. Necessary assumptions for input variables are presented in Tables 3.3 through 3.9. Default characteristics for critical receptors are presented in Table 3.1. Calculations for individual TPHCWG sub-fractions are combined into CCME "super-fractions" on a weight-percent basis, employing the formula for combining fractions presented in Appendix C and the weight percents presented in Table 3.11.

Table 3.10 : Soil allocation factors (SAF) for deriving soil quality levels for PHCs*.

Fraction	SAF	Rationale
F1	0.5	Physico-chemical properties and environmental measurements indicate co-residency in air and water. Not likely to occur in significant quantities in food due to poor contact with primary sources and volatility. Consumer products are known to off-gas PHC and data are available for some F1 sub-fractions that indicate fairly low concentrations in indoor air compared to the reference concentration. However, there is little to no information on background exposures to other F1 sub-fractions and there are other known exposures that have not yet been quantified (e.g., patrons at filling stations, adjacent residents). F1 levels may be formally developed for water.
F2	0.5	Physico-chemical properties and environmental measurements indicate co-residency in air and water but at lower concentrations than for F1. No reliable data on background exposure from indoor or outdoor air were identified. F2 to F4 fractions are known to occur in consumer products such as leather and furniture polishes, pharmaceuticals, lubricants, dust control products and motor oils. Probability of occurrence in food greater than for F1. There is potential for exposure along all four of the contaminated soil pathways. Some likelihood that levels for F2 could be developed for water.
F3	0.6	Sparingly soluble in water and very low volatility. F2 to F4 fractions are known to occur in consumer products such as leather and furniture polishes, pharmaceuticals, lubricants, dust control products and motor oils. Some exposure in food likely from barbecued and grilled foods. Exposure from soil likely to occur mainly from soil ingestion and dermal contact. Unlikely that levels will be developed for media other than soil.
F4	0.8	Physico-chemical properties indicate PHC of $C_{>34}$ cannot dissolve in water or volatilize significantly. Whatever non-soil exposure may occur is likely related principally to consumer products such as heavy lubricants, greases and waxes. Exposure from soil likely to occur mainly from soil ingestion and dermal contact. Unlikely that levels will be developed for media other than soil.

* SAF set to 1 for protection of potable groundwater (see Section 3.8)

Table 3.11: Recommended composition of designated petroleum "fractions".

TPH Sub-fraction	Fraction 1	Fraction 2	Fraction 3	Fraction 4
Aliphatics				
C_6-C_8	0.55			
$C_{>8}$-C_{10}	0.36			
$C_{>10}$-C_{12}		0.36		
$C_{>12}$-C_{16}		0.44		
$C_{>16}$-C_{21}			0.56	
$C_{>21}$-C_{34}			0.24	
$C_{>34}$				0.8
Aromatics				
$C_{>7}$-C_8				
$C_{>8}$-C_{10}	0.09			
$C_{>10}$-C_{12}		0.09		
$C_{>12}$-C_{16}		0.11		
$C_{>16}$-C_{21}			0.14	
$C_{>21}$-C_{34}			0.06	
$C_{>34}$				0.2
Sum all sub-fractions	1	1	1	1

4. Ecological Soil Quality Levels

4.1 Protocol Summary and General Issues

A necessary first step in the development of Tier 1 levels for site investigation and soil remediation is to establish the suite of ecological receptors deemed to be potentially at risk from PHC contamination. The choice of ecosystem components that should be protected must necessarily be generically applicable at Tier I; that is, sufficiently protective when applied at the vast majority of terrestrial sites within Canada where PHC releases might be encountered. Figure 4.1 illustrates a simplified set of exposure scenarios for potential ecological receptors at PHC contaminated sites.

Potentially exposed organisms across the entire landmass of Canada span a range of phylogenetic diversity, trophic levels, and physioecological attributes. The overall range includes, for example, soil-dependent organisms (plants, soil invertebrates, soil microbes) and higher order consumers (wildlife, livestock) that may be categorized as primary consumers (herbivores), secondary, tertiary and quaternary consumers. The larger conceptual model for ecological receptors also includes aquatic life in surface water bodies (wetlands, ponds, lakes, streams, rivers) which may occur at or adjacent to PHC-contaminated sites.

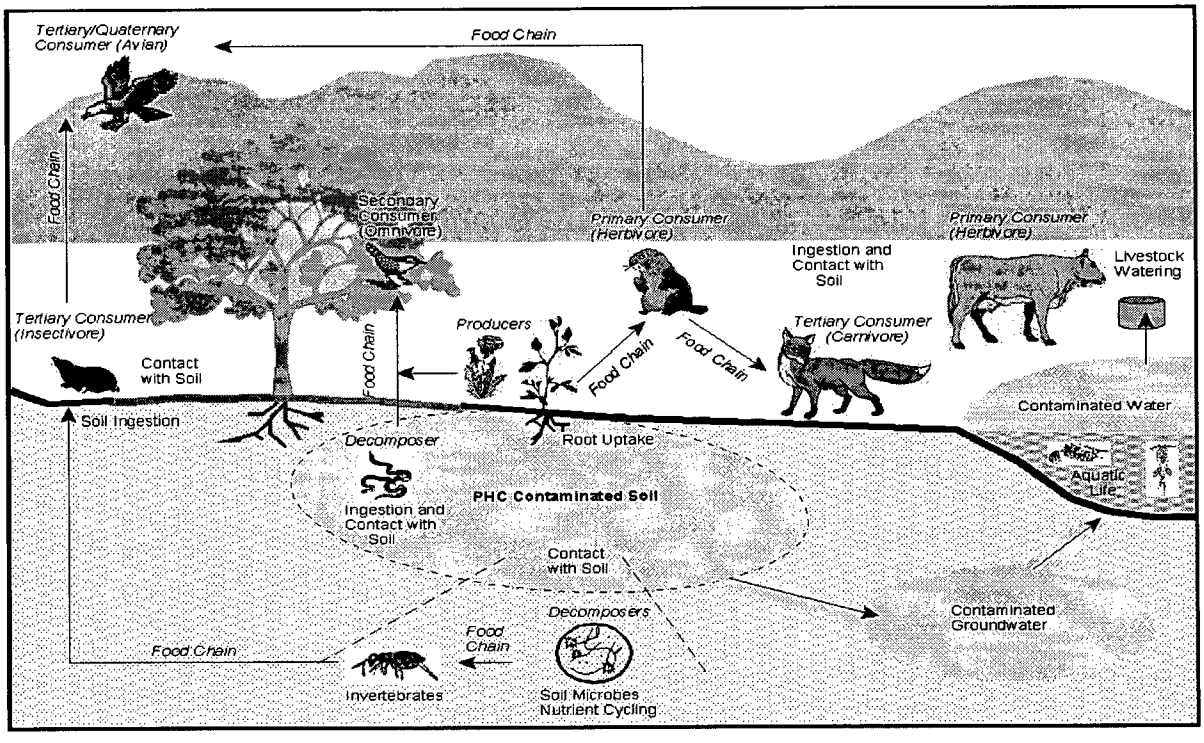


Figure 4.1. Key ecological receptors and exposure pathways of PHC contaminated soils.

The PHC CWS Tier I guidance was developed in consideration of a range of ecological receptors that might otherwise be exposed to petroleum hydrocarbons at unacceptably high levels. Because of the scarcity of ecological effects information for terrestrial organisms, however, selected key ecological receptors that maintain land activities were chosen for the development of Tier 1 levels. In particular, Table 4.1 lists the major categories of ecological receptors for each of the land uses considered as described in more detail in Chapter 2.

Specifics of the scientific rationale for the protection of soil invertebrates and plants, or protection of other ecological receptors (aquatic life, livestock drinking surface water) are provided in Sections 4.2 and 4.3, respectively.

Table 4.1: Ecological receptors and exposure scenarios used in developing the PHC CWS.

Land Use		
Agricultural	***Residential/Parkland***	***Commercial and Industrial***
· Direct contact by soil invertebrates and plants · Aquatic life in adjacent water bodies · Livestock drinking surface water (dugouts) · Livestock ingesting soil	· Direct contact by soil invertebrates and plants · Aquatic life in adjacent water bodies	· Direct contact by soil invertebrates and plants[1] · Aquatic life in adjacent water bodies

Notes: (1) Subsequent to deliberations by EcoTAG and the PHC CWS Development Committee, it was decided that soil quality levels for commercial and industrial sites would be derived primarily in consideration of plant health.

In some non-Canadian jurisdictions, as well as in detailed ecological risk assessments, the development of soil screening or remediation guidance for PHCs has focused more on vertebrate receptors – especially avian or mammalian domesticated and wild species. In Canada, the greater emphasis has been placed on exposure pathways based on direct contact between plant roots or soil invertebrates and the contaminated soils. This emphasis is based on the need to preserve the principal ecological functions performed by the soil resource. Less emphasis has been placed than in some jurisdictions on the estimation of contaminant concentrations in soils beyond which wildlife or domesticated animals might be at risk.

The focus on off-site migration and associated effects on aquatic organisms was deemed to be necessary based on the potential for the introduction of more water-soluble fractions of PHCs to surface water runoff and groundwater at PHC contaminated sites, and was supported by collective practical experience at various PHC contaminated sites. The maintenance of soil integrity based on its ability to support plant and soil invertebrate communities is deemed to be important for both

short and long term ecological sustainability, as demonstrated – for example – through no substantial decrease in primary productivity or impairment of nutrient and energy cycling within the area of interest.

The relative lack of emphasis on terrestrial vertebrate animals such as mammalian or avian wildlife is probably acceptable for PHC release sites as most PHCs are readily metabolized by vertebrates, modified into a more readily excretable form, and thus do not tend to accumulate in tissues. In addition, PHCs are not readily absorbed into and accumulated into plant tissues. The net result is that the consumption of either plants or other animals (as opposed to soil ingestion) does not tend to constitute the major component of exposure for PHCs in wildlife and livestock populations.

It was recognized when deriving the PHC CWS that both livestock and wildlife could be at risk from direct ingestion of released petroleum products. In waterfowl, for example, direct oiling of feathers from PHC spills leads to loss of insulation value and may directly lead to hypothermia. In addition, there is a huge volume of veterinary and toxicological literature that demonstrates that direct ingestion of petroleum products from the preening of feathers or fur can lead to acute toxic effects, including death. This exposure scenario, however, is based largely on the presence of free-phase petroleum hydrocarbons in the environment. For the purpose of the PHC CWS it is assumed as a starting point that the presence of free-phase PHCs from anthropogenic releases to the environment is unacceptable and that remedial activities are necessary wherever free-phase PHCs are observed.

The derivation of Canada Wide Standards for petroleum hydrocarbons (PHCs) represents one of the first attempts in Canada to develop environmental quality benchmarks for complex mixtures. The challenges in defining environmentally protective benchmarks for the complex suite of constituents in PHCs are greater than for other mixtures such as polychlorinated biphenyls (PCBs) or polychlorinated dioxins and furans (PCDDs, PCDFs), where there is thought to be a common toxicological mode of action that prevails across different constituents of the mixture. The constituents found in any petroleum hydrocarbon mixture encountered in the upstream industry, in downstream products, or in releases to the environment generally exhibit a very large range of chemical structures and properties relative to other complex mixtures, which are of direct relevance to environmental redistribution, persistence, bioavailability and toxicity.

When defining environmentally protective soil or water quality guidelines for complex mixtures, the issues go well beyond the uncertainties associated with the interactive effects of two or more individual potential contaminants. There are challenges associated with how to reconcile the disparate data types that have arisen given the diversity of analytical and experimental techniques that have been used to operationally define the mixture.

The Ecological Task Advisory Group (EcoTAG), under the direction of the PHC CWS Development Committee, recommended a strategy for deriving soil quality guidelines from complex mixtures (EcoTAG 2000). This is illustrated in Figure 4.2.

PHC toxicity data and studies for ecological receptors were used to the extent possible in order to bring the maximum amount of information to bear on the development of PHC Tier 1 soil values. For convenience, the approach adopted was described as a "weight-of-evidence" approach, which is defined as the critical evaluation and adoption of new numerical protocols, where required, to facilitate the incorporation of otherwise high quality but disparate types of information on the risks of PHCs to ecological receptors. This approach builds on the weight-of-evidence procedure introduced in the CCME (1996) soil quality guideline derivation protocol.

For the purpose of the derivation exercise, the recommended order of preference for toxicity data utilization (Figure 4.2) was –

- new toxicity data for the PHC CWS fractions;
- surrogate data "standardized" to whole fraction values, to the extent that broadly disparate estimates of PHC toxicity are not produced;
- whole product data from controlled laboratory studies and with toxicity subsequently assigned to the PHC CWS fractions; and
- field data from PHC contaminated sites.

This order of preference was established based on both data availability and perceived relevance to risks when PHC concentrations in soil are quantified as the four CWS fractions, and based on generic applicability across Canadian sites.

There were a number of critically important issues which were examined as part of the overall derivation exercise. These included –

- Conversion of effects endpoints from laboratory studies as calculated from nominal, or spiked, soil concentrations to estimates based on expected soil exposure concentrations;
- Biases in estimates of soil quality benchmarks associated with data manipulation to reconcile redundant toxicity endpoints (e.g., multiple data points for a specific taxon - toxicity endpoint combination). See Appendix D for a more detailed discussion; and
- Differences in toxicological thresholds for soil invertebrates and plants based on fresh PHC exposures versus historical releases, as well as strategies for incorporating at Tier 1 an appreciation of the importance of weathering for bioavailability and toxicity.

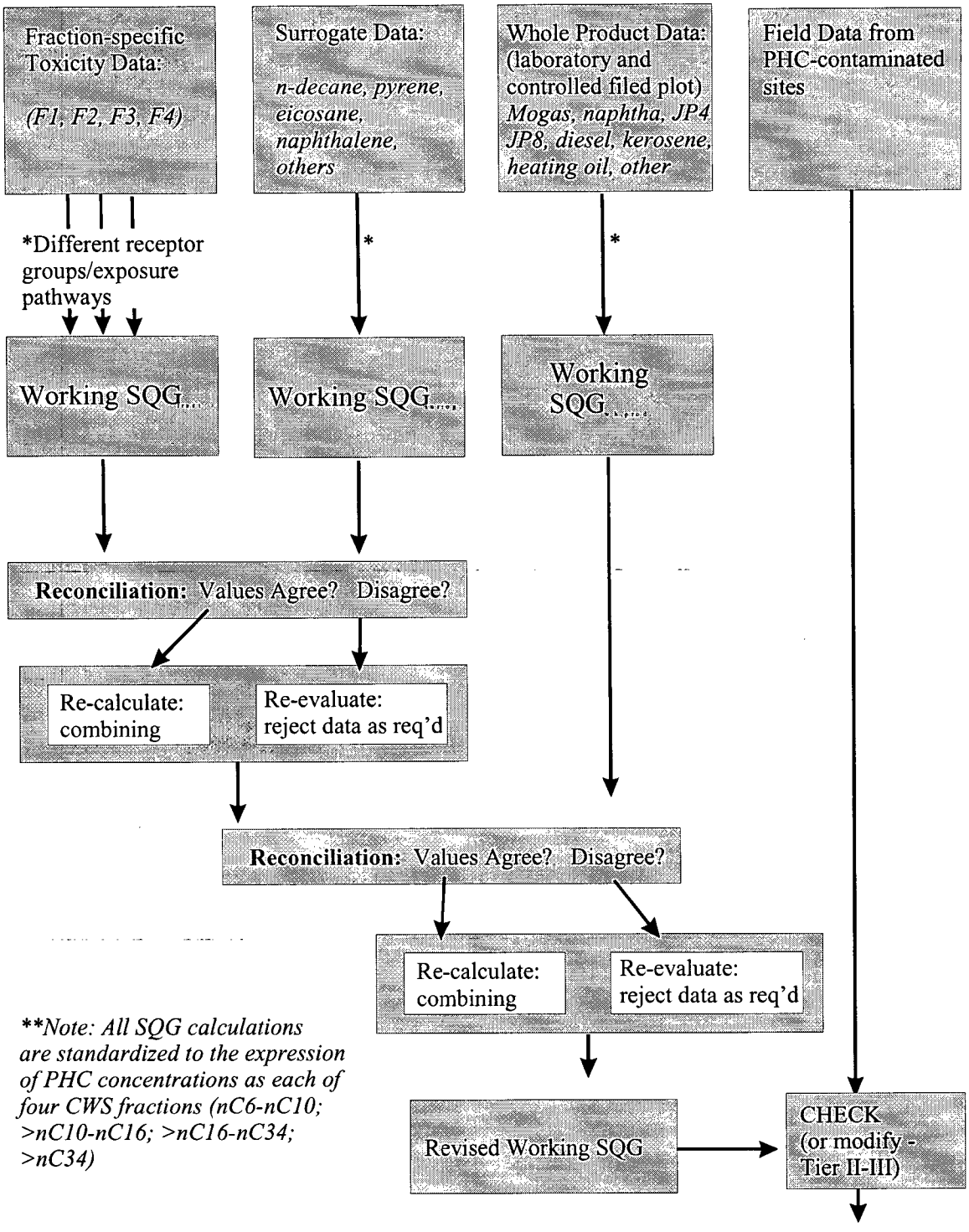


Figure 4.2: Summary of framework used for reconciling disparate data types when developing PHC Soil Quality Tier levels.

4.2 Direct Soil Contact – Protection of Soil Invertebrates and Plants

The approach taken herein was to critically evaluate the resulting soil quality benchmarks for the four PHC fractions based on a number of different data screening scenarios. The intent of description provided herein is to create as much transparency as possible in documenting how the PHC CWS Tier 1 levels were derived based on direct contact to soil invertebrates and plants.

Methods used to derive soil quality benchmarks from the PHC toxicity data, as adapted from CCME (1996), are documented in more detail in Appendix D.

4.2.1 Methods

Prior to the initiation of efforts to develop a PHC CWS, the scientific literature contained little if any information that would allow a confident prediction of the organismic and ecological responses to petroleum hydrocarbons when measured as the designated fractions (CWS F1, F2, F3, F4). A series of toxicity tests, therefore, was conducted in order to address the large data gaps for the effects of PHC mixtures on ecological receptors. The major portion of the data presently available for the derivation of PHC CWS based on effects in plants and/or soil invertebrates due to direct soil contact were produced by Stephenson *et al.* of ESG International through funding provided by the Petroleum Technology Alliance of Canada (PTAC), Alberta Environment and Canadian Association of Petroleum Producers (CAPP). Additional studies were facilitated through financial support from the Canadian Petroleum Producers Industry (CPPI), Environment Canada, Alberta Environment, Quebec Ministry of Environment, and B.C. Ministry of Environment, Lands and Parks.

Details of studies on fraction-specific toxicity for fractions F2 and F3 were provided in Stephenson *et al.* (2000a, b), while studies on motor gas toxicity (prior to the introduction of additives) as an approximation of F1 toxicity were provided in Stephenson (2000). These reports include details of:

- the larger study objectives;
- preparation of the individual fractions as vacuum distillates from fresh "Federated Crude Oil";
- detailed chemical characterization, using various pre-established analytical techniques;
- comparison of different soil spiking techniques and soil test unit configurations, based on minimizing loss of volatile PHC constituents through the test period;
- composition of and relative acute toxicities to soil invertebrates and plants of PHCs in an artificial soil and sandy loam reference soil
- acute versus chronic responses; and

- *appropriate methods for the estimation or realized exposure concentrations from nominal and measured concentrations.*

The entire toxicity database for mogas (without additives), F2, F3 and fresh Federated Whole Crude Oil is tabulated in Appendix E. The studies were based on the use of either whole products or vacuum distillates of fresh as opposed to weathered whole Federated Crude Oil, using coarse textured soils (either a standardized field soil or an artificial sandy loam). The results, therefore, are expected to be most closely applicable to coarse-grained surface soils to which a fresh petroleum hydrocarbon product has been introduced. Additional considerations pertaining to finer grained site soils, or contamination at depth, are discussed in Chapter 5.

4.2.2 Departures for the PHC CWS from the CCME (1996) Protocol

In consideration of the challenges associated with the application of the CCME (1996) protocol to the available petroleum hydrocarbon toxicity data for terrestrial receptors, the following methodological departures were applied:

- Only effects-endpoints (EC_x or LC_x) were used, as derived from interpolation within linear or non-linear regression-type approaches of appropriately constructed dose response curves;
- NOEC and LOEC data were not used if corresponding EC_x data were available;
- Toxicity endpoint response levels were standardized at or near the 50% response level for sublethal studies. Where studies provided endpoints that were not based on a 50% response, the EC_x value for the data point where 'x' was the closest to 50% was used;
- For the same species, individual toxicity data points were considered to be redundant if they (i) represented different response levels for the same type of response and under the same or highly similar exposure conditions; (ii) were for different soil types, but the objective was not to evaluate effects of soil properties; or (iii) were based on different response measures which are known to be directly, causally connected. For data points that were deemed to be redundant, a single composite response concentration was calculated as the geometric mean[1];
- For toxicity data for the same species, response type, response level and exposure conditions, but based on different exposure periods, the data for the longer exposure period were given precedence;

[1] In virtually all cases, combining ecotoxicity data for the same test species, exposure period and toxicity endpoint did not substantially reduce the number of useable toxicity endpoints available to estimate the species sensitivity distribution. Use of the geometric mean in these cases provided a conservative estimate of soil concentrations leading to toxicological responses. In theory, however, the toxicity endpoints from different soil types might have also been considered as distinct endpoints, since it is part of the overall expected variation in species and between-site sensitivity.

- Separate anaylses of the plant and soil invertebrate data sets were carried out initially to establish the relative sensitivity of these two major functional groups;
- Subsequently, the 25th, percentile of the combined effects data set for soil invertebrates and plants was used in order to derive a soil quality benchmark for agricultural and residential/parkland sites. This is very similar to the protocol for application of an Effects Concentration - Low (EC-L) under the existing CCME (1996) protocol (Appendix D)[1];
- The 50th percentile of the plant effects (not mortality) data was used to derive a soil quality benchmark for commercial and industrial land uses.

The above-mentioned procedures were adopted in direct response to some of the data manipulation issues that arose for the PHC fraction-specific toxicity results, and may or may not have value for use in the development of soil quality guidelines for other substances. The rationale for the recommendations is provided through a detailed exploration of the effects of the data manipulation protocols on the resulting soil quality benchmarks for F3, as described below.

Overall, the approach taken for the PHC CWS was based on two explicit assumptions:

(i) Effects endpoints for reduced plant growth, yield, seed germination, or productivity, or for increased mortality or reduced growth or fecundity in soil invertebrates are ecologically relevant.

(ii) Different toxicological response endpoints in the same species provide useful individual measures of intra-taxon variability in sensitivity provided that the endpoints are not directly, causally linked.

Different measurement endpoints represent an inherent part of the within-species sensitivity distribution if they arise from perturbations of different biochemical/ physiological processes. Such variability is deemed to be a relevant part of the overall species sensitivity distribution. Plant root and shoot growth responses to PHCs in soils are likely to be at least partially correlated; however, the orthogonality of the individual toxicity endpoint is not required for a ranks-based approach.

Scientific substantiation for the first of the two assumptions is as follows. The overall approach would lead to a soil quality concentration equivalent to the 25th percentile

[1] EcoTAG originally felt that the separate evaluation of soil invertebrate and plant sensitivity to the PHC CWS fractions was likely to provide a more precise indication of soil PHC levels at which risks to the different groups were likely to be elevated. This decision was based, in part, on expectations regarding the importance of different toxicological mechanisms for the vastly different phyletic groups. Indeed, soil invertebrates were observed to be generally more sensitive to mogas, F2 and F3 than plants. In comparing the relative sensitivity of the two groups, however, EcoTAG concluded that the establishment of soil protective levels based on the combined soil invertebrate and plant data would still provide adequate protection for a large proportion of the soil invertebrate community at any given site.

of the species sensitivity distribution, standardized around a 50% reduction in growth, yield, fecundity or survivorship. This, in turn, assumes that the available, screened toxicity database allows an accurate reconstruction of a species sensitivity distribution for all possible taxa that might occur at a site within Canada. The potential for biases in the re-construction of species sensitivity distributions is likely to be inversely proportional to the number and diversity of information for different taxa, toxicological endpoints, and soil types in the underlying database.

The approach is not amenable to easy translation into - for example - percent of species in the environment protected, or percentage of community diversity at risk; measures with a more intuitive appeal from a policy perspective. The only known and credible method for translating a 25^{th} percentile of an EC_x or LC_x distribution into a true community- or ecosystem-based measure of the level of protection is through the design of specific field studies, using complex ecological communities.

4.2.3 Development of Soil Quality Benchmarks for: Fraction 4 (>nC34)

No specific studies have been undertaken of the toxicity to soil invertebrates or plants of the PHC CWS Fraction 4 [petroleum hydrocarbon constituents with a greater boiling point than an nC34 aliphatic hydrocarbon (>nC34)]. Work is presently underway to characterize the toxicity of a representative F4 mixture, obtained through the distillation of fresh Federated Crude Oil. The results, however, were not available in time to guide the first round derivation of the Tier 1 levels for F4. It is anticipated that the new toxicity data will be useful in re-assessing the Tier 1 levels for F4 as part of the larger PHC CWS implementation process.

The Ecological Technical Advisory Group (EcoTAG) was of the opinion that laboratory toxicity testing is unlikely to adequately capture the range of issues associated with heavy hydrocarbons, such as asphaltenes or residual heavy hydrocarbons that may dominate soils following bioremediation or long-term weathering. The bioavailability of individual hydrocarbon constituents with molecular weights larger than nC34 is likely to be very limited (TPHCWG 1997); therefore, ecological risks are likely to be only poorly linked to internalization of the heavier PHCs and subsequent perturbation of biochemical/physiological functioning.

On the other hand, heavier hydrocarbon constituents, as potentially captured in the F4 fraction have been demonstrated to exert negative impacts on soil properties at release sites, including the production of "hydrophobic" soils. Hydrophobic soils have a severely impaired water-holding capacity, which, in turn would affect the rhizosphere and plant uptake of water and nutrients. There appears to be little relationship between either the types of PHCs introduced into soils or the total PHC concentration and the tendency for formation of hydrophobic soils. As yet to be defined soil properties appear to have a large influence on the tendency for formation of hydrophobic soils.

Given the current limitations in the scientific understanding of the possible range of mechanisms of soil ecosystem impairment, and the risks associated with the >nC34 PHC fraction, alternate approaches for the derivation of an F4 Tier 1 level were considered, including either the derivation of a value based on alternative toxicological information or a policy-based decision. A strictly policy-based Tier 1 value was rejected in favour of using toxicity data for whole Federated Crude Oil. The unfractionated fresh product probably provides a conservative estimate of toxicological thresholds for this fraction. Since the whole product contained appreciable portions of CWS fractions F1, F2 and F3 in addition to the heavier hydrocarbon fraction (including asphaltenes) found in F4, there is a strong likelihood that the actual observed toxicity thresholds would occur at higher soil concentrations had the test organisms been exposed to F4 alone. There is a limited possibility, however, that the lighter PHC fractions could exert antagonistic influence on the F4 toxicity – which cannot be ruled out without additional evidence.

The toxicity of fresh whole Federated Crude Oil is analyzed in detail in Section 4.2.9, and illustrated in Figures 4.17 and 4.18. Based on this analysis, the following endpoints were derived:

- The 25th %ile of the combined plant and soil invertebrate EC_x/LC_x toxicity data for whole Federated Crude Oil was estimated to be 4,800 mg/kg in soil, based on the nominal, or spiked concentration.
- The 50th %ile of the plant toxicity data alone was estimated to be 9,100 mg/kg in soil, based on the nominal, or spiked concentration.

As will be noted in Sections 4.2.4 through 4.2.6, the nominal concentration did not adequately represent the true exposure concentration in the soil invertebrate or plant toxicity tests. Depending on the volatility of the fractions being considered, the actual initial exposure concentration at time 'zero' was estimated to vary from <10% of the nominal concentration for mogas, to between 31 and 65% for the F3 distillate of Federated Whole Crude. The percent loss was also observed to be dependent on the magnitude of the nominal concentration.

To account for possible PHC losses from toxicity trials on whole Federated Crude Oil, the soil quality benchmarks for PHC CWS Fraction 4 were established at 2,800 mg/kg for agricultural, residential and parkland sites (i.e. – 58% of the nominal 25th %ile EC_{50}/LC_{50} soil concentration for the combined soil invertebrate and plant toxicity data). Similarly, the soil quality benchmarks were established as 3,300 mg/kg for commercial and industrial sites (i.e. – 36% of the 50th %ile of the EC_{50} soil concentration for plant toxicity test data).

4.2.4 Development of Soil Quality Benchmarks for Fraction 3 (>nC16 to nC34)

Stephenson *et al.* (2000b) derived toxicity endpoints for exposure to PHC CWS fraction F3 in soil for three species of plants; *Medicago sativa* (alfalfa), *Hordeum*

vulgare (barley), *Agrophyron dasystachyum* (northern wheatgrass) and three species of soil invertebrates; Collembola: *Onychiuris folsomi* (springtail), and *Eisenia fetida* and *Lumbricus terrestris* (earthworms). Table 4.2 provides a summary of the available data on the toxicity of Fraction 3 of Federated crude, with a boiling point range from >nC16 and nC34, inclusive.

For the barley and for acute exposure periods, the toxicity tests were carried out in two soil types: a field-collected sandy loam reference soil, and an artificial soil [details provided in Stephenson et al. (1999)]. In addition, various regression-based statistical techniques were used to calculate an EC_{20} and EC_{50} response level. Finally, tests in field soils included measurement of responses after an acute exposure period, usually 7 days, as well as a longer, chronic or "definitive" exposure period.

A pair-wise comparison was undertaken to assess the effects on calculated toxicological endpoints of soil type, exposure period, and effect size. This was done through the independent use of paired-sample t-tests for each of the three plant species, and for each factor of interest. The results are summarized below:

- **Alfalfa exposure to F3 in soil:**
  - ⇒ Tests were conducted only in field soil.
  - ⇒ EC_{20} and EC_{50} endpoints were not significantly lower after 26 day exposure than 7 day exposure [n = 4, t(1) = 1.48, p = 0.14]; however, the lack of statistical significance was due to the small number of paired data available. The 26 day and 7 day exposure endpoints were significantly correlated (Pearson r = 0.86). ***The ECx soil concentrations were on average 80% lower for the longer exposure period.***
  - ⇒ The EC_{20} soil concentrations were significantly lower than EC_{50} concentrations, with an average difference of 69% [n = 10, t(1) = -2.48, p = 0.017]. Toxicity endpoints for specific endpoint types were highly correlated (Pearson r = 0.86).
- **Barley exposure to F3 in soil:**
  - ⇒ Acute (7 day) tests were conducted in both field and artificial soil. The toxicity in field soil was consistently and significantly lower, by 46% on average, than in the artificial soil [n = 6, t(2) = -9.17, p = 0.0003; Pearson r = 0.90].
  - ⇒ EC_{20} and EC_{50} endpoints were significantly lower after 14 day exposure than 7 day exposure [n=6, t(1) = 2.24, p = 0.038]. *The 14 day exposure endpoints were on average 52% lower than 7 day endpoints.* (Pearson r = 0.22).

⇒ The EC_{20} soil concentrations were significantly lower than EC_{50} concentrations, with an average difference of only 28% [n=15, t(1) = -6.05, $p < 0.0001$]. Toxicity endpoints for specific endpoint types were highly correlated (Pearson r = 0.956).

- **Northern wheatgrass exposure to F3 in soil:**

  ⇒ Acute (7 day) tests were conducted in both field and artificial soil. The toxicity in field soil was consistently and significantly lower, by 52% on average, than in the artificial soil (n = 7, t(2) = -2.67, p = 0.037; Pearson r = 0.53).

  ⇒ EC_{20} and EC_{50} endpoints were significantly lower after 25 day exposure than 7 day exposure [n = 3, t(1) = -3.26, p = 0.0031]. *The 25 day exposure endpoints were on average 89% lower than 7 day endpoints.* (Pearson r = 0.21).

  ⇒ The EC_{20} soil concentrations were significantly lower than EC_{50} concentrations, with an average difference of 59% [n=13, t(1) = -3.26, p=0.003]. Toxicity endpoints for specific endpoint types were highly correlated (Pearson r = 0.941).

Table 4.2: Summary of Fraction 3 (>nC16 to nC34) toxicity data.

Organism	Endpoint	Parameter[1]	Value (mg/kg nominal)	# conc. in test series	# Reps. for ea. conc.	Soil	pH	Comment
Plants								
alfalfa	EC50	shoot length	51900	7(0, 15, 30, 50, 60, 70, 80 mg/g)	4	field soil: Delacour Orthic Black Chernozem		8 day test. n=10
alfalfa	EC20	shoot length	2800	as above	4	as above		as above
alfalfa	EC50	root length	10000	as above	4	as above		as above
alfalfa	EC20	root length	7200	as above	4	as above		as above
alfalfa	EC50	whole ww	72300	as above	4	as above		as above
alfalfa	EC20	whole ww	15800	as above	4	as above		as above
alfalfa	EC50	whole dw	98200	as above	4	as above		as above
alfalfa	EC20	whole dw	50200	as above	4	as above		as above
alfalfa	EC50	shoot length	8300	12 (0, 1, 3, 6, 12, 15, 20, 40, 60, 80, 100, 120 mg/g)	3-6	as above		26 day test n= 10 clear lids kept on till plants 3cm in height
alfalfa	EC20	shoot length	620	as above	3-6	as above		as above
alfalfa	EC50	root length	6300	as above	3-6	as above		as above
alfalfa	EC20	root length	920	as above	3-6	as above		as above
alfalfa	EC50	shoot ww	2100	as above	3-6	as above		as above
alfalfa	EC20	shoot ww	510	as above	3-6	as above		as above
alfalfa	EC50	shoot dw	2300	as above	3-6	as above		as above
alfalfa	EC20	shoot dw	620	as above	3-6	as above		as above
alfalfa	EC50	root ww	4400	as above	3-6	as above		as above
alfalfa	EC20	root ww	860	as above	3-6	as above		as above
alfalfa	EC50	root dw	5500	as above	3-6	as above		as above
alfalfa	EC20	root dw	1100	as above	3-6	as above		as above
barley	EC50	shoot length	53400	6 (0, 4, 10, 30, 50, 80 mg/kg)	4	field soil: Delacour Orthic Black Chernozem		6 day test. n =5

[1] ww = wet weight; dw = dry weight

Organism	Endpoint	Parameter[1]	Value (mg/kg nominal)	# conc. in test series	# Reps. for ea. conc.	Soil	pH	Comment
barley	EC20	shoot length	39400	as above	4	as above		as above
barley	EC50	root length	58200	as above	4	as above		as above
barley	EC20	root length	47600	as above	4	as above		as above
barley	EC50	shoot ww	50300	as above	4	as above		as above
barley	EC20	shoot ww	36700	as above	4	as above		as above
barley	EC50	shoot length	98200	7 (0, 15, 30, 50, 60, 70, 80 mg/g)	4	artificial: 70% silica sand; 20% kaolinite clay;10% sphagnum peat	6-7	7day test. n = 5
barley	EC20	shoot length	74800	as above	4	as above	6-7	as above
barley	EC50	root length	119600	as above	4	as above	6-7	as above
barley	EC20	root length	79000	as above	4	as above	6-7	as above
barley	EC50	shoot ww	85900	as above	4	as above	6-7	as above
barley	EC20	shoot ww	73800	as above	4	as above	6-7	as above
barley	EC50	shoot dw	87200	as above	4	as above	6-7	as above
barley	EC20	shoot dw	73600	as above	4	as above	6-7	as above
barley	EC50	root ww	90800	as above	4	as above	6-7	as above
barley	EC20	root ww	61200	as above	4	as above	6-7	as above
barley	EC50	root dw	95300	as above	4	as above	6-7	as above
barley	EC20	root dw	67400	as above	4	as above	6-7	as above
barley	EC50	shoot length	27600	10 (0, 10, 20, 30, 40, 50, 60, 70, 80, 100 mg/g)	3-6	field soil: Delacour Orthic Black Chernozem		14day test. n = 5 clear lids kept on till plants 3cm in height
barley	EC20	shoot length	3700	as above	3-6	as above		as above
barley	EC50	root length	3200	as above	3-6	as above		as above
barley	EC20	root length	120	as above	3-6	as above		as above
barley	EC50	shoot ww	54100	as above	3-6	as above		as above
barley	EC20	shoot ww	48200	as above	3-6	as above		as above
barley	EC50	shoot dw	53300	as above	3-6	as above		as above
barley	EC20	shoot dw	48700	as above	3-6	as above		as above
barley	EC50	root ww	8700	as above	3-6	as above		as above
barley	EC20	root ww	1700	as above	3-6	as above		as above

Organism	Endpoint	Parameter[1]	Value (mg/kg nominal)	# conc. in test series	# Reps. for ea. conc.	Soil	pH	Comment
barley	EC50	root dw	35100	as above	3-6	as above		as above
barley	EC20	root dw	10000	as above	3-6	as above		as above
northern wheat grass	EC50	shoot length	42100	7 (0, 15, 30, 50, 60, 70, 80 mg/g)	4	as above	0	8 day test. n = 5
northern wheat grass	EC50	root length	51100	as above	4	as above	0	as above
northern wheat grass	EC20	root length	20400	as above	4	as above	0	as above
northern wheat grass	EC50	whole ww	26700	as above	4	as above	0	as above
northern wheat grass	EC20	whole ww	13700	as above	4	as above	0	as above
northern wheat grass	EC50	whole dw	24800	as above	4	as above	0	as above
northern wheat grass	EC20	whole dw	12100	as above	4	as above	0	as above
northern wheat grass	EC50	shoot length	81900	as above	4	artificial: 70% silica sand; 20% kaolinite clay; 10% sphagnum peat	6-7	12 day test. n = 5
northern wheat grass	EC20	shoot length	17100	as above	4	as above	6-7	as above
northern wheat grass	EC50	root length	121000	as above	4	as above	6-7	as above
northern wheat grass	EC20	root length	54900	as above	4	as above	6-7	as above
northern wheat grass	EC50	whole ww	73400	as above	4	as above	6-7	as above
northern wheat grass	EC20	whole ww	34000	as above	4	as above	6-7	as above
northern wheat grass	EC50	whole dw	63900	as above	4	as above	6-7	as above
northern wheat grass	EC20	whole dw	33500	as above	4	as above	6-7	as above
northern wheat grass	EC50	shoot length	12700	11 (0, 5, 10, 15, 20, 30, 40, 50, 60, 70, 80 mg/g)	3-6	field soil: Delacour Orthic Black Chernozem	0	25 day test. n = 5 clear lids kept on till plants 3cm in height
northern wheat grass	EC20	shoot length	330	as above	3-6	as above	0	as above
northern wheat grass	EC50	root length	7300	as above	3-6	as above	0	as above
northern wheat grass	EC20	root length	4300	as above	3-6	as above	0	as above
northern wheat grass	EC50	shoot ww	610	as above	3-6	as above	0	as above
northern wheat grass	EC20	shoot ww	13	as above	3-6	as above	0	as above
northern wheat grass	EC50	shoot dw	1400	as above	3-6	as above	0	as above
northern wheat grass	EC20	shoot dw	50	as above	3-6	as above	0	as above

Organism	Endpoint	Parameter[1]	Value (mg/kg nominal)	# conc. in test series	# Reps. for ea. conc.	Soil	pH	Comment
northern wheat grass	EC50	root ww	890	as above	3-6	as above	0	as above
northern wheat grass	EC20	root ww	180	as above	3-6	as above	0	as above
northern wheat grass	EC50	root dw	1100	as above	3-6	as above	0	as above
northern wheat grass	EC20	root dw	210	as above	3-6	as above	0	as above
Soil Invertebrates								
springtail (*O.folsomi*)	LC50	mortality	6670	6 (0, 2, 4, 8, 12, 15 mg/g)	3-4	artificial 70% silica sand 20% kaolinite clay 10% sphagnum peat	6-7	7 day test n = 10 covered loosely
springtail (*O.folsomi*)	LC50	mortality	5970	as above	3-4	field soil: Delacour Orthic Black Chernozem	0	as above
springtail (*O.folsomi*)	LC50	adult mortality	3695-4280	10 (0, 0.5, 1, 2, 3, 4, 5, 5.5, 6, 7 mg/g)	10	as above	0	35-36 day test n = 10 loosely closed lids removed biweekly for air exchange. value for IC & LC
springtail (*O.folsomi*)	LC20	adult mortality	3120	as above	10	as above	0	as above
springtail (*O.folsomi*)	EC50	# juvenile	1490	as above	10	as above	0	as above
springtail (*O.folsomi*)	EC20	# juvenile	910	as above	10	as above	0	as above
springtail (*O.folsomi*)	EC50	adult fecundity	1410	as above	10	as above	0	as above
springtail (*O.folsomi*)	EC20	adult fecundity	620	as above	10	as above	0	as above
springtail (*O.folsomi*)	NOEC	adult mortality	3000	as above	10	as above	0	as above
springtail (*O.folsomi*)	LOEC	adult mortality	4000	as above	10	as above	0	as above
springtail (*O.folsomi*)	NOEC	# juvenile	1000	as above	10	as above	0	as above
springtail (*O.folsomi*)	LOEC	# juvenile	2000	as above	10	as above	0	as above
springtail (*O.folsomi*)	NOEC	adult fecundity	1000	as above	10	as above	0	as above
springtail (*O.folsomi*)	LOEC	adult fecundity	2000	as above	10	as above	0	as above
worm (*E. foetida*)	LC50	mortality	22360	10 (0, 0.5, 1, 2, 4, 8, 12, 15, 20, 50 mg/g)	3-4	as above	0	14 day test n = 5 perforated lids
worm (*E. foetida*)	IC50	# juveniles	776	11 (0, 0.5, 1, 3, 5, 7, 10, 12.5, 15, 20, 25 mg/g)	10	as above	0	57 day test n = 2 perforated lids. adults removed at day 37 & cocoons allowed to hatch. value for IC & LC
worm (*E. foetida*)	EC20	# juveniles	240	as above	10	as above	0	as above

Organism	Endpoint	Parameter[1]	Value (mg/kg nominal)	# conc. in test series	# Reps. for ea. conc.	Soil	pH	Comment
worm (*E. foetida*)	EC50	juvenile ww	854	as above	10	as above	0	as above
worm (*E. foetida*)	EC20	juvenile ww	272	as above	10	as above	0	as above
worm (*E. foetida*)	EC50	juvenile dw	809	as above	10	as above	0	as above
worm (*E. foetida*)	EC20	juvenile dw	213	as above	10	as above	0	as above
worm (*E. foetida*)	NOEC	# juveniles	0	as above	10	as above	0	as above
worm (*E. foetida*)	LOEC	# juveniles	500	as above	10	as above	0	as above
worm (*E. foetida*)	NOEC	juvenile ww	0	as above	10	as above	0	as above
worm (*E. foetida*)	LOEC	juvenile ww	500	as above	10	as above	0	as above
worm (*E. foetida*)	NOEC	juvenile dw	0	as above	10	as above	0	as above
worm (*E. foetida*)	LOEC	juvenile dw	500	as above	10	as above	0	as above
worm (*L. terrestris*)	LC50	mortality	19150	6 (0, 8, 12, 15, 20, 50 mg/g)	3-4	artificial: 70% silica sand; 20% kaolinite clay; 10% sphagnum peat	6-7	14 day test n = 3 perforated lids
worm (*L. terrestris*)	LC50	mortality	17220	7 (0, 4, 8, 12, 15, 20, 50 mg/g)	3-4	field soil: Delacour Orthic Black Chernozem	0	as above

(from Stephenson et al. 2000b)

Figure 4.3 illustrates the distribution of all plant F3 toxicity data tabulated above, irrespective of differences in exposure period or effect size of the end point. The plant data were ranked (from 1 to 77) and the rank percentile (on the y-axis) plotted against the estimated nominal F3 soil concentrations for the tabulated toxicity endpoints. The graphing of the ranked data in this plot is functionally equivalent to the CCME (1996) protocol for deriving the Threshold Effects Concentration, based on the 25th percentile of the ranked data (around 3,000 mg/kg PHCs as F3 in Figure 4.3). The plant toxicity endpoints, however, do not include any NOEC values, since these were not provided. Rather, the entire F3 plant database is made of interpolated 20% and 50% effects (EC) or inhibitory (IC) soil concentrations.

The advantage of plotting the data as shown in Figure 4.3 is that it allows better scrutiny of the underlying data distribution. Data points plotted as their rank percent in the database tend to follow a straight line when plotted along a y-axis with a probability-type scale. The fact that the data approximate a straight line distribution when the soil concentrations are plotted along a logarithmic scale suggests that the sensitivity of the plant species tested adheres to a log-normal distribution, as might be predicted. A close inspection of Figure 4.3 further suggests that the composite data actually includes two major distinct log-normal sensitivity distributions, since the plot approximates two separate straight lines that meet at a nominal F3 soil concentration of around 50,000 mg/kg. The fact that there are two major distributions within the larger database merits critical evaluation.

Figure 4.4 shows the data distribution, and corresponding 25th percentile value when the EC_{50} endpoints are used, and the EC_{20} data are omitted. The EC_{20} data where excluded in this scenario based on several reasons:

- The reduction in growth endpoints for the plants are not mortality-based endpoints; hence, it is not obvious that a twenty percent reduction in root or shoot length or mass would lead to population level effects in the environment;
- Some provincial jurisdictions (e.g., British Columbia) specify a level of protection for soil invertebrates and plants which is equivalent to an EC_{50} or an LC_{20}, not the EC_{20}; and
- The database provided for plants from the toxicity tests on the F2 fraction did not include EC_{20} data. It was deemed advantageous to screen the toxicity data for F2 and F3 in similar ways, to better allow a direct comparison of the 25th percentile values (TECs or EC-Ls) for fractions F2 and F3.

The EC_{50} endpoints for barley and northern wheatgrass, furthermore, were provided based on studies using both an artificial and standardized field soil (see Table 4.2). In most cases, EC_{50} values were similar for each plant response measured between the two soil types.

The endpoint-specific toxicological response was estimated as the geometric mean of the EC_{50}s for F3 PHC exposure in the artificial and field soil.

As shown in Figure 4.4, a 25th percentile value based on only the EC_{50} data for plants (approx. 7,000 mg/kg nominal) was higher than when the EC_{20} and EC_{50} data were combined, as in Figure 4.3 (approx. 3,000 mg/kg). The data also approximate a bimodal log-normal sensitivity distribution.

Figure 4.5 illustrates the ranked data distribution based on a further reduction of the database to exclude acute and intermediate exposure periods, in favour of "definitive" (Stephenson *et al.,* 2000b) exposure periods (i.e., the longest exposure period used in the experiment). It is clear that, for the F3 fraction, growth or yield inhibition increased substantially with longer, chronic exposure periods (26, 14, and 25 day for alfalfa, barley and northern wheat grass, respectively) relative to more acute exposures (8, 6, and 8 days, respectively). A strong unimodal log-normal sensitivity distribution is apparent in Figure 4.5. This suggests that the reduction in plant growth or yield when exposed to F3 PHCs follows a distinct log-normal sensitivity distribution. An approximate estimate of the 25th percentile of the ranked data in Figure 4.5 is 2,000 mg/kg F3, expressed as a nominal exposure concentration. The use of the term "definitive" may be a bit misleading, since there is no evidence that longer, chronic exposure periods would not have resulted correspondingly larger reductions in growth or yield relative to uncontaminated controls.

As a final check against the biases associated with possible inclusion of redundant toxicity endpoints, all available EC_{50} values for definitive exposure periods and for a single test species were combined (aggregate EC_{50}s were derived from endpoints based on shoot or root length or mass based on wet and dry weight measurements). A single EC_{50} for each plant species was calculated both as the geometric and arithmetic mean of the constituent data. Figure 4.6 shows the consolidated data based on the geometric means. The arithmetic mean EC_{50}s were similar.

The severe reduction through either culling or combination of the toxicity endpoints data as shown in Figure 4.6 shows that, while the three data points produced are too few to adequately define a reasonable 25th percentile effects concentration, the value of 1,700 mg/kg nominal F3 that was derived is close to the 25th percentile provided in Figure 4.5. Overall, an estimate of a nominal F3 exposure concentration of 2,000 mg/kg appears to be a reasonable estimate of a threshold concentration above which there may be elevated risks for plants.

Figure 4.7 and 4.8 provide a parallel analysis for the F3 soil invertebrate data set. The entire invertebrate toxicity endpoint data set is shown in Figure 4.7. The use of the entire data set in a ranks-based procedure would result in a 25th percentile nominal concentration of approximately 400 mg/kg.

The data plotted in Figure 4.8 are based on the exclusion of NOEC, LOEC and $LC(EC)_{20}$ estimates. The mortality data have been circled to distinguish them from sublethal endpoints. The lowest LC_{50} value was observed at an F3 nominal concentration of around 5,000 mg/kg, which is more than five-fold higher than the 25th percentile nominal concentration of around 800 mg/kg, based on the combined mortality-type and non-lethal endpoints.

Figure 4.9 compares the underlying data distributions and 25th percentile estimates of toxicity endpoints for plants and soil invertebrates, based on the most appropriate data manipulations as discussed above. The ranked data distribution for the combined data sets is also shown.

The preceding analysis is based entirely on the evaluation of toxicological responses of soil invertebrates or plants based on the "nominal", or spiked soil concentration of F3. The loss of compound during toxicity testing is expected to be less severe for F3 than for fractions F1 and F2; however, the actual changes in exposure concentration of F3 PHCs from the nominal to the initial or final soil concentration were examined as by Stephenson et al. (2000b) as a means of adjusting the broader suite of nominal data. Table 4.3 provides an excerpt of the data on F3 losses during toxicity testing.

Table 4.3: Change in the soil concentration during sampling unit preparation and over the exposure period.

Nominal F3 Concentration (spiked)	Initial Measured Concentration (t=0)[A]	Init.: Percent of Nominal	Final (14 day) Measured Concentration[B]	Final: Percent of Nominal
6,000 mg/kg	1,910 mg/kg	31%	550 mg/kg	9%
20,000 "	6,170 "	31%	3,440 "	17%
60,000 "	32,030 "	53%	22,160 "	37%
100,000 "	56,330 "	56%	52,580 "	53%
120,000 "	79,660 "	66 %	78,380 "	65%

Notes:
A. Based on GC analysis of TPH for a subset of test soils.
B. TPH analysis of alfalfa definitive (14 day) test units.

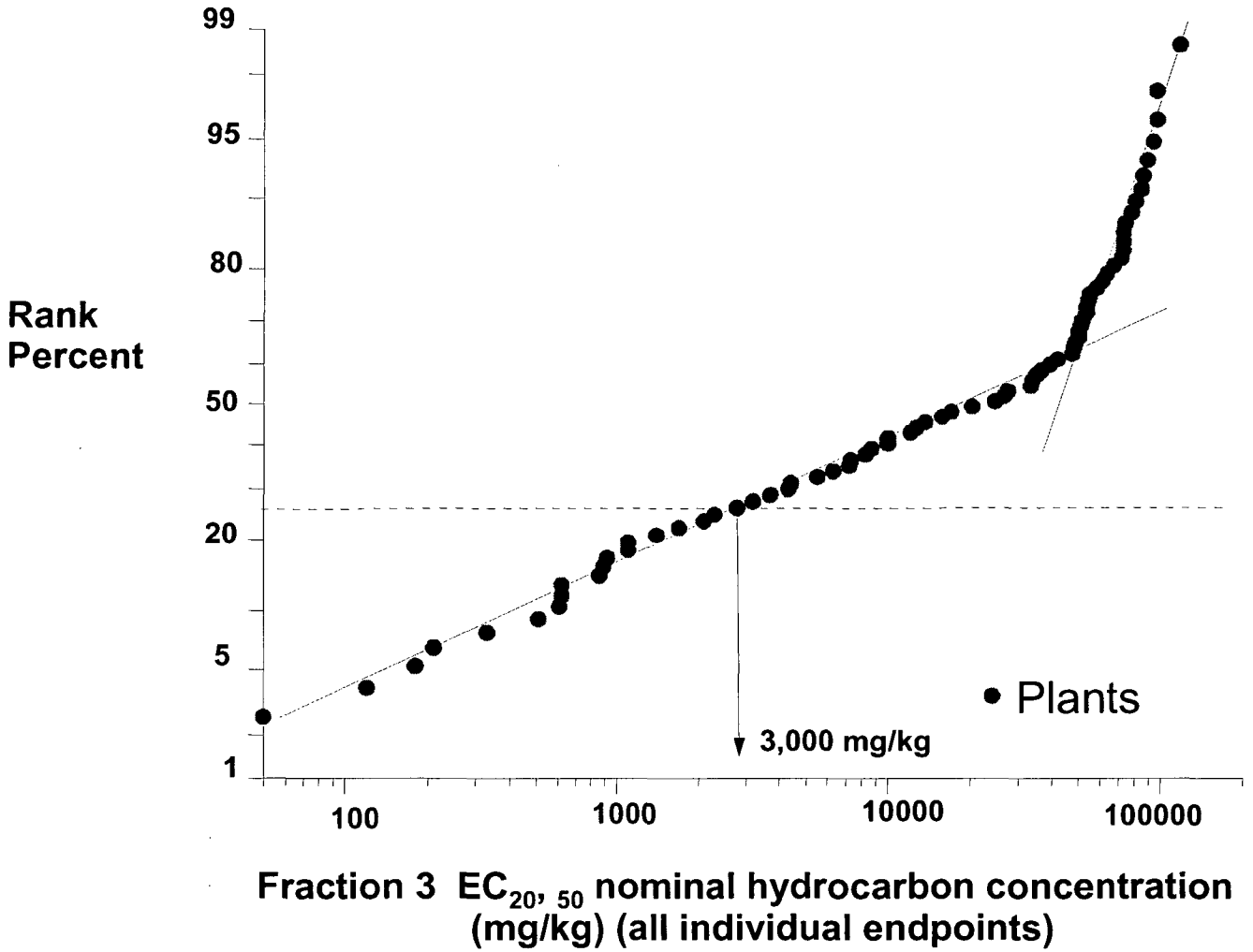


Figure 4.3: Distribution of plant toxicological endpoints for studies on F3 PHCs based on all data provided in Table 4.2.

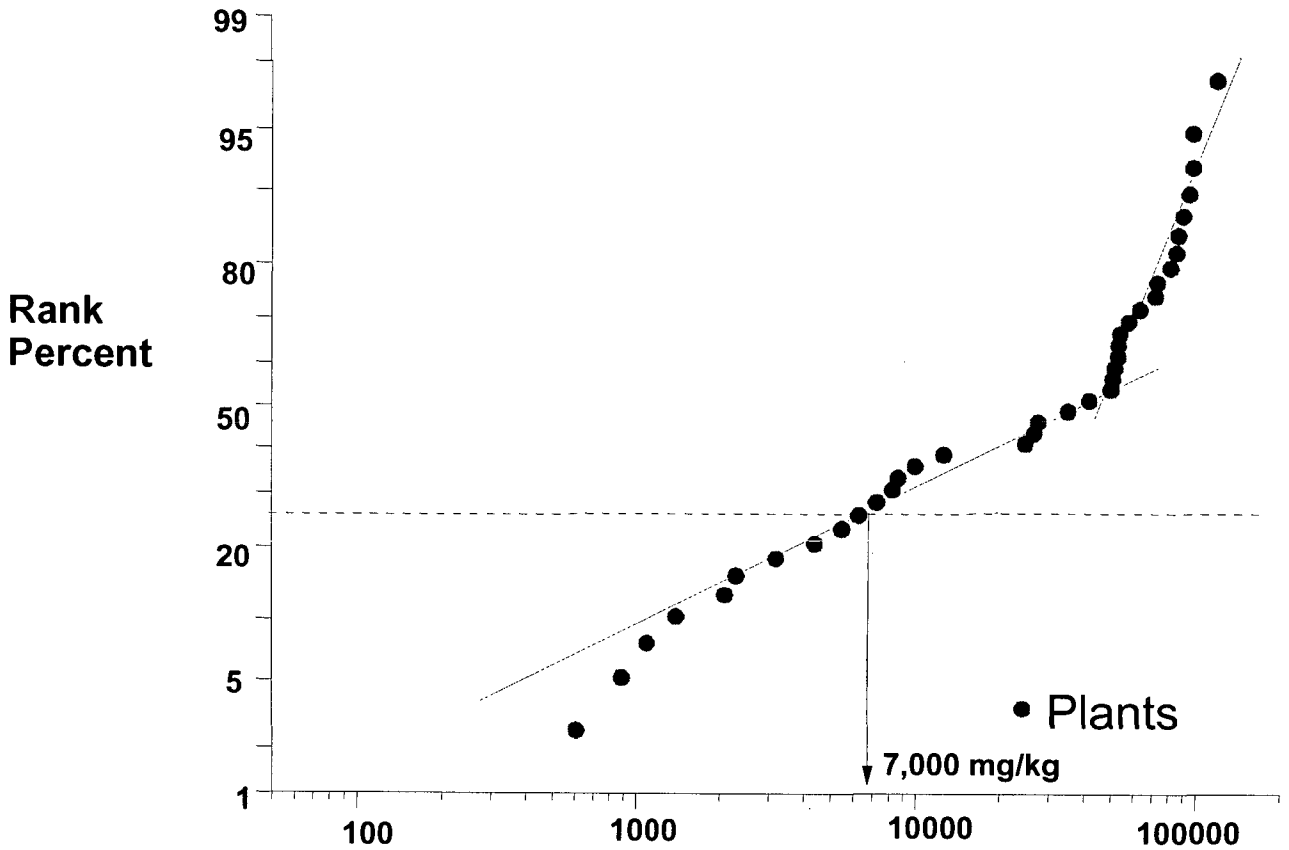


Figure 4.4: Distribution of plant toxicological endpoints for studies on F3 PHCs based on EC_{50} data.

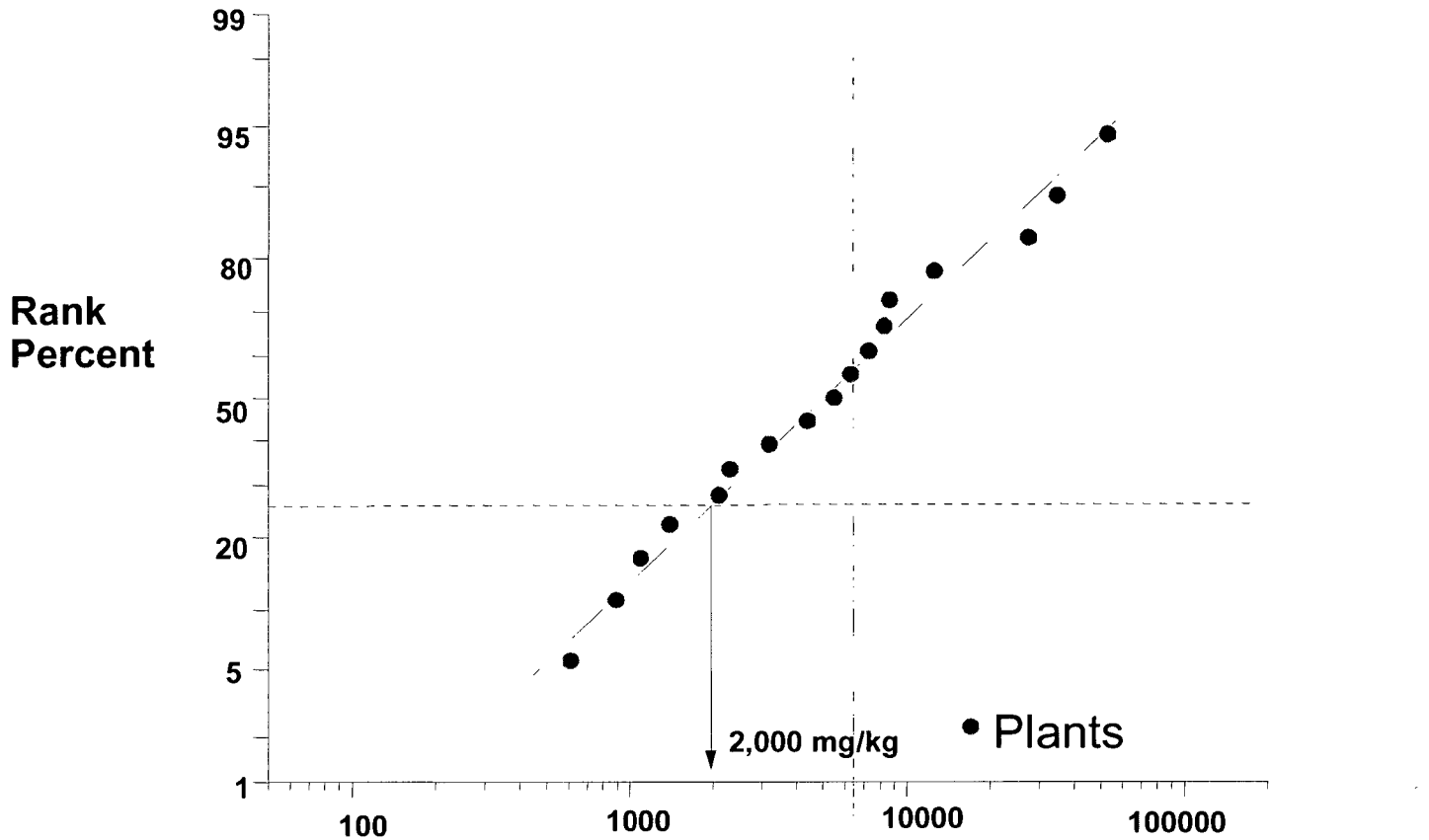


Figure 4.5: Distribution of plant toxicological endpoints for studies on F3 PHCs based on EC_{50} data and chronic ("definitive") exposure periods only.

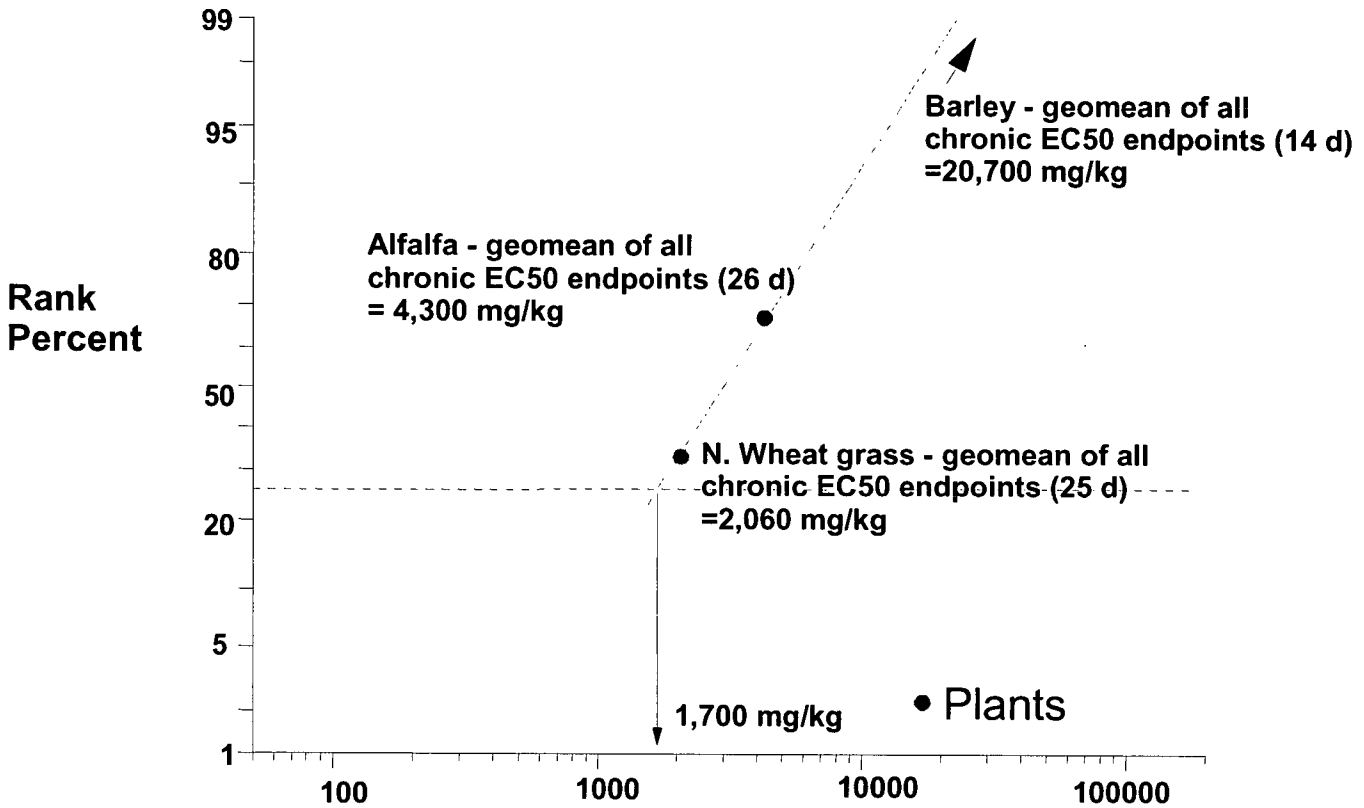


Figure 4.6: Distribution of plant toxicological endpoints for studies on F3 PHCs - consolidated EC_{50} estimates for three plant species for chronic ("definitive") exposure periods only.

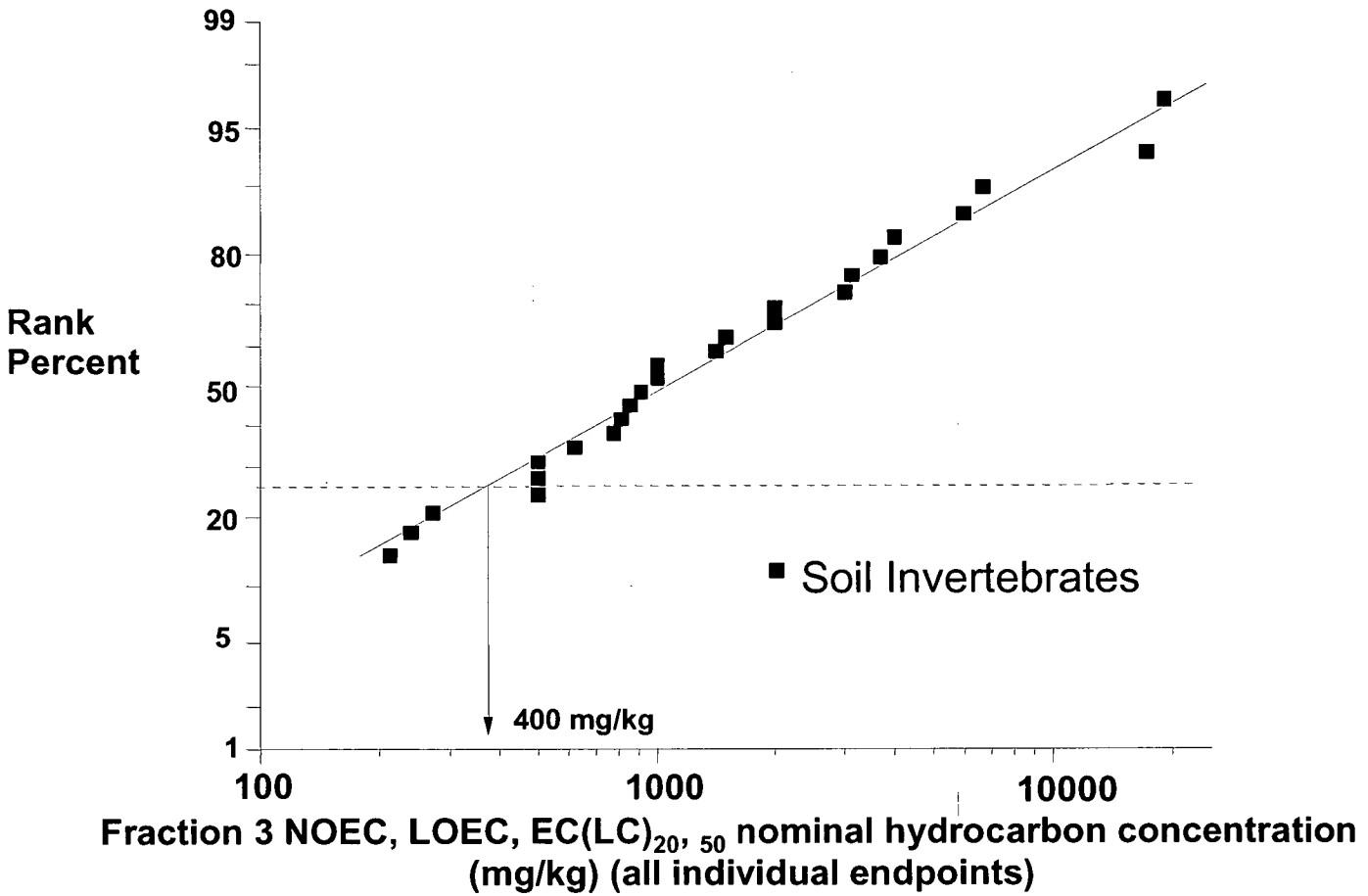


Figure 4.7: Distribution of soil invertebrate toxicological endpoints for studies on F3 PHCs based on LOEC, NOEC, $EC(LC)_{20}$ and $EC(LC)_{50}$ data across two different soil types and acute and chronic ("definitive") exposure periods.

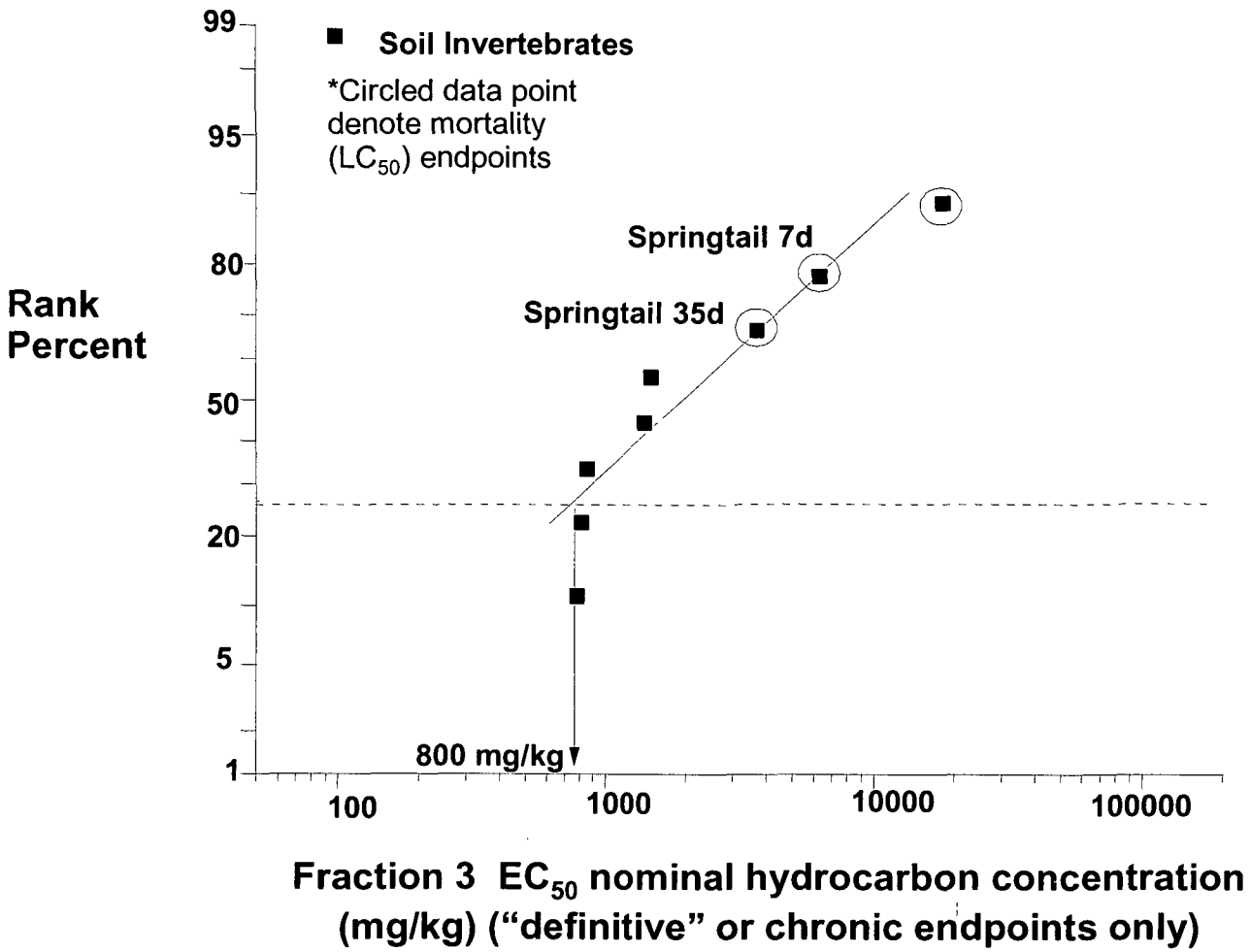


Figure 4.8: Distribution of soil invertebrate toxicological endpoints for studies on F3 PHCs based on $EC(LC)_{50}$ and primarily chronic ("definitive") exposure periods.

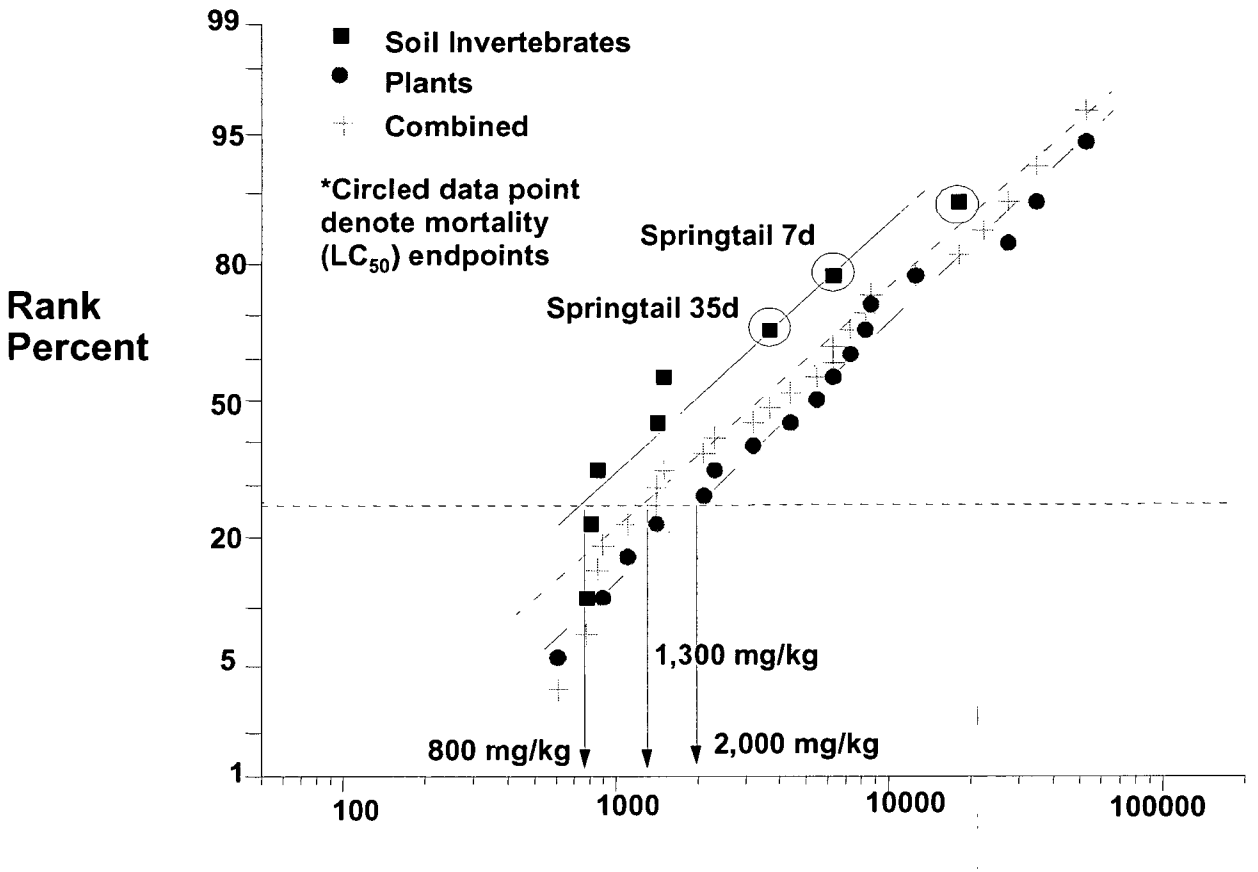


Figure 4.9: Comparison of data distributions for soil invertebrate and plant toxicological endpoints for studies on F3 PHCs.

Based on the above-documented analysis, the 25th percentile of the $EC(LC)_{50}$ nominal concentrations of F3, distilled from Federated Crude Oil, was estimated as shown in Table 4.4. The 50th percentile of the $EC(LC)_{50}$ data distribution, as illustrated in Figure 4.9 is also shown. This shows the effect of the defined ranks level on the resulting soil concentration.

Table 4.4: Threshold effects concentrations for PHC CWS fraction F3.

	Soil Invertebrates Only	Plants Only	Soil Invertebrates and Plants Combined
Est. 25th percentile of effects data based on "nominal" exposure levels: F3	**800 mg/kg**	**2,000 mg/kg**	**1,300 mg/kg**
Estimated "initial" exposure concentration as percent of "nominal" F3 concentration (see Table 4.3, above)	31%	31%	31%
Est. 25th percentile of effects data based on "initial" realized exposure levels: F3	**250 mg/kg**	**620 mg/kg**	**400 mg/kg**
Est. 50th percentile of effects data based on "nominal" exposure levels: F3	2,000 mg/kg	5,500 mg/kg	4,000 mg/kg
Est. 50th percentile of effects data based on "initial" realized exposure levels: F3	**620 mg/kg**	**1,700 mg/kg**	**1,200 mg/kg**

The resulting Threshold Effects Concentrations for the F3 fraction, based on the 25th percentile of the effects database (EC_{50}s and LC_{50}s) are lower than might have been initially anticipated. Referring back to Table 4.2, it can be seen that the following were among the lowest EC_{50}s for F3:

- northern wheatgrass shoot wet wt., 25 day EC_{50} 610 mg/kg nominal **= 190 mg/kg initial**
- worm (*E. foetida*) number of juveniles, 57 day EC_{50} 776 mg/kg nominal **= 240 mg/kg initial**
- worm (*E. foetida*) juvenile dry wt., 57 day EC_{50} 810 mg/kg nominal **= 250 mg/kg initial**
- northern wheatgrass root wet wt., 25 day EC_{50} 890 mg/kg nominal **= 280 mg/kg initial**

- springtail (*O. folsomi*) adult fecundity, 35-36 day EC_{50} 1410 mg/kg nominal
  = 440 mg/kg initial

- alfalfa shoot wet wt, 26 day EC_{50} 2100 mg/kg nominal
  = 650 mg/kg initial

4.2.5 Development of Soil Quality Benchmarks for Fraction 2 (> nC10 to C16)

Using an approach similar to that applied for the Fraction 3, the available draft data from Stephenson *et al.* (2000a) were plotted. Figure 4.10 shows the relative data distribution and corresponding 25th percentile nominal F2 concentrations for plants and soil invertebrates. The data for artificial and standardized field soil were first combined using a geometric mean. In addition, the acute exposure endpoints for plants were omitted.

For the barley and for acute exposure periods, the toxicity tests were carried out in two soil types: a field-collected sandy loam reference soil, and an artificial soil (details provided in Stephenson *et al.* (1999). In addition, various regression-based statistical techniques were used to calculate an EC_{50} response level only. Unlike F3 toxicity tests, no acute endpoints were provided for alfalfa or northern wheatgrass. In addition, the definitive tests conducted in these two plant species were carried out only in one soil type – a field collected "Delacour Orthic Black Chernozem" sandy loam.

A pair-wise comparison was undertaken to assess the effects on calculated toxicological endpoints of soil type, and exposure period for barley. This was carried out through the independent use of paired-sample t-tests for each of the three plant species, and for each factor of interest. The results are summarized below:

- **Barley exposure to F2 in soil:**

  ⇒ Acute (8 day) tests were conducted in both field and artificial soil. The toxicity in the two soil types was similar: There was a difference of only 0.3% in average EC_{50} values between the two soil types. [n = 6, t(2) = 0.068, p = 0.945; Pearson r = 0.95].

  ⇒ EC_{50} endpoints were significantly lower after 13 day exposure than 8 day exposure [n = 6, t(1) = 2.42, p = 0.030]. *The 13 day exposure endpoints were on average 46 % lower than 8 day endpoints.* (Pearson r = -0.30).

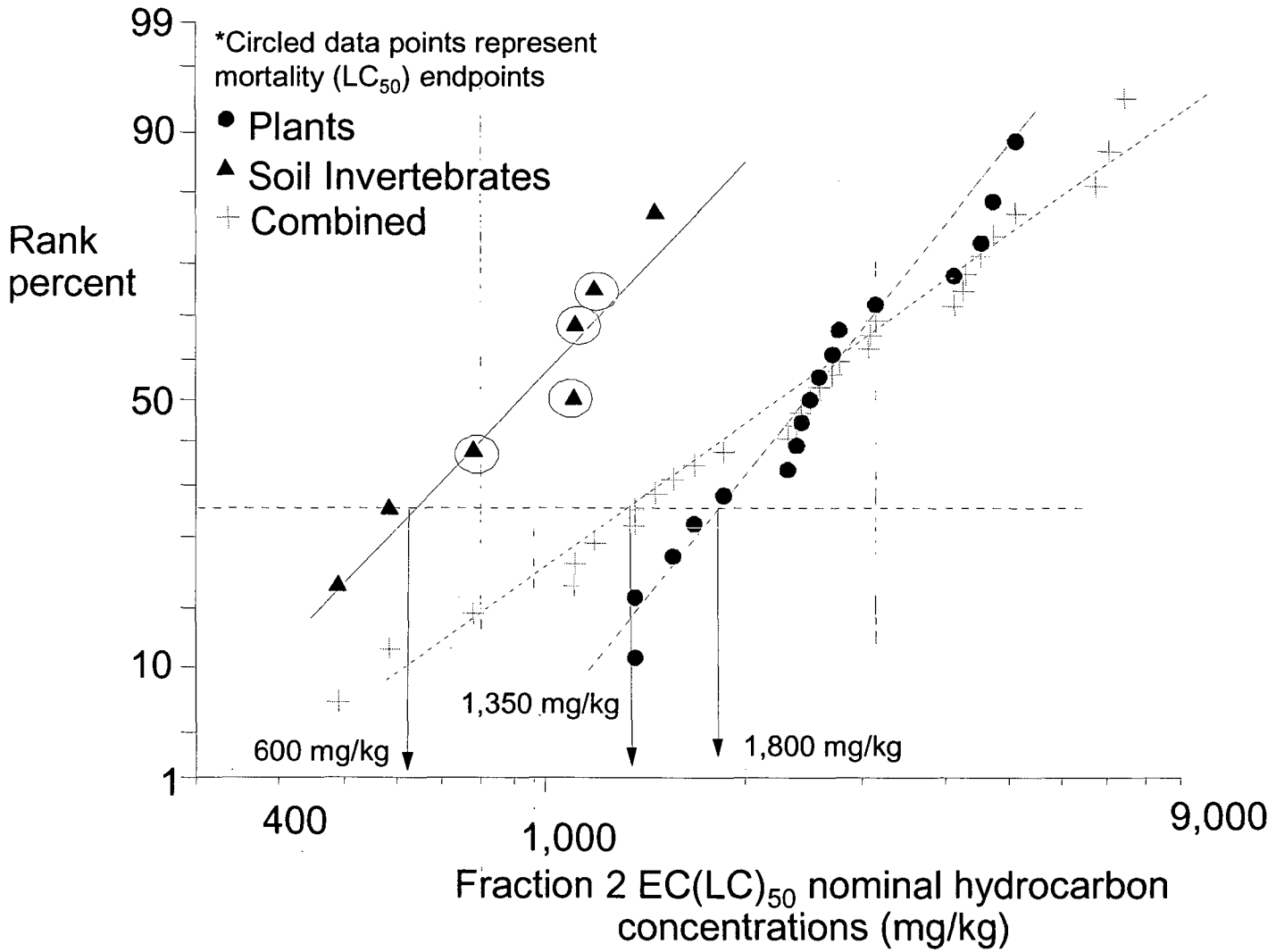


Figure 4.10: Comparison of data distributions for soil invertebrate and plant toxicological endpoints for studies on F2 PHCs.

The preceding analysis is based entirely on the evaluation of toxicological responses of soil invertebrates or plants based on the "nominal", or spiked soil concentration of F2. The actual changes in exposure concentration of F2 PHCs from the nominal to the initial or final soil concentration were examined as by Stephenson et al. (2000a) as a means of adjusting the broader suite of nominal data. Table 4.5 provides an excerpt of the F2 losses during toxicity testing:

Table 4.5: Change in the soil concentration during sampling unit preparation and over the exposure period.

Nominal F2 Concentration (spiked)	Initial Measured Concentration (t=0)[A]	Init.: Percent of Nominal	Final (14 day) Measured Concentration[B]	Final: Percent of Nominal
500 mg/kg	150 mg/kg	29%	not avail.	
1,000 "	340 "	33%	not avail.	
6,000 "	2,160 "	36%	not avail.	
8,000 "	3,380 "	42%	not avail.	
30,000 "	14,280 "	47%	not avail.	

Notes:
A. Based on GC analysis of TPH for a subset of test soils.
B. TPH analysis of northern wheatgrass definitive (14 day) test units.

Based on the above-documented analysis, the 25th percentile of the $EC(LC)_{50}$ nominal concentrations of F2, distilled from Federated Crude Oil, was estimated as shown in Table 4.6.

Table 4.6: Draft threshold effects concentrations for PHC CWS fraction F2.

	Soil Invertebrates Only	Plants Only	Soil Invertebrates and Plants Combined
Est. 25th percentile of effects data based on "nominal" exposure levels: F2	600 mg/kg	1,800 mg/kg	1,350 mg/kg
Estimated "initial" exposure concentration as percent of "nominal" F2 concentration (see Table 4.5, above)	33%	33%	33%
Est. 25th percentile of effects data based on "initial" realized exposure levels: F2	**200 mg/kg**	**600 mg/kg**	**450 mg/kg**
Est. 50th percentile of effects data based on "nominal" exposure levels: F2	900 mg/kg	2,300 mg/kg	2,100 mg/kg
Est. 50th percentile of effects data based on "initial" realized exposure levels: F2	**300 mg/kg**	**760 mg/kg**	**690 mg/kg**

The following were among the lowest $LC(EC)_{50}$s for F2:

- worm (*E. foetida*) number of juveniles, 62-63 day EC_{50} — 490 mg/kg nominal **= 160 mg/kg initial**
- worm (*E. foetida*) mortality 14 day LC_{50} — 530 mg/kg nominal **= 170 mg/kg initial**
- worm (*L. terrestris*) mortality 7 day LC_{50} — 1,100 mg/kg nominal **= 330 mg/kg initial**
- worm (*L. terrestris*) mortality 14 day LC_{50} — 1,100 mg/kg nominal. **= 330 mg/kg initial**
- alfalfa shoot dry wt. 21 day EC_{50} — 1,370 mg/kg nominal **= 450 mg/kg initial**
- northern wheatgrass 14 day EC_{50} — 1,370 mg/kg nominal **= 450 mg/kg initial**

- springtail (*O. folsomi*) number of juveniles 35 day EC_{50} 1,470 mg/kg nominal **= 490 mg/kg initial**

4.2.6 Development of Soil Quality Benchmarks for Fraction 1 (C6-nC10)

Limitations in time and funding prevented the generation of new data for the toxicity of F1, distilled from Federated crude, to soil invertebrates and plants. Toxicity data were provided by Stephenson (2000), however, for motor gas, or Mogas.

Mogas is a very common, light-end distillate which is predominantly F1 hydrocarbons when fresh. Following release to the environment, however, the relatively high volatility of mogas constituents tends to result in rapid loss from soils, often within hours to days, depending on which constituent is considered.

The characteristics of the mogas used in the soil invertebrate and plant toxicity tests is provided in Stephenson (2000). The aliphatics in the mixture were predominantly in the >C6 to C8 range. The aromatics were predominantly in the >C8 to C10 range. The mixture was approximately 70% aliphatics and 30% aromatics, including BTEX. In addition, the mogas, provided by the Environmental Technology Group of the Imperial Oil Research Department, was an additive-free refinery blend. Toxic responses, therefore, were not due to additives.

Using an approach similar to that applied for the Fraction 3, the available draft data from Stephenson (2000) were plotted. Figure 4.11 illustrates the plant and soil invertebrate $EC(LC)_{50}$ data distributions.

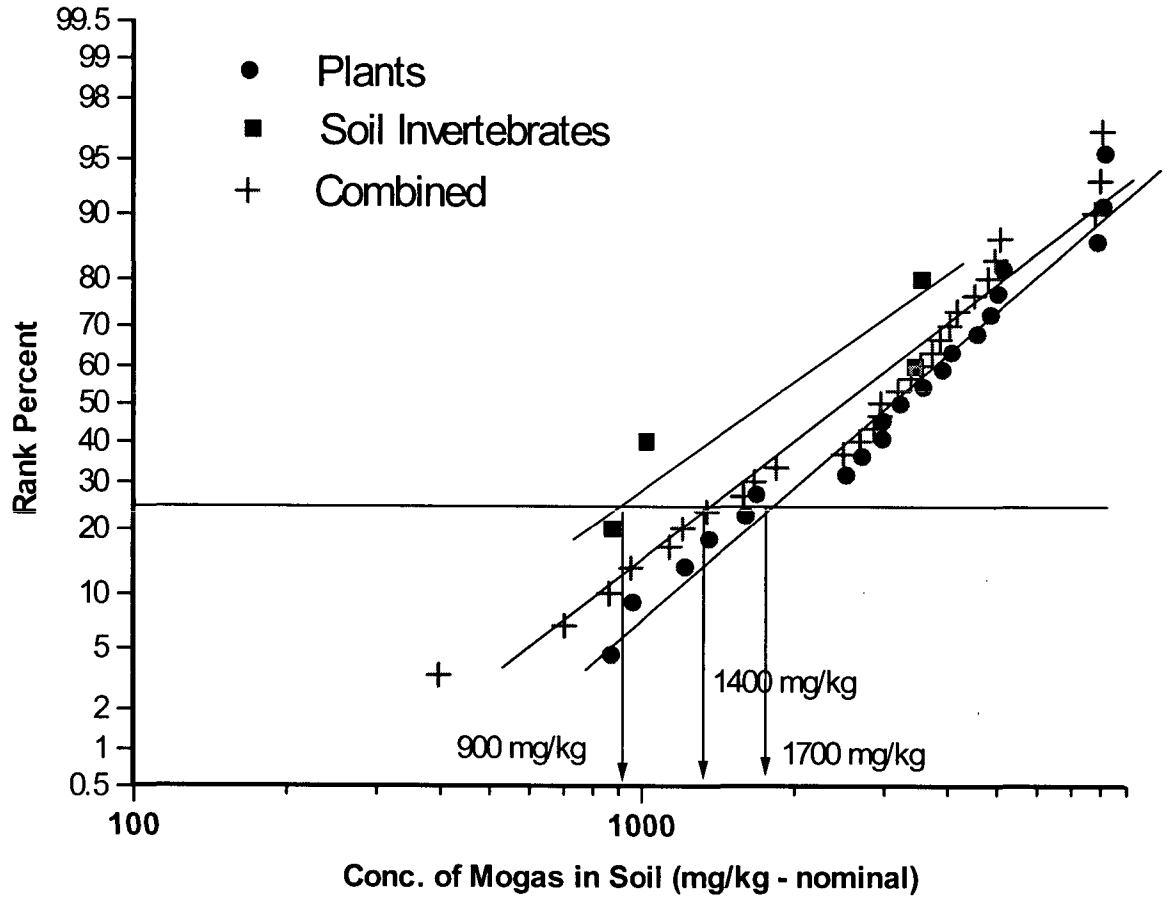


Figure 4.11: Comparison of data distributions for soil invertebrate and plant toxicological endpoints for studies on mogas.

Table 4.7 provides a brief summary of the comparative toxicity of additive-free mogas to alfalfa in two soil types, based on different exposure periods, and at a 20% versus 50% response level.

Table 4.7: Comparison of alfalfa response thresholds [mg/kg (nominal) mogas as TPH] by soil type, exposure duration, and effect size.

Soil Type	Sandy Loam Ref				Artificial Soil			
Exposure time	11 day		21 d		11 d		21 d	
Response Level	EC20	EC50	EC20	EC50	EC20	EC50	EC20	EC50
Endpoint								
shoot length	**2410**	**6600**	**2570**	**5130**	**3210**	**5450**	ND	ND
root length	**3080**	**4580**	**1890**	**2710**	**3310**	**5010**	ND	ND
whole plant ww	**5900**	**8220**	ND	ND	**3390**	**5320**	ND	ND
whole plant dw	**5100**	**6750**	ND	ND	**3400**	**4910**	ND	ND
shoot ww	ND	ND	**1850**	**2520**	ND	ND	ND	ND
shoot dw	ND	ND	**2240**	**3900**	ND	ND	ND	ND
root ww	ND	ND	**2310**	**2980**	ND	ND	ND	ND
root dw	ND	ND	**2120**	**2970**	ND	ND	ND	ND

There were differences in the variability between different response endpoints between the two soils. Overall, however, there was no significant difference in the soil concentration at which comparable response levels (EC_{20} or EC_{50}) were elicited between the artificial soil and sandy loam field soil (two-tailed paired-sample t-test; n = 8. t = 2.17, p = 0.066).

As expected, there was a highly significant difference between EC_{20} and EC_{50} values (one-tailed paired-sample t-test; n = 14. t = -6.94, $p < 0.0001$): EC_{20} soil concentrations were on average 36% lower than EC_{50} values. Finally, 11 day EC_x soil concentrations were significantly higher than 21 day EC_x soil concentrations (one-tailed paired-sample t-test; n = 4, t = 2.48, p = 0.04): the resulting effects endpoint was on average 26% lower for 21 days than 11 days exposure.

Based on the above-documented analysis, the 25th percentile of the $EC(LC)_{50}$ nominal concentrations of additive-free mogas, as an estimate of F1, was as follows (Table 4.8):

Table 4.8: Draft threshold effects concentrations for PHC CWS fraction F1, based on the toxicity of mogas:

	Soil Invertebrates Only	Plants Only	Soil Invertebrates and Plants Combined
Est. 25th percentile of effects data based on "nominal" exposure levels: F1 (mogas)	**900 mg/kg**	**1,700 mg/kg**	**1,400 mg/kg**
Estimated "initial" exposure concentration as percent of "nominal" F1 (mogas) concentration	Note A	Note A	Note A
Est. 25th percentile of effects data based on estimate of "initial" realized exposure levels: F1 (mogas)	**75 mg/kg**	**165 mg/kg**	**130 mg/kg**
Est. 50th percentile of effects data based on "nominal" exposure levels: F1 (mogas)	**1,700 mg/kg**	**3,000 mg/kg**	**2,300 mg/kg**
Est. 50th percentile of effects data based on estimate of "initial" realized exposure levels: F1 (mogas)	**170 mg/kg**	**330 mg/kg**	**240 mg/kg**

Notes:

A: Stephenson evaluated the relationship between the nominal concentration of mogas, and the initial measured concentration. For the preparation method used in Stephenson's laboratory, there was a strong correlation ($r^2 = 0.98$) over 5 orders of magnitude concentration range between the nominal concentration and initial (t = 0) concentration. The simple least-squares regression was as follows:

log (initial) = 1.232 log (nominal) -1.762 (all values in mg mogas/ kg soil dw)

This formula was used to convert at 25th percentile $EC(LC)_{50}$ concentration based on nominal concentration to one based on the expected initial realized exposure concentration in soil test units.

The following were among the lowest $LC(EC)_{50}$s for additive-free mogas:

- worm (*E. foetida*) mortality; 14 day LC_{50} (sandy loam field soil) — 710 mg/kg nominal **= 56 mg/kg initial**
- barley root wet mass; 13 day EC_{50} (sandy loam field soil) — 870 mg/kg nominal **= 72 mg/kg initial**
- alfalfa shoot dry mass, 21 day EC_{50} (artificial soil) — 2,520 mg/kg nominal **= 270 mg/kg initial**
- springtail (*O. folsomi*) number of juveniles 35 day EC_{50} nominal (artificial soil) — 2,890 mg/kg **= 320 mg/kg initial**
- springtail (*O. folsomi*) number of juveniles 35 day EC_{50} nominal (sandy loam field soil) — 4,210 mg/kg **= 500 mg/kg initial**

4.2.7 Surrogate PHC Data

4.2.7.1 - F4 Surrogate Ecotoxicity. No surrogates have been identified to the present time for the F4 fraction.

4.2.7.2 - F3 Surrogate Ecotoxicity. Of the large number of possible PHC compounds found within the >C16 to C34 equivalent boiling point range, pyrene and eicosane were selected as a minimum data set representing an aromatic and aliphatic, respectively. Sufficient data were not available for the round 1 derivation of the PHC CWS, however.

Benzo(a)pyrene (B(a)P) is a C20, five ring unsubstituted aromatic hydrocarbon that has been studied much more extensively than any other individual constituent falling in the F3 fraction. While much of the interest in benzo(a)pyrene is related to its known carcinogenicity to vertebrates, it also has the potential to produce non-specific narcosis-type effects in soil invertebrates in a manner that is similar to other non-carcinogenic aromatics and aliphatics which might be found in the F3 fraction.

Environment Canada (1996a) provides the following summary of plant and soil invertebrate toxicity studies for benzo(a)pyrene (Table 4.9).

Table 4.9: Collated data on soil invertebrate and plant responses to Benzo(a)Pyrene in soil.

Organism	Effect Endpoint	B(a)P conc. (mg/kg soil)
Worm (*E. foetida*)	Mortality 14 day – NOEC	26,000[A]
Lettuce (*Lactuca sativa*)	Seedling emergence 5 day – NOEC	4,400
	LOEC (40% red'n)	8,800
Radish (*Raphanus sativa*)	Seedling emergence 3 day – NOEC	17,500

(from Environment Canada 1996a)

Notes:
A) Initial conc.

The comparison of toxicity endpoints derived using different methodologies, and in different soil types, is undermined by the possible influence of inconsistent exposure regimes. Such comparisons, therefore, should be evaluated with some degree of skepticism, pending a more detailed analysis of the methodological details.

The toxicological response concentrations for benzo(a)pyrene in Table 4.9 are much higher in general than for the F3 fraction for soil invertebrates or plants (estimated 25th percentile for F3 was 250 to 620 mg/kg initial concentration). The F3 data, however, clearly demonstrate that exposure period is of critical importance for the effects endpoint. The F3 fraction was progressively more toxic with an increase in exposure time for both soil invertebrate and plant toxicity tests.

As will be discussed further in Section 4.2.9, the range of equivalent toxicity values across different test organisms was greater for the F3 fraction than for F2, mogas, or even the whole Federated crude oil. This might be attributable to the fact that F3 (>C16 to C34) contains compounds with a broad range of water solubility and lipophilicity. Benzo(a)pyrene is a C20 hydrocarbon; however, its strong lipophilicity (K_{ow} = 6.06; Env. Can., 1996a) and low water solubility (2.3 x 10^{-3} mg/L) probably make it among the least water soluble, most tightly soil sorbed, and least bioavailable of PHC constituents within the F3 fraction.

4.2.7.3 – F2 Surrogate Ecotoxicity. Of the large number of possible PHC compounds found within the >nC10 to C16 equivalent boiling point range, naphthalene and n-decane were selected as a minimum data set representing an aromatic and aliphatic, respectively. Toxicity studies on naphthalene were carried out in support of the PHC CWS initiative using barley, by Ministère de l'Environnment et de la Faune - Quebec, (MEF-QC), Ontario Ministry of the Environment (OMOE), Environment Canada and ESG International Inc.

The most recent data on effects of naphthalene on barley augment earlier documented data (Environment Canada, 1996b), as follows:

Table 4.10 Collated and new data on soil invertebrate and plant responses to naphthalene in soil.

Organism	Effect Endpoint	Naphthalene conc. (mg/kg)	Notes
Worm (*E. foetida*)	Mortality 14 day – NOEC	204	A
	LOEC (56%)	408	
	EC_{25}	287	
	EC_{50}	**362**	
	Mortality 7 day – NOEC	63 (33)	B
	LOEC (47%)	125 (70)	
	EC_{25}	97 (54)	
	EC_{50}	137 (**77**)	
	Mortality 7 day – **LC_{50}**	(**56.3**)	
	Mortality 14 day – LC_{50}	108	A
Lettuce (*Lactuca sativa*)	Seedling emergence 5 day – NOEC		A
	LOEC (62%)	350	
	EC_{25}	700	
	EC_{50}	470	
		630	
	NOEC	8 (2)	B
	LOEC (62%)	16 (5)	
	EC_{25}	10 (3)	
	EC_{50}	144 (**64**)	
Radish (*Raphanus sativa*)	Seed germination 3 day – NOEC		A
	LOEC (62%)	63 (58)	
	EC_{25}	125 (121)	
	EC_{50}	66 (61)	
		90 (**86**)	

(from Environment Canada 1996b)

Notes:
(A) Nominal;
(B) Nominal conc. with conc. measured at end of exposure period in brackets.

Limited studies are also underway to examine the toxicological effects of n-decane, by MEF-QC and OMOE. The results are forthcoming. The n-decane studies will allow a direct comparison of the relative toxicity of an aromatic compound (naphthalene) and aliphatic (n-decane) with a similar effective carbon size to a representative plant (barley).

Figure 4.12 shows the most recent data for the toxicity of naphthalene to barley. All researchers calculated an EC_{20} and EC_{50} effect level, which are plotted separately in Figure 4.12. This underscores the importance of decisions around data screening prior to applying a ranks-based procedure for defining toxicological thresholds.

The spread in the data (i.e., EC_{50} values that vary from around 500 to 3,000 mg/kg nominal naphthalene concentration) for a single test species is attributable to the different measurement endpoints incorporated (root and shoot length, wet weight, dry weight). The lower concentration effects endpoints tended to be for the inhibition of root growth or mass, whereas the higher endpoints tended to be for shoot growth or mass.

As shown in Table 4.6, the estimated 25th percentile of the EC_{50} data (adjusted for actual initial exposure concentration) for the F2 fraction was **200 mg/kg** for invertebrates and **600 mg/kg** for plants. The 25th percentile EC_{50} for naphthalene effects on barley (Figure 4.12) was 820 mg/kg. Assuming losses from soil during the preparation of test units similar to those documented by Stephenson for naphthalene (initial concentration of ~30% nominal), this would yield a barley growth naphthalene EC_{50} of around **250 mg/kg**. The $EC(LC)_{50}$ values shown in Table 4.9 were in the range of **56 to 86 mg/kg** initial exposure concentration.

Overall, comparison of the available naphthalene toxicity data with the F2 data indicates that naphthalene alone may be slightly more toxic to soil invertebrates and plants on a soil concentration basis than F2 distilled from Federated whole crude (by a factor of approximately two to four).

4.2.7.4 – F1 Surrogate Ecotoxicity. Surrogate compounds previously deemed to represent the F1 fraction include the aromatic toluene and the aliphatic n-hexane. No attempt was made as part of the PHC CWS development initiative to acquire additional toxicity data for surrogates that are potentially representative of the F1 fraction.

Limited data for benzene (Environment Canada, 1996c) toluene (Environment Canada, 1996d), ethylbenzene (Environment Canada, 1996d) and xylenes (Environment Canada, 1996d) on soil invertebrates and plants were collated as part of previous efforts to derive soil quality guidelines. Figure 4.13 provides a graphical summary of the Environment Canada collated ecotoxicity data for benzene.

The soil invertebrate and plant toxicity data for toluene, ethylbenzene, and xylenes is even more limited than for benzene and is not shown graphically herein.

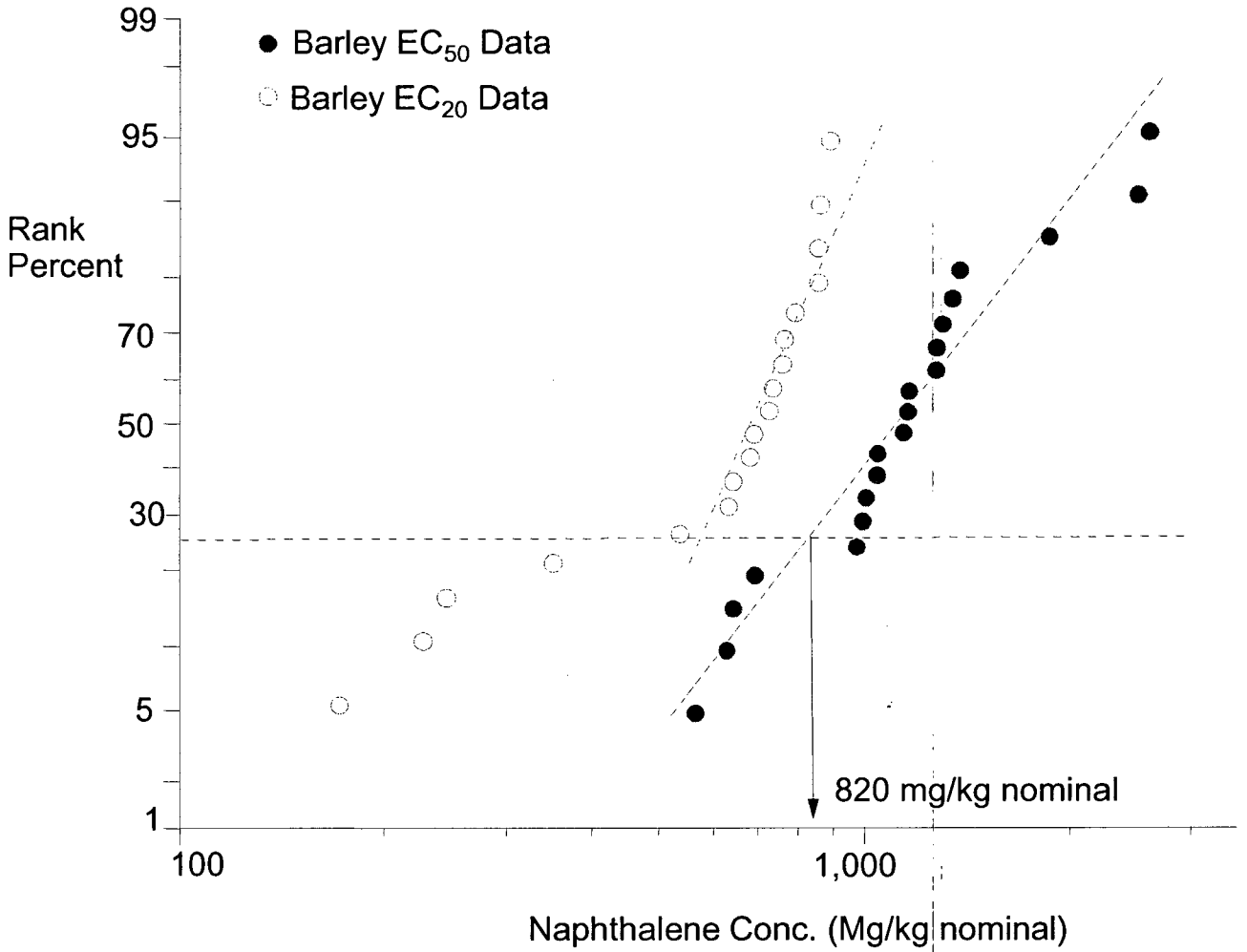


Figure 4.12: Distribution of barley ecotoxicological endpoints for studies on naphthalene based on EC_{50} and EC_{20} endpoints from four different laboratories.

There are considerable methodological challenges in conducting bulk soil toxicity tests for highly volatile compounds. Major portions of the toxicant tend to be lost during preparation of the soil test units, and substantial chemical losses are also experienced during the exposure period. Such losses might not be as great in a typical field situation with a much larger contaminated soil mass, including substantial subsurface mass of volatile organics which tend to re-supply and saturate the soil vapour phase and result in residual contaminant concentrations over much longer periods of time.

Overall, it is difficult to draw any firm conclusions based on comparison of the toxicity of mogas or F1 hydrocarbons with individual surrogates in the C6 to nC10 range.

4.2.8 Whole Product Data

Several of the peer-reviewed studies may provide useful toxicological data based on laboratory or field studies of whole upstream or downstream petroleum products, such as crude oil, mogas, diesel, or JP4 (jet fuel). The carbon range and proportion of CWS carbon-fractions for some of the whole product data are provided in Table 4.11.

Table 4.11: Comparison of whole products and the PHC CWS fractions.

Product	Carbon Range	CWS Fraction
Mogas (fresh)		15% BTEX portion; 65% Non-BTEX portion, include in F1; 20% F2
Mogas (slightly weathered)		25% BTEX; 25% non-BTEX F1; 50% F2
Naphtha (light catalytic cracked)	C4 to nC12	F1
Diesel (fresh)	nC9 to nC20.	50% F2; 50% F3
Kerosene	nC9 to nC17	F2
JP4	C4 to nC16	50% F1; 50% F2 (?)
Heavy fuel oils and lube oils (fresh)	> nC12-14	F3, F4 (?)

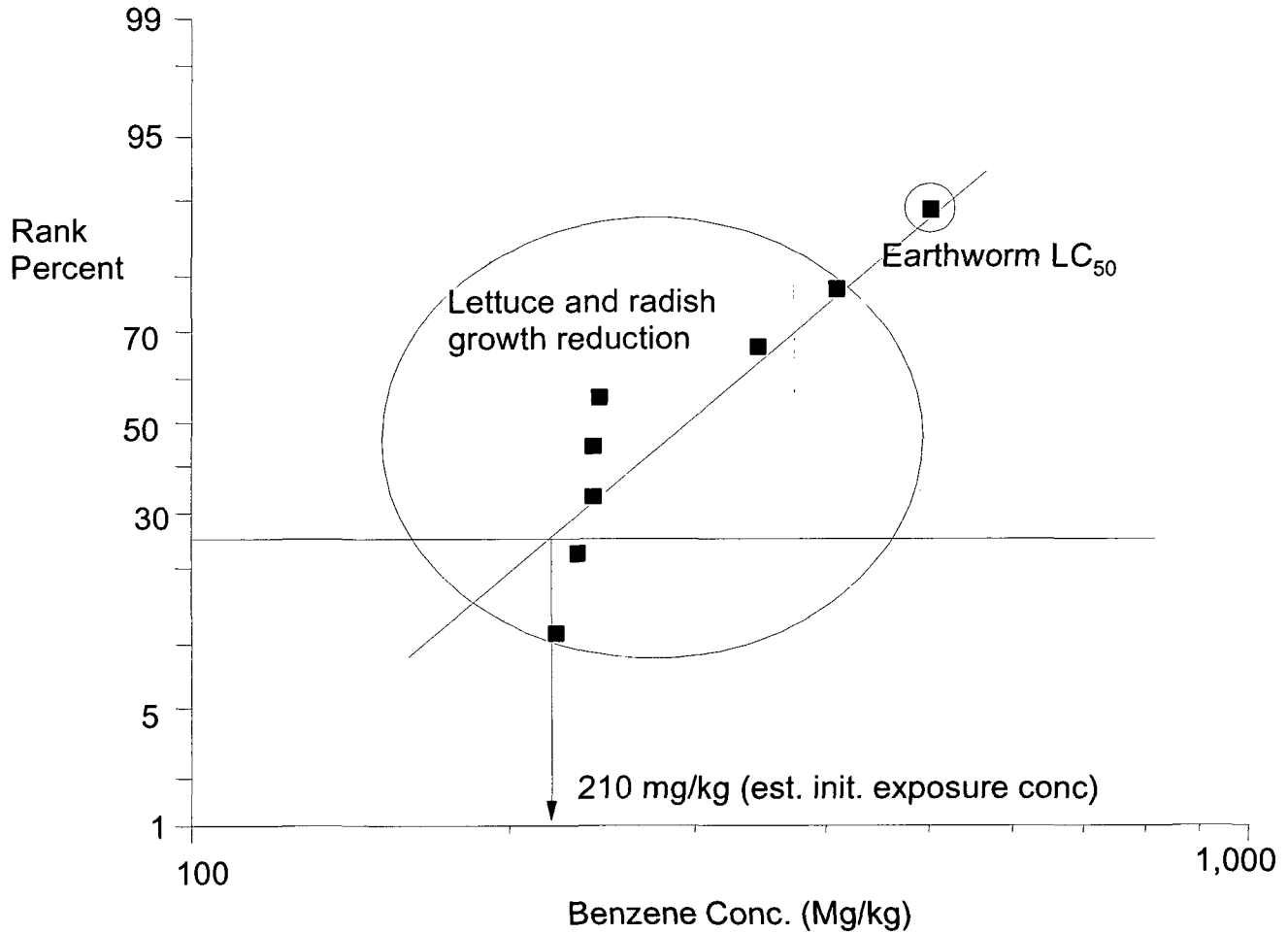


Figure 4.13: Distribution of plant and soil invertebrate ecotoxicological endpoints for benzene based on EC_{50} and LC_{50} endpoints.

In the case of products that fall entirely, or nearly so, within a single PHC CWS fraction, the studies may have value for deriving from scratch a fraction-specific sediment quality guideline (SQG). Naphtha and kerosene toxicity data, for example, may be useful for deriving an SQG for F1 and F2 respectively. Cases where a whole product spans several fractions are clearly more complicated; for example, diesel may be apportioned roughly equally between F2 and F3 (Table 4.11). It is not clear how the relative toxicity of individual fractions can be accounted for, and therefore, how whole product data can be used in the derivation of SQGs for individual carbon fractions.

The diesel or other whole product toxicity data are clearly useful as a validation check against soil values that have been derived from other data types, including fraction-specific and surrogate data. As discussed in section 4.1, this is primarily the context in which the use of whole product studies has been advocated.

4.2.9 Toxicity of Whole Federated Crude Versus CWS Fractions

Stephenson *et al.* (1999) conducted soil toxicity testing on a similar battery of test organisms, using directly comparable endpoints, for whole Federated crude oil and the F3 and F2 fractions obtained from Federated crude through careful distillation. The data are summarized in Appendix F. It is also possible to compare the toxicity of Federated crude with mogas as a reflection of F1 toxicity, based on the data generated by Stephenson (2000).

The ratios of the EC (or $LC)_{50}$ for fractions F1, F2, and F3 to whole Federated crude are summarized as frequency distributions in Figures 4.14 to 4.16.

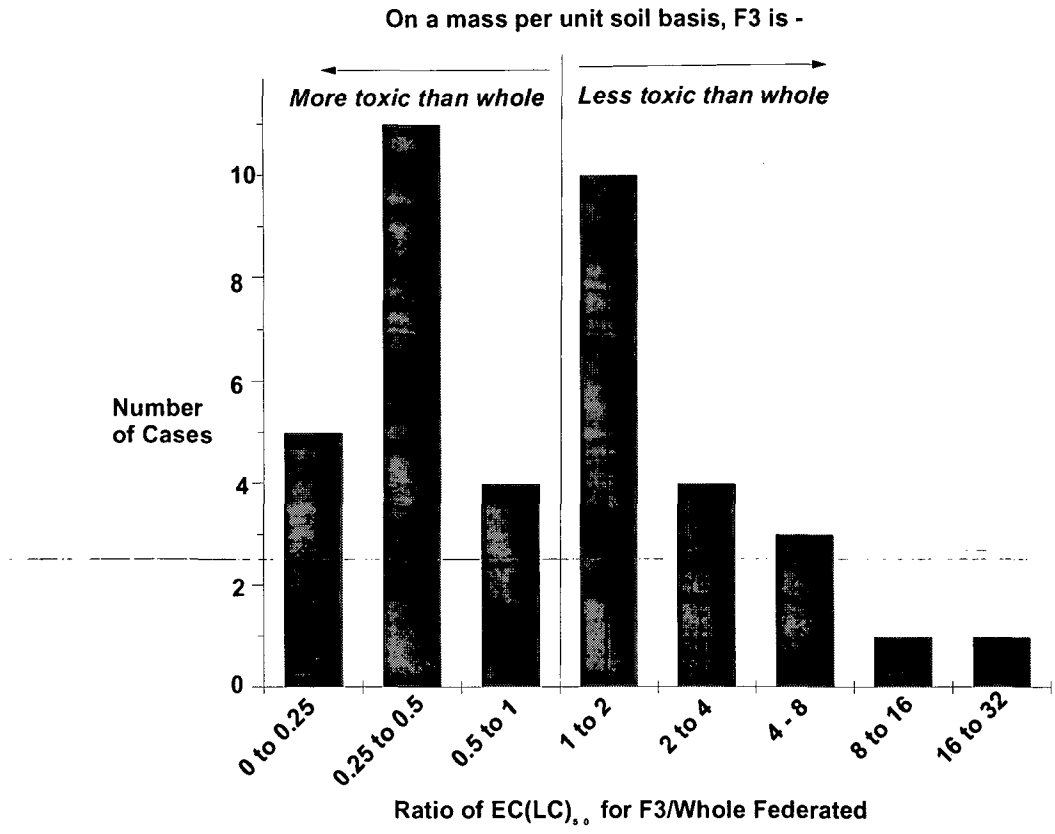


Figure 4.14: Frequency histogram of the relative toxicity of F3 to Federated Whole Crude, based on $EC(LC)_{50}$ endpoints.

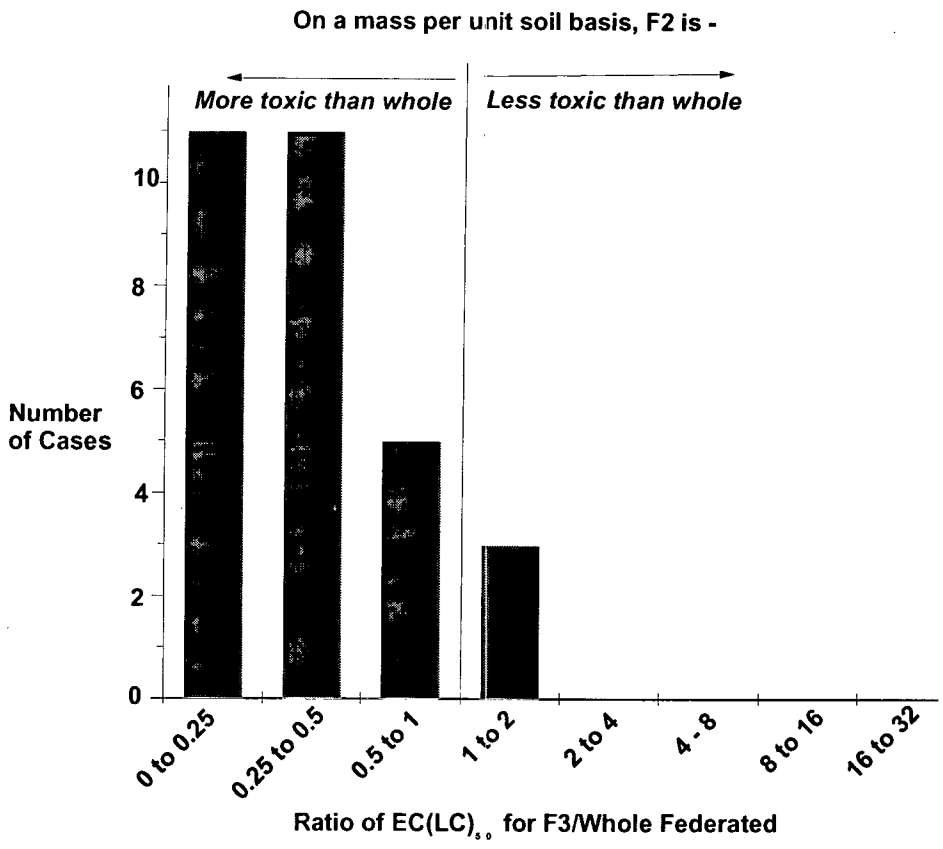


Figure 4.15: Frequency histogram of the relative toxicity of F2 to Federated Whole Crude, based on $EC(LC)_{50}$ endpoints.

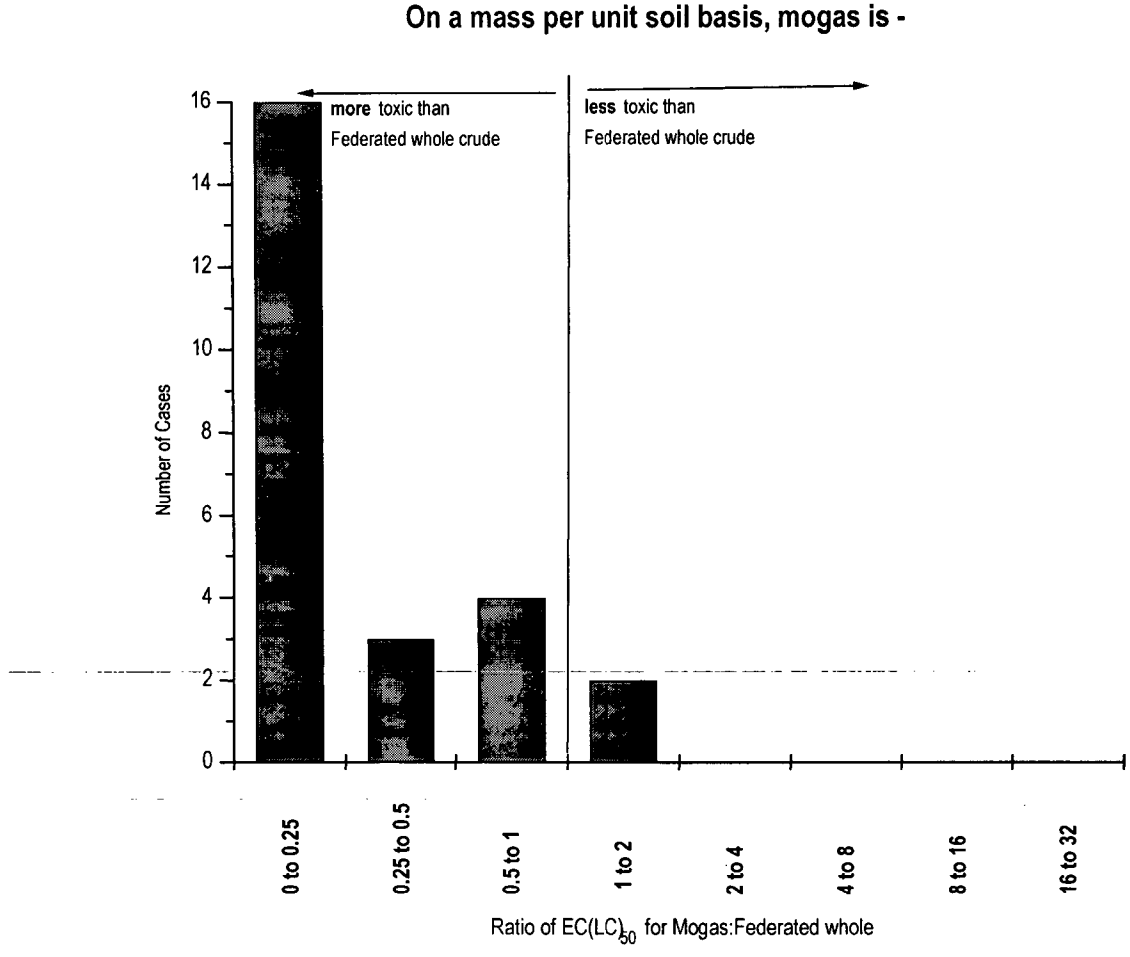


Figure 4.16: Frequency histogram of the relative toxicity of Mogas to Federated Whole Crude, based on $EC(LC)_{50}$ endpoints.

A major portion of the TPH concentration of Federated whole crude might be associated with F4 constituents (>C34) as well as F3 constituents (>C16 to C34) with a limited bioavailability, since the strong hydrophobicity would limit partitioning from soil particles. It would be expected, therefore, that a substantial portion of the whole product toxicity would be associated with the F1 and F2 portions. If these relatively more toxic fractions are isolated, then they alone should exhibit higher toxicity and lower $EC(LC)_{50}$ values than Federated whole crude. Figures 4.15 and 4.16 bear this out. Fraction 2 alone tended to be between two and ten times more toxic, per unit concentration, than whole Federated crude (Appendix F).

The range of toxicity encountered for different taxa and different endpoints for the F3 distillate was much greater than for either F2 alone or for whole crude. The $EC(LC)_{50}$ ratio for F3 to whole crude varied from 0.09 to 19. In other words, F3 alone varied from being around ten times more toxic to twenty times less toxic than whole Federated crude, depending on the test species and endpoint employed.

Figures 4.17 and 4.18 also demonstrate the spread in data for F3 toxicity endpoints relative to either the whole product or various other fractions. This further suggests that the toxicity of F3 across different taxa and exposure conditions will be less easy to predict than for F1 and F2. One possible reason for the spread in data is the large range of physicochemical properties encompassed in F3, based on constituents with a boiling point range bracketed by >C16 and C34. The mixture, therefore, is likely to include a great diversity of branched and straight-chain aliphatics, heterocyclics, N- and S-substituted compounds, and alkylated PAHs. Overall, F3 merits additional future scrutiny in terms of the associated environmental risks.

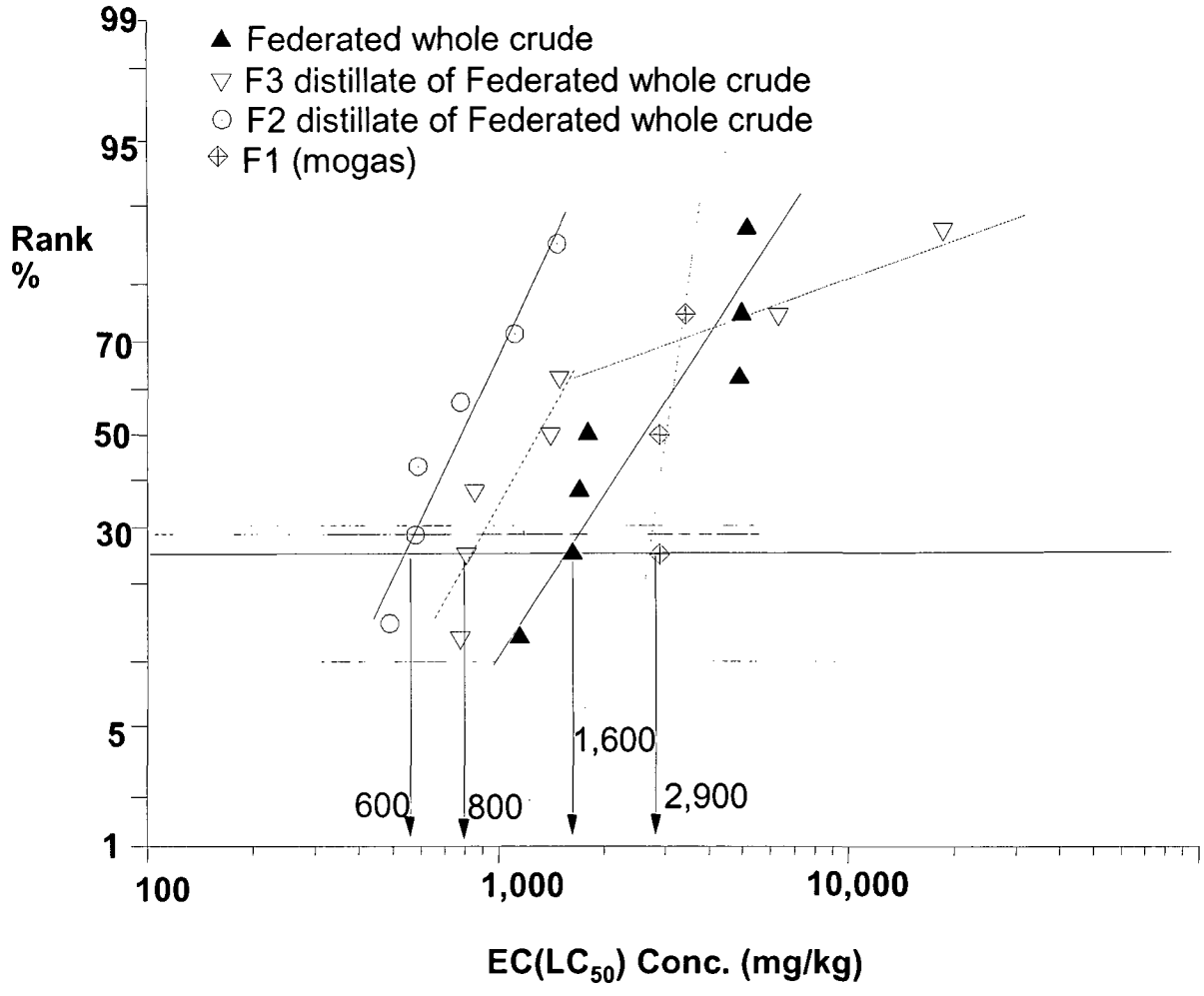


Figure 4.17: Comparison of ranked data for soil invertebrate toxicity effects.

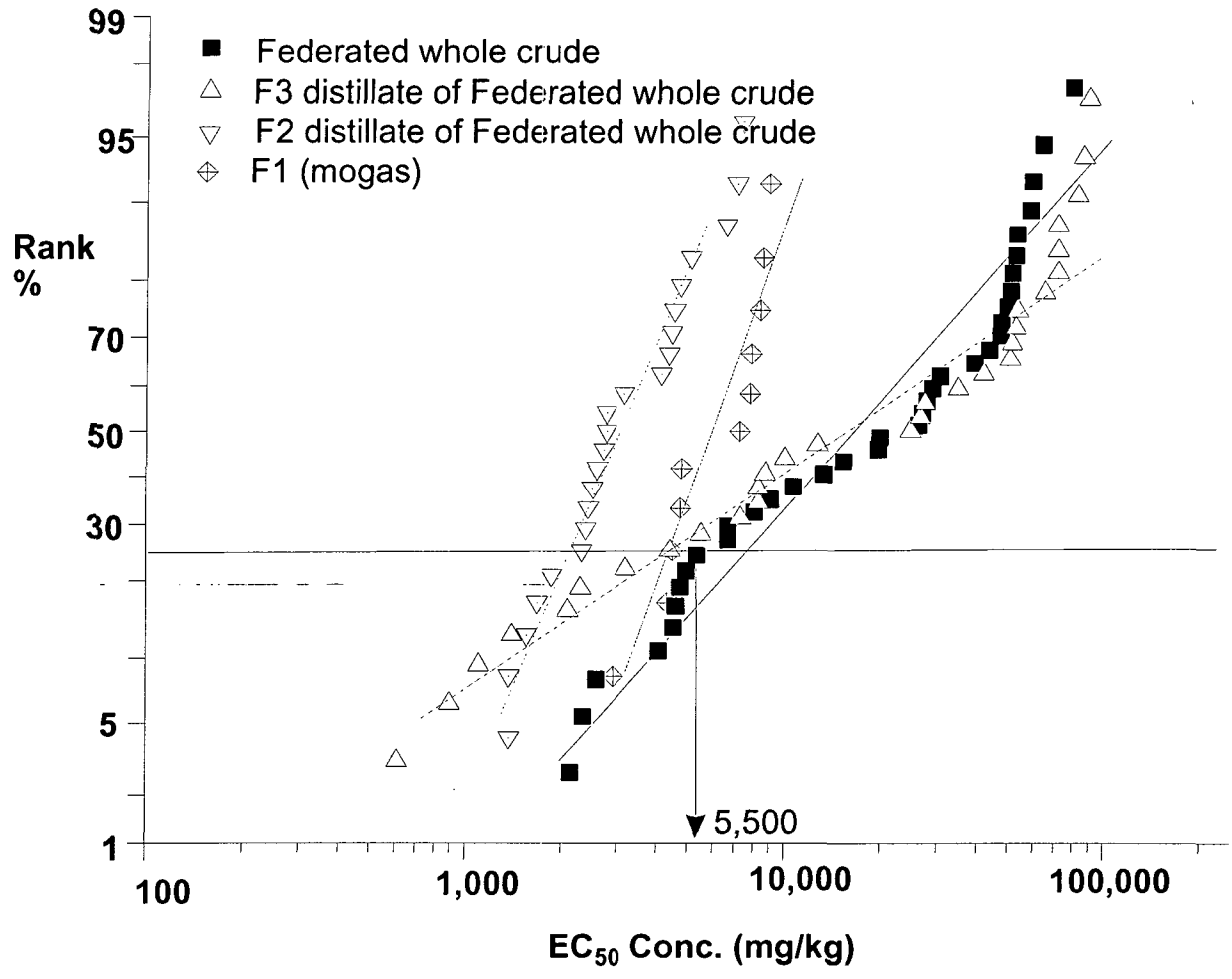


Figure 4.18: Comparison of ranked data for plant toxicity effects endpoints [EC_{50} estimates].

4.2.10 Toxicity of Weathered versus Fresh PHCs

It is commonly held that the natural or enhanced attenuation and biodegradation of PHC mixtures decreases the toxicity and risks over time, as well as the concentrations of various PHC input types. The decrease in toxicological risk is generally attributed to one or more of the following:

- Changes in composition (change in the relative proportions of the original fractions) with biases in loss of more versus less toxic substances.

- Decreased solubility and bioavailability relative to total soil concentrations, due to changes in the PHC-soil particle interaction (enhanced sorption; transfer to intercrystalline layer and/or other deeper internal portions of soil particles).

A conceptual model based on biochemical perturbations in target receptors, which includes issues around bioavailability, is as follows:

PHC input source

↓

↓

Total concentration in soil

↓

↓

Compositional change associated with partitioning and differential loss

↓

Bioavailable fraction (0 to 100% bioavailable)

↓

Internalized or surface contact dose

It is important to differentiate between changes in the toxicity following weathering or bioremediation that are associated with shifts in chemical composition as opposed to bioavailability. In particular, it has been hypothesized that the solubility, leachability, and – hence – bioavailability of petroleum hydrocarbon mixtures rapidly declines after even short periods following introduction into a soil environment (Parkerton and Stone, *in press*).

One of the major advantages of managing PHCs as four discrete fractions, as opposed to using TPH or Oil and Grease measurements, is that compositional shifts associated with weathering may be recognized through the shift in soil concentrations of CWS fractions F1 through F4. The loss of highly volatile hydrocarbons, therefore, would necessarily result in a lower residual concentration of PHCs in the F1 and F2 range. The lower toxicity of residual petroleum hydrocarbons based on loss of volatiles is expected to be reflected in

the lower F1 and F2 concentrations in the soil.

There may be compositional shifts due to weathering, however, within a fraction such that ecotoxicity data on fresh product may not be a good predictor of the risks associated with soils from historical release sites or bioremediated soils. This issue is probably the most important in the context of the CWS F3 fraction (>nC16 to C34), which may comprise a broad spectrum of PHC mixtures, and probably a broader range of relative toxicity than F1 or F2. It has been hypothesized that PHC compounds in the boiling point range >nC16 to C21 (lower molecular weight portion of F3) are relatively more toxic, but less environmentally persistent than constituents in the range >C21 to C34. If this were the case, a change in relative composition within F3 due to weathering and differential attenuation could render overly conservative any F3 soil quality value based on toxicity testing of F3 from fresh product.

The major portion of good quality data to calculate an ecological soil contact Tier 1 value is from either fresh mogas (for F1) or F2 and F3 range distillate of fresh Federated whole crude. This may bias the Tier 1 standards toward lower values typical of fresh releases, as opposed to weathered PHCs. This section specifically evaluates whether the use of laboratory-based plant and soil invertebrate toxicity tests on vacuum distillates from fresh whole product is likely to over-estimate risks at the major portion of field sites.

In particular, one or more of three specific conditions were deemed to constitute direct evidence that the Tier 1 values derived from ecotoxicity data for distillates from fresh Federated Crude Oil are overly protective when applied to a field site with a more weathered mixture:

a. There is a shift toward heavier constituents within each of the CWS fractions (especially F3) as a result of weathering and/or biodegradation;

b. Residual soil concentrations, when expressed according to boiling point ranges equivalent to those encompassed by the PHC CWS fractions, generally result in a higher concentration at which soil invertebrates or plants are affected (higher LC_x or EC_x) than has been documented for fractions derived from fresh Federated Whole Crude (Section 3); and/or

c. No-observed effect levels for F1, F2 or F3 equivalent concentrations are generally substantially higher than would be predicted by the 25^{th} % ile of the EC/LC_{50} distributions documented in Sections 4.2.4 through 4.2.6.

Considerable new information has been brought to bear on the relative risks of fresh versus weathered petroleum products within the last few years. Several studies are presently under way, and the results that will not be available until

after adoption of the first round of Tier I PHC CWS. Four major studies conducted by 1) Visser *et al.* 2) Saterbak *et al.* 3) Alberta Research Council 4) Montreal Refinery site, however, were consulted for evidence of limitations in the applicability of laboratory-based ecotoxicity data on fresh PHC fractions to field sites in Canada. A summary of the major findings is presented below. A detailed discussion of these preliminary results is provided in Appendix G.

Based on the analysis documented in Appendix G, it is concluded that it is not presently possible to adjust generic soil quality benchmarks to reflect the degree of PHC weathering at a specific release site. While some of the studies provisionally support the assertion that PHCs of an equivalent composition are less toxic following weathering, there are also clear-cut cases where the opposite has been observed.

A further rationale for rejection of any measures to adjust generic (Tier I) PHC soil quality benchmarks is as follows:

- Loehr and Webster (1997) stated that –

  "Insufficient data was available to evaluate the relationship between chemical mobility and terrestrial (bulk soil) toxicity". (p. 224)

  In other words, there is insufficient knowledge at the present time to derive defensible numerical models which account for weathering effects of PHC mixtures in bulk soils.

- Loehr and Webster (ibid.) further stated –

  "The results of these evaluations indicated the following:

  There was no apparent relationship between the measured chemical concentrations in a soil or sludge and the associated toxicity of that soil or sludge, before or after bioremediation;"

- Existing studies of mixtures have generally failed to differentiate changes in toxicological thresholds for TPH associated with mixture compositional changes (which would be better reflected in the PHC CWS analysis of 3+1 fractions) as opposed to changes in bioavailability. The existing literature, therefore, offers little guidance.

- Existing studies of weathered versus fresh toxicity thresholds for individual PHC surrogates have underlined the importance of variations in soil type (and possibly other site-specific variations) that cannot presently be accounted for in a Tier I generic site application.

- Use of a fresh/weathered conditional application at Tier I would require some robust means of defining the age of the PHC release and/or degree of weathering.

4.2.11 Reconciliation of Data Types

The toxicity of various PHC constituents in soils to plants and/or invertebrates, based on various measures of PHC concentration as discussed above, is summarized in Table 4.12.

Overall, the data generated for fractions F1, F2, F3 are within the lower effects range (25^{th} percentile of the effects endpoints) as calculated for whole products. The F1, F2 and F3 lower effects concentration were substantially higher than previously documented for individual BTEX constituents; however – as noted above – the degree of confidence in the BTEX plant and soil invertebrate toxicity test results is low.

Based on a weight-of-evidence type analysis, as previously defined (Section 4.1), the new information generated on the ecotoxicity of mogas (for F1), F2, F3, and whole Federated crude (for F4) were deemed to provide the best estimates of toxicological thresholds for the purpose of deriving Tier 1 levels.

Table 4.12: Plant and invertebrate toxicity endpoints for various PHC constituents, based on the 25th percentile of the effects [EC(LC)$_{50}$] database, or range of effects concentrations (in brackets).

PHC Measure	Soil Protective Benchmark for PHCs in Soils (in mg/kg estimated soil exposure concentration or as indicated)		
	Soil Invertebrate 25th percentile	Plant 25th percentile	Combined 25th percentile
Fraction-specific			
F4 (>nC34)	note A	note A	note A
F3 (>nC16 to C34)	**250**	**620**	**400**
F2 (>nC10 to C16)	**200**	**600**	**450**
F1 (C6 to nC10)[B]	**75**	**165**	**130**
Surrogate data			
F4	not avail.	not avail.	not avail.
F3			
Benzo(a)pyrene	NOEC = 26,000	LOEC = 8,800	
Pyrene	not avail.	note C	not avail.
Eicosene	not avail.	note C	not avail.
F2			
Naphthalene	(56 to 108)	(64 to 86) 250 (barley)	
N-decane	not avail.	note C	not avail.
F1			
Benzene	(55, 342)[D]	(26-102)[D]	210
Toluene	(5-126)[D]	(7-84)[D]	
Ethylbenzene	(155)[D]	(9-71)[D]	
Xylene	(79)[D]	(9-97)[D]	
Whole Product Data			
Fresh Federated Whole Crude	1,600 nominal	5,500 nominal	4,800 nominal
Weathered Crude Oil	800 nominal	600 nominal	
Fresh Crude Oil	1,200 nominal	8,400 nominal	
Fresh Diesel or Heating Oil	800 nominal	800 nominal	
Weathered Diesel or Heating Oil	not avail.	20,000	

Notes:
A: To be determined based on toxicity tests on asphaltene.
B: As estimated from toxicity tests on mogas.
C: In progress.
D: Excerpted from CCME (1996), Supporting Documents. Canadian Soil Quality Guidelines for Benzene, Ethylbenzene, Toluene, and Xylenes. The bracketed concentrations are final measured concentrations, which are underestimates of initial exposure concentration.

4.3 Exposure Scenarios for Ecological Receptors Based on PHCs in Groundwater

This section describes the derivation of draft petroleum hydrocarbon (PHC) concentration limits in surface and subsurface soils beyond which there might be elevated risks to ecological receptors via groundwater exposure pathways. Two different groups of ecological receptors were examined:

i) **Aquatic life** in nearby streams, rivers, and lakes, where PHC contaminated groundwater infiltration might be an issue; and

ii) **Livestock watering**, where livestock (especially cattle) might obtain drinking water from a dugout or other water body within a short distance, and with the potential to receive contaminated groundwater from petroleum hydrocarbon contaminated soils.

The exposure pathway for aquatic life is applicable to all sites and all land-use types where there is potential for risks to aquatic life in surface water bodies at or near a contaminated site. The pathway assumes the presence of a shallow aquifer that interacts directly or indirectly with contaminated soil upgradient from the water body. The exposure pathway for livestock drinking water supplies is intended to apply in agricultural settings only.

The approach used herein to model fate of PHCs in the subsurface environment is adapted from that developed by the British Columbia Contaminated Sites Soil Task Group (CSST) for "soil matrix standards" based on groundwater flow to surface water used by aquatic life. The CSST approach is outlined in "Overview of CSST Procedures for the Derivation of Soil Quality Matrix Standards for Contaminated Sites" [British Columbia Environment (BCE), 1996a]. The US EPA draft document "Soil Screening Guidance" (1994) was used as the framework for the BCE model and the mathematical simulation for the saturated groundwater transport was based on work by Domenico and Robbins (1984). The mathematical equations incorporated in the model are provided in Appendix H.

4.3.1 PHC Chemical Property Assumptions for Tier I Groundwater Fate Modeling

The input parameters to the BCE model were modified using estimates of chemical-specific characteristics for the CWS PHC fractions (Table 4.13), as well as standardized assumptions (based on input from the CWS technical advisory groups) regarding generic site properties (Appendix H).

Soil quality benchmarks for two of the four PHC CWS fractions were developed following preliminary analysis, based on the likelihood of solubilization into groundwater and subsurface transport toward a surface water body containing

aquatic organisms. As discussed previously, the PHC CWS Fraction 1 (F1) includes both aromatic and aliphatic hydrocarbon constituents in the effective boiling point range spanned by n-hexane (nC6) and n-decane (nC10), but excluding BTEX (benzene, toluene, ethylbenzene, and xylenes). The PHC CWS fraction 2 (F2) is designated as the sum of concentrations of aliphatic and aromatic PHCs in the boiling point range between nC10 and nC16. No attempt was made to derive soil quality guidelines based on groundwater transport to ecological receptors for PHC CWS fractions F3 (>nC16 to C34) or F4 (>C34): The strong hydrophobicity of heavier hydrocarbons in these fractions generally precludes significant mobilization in the groundwater in the dissolved phase.

Table 4.13: Representative physical parameters for TPHCWG sub-fractions, based on correlation to relative boiling point index (source: TPHCWG, Vol. 3; 1997).

Fraction (based on boiling point range)	Solubility (mg/L)	Henry's Law Constant (cm^3/cm^3)	Log K_{oc}
Aliphatic			
C5-C6	3.6E+01	3.3E+01	2.9E+00
>C6-C8	5.4E+00	5.0E+01	3.6 E+00
>C8-C10	4.3E-01	8.0E+01	4.5 E+00
>C10-C12	3.4E-02	1.2E+02	5.4 E+00
>C12-C16	7.6E-04	5.2E+02	6.7 E+00
>C16-C21	2.5E-06	4.9E+03	8.8 E+00
Aromatic			
C5-C7 (benzene only)	1.8E+03	2.3E-01	1.9 E+00
>C8-C10	6.5E+01	4.8E-01	3.2 E+00
>C10-C12	2.5 E+01	1.4E-01	3.4 E+00
>C12-C16	5.8 E+00	5.3E-02	3.7 E+00
>C16-C21	6.5E-01	1.2E-02	4.2 E+00
>C21-C35	6.6E-03	6.7E-04	5.1 E+00

In order to predict PHC fate and transport in the subsurface environment, it was necessary to establish applicable physical transport properties for constituent mixtures of the CWS F1 and F2 fractions. A singular estimate for the relevant physical properties was estimated for the sub-fractions designated by the Total Petroleum Hydrocarbon Criterion Working Group (TPHCWG - Vol. 3, 1997), which serves as a good starting point for the PHC CWS groundwater-based soil quality guideline efforts. In general, the TPHCWG fractions were established to limit the range of physical properties of individual constituents within the fraction to around one order of magnitude. The PHC CWS fractions, however, represent a further amalgamation of 17 TPHCWG sub-fractions into only four fractions (F1: nC6 to nC10; F2: >nC10 to nC16; F3: >nC16 to nC34; F4: >nC34). Under the

PHC CWS scheme, aliphatics and aromatics are combined. As noted previously, the BTEX fraction is subtracted from F1.

In assigning values for solubility, organic carbon partition coefficients, Henry's Law Constants or other physical properties to F1 and F2, it is important to appreciate that a given fraction is likely to be a complex mixture of individual compounds. Each of these compounds may have unique physical properties, and a set of assigned values for either the TPH CWG sub-fractions that make up CWS F1 or F2, or for F1 and F2 themselves, as a whole assume that the entire mixture behaves according to some average property which is captured in a singular estimate. This assumption neglects the change in composition of a PHC complex mixture as it moves through the subsurface environment, based on differential partitioning between various matrices, such as soil particle surfaces, interstitial air, interstitial water, or organic matrices.

For the purpose of this exercise, it is assumed herein that the chemical properties of the TPHCWG seventeen sub-fractions (Table 4.13) as previously estimated accurately reflect the environmental partitioning behaviour of these mixtures as a whole. Should relevant new scientific information arise on the fate and transport of complex PHC mixtures, this assumption may need to be re-visited.

The assumed composition of the modeled CWS fractions, as previously applied for human health protective pathways, is as follows:

(i) **CWS Fraction 1 (F1):** 55% >C6 to nC8 (100% aliphatics); 45% >nC8 to nC10 (80% aliphatics and 20% aromatics).

(ii) **CWS Fraction 2 (F2):** 45% >nC10 to nC12 (80% aliphatics and 20% aromatics); 55% >nC12 to nC16 (80% aliphatics and 20% aromatics).

For the CWS, groundwater modeling of the soil concentration below which risks to aquatic life is likely to be elevated was based on the additive contribution of the relevant TPHCWG sub-fractions contained in each PHC CWS fraction. Potential additive or other interactive effects between F1 and F2 fractions were ignored in the derivation exercise. The use of the TPHCWG sub-fractions as the basic chemical unit for modeling represents a compromise along a continuum. The choice of chemical descriptors potentially occupies the entire range from use of single PHC compounds (for example, isopropylbenzene) to the use of a whole product (for example, motor gas) as a singular chemical entity. This is shown conceptually below (Figure 4.19):

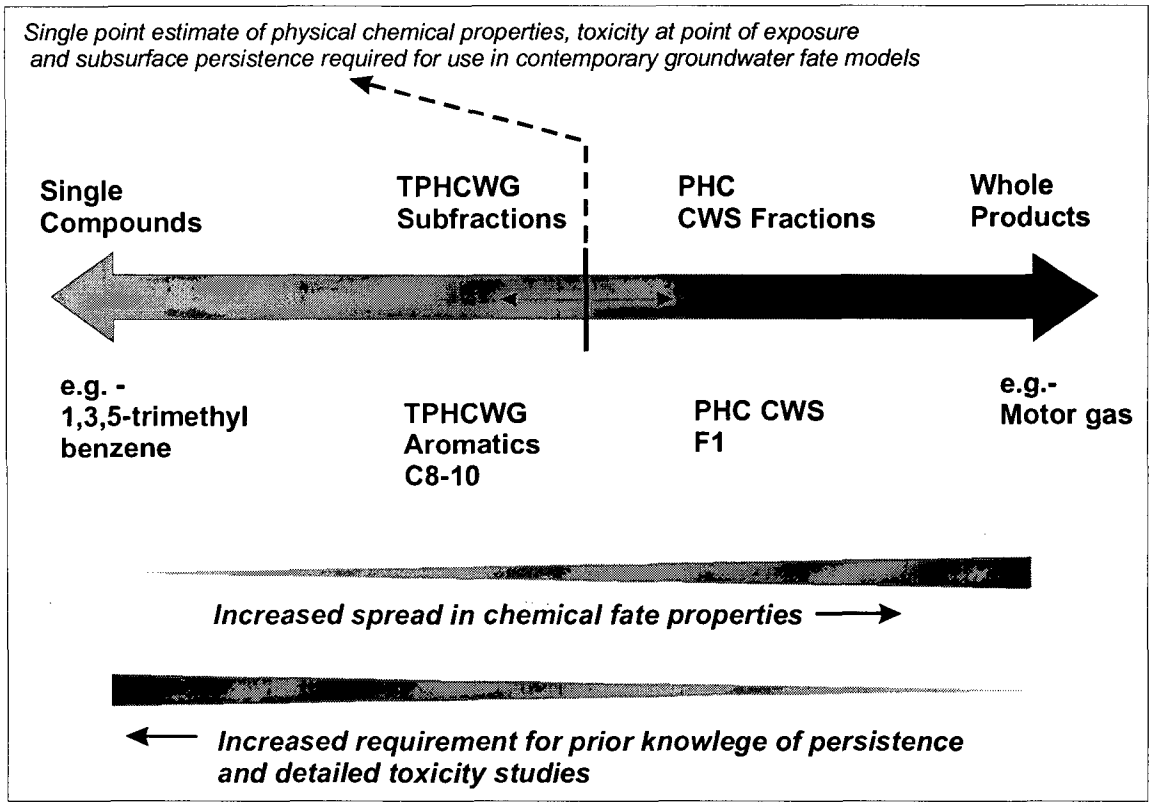


Figure 4.19: Compromise between precision of estimates and level of detailed knowledge of chemical-specific toxicity.

In order to back-calculate an environmentally acceptable soil concentration for PHCs based on groundwater transport to an ecological receptor, the following information is required for each designated chemical unit:

(i) a single point estimates of aqueous solubility, Henry's constant, and K_{oc};

(ii) an estimate of environmental persistence unless it is very conservatively assumed that no subsurface degradation occurs; and

(iii) an aquatic toxicity reference value (TRV) above which risks to relevant ecological receptors may be elevated.

This parallels the informational requirements for estimation of an environmentally acceptable soil concentration based on human health considerations (Chapter 3) although there are key differences between the modeling exercises since the aquatic life or livestock exposure scenario is largely dependent on lateral migration of PHCs in groundwater, as opposed to on-site exposure via drinking water. Where the available scientific knowledge does not adequately support

confident assignation of unique values of the above to each designated chemical unit, then it is necessary to make some more generic assumptions about point estimates that span several of the chemical units. This is discussed in more detail below.

Soil protective benchmarks calculated for the chosen chemical units - in this case the TPHCWG sub-fractions - can be combined to produce an environmentally acceptable concentration in soil for CWS F1 or F2 based on the following formula:

$$SQG_{slice\_i} = \frac{1}{\sum\left(\frac{MF_{subfraction\ j}}{SQG_{subfraction\ j}}\right)}$$

Where -

SQG_{slice_i} = soil quality guideline for the CWS fraction *i* (mg/kg)
$SQG_{subfraction\ j}$ = soil quality guideline (mg/kg) for each sub-fraction within fraction *i* for the target water quality guideline for fraction *i*
$MF_{subfraction\ j}$ = mass fraction of each sub-fraction within the fraction *i*

4.3.2 Estimation of PHC Toxicity to Aquatic Receptors

One of the challenges for developing soil quality guidelines for PHC CWS fractions that are protective of aquatic life in nearby surface water bodies was the absence of formally adopted guidance on appropriate water quality benchmarks for each of the four CWS fractions. The derivation of such soil guidelines necessarily relies on assertions about concentrations of PHCs in water that are acceptably low, and at what level in water there is a potential for elevated risks to aquatic biota.

This derivation exercise focused on CWS fractions F1 and F2, since analysis of the literature indicated that PHCs found in fractions F3 and F4 are sufficiently insoluble that movement via dissolution in groundwater is not likely to be an operable exposure pathway. In the absence of pre-existing guidance, two different approaches were investigated for defining environmentally acceptable concentrations of F1 and F2 PHCs in water bodies containing aquatic life. These were –

- **use of individual surrogates** to define the expected toxicity reference value (toxicological threshold) of the entire CWS fraction in the surrounding water, based on pre-existing aquatic toxicity studies of these surrogates; and

- **use of a "Critical Body Residue" approach**, assuming that the major portion of toxicity is associated with a narcosis-type endpoint, and that the concentration of PHC constituents in the surrounding water is less important for narcosis than the cumulative fraction on a molar basis of all PHCs present in either CWS F1 or F2.

The two approaches are described in more detail below.

4.3.2.1 Use of a Surrogates-Based Approach to Define Acceptable Ambient Water Concentrations. B.C. Environment[1] initially provided to EcoTAG and the PHC CWS Development Committee draft recommendations on aquatic life toxicity reference values for volatile (nC5-nC9) and light (nC10-C19) extractable petroleum hydrocarbons [Volatile Petroleum Hydrocarbons (VPH), and Light Extractable Petroleum Hydrocarbons (LEPH), respectively] based on aquatic life protection.

The BCE draft water quality guidelines employed a surrogates-based approach. For VPH, which is directly equivalent to CWS F1, the surrogates initially used were n-hexane to represent aliphatics toxicity, and toluene to represent the toxicity to aquatic life of the aromatics portion. For the Light Extractable Petroleum Hydrocarbons (LEPH: nC10-C19) fraction, n-decane and naphthalene were used as surrogate compounds for the aliphatics and aromatics respectively. The CWS F2 fraction (nC10-C16) employs a different cut-off than LEPHs at the upper end; however, the previously screened surrogate toxicity data (for naphthalene and n-decane) were deemed to be applicable to F2 since both are at the lighter end of this boiling point range.

For each of the VPH and LEPH fractions, toxicity data for an aliphatic and aromatic surrogate were obtained from US EPA's AQUIRE database. Following an initial review, the BCE toxicity reference values were further modified as described herein.

For the PHC CWS fractions F1 and F2, the toxicity data for each of the chosen surrogates and associated uncertainty factors initially applied were as follows:

[1] Memorandum from Mike Macfarlane and Glyn Fox to John Ward, January 7, 2000. Re: Recommendations for Aquatic Life Criteria for VPH/LEPH/HEPH.

CWS F1:

- **n-hexane**: geometric mean of 48-h LC_{50} for *Daphnia magma* and 24-h LC_{50} for *Artemia salina* = 3,700 µg/L, then divided by a twenty-fold uncertainty factor = 185 µg/L.
- **toluene**: Based on CCME (1996) re-assessment of toluene WQG. Lowest effect level for 27-d rainbow trout LC_{50} of 20 µg/L, then divided by a ten-fold uncertainty factor = 2 µg/L.

CWS F2:

- **decane**: A 48-h acute NOAEL for *Daphnia magna* of 1,300 µg/L was then divided by a ten-fold uncertainty factor to yield a WQG of 130 µ g/L.
- **naphthalene**: The geometric mean of rainbow trout hatchability in embryo-stage larvae was 11 µg/L. This was adopted with no uncertainty/application factor.

Through application of the assumed relative percent composition of either F1 or F2 as aliphatics and aromatics, a single toxicity reference value for the entire fraction was obtained. The appropriate mathematical procedure includes the use of the "inverse weighted means" formula as was used elsewhere to combine modeling results for multiple constituent TPH CWG fractions; i.e. –

$$\textit{Toxicity Reference Value (CWS Fraction)} = \frac{1}{\Sigma \left[MF_{sub\text{-}fj} / TRV_{sub\text{-}fj}\right]}$$

where –

$MF_{sub\text{-}fj}$ = mass fraction of subfraction j 0.2 for aromatic surrogate
0.8 for aliphatic surrogate

$TRV_{sub\text{-}fj}$ = toxicity reference value of subfraction j

For the F1 fraction, the result overall TRV was calculated as follows:

$$\textit{Toxicity Reference Value (CWS F1-draft)} = \frac{1}{[(0.8/185\ \mu g/L.)+(0.2\ /\ 2\ \mu g/L)]}$$

$$= 9.6\ \mu g/L$$

Similarly, for the F2 fraction, the result overall TRV was calculated as follows:

$$\textit{Toxicity Reference Value (CWS F2-draft)} = \frac{1}{\quad}$$

$$[(0.8/\ 130\ \mu g/L.)+(0.2\ /\ 11\ \mu g/L)]$$

$$= \quad 42\ \mu g/L$$

The use of n-hexane as a surrogate for the toxicity of aliphatics in a typical F1 mixture appears to be reasonable. The use of toluene, or indeed any of the BTEX suite, to characterize the toxicity of the aromatics fraction merited a more detailed examination, however – especially given the potential to strongly influence assumptions regarding the overall toxicity of the CWS F1 fraction. This fraction, by definition, excludes BTEX.

The aromatics found in F1 for a range of whole products are shown in Table 4.14, based on data provided in TPH CWG – Vol. 3.

Approximately 6% to 36% of the composition of gasoline by weight is made up of BTEX. Non-BTEX aromatics in the F1 boiling point range are estimated to comprise an additional 2% to 12% by weight of gasoline. The non-BTEX aromatic composition for the other products was estimated to account for between 0.2% and 3.9% by weight. The preceding estimates, however, are not directly equivalent to an expected aromatic composition in F1 (as opposed to in the whole product), since an appreciable portion of the overall weight percent even for gasoline would be expected to have an Effective Carbon (EC) range greater than nC10 or less than C6. The actual percent composition would be estimated as –

$$\%\ \text{composition (F1)} = \frac{\text{contribution to composition of the whole product}}{\text{fraction of whole product comprised of F1}}$$

If it is reasonably assumed that gasoline is 60% F1 (and 40% <C6 or >nc10) then the maximum percent composition of F1 would be calculated as follows:

$$\%\ \text{composition (F1)} = \frac{12\%}{0.6} = 20\%$$

An upper (worst-case) estimate that CWS F1 is comprised of 20% non-BTEX aromatics, as was previously assumed, appears to be a reasonable assumption

Table 4.14: Whole product composition of F1 aromatics (adapted from TPH CWG, Vol. 3).

Compound	Number of Carbons	EC	Crude Oil Wt%		Gasoline Wt.%		JP-4 Wt.%	JP-5 Wt.%	Diesel Wt.%	
			l.r.	*u.r.*	*l.r.*	*u.r.*	*value*	*value*	*l.r.*	*u.r.*
Benzene	6	6.5	0.04	0.4	0.12	3.5	0.5		0.003	0.1
Toluene	7	7.58	0.09	2.5	2.73	21.8	1.33		0.007	0.7
ethylbenzene	8	8.5	0.09	0.31	0.36	2.86	0.37		0.007	0.2
o-xylene	8	8.81	0.03	0.68	0.68	2.86	1.01	0.09	0.001	0.085
m-xylene	8	8.6	0.08	0.2	1.77	3.87	0.95	0.13	0.018	0.512
p-xylene	8	8.61	0.09	0.68	0.8	1.58	0.35		0.018	0.512
sub-total (% by wt)			***0.42***	***4.8***	***6.4***	***36***	***4.5***	***0.22***	***0.054***	***2.1***
Styrene	9	8.83							<0.002	<0.002
1-methyl-4-ethylbenzene	9	9.57	0.03	0.13	0.18	1	0.43			
1-methyl-2-ethylbenzene	9	9.71	0.01	0.09	0.19	0.56	0.23			
1-methyl-3-ethylbenzene	9	9.55	0.04	0.4	0.31	2.86	0.49			
1,2,3-trimethylbenzene	9	10.1	0.1	0.1	0.21	0.48				
1,2,4-trimethylbenzene	9	9.84	0.13	0.9	0.66	3.3	1.01	0.37		
1,3,5-trimethylbenzene	9	9.62	0.05	0.18	0.13	1.15	0.42		0.09	0.24
n-propylbenzene	9	9.47			0.08	0.72	0.71		0.03	0.048
isopropylbenzene (cumene)	9	9.13			<0.01	0.23	0.3		<0.01	<0.01
n-butylbenzene	10	10.5			0.04	0.44			0.031	0.046
isobutylbezene	10	9.96			0.01	0.08				
sec-butylbenzene	10	9.98			0.01	0.13				
t-butylbenzene	10	9.84			0.12	0.12				
1-methyl-2-n-propylbenzene	10				0.01	0.17				
1-methyl-3-n-propylbenzene	10				0.08	0.56				
1-methyl-4-isopropylbenzene	10	10.1							0.003	0.026
1-methyl-2-isopropylbenzene	10				0.01	0.12	0.29			
sub-total (% by wt)			***0.36***	***1.8***	***2.0***	***12***	***3.9***	***0.4***	***0.2***	***0.4***

Note: l.r. – lower value of reported range; u.r. – upper value of reported range.

The expected relative contribution of individual non-BTEX aromatics to F1 is also shown in Figure 4.20: Based on expected composition, some of the alkylbenzene compounds were deemed be potentially more representative aromatic surrogates of CWS F1 than toluene. The dominant non-BTEX aromatics in the F1 fraction of gasoline and crude oil tend to be trialkylbenzenes such as (in order of relative contribution) 1,2,4-trimethylbenzene; 1-methyl-3-ethylbenzene; 1,3,5-trimethylbenzene; and 1–methyl-4-ethylbenzene. Ideally, assertions about the toxicity of non-BTEX aromatics in CWS F1 using a surrogates approach should be based on studies of these dominant trialkylbenzenes.

The results of a subsequent search for aquatic toxicity data for C9 and C10 alkylbenzenes are provided as Table 4.15, and summarized in Figures 4.21 through 4.23. The lowest tabulated value was for *Daphnia magna* exposed to isopropylbenzene (cumene): Bobra *et al* (1983) observed a 48 h EC_{50} for immobilization of 5 mmol/m^3, or 601 µg/L. As noted in the figures and table, this value falls below the 5th %ile of the species sensitivity distribution for effects on aquatic organisms (including mortality) observed for several C9 and C10 alklybenzenes. In fact, this low value for a 48 h LC_{50} is in disagreement with observed toxicity endpoints derived by others (Table 4.15), and is deemed to be a perhaps overly protective surrogate value for the aquatic risks of CWS F1 aromatics. Immobility in aquatic animals, especially as associated with narcosis-type effects (see below) will generally be followed by mortality unless exposure to the stressor is curtailed. One of the challenges in assessing immobility endpoints in daphnids and other small aquatic animals is that a high degree of variability between different observers sometimes occurs.

In order to account for chronic versus sub-chronic response, a five-fold uncertainty factor was applied to the Bobra *et al.* endpoint, to arrive at an aromatics surrogate toxicity threshold of 120 µg/L. The application of a lower uncertainty factor than is often applied for extrapolating from acute or sub-chronic to chronic endpoints is justified by the fact that the data point falls well below the 5th %ile of the reconstructed species sensitivity distribution, and the endpoint was an immobility EC_{50}, not – strictly speaking – an acute endpoint. No further uncertainty factor was applied to account for additional inter-taxon variability, given that alkylbenzene toxicity data were available for a wide variety of organisms, spanning invertebrates, fish, and algae.

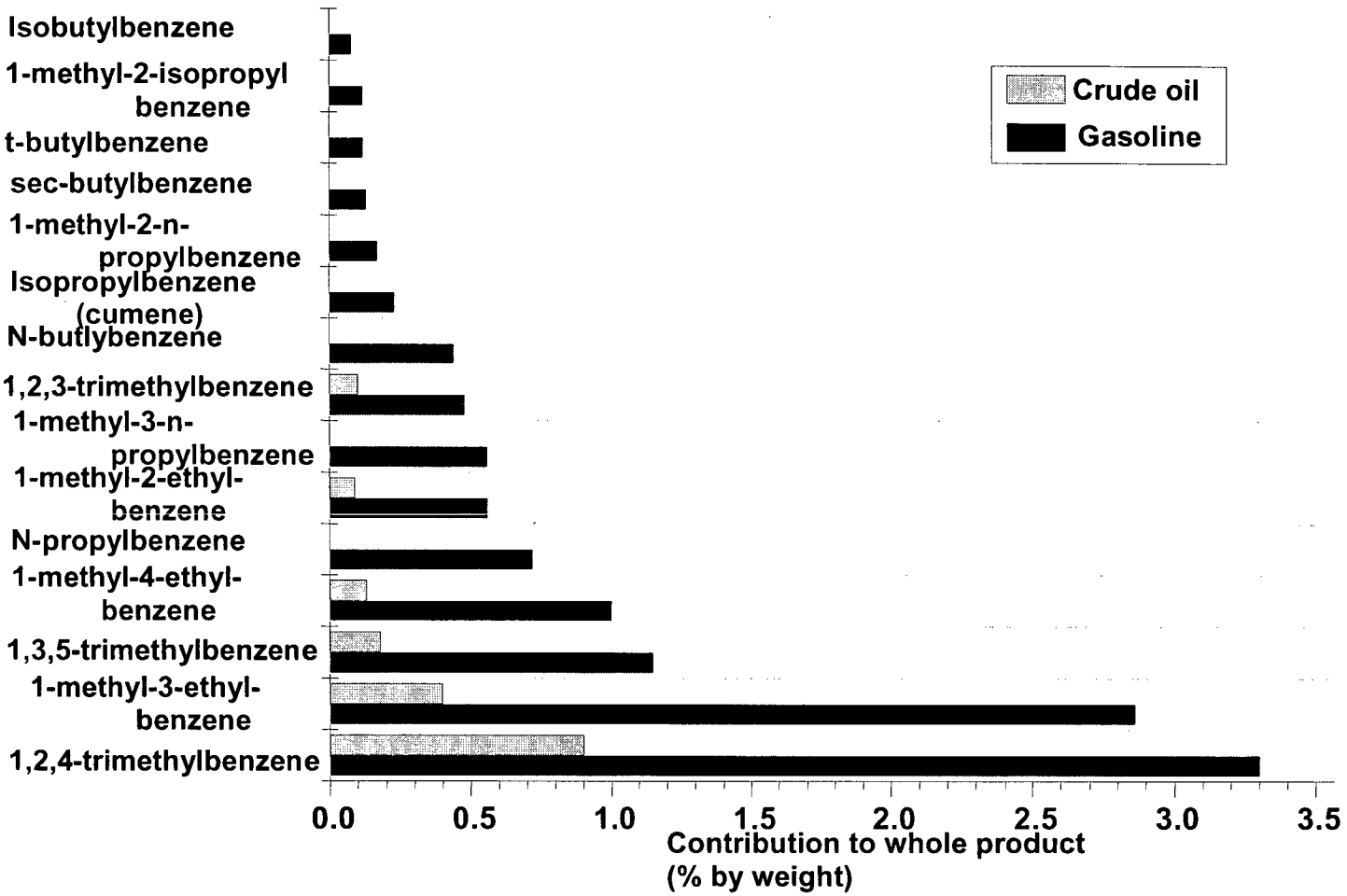


Figure 4.20: Relative abundance of different non-BTEX aromatics in F1.

Table 4.15: Compiled aquatic toxicity data for F1 alkylbenzenes.

Chemical Name	mol. Wt.	sol (mg/L)	H[c/c]	log Kow	Scientific Name	Common Name	Endpoint	Effect	Media Type	Test Duration	Duration Units	Concentration Mean (ug/L)	Author	Title
1,2,4-Trimethylbenzene	120.2	57	2.30E-01	3.60E+00	*Artemia salina*	Brine shrimp	LC50	MOR	SW	24	H	**12020**	ABERNETHY, S., A.M. BOBRA, W.Y. SHIU, P.G. WELLS, AND D. MACKAY	1986. Acute Lethal Toxicity of Hydrocarbons and Chlorinated Hydrocarbons to Two Planktonic Crustaceans: The Key Role of Organism-Water Partitioning.Aquat Toxicol 8(3):163-174 (Publ in Part As 11936)
1,2,4-Trimethylbenzene	120.2	57	2.30E-01	3.60E+00	*Daphnia magna*	Water flea	EC50	Immobil.	FW	48	H	**3606**	BOBRA, A.M., W.Y. SHIU, AND D. MACKAY	1983. A Predictive Correlation for the Acute Toxicity of Hydrocarbons and Chlorinated Hydrocarbons to the Water Flea (Daphnia magna). Chemosphere 12(9-10):1121-1129
1,2,4-Trimethylbenzene	120.2	57	2.30E-01	3.60E+00	*Pimephales promelas*	Fathead minnow	LC50	MOR	FW	96	H	**7720**	GEIGER, D.L., S.H. POIRIER, L.T. BROOKE, AND D.J. CALL	1986. Acute Toxicities of Organic Chemicals to Fathead Minnows (Pimephales promelas), Vol. 3. Center for Lake Superior Environmental Studies, University of Wisconsin, Superior, W I:328
Mesitylene (1,3,5-Trimethylbenzene)	120.2	50	3.15E-01	3.58	*Artemia salina*	Brine shrimp	LC50	MOR	SW	24	H	**14184**	ABERNETHY, S., A.M. BOBRA, W.Y. SHIU, P.G. WELLS, AND D. MACKAY	As above
Mesitylene	120.2	50	3.15E-01	3.58	*Carassius auratus*	Goldfish	LC50	MOR	FW	24	H	**20570**	BRENNIMAN, G., R. HARTUNG, W.J. WEBER, AND J	1976. A Continuous Flow Bioassay Method to Evaluate the Effect of Outboard Motor Exhausts and Selected Aromatic Toxicants on Fish. Water Res 10(2):165-169
Mesitylene	120.2	50	3.15E-01	3.58	*Carassius auratus*	Goldfish	LC50	MOR	FW	48	H	**16170**	BRENNIMAN, G., R. HARTUNG, W.J. WEBER, AND J	As above.
Mesitylene	120.2	50	3.15E-01	3.58	*Carassius auratus*	Goldfish	LC50	MOR	FW	72	H	**13650**	BRENNIMAN, G., R. HARTUNG, W.J. WEBER, AND J	As above.
Mesitylene	120.2	50	3.15E-01	3.58	*Carassius auratus*	Goldfish	LC50	MOR	FW	96	H	**12520**	BRENNIMAN, G., R. HARTUNG, W.J. WEBER, AND J	As above.
Mesitylene	120.2	50	3.15E-01	3.58	*Daphnia magna*	Water flea	LC0 (NOEC)	MOR	FW	24	H	**40000**	KUHN, R., M. PATTARD, K. PERNAK, AND A. WINTER	1989. Results of the Harmful Effects of Water Pollutants to Daphnia magna in the 21 Day Reproduction Test. Water Res 23(4):501-510.
Mesitylene	120.2	50	3.15E-01	3.58	*Daphnia magna*	Water flea	EC50	Immobil.	FW	24	H	**50000**	KUHN, R., M. PATTARD, K. PERNAK, AND A. WINTER	As above.
Mesitylene	120.2	50	3.15E-01	3.58	*Daphnia magna*	Water flea	EC50	Immobil.	FW	48	H	**6010**	BOBRA, A.M., W.Y. SHIU, AND D. MACKAY	As above.
Mesitylene	120.2	50	3.15E-01	3.58	*Daphnia magna*	Water flea	NOEC	REP	FW	21	D	**890**	KUHN, R., M. PATTARD, K. PERNAK, AND A. WINTER	As above.
Mesitylene	120.2	50	3.15E-01	3.58	*Scenedesmus subspicatus*	Green algae	EC10	absorb. @578 nm	FW	48	H	**8100**	KUHN, R. AND M. PATTARD	1990. Results of the Harmful Effects of Water Pollutants to Green Algae (Scenedesmus subspicatus) in the Cell Multiplication Inhibition Test. Water Res 24(1):31-38.

Chemical Name	mol. Wt.	sol (mg/L)	H[c/c]	log Kow	Scientific Name	Common Name	Endpoint	Effect	Media Type	Test Duration	Duration Units	Concentration Mean (ug/L)	Author	Title
Mesitylene	120.2	50	3.15E-01	3.58	*Scenedesmus subspicatus*	Green algae	EC50	absorb. @578 nm	FW	48	H	**25000**	KUHN, R. AND M. PATTARD	As above.
Mesitylene	120.2	50	3.15E-01	3.58	*Scenedesmus subspicatus*	Green algae	EC10	turbidity as est. of pop'n density	FW	48	H	**53000**	KUHN, R. AND M. PATTARD	As above.
Mesitylene	120.2	50	3.15E-01	3.58	*Scenedesmus subspicatus*	Green algae	EC50	turbidity as est. of pop'n density	FW	48	H	**53000**	KUHN, R. AND M. PATTARD	As above.
o-Ethyltoluene (1-methyl-2-ethylbenzene)	120.2	75	2.14E-01	3.63	*Chlamydomonas angulosa*	Green algae	EC50	PHY	NR	3	H	**18631**	HUTCHINSON, T.C., J.A. HELLEBUST, D. TAM, D. MACKAY, R.A. MASCARENHAS, AND W.Y. SHIU	1980. The Correlation of the Toxicity to Algae of Hydrocarbons and Halogenated Hydrocarbons with Their Physical-Chemical Properties. Environ Sci Res 16:577-586.
o-Ethyltoluene	120.2	75	2.14E-01	3.63	*Chlorella vulgaris*	Green algae	EC50	PHY	NR	3	H	**40868**	HUTCHINSON, T.C., J.A. HELLEBUST, D. TAM, D. MACKAY, R.A. MASCARENHAS, AND W.Y. SHIU	As above.
p-Ethyltoluene (1-methyl-4-ethylbenzene)	120.2	94	2.02E-01	3.63	*Chlamydomonas angulosa*	Green algae	EC50	PHY	NR	3	H	**54090**	HUTCHINSON, T.C., J.A. HELLEBUST, D. TAM, D. MACKAY, R.A. MASCARENHAS, AND W.Y. SHIU	As above.
p-Ethyltoluene	120.2	94	2.02E-01	3.63	*Chlorella vulgaris*	Green algae	EC50	PHY	NR	3	H	**48080**	HUTCHINSON, T.C., J.A. HELLEBUST, D. TAM, D. MACKAY, R.A. MASCARENHAS, AND W.Y. SHIU	As above.
Propyl benzene (n-propylbenzene)	120.2	52	4.20E-01	3.69	*Chlamydomonas angulosa*	Green algae	EC50	PHY	NR	3	H	**18030**	HUTCHINSON, T.C., J.A. HELLEBUST, D. TAM, D. MACKAY, R.A. MASCARENHAS, AND W.Y. SHIU	As above.
Propyl benzene	120.2	52	4.20E-01	3.69	*Chlorella vulgaris*	Green algae	EC50	PHY	NR	3	H	**16227**	HUTCHINSON, T.C., J.A. HELLEBUST, D. TAM, D. MACKAY, R.A. MASCARENHAS, AND W.Y. SHIU	As above.

Chemical Name	mol. Wt.	sol (mg/L)	H[c/c]	log Kow	Scientific Name	Common Name	Endpoint	Effect	Media Type	Test Duration	Duration Units	Concentration Mean (ug/L)	Author	Title
Propyl benzene	120.2	52	4.20E-01	3.69	*Daphnia magna*	Water flea	LC50	MOR	FW	24	H	**2000**	TOSATO, M.L., L. VIGANO, B. SKAGERBERG, AND S. CLEMENT	1991. A New Strategy for Ranking Chemical Hazards. Framework and Application. Environ Sci Technol 25:695-702.
Propyl benzene	120.2	52	4.20E-01	3.69	*Oncorhynchus mykiss*	Rainbow trout,donaldson trout	LC50	MOR	FW	96	H	**1550**	GALASSI, S., M. MINGAZZINI, L. VIGANO, D. CESAREO, AND M.L. TOSATO	As above.
Propyl benzene	120.2	52	4.20E-01	3.69	*Selenastrum capricornutum*	Green algae	EC50	GRO	FW	72	H	**1800**	GALASSI, S., M. MINGAZZINI, L. VIGANO, D. CESAREO, AND M.L. TOSATO	As above.
Cumene (isopropylbenzene)	120.2	50	5.92E-01	3.63	*Artemia*	Brine shrimp	EC50	ITX	FW	48	H	**7400**	MACLEAN, M.M. AND K.G. DOE	1989. The Comparative Toxicity of Crude and Refined Oils to Daphnia magna and Artemia. Environment Canada, EE-111, Dartmouth, Nova Scoti a:64
Cumene	120.2	50	5.92E-01	3.63	*Artemia*	Brine shrimp	EC50	ITX	FW	48	H	**7500**	MACLEAN, M.M. AND K.G. DOE	As above.
Cumene	120.2	50	5.92E-01	3.63	*Artemia*	Brine shrimp	LC50	MOR	FW	48	H	**7400**	MACLEAN, M.M. AND K.G. DOE	As above.
Cumene	120.2	50	5.92E-01	3.63	*Artemia*	Brine shrimp	LC50	MOR	FW	48	H	**8000**	MACLEAN, M.M. AND K.G. DOE	As above.
Cumene	120.2	50	5.92E-01	3.63	*Artemia salina*	Brine shrimp	LC50	MOR	SW	24	H	**13703**	ABERNETHY, S., A.M. BOBRA, W.Y. SHIU, P.G. WELLS, AND D. MACKAY	As above.
Cumene	120.2	50	5.92E-01	3.63	*Artemia salina*	Brine shrimp	LC50*	MOR	SW	24	H	**1E+05**	PRICE, K.S., G.T. WAGGY, AND R.A. CONWAY	1974. Brine Shrimp Bioassay and Seawater BOD of Petrochemicals. J Water Pollut Control Fed 46(1):63-77.
Cumene	120.2	50	5.92E-01	3.63	*Chlamydomonas angulosa*	Green algae	EC50	PHY	NR	3	H	**8775**	HUTCHINSON, T.C., J.A. HELLEBUST, D. TAM, D. MACKAY, R.A. MASCARENHAS, AND W.Y. SHIU	As above.
Cumene	120.2	50	5.92E-01	3.63	*Chlorella vulgaris*	Green algae	EC50	PHY	NR	3	H	**21275**	HUTCHINSON, T.C., J.A. HELLEBUST, D. TAM, D. MACKAY, R.A. MASCARENHAS, AND W.Y. SHIU	As above.
Cumene	120.2	50	5.92E-01	3.63	*Daphnia magna*	Water flea	EC50	ITX	FW	24	H	**1400**	TOSATO, M.L., L. VIGANO, B. SKAGERBERG, AND S. CLEMENT	As above.
Cumene	120.2	50	5.92E-01	3.63	*Daphnia magna*	Water flea	EC50	ITX	FW	48	H	**601**	BOBRA, A.M., W.Y. SHIU, AND D. MACKAY	As above.

Chemical Name	mol. Wt.	sol (mg/L)	H[c/c]	log Kow	Scientific Name	Common Name	Endpoint	Effect	Media Type	Test Duration	Duration Units	Concentration Mean (ug/L)	Author	Title
Cumene (listed as "cumol" in German)	120.2	50	5.92E-01	3.63	*Daphnia magna*	Water flea	LC0	MOR	FW	24	H	**83000**	BRINGMANN, G. AND R. KUHN	1977. The Effects of Water Pollutants on Daphnia magna. Z Wasser-Abwasser-Forsch 10(5):161-166 (GER) (ENG ABS).
Cumene (listed as "cumol" in German)	120.2	50	5.92E-01	3.63	*Daphnia magna*	Water flea	LC50	MOR	FW	24	H	**95000**	BRINGMANN, G. AND R. KUHN	As above.
Cumene (listed as "cumol" in German)	120.2	50	5.92E-01	3.63	*Daphnia magna*	Water flea	LC100	MOR	FW	24	H	**1E+05**	BRINGMANN, G. AND R. KUHN	As above.
Cumene	120.2	50	5.92E-01	3.63	*Oncorhynchus mykiss*	Rainbow trout,donaldson trout	LC50	MOR	FW	96	H	**2700**	GALASSI, S., M. MINGAZZINI, L. VIGANO, D. CESAREO, AND M.L. TOSATO	As above.
Cumene	120.2	50	5.92E-01	3.63	*Pimephales promelas*	Fathead minnow	LC50	MOR	FW	96	H	**6320**	GEIGER, D.L., S.H. POIRIER, L.T. BROOKE, AND D.J. CALL	As above.
Cumene	120.2	50	5.92E-01	3.63	*Poecilia reticulata*	Guppy	LC50	MOR	FW	96	H	**5100**	GALASSI, S., M. MINGAZZINI, L. VIGANO, D. CESAREO, AND M.L. TOSATO	As above.
Cumene	120.2	50	5.92E-01	3.63	*Selenastrum capricornutum*	Green algae	EC50	GRO	FW	72	H	**2600**	GALASSI, S., M. MINGAZZINI, L. VIGANO, D. CESAREO, AND M.L. TOSATO	As above.
tert-Butylbenzene	134.2	30	5.17E-01	4.11	*Daphnia magna*	Water flea	LC50	MOR	FW	24	H	**41000**	BRINGMANN, G. AND R. KUHN	As above.
Isobutyl benzene	134.2	10.1	1.34	4.01	*Chlamydomonas angulosa*	Green algae	EC50	PHY	NR	3	H	**3087**	HUTCHINSON, T.C., J.A. HELLEBUST, D. TAM, D. MACKAY, R.A. MASCARENHAS, AND W.Y. SHIU	As above.
Isobutyl benzene	134.2	10.1	1.34	4.01	*Chlorella vulgaris*	Green algae	EC50	PHY	NR	3	H	**3490**	HUTCHINSON, T.C., J.A. HELLEBUST, D. TAM, D. MACKAY, R.A. MASCARENHAS, AND W.Y. SHIU	As above.

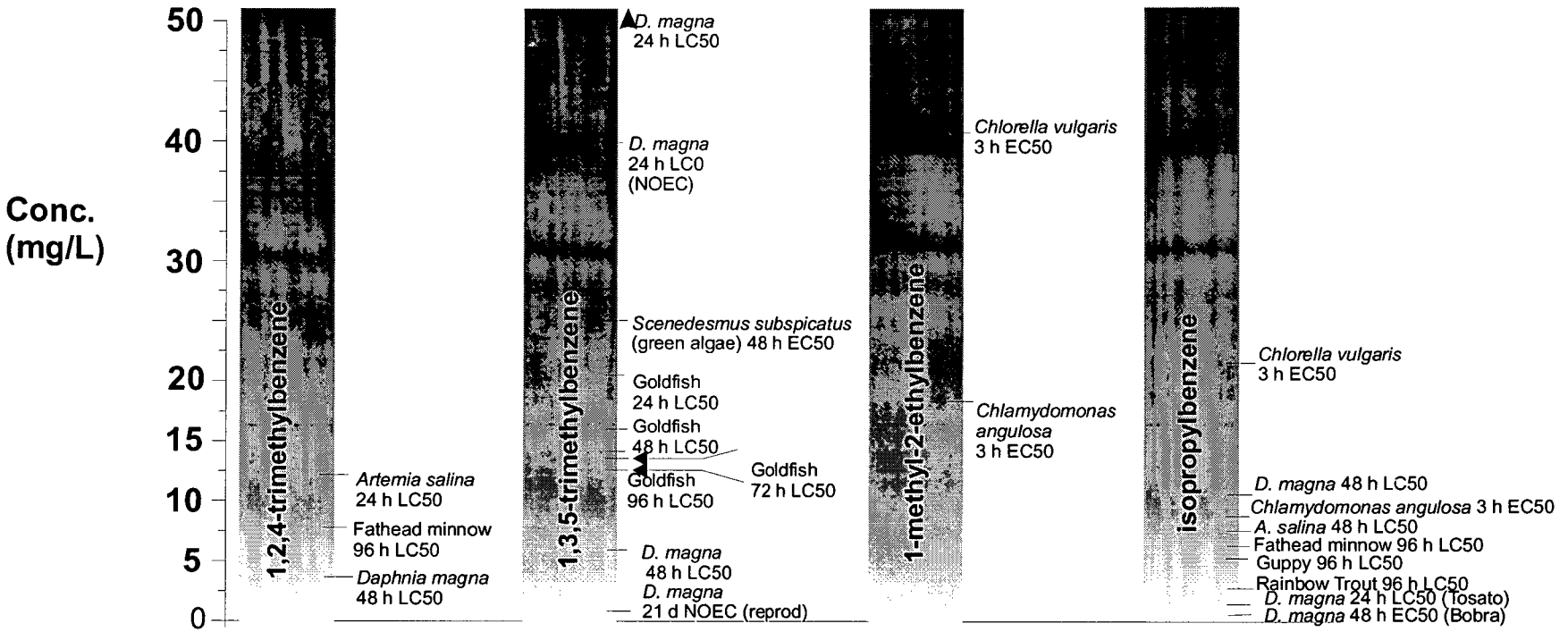


Figure 4.21: Illustration of the aquatic toxicity of alkylbenzenes.

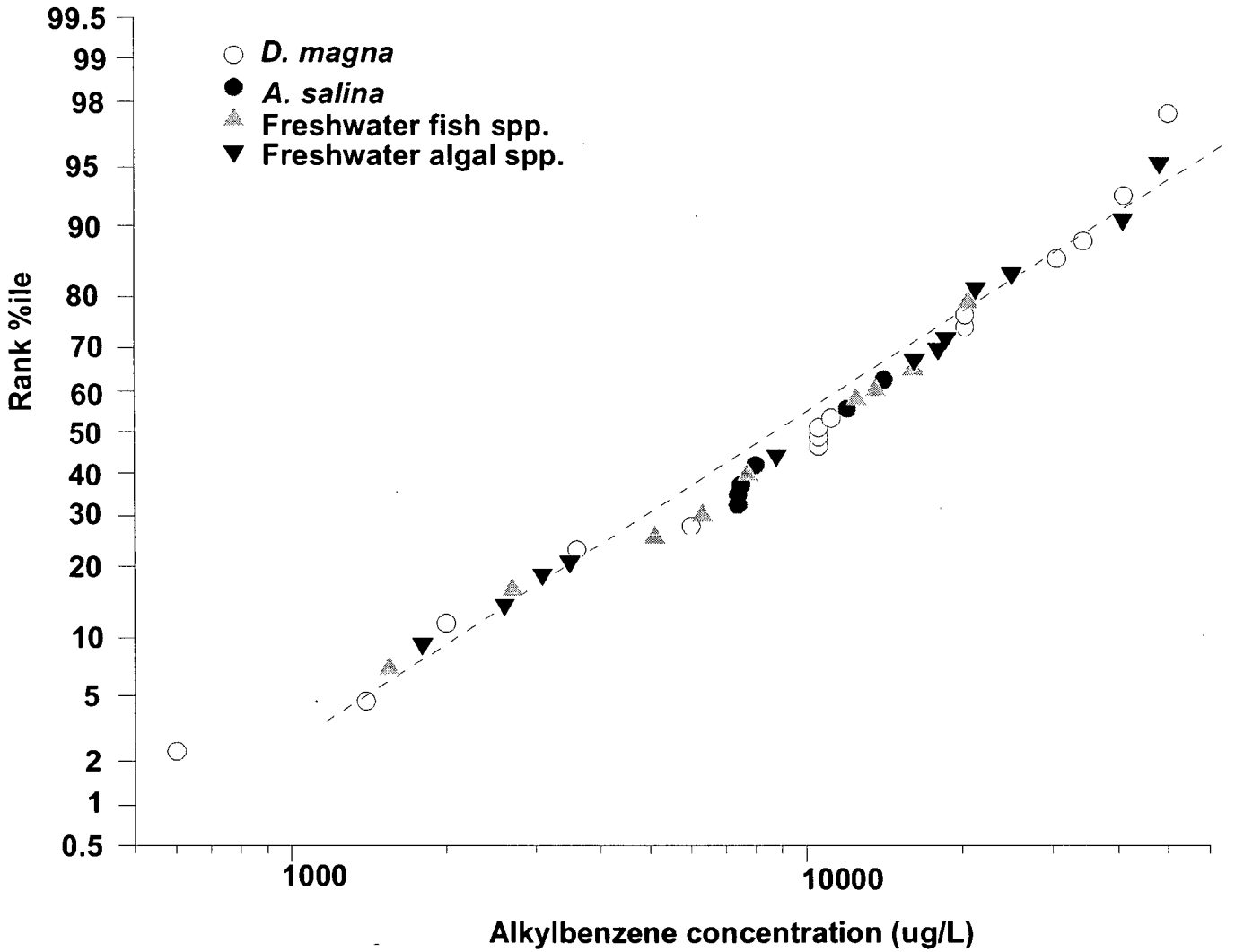


Figure 4.22: Re-constructed aquatic species sensitivity distribution based on the available toxicity data for alkylbenzenes.

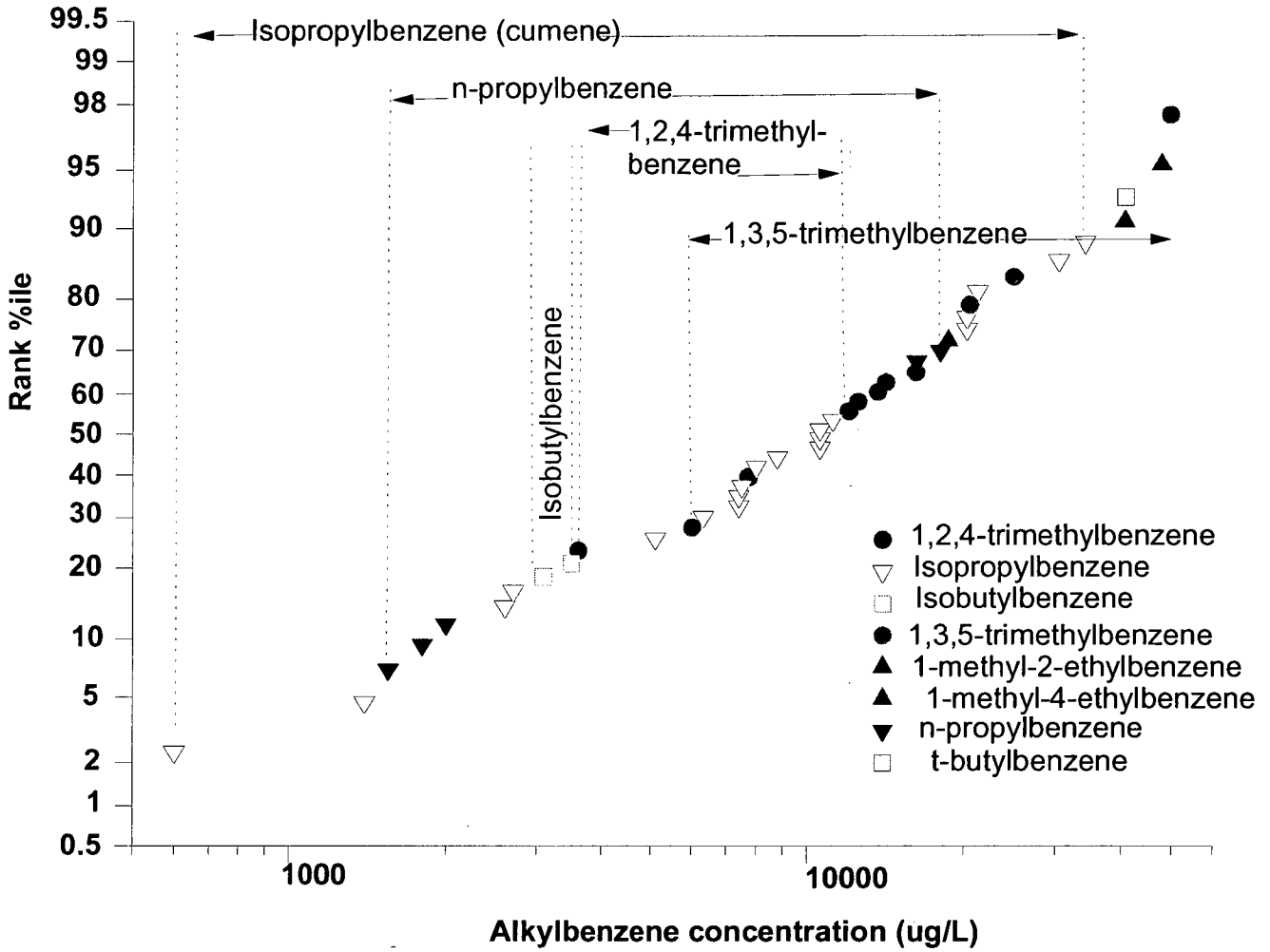


Figure 4.23: Re-constructed aquatic species sensitivity distribution based on the available toxicity data for alkylbenzenes – Relative toxicity of different alkylbenzenes.

The combined aliphatics and aromatics draft toxicity reference value for CWS F1, therefore, was modified as follows:

$$\textit{Toxicity Reference Value (CWS F1- Draft)} = \frac{1}{[(0.8/185\ \mu g/L.)+(0.2/120\ \mu g/L)]}$$

$$= 167\ \mu g/L$$

Within British Columbia, Contaminated Sites Soils Taskgroup policy decisions further allow for a ten-fold dilution within an initial mixing zone once the contaminant has reached the surface water body. A ten-fold dilution was not used herein, since policy decisions regarding allowances for dilution within the receiving environment vary across jurisdictions within Canada.

4.3.2.2 The Critical Body Residues Approach. Michelson (1997) recently refined a regulatory approach for establishing narcosis-type toxicity thresholds based on the internalized 'dose' of lipophilic substances. Such an approach is well suited for evaluating and managing the risks of complex, predominantly hydrophobic mixtures such as petroleum hydrocarbons. Michelson's (1997) work builds on studies and suggested approaches by Golder Associates and McCarty (1995), which are in turn based on studies by Abernathy et al. (1988), McCarty and Mackay, (1993), (McCarty, 1991) and EPA (1988). These authors have variously demonstrated and established conceptual models asserting that narcotic effects of hydrophobic organic contaminants occur at similar levels for different taxa as well as different compounds when the 'dose' is expressed based on the cumulative molar fraction of the contaminant(s) taken up into lipid membranes. A dose expressed in this form has been termed the "critical body residue" (CBR).

Narcosis is a long-recognized, non-specific type of toxicity, in which the internalization of lipophilic contaminants in lipid-rich structures in an organism broadly interferes with a myriad of biochemical functions. For example, critically high residues of hydrophobic organic contaminants in the lipid bilayer cell membrane of nerve fibres within animals could adversely affect membrane potential, depolarization and re-polarization, nerve transition, and ultimately behavioural and locomotory function. Manifestations of narcosis in animals might include lethargy and anaesthetic-type effects. Strictly speaking, narcosis occurs only in animals (protozoa and metazoa); however, there are undoubtedly functional equivalents in algae, plants, and fungi. Any internalization of lipophilic contaminants into the lipid bilayer membranes of cells and organelles in living organisms at critically high concentrations is expected to be accompanied by an increased potential for disruption of the fluid mosaic, including embedded proteins.

The "critical body residues" (CBR) approach is predicated on the following assumptions:

- A major component of the toxicity of PHCs to aquatic life is via narcosis-type effects. This ignores more specific toxicological mechanisms based on toxicant-molecular receptor interactions, such as endocrine disruption, MFO induction, mutagenesis, or carcinogenesis.

- The risks of narcosis are directly related to the cumulative molar fraction of all lipophilic toxicants taken up into lipid pools within an organism, and the tendency of different toxicants to induce narcosis once internalized in lipid is similar.

- The concentration of hydrophobic contaminants in internal lipid pools of aquatic organisms at any given time is related to equilibrium partitioning from the exposure medium.

- The risks are much less directly related to the actual concentration in water of individual toxicants or mixtures thereof; the internalized dose (on a molar/lipid weight basis) is a much better predictor of narcotic effects.

- Toxicants are neither substantially metabolized nor eliminated from internal lipid pools. While we know that this is not true for the major portion of organic contaminants, and is highly dependent of phyletic differences, the assumption is conservative and thus protective by driving a routine over-estimate of CBR toxicity.

As stated by Michelson (1997) –

> "In addition, the narcotic effect is not dependent on the specific lipophilic chemical or chemicals present (Call *et al.*, 1985). Various studies (Ferguson, 1939; McGowan, 1952; Hermens *et al.*, 1984; Hermens *et al.*, 1985a,b; Deneer *et al.*, 1988) have demonstrated that the narcotic effect is instead related to the total number of foreign molecules present, and therefore effects in tissue can be predicted from the total molar concentration of contaminants in the tissue. Thus it is not necessary to know the identity or toxicity of each individual chemical, just the molar concentration of all the chemicals in tissue combined".

In the context of soil quality guidelines, the CBR approach would be viable if –

- firstly, there is a definable CBR below which risks from narcosis to aquatic life are likely to be negligible;

- secondly, the CBR can be related to concentrations of the toxicant(s) in the surrounding medium;

- thirdly, the major uptake pathway for CBRs is from the surrounding water (as opposed to through diet or from sediments); and,

- fourthly, threshold soil contaminant concentrations can reasonably be predicted from water ambient concentrations using an appropriate fate and transport model.

The third and fourth requirements hold for both a CBR-based and other approaches for the derivation of soil quality guidelines that are protective of aquatic life.

Critical body residues have been related to concentrations of various contaminants in the surrounding water through the development of and subsequent predictive use of fugacity-type approaches and physical-chemical properties. This is an approach that has a long history of use in environmental fate and toxicity studies, spanning more than three decades. The critical body residue is related to the concentration in the surrounding water for any given contaminant based primarily on its octanol-water partition co-efficient (K_{ow}), which is expected to be directly equivalent to the chemical specific bioconcentration factor. This, in turn, assumes that octanol is a reasonable surrogate for functional lipids in the myriad of aquatic life, an assertion that has been challenged by some researchers.

Non-polar contaminant body residues are based on contaminant molar concentrations in lipid, as follows:

$$BR_L = C_W \times BCF_l$$
$$= C_W \times K_{ow}$$

where:

BR_L	=	body residue, expressed as molar concentration in the lipid (mmol/kg lipid)
C_W	=	concentration in the water (mmol/L)
BCF_l	=	lipid-normalized bioconcentration factor (unitless)
K_{ow}	=	octanol-water partitioning coefficient (unitless)

The second of the two equations assumes that the lipid-normalized BCF is essentially equal to the K_{ow}, which in turn is based on an assumption that octanol is a very similar substance to lipid tissues, and can be used as a surrogate for lipid partitioning. Michelson (1997) reviews the scientific support for this assumption.

A body residue value based on whole tissue wet weight rather than lipid-normalized weight could also be used, provided that percent lipid (by weight) is measured and subsequently applied; however, this further complicates the task of deriving generically protective contaminant benchmarks, since different organisms vary in their lipid content.

Michelson (1997) discusses the range of BR_Ls for at which narcosis-type effects are likely to be manifested. The following is excerpted without amendment:

> "Much of the literature is reported as whole-body critical body residues (CBRs) at which acute mortality is observed. However, lipid content is generally also reported, allowing calculation of lipid-normalized CBRs. The whole body acute CBR is reported to range from approximately 2-8 mmol/kg wet tissue (McCarty and Mackay, 1993; McCarty, 1991; van Hoogan and Opperhuizen, 1998; Carlson and Kosian, 1987; McKim and Schmieder, 1991). Lipid-normalization of these values (using actual lipid data provided in the references), along with additional lipid-normalized values in the literature (Abernathy et al., 1998; van Wezel et al., 1995), produces a range of lipid-normalized acute CBRs of 30-200 mmol/kg-lipid.
>
> State and federal water quality laws require that water quality standards be protective of both acute and chronic toxicity. Chronic exposure by benthic organisms to a groundwater plume continuously discharging into surface water would be expected, so it is reasonable to set a tissue criterion that represents a chronic narcosis endpoint. Fewer data are available on chronic CBRs, and none are lipid-normalized. Whole-body chronic CBRs are reported in McCarty and Mackay (1993), Donkin et al. (1989), Carlson and Kosian (1987), Borgmann et al. (1990), Mayer et al. (1977), Mauck et al. (1978) and Opperhuizen and Schrap (1988), producing a range of 0.2 - 0.8 mmol/kg (wet tissue) and an acute-chronic ratio of 10. An acute-chronic ratio of about 10 has been reported by a number of researchers for a wide variety of organisms (Abernathy et al. 1988; McCarty, 1986; Call et al., 1985)."

Based on this analysis, a lipid-based CBR of 30-200 mmol/kg-lipid might be used as a basis for establishing aquatic life acute toxicity reference values for petroleum hydrocarbons. As discussed, chronic toxicity based on narcosis would be expected to occur over a lower range of body residues.

It was of interest to evaluate whether this approach would lead to more or less conservative water-based levels of F1 and F2 PHCs relative to the previously described approach (Section 4.3.2.1). Hence, the available aquatic toxicity data for alkylbenzenes (Table 4.15) were converted first to molar concentrations in water, and subsequently to lipid-based body residue concentrations, by assuming that the bioconcentration factor is directly equivalent to the K_{ow} for each of the alkylbenzenes.

The reconstructed species sensitivity distribution based on the available toxicity data as plotted in Figure 4.22 was re-plotted (Figure 4.24), with dose expressed as BR_L instead of as the concentration in water. Also indicated on the figure is the expected CBR range as defined by Michelson (1997)

The conversion of the water-based, chemical-specific toxicity data to critical body residue values did not substantively affect the spread in the data. The variability in

experimentally derived acute toxicity was around two orders of magnitude regardless of whether it was expressed based on water concentration (µg/L) or as a CBR (mmol/kg-lipid). The relative ranking of the various data points was not substantively altered either.

It is concluded, therefore, that for C9-C10 alkylbenzenes, and expression of dose that accounts for differences in potential for bioaccumulation and evaluation of toxicity on a molar rather than gravimetric basis did not substantively alter perceptions about toxicity (nor the value of F1 aromatic PHCs in water on which to model acceptable soil concentrations). A different result may have been achieved had the CBR approach been applied to mixtures of narcotic compounds with a much larger variation in K_{ow} or molecular weight (e.g. – if one were interested in the combined narcotic effects of F1 and F2 PHCs, or if the preceding analyses were conducted on the larger range of aliphatics and aromatics likely to be found in CWS F1.

The CBR acute threshold as defined by Michelsen (20-300 mmol/kg-lipid) falls at the lower end of the range of CBR estimates from experimentally derived data. This would be expected, since – as previously stated – it is derived based on some conservative assumptions. This approach merits additional development.

Only one toxicity data point was observed at a concentration lower than the lowest range of the CBR. As discussed in Section 4.3.2.1, *Daphnia magna* exposed to isopropylbenzene (cumene) exhibited a 48 h EC_{50} for immobilization of 5 mmol/m^3, or 601 µg/L [the lower and upper 95% confidence interval estimates for the EC50 value as provided Bobra *et al* (1983) was 1 mmol/m^3 and 30 mmol/m^3, respectively – underscoring the limited confidence in the accuracy of this endpoint]. There is no technical basis, however, in light of the methods description in the Bobra *et al.* paper for the exclusion of this data point when considering alkylbenzene toxicity. It is, nonetheless, recognized to be an outlier relative to the larger probability distribution. In section 4.3.2.1, the uncertainty factor applied in extrapolating from a sub-chronic to chronic endpoint was adjusted in light of this.

Di Toro *et al.* (2000) recently applied the critical body residue approach to develop water quality criteria for narcotic contaminants in general, and PAHs in particular. The reader is referred to the original paper for a state-of-the-science validation and application of the CBR approach. The authors note that, while the underlying mechanisms of toxicity are similar across widely different aquatic animal taxa, there are variations in toxicity and the CBR associated with acute toxicity. Such variation is

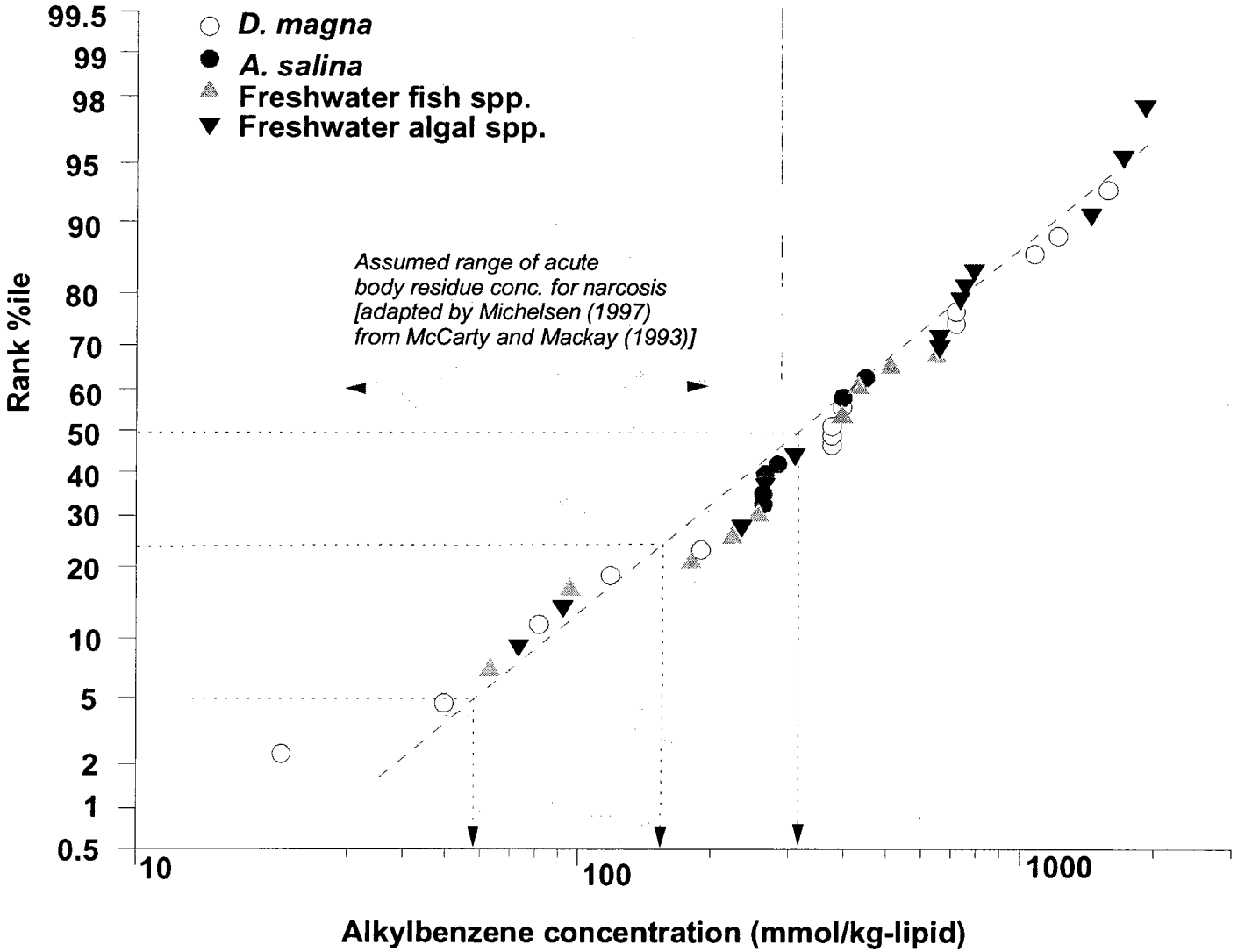


Figure 4.24: Range of critical body residues calculated from experimentally derived acute toxicity (primarily LC_{50}) endpoints for alkylbenzenes. [NB: plant endpoints were acute impairment of photosynthetic pigments (absorbance) and cell division (culture turbidity)].

predictable, however, and Di Toro *et al.* provide validated models that account for the inter-taxon variability. The authors provide a species sensitivity distribution for toxicity based on body burden, develop multi-species thresholds based on the 5th %ile of the ranked data (as specified in the USEPA guidelines for establishing water quality criteria), and provide a universal acute-chronic ratio adjustment.

Table 4.16 is adapted from Di Toro *et al.* (2000), and shows the "Final Chronic Values for Narcotic Chemicals" as calculated using the CBR approach, and based on application of an acute-chronic ratio (ACR) of 5.09. This ACR was derived as the geometric mean value of 35 data pairs of acute and chronic toxicity, encompassing 20 individual chemicals and six distinct aquatic species of animals.

Table 4.16: Final chronic values for narcotic contaminants and aquatic life - Lipid-based tissue residue concentration thresholds for chronic toxicity across multiple taxa (mmol/kg-lipid).

Chemical Class					
Baseline	**Halogenated Baseline**	**Ketones**	**Halogenated Ketones**	**PAHs**	**Halogenated PAHs**
6.94	3.96	3.95	2.25	3.79	2.16

Among the above-listed CBR-based chronic toxicity thresholds for aquatic life, the value for PAHs is most directly applicable to CWS F1 or F2 petroleum hydrocarbon constituents in general. In the absence of more detailed evaluation, however, a chronic CBR-based value of 3.0 mmol/kg-lipid appears to be a reasonable threshold for protection against adverse aquatic effects due to narcosis.

Using a chronic CBR-based toxicity threshold of 3.0 mmol/kg-lipid, it is then possible to calculate a toxicity reference value (C_w) for each of the TPHCWG sub-fractions that make up CWS F1 or F2. As shown above -

$$C_W = \frac{BR_L}{K_{ow}}$$

Table 4.17: Derivation of sub-fraction chronic toxicity reference values using a CBR-based chronic tissue residue benchmark of 3.0 mmol/kg-lipid.

TPHCWG sub-fraction	$logK_{OC}$ [A]	$logK_{OW}$ [B]	Mol. Wt.[A] (g/mole)	Solubility (mg/L)	C_W - Estimated CBR-based tox. ref. value (µg/L)
Aliphatics					
AlC6-8	3.6	3.81	100	5.4	46.5
AlC8-10	4.5	4.71	130	0.43	7.6
AlC10-12	5.4	5.61	160	0.034	1.18
AlC12-16	6.7	6.91	200	0.00076	0.074
Aromatics					
ArC8-10	3.2	3.41	120	65	140
ArC10-12	3.4	3.61	130	25	96
ArC12-16	3.7	3.91	150	5.8	55.4

A: from TPHGWG Vol. 3

B: Based on empirical relationship between Koc and Kow developed by Karickhoff *et al.* (1979).

4.3.2.3 Final Reconciliation of Approaches. The F1 (167 µg/L) and F2 (42 µg/L) toxicity reference values developed in Section 4.3.2.1 were compared to LC_{50} values for a variety of whole products, including fuel oil #2 and gasoline. The whole product LC_{50}s for a variety of fish or invertebrate species were in the range of 1,500 to > 560,000 µg/L (Table 4.18).

These lethality endpoints for whole products are generally an order of magnitude or more higher than the previously documented F1 and F2 toxicity reference values; however, sub-lethal effects endpoints are generally considered to be more appropriate for the calculation of environmentally protective thresholds than mortality endpoints. In addition, it is not unreasonable to assume that chronic sensitivity to PHCs and more sensitive toxicity endpoints (e.g. reproduction) would be up to an order of magnitude or more lower than acute mortality thresholds.

Using gasoline as comparable with F1, the lowest LC_{50} was 1,500 µg/L (for grass shrimp; based on five fish or invertebrate spp. total). If this is divided by an uncertainty factor (UF) of 20 to account for the fact that LC_{50} endpoints were the only ones available and to account for the likelihood that at least some species may be lower on the overall species sensitivity distribution, then a whole product toxicity reference value would be around 75 µg/L. If a 10-fold UF is applied (assuming that inter-taxon variability has been adequately addressed based on the species examined and choice of the lowest relevant LC50) the value derived is 150 µg/L - not far different from 167 ug/L.

Table 4.18: PHC Whole Product literature values for toxicity to aquatic life (adapted from MacFarlane and Fox, Jan. 7, 2000).

Product	Organism	LC_{50} value (µg/L)	Ref.
Fuel Oil #2	Juvenile American Shad	2E+05	A
	Bluegill	9.8e+3 to >1.8e+5	"
	Banded Killifish	1.1e+3 to 2.9e+4	"
	Striped Bass	9.1e+2 to 3.1e+4	"
	Pumpkin Seed	1.1e+3 to 4.3e+4	"
	White Perch	1.4e+3 to 4.2e+4	"
	American Eel	4.6e+3 to 2.8e+4	"
	Carp	6.2e+3 to 5.3e+4	"
	Rainbow trout (eggs)	1.2e+4 to 2.0e+4	"
	Gulf Menhaden	7.0e+5	"
	Sand Lance	5.8e+3 to 1.4e+4	"
	Striped Mullet	3.2e+5 to > 5.6e+5	"
	Mullet	1.3e+4	"
	Menhaden	5e+3	"
	Grass Shrimp	2e+3	"
	Paleomonetes vulgaris	1.8e+5	"
Gasoline	Rainbow trout	4.0e+4 to 1.0e+5	"
	Salmon fingerling	1.0e+5	"
	Juvenile American shad	6.8e+4 to >1.1e+5	"
	Mullet	2e+3 to 4e+4	"
	Menhaden	2e+3	"
	Grass Shrimp	1.5e+3	"
Diesel	*Daphnia magna*	7.2e+3	B
"	*Salmo gairdneri* (= *O. mykiss)*	2.5e+3	C
#2 Fuel Oil	*Daphnia magna*	2.2e+3	B
Leaded gasoline	" "	5.4e+3	"
Unleaded gasoline	" "	5.0e+4	B
" "	*Salmo gairdneri* (= *O. mykiss)*	5.4e+3	C
New crankcase oil	*Daphnia magna*	3.8+2	B
Used crankcase oil	" "	4.9e+4	"

References" A) 1997 Micromedex Inc., Vol. 32 OHM/TADS – Oils and Hazardous Materials/Technical Assistance Data System; B) MacLean (1988), as summarized in MADEP (1996); C) Lockhart (1987), as summarized in MADEP (1996)

For F2, diesel and fuel oil #2 have some relevance. The lowest tabulated LC50 was 1,100 µg/L. Using an UF of 10, a whole product toxicity threshold of 110 µg/L is calculated. Using 20-fold UF, a toxicity threshold of 55 µg/L is calculated (close to but still higher than the originally 'calculated' 42 µg/L).

We might expect that the whole product toxicity data, surrogate-based toxicity data and CBR-based water concentrations would be similar provided that a petroleum product has been introduced directly to surface water at a sufficiently low concentration that the proportion of constituents in the bioavailable water-accommodated fraction is similar to that of the original mixture, at least within the EC range encompassed by each of CWS F1 and F2. For example, a lower value for F2 than for F1 would be expected based on a Critical Body Residue approach - since the potential for bioconcentration increases from F1 to F2.

Using a CBR approach, the aromatics toxicity reference value derived for C8-C10 aromatics based on an assumed chronic threshold body residue of 3.0 mmol/kg-lipid was 140 µ/L (Table 4.17). This compares favourably with a threshold toxicity reference value of alkylbenzenes as discussed in Section 4.3.2.1 based on dividing the Bobra *et al.* (1983) 48 h EC_{50} value of 601 µg/L by an uncertainty factor of five, to arrive at a chronic value of 120 µg/L.

The preceding discussion illustrates that different approaches for defining aquatic toxicity provide similar conclusions regarding toxicological thresholds, at least where aquatic organisms have been directly exposed to the narcotic contaminant suite of interest. In light of the need to also account for compositional change between source and aquatic receptor, due to differential partitioning in along subsurface pathways, the use of a CBR approach was chosen for subsequent modeling. This allowed the derivation of a chronic toxicity reference value for each of the TPHCWG sub-fractions, and therefore better accounted for compositional change during leaching into groundwater and subsurface transport than if a single toxicity reference values had been used for each of CWS PHC fractions F1 and F2.

In conclusion, the water quality benchmarks for the TPHCWG sub-fractions, as shown in Table 4.17 were used in the modeling exercise: i.e. -

CWS F1

TPHCWG Aliphatics C6-8	46.5 µg/L
TPHCWG Aliphatics C8-10	7.6 µg/L
TPHCWG Aromatics C8-10	140 µg/L

CWS F2

TPHCWG Aliphatics C10-12	1.18 µg/L
TPHCWG Aliphatics C12-16	0.074 µg/L
TPHCWG Aromatics C10-12	96 µg/L
TPHCWG Aromatics C12-16	55.4 µg/L

4.3.3 Estimation of PHC Toxicity to Livestock Based on Drinking Water Uptake From a Surface Water Body

A literature review was undertaken of the documented effects of petroleum hydrocarbons on livestock, based on ingestion-type studies. Cattle, in particular, might be exposed to PHCs through:

- ingestion of contaminated surface soils, especially during grazing;
- ingestion of contaminated plants, where there has been uptake from the soil;
- internalization through drinking water from surface dugouts and other water bodies affected by PHC-contaminated soils;
- dermal absorption; and
- inhalation in the vapour phase.

For a multi-media exposure, CCME (1996) established an allocation factor for the allowable or threshold dose of 0.75 based on the evaluation of contaminated soil and plants in isolation from the other three pathways. This allocation factor is set based on the recognition that these are likely to be the quantitatively the major contributors to internalized dose. For PHCs, many scientific studies have shown that the phyto-accumulation is very limited, suggesting that soil ingestion alone will account for the vast majority of the contribution to internal dose at the majority of PHC-contaminated agricultural sites.

Dermal absorption is thought to have very limited contribution to contaminant exposure in terrestrial mammals with thick coats, including cows, except where the contaminant is directly ingested from the skin through grooming activities. In addition, vapour-phase accumulation is assumed herein to be a minor contributor to expected dose, relative to direct soil and water ingestion.

This section provides estimates of toxicological thresholds based on chronic drinking water ingestion by livestock, especially cattle. An allocation factor of 0.2 is assumed, recognizing that cattle inhabiting an area where PHCs have been released may also be exposed through the other four pathways, and may also experience limited background exposure, especially through proximity to farm machinery being operated and maintained.

A limited number of studies are available with which to estimate a "Daily Threshold Effects Dose" for livestock drinking water ($DTED_{LDW}$). In particular, Coppock and Campbell, in Chalmers (1999), provided a thorough and up-to-date review of PHC risks to livestock. This document should be consulted for more information on the state of the science. There is a large body of published information, especially in veterinary journals, on the accidental poisoning of livestock, often through the ingestion of mineral spirit carriers for topical remedies applied to the coat, or through the direct ingestion of

petroleum products such as mogas or diesel. Many of these studies provide details of symptoms and acute pathology, which may be diagnostic of PHC poisoning.

Less than a half-dozen studies have value in assigning a threshold PHC dose for cattle. Page 56 of Chalmers (1999) includes tabulated threshold dose estimates for crude oil in cattle, which range from > 1.25 to 8 mL/kg bw. This table is reproduced herein (Table 4.19). Unweathered oil (with a specific gravity of 0.843) exhibited a threshold dose of 2.5 mL/kg (adapted from Stober, 1962).

Table 4.19: Threshold doses for crude oil in cattle (adapted from Chalmers, 1999).

Oil Type	Composition	Threshold Dose
Unweathered Oil	100 mL = 84.3 g Carbon = 84.6% (19% arom.) Hydrogen = 11.92% Nitrogen = 0.71% Sulfur = 2.46%	2.5 to 5 mL/kg bw = 2.1 to 4.2 g/kg bw
Weathered oil	Water 10% by wt. 100 mL = 91.0 g Carbon = 83.6% (21% arom.) Hydrogen = 11.56% Nitrogen = 0.49% Sulfur = 2.8%	8 mL/kg bw = 7.3 g/kg bw
Venezeule crude oil (naphtha-based)	100 mL = 87.5 g Carbon = 85.6% (19% arom.) Hydrogen = 12.95% Nitrogen = 0.46% Sulfur = 1.58%	= 4.0 mg/kg
Bunker "C" oil	Carbon = 86% (19% arom.) Hydrogen = 11% Nitrogen and Oxygen = 0.46% Sulfur = 2.5%	> 1.25 mL/kg = > 1.1 g/kg bw

Coppock and Campbell (in Chalmers, 1999) more formally evaluate risks, including safe PHC exposure levels for cattle. They used a "Tolerable Daily Intake" (TDI) approach, based on CCME (1993) for crude oil, as follows:

- Cited Literature value LOAEL (after Stober, 1962) = 2.5 mL/kg bw
- Oil Specific gravity = 0.85 g/ml
- LOAEL = 2.5 mL/kg bw x 0.85 g/mL = 2.1 g fresh crude/kg bw

- Estimated NOAEL = LOAEL/5.6 = 2.13 g/kg bw/5.6 = 0.38 g/kg bw

(i) Livestock TDI = $(LOAEL \times NOAEL)^{0.5}/UF = (2.13 \text{ g/kg bw} \times 0.38 \text{ g/kg bw})_{0.5}/UF$

Where -

UF = Uncertainty Factor: set at 10

and –

(ii) TDI = 0.9 g fresh crude/kg bw/10 = 0.09 g fresh crude/kg bw

It is assumed that Coppock and Campbell implicitly assume this to be a daily exposure threshold, in other words – 0.09 g/kg bw/day.

The CCME (1993) TDI approach was intended to apply to human health risk assessments. CCME (1996) provides a protocol for estimating toxicological thresholds for livestock and wildlife based on the "Daily Threshold Effects Level" (DTED) for livestock drinking water (LDW). The DTED is estimated as follows:

(iii) $\mathbf{DTED_{LDW}}$ = Lowest Documented Effects Dose (ED)/ Uncertainty Factor

(iv) = 2.1 g fresh crude/kg bw/day / UF of 10 = 0.21 g/kg bw/d

= 210 mg/kg bw/d

(Assuming that the Lowest Effects Dose is the previously discussed LOAEL of 2.1 g/kg bw/d)

From this, a reference concentration (RfC_{LDW}) for whole fresh crude ingested in livestock drinking water is established as follows:

(v) $\mathbf{RfC_{LDW}} = (DTED_{LDW} \times AF \times BW)/WIR,$

where -

$DTED_{LDW}$ = Daily Threshold Effects Dose for Livestock Drinking Water (as above)

AF	=	Allocation Factor for allowable dose (set at 0.2)
BW	=	Cow Body Wt., set at 550 kg for an adult cow
WIR	=	Water Ingestion Rate (set at 100 L/day)

Coppock and Campbell (in Chalmers, 1999) consulted a study by Pal (1988), which demonstrated that cattle drink between 25 and 66 L/cow/day. Additional consumption occurs in lactating cows (an additional 5.4 L of water/L milk produced, as well as for cows fed on dry feed (3 to 10 L of water/kg dry feed consumed). An appropriate water ingestion rate (WIR) for adult cows is taken to be around 100 L/d.

The final RfC_W is estimated as follows:

(vi) $\mathbf{RfC_W}$ = (210 mg/kg bw/d x 0.2 x 550 kg bw)/100 L/d

= **23 mg/L fresh crude**

Coppock and Campbell, based on the study by Stober (1962), suggested that the value for a weathered crude oil (after adjusting for calculations areas) would be 3.7 x higher, or 85 mg/L weathered crude.

The preceding calculations assume a proportional transfer of the different constituents of a crude oil to a drinking water reservoir, such that the dose derived from drinking water would be equivalent to experimental doses in the consulted studies. Such an assumption ignores known differential solubilities and partitioning of different hydrocarbon classes. In addition, the RfC_W must be converted to an RfC_W for each of the CWS fractions, in order to back-calculate a soil protective benchmark based on a livestock drinking water exposure scenario.

If it is assumed that the fresh crude used in cattle toxicology experiments had a composition similar to Federated Whole crude, then the relative composition of the original dose as PHC CWS F1-F4 can be estimated. The underlying studies do not allow us to know which of the fractions (or single compounds within the fractions) might have resulted in the toxicological response. In subdividing the original RfC_W among the CWS fractions, therefore, one runs the risk of attributing a LOAEL response to one of the non-toxic CWS fraction. It can be confidently stated, however, that the redefined composition as CWS fractions represents the lowest possible dose for each fraction, below which toxicity would be unlikely (for each Fraction, the concentration would represent either the LOAEC, or – if not the responsible toxicant, a documented NOAEC.

Recent studies sponsored by PTAC/CAPP (Stephenson et al, 1999) provided the following carbon distribution for fresh Federated Crude Oil. Fresh Federated Crude (from Swan Hills area of Alberta) had the following composition:

C1-C5:	2.8%
C6-C10 (CWS F1):	23.2%
C11-C16 (CWS F2):	21.3%
C17-C22:	16.0%
C23-C35:	8.5%
SUM OF LAST 2 (CWS F3):	34.5%
>C35 (CWS F4):	18.2%

Assuming that the unweathered crude oil has a similar composition, the $DTED_{LDW}$ can be apportioned among the CWS fractions, to produce the following provisional RfC_{LDW} estimates:

PHC CWS F1:	= 0.232 x 23 mg/L	=	**5.3 mg/L;**
PHC CWS F2:	= 0.213 x 23 mg/L	=	**4.9 mg/L;**
PHC CWS F3:	= 0.345 x 23 mg/L	=	**7.9 mg/L;**
PHC CWS F4:	= 0.182 x 23 mg/L	=	4.2 mg/L.

Fraction F4 was removed from further consideration since (i) the bioavailability and gastrointestinal absorption of petroleum hydrocarbons >C34 is expected to be exceedingly limited, and (ii) the particulars of groundwater transport would preclude any substantial migration of this fraction into adjacent surface water bodies, including livestock watering dugouts.

4.3.3.1 Additional Toxicological Literature Review. Mitchell et al (1978) exposed cross-bred barrow pigs to 0, 1, 2, or 3 ppm (µL/L) gasoline in drinking water (8 pigs per treatment level: approximate initial weight was 85 kg). No effect was detected over a five week exposure period on weight gain, feed efficiency, or water consumption rates. In a second experiment, young, recently weaned swine were fed ad libitum drinking water with gasoline at the solubility limit. There was no difference between control and exposed swine.

The study by Rowe et al (1973) involved the treatment of 11 cattle (varying in age from 6 mo. to 3.5 y) total with either a sweet crude, sour crude, or kerosine. Crude oil dosages ranged from 37 mL/kg body weight, given as a single dose, to 123 mL/kg bw given as five doses over a five day period. Kerosine dosages ranged from a single dose of 19.8 mL/kg bw to 61.6 mL/kg bw given as five doses over five days. In addition, 3 separate groups of five calves were administered crude oils and kerosine at a rate of 8 mL/kg bw/d for up to 14 consecutive days. A dose of 8 mL/kg bw/day to one calf

produced only mild signs of pneumonia, from which recovery occurred. Higher single doses to calves or adults resulted in a variety of more severe effects, including mortality for some doses and individuals. A threshold dose of 8 ml/kg bw/day for 14 day is consistent with the LOAEL derived by Coppock and Campbell (1997).

4.3.4 Model Predictions – Aquatic Life

For the CWS Tier I default site assumptions, preliminary model calculations were run for each of the F1 and F2 fractions, and sensitivity analyses were run on a number of model inputs, as follows:

- *Fraction Physical Properties:*
  - ⇒ solubility
  - ⇒ Henry's Law Constant
  - ⇒ Log K_{oc}
  - ⇒ Subsurface degradation half-life
- *Site Generic Parameters:*
  - ⇒ soil organic carbon content (F_{oc})
  - ⇒ Darcy's velocity
  - ⇒ distance to surface water body

Preliminary analyses revealed that model estimates of soil concentrations for various TPHCWG subfractions were very sensitive to estimates of solubility and the organic carbon – water partition coefficient (K_{oc}), but insensitive to variations in the Henry's Law Constant. This is likely due to the relative unimportance of PHC fate in the unsaturated zone, since generic site assumptions provide for the direct interaction between the bottom of the contaminated soil zone and the saturated zone. Varying the depth of the unconfined aquifer had no influence on model predictions.

Preliminary analyses further revealed that the resulting soil quality benchmarks for each TPHCWG sub-fraction, as well as for the CWS fractions derived from these, were heavily influenced by assumptions regarding the possibility of and rate of subsurface hydrocarbon degradation. The allowance of even highly conservative degradation rates produced much higher soil quality benchmarks for PHCs in the CWS F1 range, in particular, than if attenuation through *in situ* biodegradation is discounted entirely. In response to this issue, the default assumption of infinite subsurface half-lives for PHCs was re-visited. This assumption was initially adopted in parallel with guidance by PIWG in the context of human health-protective pathways, and parallels Tier I assumptions within the Risk Based Corrective Action (RBCA) model. The assumption merited re-consideration in the context of exposure pathways for ecological receptors, since the primary compartment of interest for fate calculations is the subsurface saturated zone. An environmental persistence half life in the saturated zone should be less variable across sites than in the unsaturated zone, and there are probably fewer factors that influence biodegradation rates.

Appendix G provides a brief summary of the environmental persistence of PHCs in the subsurface environment. In addition, generic environmental persistence half-lives are defined for the CWS F1 and F2 fractions using conservative estimates which in their application would tend to over-estimate rather than underestimate the of an ecological receptor at the vast majority of Canadian sites. The consequences of the environmental degradation rate estimates are further explored in this section, as part of the detailed derivation exercise.

The existing environmental persistence data are insufficient to allow a confident derivation of degradation half-lives (t1/2) at a chemical unit lower than the CWS fractions (F1, F2). Even at this level, the derived values are highly conservative, given the uncertainty in their applicability and any given PHC release site in Canada. Degradation half-lives in both the saturated and unsaturated zone, therefore, where established as follows:

CWS F1: t1/2 (saturated and unsaturated zone) = 712 d (~ 2 yr)

(and t1/2 for TPHCWG Aliphatics C6-8; Aliphatics C8-10; and Aromatics C8-10 = 712 d)

CWS F2: t1/2 (saturated and unsaturated zone) = 1750 d

(and t1/2 for TPHCWG Aliphatics C10-12; Aliphatics C12-16; Aromatics C10-12 and C12-16 = 1750 d)

As discussed in Section 4.3.1, a necessary first step in calculating a soil quality benchmark for the protection of aquatic life for PHC CWS fractions F1 and F2 is the modeling of an appropriate SQG for each of the constituent TPHCWG subfractions. For CWS F1, the TPHCWG subfractions included –

TPHCWG Aliphatics C6-C8 (55% of CWS F1 by mass);

TPHCWG Aliphatics C8-C10 (36% of CWS F1 by mass);

TPHCWG Aromatics C8-C10 (9% of CWS F1 by mass).

Similarly, the assumed composition of PHC CWS F2 is –

TPHCWG Aliphatics C10-C12 (36% by mass);

TPHCWG Aromatics C10-C12 (9% by mass);

TPHCWG Aliphatics C12-C16 (44% by mass);

TPHCWG Aromatics C12-C16 (11% by mass).

4.3.4.1 TPHCWG Aliphatics C6-C8. Table 4.20 provides the output of runs on the

BCE groundwater model for TPHCWG subfraction C6-C8 (aliphatics), using the PIWG/CWS default site assumptions for a coarse-textured site (Appendix H) and chemical property assumptions as documented in Table 4.13.

Table 4.20: Calculated SQGs (mg/kg) for the TPHCWG aliphatics C6-C8 subfraction.

	Assumed Environmental Degradation Half Live (t1/2) in Days							
Distance from source area (m)	1.0E+09	1.0E+06	1.0E+05	1.0E+04	6.0E+03	3.0E+03	1.5E+03	712
10	4.8	4.8	5.0	7.4	9.5	18	51	357[A]
20				11	18	51		
30	4.8	4.9	5.5	16	31	130		
40					53			
50	5.0	5.1	6.2	32	86			
60					141			
70								
80				93	*No solution provided since fraction at solubility limit at source would still be too low to result in toxic concentration at aquatic receptor*			
90				131				
100	6.8	7.1	10					
150			15					
200	12	13	27					

Notes: A) Solubility limit increased 10X to obtain model solution

4.3.4.2 TPHCWG Aliphatics C8-C10. Even at a distance of 10 m from source to receptor, and without allowing for any subsurface degradation of this fraction, model runs failed to provide an appropriate sub-fraction SQG. This is due to the fact that the overall transport toward the aquatic receptor is constrained by the limited solubility of the fraction at the interface between the PHC contaminated soil mass. Introduction of leachate into the subsurface environment at the solubility limits provides an upgradient concentration that is lower than that required to result in a threshold toxic concentration at the aquatic receptor, after accounting for attenuation through dilution and degradation. Furthermore, relaxing solubility constraints by increasing the assumed solubility of the TPHCWG sub-fraction by and order of magnitude did not alleviate this constraint.

4.3.4.3 TPHCWG Aromatics C8-C10. Table 4.21 provides the output of runs on the BCE groundwater model for TPHCWG subfraction C8-C10 (aromatics), using the PIWG/CWS default site assumptions for a coarse-textured site and chemical property assumptions as documented in Table 4.13.

Table 4.21: Calculated SQGs (mg/kg) for the TPHCWG aromatics C8-C10 subfraction.

Distance from source area (m)	Assumed Environmental Degradation Half Live (t1/2) in Days							
	1.00E+09	1.00E+06	1.00E+05	1.00E+04	6.00E+03	3.00E+03	1.50E+03	712
10	4.1	4.1	4.2	4.9	5.5	7.2	12	33
20							30	161
30				6.9	9.4	19	66	
40							138	
50	4.3	4.3	4.7	9.7	16	46	277	
60								
70								
80					28	110		
90						253		
100	5.8	5.9	6.9	27	63	376		
150				70	221			
200	10	11	14	164				

4.3.4.4 TPHCWG Aliphatics C10-C12 and C12-C16. Even at a distance of 10 m from source to receptor, and without allowing for any subsurface degradation of this fraction, model runs failed to provide an appropriate SQG for these two subfractions. In the case of C12-C16 (aliphatics) the model algorithms failed to converge on a solution, even after manipulation of assumed solubility limits. Thus, the concentration of PHCs in the soil would not theoretically impose limits on the concentration in groundwater down gradient from the source area at a distance of 10 m or more, assuming transport in dissolved form. Rather, the solubility limits at the point where contaminated soil and groundwater interacts is deemed to be the major limiting factor.

Table 4.22: Calculated SQGs (mg/kg) for the TPHCWG Aliphatics C10-C12 subfraction.

Distance from source (m)	Assumed Environmental Degradation Half Live (t1/2) in Days							
	1.00E+09	1.00E+06	1.00E+05	1.00E+04	6.00E+03	3.00E+03	1.75E+03	875
10	35	44	[A]285					
20								
30								
40								
50								
60								
70								
80								
90								
100								
150								
200								

Notes: A) Solubility limit increased 10X to obtain model solution

4.3.4.5 TPHCWG Aromatics C10-C12. Table 4.23 provides the output of runs on the BCE groundwater model for TPHCWG subfraction C10-12 (aromatics), using the PIWG/CWS default site assumptions for a coarse-textured site (Appendix H) and chemical property assumptions as documented in Table 4.13.

Table 4.23: Calculated SQGs (mg/kg) for the TPHCWG aromatics C10-C12 subfraction.

Distance from source (m)	Assumed Environmental Degradation Half Live (t1/2) in Days							
	1.00E+09	1.00E+06	1.00E+05	1.00E+04	6.00E+03	3.00E+03	1.75E+03	875
10	4.5	4.5	4.6	5.8	6.9	10	18	56
20						22	57	
30				9.7	15	43	152	
40						80		
50	4.6	4.7	5.3	16	32	145		
60						259		
70					68			
80					98			
90					140			
100	6.3	6.4	8.2	61	198			
150				204				
200	11	12	19					

4.3.4.6 TPHCWG Aromatics C12-C16. Table 4.24 provides the output of runs on the BCE groundwater model for TPHCWG subfraction C12-C16 (aromatics), using the PIWG/CWS default site assumptions for a coarse-textured site (Appendix H) and chemical property assumptions as documented in Table 4.13.

Table 4.24: Calculated SQGs (mg/kg) for the TPHCWG aromatics C12-C16 subfraction.

Distance from Source (m)	Assumed Environmental Degradation Half Live (t1/2) in Days							
	1.00E+09	1.00E+06	1.00E+05	1.00E+04	6.00E+03	3.00E+03	1.75E+03	875
10	5.1	5.1	5.4	8.6	12	25	63	
20				14	25	89		
30			6.0	22	48			
40				33	90			
50	5.3	5.4	6.9	50				
60				76				
70				115				
80			9.6					
90								
100	7.2	7.6	12					
150			21					
200	13	14	34					

4.3.4.7 Associated Issues: The Influence of Soil Organic Carbon Content (Foc). The calculated sub-fraction soil quality guidelines presented in Tables 4.20-4.24 show that the derivation methods, and resulting Tier I guidance for soil concentration thresholds that are protective of aquatic life, are strongly influenced by both the expected rate of hydrocarbon biodegradation in the saturated zone and the distance separating the contaminated soil mass and the aquatic receptor.

The assumed hydrophobicity of several of the sub-fractions prevented the calculation of a sub-fraction SQG. Even for those fractions addressed in Tables 4.20-4.23 however, the calculated SQG is highly sensitive to minor changes in the assumed (or measured) organic carbon content of subsurface soils at a site. This is shown graphically in Figure 4.25:

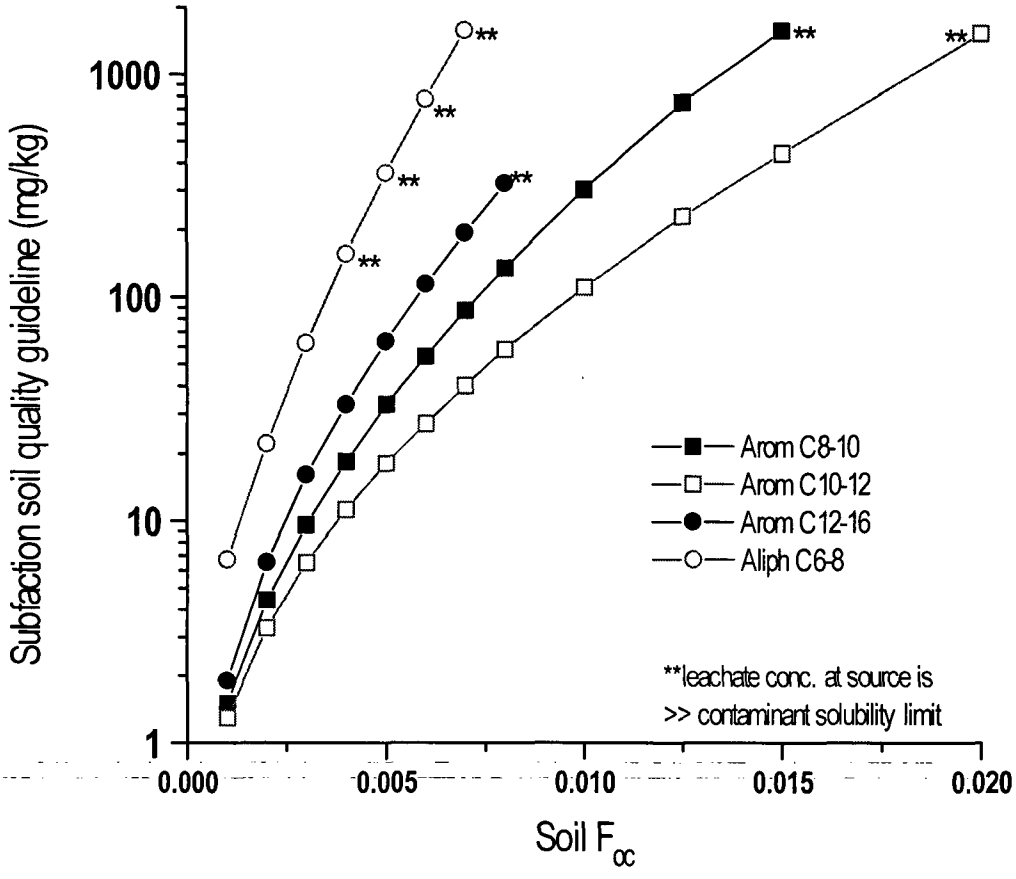


Figure 4.25: Change in modeled PHC soil quality benchmarks based on changes in soil organic carbon content.

4.3.4.8 Calculation of SQGs for PHC CWS Fractions F1 and F2. For Tier I calculations, based on a generic site wherein a surface water body is separated from petroleum hydrocarbon contaminated, coarse-grained soil by a distance of 10 m, the following estimates of appropriate sub-fraction soil quality thresholds were calculated:

i) **PHC CWS F1:**

TPHCWG Aliphatics C6-C8 (55% of CWS F1 by mass): **357 mg/kg**
TPHCWG Aliphatics C8-C10 (36% of CWS F1 by mass): no value (assume **20,000 mg/kg**; i.e. limits below which free product would be expected)
TPHCWG Aromatics C8-C10 (9% of CWS F1 by mass): **33 mg/kg**

ii) **PHC CWS F2:**

TPHCWG Aliphatics C10-C12 (36% by mass): no value (assume **20,000 mg/kg**; i.e. limits below which free product would be expected)
TPHCWG Aromatics C10-C12 (9% by mass): **18 mg/kg**
TPHCWG Aliphatics C12-C16 (44% by mass): no value (assume **20,000 mg/kg**; i.e. limits below which free product would be expected)
TPHCWG Aromatics C12-C16 (11% by mass): **63 mg/kg**

The sub-fractions for which no SQG could be calculated are not deemed to be limiting for aquatic life based on transport in the dissolved phase, up to a concentration of 100% in soil: The solubility limits at the point of interception between contaminated soil and groundwater are the major limiting factor to increased concentrations in groundwater and surface water down –gradient from the site. Based on inclusion of the "no value" subfractions at a 20% soil concentration (an approximate threshold for the presence of free product), the following CWS SQGs are calculated:

$$SQG_{slice\_i} = \frac{1}{\sum\left(\frac{MF_{subfraction\ j}}{SQG_{subfraction\ j}}\right)}$$

Where -

SQG_{slice_i} = soil quality guideline for the CWS fraction *i* (mg/kg)
$SQG_{subfraction\ j}$ = soil quality guideline (mg/kg) for each sub-fraction within fraction *i* for the target water quality guideline for fraction *i*
$MF_{subfraction\ j}$ = mass fraction of each sub-fraction within the fraction *i*

CWS F1:

SQG = 1/[(0.55/357 mg/kg) + (0.36/20000 mg/kg) + (0.09/33 mg/kg)]

= 233 mg/kg

CWS F2:

SQG = 1/[(0.36/20000 mg/kg) + (0.44/20000 mg/kg) + (0.09/18 mg/kg) + (0.11/6.3 mg/kg)]

= 147 mg/kg

Rounding these numbers to two significant figures, the following provisional guidelines are derived:

i) PHC CWS F1: SQG_{AL} (provisional) = 230 mg/kg
ii) PHC CWS F2: SQG_{AL} (provisional) = 150 mg/kg

Based on the analysis provided herein, the recommended Tier I SQG_{AL} for coarse-grained soils for CWS fractions F1 and F2 is 230 mg/kg and 150 mg/kg respectively.

PIWG also provided default assumptions for Tier I sites with fine-grained (silt-clay) soils. Use of an assumed Darcy velocity of 0.016 m/y, coupled with other assumed model input parameters for fine textured soils did not lead to reasonable estimates of subfraction SQGs for any of the TPHCWG subfractions. It is recommended, therefore, that a soil quality guideline based on groundwater transfer to surface water bodies should not apply to fine-grained sites at Tier I. Not withstanding the absence of an adopted soil protective standard based on the aforementioned exposure scenario, the regulator or other stakeholder may require additional investigation and/or risk management activities in cases where there is evidence of PHC inputs to adjacent water bodies containing aquatic life, either through aeolian transport and particle erosion, groundwater transport, or other pathways.

4.3.5 Model Predictions – Livestock Watering

Estimates of toxicological thresholds for livestock drinking water, as fraction-specific reference concentrations (RfC_{LDW}s), are provided in Section 4.3.5. These RfC_{LDW}s were used to back-calculate soil concentrations for PHCs above which risks to livestock ingesting drinking water might be expected – based on an approach similar to that used calculating soil benchmarks for the protection of aquatic life.

The BCE groundwater model was used to estimate appropriate threshold source soil concentrations, using the assumptions for a generic site with coarse-textured soil, as documented in Table 4.13. In addition, the model was run firstly under the assumption

that no PHC degradation would occur in the saturated or unsaturated environment. Model calculations were subsequently run assuming an environmental persistence in both the saturated and unsaturated zone of 2 years (712 days) and slightly less than 5 years (1750 days) for CWS fractions F1 and F2, respectively (as applied to the TPHCWG sub-fractions). Table 4.25 summarizes the model runs.

Table 4.25: Back-calculated predictions of soil quality benchmarks (in mg/kg) for TPHCWG subfractions based on protection of livestock ingesting drinking water.

	$t_{1/2}$ = 1.0e+09			$t_{1/2}$ (F1: 712 days; F2: 1,750 days)		
CWS F1						
TPHCWG-AIC6-8	>sol [A]	390	at 4x sol [C]	>sol	29,000	at 350x sol
TPHCWG-AIC8-10	>sol	3100	at 10x sol	>sol	no solution at sol = 100% conc	
TPHCWG-ArC8-10	**155 mg/kg** [B]			>sol	920	at 3x sol
CWS F2						
TPHCWG-AIC10-12	>sol	28000	At 100x sol	>sol	no solution at sol = 100% conc	
TPHCWG-AIC12-16	>sol			>sol	no solution at sol = 100% conc	
TPHCWG-ArC10-12	**230 mg/kg**			**360 mg/kg**		
TPHCWG-ArC12-16	>sol	450	at 4x sol	>sol	5600	at 20x sol

Notes: A) No solution returned based on TPHCWG estimates for subfraction physico-chemical properties. The groundwater leachate concentration at the source soils would exceed the assumed sub-fraction solubility limits in order to result in a surface water concentration deemed to constitute a risk.
B) Bolded values are model calculations that were reached within the TPHCWG estimated solubility limits for the subfraction.
C) Where the solubility limits were exceeded by the leachate concentration, an arbitrarily elevated solubility limit was used to back-calculate a soil concentration that would result in the target RfCs if solubility was not a limiting factor.

Note that no results are provided for the TPHCWG subfractions that fall within the CWS F3 fraction. Model runs reinforced the view that the strong hydrophobicity of >nC16 to C34 PHCs would render groundwater exposure pathways inoperative.

The tabulated TPHCWG subfraction values were used to calculate a soil quality benchmark for CWS fractions F1 and F2 using the following algorithm (see also Section 4.3.2):

$$SQG_{slice\_i} = \frac{1}{\sum\left(\frac{MF_{subfraction\ j}}{SQG_{subfraction\ j}}\right)}$$

Where -

SQG_{slice_i} = soil quality guideline for the CWS fraction *i* (mg/kg)

$SQG_{subfraction\ j}$ = soil quality guideline (mg/kg) for each subfraction within fraction *i* for the target water quality guideline for fraction *i*

$MF_{subfraction\ j}$ = mass fraction of each subfraction within the fraction *I*

The SQGs for subfractions for which the groundwater leachate concentration at the source soils would exceed the assumed sub-fraction solubility limits were estimated as either (i) the soil concentration required to produce the target surface water concentration had solubility not been a limiting factor, or (ii) a 100% soil concentration. This resulted in the following soil quality guideline estimates for CWS fractions F1 and F2:

CWS Fraction	$T_{1/2}$ = 1.0e+09 day	$T_{1/2}$ = 712 and 1750 days for F1,2
F1	550 mg/kg	9,000 mg/kg
F2	1,500 mg/kg	4,000 mg/kg

4.4 Tier I Guidance for Ecological Receptors

An analysis was undertaken to derive a soil quality guideline for PHCs which will be protective of aquatic life where there is an adjacent surface water body. Based on the sensitivity analysis contained herein, this exposure pathway would be important when the aquatic-life containing water body is less than 100 m from the contaminant source area. In addition risks to aquatic life in an adjacent water body would be important to consider where massive PHC releases have occurred, and/or there are aspects of PHC transport which fall outside of the assumptions of the modeling exercise (channelized flow, presence of non-aqueous phase lipids or large co-solvent concentrations).

Detailed new toxicology studies, coupled with a detailed analysis of existing and new data (herein) provided guidance on environmentally protective thresholds for PHCs in relatively coarse surface soils of relevance to soil invertebrates and plants.

Table 4.26 provides a summary of Tier I guidance for ecological receptors in surface, coarse soils, based on the preceding analysis. Toward the final derivation of the Tier I PHC CWS, additional values were provided based on the prevention of ecological risks, for fine-grained soils as well as subsurface soils. The extension of the numbers provided in Table 4.26 to fine-textured and/or subsurface soils is discussed in Chapter 5.

Table 4.26: Summary of generic PHC soil quality guidelines (mg/kg soil) recommended for coarse-textured surface soils in Canada.

Receptor	PHC CWS Fraction				Rationale
	F1	F2	F3	F4	
Soil Invertebrates and Plants					
· *Agricultural and Residentiall Parkland*	130	450	400	2,800[1]	-25thpercentile of combined soil invertebrates and plants species sensitivity dist'n - 50thpercentile of plant effects dist'n
· *Commercial and Industrial*	330	760	1,700	3,300	
Aquatic Life · *All land use categories*	230	150	NA[2]	NA	-Based on a narcosis/ critical body residue approach. A chronic lipid-based threshold of 3.0 mmol PHCs/kg-lipid was used to establish acceptable water concentrations in a surface body 10 m away from the mass of PHC-contaminated soils for each of seven TPHCWG sub-fractions.
Livestock Drinking surface Water · *Agricultural*	9,000	4,000	NA	NA	

Notes: (1) provisional guidance only, based on ecotoxicity of fresh whole Federated Crude Oil (Section 4.2.3); (2) NA – not applicable

Some direct scientific guidance is also provided herein on groundwater mediated exposure pathways and risks to aquatic life or livestock in fine soils. The groundwater model exercise predicts that the transport of PHCs (especially the F1 and F2 fractions) within the dissolved phase in groundwater in a homogeneous, fine-textured soil in unlikely to lead to exposure concentrations in surface water bodies of concern. One possible exception to this is when a mass of PHC contaminated soil is in intimate contact with a surface water body. Such a situation is deemed to be outside of the assumptions used in the derivation of Tier I PHC CWS.

5. Integration of Ecological and Human Health Levels

5.1 General

Tabular Tier 1 levels in the PHC CWS present the lower of the values generated for human health and ecological protection such that both are protected when Tier 1 levels are applied. This roll-up is essential to establish the risk management goals applicable to the most sensitive sites under each land use – i.e., sites where all potential receptors and exposure pathways are operative. In practice, the number of such sites in a particular jurisdiction may be small and detailed results applicable to individual pathway/receptor combinations are needed in order to identify practical management strategies. This chapter provides a summary of the risk-based values developed for each pathway/receptor combination in the individual land use categories. In addition, rationale is provided for certain risk management decisions made in the final integration of human health and ecotoxicological inputs.

The principal features added to the PHC CWS at the integration stage were:

- Adjustment of eco-contact levels with respect to soil texture, and
- Addition of generic levels for subsoils – defined as earthy materials below 1.5 m depth.

In the process of developing these features the Development Committee considered several factors that are not easily accommodated in explicit, quantitative exposure and risk estimates. These factors included:

- Capabilities of current and emerging remediation technologies,
- Likelihood of subsoil disturbance and excavation under different scenarios,
- Potential effects of PHC on buried infrastructure,
- Aesthetics,
- Role of subsoil in terrestrial ecology,
- Costs of risk reduction measures,
- Property values and environmental stewardship.

A description of the roles played by the above scientific, technical and socio-economic factors in finalizing the Tier 1 PHC CWS levels is provided in this chapter.

5.2 Eco Soil Contact Pathway – Role of Soil Texture

Soil texture, and clay content in particular, has long been recognized as an important influence on the behaviour of chemicals in soils. The clay fraction is responsible for most of the surface area of soils and also provides unique colloidal properties that support well-documented phenomena such as cation exchange. It is now accepted that clay plays an important role in stabilizing naturally occurring organic residues against microbial attack (Stevenson 1983). As a result, fine

textured soils tend to accumulate greater amounts of organic matter and exhibit lower rates of decomposition than coarse textured soils under similar climatic and vegetative conditions.

Colloidal properties are now being shown to be influential on contaminant behaviour in soils also. Recent scientific literature indicates that toxicity of PHCs in soils declines with time (see, for example Loehr and Webster 1996, Salanitro et al. 1997). In part, as discussed in Chapter 4, this is due to dissipative mechanisms such as volatilization, leaching and biodegradation. However, some evidence suggests that "aging" of PHCs results in reduced bioavailability as well. Several mechanisms of aging have been hypothesized and investigated including, attrition of lower molecular components due to biodegradation, physical occlusion of PHCs in pores inaccessible to organisms, and stabilization of PHCs by association with soil colloidal material. Irrespective of which of these mechanisms predominates, there is agreement that "aging" is a factor in ecotoxicological response in the field. The degree of amelioration has been observed to be greater in fine textured soils; consistent with predictions from consideration of colloidal properties.

Chung and Alexander (1998) and Kelsey and Alexander (1997) described differences in bioavailability of individual hydrocarbons added to soils of varying texture and how bioavailability decreases with aging. Salanitro et al. (1997) reported similar trends in soils contaminated by crude oil and concluded that soil conditions are among the chief determinants of hydrocarbon phytotoxicity in soil. While mechanisms by which soil colloids reduce bioavailability of PHCs are not clearly established, it is highly likely that they include those applicable to biological residues, such as H-bonding, van der Waals forces, ion exchange, geometric complementarity, physical occlusion, etc. Many researchers ascribe reductions in bioavailability of hydrocarbons in soil to a generalized "sequestration".

5.2.1 Socio-Economic and Technological Factors

Considerable work has been carried out over the past two years to provide information on response of soil dwelling organisms to the PHC CWS fractions and certain whole products. Chapter 4 describes how standardized acute and chronic bioassays of plant and invertebrate toxicity response in artificial and coarse textured field soils have been conducted on Federated Crude, Mogas and four fractions cut from the Federated Crude. Analyses of these data using modified concepts and procedures from the CCME (1996) soil protocol indicate an appreciable toxicity for all investigated fractions. However, direct application of the Tier 1 values calculated for coarse textured surface soils to fine textures and deep subsoils would pose significant challenges to the biotreatment technologies typically applied to PHC contaminated soils.

CCME carried out a screening socio-economic analysis in support of the PHC CWS (Komex 2000) that analyzed theoretical Tier 1 values ("seed values" and upper and lower limit values around the seed values) in order to estimate options and costs for

remediation of affected Canadian soils. This analysis indicated to the Development Committee that well-established biotreatment technologies can be used to attain Tier 1 values for coarse soils as derived above but would often fail to meet these same targets were they applied to fine textured soils. Attainment of Tier 1 levels for F3 would be particularly problematic. The analysis further indicated that the probable outcome of application of Tier 1 eco contact values for coarse soils to fine soils would be that extensive volumes of soil and subsoil would be directed to landfills rather than receiving remedial treatment. This, in turn, would fail to conserve otherwise useful soil and put additional pressure on scarce landfilling capacity. The CCME Development Committee considered this information carefully and concluded that some amendment to eco-contact values applicable to fine textured soils should provide a net geo-environmental benefit.

5.2.2 Risk Management Decision

While systematic, quantitative relationships between soil toxicity of PHC and texture are not yet published, it was judged to be a conservative assumption that, over practical exposure durations in field soils, toxic response in fine textured soils would be not greater than half that seen in coarse textured soils. As described in Chapter 4, the bulk of the contributing data for development of the PHC CWS were derived from coarse textured soils (e.g., OECD mix). Thus, a risk management decision was made to increase Tier 1 levels for eco-contact in surface soils by 2-fold over those derived for coarse textured soils. Eco Soil Contact entries in Table 5.1 (applicable to fine-textured soils) are, with one exception, double those in Table 5.2 (applicable to coarse textured soils). An upset limit of 2,500 mg/kg was used for commercial and industrial lands in consideration of the relatively non-conservative ecotoxicity endpoint used for the coarse textured case (see Chapter 4).

Note that this risk management decision regarding soil texture applies only to the eco-contact pathway, where experimental evidence for the adjustment exists. It should be further noted that this is strictly a practical decision that responds to the differences in biotreatment efficiency in soils of differing efficiency. Loehr and Webster (1996) showed that fine textured soils reached a non-toxic biotreatment endpoint at higher residual hydrocarbon concentrations than did coarse textured soils.

As research results accumulate, it will be possible to re-visit the professional judgment basis of eco-contact values for fine textured soils.

5.3 Approach to Subsoil Values

Information is presented in Tables 5.3 and 5.4 on generic levels applicable to subsoils, defined as earthy materials below 1.5 m depth. This section describes the general rationale for subsoil values, principles used in their derivation, pathway analysis and specific risk management decisions supporting the generic values.

Experience has shown that technical and socio-economic factors constrain risk management decision-making at contaminated sites. At larger and/or more severely contaminated sites this frequently means that numerical guidelines are applied only to surface soils and deeper contamination is addressed using site-specific risk assessment and management. Commonly, risk management plans based on site-specific risk assessment allow higher contamination concentrations at depth than would be acceptable under a guideline-based approach. Details vary but reduced accessibility of contamination at depth is a very common rationale for these higher concentrations. Monitoring of these higher concentrations and some form of notification or administrative control is usually required for regulatory acceptance. Recently, some jurisdictions have incorporated this form of risk management - stratified remediation - into their generic guidelines (e.g., MADEP 1994, OMEE 1996, Atlantic PIRI 1999). This approach has the advantage of presenting an economical risk management option without triggering the need for a site-specific risk assessment. CCME decided to develop generic values for subsoils as a risk management option under the PHC Canada-Wide Standard.

5.3.1 Principles for Development of Generic Subsoil Levels

While practical advantages have been identified, these could be realized only if a number of principles and conditions were followed:

- Generic subsoil levels must be risk-based and take account of all relevant and applicable pathways for both human and ecological receptors;
- All pathways applicable to surface soil must be assessed in the determination of appropriate subsoil pathways;
- Generic subsoil levels must not compromise aesthetic values or pose an unacceptable risk to infrastructure;
- An acceptable subsoil definition must exclude zones of high biological activity;
- Subsoil contamination must not serve as significant source for upward contamination of overlying soil through diffusion or "wicking" under evapotranspiration gradients;
- Subsoil contamination should not pose an unacceptable risk to workers who may occasionally come into contact with contamination through excavation or infrastructure service activities.

5.3.2 Review of Pathways

Human Health

(a) Soil ingestion – Not applicable under non-disturbance conditions. Could apply to construction and infrastructure workers under occasional conditions. For surface soil, only residential land use shows values below residual levels -"RES" - (>3%) for surface – 1.6% and 2.9% for F2 and F3 respectively. Given these values and the sharply reduced exposure for

workers as compared to continuously exposed children, a worker exposure scenario would be expected to return a value of "RES".

(b) Soil dermal contact -- Not applicable under non-disturbance conditions. Could apply to construction and infrastructure workers under occasional conditions. All surface exposure pathways assessed as "RES". Occasional, short duration exposure to subsoil would be expected to return "RES" also.

(c) Vapour inhalation – Risk-based values for soil are based on a minimum vertical distance from base of slab to contamination ("L_t") of 30 cm. For the basement and subsoil scenario, the same 30 cm vertical distances applies. However, for slab-on-grade construction, the default value of L_t is 139 cm – 150 cm to subsoil less the nominal slab thickness of 11 cm. L_t may be further increased for contamination positioned below 150 cm depth.

(d) Potable groundwater protection – Applies in same manner as for surface soil.

Ecological Health

(a) Direct soil contact – Very deep-rooted species may explore soil to this depth. Also, certain invertebrates may migrate deeply to avoid moisture stress periodically (Coleman and Crossley 1995). In the former case, the proportion of root biomass involved is minor and would be expected to pose minimal risk so long as values do not exceed those applicable to surface soil by a wide margin. In the latter case, the proportion of species making deep vertical migrations is small, and of those that do, time spent at depth is small and may be partially avoided. Given the present reliance on fresh product ecotoxicity data, which provide a conservative estimate of biological response, a five-fold increment in the Tier 1 value applicable to surface soil should be protective of ecological functions at depth.

(b) Soil and food ingestion/bioaccumulation – Does not apply.

(c) Protection of groundwater for aquatic life, livestock watering – Applies in same manner as for surface soil.

Miscellaneous

(a) Off-site migration of Soil/Dust – Does not apply for subsoils.

5.3.3 Risk Management Decisions

Depth to Subsoil

Based on consideration of the depth of soil development in Canada and zones of high biological activity, including rooting depths of common and valued plants, and common depths of routine excavation, a depth of 1.5 m was used to define the transition from soil to subsoil. This is also consistent with OMEE (1996).

Applicable Pathways

Based on the pathways analysis in Section 5.3.2 generic subsoil values are presented only for the vapour inhalation pathway, groundwater protection pathways, and Eco-soil contact pathways. The values for vapour inhalation and groundwater protection were calculated as indicated in Section 5.3.2 and differ very little, if at all, from values applicable to surface soils. The Eco Soil Contact pathway includes the factors discussed in Section 5.3.2 as well as any considerations related to aesthetics and protection of infrastructure. This decision was taken in consideration of the following points:

- At some sites, neither the vapour inhalation pathway nor groundwater protection pathways will apply whereas the Eco Soil Contact pathway is considered applicable at all times;
- There is a need, generically, to indicate an upset limit for subsurface PHC contamination;
- Definitive studies clearly delineating tolerable limits for PHC contamination from a standpoint of aesthetics and infrastructure protection are lacking. Nevertheless, there is evidence that high levels of PHC in subsoil can adversely affect aesthetics and infrastructure.

Thus, data were judged insufficient to allow "standalone" risk-based derivations for aesthetics and infrastructure, and they were addressed qualitatively as risk management considerations constraining the degree of expansion of surface ecotoxicity values applicable to subsoil.

Upset Limits

Free Product Formation – Theoretically, free-phase hydrocarbon can form in soil once a constituent exceeds its solubility limit in soil water, which is reached at a total soil concentration determined by the partitioning isotherm applicable to the particular soil and substance under consideration. For lower molecular weight constituents of particular environmental concern, these saturation limits can be reached at concentrations less than 50 mg/kg for C12-C16 aliphatics to about 1600 mg/kg for C5-C7 aromatics (TPHCWG 1999). In practice, lower molecular weight constituents tend to partition strongly into any residual (immobile) hydrocarbon phase that may be present. Appearance of residual hydrocarbon as a perceptible free phase in soil depends on a number of factors including soil texture, porosity, aeration porosity and hydrocarbon type (US EPA 1992b). Nevertheless, across a range of soil and petroleum hydrocarbon types, 3% PHC is generally sufficient for many to identify a hydrocarbon phase. Allowing for a margin of safety, a decision was taken that generic subsoil concentrations should not exceed 2%, of which not more than 1% should be in the sum of F1-F3. In consideration of the mobility and flammability risk posed by F1, it was further decided that F1 concentrations should not exceed 1,000 mg/kg.

Effect of Texture -- It was felt that clay content would contribute to general stabilization of F1-F3 at depth. Within a land use and fraction, fine textured soils were assigned higher generic subsoil PHC values than were coarse textured soils. Given the viscosity, insolubility, low bioavailability and resistance to attack of F4 it was felt that texture was relatively unimportant in the environmental risk posed by PHC in subsoil. Consequently, an upset limit of 10,000 mg/kg was established for F4 for both coarse- and fine-textured subsoil.

Technological Factors -- Bioremediation is presently the preferred technology for dealing with percent range PHC contamination of soils and subsoils, based on its effectiveness and cost (Komex 2000). Several studies have shown that bioremediation is most effective on low- to mid-range PHC (i.e., less than about C25). Larger PHC are biodegraded, but at much slower rates and, possibly, at lower rates still with soil "aging". This means that the major challenge for bioremedial systems is in dealing with F3, which is present in varying amount across a broad range of PHC release types and, unlike F4, is substantially toxic to plants and soil invertebrates (see Chapter 4). The following upset limits were established for F3 in subsoils in consideration of toxic risk, aesthetics, effects on infrastructure and bioremedial capabilities:

- Coarse textured subsoil, agricultural and residential uses: 2,500 mg/kg
- Coarse textured subsoil, commerical and industrial uses: 3,500 mg/kg
- Fine textured subsoil, agricultural and residential uses: 3,500 mg/kg
- Fine textured subsoil, commerical and industrial uses: 5,000 mg/kg

Subsoil Procedures for F1

Generic levels for F1 in fine textured subsoil under commercial/industrial uses were established at the upset limit of 1,000 mg/kg described above under "free product formation". Subsoil values for coarse textures under commercial/industrial use were established at twice the value applied to agricultural and residential uses. For agricultural and residential uses, an approximate 3-fold increment over the surface soil values was used for subsoil values.

Subsoil Procedures for F2

Generic levels for coarse textured were established at approximately 3-fold above the values applicable to coarse textured surface soil. Finally, generic levels for fine-textured subsoil were established at the approximate means of values established for F1 and F3 within the same texture and land use class.

5.4 Summary of Risk Management Decisions

Generic subsoil levels for PHC are judged to be protective of human health and environment so long as subsoil remains at depth. In addition, allowance has been made for certain exposures that could occur as a consequence of excavation.

A number of assumptions and interpretations have been made with respect to effects of subsoil PHC contamination on ecological functions, infrastructure and aesthetics. The risk management decision made in regard to these factors rely principally on input from stakeholders and experts. More quantitative information from future studies will allow validation or adjustment of these risk management decisions.

It is recognized that jurisdictions have discretion in the application of generic subsoil PHC levels with regard to any relevant conditions for on-going management.

5.5 Tabular Presentation of Generic PHC CWS Levels

Tables 5.1 through 5.4 on the following pages summarize the outcomes of the risk assessment and risk management procedures discussed in detail in Chapters 1 through 5. Four tables are presented:

- Table 5.1: Tier 1 levels for fine-grained surface soil.
- Table 5.2: Tier 1 levels for coarse-grained surface soil.
- Table 5.3: Generic levels for fine-grained subsoil.
- Table 5.4: Generic levels for coarse-grained subsoil.

Generic subsoil values are not listed as Tier 1 because their use may pose on-going risk management considerations in some situations.

Table 5.1. Tier 1 levels (mg/kg soil) for PHCs for fine-grained surface soils.

Land Use	Exposure Pathways	F1 (C6-C10)	F2 (>C10-C16)	F3 (>C16-C34)	F4 (>C34)
Agricultural	Soil Ingestion	15,000	8000	18,000	25,000
	Dermal Contact	RES	RES	RES	RES
	Vapour Inhalation (indoor, 30 m offset)	2100	11,400	NA	NA
	Protection of Potable GW[1]	180	250	NA	NA
	Protection of GW for Aquatic Life[2]	TBD	TBD	NA	NA
	Protection of GW for Livestock Watering[3]	TBD	TBD	NA	NA
	Nutrient Cycling	TBD	TBD	TBD	TBD
	Eco Soil Contact[4]	260	900	800	5600
	Eco Soil Ingestion	TBD	TBD	TBD	TBD
	Produce, Meat and Milk	NC	NC	NC	NC
Residential	Soil Ingestion	15,000	8000	18,000	25,000
	Dermal Contact	RES	RES	RES	RES
	Vapour Inhalation (indoor)	940	5200	NA	NA
	Protection of Potable GW[1]	180	250	NA	NA
	Protection of GW for Aquatic Life[2]	TBD	TBD	NA	NA
	Nutrient Cycling	TBD	TBD	TBD	TBD
	Eco Soil Contact[4]	260	900	800	5600
	Produce	NC	NC	NC	NC
Commercial	Soil Ingestion	RES	29,000	RES	RES
	Dermal Contact	RES	RES	RES	RES
	Vapour Inhalation (indoor)	4600	25,000	NA	NA
	Protection of Potable GW[1]	180	250	NA	NA
	Protection of GW for Aquatic Life[2]	TBD	TBD	NA	NA
	Nutrient Cycling	TBD	TBD	TBD	TBD
	Eco Soil Contact[4]	660	1500	2500	6600
Industrial	Soil Ingestion	RES	RES	NA	NA
	Dermal Contact	RES	RES	RES	NA
	Vapour Inhalation (indoor)	4600	25,000	NA	NA
	Protection of Potable GW[1]	180	250	NA	NA
	Protection of GW for Aquatic Life[2]	TBD	TBD	NA	NA
	Nutrient Cycling	TBD	TBD	TBD	TBD
	Eco Soil Contact[4]	660	1500	2500	6600
	Offsite Migration	NA	NA	12,000	RES

NA = Not applicable. Calculated value exceeds 1,000,000 mg/kg or pathway excluded.
RES = Residual PHC formation. Calculated value exceeds 30,000 mg/kg and solubility limit for PHC fraction.
NC = Not calculated. Insufficient data to allow derivation.
TBD = To be determined

1 = Assumes site is underlain by groundwater of potable quality in sufficient yield (K of 10^{-4} cm/sec or greater).
2 = Assumes surface water body at 10 m from site.
3 = Generally applicable for this land use as related to use of dugouts and wells for supply of livestock water.
4 = Tier 1 values based primarily on laboratory bioassay response to fractions derived from fresh Federated Crude Oil and adjusted for textural factors.

Table 5.2 Tier 1 levels (mg/kg soil) for PHCs for coarse-grained surface soils.

Land Use	Exposure Pathways	F1 (C6-C10)	F2 (>C10-C16)	F3 (>C16-C34)	F4 (>C34)
Agricultural	Soil Ingestion	15,000	8000	18,000	25,000
	Dermal Contact	RES	RES	RES	RES
	Vapour Inhalation (indoor, 30 m offset)	200	1100	NA	NA
	Protection of Potable GW	860	1200	NA	NA
	Protection of GW for Aquatic Life[1]	230	150	NA	NA
	Protection of GW for Livestock Watering[2]	*9000*	*4000*	NA	NA
	Nutrient Cycling	TBD	TBD	TBD	TBD
	Eco Soil Contact[3]	130	450	400	2800
	Eco Soil Ingestion	TBD	TBD	TBD	TBD
	Produce, Meat and Milk	NC	NC	NC	NC
Residential	Soil Ingestion	15,000	8000	18,000	25,000
	Dermal Contact	RES	RES	RES	RES
	Vapour Inhalation (indoor, basement)	50	240	NA	NA
	Vapour Inhalation (indoor, slab-on-grade)	30	150	NA	NA
	Protection of Potable GW	860	1200	NA	NA
	Protection of GW for Aquatic Life[1]	230	150	NA	NA
	Nutrient Cycling	TBD	TBD	TBD	TBD
	Eco Soil Contact[3]	130	450	400	2800
	Produce	NC	NC	NC	NC
Commercial	Soil Ingestion	RES	29,000	RES	RES
	Dermal Contact	RES	RES	RES	RES
	Vapour Inhalation (indoor)	310	1700	NA	NA
	Protection of Potable GW	860	1200	NA	NA
	Protection of GW for Aquatic Life[1]	230	150	NA	NA
	Nutrient Cycling	TBD	TBD	TBD	TBD
	Eco Soil Contact[3]	330	760	1700	3300
Industrial	Soil Ingestion	RES	RES	NA	NA
	Dermal Contact	RES	RES	RES	NA
	Vapour Inhalation (indoor)	310	1700	NA	NA
	Protection of Potable GW	860	1200	NA	NA
	Protection of GW for Aquatic Life[1]	230	150	NA	NA
	Nutrient Cycling	TBD	TBD	TBD	TBD
	Eco Soil Contact[3]	330	760	1700	3300
	Offsite Migration	NA	NA	RES	RES

NA = Not applicable. Calculated value exceeds 1,000,000 mg/kg or pathway excluded.
RES = Residual PHC formation. Calculated value exceeds 30,000 mg/kg and solubility limit for PHC fraction.
NC = Not calculated. Insufficient data to allow derivation.
TBD = To be determined
1 = Assumes surface water body at 10 m from site.
2 = Includes use of dugouts and wells for supply of livestock water.
3 = Tier 1 values based mainly on laboratory bioassay response to fractions derived from fresh Federated Crude Oil.

Table 5.3. Generic levels for PHCs in fine-grained subsoil (> 1.5 m depth).

Land Use	Exposure Pathways	F1 (C6-C10)	F2 (>C10-C16)	F3 (>C16-C34)	F4 (>C34)
Agricultural	Soil Ingestion	RES	RES	RES	RES
	Dermal Contact	RES	RES	RES	RES
	Vapour Inhalation (indoor, 30 m offset)	2100	11,400	NA	NA
	Protection of Potable GW[1]	180	250	NA	NA
	Protection of GW for Aquatic Life[2]	TBD	TBD	NA	NA
	Protection of GW for Livestock Watering[3]	TBD	TBD	NA	NA
	Nutrient Cycling	NA	NA	NA	NA
	Eco Soil Contact[4]	750	2200	3500	10,000
	Eco Soil Ingestion	*TBD*	*TBD*	*TBD*	*TBD*
	Produce, Meat and Milk	NA	NA	NA	NA
Residential	Soil Ingestion	RES	RES	RES	RES
	Dermal Contact	RES	RES	RES	RES
	Vapour Inhalation (indoor: basement, slab)	(940, 990)	(5200, 5500)	NA	NA
	Protection of Potable GW[1]	180	250	NA	NA
	Protection of GW for Aquatic Life[2]	TBD	TBD	NA	NA
	Nutrient Cycling	NA	NA	NA	NA
	Eco Soil Contact[4]	750	2200	3500	10,000
	Produce	NA	NA	NA	NA
Commercial	Soil Ingestion	RES	RES	RES	RES
	Dermal Contact	NA	RES	NA	NA
	Vapour Inhalation (indoor)	4800	26,000	NA	NA
	Protection of Potable GW[1]	180	250	NA	NA
	Protection of GW for Aquatic Life[2]	TBD	TBD	NA	NA
	Nutrient Cycling	NA	NA	NA	NA
	Eco Soil Contact[4]	1000	3000	5000	10,000
Industrial	Soil Ingestion	NA	NA	NA	NA
	Dermal Contact	NA	NA	NA	NA
	Vapour Inhalation (Indoor)	4800	26,000	NA	NA
	Protection of Potable GW[1]	180	250	NA	NA
	Protection of GW for Aquatic Life[2]	TBD	TBD	NA	NA
	Nutrient Cycling	NA	NA	NA	NA
	Eco Soil Contact[4]	1000	3000	5000	10,000
	Offsite Migration	NA	NA	NA	NA

NA = Not applicable. Calculated value exceeds 1,000,000 mg/kg or pathway excluded.
RES = Residual PHC formation. Calculated value exceeds 30,000 mg/kg and solubility limit for PHC fraction.
NC = Not calculated. Insufficient data to allow derivation.
TBD = To be determined

1 = Assumes site is underlain by groundwater of potable quality in sufficient yield (K of 10^{-4} cm/sec or greater).
2 = Assumes surface water body at 10 m from site.
3 = Generally applicable for this land use as related to use of dugouts and wells for supply of livestock water.
4 = Values based primarily on laboratory bioassay response to fractions derived from fresh Federated Crude Oil and adjusted for texture, depth factors and other physical hazard considerations.

Table 5.4. Generic levels for PHC in coarse-grained subsoil (> 1.5 m depth).

Land Use	Exposure Pathways	F1 (C6-C10)	F2 (>C10-C16)	F3 (>C16-C34)	F4 (>C34)
Agricultural	Soil Ingestion	RES	RES	RES	RES
	Dermal Contact	RES	RES	RES	RES
	Vapour Inhalation (indoor, 30 m offset)	200	1100	NA	NA
	Protection of Potable GW	860	1200	NA	NA
	Protection of GW for Aquatic Life[1]	230	150	NA	NA
	Protection of GW for Livestock Watering[2]	*9000*	*4000*	NA	NA
	Nutrient Cycling	NA	NA	NA	NA
	Eco Soil Contact[3]	350	1500	2500	10,000
	Produce, Meat and Milk	NA	NA	NA	NA
Residential	Soil Ingestion	RES	RES	RES	RES
	Dermal Contact	RES	RES	RES	RES
	Vapour Inhalation (indoor, basement)	50	240	NA	NA
	Vapour Inhalation (indoor, slab-on-grade)	40	190	NA	NA
	Protection of Potable GW	860	1200	NA	NA
	Protection of GW for Aquatic Life[1]	230	150	NA	NA
	Nutrient Cycling	NA	NA	NA	NA
	Eco Soil Contact[3]	350	1500	2500	10,000
	Produce	NA	NA	NA	NA
Commercial	Soil Ingestion	RES	RES	RES	RES
	Dermal Contact	NA	RES	NA	NA
	Vapour Inhalation (indoor)	340	1800	NA	NA
	Protection of Potable GW	860	1200	NA	NA
	Protection of GW for Aquatic Life[1]	230	150	NA	NA
	Nutrient Cycling	NA	NA	NA	NA
	Eco Soil Contact[3]	700	2000	3500	10,000
Industrial	Soil Ingestion	NA	NA	NA	NA
	Dermal Contact	NA	NA	NA	NA
	Vapour Inhalation (indoor)	340	1800	NA	NA
	Protection of Potable GW	860	1200	NA	NA
	Protection of GW for Aquatic Life[1]	230	150	NA	NA
	Nutrient Cycling	NA	NA	NA	NA
	Eco Soil Contact[3]	700	2000	3500	10,000
	Offsite Migration	NA	NA	NA	NA

NA = Not applicable. Calculated value exceeds 1,000,000 mg/kg or pathway excluded.
RES = Residual PHC formation. Calculated value exceeds 30,000 mg/kg and solubility limit for PHC fraction.
NC = Not calculated. Insufficient data to allow derivation.
TBD = To be determined

1 = Assumes surface water body at 10 m from site.
2 = Includes use of dugouts and wells for supply of livestock water.
3 = Values based primarily on laboratory bioassay response to fractions derived from fresh Federated Crude Oil and adjusted for depth factors and other physical hazard considerations.

6. Background to the Development of Analytical Methodology

6.1 Introduction

Methods for quantifying and reporting environmental contaminants generally influence the scope and interpretation of the results, and this is particularly important in the case of PHCs. Petroleum hydrocarbons in soil have been reported as extractable, purgeable or total depending on how they have been recovered from soil and measured. In addition, variations in the degree of analytical "clean up" and the manner of detection/quantification affect the results obtained and the reporting terminology. Analytical cleanup is normally undertaken to reduce interference from co-extracted biochemicals that are not PHCs. Quantification can occur by gravimetric, spectrophotometric or chromatographic methods.

Various combinations of extraction, cleanup and detection methods contribute to a proliferation of terms, which include oil and grease, mineral oil and grease, extractable hydrocarbons, purgeable hydrocarbons, and total petroleum hydrocarbons. This array of terms is confusing to users and contributes to uncertainty around what is being observed and what environmental significance a given set of data might have.

Inter laboratory studies of PHC analytical methods conducted by Environment Canada's Wastewater Technology Centre in the mid-1990s showed highly variable results from laboratory to laboratory when extraction, purification and detection steps were not specified. However, much of the variability depended on systematic factors – i.e., fundamental differences in extraction, detection, quantification and reporting. Stakeholders confirmed the need for consistent nomenclature, analytical methodology and linkage between the two at the first national PHC workshop in October 1997. The CCME PHC CWS thus includes a reference analytical method that must be followed to ensure the validity of the assessment and remediation program. The reference method combines prescriptive and performance-based elements.

6.2 Sampling and Analysis of PHC in Soil

The reference method for measurement of PHC in soil and subsoil described in this section was developed under the guidance of a national, multistakeholder Analytical Methods Technical Advisory Group (AM TAG). The method was developed to ensure that measurements made in support of the PHC CWS:

- Link to the fractions used in the risk analysis;
- Are technically and scientifically defensible;
- Provide users with accurate and consistent results;

- Can be delivered by competent laboratories using routine equipment;
- Can incorporate knowledge and experience of analysts to improve results and costs within a performance-based framework.

While the procedures described below are required to characterize contamination and confirm remedial results, it is recognized that certain simplifications will occur on a site-by-site basis or within the overall management process at a given site. As examples:

a) Site characterization may confirm that only a subset of CWS PHC fractions is present at a particular release site and this information may be used to reduce the cost and complexity of PHC analysis. For example, investigation of a site confirmed to be contaminated by fresh gasoline need not include observations on F3 and F4. Similarly, if weathered lubricants are the sole PHC contaminants, observations on F1 and possibly F2 will not be needed.

b) It may be possible at many sites to correlate inexpensive screening analyses with standardized reference analyses (CCME 2000). While such analyses would not be adequate for confirmation or regulatory purposes, they may be useful in the delineation of contamination and preparation of remedial action plans.

It is further recognized that analytical results are strongly influenced by sampling procedures including the approach to delineation, sample collection technique, handling and storage. These considerations are touched on only briefly below but are considered in greater detail in both the analytical method documentation (CCME 2000) and the PHC CWS User Guidance (CCME 200X).

6.3 Sample Collection and Handling

Sampling is generally undertaken to assess the nature and extent of contamination and, depending on assessment outcome, guide any necessary remedial actions and confirm their effectiveness. Ultimately, sampling and analysis information will be used to create a record of environmental condition that will allow stakeholders to make appropriate land and water use decisions. Concentrations of the PHC fractions in contaminated soil and subsoil are needed to assess management options including the urgency of any indicated remedial action and the technologies that may be able to deal with the contamination.

Given the above applications, sampling for site characterization must be conducted so as to:

- delineate the lateral and vertical extent of "non-compliant" soil and subsoil,

- maximize retention of all fractions (F1, F2, F3, F4) in the sample,
- determine the concentration of contamination in the non-compliant areas.

Sampling for confirmation of site condition must be able to show that non-compliant soil and subsoil has been remediated and that margins of the affected area "test clean". The definitions of compliant and non-compliant material depend on land use, texture, depth and various site properties and use patterns as described in CCME (200X).

Retention of PHC in soil and subsoil samples is critical in achieving valid analytical results, especially for the volatile fraction F1. Dissipation of low molecular weight PHC via volatilization and biodegradation is the principal concern. Biodegradation is also a concern for other PHC fractions. Use of air-tight vessels and low temperature storage for minimizing this dissipation is described in CCME (2000).

Technical guidance to assist in achieving the goals of accurate and precise characterization of site conditions is provided in **CCME (1993, 1994**, 200X). The CWS PHC method does not address in detail sampling of PHC contaminated sites. It does provide general guidance using CCME and U.S.EPA published procedures and the necessity of following a strict protocol and the need for samplers to develop QA/QC procedures for sampling and transfer to the laboratory.

The quality and quantity of site characterization data necessary for assessment and closure of a PHC-contaminated site are determined by jurisdictions.

It is essential to note that many different sampling strategies can yield acceptable and comparable site characterization data. The choice of strategy is up to the user.

6.4 Analysis of PHC in Soil Samples

Determination of PHC in solid matrices such as soils generally includes extraction and detection steps and may include a purification or clean-up step in between. Historically, a great diversity of extraction and detection systems have been used. The CCME reference method (CCME 2000) is based on proven approaches that mate well with the four PHC fractions and make use of technologies that are routinely available in laboratories accredited by the Canadian Association of Environmental Analytical Laboratories or the Ministère de l'environment du Quebèc. The method blends prescriptive (procedures that must be followed) and performance-based elements (a range of procedures meeting performance criteria which may be used). The balance between prescriptive and performance-based procedures was reached by consensus among members of the AM TAG in consideration of professional experience and results of round robin trials aimed at identifying sources of error in PHC methods.

6.4.1 Outline of Method

PHCs are divided into two practical categories that differ in analytical procedures: (1) volatile PHCs (F1), and (2) extractable PHCs (F2-F4). Depending on the amount of F4 material in the sample and user/analyst preferences, extractable PHCs may be further sub-divided on the basis of detection method (chromatographic/gravimetric).

Volatile PHCs are recovered by extracting the sample with methanol in a sealed container. Volatile PHCs dissolved in the methanol are then purged directly to a gas chromatograph (GC) equipped with a 100% poly(dimethylsiloxane) (DB-1 or equivalent) column and flame ionization detector (FID). Area counts between C6 and C10 are then integrated and adjusted for BTEX (which are measured and reported separately) and reported in concentration units as F1.

Extractable PHCs are recovered by Soxhlet extraction in 50:50 hexane-acetone. The extract is dried over sodium sulfate and treated with silica gel to remove polar material (fats, plant waxes etc.). A sample of the extract is then injected into a GC-FID equipped with a poly(dimethylsiloxane) column. Area counts are integrated and then quantified in the following ranges: (1) nC10 to nC16 – "F2", (2) nC16 to nC34 – "F3", and (3) nC34 to nC50 - "F4". This determination of F4 is adequate provided the GC-FID chromatogram has returned to the baseline at nC50. If this is not the case, or other evidence suggests that PHCs greater than nC50 are present in appreciable quantities, residual PHCs may be determined gravimetrically or through extended, high temperature chromatography. If determinations of target PAH (e.g., napthalene, phenanthrene, chrysene, benzo(a)pyrene) have been made, these should be subtracted from the appropriate PHC CWS fractions (generally F3, except F2 for naphthalene).

Comparison to other methods for PHCs:

There is an incredible diversity of methods for analyzing PHCs. This meant that compromises had to be struck. For example, considerable debate was held by the AMTAG regarding use of solvents e.g. dichloromethane (DCM) versus hexane or hexane/acetone. The success of silica gel clean up to remove compounds other than hydrocarbons before gas chromatography is very much dependent on experience, degree of activation, and the solvent used for elution. This confirms the need for on-going improvement and further standardization in analytical methods for PHCs.

6.5 Linkage to Effects Database

The toxic response of plants and invertebrates to the above analytically-defined fractions was determined in soil microcosms. Concentrations of the fractions were measured at various times during the exposure period using the reference method.

No uncertainty factors were added to the toxic response endpoints (see Section 4.2). Thus, to maximize applicability of results, analytical determinations from field sites should use the reference method.

Similarly, human health toxicological endpoints were drawn from work of the TPHCWG and are specific to sub-fractions defined within the four PHC CWS fractions. Again, appropriate comparison to the risk-based endpoints derived from the TPHCWG toxicological reference values requires that PHC be measured and reported consistent with the reference method.

6.6 Notes on the PHC CWS Analytical Method

6.6.1 Development, Validation, and Calibration Issues

Although it is the intention of the CCME that jurisdictions adopt the analytical method as a standard, jurisdictions may choose to use it as a benchmark against which laboratories can establish their performance using equivalent methods (in areas where flexibility is indicated). The need to follow the four fractions in the CWS and a need for a consistent approach to calibration have been captured within the method. Reference Materials are not available at this time. However, the Canadian Association for Environmental Analytical Laboratories have been approached to consider one more preliminary inter-laboratory study, followed by a regular Proficiency Testing program. This program would allow Canadian laboratories accredited by the Standards Council of Canada to include PHCs by this method in their scope of accreditation.

6.6.2 Data Quality Objectives

Method detection limits are not available at this time. Consideration is being given to the development of a single laboratory validation to determine method detection limits. This could be verified by the preliminary inter-laboratory study discussed earlier. Recoveries, as normally defined, are not addressed in the method due to a lack of appropriate surrogates. One of the conclusions from a recent inter-laboratory study was that good laboratories, with experience in the PHC CWS method, routinely generated results within 25% of design values -- a vast improvement on past inter laboratory performance.

6.6.3 BTEX and PAH Analysis

The method does require analysis of BTEX so that values for BTEX can be subtracted from fraction F1. However, it is left to jurisdictions to choose among a variety of good, available methods. Most use GC-MS to aid identification of BTEX

components. It is not possible to measure BTEX components by the PHC CWS method as compounds are not uniquely resolved in the C6-C10 region by GC-FID. The PHC CWS method also requires subtraction of selected PAHs if they are present in sufficient quantity to affect the PHC result. Sites showing considerable quantities of PAHs would have to be treated as such.

6.6.4 Constraining PHC Quantitation Range

Inclusive procedures in the analytical method are provided on the assumption that PHC contamination may be "broad-band" and poorly characterized – as might occur in the case of a crude oil release, or when different product/waste streams coalesce in a downstream scenario. However, in some cases, reliable information exists to indicate that a PHC release is of a single type that is well-characterized and confined to (1) three or less of the PHC CWS fractions, or (2) F1-F3 plus only a portion of F4. The latter case is discussed in some detail in the analytical method – the go/no-go decision regarding extending chromatography beyond C50 or performing a gravimetric determination based on chromatogram characteristics and knowledge of release type.

In principle, similar approaches may be applied with respect to the first case. For example, if PHC contamination is understood to be related to a recent release of a single grade of gasoline, and comprehensive gas chromatography of representative samples confirms this knowledge, F4 and possibly F3 can be eliminated from the analysis. Similarly, other simple fuel types may be confirmed by return of the chromatographic trace to the baseline region within the F3 envelope. In such cases it may be unnecessary to extend chromatography to the C50 range.

Specific approved procedures must be confirmed with the jurisdictional authority.

6.6.5 Additional Comments

Screening approaches were not considered. They exist but generally are not applicable to what is essentially a reference method, the results of which will decide which action is to be taken. Screening or rapid on-site techniques can be useful during remediation and in defining site boundaries.

It was noted that unusual soils may require different treatments of the results (e.g. soils with very organic levels or soils partially remediated with straw and manure). Such results are useful, despite their limitations, in deciding which Tier-level provides the best approach to remediation.

7. Summary and Recommendations

7.1 Scientific Overview

PHCs released to soil pose a variety of risks in the geo-environment. These risks include combustion hazards, direct toxic risks to humans, plants and animals, effects on soil processes such as water retention and nutrient cycling, movement to water and air, and aesthetic problems such as objectionable odour and sheen. Left unmanaged, PHCs in the geo-environment can cause important adverse effects.

PHC release sites are present in all Canadian jurisdictions and the total number of actual and potential sites number in the hundreds of thousands. Jurisdictions presently assess and manage PHC-contaminated sites under different processes with different yardsticks and different terminologies, producing a patchwork of environmental results and costs. This is both confusing to stakeholders and an inefficient use of resources. Nationally consistent understandings and outcomes are needed.

This document presents the consensus recommendations of the CCME Development Committee for the Tier 1 standards of the Canada-Wide Standard for Petroleum Hydrocarbons in Soil. These Tier 1 standards for soil and subsoil reside within a 3-tiered, risk-based framework that can be applied to assess and manage sites contaminated by petroleum hydrocarbons in the range of C6 to C50+. Tier 2 and Tier 3 procedures are described in CCME (200X).

The Tier 1 standards are science-based and designed to be protective of human and ecological health for four land use categories – agricultural, residential, commercial and industrial. For each of these land-use categories an exposure scenario was developed to illustrate a sensitive use. The exposure scenario defined the receptors present and pathways by which these could be exposed to contamination in soil, subsoil and cross-contaminated groundwater. Knowledge of receptor response to PHC contamination was used to calculate or estimate environmentally acceptable concentrations in the soil and subsoil.

Because environmental behaviour and effects of PHCs in the geo-environment are related to chemical properties (e.g., size, geometry and extent of oxidation) it was advantageous to consider these substancesin broad categories or fractions. Four fractions were defined by combining sub-fractions provided in the work of the US TPH Criteria Working Group. For the purposes of human health protection, it was assumed that within the four fractions aliphatics and aromatics were present in a ratio of 4:1. The combined sub-fractions in the appropriate ratios then served as surrogates for the entire fraction.

A review of scientific literature indicated that there was insufficient information to support a similar approach for protection of ecological receptors. Research was commissioned by several stakeholder groups to provide information to support a weight-of-evidence approach that combined biological response data from chemical surrogates, whole fractions, and whole products. Both on-site and off-site receptors were considered.

Offsite receptors were considered primarily as users of PHC-contaminated groundwater. Groundwater protection goals were defined either at the downgradient boundary of a PHC-contaminated area (potable uses) or at a nominal 10 m offset (livestock watering or aquatic life receptor). This distance can be replaced by site data in a Tier 2 assessment.

The above procedures taken together provide a strong and much-improved scientific basis for Tier 1 standards applicable to PHC contamination of soil and subsoil in Canada. Coupled to the tiered assessment framework (CCME 200X), it is expected that greater precision and efficiency in remedial efforts will be realized.

7.1.1 Uncertainty

Many uncertainties are present in the science underlying the PHC CWS. Some of the uncertainty represents lack of knowledge. For example, the intrusion rates of F1 vapours into enclosed spaces are generally not known. Rather, these rates are estimated through use of mechanistic vapour transport models. It is expected that models will improve through testing and refinement, also less reliance on models will be required as methods for on-site vapour intrusion measurement evolve. Some uncertainty is caused also by random and or complex future events such as the likelihood that groundwater not presently used will be used.

Efforts were made throughout the PHC CWS development process to identify key areas of uncertainty that could be reduced through research. These areas are discussed under the Recommendations section below.

Uncertainties in exposure and effects were generally addressed by ensuring that conservative assumptions were made regarding contaminant types, mobilities, toxicities and exposure patterns. This approach was balanced with the need for practical Tier 1 standards that take account of technological capabilities and socio-economic factors.

7.2 Socio-economic Considerations

The PHC CWS Tier 1 standards were designed to be attainable. Socio-economic screening analyses were undertaken that confirmed that liabilities for remediation of PHC-contaminated sites in Canada are in the multi-billion dollar range. It was noted

that bioremedial technologies are the most accessible, affordable and reliable approaches presently available.

Performance capabilities of bioremedial technologies were considered in the interpretation of scientific uncertainties in development of the Tier 1 standards. For example, bio-treatability was influential in the interpretation of ecotoxicological response to F3. Dispersion in data between laboratory and field conditions, fresh versus weathered PHC and coarse versus fine textures indicated that the 400 mg/kg ecotoxicity standard applicable to coarse textured surface soils under sensitive land uses could safely be relaxed to 800 mg/kg for fine textures and better accommodate bioremedial performance factors.

Similarly, socio-economic factors were the principal risk management consideration in basing ecological protection for commercial and industrial soils solely on the response of plants. The PHC CWS is a practical standard. Practical endpoints and management decisions are delivered, however, within the scientific uncertainty around the definition of acceptable environmental quality. In other words, soils remediated to the Tier 1 standards are expected to pose no adverse effects to human health or the environment within the conservative exposure scenarios used.

The principal benefits expected from implementation of the PHC CWS include:

- Documented scientific basis for risk management decisions for PHC-contaminated sites;
- Standards are protective of human and environmental health;
- Consistent approach to measurement, assessment and remediation levels the playing field for responsible parties and stakeholders;
- Attainable standards encourages responsible action and brings affected areas back into use at a faster rate;
- Tiered assessment framework allows efficient use of remedial resources while ensuring protection – avoids over- and under-management of sites;
- Clear land and water use decisions at PHC-contaminated sites.

7.3 Recommendations for Further Development and Research

Significant progress was made in applying current science to the development of the PHC CWS. Nevertheless, there are still important gaps in information and understanding that, if filled, would lead to further improvements in the management of PHC in Canada's geo-environment. The following sections list the principal areas

where the Development Committee and Technical Advisory Groups felt that research investment was needed.

7.3.1 Research Related to Human Health Protection

Toxicity of PHC fractions

- deficiencies were noted in understanding of toxic actions of aromatic components of F3 and F4. Pyrene was used as a surrogate but this will not be satisfactory in the long term because it does not chromatograph with F4 compounds. An appropriate, non-carcinogenic F4 aromatic compound needs to be identified.

- Commercial hexane was used as a surrogate for F1 aliphatics. However, some components of the F1 aliphatics – those, such as n-hexane, metabolized to gamma-diketones - have unique modes of toxic action and, apparently, high potencies. These may need to be managed separately or F1 aliphatic potency may need revision. There are presently inconsistencies in the available regulatory toxicity evaluations for commercial hexane and pure hexane.

- Heterocyclic components of PHCs were not considered in the present development work. Certain thiophenes and quinolines exhibit ecotoxicity and may be present at low levels in a variety of PHC sources. Further information is needed on their occurrence in common PHC release types and effects in mammalian systems. Once this information is available, the appropriateness of the toxicological benchmarks for F3 and F4 must be assessed to identify any necessary changes.

Vapour Intrusion to Buildings

- Vapour movement under and around building foundations – relative contributions of advective and diffusive transport. In the PHC CWS, advection is included only for coarse-textured soils. However, the relative contributions of the two transport mechanisms in soils of intermediate texture are not known and may be important in the vapour intrusion process.

- Adaptation of Darcy's Law to gaps and imperfections in building foundations. The PHC CWS applies a description of vapour intrusion based on movement of gases to a buried perimeter pipe adapted by Johnson and Ettinger (1991) from research on radon infiltration. Research is needed to explore infiltration through differing spacings and geometries in response to pressure and concentration gradients across building substructures.

- Development of field methods for determination of peri-foundational PHC concentrations and rates of intrusion – such that reliance on models may be reduced. While improvements to models are needed to support pro-active

management – including better generic standards – in cases where vapours are at or near the foundation some form of exposure management is often required on an urgent basis. Improved methods are needed for obtaining relevant and representative soil gas measurements near foundations and interpreting these data such that appropriate interventions are taken.

Aesthetics

Management decisions regarding PHC contamination of soils are sometimes driven by odour considerations. These decisions are generally made on the basis of qualitative, site-specific information – i.e., the material is deemed unsuitable for the present or proposed use on the basis of odours disagreeable to one or more stakeholders. Such situations are difficult to forecast and are therefore a potential concern in re-development of PHC-affected sites. A systematic and objective approach to evaluation of PHC odours could reduce the frequency of such events. Information is needed on:

- Odour thresholds of commonly occurring PHC constituents;
- Occurrence and abundance of malodorous components in common PHC release types;
- Vapour pressures and mobilities of these compounds;
- Options for incorporation of this information into a risk-based approach.

7.3.2 Research Related to Ecological Protection

Effects of PHCs in Field Trials

- Information is needed on the fate of individual fractions over time. Current data present information on dissipation and toxicity of mainly whole products. Effects from balance of fractions cannot be segregated from bioavailability within fractions.

Effects of Different PHC Mixtures

- Ecotox information is needed on cuts prepared from different PHC sources. It is not known how well the Federated Crude oil represents the diversity of PHC sources in Canada.

Bioassay

- A broader range of plants and soil organisms need study. Effects of vapour perfusion from below on roots, soil organisms have not received much study.

- Thorough, toxicity-based guidelines for aquatic receptors are needed based on direct testing of F1 and F2 fractions.

7.3.3 Research Related to Fate, Behaviour and Effects of PHC in and on the Geo-Environment

- Genesis of hydrophobicity. What soil properties, PHC properties and management histories lead to this phenomenon?

- Aqueous and vapour phase partitioning of low molecular weight PHCs in the presence of variable amounts of F2, F3 and F4 material. The practical application of Raoult's Law to better estimate vapour and dissolved phase concentrations contributing to leaching and vapour intrusion fluxes.

- Biodegradation rates in the vadose zone in relation to season, soil moisture content, depth and nutrient availability. Methods to measure biodegradation rates throughout the year at individual sites are needed.

- Harmonization of groundwater modeling for on- and off-site receptors. Research to identify a single modeling approach that can be applied to receptors at various distances from a source is needed. Also needed is a review of vertical mixing and dispersion phenomena and appropriate mathematical descriptions.

- Guidance on sampling, storage and handling of PHC-contaminated soil, subsoil and groundwater is also required.

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Appendix A: Overview of CCME developmental and consultative processes for the PHC CWS

A.1 Canada-Wide Standards

In January of 1998 twelve Canadian Ministers of the Environment (members of the Canadian Council of Ministers of the Environment (CCME)) signed a Harmonization Accord and three associated sub-agreements, including the Sub-Agreement on Environmental Standards[1]. The Canada-wide Environmental Standards Sub-Agreement is a framework for federal, provincial and territorial Environmental Ministers to work together to address key environmental protection and health risk reduction issues that require a common standard across the country. The standards sub-agreement sets out principles for governments to jointly agree on priorities, to develop standards, and to prepare complementary workplans to achieve those standards, based on the unique responsibilities and legislation of each government.

Six priority substances were announced at the time of signing of the Canada-wide Environmental Standards Sub-Agreement. PHCs in soil were one such priority; a problem shared by all jurisdictions throughout Canada.

In June 2000, the PHC CWS was accepted in principle by the Canadian Council of Ministers of the Environment[2] (CCME).

A.1.1 Developmental Process for the PHC CWS

Release of the PHC CWS represents the culmination of a three-year multi-stakeholder development process, reflecting the efforts of representatives from government, petroleum and environmental industries, academia and non-governmental organizations.

The PHC CWS was developed under the direction of a national Development Committee co-chaired by Alberta and Canada. Alberta was the champion of the PHC CWS, having responsibility for providing leadership and overall management of the development of the standard including preparation of workplans; initiating, tracking and integrating the necessary pieces; liaising with stakeholders and the Environmental Planning and Protection Committee; coordinating activities with other Development Committees; and presenting the standard to the Council of Ministers.

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[1] Nunavut Signed on to the Harmonization Accord and Subagreements when they joined the Council in November 1999.

[2] The CCME is the major inter-governmental forum in Canada for discussion and joint action on environmental issues of national and international concern. The council is made up of environment ministers from the federal, provincial and territorial governments. The CCME undertakes activities associated with environmental protection and sustainable development through coordinated action, which includes the development of Canada-wide Standards.

Four multi-stakeholder technical advisory groups and one working group supported the work of the Development Committee. Consensus process was used to generate recommendations to the Development Committee from the advisory and working groups, and consensus among jurisdictions was used to generate recommendations in the Development Committee. National, multi-stakeholder workshops were used to set the initial direction of development (October 1997) and confirm results and direction as development proceeded.

In the early stages of the development of the standard, technical advisory groups (TAGs) were tasked to provide expert scientific advice to the PHC CWS Development Committee including the: Analytical Methods TAG (AMTAG), Human Health Fate and Transport TAG (HHFTTAG), Ecological TAG (ECOTAG), and Socioeconomic Analysis TAG (SEATAG). In addition, the Protocol Improvement Working Group (PIWG) was established to evaluate and compare established protocols for the derivation of human health-based soil quality assessment values for petroleum hydrocarbons. In particular, the PIWG reviewed the CCME Protocol for the derivation of environmental and human health soil quality guidelines (CCME 1996) and the Atlantic Partnership in RBCA (Risk-Based Corrective Action) for Petroleum Impacted (PIRI) Sites (Atlantic PIRI 1999). The establishment of the TAGs and PIWG, which reported on a regular basis to the Development Committee, resulted in a process that ensured a high level of multi-stakeholder consultation and transparency throughout the development of the standard.

A.2.0 Membership of PHC CWS Committees

A.2.1 PHC CWS Development Committee

Member	Jurisdiction
Ted Nason (co-chair)	Alberta
Glyn Fox	British Columbia
David Thornton (co-chair) Connie Gaudet, Kathie Adare	Canada
Edwin Yee	Manitoba
Ray Morin	New Brunswick
Toby Matthews	Newfoundland
Harvey Gaukel	Northwest Territories

John Henderson, Sharon Vervaet	Nova Scotia
Earle Baddaloo	Nunavut
Marius Marsh	Ontario
Danny McInnis	Prince Edward Island
Renée Gauthier	Quebec
Sam Ferris	Saskatchewan
Kevin McDonnell, Ruth Hall	Yukon
Fred O'Brien (Yukon)	CEOH
Scott Tessier, Margaret Gibbs, Nancy Gehlen	CCME

A.2.2 Human Health Fate and Transport Technical Advisory Group (HHFT TAG)

The CCME Human Health/Fate and Transport Technical Advisory Group (HHFT TAG) was mandated to assist with delivery of of the PHC CWS by:

- providing advice on technical issues or questions posed by the PHC DC;
- assisting in the selection of optimum solutions from technical options;
- evaluating models for best predictive power under diverse Canadian conditions.

The primary purpose of the HHFT TAG is to enable the PHC DC to deliver on a timely basis Tier 1 levels for petroleum hydrocarbons (PHCs) in soil that are scientifically sound and consistent with stakeholder advice on consideration of direct and indirect exposure pathways for humans under the four land uses defined in the CCME framework.

Membership of the HHFT TAG was designed to ensure the required complement of expertise in toxicology, soil science, hydrogeology and risk analysis. As well, a balance was sought across sectors and between basic and applied fields.

Name	Affiliation
HHFT TAG I:	
Warren Kindzierski (Chair)	University of Alberta
Adolfo Silva	Canadian Petroleum Products Institute
Chris Severson-Baker	Pembina Institute
Donna Vorhees	Menzie-Cura
Glyn Fox	BC Environment
Jean-Pierre Trepanier	Sanexen
John Cracknell	Jacques-Whitford
Mark Allen	New Brunswick Health Committee for Environmental and Occupational Health (CEOH)
Michel Charbonneau	University of Quebec
Reidar Zapf-Gilje	Golder Associates
Rob Hoffman	Chevron Canada
Corresponding Members:	
Christine Moore	CanTox
David Williams	O'Connor Associates
John Wiens	AGRA
Mike Zemanek	Alberta Environment
Paul Kostecki	University of Massachusetts
Reginal North	Keystone Environmental
HHFT TAG II:	
Warren Kindzierski (Chair)	University of Alberta
Adolfo Silva	Canadian Petroleum Products Institute
Andrea Walters	Petro Canada
Claude Chamberland	Shell Canada
Donna Vorhees	Menzie-Cura
Eliot Sigal	CanTox
Glyn Fox	BC Environment
Ian Hers	Golder Associates
Mark Cameron	Keystone Environmental
Mike Zemanek	Alberta Environment

A.2.3 Ecological Technical Advisory Group (Eco TAG)

Name	Affiliation
EcoTAG core members:	
Doug Bright, Chair	Royal Roads University
Lin Callow	Gulf Canada Resources Inc.
Anne-Marie Lafortune	Ministère de l'Environnement et de la Faune
Wayne Landis	Western Washington University
Bill McGill	University of Alberta
Peter Miasek	Imperial Oil
Christine Moore	CanTox
Norman Sawatsky	Alberta Environment
Rick Scroggins	Environment Canada
Gladys Stephenson	ESG International Inc.
Graham van Aggelen	Environment Canada
Susanne Visser	University of Calgary
Ex officio:	
Kathie Adare	Environment Canada
Connie Gaudet	Environment Canada
Trisha Murray	Environment Canada
Sylvain Ouellet	Environment Canada
Tracy Schneider	Environment Canada
Sherri Smith	Environment Canada
Corresponding Members:	
Nigel Blakley	Washington State Department of Ecology
James Clark	
Anne Fairbrother	ParaMetrix
Stephen Goudey	HydroQual Labs
Sue Halla	Alberta Energy and Utilities Board
Michael Kangas	
Francis Law	Simon Fraser University
Mike MacFarlane	BC Environment
Lynn McCarty	Golder Associates
Rodger Melton	
Charles Menzie	Menzie-Cura and Associates
Dwayne Moore	Cadmus Group
Stan Pauwels	Mclaren-Hart.com
Mike Rankin	Golder Associates Ltd.
Andrew Teal	Imperial Oil

A.2.4 Analytical Methods Technical Advisory Group (AM TAG)

The CCME Analytical Methods Technical Advisory Group (AM TAG) was mandated to assist with delivery of the PHC CWS by:

- Providing advice on technical issues or questions posed by the PHC DC;
- Reviewing existing methods for the determination of PHC in solid matrices;
- Developing recommendations for a benchmark analytical method to support the PHC CWS;
- Testing the recommended benchmark method and providing advice on operating parameters, data analysis and performance-based measures for validation of equivalent or better methods.

The primary purpose of the AM TAG was to enable the PHC DC to deliver on a timely basis a Canada-Wide Standard for petroleum hydrocarbons (PHC) in soil that is scientifically sound and accompanied by a reliable, accurate, precise and practical analytical method.

Membership of the AM TAG was designed to ensure the required complement of expertise in environmental and analytical chemistry and experience with analysis of organic mixtures in solid matrices. As well, a balance was sought among private, government and industrial laboratories.

The following members of the Analytical Methods Technical Advisory Group (AMTAG) of the CCME contributed to the establishment and validation of this method.

Name	Affiliation
Richard Turle	Environment Canada (AMTAG Chair)
Renée Gauthier	Ministère de l'Environnement du Québec
Scott Hannam	ASL Analytical Service Laboratories Ltd.
George Kanert	Ontario Ministry of the Environment
Abdel Kharrat	Alberta Research Council
Don Laberge	Envirotest Laboratories (CAEAL Representative)
Todd Arsenault	Environment New Brunswick
Tim Munshaw	Philip Analytical (IAETL Representative)
Carol Drury	Shell Canada (Petroleum industry Representative)
Ileana Rhodes	Equilon Enterprises LLC (Petroleum industry representative)
François Messier	CEAEQ, Ministère de l'Environnement du Québec
Dave Morse	Ontario Ministry of the Environment
Peter Fowlie	Cornerstone Science

A.2.5 Socio-Economic Technical Advisory Group (SEA TAG)

The CCME Socio-Economic Assessment Technical Advisory Group (SEA TAG) was mandated to assist with delivery of the PHC CWS by:

- providing advice on technical issues or questions posed by the PHC DC;
- assisting in the selection of scenarios and models for assessment of socio-economic factors;
- evaluating recommendations for incorporation of socio-economic factors into the PHC CWS.

The primary purpose of the SEA TAG was to enable the PHC DC to deliver on a timely basis a Canada-Wide Standard for petroleum hydrocarbons (PHC) in soil that is scientifically sound and takes account of the limitations and potentials posed by social, economic and technological factors.

Membership of the SEA TAG was designed to ensure the required complement of expertise in environmental science and engineering, risk analysis, social science, and economics. As well, a balance as sought across sectors and between basic and applied fields.

Name	Affiliation
Dana Atwell	Shell Canada
Robert Lee	Cantox Environmental Inc., Calgary, AB
Charles Hammond	Independent Retail Gasoline Marketers Association, St. Marys, ON
Chris Severson-Baker	Pembina Institute, Drayton Valley, AB
Alan Wood	Insurance Bureau of Canada, Edmonton, AB
Paul Young	Petro-Canada
Doug Younie	Alberta Environment, Edmonton, AB

A.2.6 Protocol Improvement Working Group (PIWG):

The Protocol Improvement Working Group (PIWG) was a fixed-duration working group created to compare human health protection aspects of the Canadian Council of Ministers of the Environment (CCME) and the Atlantic Partnership in Risk-based Corrective Action Implementation (Atlantic PIRI) protocols for development of a Canada Wide Standard for petroleum hydrocarbons in soil. An objective of the comparison was to identify and make recommendations for a new protocol that integrates these best aspects of each. A main priority of the PIWG was the direct comparison and consideration of the two protocols in making their recommendations. The PIWG also considered additional fate and transport information from other protocols. Ecological protection aspects of the protocols was

not considered by this group. The PIWG provided its recommendations to CCME Petroleum Hydrocarbon Committee Technical Advisory Groups. The PHC Development Committee considered recommendations of the Technical Advisory Groups in preparing a complete Canada Wide Standard for consideration by senior CCME committees and, ultimately, the Council of Ministers.

Name	Affiliation
Warren Kindzierski (Chair)	University of Alberta
Claude Chamberland	Shell Canada
Lin Callow	Gulf Canada Resources
Sharon Vervaet	Nova Scotia Department of Environment and Labour
Ted Nason / Mike Zemanek (Alternate)	Alberta Environment

Appendix B: Brief historical review of soil quality guidelines for PHCs

B.1.0 History of PHC Management Tools for Contaminated Sites

The CCME *Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines* (CCME 1996) was published in 1996 following 4 years of developmental work by the CCME Subcommittee on Environmental Quality Criteria for Contaminated Sites to devise science-based procedures for deriving soil quality guidelines for human and ecological receptors which have a basis in risk assessment. That *Protocol* underwent extensive peer review and has now been applied to the derivation of risk-based soil quality guidelines for a variety of inorganic and organic contaminants. However, the CCME *Protocol* had not been applied to petroleum hydrocarbon mixtures due to scientific difficulties in applying that framework to complex mixtures.

Currently in Canada, various provinces have existing regulations and/or regulatory policies that prescribe soil quality criteria for sites contaminated with PHCs. A graphical depiction of the carbon fractions represented by these current guidelines is presented in Figure 2.2.

Existing Canadian PHC guidelines differ in their definition of the substance. PHCs have been varyingly defined in terms of:

- petroleum products (gas, diesel, heavy oils) (Ontario);
- physical-chemical characteristics, particularly boiling point (volatile, light extractable, heavy extractable) (B.C.);
- carbon range (C_{10}-C_{50}; that encompasses the potential full range of gas, diesel and heavy oils in the "extractable" range, but excludes BTEX and other more volatile components) (Quebec);
- analytical methods without necessarily defining other characteristics of the mixture (Alberta);
- limited sub-fractions of the carbon number range, (C_5-C_{10}, $C_{>10}$-C_{12}, $C_{>12}$-C_{16}, etc.) adopting definitions, physical-chemical properties, reference doses, and other assumptions, as proposed by the Total Petroleum Hydrocarbon Criteria Working Group (Atlantic provinces).

B.2.0 Review of Some Risk-based Approaches to PHC Assessment / Management

Over the past few years, there have been four primary initiatives in North America to establish a viable, scientifically defensible, risk-based approach to the assessment and management of PHC-contaminated sites. These four approaches have been undertaken by the Massachusetts Department of Environmental Protection (MADEP 1994, 1996, 1997); the Total Petroleum Hydrocarbon Criteria Working Group (Edwards et al. 1997, Gustafson et al. 1997, Potter and Simmons 1998, Weisman

1998); the B.C. Ministry of Environment (Golder Assoc. 1995); by CanTox Inc. (1997); and by the Atlantic provinces (which modified the work of the TPHCWG). These approaches are similar in that they propose to subdivide the complex mixture that is PHC according to specified ranges of equivalent carbon number (ECN), and assign to each 'fraction' the necessary physical-chemical properties (solubility, Henry's Law constant, etc.) and toxicological characteristics (i.e., TDI and/or RfC) which permit the prediction of chemical fate, exposure and potential risk. Refer to Figure 2.2 for a graphical depiction of the carbon number ranges encompassed by the fractions defined by each of these approaches.

These methods differ in the number of, and classification of, carbon number fractions. They also differ in the values that have been assigned for physical-chemical properties and toxicological tolerable daily intakes (TDIs).

In North America, three approaches have been proposed for establishing reference doses for PHC fractions and to subsequently derive risk-based soil quality guidelines. Methods have been proposed by: 1) the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) established by the U.S. Air Force; 2) the Massachusetts Department of Environmental Protection (MADEP); and 3) by CanTOX Inc. Atlantic PIRI has adapted the TPHCWG methodology to the maritime provinces' needs, modifying the approach to reflect risk-based methods, procedures and assumptions prescribed by Health Canada and the Canadian Council of Ministers of Environment.

Other provincial and state agencies have PHC criteria but they are not generally derived via a risk-based approach. A review of the available PHC guidelines/methodologies of these various agencies and organizations follows.

B.3.0 The Total Petroleum Hydrocarbon Criteria Working Group

In 1994, the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) was established in the United States as a result of an initiative of the U.S. Department of Defence. The goal was to devise a scientific basis for assessment of petroleum-contaminated sites within a risk assessment/risk management framework (in particular, the framework provided by the ASTM Standard for Risk Based Corrective Action - RBCA). The work of the TPHCWG culminated in the publication of a four volume series of documents (Edwards et al. 1997, Gustafson et al. 1997, Potter and Simmons 1998, Weisman 1998) evaluating and defining the characteristics of TPH related to environmental fate, toxicity, and other factors pertinent to applying the ASTM RBCA framework to petroleum-contaminated soil and groundwater.

The TPHCWG recommended that PHCs be considered as 14 separate and independent (toxicologically, and with respect to environmental fate) sub-fractions defined by effective carbon number ranges, and further divided between aliphatics and aromatics. This large number of sub-fractions was devised based on a thorough and extensive compilation and evaluation of environmental fate and

transport considerations. The TPHCWG defined the effective carbon number ranges for PHC sub-fractions such that solubility, leachability and the volatility did not span more than approximately one order of magnitude. This degree of uncertainty was considered acceptable within the overall uncertainties of PHC risk assessment/risk management.

The TPHCWG specifically set out to apply the ASTM RBCA (1995) risk-based approach to the issue of PHC contamination. TPHCWG evaluated 275 individual hydrocarbon compounds from the following 11 homologous series:

- straight chain alkanes
- straight chain alkenes
- straight chain alkynes
- branched chain alkanes
- branched chain alkenes
- cylcloalkanes
- cycloalkenes
- alkyl benzenes (including benzene)
- naphtheno benzenes
- alkyl naphthalenes (including naphthalene)
- polynuclear aromatics

Of the 275 individual compounds evaluated, information on all required physico-chemical parameters (carbon number, equivalent carbon number, molecular weight, solubility, specific gravity, vapour pressure, Henry's Law constant, octanol-water partition coefficient, organic carbon partition coefficient, boiling point, diffusivity in air, diffusivity in water) were available for about 180, while partial information existed for the remainder.

As previously mentioned, the TPHCWG methodology was defined as an extension of the ASTM's standard E-1739 for Risk Based Corrective Action (1995). Within the ASTM RBCA approach to deriving risk-based screening levels, two factors have significant influence: LF - leaching factor; and VF - volatilization factor. Due to the influence of these two variables, the TPHCWG grouped carbon sub-fractions of PHC where individual components had values of LF and VF ranging about one order of magnitude. This was considered a reasonable degree of accuracy or consistency given the numerous uncertainties in the risk assessment process. Also, specified carbon sub-fractions were further divided between aromatics and aliphatics. Selected carbon sub-fractions are presented in Table B.1.

Physico-chemical properties of individual components and homologous series were extensively evaluated by direct comparison and correlation. Representative properties for carbon sub-fractions were estimated by arithmetic averaging, weighted averaging and correlation techniques. Sub-fraction-specific physico-

chemical properties ultimately selected by the TPHCWG are also presented in Table B.1.

Sub-fraction specific TDIs and RfCs selected by TPHCWG are presented in Table B.1. Toxicity data were evaluated for both individual compounds and for specific hydrocarbon mixtures where data were available. Emphasis was placed on data pertaining to mixtures as these studies were considered most applicable to, and representative of, PHCs.

On behalf of the TPHCWG, Exxon Biomedical Sciences Inc. conducted a comprehensive search for literature pertaining to the toxicity of all individual hydrocarbon compounds identified in Volume 3 of the TPHCWG's methodology. Literature pertaining to the toxicity of hydrocarbon mixtures was also searched. All relevant studies and reports identified by this search were compiled and are summarized in volume 4 of the TPHCWG Methodology (Edwards et al. 1997). All data were evaluated relevant to the PHC sub-fractions identified in Table B.1.

Where possible and appropriate, suggested TDIs and RfCs were based on the evaluation of studies pertaining to mixtures of hydrocarbons spanning or including the carbon sub-fractions under consideration. Where data and information on mixtures were unavailable or of insufficient quality or relevance, RfCs for individual compounds were selected/defined and used as a surrogate for an entire specified PHC sub-fraction. In some cases, TDI/RfC values for a mixture were based on the weighted averaging of the TDI/RfC of two or more individual components of the mixture.

For the most part, TDIs and RfCs for individual compounds were drawn from U.S.EPA's Integrated Risk Information System and Health Effects Assessment Summary Tables. In some cases, TDIs and RfCs for individual compounds were derived from appropriate studies identified via the literature search, employing methods prescribed by U.S.EPA for the derivation of these reference exposure values. In all cases, TDI/RfC values based on toxicity data pertaining to mixtures were derived by the TPHCWG following procedures prescribed by U.S.EPA.

Demonstration of the TPHCWG approach to PHC mixtures has been completed by the Association of American Railroads (Nakles et al. 1996). Following the TPHCWG proposed approach, Nakles et al. (1996) derived PHC fraction-specific risk-based screening levels (RBSLs). Nakles et al. (1996) also derived RBSLs for gasoline and diesel fuel (BTEX excluded), expressed as the sum of the relative concentrations of these PHC fractions in the weathered whole products.

B.3.1 General Acceptance of the TPHCWG Approach

The work and proposals of the TPHCWG are now widely accepted in the U.S.A., and are becoming accepted in Canada, for the assessment and management of petroleum-contaminated sites. Its root in the ASTM RBCA framework, and the

broad inter-disciplinary and inter-jurisdictional participation in this Working Group has resulted in its general acceptance. In Canada, the Atlantic provinces have adopted this approach within their PIRI (Partnership In RBCA Implementation) initiative. Other provinces have been generally accepting of site-specific risk assessments of PHC-contaminated soils using the TPHCWG approach, particularly the recommended TDIs/RfCs and the assigned physical-chemical properties, with or without the use of the RBCA models and framework.

Based on the foregoing work of the TPHCWG, and on its general regulatory acceptance in North America, the CCME Development Committee on Canada Wide Standards for Petroleum Hydrocarbons has adopted the work of the TPHCWG into the Canada Wide Standard on Petroleum Hydrocarbon. However, some modifications have been introduced in order to accommodate the need for soil quality guidelines for specified "fractions" of PHC.

B. 4.0 Massachusetts Department of Environmental Protection (MADEP)

In 1994, MADEP was the first regulatory agency to formally propose a fraction-specific approach to PHCs (MADEP 1994). Draft regulations respecting numerical criteria were published for public comment on November 1, 1996 and subsequently revised and re-released for further comment on January 17, 1997.

MADEP proposed that PHC be evaluated as the sum of exposures to specific PHC fractions, each with a specified human reference dose thus providing human health risk-based PHC criteria. MADEP established fraction-specific TDIs for individual (surrogate) hydrocarbon compounds published by the U.S.EPA. Where a specified PHC fraction had only one compound with a published TDI (n-hexane within the alkanes, for example), that TDI was adopted as the TDI for the entire fraction. Where a specified fraction had two or more components with published TDIs, the TDI of lowest value (i.e., the TDI for the most potent component) was selected as the representative TDI. Again, the selected TDI was applied to the entire hydrocarbon fraction.

Following comments provided during the public consultation period following the release of proposed revisions to the PHC criteria dated November 1, 1996, and considering recent developments in PHC criteria, particularly the work of TPHCWG, MADEP revised the November 1996 proposals, releasing these revisions for further public consultation on January 17, 1997. Revisions addressed concerns expressed regarding over-conservatism of the proposed guidelines. Research conducted by MADEP on the partitioning of volatile petroleum hydrocarbons between adsorbed, dissolved and vapour phases in soil (which suggested earlier assumptions over-estimated partitioning to the gaseous phase by an order of magnitude) and the toxicological review by the TPHCWG (which indicated uncertainty in the toxicity of certain fractions spanning an order of magnitude) resulted in revised PHC criteria that reflected considerable professional judgement in addition to the calculation of

risk-based criteria derived following standard procedures outlined in the Massachusetts Contingency Plan.

B.5.0 CanTOX Inc.

CanTOX Inc. (1997) has proposed a risk-based approach for petroleum hydrocarbons which it has applied at a variety of sites for the military and other clients. Their approach is similar to that of MADEP in that the toxicological and physico-chemical characteristics of specific, individual compounds within particular PHC fractions are assumed to be representative to the entire fraction. CanTOX increased the representativeness of a surrogate compound for the toxicological characteristics of the specified fraction by defining oral or inhalation reference doses/slope factors for numerous individual petroleum hydrocarbons, thereby eliminating these compounds of known toxicity from PHC fraction analysis to which surrogates would be applied. These compounds of known toxicity would be quantified through chemical analysis of site samples and subtracted from the remaining PHC components. Surrogate toxicities are then applied only to the remaining, chemically-undefined PHC fractions. The prescribed reference doses lend themselves to application to ASTM Standard E-1739 or other risk-based methods of risk assessment and guidelines development.

B.6.0 B.C. MOE - Working Document: Recommendations to B.C. Environment for Development of Remediation Criteria for Petroleum Hydrocarbons in Soil and Groundwater

On behalf of B.C.MOE, Golder Associates prepared a review of national and international approaches to developing risk-based criteria for PHCs (Golder Assoc. 1995). The proposals and recommendations do not represent B.C.MOE policy, and current B.C.MOE guidelines for PHCs in soil and groundwater were based largely on professional judgement rather than quantitative risk assessment (G. Fox, B.C.MOE, personal communication).

This working document was used as a resource document by the TPHCWG and, therefore, many of its components are similar to the TPHCWG methodology. A unique aspect of the proposed approach was to define the proportion of each surrogate in its respective PHC fraction and derive exposures and risks only for the proportion of the fraction that was the surrogate chemical. This approach effectively assumed that the remaining components of the mixture have no toxicity or at least that their toxicity is negligible compared to the remaining components.

B.7.0 Atlantic Partnership in RBCA Implementation

The Atlantic provinces, through the efforts of the Partnership In Risk-Based Corrective Action Implementation (PIRI) initiative, have established a quantitative risk assessment/risk management approach for PHC-contaminated sites. This approach is based on the work of the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) and the American Society for Testing and Materials (ASTM)

Risk-Based Corrective Action (RBCA) framework (ASTM, 1995c).

In 1997, New Brunswick initiated a project to evaluate the applicability of the ASTM RBCA Standard and the work of the TPHCWG to assessing risks posed by petroleum-contaminated soils in that province. A modified RBCA standard was devised which substituted Canadian data and assumptions within the ASTM RBCA framework. Subsequently, the Partnership in RBCA Implementation (PIRI) was established whereby regulatory representatives of the Atlantic Provinces (New Brunswick, Nova Scotia, Prince Edward Island and Newfoundland), affected industries (Canadian Petroleum Products Institute), as well as environmental engineering and remediation consulting firms, combined their efforts to devise and implement a risk-based approach to assessing and managing petroleum-contaminated sites. The approach that evolved was based largely on the modified RBCA standard developed by New Brunswick.

Modifications introduced to reflect Canadian approaches and assumptions for risk assessment included:

- Canadian reference doses or tolerable daily intakes, where available;
- Alteration of numerous assumptions (averaging times, exposure rates and frequencies, water and air intake rates, etc.) to reflect the Canadian population;
- Alteration of assumed site characteristics (required to derive screening level criteria) to reflect conditions of Atlantic Canada.

B.8.0 Other Canadian Provincial PHC Criteria

PHC criteria for soil and groundwater currently in use by the Ontario Ministry of Environment and Energy (MOEE), the Ministère de L'Environnement du Québec (MENV), Alberta Environment and the British Columbia Ministry of Environment, Lands and Parks (BCMELP) are presented in Table B.2.

MOEE criteria are based primarily on the recommendations of a multi-stakeholder workgroup (OMEE 1993) with some modifications to reflect additional considerations and information presented by OMEE (1996). The current OMEE PHC criteria have a qualitative but not a quantitative basis in risk. OMEE derived a Generic Site Sensitivity Analysis flowchart to differentiate sites into three relative levels of risk/concern (high, moderate and low). Subsequently, guidelines were proposed for PHCs as gasoline/diesel, and PHC as heavy oils. Alternate analytical procedures were also prescribed for extraction and quantification of total PHC in these different products.

MENV has recently released a revised strategy for the rehabilitation of contaminated lands (MENV 1996). Criteria for petroleum hydrocarbons (carbon range C_{10} to C_{50}) replaced earlier criteria for oil and grease as of January 1996. MEFQ prescribes soil and groundwater criteria for three qualitatively different levels of risk:

Level A — Typical background concentrations for inorganic parameters; limit of analytical detection for organics (analytical methods available on Quebec Ministry's website).

Level B — Maximum acceptable concentrations for residential, recreational and institutional lands and commercial properties near residential areas.

Level C — Maximum acceptable concentration for commercial (not situated near residential properties) and industrial lands.

No scientific rationale for the prescribed A, B and C PHC criteria is presented.

PHC soil criteria have been promulgated by BCMELP in Part 3.1 (Contaminated Site Remediation) of the Waste Management Amendment Act, 1993 (BCMELP 1993). Under that Act, criteria have been published (Schedule 4: Generic Numerical Soil Standards) for volatile petroleum hydrocarbons (VPHs), light extractable petroleum hydrocarbons (LEHPs) and heavy extractable petroleum hydrocarbons (HEPHs). Generic standards for these parameters range from 200 to 5000 ppm and vary according to land use (agricultural, urban park, residential, commercial, industrial). The standards are based on professional judgement; no rationale for their derivation has been published (G. Fox, BCMELP, personal communication).

On behalf of Alberta Environmental Protection, OAEI undertook the Development of Remediation Guidelines for Petroleum Storage Tank Sites (OAEI 1996), which included total petroleum hydrocarbons among numerous other contaminants. A variety of methods were examined as a basis for the derivation of quantitative and qualitative risk-based PHC criteria. Final criteria were based on qualitative considerations including human organoleptic, aesthetic and phytotoxicological/ecotoxicological considerations. Criteria were defined for three levels of site sensitivity, loosely interpretable as residential (Level I), commercial (Level II) and industrial (Level III) sites. Potential off-site receptors located on a more sensitive site were also considered.

B.9.0 State-by-State Summary of PHC Criteria from the US

A state-by-state summary of soil PHC action and cleanup standards used across the United States has been recently presented in the *Journal of Soil Contamination* (Anonymous 1997). State criteria respecting PHCs are summarized in Table B.3. These PHC and related criteria are largely based on professional judgements. MADEP, the only state to actively evaluate a risk basis for PHC criteria, has not yet promulgated risk based PHC criteria.

Table B.1: Carbon sub-fractions (as Equivalent Carbon number - EC), physico-chemical parameters, reference doses and reference air concentrations proposed by the Total Petroleum Hydrocarbon Criteria Working Group.

TPH Sub-fraction	BP (°C)	EC (n)	MW (g/mole)	S (mg/L)	VP (atm)	H (cm^3/cm^3)	log Koc	TDI (mg/kg-day)	RfC (mg/m^3)
Aliphatics									
EC 5-6	5.1 E+01	5.5 E+00	8.1 E+01	3.6 E+01	3.5 E-01	3.3 E+01	2.9 E+00	5.0	18.4
EC >6-8	9.6 E+01	7.0 E+00	1.0 E+02	5.4 E+00	6.3 E-02	5.0 E+01	3.6 E+00	5.0	18.4
EC >8-10	1.5 E +02	9.0 E+00	1.3 E+02	4.3 E-01	6.3 E-03	8.0 E+01	4.5 E+00	0.1	1.0
EC >10-12	2.0 E+2	1.1 E+01	1.6 E+02	3.4 E-02	6.3 E-04	1.2 E+02	5.4 E+00	0.1	1.0
EC >12-16	2.6 E+02	1.4 E+01	2.0 E+02	7.6 E-04	4.8 E-05	5.2 E+02	8.8 E+00	0.1	1.0
EC >16-21	3.2 E +02	1.9 E+01	2.7 E+02	2.5 E-06	1.1 E-06	4.9 E+03	9.0 E+00	2.0	NA [1]
Aromatics									
EC >8-10	1.5 E+02	9.0 E+00	1.2 E+02	6.5 E+01	6.3 E-03	4.8 E-01	3.2 E+00	0.04	0.2
EC >10-12	2.0 E+02	1.1 E+01	1.3 E+02	2.5 E+01	6.3 E-04	1.4 E-01	3.4 E+00	0.04	0.2
EC >12-16	2.6 E+02	1.4 E+01	1.5 E+02	5.8 E+00	4.8 E-05	5.3 E -02	3.7 E+00	0.04	0.2
EC >16-21	3.2 E+02	1.9 E+01	1.9 E+02	6.5 E-01	1.1 E-06	1.3 E-02	4.2 E+00	0.03	NA [1]
EC >21-34	3.4 E+02	2.8 E+01	2.4 E+02	6.6 E-03	4.4 E-10	6.7 E-04	5.1 E+00	0.03	NA [1]

(from Gustafson et al. 1996; Edwards et al., 1996)

1 NA = not available; specified sub-fraction considered non-volatile.

Table B.2: Criteria for "Petroleum Hydrocarbons" (mg/kg soil) currently in use in Ontario, Quebec, Alberta and British Columbia.

Ontario Ministry of Environment and Energy (OMEE)					
	Agricultural [1]	Residential/Parkland [1]		Industrial/Commercial [1]	
	Potable or Nonpotable GW	Potable GW	Nonpotable GW	Potable GW	Nonpotable GW
gas/diesel	100	100	1000	100	1000
heavy oils	1000	1000	1000	1000	5000
Ministère de L'Environnement et de la Faune Québec (MEFQ)					
	Level A - Background/Detection Limit	Level B- Maximum for Residential, Parkland and Institutional Properties		Level C - Maximum for Commercial and Industrial	
C_{10} - C_{50}	<100	700		3500	
British Columbia Ministry of Environment, Lands and Parks (BCMELP)					
	Agricultural	Urban Park	Residential	Commercial	Industrial
VPHs [2]	200	200	200	200	200
LEPHs [2]	1000	1000	1000	2000	2000
HEPHs [2]	1000	1000	1000	5000	5000
Alberta Environment – PST Guidelines [3]					
		Level I [4]		Level II [4]	Level III [4]
Product or fraction not specified		Coarse-grained soil: 1000 Fine-grained soil: 2000		2000 4000	5000 5000
Alberta Environment – Tier I Criteria for Contaminated Soil Assessment and Remediation [5]					
	Agricultural	Residential			
Mineral oil and grease	1,000	1,000			

(from BCMELP 1993; MEFQ 1996; OAEI 1996; OMEE 1996)

[1] Criteria apply to both surface and subsurface soils;
[2] VPH=volatile petroleum hydrocarbon, LEPH=light extractable petroleum hydrocarbon, HEPH=heavy extractable petroleum hydrocarbon (extraction and
analytical methods not specified in B.C. Contaminated Sites regulations)
[3] Petroleum Storage Tank (PST) guidelines applied to downstream facilities (gas stations, etc.) and refinery sites.
[4] Level I, II and III sites approximate but do not match precisely the categories residential, commercial and industrial
[5] Tier I guidelines applied to upstream oil and gas sites and to sensitive sites, such as agricultural and residential lands, with surface soil contamination.

Table B.3: Total petroleum hydrocarbon cleanup levels for contaminated soils in the United States of America*.

STATE	PRODUCT	PARAMETER/ CONSTITUENT	ANALYTICAL METHOD	NUMERIC CRITERION (mg/kg)	DEPARTMENT	COMMENTS
Alabama	Gasoline	TPH**	EPA 4030, 9071, 418.1 SM 5520	100	Alabama Department of Environmental Management	
	Diesel	TPH	EPA 4030, 9071, 418.1, SM 5520	100		
	Waste Oil	TPH	EPA 4030, 9071, 418.1, SM 5520	100		
Alaska	See AEHS, 1999.				Alaska Department of Environmental Conservation	
Arkansas	NA	NA	NA	NA	Arkansas Department of Environmental Quality	Note: Hydrocarbon remediation based on ASTM Method, E 1739.
Arizona	Gasoline	TPH [1]	AZ 418.1	7,000 [3] 24,000 [4]	Arizona Department of Environmental Quality	(1) Applies only to sites characterized prior to 12/4/97, and remediating pursuant to interim soil remediation standards (final rule *doesn't* have TPH standard). (2) Refer to AAC R18-7-201. (3) Cleanup Level Residential. (4) Cleanup Level Non-Residential.

STATE	PRODUCT	PARAMETER/ CONSTITUENT	ANALYTICAL METHOD	NUMERIC CRITERION (mg/kg)	DEPARTMENT	COMMENTS
	Kerosene	C10-C32	AZ 8015	(2)		
	Diesel	C10-C32	AZ 8015	(2)		
	Jet Fuel	C10-C32	AZ 8015	(2)		
	Heavy Fuel Oil	TPH(2)	AZ 418.1	(2)		
		C10-C32	AZ 8015	(2)		
	Waste Oil	TPH(2)	AZ 418.1	(2)		
		C10-C32	AZ 8015	(2)		
California	Gasoline	TPH	(1)	Site Specific	California Regional Water Quality Control Board	(1) There is no statewide requirement for a specific laboratory test. Contact the lead agency for guidance.
	Diesel	TPH	(1)	Site Specific		
		TAPH	(1)	Site Specific		
Colorado	Subsurface Soil	TPH(1)	NA	500	Colorado Department of Labor and Employment, Oil Inspection Section	(1) TPH threshold values (2) For Residential and Industrial Land Uses.
	Surficial Soil	TPH(1)	NA	500(2)		
Connecticut	NA***	NA	NA	NA	Department of Environmental Protection Underground Storage Tank Program	Contact Department
DC	Gasoline	GRO*	EPA 8015 M	100	NA	Note: Soil Quality Standards are from UST Regulation (20 DCMR Chapter 55).
	Diesel	DRO**	EPA 8015 M	100		
	Waste Oil	DRO	EPA 8015 M	100		

STATE	PRODUCT	PARAMETER/ CONSTITUENT	ANALYTICAL METHOD	NUMERIC CRITERION (mg/kg)	DEPARTMENT	COMMENTS
Deleware	Gasoline	TPH GRO	(1)	100	Deleware Department of Natural Resources & Environmental Control	Note: Contact Deleware's UST Branch for required methodologies. (1) Different Tiers, TPH criterion may be replaced by a list of COCs (Chemicals of Concern) (2) Tier O Action/Cleanup Level; Applies to all new sites entering the program, such as removal or abandonment. Note: Above Tier O, TPH-GRO and TPH-DRO are replaced by a list of chemicals of concern.
	Kerosene	TPH GRO	(1)	100**		
		TPH DRO	(1)	1000[2]		
	Jet Fuel	TPH GRO	(1)	100[2]		
		TPH DRO	(1)	1000[2]		
	Diesel	TPH DRO	(1)	1000[2]		
	Heating Fuel	TPH DRO	(1)	1000[2]		
	Used Oil	TPH GRO	(1)	100[2]		
		TPH DRO	(1)	1000[2]		
	Aviation Gas	TPH GRO	(1)	100[2]		
Florida	TRPHs***	TRPH	FL-PRO	340[1]	Florida Department of Environmental Protection	(1) For Direct Exposure Residential and Leachability Based on Groundwater Criteria.

STATE	PRODUCT	PARAMETER/ CONSTITUENT	ANALYTICAL METHOD	NUMERIC CRITERION (mg/kg)	DEPARTMENT	COMMENTS
Georgia	Gasoline, Aviation Gas	TPH	EPA 8015 (GRO)	10	Georgia Department of Natural Resources	**Note: Soil cleanup levels shown are the most stringent threshold values for average or higher groundwater pollution susceptibility area and public or non-public water supplies or surface water are located less than or equal to 500 feet away.** Note: For information on lower susceptibility areas and/or different distances from water sources or withdrawal points, call the department.
	Diesel, Kerosene, Jet Fuel A, #2 and #4 Fuel Oil	TPH	EPA 8015 (GRO & DRO)	10		
	Hydraulic Oil, #5 and #6 Fuel Oil, Motor Oil, Used Oil	TPH	EPA 418.1	10		
	Mineral spirits, Jet Fuel B, or unknown petroleum contents	TPH	EPA 8015 (GRO & DRO)	10		

STATE	PRODUCT	PARAMETER/ CONSTITUENT	ANALYTICAL METHOD	NUMERIC CRITERION (mg/kg)	DEPARTMENT	COMMENTS
Hawaii	*Gasoline*	*TPH as Gasoline*	EPA 5030/8015, LUFT	*Site-Specific*	*Hawaii Dept. of Health*, Solid and Hazardous Waste Branch	*Note: Hawaii Risk Based* Corrective Action (RBCA) program can be used to develop more site-specific action levels for soil.
		TPH as Residual Fuels	EPA 5030/8015, LUFT	Site-Specific		
		TPH as Residual Distillates	EPA 5030/8015 LUFT	Site-Specific		
Idaho	Gasoline	NA	NA	NA	Iowa Department of Natural Resources	Note: Idaho has developed a RBCA program for assessment and cleanup of petroleum contamination.
Illinois	NA	NA	NA	NA	Illinois Environmental Protection Agency	Note: The Illinois EPA has adopted RBCA Regulations to determine cleanup objectives.
Indiana	Kerosene, Gasoline	TPH	EPA 8015 M or 8240/8260	<100[1] 20[2]	Indiana Department of Environmental Management (IDEM)	(1) On-site cleanup level. (2) Off-site cleanup level. Note: IDEM is currently developing RBCA guidance.
	Naplha, Diesel	TPH	EPA 8015 M or 8270	<100[1] 20[2]		
	Aviation Gas	TPH	EPA 4181	<100[1] 20[2]		
Iowa	See AEHS, 1999.				Idaho Division of Environmental Quality	Note: Iowa has adopted the ASTM RBCA method for addressing Petroleum Contaminated Sites.

STATE	PRODUCT	PARAMETER/ CONSTITUENT	ANALYTICAL METHOD	NUMERIC CRITERION (mg/kg)	DEPARTMENT	COMMENTS
Kansas	Gasoline	TPH	(1)	100	Kansas Department of Health & Environment	(1) Purge and trap with summation of peaks chromatography; EPA 418.1 can be used for TPH analysis of waste oil only. Note: Kansas expects to implement a Risk-Based Corrective Action approach but these standards will remain in place as baseline standards.
	Diesel	TPH	(1)	100		
	Waste Oil	TPH	(1)	100		
Kentucky	See AEHS, 1999.				Kentucky Division of Waste Management	
Louisiana	See AEHS, 1999.				Louisiana Department of Environmental Quality	Note: Has a Risk Evaluation/Corrective Action Program similar to RBCA.
Maryland	Gasoline	TPH	EPA 8015M GRO	Site specific or 10	Maryland Department of the Environment	Note: There are no promulgated cleanup standards. All decisions are made via site-specific risk characterization.
	Diesel Fuel, #2 Heating Oil	TPH	EPA 8015M DRO	Site specific or 10		
	Heavy Oil #4, 5, and 6, Bunker Oil	TPH	EPA 1664	Site specific or 10		
	Used Oil	TPH	EPA 1664	Site specific or 10		

STATE	PRODUCT	PARAMETER/ CONSTITUENT	ANALYTICAL METHOD	NUMERIC CRITERION (mg/kg)	DEPARTMENT	COMMENTS
Massachusetts	Gasoline	C5-C8 Aliphatic Hydrocarbons	MADEP VPH	0.1-0.5[1] or site specific	Massachusetts Department of Environmental Protection	(1) Nine generic cleanup standards have been established depending upon exposure potential/accessibility of soil, and use/classification of underlying groundwater.
		C9-C12 Aliphatic Hydrocarbons	MADEP VPH	1.0-5.0[1] or site specific		
		C9-C10 Aliphatic Hydrocarbons	MADEP VPH	0.1-0.5[1] or site specific		
	Diesel, #2 Fuel Oil	C9-C18 Aliphatic Hydrocarbons	MADEP EPH	0.1-0.5[1] or site specific	Massachusetts Department of Environmental Protection	
		C19-C36 Aliphatic Hydrocarbons	MADEP EPH	2.5-5.0[1] or site specific		
		C11-C22 Aliphatic Hydrocarbons	MADEP EPH	0.2-0.5[1] or site specific		

STATE	PRODUCT	PARAMETER/ CONSTITUENT	ANALYTICAL METHOD	NUMERIC CRITERION (mg/kg)	DEPARTMENT	COMMENTS
Maine	Gasoline	Total Gasoline	GRO	5(1)	Maine Department of Environmental Protection (DEP)	Note: Maine DEP uses a Decision Tree approach to establish remediation standards. Four Categories of sites exist: Baseline 1 (BL-1), Baseline 2 (BL-2), Intermediates (IN), and Stringent (ST). (1) Applies to ST and IN sites only. BL-1 sites require only removal of tree product and product-saturated soils. BL-2 sites may be cleaned to 500-1000 mg/kg measured by field/headspace for gasoline or 200-400 mg/kg for diesel.
	Diesel	Total Fuel Oil	DRO	10(1)		
Michigan	NA	NA	NA	NA	Michigan Department of Environmental Quality; Environmental Response Division	
Minnesota	Gasoline	TPH	Wisconsin DNR GRO	Site Specific	Minnesota Pollution Control Agency	
	Diesel	TPH	Wisconsin DNR GRO	Site Specific		
	Waste Oil	TPH	Wisconsin DNR GRO	Site Specific		
Missouri	See AEHS, 1999.			50-100	Missouri Department of Natural Resources	Note: Site gets assigned a score based on site features – TPH criteria depends on score.
Mississippi	Gasoline	NA	NA	NA	Mississippi Underground Storage Tank Division	(1) If no sensitive environmental receptors are present.

STATE	PRODUCT	PARAMETER/ CONSTITUENT	ANALYTICAL METHOD	NUMERIC CRITERION (mg/kg)	DEPARTMENT	COMMENTS
	Diesel	TPH	EPA 418.1	<100[1]		
	Waste Oil	TPH	EPA 418.1	<100[1]		
North Carolina	See AEHS. 1999.				North Carolina Division of Waste Management	Note: Contact UST section of NC Department of Natural Resources, Division of Waste Management.
North Dakota	Gasoline	TPH	EPA 8015M	Site Specific	North Dakota State Department of Health	
	Diesel	TPH	EPA 8015M	Site Specific		
	Waste Oil	NA	NA	NA		
Nebraska	Gasoline	TRPH	OA1	Site Specific[1]	Nebraska Department of Environmental Quality	(1) Soil cleanup levels are based on site specific contaminants and exposure parameters.
	Diesel	TRPH	OA1, OA2	Site Specific[1]		
	Waste Oil	TRPH	OA1, OA2	Site Specific[1]		
New Hampshire	Gasoline	TPH (as gasoline)	(1)	10 000	New Hampshire Department of Environmental Services	(1) Initially EPA 8250 plus MTBE and P&T – GC/FID for TPH. All other samples EPA 8020 plus MTBE and P&T GC/FID for TPH. (2) Initially EPA 8260, 8270/8310 and extraction GC/FID for TPH. All other samples 8020, 8240, 8260, 8270/8310 and extraction GC/FID for PAH.
	No's 2,4,5,6 Fuel Oil and Diesel	TPH (as oil)	(2)	10 000		

STATE	PRODUCT	PARAMETER/ CONSTITUENT	ANALYTICAL METHOD	NUMERIC CRITERION (mg/kg)	DEPARTMENT	COMMENTS
New Jersey	NA	NA	NA	NA	New Jersey Department of Environmental Protection; Site Remediation	
New Mexico	Gasoline	TPH	EPA 8021	100	New Mexico Environment Department	
	Diesel	TPH	EPA 8015M	100		
	Waste Oil	TPH	EPA 8015M	100		
Nevada	Gasoline	TPH	EPA 8015M	100	Nevada Department of Conservation and Natural Resources	
	Diesel	TPH	EPA 8015M	100		
	Waste Oil	TPH	EPA 8015M	100		
New York	NA	NA	NA	NA	New York Department of Environmental Conservation	
Ohio	Gasoline	TPH	EPA 8015M	Site Specific	Ohio Department of Commerce	
	Diesel	TPH	EPA 418.1	Site Specific		
	Waste Oil	TPH	EPA 418.1	Site Specific		
Oklahoma	Gasoline, Diesel, and Kerosene	TPH	EPA 8015	Site Specific	Oklahoma Corporation Commission, UST Program	Note: Oklahoma uses a Remediation Index in determining cleanup standards on a site-by-site basis. EPA 418.1 is not accepted testing method for TPH.
Oregon	See AEHS, 1999.				Oregon Department of Environmental Quality	Note: Oregon's UST Cleanup Rules (OAR 340-122-0205 through 340-122-0360) provide responsible parties with four options for remediating sites.
Pennsylvania	NA	NA	NA	NA	Commonwealth of Pennsylvania Department of Environmental Protection	

STATE	PRODUCT	PARAMETER/ CONSTITUENT	ANALYTICAL METHOD	NUMERIC CRITERION (mg/kg)	DEPARTMENT	COMMENTS
Rhode Island	See AEHS, 1999.				Rhode Island Department of Environmental Management	Note: Rhode Island has Direct Exposure TPH criteria and Leachability criteria for contaminated soils. See AEHS for more information.
South Carolina	Gasoline, Diesel, and Kerosene	NA	NA	NA	South Carolina Department of Health & Environmental Control	(1) No action or cleanup levels. TPH is used solely to determine necessity of performing expanded analyses.
	Waste Oil	TPH	EPA 9071	(1)		
South Dakota	Gasoline	TPH	(1)	(2)	South Dakota Department of Environmental and Natural Resources	(1) California/USGS method or similar methods that can quantify TPH by integrating all detectable peaks within the time period in which 95% of the recoverable hydrocarbons are eluted. (2) Cleanup is not required if no risks to human health present. Source removal required. If risks present – site specific.
	Diesel	TPH	(1)	(2)		
	Waste Oil	TPH	(1)	(2)		
Tennessee	Gasoline	TPH-GRO	TN TPH-GRO	100-1000[1]	Tennessee Department of Environment and Conservation; Division of UST	(1) Cleanup levels are based on groundwater classification and soil permeability.
	Diesel	TPH-EPH	EPH	100-1000[1]		
	Waste Oil	TPH-EPH	EPH	100-1000[1]		

STATE	PRODUCT	PARAMETER/ CONSTITUENT	ANALYTICAL METHOD	NUMERIC CRITERION (mg/kg)	DEPARTMENT	COMMENTS
Texas	Gasoline	TPH	TNRCC 1005	Site Specific/ Risk Based	Texas Natural Resource Conservation Commission	
	Diesel	TPH	TNRCC 1005	Site Specific/ Risk Based		
	Used Oil	TPH	TNRCC 1005	Site Specific/ Risk Based		
Utah	NA	NA	NA	Site Specific	Utah Division of Environmental Response and Remediation	Note: Utah has RBCA Tier 2 process for determining site-specific cleanup values.
Virginia	Gasoline	TPH	CA UFT Method	Site Specific/ Risk Based	Virginia Department of Environmental Quality	
	Diesel	TPH	CA UFT Method	Site Specific/ Risk Based		
	Waste Oil	TPH	EPA – approved GC Methods	Site Specific/ Risk Based		
Vermont	Gasoline	NA	NA	NA	Vermont Agency of Environmental Conservation	
	Diesel	TPH	EPA 418.1 or Extended GC	Site Specific/ Risk Based		
	Waste Oil	NA	NA	NA		
Washington	Gasoline	TPH	NWTPH-GX	100	Washington Department of Natural Resources	Note: Cleanup level shown is for Method A for routine cleanups. Method B and C also exist for residential and industrial cleanups which are risk-based.
	Diesel	TPH	NWTPH-DX	500		
	Waste Oil	NA	NA	NA		
Wisconsin	Gasoline	GRO	WI DNR Modified GRO	Site Specific	Wisconsin Department of Natural Resources	
	Diesel	GRO	WI DNR Modified DRO	100 or Site Specific		
	Waste Oil	DRO	WI DNR Modified DRO	Site Specific		
West Virginia	Gasoline	TPH	EPA 5015 M(1)	Site Specific	West Virginia Department of Environmental Protection	(1) Report GRO and DRO separately.

STATE	PRODUCT	PARAMETER/ CONSTITUENT	ANALYTICAL METHOD	NUMERIC CRITERION (mg/kg)	DEPARTMENT	COMMENTS
	Diesel	TPH	EPA 5015 M[1]	Site Specific		
Wyoming	Gasoline	NA	NA	NA	Wyoming Department of Environmental Quality	(1) If groundwater is <50 feet. (2) If groundwater is >50 feet.
	Leaded Gas	TPH	EPA 8015 M GRO C5-C10	30[1] 100[2]		
	Fuel Oils	TPH	EPA 8015 M GRO C10-C32	100		
	Lubricating Oils	TPH	EPA 8015 M GRO C10-C32	100		
	Waste Oil	TPH	EPA 8015 M GRO (GC)	100		

(from: Komex Inc., 2000)

NOTES:

* Information obtained from Associates for the Environmental Health of Soils (AEHS) State by State Soil Survey

** TPH = Total Petroleum Hydrocarbon

*** NA = Not Available

\+ GRO = Gasoline Range Organics

++ DRO = Diesel Range Organics

+++ TRPH = Total Recoverable Petroleum Hydrocarbon

Appendix C: Equations used for the derivation of human health-based Tier 1 Levels and example derivation.

Part A: Tier 1 Level Equations

Algorithm used to sum TPHCWG sub-fractions within each fraction:
To derive soil quality guidelines for a PHC fraction, guidelines must first be estimated for each individual TPHCWG sub-fraction, for the target Hazard Quotient desired. Then, the guidelines for sub-fractions must be combined according to their mass fraction within the fraction, according to the algorithm below.

$$SQG_{Fraction\_i} = \frac{1}{\sum\left(\frac{MF_{subfraction\ j}}{SQG_{subfraction\ j}}\right)}$$

$SQG_{fraction\_i}$ = soil quality guideline for the fraction *i* (mg/kg)
$SQG_{sub\text{-}fraction\ j}$ = soil quality guideline (mg/kg) for each sub-fraction within fraction *i* for the target Hazard Quotient for fraction *i*
$MF_{sub\text{-}fraction\ j}$ = mass fraction of each sub-fraction within the fraction *i*

Soil Ingestion Pathway:

$$SQG_{SI} = [(TDI - EDI)(SAF)(BW)(10^3\ g/kg)]/[(SIR)(AF_G)(ET)] + BSC$$

Where:
SQG_{SI} = soil quality guideline by soil ingestion (mg/kg)
TDI = tolerable daily intake (reference dose) (mg/kg-d)
EDI = estimated daily intake (mg/kg-d)
SAF = Soil Allocation Factor (unitless)
BW = body weight (kg)
SIR = soil ingestion rate (g/d)
AF_G = gastrointestinal absorption factor (unitless)
ET = exposure term (unitless)
BSC = background soil concentration (mg/kg)

Dermal Contact Pathway:

$$SQG_{DC} = [(TDI - EDI)(SAF)(BW)(10^6 mg/kg)]/[(AF_D)\{SA_{HANDS})(DL_{HANDS}) + (SA_{OTHER})(DL_{OTHER})\}(EF)(ET)] + BSC$$

Where:

SQG_{DC}	= soil quality guideline by soil ingestion (mg/kg)
TDI	= tolerable daily intake (reference dose) (mg/kg-d)
EDI	= estimated daily intake (mg/kg-d)
SAF	= Soil Allocation Factor (unitless)
BW	= body weight (kg)
AF_D	= dermal absorption factor (unitless)
SA_{HANDS}	= surface area of hands (m^2)
SA_{OTHER}	= surface area of exposed body surfaces other than hands (m^2)
DL_{HANDS}	= dermal loading of soil to hands (mg/m^2-event)
DL_{OTHER}	= dermal loading of soil to other skin surfaces (mg/m2-event)
EF	= exposure frequency (events/d)
ET	= exposure term (unitless)
BSC	= background soil concentration (mg/kg)

Protection of Potable Groundwater:

$$SQG_{GW} = [(TDI - EDI)(K_d + (\theta_m / \rho_w))(SAF)(BW)(DF_W)] / (IR_W)$$

Where:

SQG_{GW}	= soil quality guideline to protect potable groundwater (mg/kg)
TDI	= tolerable daily intake (reference dose) (mg/kg-d)
EDI	= estimated daily intake (mg/kg-d)
K_d	= distribution coefficient (mL/g)
θ_m	= ratio: mass of water in soil / dry mass of soil (unitless)
ρ_w	= density of water (g/cm^3)
SAF	= Soil Allocation Factor (unitless)
BW	= body weight (kg)
IR_W	= water ingestion rate (L/d)
DF_W	= aquifer dilution factor (unitless)

= $\{[(B \times K \times i) / (R \times L)] + 1\}/(L_1/L_2)$

where: B = effective mixing depth in aquifer (m)

K = saturated hydraulic conductivity of aquifer (m/y)

i = hydraulic gradient (unitless)

R = recharge rate (m/y)

L = site length (m)

L_1 = thickness of affected subsurface soils (cm)

L_2 = distance from top of affected soils to groundwater (cm)

Indoor Infiltration and Inhalation Pathway:

$$SQG_{ii,a} = [(TDI - EDI)(BW)\{\theta_w + (K_{oc})(f_{oc})(\rho_b) + (H/RT)(\theta_a)\}(SAF)(DFi)(10^3 g/kg)]/$$
$$[(IR)(H/RT)(\rho_b)(ET)(10^6 cm^3/m^3)] + BSC$$

$$SQG_{ii,b} = [(RfC - C_a)\{\theta_w + (K_{OC})(f_{OC})(\rho_b) + (H/RT)(\theta_a)\}(SAF)(DFi)(10^3 g/kg)]/$$
$$[(H/RT)(\rho_b)(ET)(10^6 cm^3/m^3)] + BSC$$

Where:

$SQG_{ii,a}$	= soil quality guideline by indoor infiltration for volatile PHCs using TDI (i.e., sub-fraction has no prescribed RfC) (mg/kg)
$SQG_{ii,b}$	= soil quality guideline by indoor infiltration for volatile PHCs using RfC (mg/kg)
TDI	= tolerable daily intake (reference dose) (mg/kg-d)
EDI	= estimated daily intake (mg/kg-d)
RfC	= reference air concentration (mg/m^3)
C_a	= background indoor/outdoor air concentration (mg/m^3)
SAF	= Soil Allocation Factor (unitless)
BW	= body weight (kg)
IR	= inhalation rate (m^3/d)
θ_w	= moisture-filled porosity (unitless)
θ_a	= vapour-filled porosity (unitless)
K_{OC}	= organic carbon partition coefficient (mL/g)
f_{OC}	= fraction organic carbon (g/g)
ρ_b	= dry bulk density (g/cm^3)
H	= Henry's Law Constant ($atm\text{-}m^2/mol$)
R	= gas constant (8.2×10^{-5} $atm\text{-}m^2/mol\text{-}^OK$)
T	= absolute temperature (^OK)
DF_i	= dilution factor from soil gas to indoor air (unitless): ***see derivation below***
ET	= exposure term (unitless)
BSC	= background soil concentration (mg/kg)

Calculation of DF for indoor infiltration pathway:

$$DF_i = \frac{1}{\alpha}$$

DF_i = dilution factor from soil gas concentration to indoor air concentration (unitless)
α = attenuation coefficient
= (contaminant vapour concentration in the building)/(vapour concentration at the contaminant source)

Coarse textured soils (considers advection only)

$$\alpha = \frac{\left(\frac{D_T^{eff} A_B}{Q_B L_T}\right)}{\left(\frac{D_T^{eff} A_B}{Q_{soil} L_T}\right) + 1}$$

D_T^{eff} = effective porous media diffusion coefficient (cm^2/s)
A_B = building area (cm^2)
Q_B = building ventilation rate (cm^3/s)
L_T = distance from contaminant source to foundation (cm)
Q_{soil} = volumetric flow rate of soil gas into the building (cm^3/s)

$$D_T^{eff} \approx D_a \left(\frac{\theta_a^{10/3}}{n^2}\right)$$

D_T^{eff} = overall effective porous media diffusion coefficient based on vapour-phase concentrations for the region between the source and foundation (cm^2/s)
D_a = diffusion coefficient in air (cm^2/s)
θ_a = air-filled porosity (unitless)
n = total soil porosity (unitless)

$$Q_B = L_B W_B H_B (ACH) / (3600\ s/h)$$

Q_B = building ventilation rate (cm^3/s)
L_B = building length (cm)
W_B = building width (cm)
H_B = building height, including basement (cm)
ACH = air exchanges per hour (h^{-1})

$$Q_{soil} = \frac{2\pi\,\Delta P\,k_v\,X_{crack}}{\mu \ln\left[\frac{2(Z_{crack})}{r_{crack}}\right]}$$

Q_{soil} = volumetric flow rate of soil gas into the building (cm^3/s)
ΔP = pressure differential ($g/cm{\cdot}s^2$)
k_v = soil vapour permeability to vapour flow (cm^2)
X_{crack} = length of idealized cylinder (cm)
μ = vapour viscosity ($g/cm{\cdot}s$)
Z_{crack} = distance below grade to idealized cylinder (cm)
r_{crack} = radius of idealized cylinder (cm)

Fine textured soils (considers diffusion only)

$$\alpha = \frac{\left(\frac{D_T^{eff} A_B}{Q_B L_T}\right)}{1+\left(\frac{D_T^{eff} A_B}{Q_B L_T}\right)+\left(\frac{D_T^{eff} A_B L_{crack}}{D^{crack} A_{crack} L_T}\right)}$$

D_T^{eff} = effective porous media diffusion coefficient (cm^2/s)
A_B = building area (cm^2)
Q_B = building ventilation rate (cm^3/s)
L_T = distance from contaminant source to foundation (cm)
L_{crack} = thickness of the foundation (cm)
D^{crack} = effective vapour-pressure diffusion coefficient through the crack (cm^2/s)
A_{crack} = area of cracks through which contaminant vapours enter building (cm^2)

Tier 2: (requires consideration of both advection and diffusion)
For derivation of site-specific soil quality objectives, calculations must consider both advective and diffusive vapour transport mechanisms, according to the following equations.

$$DF_i = \frac{1}{\alpha}$$

DF_i = dilution factor from soil gas concentration to indoor air concentration (unitless)
α = attenuation coefficient
= (contaminant vapour concentration in the building)/(vapour concentration at the source)

$$D_T^{eff} \approx D_a \left(\frac{\theta_a^{10/3}}{n^2} \right)$$

D_T^{eff} = overall effective porous media diffusion coefficient based on vapour-phase concentrations for the region between the source and foundation (cm^2/s)
D_a = pure component molecular diffusivities in air (cm^2/s)
θ_a = air-filled porosity (unitless)
n = total soil porosity (unitless)

$$Q_B = L_B W_B H_B (ACH) / (3600\ s/h)$$

Q_B = building ventilation rate (cm^3/s)
L_B = building length (cm)
W_B = building width (cm)
H_B = building height, including basement (cm)
ACH = air exchanges per hour (h^{-1})

$$Q_{soil} = \frac{2\pi\,\Delta P\,k_v\,X_{crack}}{\mu \ln\left[\frac{2(Z_{crack})}{r_{crack}}\right]}$$

Q_{soil} = volumetric flow rate of soil gas into the building (cm^3/s)
ΔP = pressure differential ($g/cm{\cdot}s^2$)
k_v = soil vapour permeability to vapour flow (cm^2)
X_{crack} = length of idealized cylinder (cm)
μ = vapour viscosity ($g/cm{\cdot}s$)
Z_{crack} = distance below grade to idealized cylinder (cm)
r_{crack} = radius of idealized cylinder (cm)

$$\alpha = \frac{\left(\frac{D_T^{eff} A_B}{Q_B L_T}\right)\exp\left(\frac{Q_{soil} L_{crack}}{D^{crack} A_{crack}}\right)}{\exp\left(\frac{Q_{soil} L_{crack}}{D^{crack} A_{crack}}\right)+\left(\frac{D_T^{eff} A_B}{Q_B L_T}\right)+\left(\frac{D_T^{eff} A_B}{Q_{soil} L_T}\right)\left[\exp\left(\frac{Q_{soil} L_{crack}}{D^{crack} A_{crack}}\right)-1\right]}$$

D_T^{eff} = effective porous media diffusion coefficient (cm^2/s)
A_B = building area (cm^2)
Q_B = building ventilation rate (cm^3/s)
L_T = distance from contaminant source to foundation (cm)
Q_{soil} = volumetric flow rate of soil gas into the building (cm^3/s)
L_{crack} = thickness of the foundation (cm)
D^{crack} = effective vapour-pressure diffusion coefficient through the crack (cm^2/s)
A_{crack} = area of cracks through which contaminant vapours enter the building (cm^2)

Part B: Example Derivaton

The equations presented in Part A are applied as appropriate for the PHC fraction and soil texture under consideration. Derivations for F1 in a coarse textured soil case are the most complex and inclusive case. Complete calculations for this fraction/texture combination are presented below.

Fraction 1, Aliphatics $C_{>6}$-C_8, Coarse-grained soil, Residential with Basement, Toddler

Soil Ingestion Pathway:

$$SQG_{SI} = [(TDI - EDI)(SAF)(BW)(10^3\ g/kg)]/[(SIR)(AF_G)(ET)] + BSC$$

Where:

TDI	= tolerable daily intake (reference dose) (mg/kg-d) = 5
EDI	= estimated daily intake (mg/kg-d) = 0.02334
SAF	= Soil Allocation Factor (unitless) = 0.5
BW	= body weight (kg) = 16.5
SIR	= soil ingestion rate (g/d) = 0.08
AF_G	= gastrointestinal absorption factor (unitless) = 1
ET	= exposure term (unitless) = 1
BSC	= background soil concentration (mg/kg) = 0

Therefore,

SQG_{SI}	= soil quality guideline by soil ingestion (mg/kg) = 513 218 mg/kg

Dermal Contact Pathway:

$$SQG_{DC} = [(TDI - EDI)(SAF)(BW)(10^6\ mg/kg)]/[(AF_D)\{SA_{HANDS})(DL_{HANDS}) + (SA_{OTHER})(DL_{OTHER})\}(EF)(ET)] + BSC$$

Where:

TDI	= tolerable daily intake (reference dose) (mg/kg-d) = 5
EDI	= estimated daily intake (mg/kg-d) = 0.02334
SAF	= Soil Allocation Factor (unitless) = 0.5
BW	= body weight (kg) = 16.5
AF_D	= dermal absorption factor (unitless) = 0.2
SA_{HANDS}	= surface area of hands (m^2) = 0.0430
SA_{OTHER}	= surface area of exposed body surfaces other than hands (m^2) = 0.2580

DL_{HANDS} = dermal loading of soil to hands (mg/m^2-event) = 1000
DL_{OTHER} = dermal loading of soil to other skin surfaces (mg/m2-event) = 100
EF = exposure frequency (events/d) = 1
ET = exposure term (unitless) = 1
BSC = background soil concentration (mg/kg) = 0

Therefore,
SQG_{DC} = soil quality guideline by soil ingestion (mg/kg)
= 2 983 826 mg/kg

Protection of Potable Groundwater:

$$SQG_{GW} = [(TDI - EDI)(Kd + (\theta_m / \rho_w))(SAF)(BW)(DF_W)] / (IR_W)$$

Where:

TDI = tolerable daily intake (reference dose) (mg/kg-d) = 5
EDI = estimated daily intake (mg/kg-d) = 0.02334
K_d = distribution coefficient (mL/g) = 19.905
= Koc x foc
where: Koc = organic carbon partition coefficient (mL/g) = $10^{3.6}$
foc = fraction organic carbon (g/g) = 0.005
θ_m = ratio: mass of water in soil / dry mass of soil (unitless) = 0.07
ρ_w = density of water (g/cm^3) = 1.0
SAF = Soil Allocation Factor (unitless) = 1.0
BW = body weight (kg) = 16.5
IR_W = water ingestion rate (L/d) = 0.6
DF_W = aquifer dilution factor (unitless) = 12.4
= $\{[(B \times K \times i) / (R \times L)] + 1\}/(L_1/L_2)$
where: B = effective mixing depth in aquifer (m) = 2
K = saturated hydraulic conductivity of aquifer (m/y) = 320
i = hydraulic gradient (unitless) = 0.05
R = recharge rate (m/y) = 0.28
L = site length (m) = 10
L_1 = thickness of affected subsurface soils (cm)
L_2 = distance from top of affected soils to groundwater (cm)
L_1/L_2 = 1 (i.e., the affected soils are in contact with groundwater)

Therefore,

SQG_{GW} = soil quality guideline to protect potable groundwater (mg/kg)
= 33 898 mg/kg

Indoor Infiltration and Inhalation Pathway:

$$\mathbf{SQG_{ii,a}} = [(TDI - EDI)(BW)\{\theta_w + (K_{oc})(f_{oc})(\rho_b) + (H/RT)(\theta_a)\}(SAF)(DFi)(10^3\, g/kg)]/$$

$$[(IR)(H/RT)(\rho_b)(ET)(10^6\, cm^3/m^3)] + BSC$$

$$\mathbf{SQG_{ii,b}} = [(RfC - C_a)\{\theta_w + (K_{OC})(f_{OC})(\rho_b) + (H/RT)(\theta_a)\}(SAF)(DFi)(10^3\, g/kg)]/$$

$$[(H/RT)(\rho_b)(ET)(10^6\, cm^3/m^3)] + BSC$$

Where:

$SQG_{ii,a}$	= soil quality guideline by indoor infiltration for volatile PHCs using TDI (i.e., sub-fraction has no prescribed RfC) (mg/kg)
$SQG_{ii,b}$	= soil quality guideline by indoor infiltration for volatile PHCs using RfC (mg/kg)
TDI	= tolerable daily intake (reference dose) (mg/kg-d)
EDI	= estimated daily intake (mg/kg-d)
RfC	= reference air concentration (mg/m^3) = 18.4
C_a	= background indoor/outdoor air concentration (mg/m^3) = 0.09111
SAF	= Soil Allocation Factor (unitless) = 0.5
BW	= body weight (kg) = 16.5
IR	= inhalation rate (m^3/d) = 9.3
θ_a	= vapour-filled porosity (unitless) = 0.281
θ_w	= moisture-filled porosity (unitless) = 0.119
K_{OC}	= organic carbon partition coefficient (mL/g) = $10^{3.6}$
f_{OC}	= fraction organic carbon (g/g) = 0.005
ρ_b	= dry bulk density (g/cm^3) = 1.7
H	= Henry's Law Constant ($atm\text{-}m^2/mol$) = 1.2
R	= gas constant ($atm\text{-}m^2/mol\text{-}^OK$) = 8.2×10^{-5}
T	= absolute temperature (^OK) = 294
DF_i	= dilution factor from soil gas to indoor air (unitless): ***see derivation below***
ET	= exposure term (unitless) = 1
BSC	= background soil concentration (mg/kg) = 0

Calculation of DF for indoor infiltration pathway:

$$DF_i = \frac{1}{\alpha}$$

DF_i = dilution factor from soil gas concentration to indoor air concentration

(unitless)

α = attenuation coefficient
= (contaminant vapour concentration in the building)/(vapour concentration at the source)

$$D_T^{eff} \approx D_a \left(\frac{\theta_a^{10/3}}{n^2} \right)$$

D_T^{eff} = overall effective porous media diffusion coefficient based on vapour-phase concentrations for the region between the source and foundation (cm^2/s)
D_a = diffusion coefficient in air (cm^2/s) = 0.05
θ_a = vapour-filled porosity (unitless) = 0.281
n = total soil porosity (unitless) = 0.4

$$Q_B = L_B W_B H_B (ACH) / (3600\ s/h)$$

Q_B = building ventilation rate (cm^3/s)
L_B = building length (cm) = 1225
W_B = building width (cm) = 1225
H_B = building height, including basement (cm) = 488
ACH = air exchanges per hour (h^{-1}) = 1

$$Q_{soil} = \frac{2\pi\, \Delta P\, k_v\, X_{crack}}{\mu \ln\left[\frac{2(Z_{crack})}{r_{crack}} \right]}$$

Q_{soil} = volumetric flow rate of soil gas into the building (cm^3/s)
ΔP = pressure differential ($g/cm \cdot s^2$) = 40
k_v = soil vapour permeability to vapour flow (cm^2) = 10^{-8}
X_{crack} = length of idealized cylinder (cm) = 4900
μ = vapour viscosity ($g/cm \cdot s$) = 1.73×10^{-4}
Z_{crack} = distance below grade to idealized cylinder (cm) = 244
r_{crack} = radius of idealized cylinder (cm) = A_{crack} / X_{crack} = 0.20296

$$\alpha = \frac{\left(\frac{D_T^{eff} A_B}{Q_B L_T} \right) \exp\left(\frac{Q_{soil} L_{crack}}{D^{crack} A_{crack}} \right)}{\exp\left(\frac{Q_{soil} L_{crack}}{D^{crack} A_{crack}} \right) + \left(\frac{D_T^{eff} A_B}{Q_B L_T} \right) + \left(\frac{D_T^{eff} A_B}{Q_{soil} L_T} \right) \left[\exp\left(\frac{Q_{soil} L_{crack}}{D^{crack} A_{crack}} \right) - 1 \right]}$$

D_T^{eff} = effective porous media diffusion coefficient (cm^2/s) = 0.00454
A_B = building area (cm^2) = 1 500 625

Q_B = building ventilation rate (cm^3/s) = 203 418
L_T = distance from contaminant source to foundation (cm) = 30
Q_{soil} = volumetric flow rate of soil gas into the building (cm^3/s) = 9.14382
L_{crack} = thickness of the foundation (cm) = 11.25
D^{crack} = effective vapour-pressure diffusion coefficient through the crack (cm^2/s)
= 0.00454 (i.e., coarse-grained soil in the crack with θ_a = 0.281 and n = 0.4)
A_{crack} = area of cracks through which contaminant vapours enter the building (cm^2)
= 994.5

Therefore,

α = 4.3211×10^{-5}

DF_i = $1/\alpha$ = 23 142

$SQG_{ii,b}$ = soil quality guideline by indoor infiltration for volatile PHCs using RfC (mg/kg)
= 120 mg/kg

Algorithm used to sum TPHCWG sub-fractions within Fraction 1 (soil ingestion pathway):

To derive soil quality guidelines for Fraction 1, guidelines must first be estimated for each individual TPHCWG sub-fraction within Fraction 1, for the desired target Hazard Quotient (equivalent to the soil allocation factor discussed herein). Then, the guidelines for sub-fractions must be combined according to their mass fraction within Fraction 1, according to the algorithm below.

$$SQG_{Fraction\_i} = \frac{1}{\sum\left(\frac{MF_{subfraction\ j}}{SQG_{subfraction\ j}}\right)}$$

$SQG_{Fraction\_i}$ = soil quality guideline for the fraction *i* (mg/kg)
$SQG_{sub\text{-}fraction\ j}$ = soil quality guideline (mg/kg) for each sub-fraction within fraction *i* for the target Hazard Quotient for fraction *i*
$MF_{sub\text{-}fraction\ j}$ = mass fraction of each sub-fraction within fraction *i*

For the soil ingestion pathway:

$SQG_{sub\text{-}fraction\ C>6\ to\ C8\ aliphatics}$ = 513 218 mg/kg

(as shown in calculations above)

$SQG_{sub\text{-}fraction\ C>8\ to\ C10\ aliphatics}$ = 9 250 mg/kg

$SQG_{sub\text{-}fraction\ C>8\ to\ C10\ aromatics}$ = 3 158 mg/kg

And,

$MF_{sub\text{-}fraction\ C>6\ to\ C8\ aliphatics}$ = 0.55
$MF_{sub\text{-}fraction\ C>8\ to\ C10\ aliphatics}$ = 0.36
$MF_{sub\text{-}fraction\ C>8\ to\ C10\ aromatics}$ = 0.09

Therefore,

$SQG_{Fraction\ 1}$ = 1 / { [0.55/513218] + [0.36/9250] + [0.09/3158]}

= 14 600 mg/kg

Appendix D: Application of the CCME 1996 Soil Protocol to the derivation of Tier 1 ecological values.

The CCME protocol for the derivation of soil quality guidelines based on direct soil contact to soil invertebrates and plants is provided in CCME (1996). Briefly, where sufficient data exist (at least ten data points from at least three studies; minimum of each of two soil invertebrate and two crop/plant data points), the following protocol is applied:

> **"Threshold Effects Concentration" (TEC).** Applicable to Agricultural and Residential/ Parkland land use, where -
>
> TEC = 25^{th} percentile of the effects and no effects data distribution;
>
> **"Effects Concentration - Low" (EC-L).** Applicable to Commercial and Industrial land use, where -
>
> EC-L = 25^{th} percentile of effects data distribution (LOEC, ECx, LCx values from toxicity database).

Where the above-mentioned minimum data requirements have not been met, the *"Provisional Method: Toxicity to Soil Invertebrates and Plants"* is applied as follows:

> For Agricultural and Residential/Parkland, use lowest of toxicity values (usually EC_{25} values) in published literature and divide by uncertainty factor (UF) based on the following: Uncertainty Factors: 5 if EC_{50} is the lowest toxicity value, 10 if LC_{50}.
>
> For Commercial and Industrial land use, use geometric mean of available endpoints (usually LOECs or EC_{25}s). Commerical/Industrial - $1 \leq UF \geq 5$.

The minimum data requirements for the Provisional Method include a minimum of three studies, and at least one terrestrial plant and one soil invertebrate toxicity endpoint.

EcoTAG (2000a) specifically advocated against the use of the provisional method where possible to avoid the use of uncertainty factors. Part of the discomfort in the provisional method is associated with the long history of use of petroleum hydrocarbon products, their relative ubiquity, and recognition that PHCs are neither highly persistent, nor highly bioaccumulative.

In addition, most EcoTAG members felt that the separate evaluation of soil invertebrate and plant endpoints was scientifically more defensible than combining the two highly disparate groups, and that the separation of the two major taxa would result in more accurate and precise estimates of the range of toxicological thresholds. There was concern, however, that the further subdivision of the available

plant and soil invertebrate toxicity data might result in a reduction in the size of data set which might be used for defining species sensitivity distribution based on direct soil contact.

The CCME (1996) protocol for calculating either the Threshold Effects Concentration or the Effects Concentration - Low is often difficult to apply when there is a relatively large database to work with as is the case of various PHC categorizations. This is due to the amount of latitude available in screening and either rejecting or including no effects or effects data prior to ranking and subsequently establishing a 25th percentile soil concentration.

Following an initial screening to ensure minimum quality requirements for toxicity data, scientific/professional judgment is routinely used to ascertain whether there is further redundancy, or inappropriate co-variations between individual data points that would lead to biases in establishing environmental quality benchmarks which are suitably protective when extrapolated to the larger soil invertebrate and plant communities present at a given locale. For example, Stephenson *et al.* (2000b) derived the following toxicity endpoints based on studies of the toxicity of the F3 fraction, distilled from federated crude oil, on springtail collembolans (*Onychiuris folsomi*) (Table D.1, below)

Table D.1: Example of soil invertebrate toxicity endpoints available.

Endpoint		Response		Exposure Period
• NOEC • LOEC • $EC(LC)_{20}$ • $EC(LC)_{50}$	X	• fecundity • no. of juveniles • adult mortality	X	• 7 day (acute) • 35-36 day (definitive)

For plants tested with the F3 fraction, the individual endpoints examined included -

- shoot length
- root length
- shoot wet weight
- shoot dry weight
- root wet weight
- root dry weight

A toxicologist might derive from a single dose-response curve a large number of EC_x or LC_x endpoints (e.g., an EC_5, EC_{10}, EC_{25}, EC_{50}, EC_{75}, EC_{90}, and EC_{95} as well as NOEC and LOEC). The soil invertebrate and plant LOECs defined from the Stephenson *et al.* (2000b) study on the toxicity of the F3 fraction where generally

associated with an effect size greater than 50% (i.e., the nominal F3 soil concentration for the LOEC endpoint was greater than the calculated nominal concentration for the EC_{50} or LC_{50}).

One of the questions which invariably arises when screening data before applying a ranks-based approach is whether two data points are effectively redundant and should be combined. For example, it might be argued that plant shoot wet weight and dry weight measurements capture essentially the same suite of physiological and biochemical responses to a toxicant. Alternatively, it might be argued that dry weight measurements capture perturbations in the deposition of structural proteins and carbohydrates, and starches for energy storage, whereas perturbations in wet weight might independently reflect hydration state, plant water balance, and/or stomatal functioning.

The use of NOEC and LOEC values to examine risks has been challenged by a number of researchers, since the values derived are in large part an artifact of (i) the experimental protocol (specific concentrations to which the test organism is exposed), and (ii) shortcomings of the Analyis of Variance (ANOVA) model in allowing the identification of statistically significant differences between different exposure concentrations and the control (issues associated with statistical power).

The CCME (1996) TEC and EC-L protocols allow the combination of mortality endpoints (LC_x) with ecologically-relevant sublethal endpoints such as decreased plant growth or crop yield, which may or may not be accompanied by corresponding mortality. This aspect of the protocol has been rejected by the Contaminated Sites Soils Taskgroup (B.C.MELP 1996) of the British Columbia Ministry of Environment in favour of methods that separately utilize the ECx and LCx portions of an available database. If due care and attention is not paid to the relative proportion of either short-term/acute versus longer-term/chronic, or sublethal effects versus mortality data, then the resulting TEC or EC-L might result in a highly variable realized level of environmental protection achieved.

There is invariably considerable latitude in how toxicological data are screened and occasionally transformed prior to being subjected to a weight-of-evidence ranks-based protocol for the derivation of environmentally protective benchmarks. While some aspects of data manipulation are amenable to standardization of methods through detailed guidance, others invariably will not be – especially when ecotoxicity data have been salvaged from a variety of sources. The challenges are actually greater in cases where the underlying database is larger, since the amount of latitude available in screening data is correspondingly larger.

Appendix E: New ecotoxicity data for soil invertebrates and plants exposed to PHC CWS fractions of fresh Federated Whole Crude, and unfractionated whole product.

Table E.1: PHC CWS fraction F3 (>nC16 to nC34) toxicity data for direct contact to soil invertebrates and plants.

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
Alfalfa	shoot length	EC20	2800	7 (0,15,30,50,60, 70,80 mg/g)	4	nominal	field soil	8d test. n=10
	root length	EC20	7200				- Delacour Orthic Black Chernozem	
	whole ww	EC20	15800					
	whole dw	EC20	50200					
	shoot length	EC50	51900	7 (0,15,30,50,60, 70,80 mg/g)	4	nominal		8d test. n=10
	root length	EC50	10000					
	whole ww	EC50	72300					
	whole dw	EC50	98200					
	shoot length	EC20	620	12 (0,1,3,6,12, 15,20,40,60,80, 100,120 mg/g)	3-6	nominal		26d test. n=10 clear lids kept on till plants 3cm in height
	root length	EC20	920					
	shoot ww	EC20	510					
	shoot dw	EC20	620					
	root ww	EC20	860					
	root dw	EC20	1100					
	shoot length	EC50	8300	12 (0,1,3,6,12,15, 20,40,60,80, 100,120 mg/g)	3-6	nominal		26d test. n=10 clear lids kept on till plants 3cm in height
	root length	EC50	6300					
	shoot ww	EC50	2100					
	shoot dw	EC50	2300					
	root ww	EC50	4400					
	root dw	EC50	5500					

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
Barley	shoot length	EC20	74800	7 (0,15,30,50, 60,70, 80 mg/g)	4	nominal	Artificial - 70% silica sand, 20% keolinite clay 10% sphagnum peat	7d test. n=5
	root length	EC20	79000					
	shoot ww	EC20	73800					
	shoot dw	EC20	73600					
	root ww	EC20	61200					
	root dw	EC20	67400					
	shoot length	EC50	98200	7 (0,15,30,50,60, 70, 80 mg/g)	4	nominal		7d test. n=5
	root length	EC50	119600					
	shoot ww	EC50	85900					
	shoot dw	EC50	87200					
	root ww	EC50	90800					
	root dw	EC50	95300					
	shoot length	EC20	39400	6 (0,4,10,30,50,80 mg/kg)	4	nominal	field soil - Delacour Orthic Black Chernozem	6d test. n=5
	root length	EC20	47600					
	shoot ww	EC20	36700					
	shoot length	EC50	53400	6 (0,4,10,30,50,80 mg/kg)	4	nominal		6d test. n=5
	root length	EC50	58200					
	shoot ww	EC50	50300					
	shoot length	EC20	3700	10 (0,10,20,30,40, 50,60,70,80,100 mg/g)	3-6	nominal		14d test. n=5 clear lids kept on till plants 3cm in height
	root length	EC20	120					
	shoot ww	EC20	48200					
	shoot dw	EC20	48700					
	root ww	EC20	1700					
	root dw	EC20	10000					
Barley (cont'd)	shoot length	EC50	27600	10 (0,10,20,30,40, 50,60,70,80,100 mg/g)	3-6	nominal	field soil	14d test. n=5 clear lids kept on till plants 3cm in height
	root length	EC50	3200				- Delacour Orthic	

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
	shoot ww	EC50	54100				Black Chernozem	
	shoot dw	EC50	53300					
	root ww	EC50	8700					
	root dw	EC50	35100					
Northern wheat-grass	root length	EC20	20400	7 (0,15,30,50,60, 70,80 mg/g)	4	nominal		8d test. n=5
	whole ww	EC20	13700					
	whole dw	EC20	12100					
	shoot length	EC50	42100	7 (0,15,30,50,60, 70,80 mg/g)	4	nominal		8d test. n=5
	root length	EC50	51100	7 (0,15,30,50,60, 70,80 mg/g)	4	nominal		8d test. n=5
	whole ww	EC50	26700					
	whole dw	EC50	24800					
	shoot length	EC20	330	11 (0,5,10,15,20, 30,40,50,60,70, 80 mg/g)	3-6	nominal		25d test. n=5 clear lids kept on till plants 3cm in height
	root length	EC20	4300					
	shoot ww	EC20	13					
	shoot dw	EC20	50					
	root ww	EC20	180					
	root dw	EC20	210					
	shoot length	EC50	12700	11 (0,5,10,15,20, 30,40,50,60,70, 80 mg/g)	3-6	nominal		25d test. n=5 clear lids kept on till plants 3cm in height
	root length	EC50	7300					
	shoot ww	EC50	610					
	shoot dw	EC50	1400					
Northern wheat-grass (cont'd)	root dw	EC50	1100				field soil	
	root ww	EC50	890					
	shoot length	EC20	17100	7 (0,15,30,50,60,	4	nominal	Artificial - 70%	12d test. n=5

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
				70,80 mg/g)				
	root length	EC20	54900				silica sand, 20% keolinite clay 10% sphagnum peat	
	whole ww	EC20	34000					
	whole dw	EC20	33500					
	shoot length	EC50	81900	7 (0,15,30,50,60, 70,80 mg/g)	4	nominal		12d test. n=5
	root length	EC50	121000					
	whole ww	EC50	73400					
	whole dw	EC50	63900					
Worms (*E.foetida*)	# juveniles	EC20	240	11 (0,0.5,1,3,5,7, 10,12.5,15,20,25 mg/g)	10	nominal	field soil - Delacour Orthic Black Chernozem	57d test. n=2 perforated lids. adults removed at D37 & cocoons allowed to hatch. value for IC & LC
	# juveniles	EC50	776					
	juvenile ww	EC20	272					
	juvenile ww	EC50	854					
	juvenile dw	EC20	213					
	juvenile dw	EC50	809					
	# juveniles	NOEC	0					
	# juveniles	LOEC	500					
	juvenile ww	NOEC	0					
	juvenile ww	LOEC	500					
	juvenile dw	NOEC	0					
	juvenile dw	LOEC	500					
	mortality	LC50	22360	10 (0,0.5,1,2,4,8, 12,15,20,50 mg/g)	3-4	nominal	field soil Delacour Orthic Black Chernozem	14d test. n=5 perforated lids
Worms (*L. terrestris*)	mortality	LC50	19150	6 (0,8,12,15,20,50 mg/g)	3-4	nominal	Artificial - 70%silica sand, 20% keolinite clay, 10% sphagnum peat	14d test. n=3 perforated lids

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
	mortality	LC50	17220	7 (0,4,8,12,15,20, 50 mg/g)	3-4	nominal	field soil Delacour Orthic Black Chernozem	14d test. n=3 perforated lids
Springtail (*O. folsomi*)	mortality	LC50	6670	6 (0,2,4,8,12,15 mg/g)	3-4	nominal	artificial 70% silica sand 20% keolinite clay 10 % sphagnum peat	7d test. n=10 covered loosly
	mortality	LC50	5970					
	# juvenile	NOEC	1000	10 (0,0.5,1,2,3,4,5, 5.5,6,7 mg/g)	10	nominal	field soil Delacour Orthic Black Chernozem	35-36d test. n=10. loosely closed lids removed biweekly for air exchange. value for IC & LC
	# juvenile	LOEC	2000					
	# juvenile	EC20	910					
	# juvenile	EC50	1490					
	adult fecundity	NOEC	1000	10 (0,0.5,1,2,3,4,5, 5.5,6,7 mg/g)	10	nominal	field soil Delacour Orthic Black Chernozem	35-36d test. n=10. loosely closed lids removed biweekly for air exchange. value for IC & LC
	adult fecundity	LOEC	2000					
	adult fecundity	EC20	620					
	adult fecundity	EC50	1410					
Springtail (*O. folsomi*) (cont'd)	adult mortality	NOEC	3000	10 (0,0.5,1,2,3,4,5, 5.5,6,7 mg/g)	10	nominal	field soil Delacour Orthic Black Chernozem	35-36d test. n=10. loosely closed lids removed biweekly for air exchange. value for IC & LC
	adult mortality	LOEC	4000					
	adult mortality	EC20	3120					

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
	adult mortality	EC50	3695-4280					

(after Stephenson et al., 2000b)

Table E.2: PHC CWS fraction F2 (>nC10 to nC16) toxicity data for direct contact to soil invertebrates and plants.

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
Alfalfa	shoot length	EC50	2710	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 20 mg/g)	3-6	nominal	field soil – Delacour, Orthic Black Chernozem	21d test. n=10
	root length	EC50	1860					
	shoot ww	EC50	1680					
	shoot dw	EC50	1370					
	root ww	EC50	4740					
	root dw	EC50	5120					
Barley (*H.vulgare*)	shoot length	EC50	6370	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 25 mg/g)	4	nominal	Artificial: 70% sand; 20% clay; 10% peat	8d test. n=5
	root length	EC50	3440					
	shoot ww	EC50	7510					
	shoot dw	EC50	7830					
	root ww	EC50	4160					
	root dw	EC50	4180					
	shoot length	EC50	7150	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 25 mg/g)	4	nominal	field soil – Delacour, Orthic Black Chernozem	8d test. n=5
	root length	EC50	2770					
	shoot ww	EC50	6610					
	shoot dw	EC50	8240					
	root ww	EC50	4460					
	root dw	EC50	4370					
	shoot length	EC50	4130	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 20 mg/g)	3-6	nominal	field soil – Delacour, Orthic Black Chernozem	13d test. n=5
	root length	EC50	4550					
	shoot ww	EC50	2430					
	shoot dw	EC50	2590					
	root ww	EC50	2390					
	root dw	EC50	2510					
Northern	shoot length	EC50	7440	11 (0, 0.5, 1, 3, 5, 6,	3-6	nominal	field soil – Delacour,	14d test. n=5

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
wheatgrass				8, 12, 15, 20, 30 mg/g)			Orthic Black Chernozem	
	root length	EC50	2320					
	shoot ww	EC50	2770					
	shoot dw	EC50	3150					
	root ww	EC50	1560					
	root dw	EC50	1370					
Worms (*E.foetida*)	mortality	LC50	1190	8 (0, 0.1, 0.3, 0.5, 0.8, 1, 2, 3 mg/g)	3	nominal	Artificial: 70% sand; 20% clay; 10% peat	7d test. loose lids. n=5
	mortality	LC50	1030	8 (0, 0.1, 0.3, 0.5, 1, 2, 3, 6 mg/g)	3	nominal	field soil – Delacour, Orthic Black Chernozem	7d test. loose lids. n=5
	mortality	LC50	1150	8 (0, 0.1, 0.3, 0.5, 0.8, 1, 2, 3 mg/g)	3	nominal	Artificial: 70% sand; 20% clay; 10% peat	14d test. loose lids. n=5
Worms (*E.foetida*)	mortality	LC50	530	8 (0, 0.1, 0.3, 0.5, 1, 2, 3, 6 mg/g)	3	nominal	field soil – Delacour, Orthic Black Chernozem	14d test. loose lids. n=5
	# of juveniles	EC50	490	10 (0, 0.029, 0.041, 0.059, 0.084, 0.12, 0.17, 0.245, 0.35, 0.5 mg/g)	10	nominal	field soil – Delacour, Orthic Black Chernozem	62-63d test. n=2. perforated lids. adults removed at D27 & cocoons allowed to hatch
	juvenile ww	EC50	590					
	juvenile dw	EC50	580					
Worms (*L.terrestris*)	mortality	LC50	1100	8 (0, 0.1, 0.3, 0.5, 0.8, 1, 2, 3 mg/g)	3	nominal	Artificial: 70% sand; 20% clay; 10% peat	7d test. loose lids. n=3
	mortality	LC50	1290	8 (0, 0.1, 0.3, 0.5, 0.8, 1, 2, 3 mg/g)	3	nominal	field soil – Delacour, Orthic Black Chernozem	7d test. loose lids. n=3
	mortality	LC50	1100	8 (0, 0.1, 0.3, 0.5, 0.8, 1, 2, 3 mg/g)	3	nominal	field soil – Delacour, Orthic Black Chernozem	14d test. loose lids. n=3

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
Worms (*L.terrestris*) (cont'd)	mortality	LC50	1120	8 (0, 0.1, 0.3, 0.5, 0.8, 1, 2, 3 mg/g)	3	nominal		14d test. loose lids. n=3
Springtail (*O.folsomi*)	mortality	LC50	2920	9 (0, 0.5, 1, 2, 3, 5, 8, 10, 25 mg/g)	3	nominal	Artificial: 70% sand; 20% clay; 10% peat	7d test. loose lids. n=10
	mortality	LC50	3230	9 (0, 0.5, 1, 2, 3, 5, 8, 10, 25 mg/g)	3	nominal	field soil – Delacour, Orthic Black Chernozem	7d test. loose lids. n=10
	# juveniles	EC50	1470	(0, 0.025, 0.05, 0.1, 0.3, 0.5, 0.8, 1, 2, 3 mg/g)	10	nominal	field soil – Delacour, Orthic Black Chernozem	35-36d test. n=10. loose lids

(after Stephenson et al., 2000a)

Table E.3: Additive-free mogas toxicity data as an estimate of CWS F1 (C6 to nC10) toxicity, based on direct contact to soil invertebrates and plants.

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. (mg/g)	# reps.	Conc. type nom./init./final	Soil type	Comments
Alfalfa	shoot length	EC20	**3210**	10 (0,1,2,3,5, 6,8,12,15, 25)	3	nominal	artificial	11 d test (n=3 closed test units mech. mixing
	root length	EC20	**3310**					
	ww	EC20	**3390**					
	dw	EC20	**3400**					
	shoot length	EC20	**2410**	10 (0,1,2,3,5, 6,8,12,15, 25)	3	nominal	SLR	11 d test (n=3 closed test units mech. mixing
	root length	EC20	**3080**					
	ww	EC20	**5900**					
	dw	EC20	**5100**					
	shoot length	EC50	**5450**	10 (0,1,2,3,5, 6,8,12,15, 25)	3	nominal	artificial	11 d test (n=3 closed test units mech. mixing
	root length	EC50	**5010**					
	ww	EC50	**5320**					
	dw	EC50	**4910**					
	shoot length	EC50	**6600**	10 (0,1,2,3,5, 6,8,12,15, 25)	3	nominal	SLR	11 d test (n=3 closed test units mech. mixing
	root length	EC50	**4580**					
	ww	EC50	**8220**					
	dw	EC50	**6750**					
	shoot length	EC20	**2570**	10 (0,1,2,3,5, 6,8,12,15 25)	3	nominal	SLR	21 d test (n=3-6; closed test units for first 7 d only; mech. mixing)
	root length	EC20	**2240**					
	shoot ww	EC20	**1890**					
	shoot dw	EC20	**1850**					
	root ww	EC20	**2310**					
	root dw	EC20	**2120**					
Alfalfa	shoot	EC50	**5130**	10 (0,1,2,3,5,	3	nominal	SLR	21 d test (n=3-6; closed test units for

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. (mg/g)	# reps.	Conc. type nom./init./final	Soil type	Comments
(cont'd)	length			6,8,12,15, 25)				first 7 d only; mech. mixing)
	root length	EC50	**3900**					
	shoot ww	EC50	**2710**					
	shoot dw	EC50	**2520**					
	root ww	EC50	**2980**					
	root dw	EC50	**2970**					
Barley (*H.vulgare*)	shoot length	EC20	**4430**	7 (0,2.5,5, 10,25,50, 100 mg/g)	3	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	7d test. n=5 open plastic test units. mech mix
	shoot ww	EC20	**5530**					
	shoot dw	EC20	**5740**					
	root length	EC20	**2310**					
	root ww	EC20	**2180**					
	root dw	EC20	**2320**					
	shoot length	EC20	**2850**	7 (0,2.5,5, 10,25,50, 100 mg/g)	3	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	7d test. n=5 closed plastic test units. mech mix
	shoot ww	EC20	**4390**					
	shoot dw	EC20	**3560**					
	root length	EC20	**1590**					
	root ww	EC20	**1930**					
	root dw	EC20	**1620**					
	shoot length	EC20	**1900**	7 (0,2.5,5, 10,25,50, 100 mg/g)	3	nominal	SLR	7d test. n=5 closed plastic test units. mech mix
	shoot ww	EC20	**1210**					
	shoot dw	EC20	**1210**					
	root length	EC20	**1380**					

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. (mg/g)	# reps.	Conc. type nom./init./final	Soil type	Comments
	root ww	EC20	**1130**					
Barley	root dw	EC20	**910**					
(cont'd)	shoot length	EC50	**3100**	7 (0,2.5,5, 10,25,50, 100 mg/g)	3	nominal	SLR	7d test. n=5 closed plastic test units. mech mix
	shoot ww	EC50	**2320**					
	shoot dw	EC50	**2520**					
	root length	EC50	**2220**					
	root ww	EC50	**1770**					
	root dw	EC50	**1950**					
	shoot length	EC50	**5000**	7 (0,2.5,5, 10,25,50, 100 mg/g)	3	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	7d test. n=5 closed plastic test units. mech mix
	shoot ww	EC50	**5500**					
	shoot dw	EC50	**5440**					
	root length	EC50	**2760**					
	root ww	EC50	**3660**					
	root dw	EC50	**3590**					
	shoot length	EC50	**7240**	7 (0,2.5,5, 10,25,50, 100 mg/g)	3	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	7d test. n=5 open plastic test units. mech mix
	shoot ww	EC50	**7860**					
	shoot dw	EC50	**7790**					
	root length	EC50	**4480**					
	root ww	EC50	**4310**					
	root dw	EC50	**4780**					

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. (mg/g)	# reps.	Conc. type nom./init./final	Soil type	Comments
Barley (cont'd)	shoot length	EC20	**890**	10 (0, 0.25, 0.5,0.75,1, 1.5,2,4,6, 10)	3	nominal	SLR	13d test. n=5 closed plastic test units, for firt seven days only, mech mix
	shoot ww	EC20	**770**					
	shoot dw	EC20	**680**					
	root length	EC20	**640**					
	root ww	EC20	**580**					
	root dw	EC20	**590**					
	shoot length	EC50	**1680**	10 (0, 0.25, 0.5,0.75,1,1 .5,2,4,6,10)	3	nominal	SLR	13d test. n=5 closed plastic test units, for firt seven days only, mech mix
	root length	EC50	**1600**					
	shoot ww	EC50	**1360**					
	shoot dw	EC50	**1220**					
	root ww	EC50	**870**					
	root dw	EC50	**960**					
Corn (*Zea mays*)	shoot length	EC20	**3230**	11 (0,1,2,3,5, 6,8,15,25, 50,100 mg/g)	3	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	acute test. n=5 closed glass jars. tumble mixing
	shoot ww	EC20	**5260**					
	shoot dw	EC20	**4230**					
	root length	EC20	**1920**					
	root ww	EC20	**6830**					
	root dw	EC20	**6730**					
	shoot length	EC20	**3080**	11 (0,1,2,3,5, 6,8,15,25, 50,100 mg/g)	3	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	acute test. n=5 closed glass jars. mech. mixing
	shoot ww	EC20	**6670**					
	shoot dw	EC20	**6250**					
	root length	EC20	**1000**					
	root ww	EC20	**6750**					

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. (mg/g)	# reps.	Conc. type nom./init./final	Soil type	Comments
	root dw	EC20	**5470**					
Corn (cont'd)	shoot length	EC50	**4880**	11 (0,1,2,3,5,6, 8,15,25,50, 100 mg/g)	3	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	acute test. n=5 closed glass jars. tumble mixing
	shoot ww	EC50	**7590**					
	shoot dw	EC50	**7710**					
	root length	EC50	**3140**					
	root ww	EC50	**9090**					
	root dw	EC50	**9610**					
	shoot length	EC50	**4650**	11 (0,1,2,3,5, 6,8,15,25, 50,100 mg/g)	3	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	acute test. n=5 closed glass jars. mech. mixing
	shoot ww	EC50	**9250**					
	shoot dw	EC50	**9620**					
	root length	EC50	**2700**					
	root ww	EC50	**8930**					
	root dw	EC50	**8440**					
	shoot length	EC20	**3840**	11 (0,1,2,3,5, 6,8,15,25, 50,100 mg/g)	3	nominal	SLR	acute test. n=5 closed glass jars. mech. mixing
	shoot ww	EC20	**6270**					
	shoot dw	EC20	**6240**					
	root length	EC20	**2290**					
	root ww	EC20	**6260**					
	root dw	EC20	**6020**					
	shoot length	EC50	**5020**	11 (0,1,2,3,5, 6,8,15,25, 50,100 mg/g)	3	nominal	SLR	acute test. n=5 closed glass jars. mech. mixing
	shoot ww	EC50	**6960**					
	shoot dw	EC50	**7100**					
	root length	EC50	**3960**					
	root ww	EC50	**6910**					

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. (mg/g)	# reps.	Conc. type nom./init./final	Soil type	Comments
	root dw	EC50	**6650**					
Red fescue	shoot length	EC20	**2790**	10 (0,1,2,3,5, 6,8,12,15, 25 mg/g)	3	nominal	artificial	9 d. acute test. n=5 closed glass jars. mech. mixing
	root length	EC20	**2440**					
	ww	EC20	**4240**					
	dw	EC20	**3370**					
	shoot length	EC20	**2680**	10 (0,1,2,3,5, 6,8,12,15, 25 mg/g)	3	nominal	SLR	9 d. acute test. n=5 closed glass jars. mech. mixing
	root length	EC20	**1430**					
	ww	EC20	**3400**					
	dw	EC20	**2970**					
	shoot length	EC50	**5070**	10 (0,1,2,3,5, 6,8,12,15, 25 mg/g)	3	nominal	artificial	9 d. acute test. n=5 closed glass jars. mech. mixing
	root length	EC50	**4350**					
	ww	EC50	**5790**					
	dw	EC50	**4250**					
	shoot length	EC50	**4110**	10 (0,1,2,3,5, 6,8,12,15, 25 mg/g)	3	nominal	SLR	9 d. acute test. n=5 closed glass jars. mech. mixing
	root length	EC50	**2930**					
	ww	EC50	**4330**					
	dw	EC50	**3890**					
Springtails (*O.folsomi*)	adult mortality	LC50	**3420**	10 (0,0.025, 0.05,0.1, 0.5,1,2,3,5, 8 mg/g)	10	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	35-36d test. n=10. ? results due to low repro of control. closed units till D7 then loosely closed
	# juveniles	EC50	**2890**					
Springtails (cont'd)	adult mortality	LC50	**3760**					
	# juveniles	EC50	**4210**					

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. (mg/g)	# reps.	Conc. type nom./init./final	Soil type	Comments
	mortality	LC50	**4720**	8 (0,0.5,1,2, 3,5,8,10 mg/g)	3	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	7d test. n=? closed units
	mortality	LC50	**5960**	8 (0,0.5,1,2, 3,5,8,10 mg/g)	3			
	mortality	LC50	**4190**	8 (0,0.5,1,2, 3,5,8,10 mg/g)	3	nominal	sandy loam 60.8% sand 27.8% silt 11.4% clay	7d test. n=? closed units
	adult mortality	LC20	**1940**	10 (0,0.025, 0.05,0.1, 0.5,1,2,3,5, 8 mg/g)	10	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	35-36d test. n=10. ? results due to low repro of control. closed units till D7 then loosely closed
	# juveniles	EC20	**2170**					
	adult mortality	LC20	**2630**	10 (0,0.025, 0.05,0.1, 0.5,1,2,3,5, 8 mg/g)	10	nominal	sandy loam 60.8% sand 27.8% silt 11.4% clay	35-36d test. n=10 ? results due to low repro of control. closed units till D7 then loosely closed
	# juveniles	EC20	**2350**					
	adult mortality	LOEC	**3000**	10 (0,0.025, 0.05,0.1, 0.5,1,2,3,5, 8 mg/g)	10	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	35-36d test. n=10 ? results due to low repro of control. closed units till D7 then loosely closed
	# juveniles	LOEC	**25**		10	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	35-36d test. n=10 ? results due to low repro of control. closed units till D7 then loosely closed. ? inclusion because higher concent were not stat signif from control - son not dose-dep responce!
	adult mortality	NOEC	**2000**		10	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	35-36d test. n=10 ? results due to low repro of control. closed units till D7 then loosely closed
	# juveniles	NOEC	**0**		10	nominal	artificial	35-36d test. n=10 ? results due to low repro of control. closed units till D7 then

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. (mg/g)	# reps.	Conc. type nom./init./final	Soil type	Comments
								loosely closed
Worms (*E.fetida*)	mortality	LC50	**630**	7 (0,0.1,0.5, 1,2,3,5 mg/g)	2	nominal	sandy loam 60.8% sand 27.8% silt 11.4% clay	mech. mixing. 7d test. closed test container
	mortality	LC50	**1230**		2	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	mech. mixing. 7d test. closed test contaner
	mortality	LC50	**710**		2	nominal	sandy loam 60.8% sand 27.8% silt 11.4% clay	mech. mixing. 7d test. open test container
	mortality	LC50	**2080**		2	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	mech. mixing. 7d test. open test container
	mortality	LC50	**1150**	7 (0,0.1,0.5, 1,2,3,5 mg/g)	2	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	mech. mixing. 14d test. closed test container
	mortality	LC50	**400**		2	nominal	sandy loam 60.8% sand 27.8% silt 11.4% clay	mech. mixing. 14d test. closed test container
	mortality	LC50	**1860**		2	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	mech. mixing. 14d test. open test container
	mortality	LC50	**710**		2	nominal	sandy loam 60.8% sand 27.8% silt 11.4% clay	mech. mixing. 14d test. open test container

(after Stephenson 2000)

Table E.4: Toxicity of fresh, Whole Federated Crude Oil to soil invertebrates and plants.

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
Alfalfa	shoot length	EC20	6550	10 (0, 2.5, 5, 10, 30, 60, 80, 100, 120, 150 mg/g)	4 control 3 trt	nominal	Artificial: 70% silica sand; 20% keolinite clay;10% sphagnum peat	11d test. n=10
	root length	EC20	339					
	whole dw	EC20	587					
	shoot length	EC20	3382	10 (0, 2.5, 5, 10, 30, 60, 80, 100, 120, 150 mg/g)	4 control 3 trt	nominal	Artificial: 70% silica sand; 20% keolinite clay;10% sphagnum peat	11d test. n=10
	root length	EC20	277					
	whole dw	EC20	113882					
	whole ww	EC20	66114					
	shoot length	EC50	149054	10 (0, 2.5, 5, 10, 30, 60, 80, 100, 120, 150 mg/g)	4 control 3 trt	nominal	Artificial: 70% silica sand; 20% keolinite clay;10% sphagnum peat	11d test. n=10
	root length	EC50	1054					
	whole dw	EC50	302221					
	whole ww	EC50	152357					
	shoot length	EC50	10506	10 (0, 2.5, 5, 10, 30, 60, 80, 100, 120, 150 mg/g)	4 control 3 trt	nominal	Field soil Delacour Orthic Black Chernozem	11d test. n=10
	root length	EC50	5175					
	whole dw	EC50	242415					

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
Alfalfa (cont'd)	shoot length	EC20	3109	13 (0, 0.5, 1, 2.5, 5, 10, 30, 60, 80, 100, 120, 135, 150 mg/g)	6 control 3-4 trt	nominal	Field soil Delacour Orthic Black Chernozem	20d test. n=10
	root length	EC20	9905					
	shoot ww	EC20	1526					
	shoot dw	EC20	5286					
	root ww	EC20	131344					
	root dw	EC20	36276					
	shoot length	EC50	19877	13 (0, 0.5, 1, 2.5, 5, 10, 30, 60, 80, 100, 120, 135, 150 mg/g)	6 control 3-4 trt	nominal	Field soil Delacour Orthic Black Chernozem	20d test. n=10
	root length	EC50	30768					
	shoot ww	EC50	5358					
	shoot dw	EC50	13330					
	root ww	EC50	50187					
	root dw	EC50	60194					
Barley (CDC Buck)	shoot length	EC20	61622	9 (0, 0.5, 1, 5, 10, 15, 30, 60, 120 mg/g)	4 control 3 trt	nominal	Field soil Delacour Orthic Black Chernozem	9d test. n=5
	root length	EC20	16683					
	shoot dw	EC20	54832					
	shoot ww	EC20	39386					
	root dw	EC20	45332					
	shoot length	EC50	80598	9 (0, 0.5, 1, 5, 10, 15, 30, 60, 120 mg/g)	4 control 3 trt	nominal	Field soil Delacour Orthic Black Chernozem	9d test. n=5
	root length	EC50	44004					
	shoot ww	EC50	53712					
	shoot dw	EC50	64965					
	root dw	EC50	59161					
Barley (Chapais)	shoot length	EC20	3431	13 (0, 0.5, 1, 2.5, 5, 10, 30, 60, 80, 100, 120,	6 control 3-4 trt	nominal	Field soil Delacour Orthic Black Chernozem	13d test. n=5

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
				135, 150 mg/g)				
	root length	EC20	2982					
	shoot ww	EC20	2570					
	shoot dw	EC20	723					
	root ww	EC20	1370					
	root dw	EC20	1171					
	shoot length	EC50	15268	13 (0, 0.5, 1, 2.5, 5, 10, 30, 60, 80, 100, 120, 135, 150 mg/g)	6 control 3-4 trt	nominal	Field soil Delacour Orthic Black Chernozem	13d test. n=5
	root length	EC50	10682					
	shoot ww	EC50	9060					
	shoot dw	EC50	4519					
	root ww	EC50	4052					
	root dw	EC50	4740					
Corn (Kandy Korn)	shoot length	EC20	103361	10 (0, 2.5, 5, 10, 30, 60, 80, 100, 120, 150 mg/g)	4 control 3 trt	nominal	Field soil Delacour Orthic Black Chernozem	7d test. n=3
	root length	EC20	2434					
	root ww	EC20	100632					
	root dw	EC20	104951					
	shoot length	EC50	116500	10 (0, 2.5, 5, 10, 30, 60, 80, 100, 120, 150 mg/g)	4 control 3 trt	nominal	Field soil Delacour Orthic Black Chernozem	7d test. n=3
	root length	EC50	62041					
	root ww	EC50	111257					
	root dw	EC50	108321					
	shoot length	EC20	94723	10 (0, 2.5, 5, 10, 30, 60, 80, 100, 120, 150 mg/g)	4 control 3 trt	nominal	Artificial: 70% silica sand; 20% keolinite clay;10% sphagnum peat	6d test. n=3
Corn (Kandy Korn) (cont'd)	root length	EC20	2604					
	shoot ww	EC20	97670					
	shoot dw	EC20	92670					

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
	root ww	EC20	82248					
	root dw	EC20	67736					
	shoot length	EC50	130639	10 (0, 2.5, 5, 10, 30, 60, 80, 100, 120, 150 mg/g)	4 control 3 trt	nominal	Artificial: 70% silica sand; 20% keolinite clay;10% sphagnum peat	6d test. n=3
	root length	EC50	26485					
	shoot ww	EC50	140732					
	shoot dw	EC50	132712					
	root ww	EC50	125753					
	root dw	EC50	114903					
	shoot length	EC20	10928	13 (0, 0.5, 1, 2.5, 5, 10, 30, 60, 80, 100, 120, 135, 150 mg/g)	6 control 3-4 trt	nominal	Field soil Delacour Orthic Black Chernozem	14d test. n=5 initial measures are provided
	root length	EC20	1168					
	shoot ww	EC20	34031					
	shoot dw	EC20	34458					
	root ww	EC20	8452					
	root dw	EC20	35224					
	shoot length	EC50	47680	13 (0, 0.5, 1, 2.5, 5, 10, 30, 60, 80, 100, 120, 135, 150 mg/g)	6 control 3-4 trt	nominal	Field soil Delacour Orthic Black Chernozem	14d test. n=5 initial measures are provided
	root length	EC50	8103					
	shoot ww	EC50	53532					
	shoot dw	EC50	51973					
	root ww	EC50	26253					
	root dw	EC50	47964					
Northern wheatgrass	shoot length	EC20	7373	11 (0, 1, 2.5, 5, 10, 30, 60, 80, 100, 120, 150 mg/g)	4 control 3 trt	nominal	Artificial: 70% silica sand; 20% keolinite clay;10% sphagnum peat	9d test. n=5
	root length	EC20	3505					
	whole ww	EC20	22917					
	whole dw	EC20	6538					

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
	shoot length	EC50	29862	11(0, 1, 2.5, 5, 10, 30, 60, 80, 100, 120, 150 mg/g)	4 control 3 trt	nominal	Artificial: 70% silica sand; 20% keolinite clay;10% sphagnum peat	9d test. n=5
	root length	EC50	16636					
	whole ww	EC50	51836					
	whole dw	EC50	22371					
	shoot length	EC20	10557	11 (0, 1, 2.5, 5, 10, 30, 60, 80, 100, 120, 150 mg/g)	4 control 3 trt	nominal	Field soil Delacour Orthic Black Chernozem	9d test. n=5
	root length	EC20	7794					
	whole ww	EC20	25588					
	whole dw	EC20	21342					
	shoot length	EC50	26120	11 (0, 1, 2.5, 5, 10, 30, 60, 80, 100, 120, 150 mg/g)	4 control 3 trt	nominal	Field soil Delacour Orthic Black Chernozem	9d test. n=5
	root length	EC50	23187					
	whole ww	EC50	50899					
	whole dw	EC50	37791					
	shoot length	EC20	837	10 (0, 0.5, 1, 2.5, 5, 10, 30, 60, 80, 100 mg/g)	6 control 3-4 trt	nominal	Field soil Delacour Orthic Black Chernozem	20d test. n=5
	root length	EC20	782					
	shoot ww	EC20	2140					
	shoot dw	EC20	525					
	root dw	EC20	1598					
	root ww	EC20	1480					
Northern Wheatgrass	shoot length	EC50	6671	10 (0, 0.5, 1, 2.5, 5, 10, 30, 60, 80, 100 mg/g)	6 control 3-4 trt	nominal	Field soil Delacour Orthic Black Chernozem	20d test. n=5
(cont'd)	root length	EC50	5876					
	shoot ww	EC50	2140					
	shoot dw	EC50	2576					
	root ww	EC50	4598					
	root dw	EC50	4963					

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
Springtails (*O. folsomi*)	mortality	LC50	7588	9 (0, 0.5, 1, 2, 4, 8, 15, 25, 50 mg/g)	6 control 3 trt	nominal	Artificial: 70% silica sand; 20% keolinite clay;10% sphagnum peat	7d test. n=10 loosely sealed lids
	mortality	LC50	4858	10 (0, 1, 2, 4, 6, 8, 10, 15, 25, 50 mg/g)	6 control 3 trt	nominal	Field soil Delacour Orthic Black Chernozem	7d test. n=10 loosely sealed lids
	mortality	LC50	4678					
	# juveniles	EC50	4882	9 (0, 0.5, 1, 2, 4, 5, 6, 7, 7.5 mg/g)	10	nominal	Field soil Delacour Orthic Black Chernozem	35-36d test. n=10 loosely fitting lids. air exchanged biweekly
	fecundity	EC50	4977					
Worms (*E.fetida*)	mortality	LC50	3984	8 (0, 0.5, 1, 3, 5, 7, 10, 15 mg/g)	6 control 3 trt	nominal	Field soil Delacour Orthic Black Chernozem	14d test. n=10 perforated lids
	mortality	LC50	5251	7 (0, 1, 3, 6, 8, 10, 24 mg/g)	6 control 3 trt	nominal	Artificial: 70% silica sand; 20% keolinite clay;10% sphagnum peat	14d test. n=10 perforated lids
	mortality	LC50	5729	7(0, 1, 3, 6, 8, 10, 24 mg/g)	6 control 3 trt	nominal	Artificial: 70% silica sand; 20% keolinite clay;10% sphagnum peat	14d test. n=10 perforated lids
	mortality	LC50	4200	8 (0, 1, 2, 3, 4, 6, 8, 10 mg/g)	6 control 3 trt	nominal	Artificial: 70% silica sand; 20% keolinite clay;10% sphagnum peat	14d test. n=3 perforated lids
Worms (*E.fetida*) (cont'd)	# juveniles	EC20	842	10 (0, 0.075, 0.125, 0.25, 0.5, 0.8, 1, 2, 3, 4 mg/g)	10	nominal	Field soil Delacour Orthic Black Chernozem	61d test. n=2 adults removed D33 & cocoons allowed to hatch. perforated lids. values for IC/EC
	juvenile ww	EC20	1183	10 (0, 0.075, 0.125, 0.25, 0.5, 0.8, 1, 2, 3, 4 mg/g)	10	nominal	Field soil Delacour Orthic Black Chernozem	61d test. n=2 adults removed D33 & cocoons allowed to hatch. perforated lids. values for IC/EC
	juvenile dw	EC20	968	10 (0, 0.075, 0.125, 0.25, 0.5, 0.8, 1, 2, 3, 4 mg/g)	10	nominal	Field soil Delacour Orthic Black Chernozem	61d test. n=2 adults removed D33 & cocoons allowed to hatch. perforated lids. values for IC/EC
	# juveniles	EC50	1633	10 (0, 0.075, 0.125, 0.25, 0.5, 0.8, 1, 2, 3, 4 mg/g)	10	nominal	Field soil Delacour Orthic Black Chernozem	61d test. n=2 adults removed D33 & cocoons allowed to hatch. perforated lids. values for IC/EC

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
	juvenile ww	EC50	1807	10 (0, 0.075, 0.125, 0.25, 0.5, 0.8, 1, 2, 3, 4 mg/g)	10	nominal	Field soil Delacour Orthic Black Chernozem	61d test. n=2 adults removed D33 & cocoons allowed to hatch. perforated lids. values for IC/EC
	juvenile dw	EC50	1714	10 (0, 0.075, 0.125, 0.25, 0.5, 0.8, 1, 2, 3, 4 mg/g)	10	nominal	Field soil Delacour Orthic Black Chernozem	61d test. n=2 adults removed D33 & cocoons allowed to hatch. perforated lids. values for IC/EC
Worms (***L. terrestris***)	mortality	LC50	4112	8 (0, 1, 2, 3, 4, 6, 8, 10 mg/g)	6 control 3 trt	nominal	Artificial: 70% silica sand; 20% keolinite clay;10% sphagnum peat	14d test. n=3 perforated lids
	mortality	LC50	64158	(0, 1, 2, 3, 4, 6, 8, 10 mg/g)	6 control 3 trt	nominal	Field soil Delacour Orthic Black Chernozem	14d test. n=3 perforated lids

(after Stephenson et al., 1999)

Appendix F: Toxicity comparison of Federated Whole Crude Oil and its derived fractions.

Table F.1: Direct comparison of the toxicity of Federated Whole Crude with CWS fractions derived from it (and with Mogas) (expressed as $EC(LC)_{50}$ nominal soil concentrations, in mg/kg).

Taxon	Endpoint	Exposure Period	$LC(EC)_{50}$ PHC conc.						
			whole crude	F3	F3/ whole	F2	F2/ whole	mogas (F1)	mogas/ crude
springtail (*O.folsomi*)	mortality	7 day (all)	6070	6300	**1.04**	3070	**0.51**	5000	**0.82**
	# juveniles	35-36 day (all)	4880	1490	**0.31**	1470	**0.30**	2890	**0.59**
	fecundity		4980	1410	**0.28**			3420	**0.69**
worms (*E. foetida)*	mortality (open container)	14 day (all)	1150	22360	**19.4**	780	**0.68**	1860	**1.62**
	# juveniles	61, 57, 62 day	1,630	776	**0.48**	490	**0.30**		
	juvenile ww		1,810	854	**0.47**	590	**0.33**		
	juvenile dw		1,710	809	**0.47**	580	**0.34**		
worm (*L.terrestris*)	mortality	14 day (all)	5,140	18,600	**3.62**	1110	**0.22**		
alfalfa	shoot length	11, 8, n/a, 11 day	39,600	51900	**1.31**			6600	**0.17**
	root length		2,340	10000	**4.27**			4580	**1.96**
	whole dw		27,100	72300	**2.67**			8220	**0.30**
	whole ww		270,000	72300	**0.27**			6750	**0.03**
	shoot length	20, 26, 21, 21 day	19877	8300	**0.42**	2710	**0.14**	5130	**0.26**
	root length		30768	8300	**0.27**	1860	**0.06**	3900	**0.13**
	shoot wet wt		5358	2100	**0.39**	1680	**0.31**	2710	**0.51**
	shoot dry wt		13330	2300	**0.17**	1370	**0.10**	2520	**0.19**
	root wet wt		50187	4400	**0.09**	4740	**0.09**	2980	**0.06**
	root dry wt		60194	5500	**0.09**	5120	**0.09**	2970	**0.05**
barley (*H. vulgare*)	shoot length	7, 7, 8, 7 day	80598	72400	**0.90**	7150	**0.09**	7240	**0.09**
	root length		44004	83400	**1.90**	2770	**0.06**	4480	**0.10**
	shoot ww		53712	65700	**1.22**	6610	**0.12**	7860	**0.15**
	shoot dw		64965	87200	**1.34**	8240	**0.13**	7790	**0.12**
	root ww			90800		4460		4310	
	root dw		59161	95300	**1.61**	4370	**0.07**	4780	**0.08**
barley (Chapais)	shoot length	13, 14, 13, 13 day	15268	27600	**1.81**	4130	**0.27**	1680	**0.11**
	root length		10682	3200	**0.30**	4550	**0.43**	1600	**0.15**
	shoot ww		9060	54100	**5.97**	2430	**0.27**	1360	**0.15**

Taxon	Endpoint	Exposure Period	$LC(EC)_{50}$ PHC conc.						
			whole crude	F3	F3/ whole	F2	F2/ whole	mogas (F1)	mogas/ crude
	shoot dw		4519	53300	**11.79**	2590	**0.57**	1220	**0.27**
	root ww		4052	8700	**2.15**	2390	**0.59**	870	**0.21**
	root dw		4740	35100	**7.41**	2510	**0.53**	960	**0.20**
corn (*Z. mays*)	shoot length	6 day						8379	
	root length							9006	
	shoot ww							2912	
	shoot dw							9010	
	root ww							8612	
	root dw							4764	
corn (Kandy Korn)	shoot length	14 day	47680						
	root length		8103						
	shoot ww		53532						
	shoot dw		51973						
	root ww		26253						
	root dw		47964						
northern wheat grass	shoot length	9, 7 day	27900	42100	**1.51**				
	root length		19600	51100	**2.61**				
	whole ww		51400	26700	**0.52**				
	whole dw		29100	24800	**0.85**				
	shoot length	20, 25, 14 day	6671	12700	**1.90**	7440	**1.12**		
	root length		6671	7300	**1.09**	2320	**0.35**		
	shoot ww		2140	610	**0.29**	2770	**1.29**		
	shoot dw		2576	1400	**0.54**	3150	**1.22**		
	root ww		4598	890	**0.19**	1560	**0.34**		
	root dw		4963	1100	**0.22**	1370	**0.28**		

Appendix G: Toxicity of PHCs in weathered soils.

For soil invertebrates and plants, toxicity tends to occur when the molar concentration of the organic toxicant in an organism's lipid pool exceeds a critical threshold (McCarthy and Mackay 1993). Non-specific mechanisms associated with membrane disruption, increased membrane fluidity, loss of membrane polarization, and a host of related biochemical perturbations (often termed 'narcosis' in animals) are often assumed to be the major mode of toxicological action (Van Wenzel *et al.* 1996). The contribution of individual non-polar toxicants to such a common, non-specific toxicological response is often assumed to be additive, with the contribution of individual toxicants being influenced primarily by bioavailability, lipophilicity, and resistance to rapid metabolic modification and elimination from the body. The bioavailability, in particular, is expected to be controlled by specifics of the interaction between an organism and the immediate soil microenvironment. Narcosis-type modes of action are often taken as the base case for toxicity in soil invertebrates and plants (Parkerton and Stone, *in press*); however, more specific toxicological modes of action should not be discounted – e.g., for PAHs effects on earthworms through photo-induced toxicity (Erickson et al. 1999).

Weathering of petroleum hydrocarbons in a soil environment through biodegradation and other loss mechanisms results in the differential loss of more easily degraded constituents among the original mix of unsubstituted and alky-PAHs, alkane, hopanes, isoprenoids (aliphatic and non-aromatic cyclic hydrocarbons) and other compounds. The loss of PHC mass can occur through either partial or complete mineralization, to produce CO_2 and H_20. Partial breakdown can lead to metabolic intermediates with similar or greater toxic potency than the parent substance.

The relative composition of PAHs, n-alkanes and isoprenoids has been used to evaluate the degree of weathering, and specific processes involved during biodegradation and environmental partitioning (Didyk and Simoneit 1989, Rogues *et al.* 1994, Wang *et al.* 1995). A slightly degraded oil is usually indicated by the partial depletion of n-alkanes; a moderately degraded one is often indicated by the substantial loss of n-alkanes and partial loss of lighter PAHs. Highly degraded mixtures may be accompanied by almost complete loss of n-alkanes along with unsubstituted, but less so more highly alkylated PAHs. Several indices have been proposed to provide a measure of weathering (Rogues et al. 1994). One index is the nC17/pristine and nC18/phytane ratios. As the more easily degraded normal hydrocarbons (nC17 and nC18) are lost, the more recalcitrant isoprenoids (pristane and phytane) are conserved. The corresponding n-alkane/isoprenoid ratio in a moderately weathered sample is less than one. In very highly weathered samples, a substantial proportion of the isoprenoids is also lost. Hopanes, however, tend to be preserved until the latter stages of overall PHC degradation, and are especially prevalent if weathering occurs by biodegradation.

One of the challenges in assessing the relative toxicity of fresh versus weathered PHCs is that the relative toxicity of the above-mentioned classes of PHCs is not

known. Where residual hydrocarbons fall in the >nC34 range, the relative toxicity is likely not an issue, since the bioavailability, and – hence – toxicity of all individual constituents is expected to be very limited (TPHCWG 1999). For the F3 fraction, however, it is not known whether n-alkanes, isoprenoids, and hopanes have equivalent bioavailability and ecotoxicity.

The above-mentioned indices are applicable primarily to crude oils, and the degree of weathering is most easily assessed when complex compositional data are available for the fresh product that was released at a site. If a management approach is to be used that accounts for effects of weathering at a field site, then there is an added requirement to be able to objectively and transparently define the degree of weathering which has occurred, either generically or on a site-specific basis.

According to Irwin et al. (1997) –

> "The word "fresh" cannot be universally defined because oil breaks down faster in some environments than in others. In a hot, windy, sunny, oil-microbe-rich, environment in the tropics, some of the lighter and more volatile compounds (such as the Benzene, Toluene, Ethyl Benzene, and Xylene compounds) would be expected to disappear faster by evaporation into the environment and by biodegradation than in a cold, no-wind, cloudy, oil-microbe-poor environment in the arctic. In certain habitats, BTEX and other relatively water-soluble compounds will tend to move to groundwater and/or subsurface soils (where degradation rates are typically slower than in a sunny well aerated surface environment). Thus, the judgement about whether or not oil contamination would be considered "fresh" is a professional judgement based on a continuum of possible scenarios.
>
> The closer in time to the original spill of non-degraded petroleum product, the greater degree the source is continuous rather than the result of a one-time event, and the more factors are present which would retard oil evaporation or breakdown (cold, no-wind, cloudy, oil-microbe-poor conditions, etc.) the more likely it would be that in the professional judgement experts the oil would be considered "fresh." In other words, the degree of freshness is a continuum which depends on the specific product spilled and the specific habitat impacted. Except for groundwater resources (where the breakdown can be much slower), the fresher the middle distillate oil contamination is, the more one has to be concerned about potential impacts of BTEX compounds, and other lighter and more volatile petroleum compounds."

G.1.0 Studies by Visser et al. (in progress)

Visser (in progress) is conducting a study of the effects of aging on the toxicity of Federated Whole Crude to soil invertebrates and plants. The experiment was conducted in three different soil types:

i) Sandy soil (82.5% sand, 9% silt, 9% clay);
ii) Loam (18% sand, 48% silt, 34% clay); and
iii) Clay (16% sand, 33% silt, 51% clay).

Toxicity endpoints included a 14 day survival assay for earthworms *(E. fetida)* and 4-5 day germination and root elongation test for lettuce and barley. Residual soil concentrations for PHCs were generated by adding fresh crude oil to each soil treatment and incubating the soil at room temperature for three months; at this point all of the treatments had achieved a stable or near stable endpoint (Visser, pers. comm.). Preliminary results are shown in Tables G.1 through G.6.

Visser et al., as well as Stephenson et al. (1999) also characterized the fresh Federated Whole Crude oil. The initial composition, prior to weathering is as follows:

C1-C5:	2.8%
C6-C10 (CWS F1):	**23.2%**
C11-C16 (CWS F2):	**21.3%**
C17-C22:	16.0%
C23-C35:	8.5%
SUM OF LAST 2 (CWS F3):	**34.5%**
>C35 (CWS F4):	**18.2%**

Table G.1: Ecotoxicity of artificially weathered Federated Whole Crude residuals in sand: Earthworm (*Eisenia fetida)* survival.

- 14 days exposure in soil (Data are means ± standard deviation) (n = 3; 15 worms/replicate)

Original Oil Dosage (mg/kg)	Crude Oil Residual (mg/kg)					% Earthworm Survival
	Total	CWS F1 (C6-C10)	CWS F2 (>C10-C16)	CWS F3 (>C16-C34)	Fraction 4 (>C34-C60+)	
0	137	0 (0%)	0 (0%)	19 (13.95)	118 (86.1%)	**100**
6000	1785	0 (0%)	21 (1.2%)	645 (36.1%)	1119 (62.7%)	**100**
12000	3473	0 (0%)	49 (1.4%)	1145 (3.0%)	2279 (65.6%)	**96.7 ± 5.8**
***24000**	7433	**1** (0%)	**240** (3.2%)	**2711** (36.5%)	**4481** (60.3%)	**100**
48000	17251	6 (0%)	794 (4.6%)	6797 (39.4%)	9654 (56.0%)	**13.3 ± 15.3**
96000	44465	15 (0%)	3097 (7.0%)	20842 (46.9%)	20511 (46.1%)	**0**

*shaded row represents NOEC.

Table G.2: Ecotoxicity of artificially weathered Federated Whole Crude residuals in sand: Seed germination, root elongation by lettuce and barley in soil.

- Butter lettuce – 5 day assay (30 seeds/rep); Barley – 4 day assay (20 seeds/rep)
- Data are means ± standard deviation (n = 3)

Orig. Oil Dosage (mg/ kg)	Crude Oil Residual (mg/kg)					Lettuce % germin.	Lettuce (cm root/ plant)	Barley (% germ.)	Barley (cm root/ plant)
	Total	CWS F1	CWS F2	CWS F3	CWS F4				
0	137	0	0	19	118	78.9± 11.7	4.7±0.1	85±8.7	8.0±0.6
6000	1785	0	21	645	1119	71.1± 7.7	8.6±0.6	85±13	8.4±0.4
12000	3473	0	49	1145	2279	81.1± 5.1	8.2±1.3	90±0	9.9±0.6
*24000	7433	**1**	**240**	**2711**	**4481**	70.0± 23.3	6.6±1.4	80±10.0	10.0±0.9
48000	17251	6	794	6797	9654	28.9± 28.8	3.2±2.8	73.3±34	4.6±3.1
96000	44465	15	3097	20842	20511	0	0	50± 32.8	1.3±0.2

*shaded row represents NOEC.

Table G.3: Ecotoxicity of artificially weathered Federated Whole Crude residuals in loam: Earthworm (*Eisenia fetida)* survival.

– 14 days exposure in soil (Data are means ± standard deviation) (n = 3; 15 worms/replicate)

Original Oil Dosage (mg/kg)	Crude Oil Residual (mg/kg)					% Earthworm Survival
	Total	CWS F1	CWS F2	CWS F3	CWS F4	
0	1416	0 (0%)	7 (0.5%)	106 (7.5%)	1303 (92.0%)	100
6000	6906?	0 (0%)	68 (1.0%)	1637 (23.7%)	5201 ((75.3%)	100
12000	7990	1 (0.0%)	143 (1.8%)	2435 (30.5%)	5411 (67.7%)	100
24000	11240	1 (0.0%)	209 (1.9%)	3915 (34.8%)	7115 (63.3%)	100
48000	23912	2 (0.0%)	662 (2.8%)	8535 (36.7%)	14713 (61.5%)	100
*96000	29603	**3 (0.0%)**	**780 (2.6%)**	**10253 (34.6%)**	**18567 (62.7%)**	100

*shaded row represents NOEC.

Table G.4: Ecotoxicity of artificially weathered Federated Whole Crude residuals in loam: Seed germination, root elongation by lettuce and barley in soil.

- Butter lettuce – 5 day assay (30 seeds/rep); Barley – 4 day assay (20 seeds/rep)
  - Data are means ± standard deviation (n = 3)

Original Oil Dosage (mg/kg)	Crude Oil Residual (mg/kg)					Lettuce % germ.	Lettuce (cm root/ plant)	Barley (% germin.)	Barley (cm root/ plant)
	Total	CWS F1	CWS F2	CWS F3	CWS F4				
0	1416	0	7	106	1303	78.9± 10.7	4.7±0.5	86.7±7.6	7.1±0.3
6000	6906	0	68	1637	5201	38.7± 18.9	4.6±0.3	86.7±2.9	7.2±0.7
12000	7990	1	143	2435	5411	56.7± 12.1	5.2±0.3	95±5	7.0±0.4
24000	11240	1	209	3915	7115	55.6± 11.7	6.1±0.2	91.7±10.4	7.8±0.6
48000	23912	2	662	8535	14713	51.1±7.7	8.9±0.3	91.7±2.9	10.3±0.7
*96000	29603	**3**	**780**	**10253**	**18567**	57.8± 11.7	9.2±0.6	88.3± 7.6	10.2±0.6

*shaded row represents NOEC.

Table G.5: Ecotoxicity of artificially weathered Federated Whole Crude residuals in clay: Earthworm (*Eisenia fetida)* survival.

- 14 days exposure in soil (Data are means ± standard deviation) (n = 3; 15 worms/replicate)

Original Oil Dosage (mg/kg)	Crude Oil Residual (mg/kg)					% Earthworm Survival
	Total	CWS F1	CWS F2	CWS F3	CWS F4	
0	904	0 (0.0%)	2 (0.2%)	70 (7.7%)	832 (92.0%)	100
6000	3765	1 (0.0%)	128 (3.4%)	1359 (36.1%)	2277 (60.5%)	100
12000	6201	3 (0.0%)	243 (3.9%)	2290 (36.9%)	3665 (59.1%)	100
24000	16514	8 (0.0%)	993 (6.0%)	7462 (45.2%)	8051 (48.8%)	100
*48000	28554	**13 (0.0%)**	**1942 (6.8%)**	**13717 (48.0%)**	**12882 (45.1%)**	100
96000	62427	22 (0.0%)	6049 (9.7%)	32430 (51.9%)	23926 (38.3%)	23.3±40.4

*shaded row represents NOEC.

Table G.6: Ecotoxicity of artificially weathered Federated Whole Crude residuals in clay: Seed germination, root elongation by lettuce and barley in soil.

- Butter lettuce – 5 day assay (30 seeds/rep); Barley – 4 day assay (20 seeds/rep)
- Data are means ± standard deviation (n = 3)

Original Oil Dosage (mg/kg)	Crude Oil Residual (mg/kg)					Lettuce % germin.	Lettuce (cm root/ plant)	Barley (% germin.)	Barley (cm root/ plant)
	Total	CWS F1	CWS F2	CWS F3	CWS F4				
0	904	0	2	70	832	67.8± 10.7	5.6±0.1	93.3±2.9	10.0±1.0
6000	3765	1	128	1359	2277	67.8±5.1	6.9±0.3	88.3±2.9	10.2±0.7
12000	6201	3	243	2290	3665	70.0± 10.0	9.2±0.8	95.0±5.0	11.8±0.6
24000	16514	8	993	7462	8051	57.8± 15.7	9.2±0.9	91.7±7.6	11.4±0.1
48000	28554	13	1942	13717	12882	57.8±8.4	8.7±0.5	93.7±7.1	10.4±0.2
*96000	62427	**22**	**6049**	**32430**	**23926**	50.0±8.8	7.5±0.5	96.7± 5.8	9.5±0.6

*shaded row represents NOEC.

These results clearly show that a measured F3 soil concentration between 2,700 and 32,000 mg/kg soil did not correspond to increased mortality to earthworms (14 day exposure), or reduced germination or reduced root elongation in lettuce and barley (4-5 day exposure). This is substantially higher than the estimated 25th percentile of the LC/EC_{50} data (250 to 620 mg/kg F3) for toxicity of F3 from fresh federated crude oil to soil invertebrates and plants (Section 4.2.4). It should be noted, however, that the lowest ECx from the Stephenson et al (2000b) study were for much longer exposure periods, and for potentially more sensitive endpoints, such as worm reproduction, as opposed to mortality.

The most sensitive EC_{50} endpoints from Stephenson et al (2000b) for F3 are reproduced immediately below for direct comparison:

- northern wheatgrass shoot wet wt., 25 day EC_{50} — 610 mg/kg nom. = 190 mg/kg init.
- worm (*E. foetida*) number of juveniles, 57 day EC_{50} — 776 mg/kg nom. = 240 mg/kg init.
- worm (*E. foetida*) juvenile dry wt., 57 day EC_{50} — 810 mg/kg nom. = 250 mg/kg init.
- northern wheatgrass root wet wt., 25 day EC_{50} — 890 mg/kg nom. = 280 mg/kg init.
- springtail (*O. folsomi*) adult fecundity, 35-36 day EC_{50} — 1410 mg/kg nom. = 440 mg/kg init.
- alfalfa shoot wet wt, 26 day EC_{50} — 2100 mg/kg nom.

The NOEC levels from Visser (in progress) for the CWS F2 fraction also occurred at much higher residual PHC concentrations that the 25th percentile of EC/LC_{50} concentration based on the study by Stephenson et al. (2000a) with one exception. The plant germination/growth or worm mortality NOEC test unit had a measured F2 concentration of 240 mg/kg. The sand test unit with a residual F2 and F3 concentration of around 790 mg/kg and 6800 mg/kg, respectively, corresponded to an average earthworm survivorship of 13%, and a reduction in germination or root length from around 10 to 70%.

Visser's study also shows that weathering has the potential to reduce PHC concentrations for the F1 and F2 fractions to levels that are lower than the previously discussed 25th percentile of soil invertebrate EC(LC)$_{50}$ values, but less so for the F3 fraction.

The degree to which weathering changes the relative proportions of the light to heavy CWS fractions varies as a function of both soil type and initial soil concentration.

G.2.0 Studies by Saterbak et al.

Saterbak et al. have carried out extensive studies on the effects of PHC weathering and bioremediation on toxicity to soil invertebrates and plants, using methods similar to those of Stephenson et al. and Visser (summarized briefly above). Details of the larger set of studies are provided in Saterbak et al. (1999; in press) and in Wong et al. (1999).

Seven field-collected soils contaminated with crude oil and one contaminated with a spilled lubricating oil, were used for toxicity testing before and after a period of 11-13 months of bioremediation, simulated in the laboratory. Toxicity test organisms and endpoints included earthworm (*E. fetida*) avoidance, survival and reproduction, as well as seed germination and root elongation in four plant species. Saterbak (*in press*) clearly demonstrated that the survival, reproduction, or growth of test organisms remained high or was improved following bioremediation.

Saterbak et al (1999) focused their objectives on the evaluation of ecotoxicity test methods applicable to use in Tier II or III evaluations of PHC contaminated sites. This guidance, along with subsequent work by Stephenson et al., is directly applicable to the possible adoption of site-specific toxicity test methods for PHC CWS Tier II evaluations.

The study by Wong et al. (1999) applied multivariate statistical techniques to detailed physical and chemical soil characterization data (e.g. soil particle size, asphaltenes, TPH, aromatics, ring saturates) for the same eight PHC-contaminated soils as predictors of toxicity to earthworms and plants.

Saterbak kindly made the larger ecotoxicity and soil chemistry database available to EcoTAG, in support of PHC CWS derivation efforts. The eight soils studied were analyzed prior to and following a year of laboratory-based remediation for TPH (C6 to C25) by GC-FID, following pentane extraction. Results are provided in Figures G.1 and G.2.

The results of this analysis allowed the re-allocation of TPH results into the PHC CWS fractions F1 and F2, as well as the lighter end of F3 (>nC16 to C25). A more complex speciation of samples prior to bioremediation provided a more complete breakdown from C5 up to C60+, and included the quantification of *n*- and *iso*-alkanes, aromatics, polar compounds, and asphaltenes. This allowed for the further reconstruction of soil (and exposure) concentrations of all four CWS fractions including all of F3 and F4; however, similar data were lacking for the post-remediation soils.

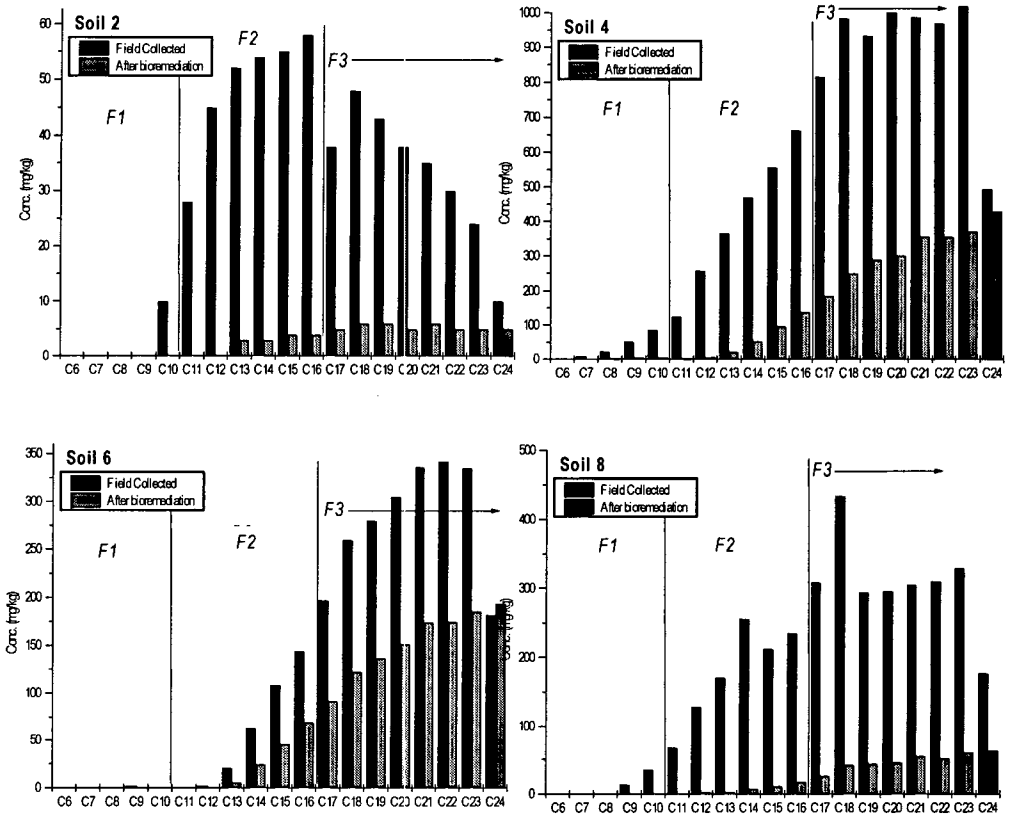


Figure G.1: C6 to C24 PHC carbon profiles for field collected and subsequently bioremediated soils.

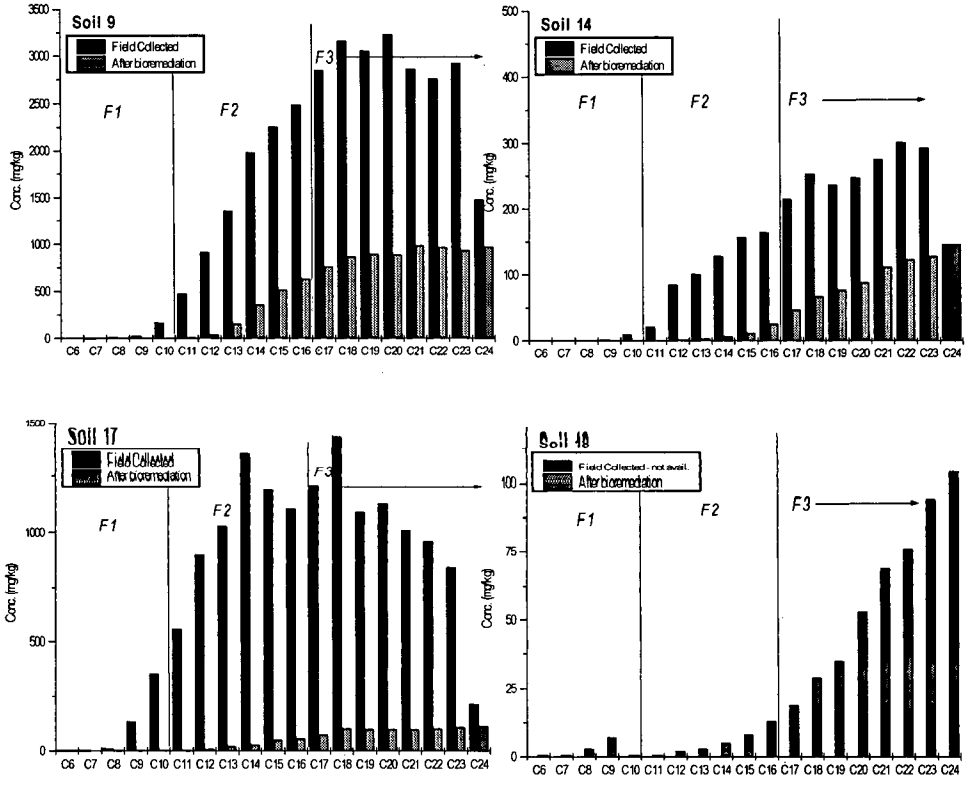


Figure G.2: C6 to C24 PHC carbon profiles for field collected and subsequently bioremediated soils.

Table G.7: Summary of ecotoxicity data from Saterbak et al.

		Soil Conc. (mg/kg)															
		Soil 2		Soil 4		Soil 6		Soil 8		Soil 9		Soil 14		Soil 17		Soil 18	
	Date	Dec-95	Jul-97	Dec-95	Jul-97	Dec-95	Jul-97	Dec-95	Jul-97	Dec-95	Jul-97	Dec-95	Jul-97	Dec-95	Jul-97	Dec-95	Jul-97
Carbon Number																	
c6-nC10		0	0	88	5.3	1.6	0	14	0	54	0	2	0	155	3		12
>nC10-C16		244	10	1864	185	196	77	871	25	7176	1103	505	28	5388	123		20
>C16-C34		1053		25539		9474		4518		38735		4144		14870		10379	
>C16-C21	TPH	224	26	4402	1172	1187	575	1568	178	14784	4076	1117	311	5998	437	0	150
>C16-C21	BDC data	392		7633		2238		1336		10511		975		5704		735	
>C21-C34	BDC data	662		17906		7236		3181.6		28224		3168		9166		9644.1	
>C34	BDC data	1415		21596		16935		2799.2		28827		6103		4484		8928	
TPH by GC		567	56	9830	2880	2580	1380	3580	433	32000	9050	2640	851	14600	992	1490	523
Soil - percent of original, mixed with clean site ref.																	
Earthworm - E. fetida - Average																	
7-Day Acute	LC25		>100		>100		>100		>100		15.2		>100		>100		>100
14-Day Acute	LC25	>100	>100	7.8	>100	78	>100	>100	>100		15.0	>100	>100	10	>100	>100	>100
Chronic	LC25		>100		>100		>100		>100	-	15.0		>100		>100		>100
Juveniles/Adult/Week	EC25	28	no data	10	6.3	23	0.91	0.9	8.9	-	0.36	-	17.4	1.2	6.6	4.0	50
Cocoons/Adult/Week	EC25	no data	no data	7.9	12.1	24	32	4.3	7.8	-	0.39	-	16.5	2.8	22	1.7	>100
Plant germination - Average																	
Corn	EC25	100	100	100	100	90	100	100	100	50	23	100	100	100	100	100	100
Lettuce	EC25			4.9	14	26	94	7.5	99	1.4	0.26	2.0	94	31	21	77	79
Mustard	EC25	8.0	55	8.7	15	18	88	23	98	0.70	0.17	1.3	41	18.8	100	87	88
Wheat	EC25	100	100	87	90	64	88	100	100	32	25	100	100	100	100	100	100
Plant root elongation - Average																	
Corn	EC25	100	100	25	45	35	100	14	19	20	18	100	100	28.75	100	100	46
Lettuce	EC25			7.8	1.8	14	70	14	65	0.90	0.14	1.5	32	20	7.3	100	74
Mustard	EC25	24		14	38	7.4	53	81	100	0.55	0.23	18	70	14	100	100	100
Wheat	EC25	100	100	55	41	30	72	100	89	17	3.8	50	88	50	100	100	100

Table G.8: Estimation of F2 and F3 EC25-equivalent concentrations for eight field-collected and subsequently bioremediated PHC contaminated soils (after Saterbak et al).

	Soil 2		Soil 4		Soil 6		Soil 8		Soil 9		Soil 14		Soil 17		Soil 18	
Date	**Dec-95**	**Jul-97**	**Dec-95**	**Jul-97**	**Dec-95**	**Jul-97**	**Dec-95**	**Jul-97**	**Dec-95**	**Jul-97**	**Dec-95**	**Jul-97**	**Dec-95**	**Jul-97**	**Dec-95**	**Jul-97**
Lowest observed EC25 (% of PHC contaminated soil)																
min (%)	**8.0**	**55**	**4.9**	**1.8**	**7.4**	**0.91**	**0.90**	**7.8**	**0.55**	**0.14**	**1.3**	**17**	**1.2**	**6.6**	**1.7**	**46**
Estimated concentration of PHCs in test unit, expressed as PHC CWS F2 and F3 (in mg.kg soil)																
F2	*20*	*5.4*	*91*	*3.3*	*15*	*0.7*	*7.8*	*2.0*	*39*	*1.5*	*6.6*	*4.7*	*65*	*8.1*		*8.9*
F3a	*18*	*14*	*214*	*21*	*88*	*5.2*	*14*	*14*	*81*	*5.7*	*15*	*51*	*72*	*29*		*68*
F3	*85*		*1243*		*701*		*41*		*213*		*54*		*178*		*176*	
Lowest observed EC25, excluding worm reproductive endpoints (% of PHC contaminated soil)																
min(2)(%)	**8.0**	**55**	**4.9**	**1.8**	**7.4**	**53**	**7.5**	**19**	**0.55**	**0.14**	**1.3**	**32**	**10**	**7.3**	**77**	**46**
Estimated concentration of PHCs in test unit, expressed as PHC CWS F2 and F3 (in mg.kg soil)																
F2	*20*	*5.4*	*91*	*3.3*	*15*	*41*	*65*	*4.8*	*39*	*1.5*	*6.6*	*9.1*	*539*	*8.9*		*8.9*
F3a	*18*	*14*	*214*	*21*	*88*	*306*	*117*	*34*	*81*	*5.7*	*15*	*101*	*600*	*32*		*68*
F3	*85*		*1243*		*701*		*337*		*213*		*54*		*1487*		*7940*	

Notes: 1) F3a comprises all PHCs in the boiling point range spanned by >nC16 to nC21.

The re-interpreted results shown in Table G.7 and G.8 show that both field collected and bioremediated soils can result in inhibition of growth and plant germination, as well as mortality in earthworms, when they contain concentrations between 2 and 540 mg/kg when expressed as CWS F2, or between 54 and 8000 mg/kg when expressed as CWS F3.

Because the soils used in these series of experiments were field-collected soils, there is a possibility that an appreciable portion of the observed toxicity was due to the presence of co-contaminants such as metals, as opposed to the PHCs present.

The lack of detailed chemical characterization of the soils following bioremediation for the >C24 range limits the conclusions that can be drawn regarding environmentally protective thresholds for this PHC fraction. It also limits any examination of the relative compositional change within the F3 fraction as a result of bioremediation; e.g., the relative composition of F3 as >nC16 to C21 versus >C21 to C34.

PERF (1999) concluded–

> "...that acute toxicity to earthworms was unlikely to occur at concentrations less than 4,000 mg/kg TPH (by GC) and should be expected to occur at TPH concentrations in excess of 10,000 mg/kg. Within the range of 4,000 mg/kg to 10,000 mg/kg, it is uncertain whether acute effects on individual earthworms will occur."

It is difficult to understand the basis for this conclusion based on the underlying studies. In addition, PERF (1999) ignored the data on worm reproduction and plant responses in their conclusions regarding "Hydrocarbon Uptake by Ecological Receptors".

Of the original eight soils, all induced detrimental effects in at least one test organism and endpoint prior to remediation. In most cases, bioremediation reduced the presence or severity of adverse effects, as indicated by an improvement in the EC_{25} (as % of soil used in test unit). It is interesting to note, from Table G.8, however, that there was evidence for an increase in the toxicity of some bioremediated soils relative to pre-remediation soils (e.g.: Soil 18: corn and lettuce root elongation; Soil 9: virtually all plant growth and germination endpoints). The studies suggest that earthworm mortality endpoints are relatively insensitive to PHCs relative to other measures. In addition, the studies highlight very large variability in ecotoxicological concentration-response curves across different soil types. Finally, this study highlights the large variations in toxicity associated with soil type.

G.3.0 Alberta Research Council, 1999 Studies

Slaski et al (1999) and Sawatski and Li (1999) summarized studies on the bioremediation of three different land-treated soils (crude oil and brine contaminated top soil; diesel invert mud residue; flare pit sludge). All three wastes were bioremediated using a bioreactor system for 1, 2 or 3 years, and subsequently land-farmed in 1996. Subsequent land-based remediation has been followed for three years after the initial

placement. As of 1998, decreased ecotoxicity of the three wastes has been observed; however, all three materials exhibited significantly greater toxicity than controls in 1998.

The results of this study do not lend themselves to an evaluation of toxicological thresholds (a dilution series was not used to estimate a soil dilution with clean soil corresponding to a pre-defined ECx).

Sawatski and Li (1999) documented changes over time in the n-alkane composition. This is shown in Table G.9, based on the relative composition of C15-C20, C20-C30, and >C30.

Table G.9: PHC Compositional change in three bioremediated wastes.

	Time 1	Time 2	Time 3	Time 4
Waste 1				
c10-c15	0	0	15.9	15.3
c15-c20	2690	821	400	138
c20-c25	8740	3000	1065	1300
c25-c30	6160	2200	827	1240
>c30	9860	3890	3260	2650
sum	27450	9911	5567.9	5343.3
c15-20 (% of ~F3)	**15.3%**	**13.6%**	**17.5%**	**5.2%**
Waste 2				
c10-c15	50700	84	56	0
c15-c20	41000	2410	1550	745
c20-c25	3900	1340	792	1600
c25-c30	0	54	140	494
>c30	0	0	13	0
sum	95600	3888	2551	2839
c15-20 (% of ~F3)	**91.3%**	**63.4%**	**62.4%**	**26.2%**
Waste 3				
c10-c15	675	270	0	0
c15-c20	12730	3700	1995	1630
c20-c25	16100	6960	1570	4230
c25-c30	15800	9460	1425	1530
>c30	19900	14900	9785	4740
sum	65205	35290	14775	12130
c15-20 (% of ~F3)	**28.5%**	**18.4%**	**40.0%**	**22.1%**

(Adapted from Sawatski and Li, 1999)

G.4.0 Study of Soils from a Former Refinery Site in Montreal

Miasek (pers. com.) provided a summary of a study commenced in 1996 and undertaken jointly by Imperial Oil, Exxon Biornedical Sciences Inc., Environment Canada, and Quebec MEF on the remediation and ecotoxicity of PHC-contaminated soils found at a former refinery site in Montreal, Quebec. Five soils were tested, as follows:

Table G.10: Summary of Montreal former refinery test soils.

Soil	Mineral Oil and Grease Conc. (mg/kg)	GC Boiling Pt. Range, C	Weight percent of – saturated/ aromatics/ polars	Weight percent of aromatic carbon	No. of soil toxicity tests (4 different test organisms ea.)
Reference	< 40	n/a	n/a	n/a	0
Thermally treated	< 40	n/a	n/a	n/a	3
Contam.at < criterion	2,000	170/430/640	26/48/26	29	1
Biotreated	3,100	220/460/590	25/46/29	27	0
Contam.at > criterion	6,900	160/410/600	29/42/29	29	3

The PHC-contaminated soil "age" was greater than 10 years. The relative composition, redefined as the PHC CWS fractions is as follows:

Table G.11: Percent composition of tested soils.

EC	Contam. at < criterion	Biotreated	Contam. at > criterion
CWS F1	*nd (0.0%)*	*nd (0.0%)*	*nd (0.0%)*
>C8-C10	nd	nd	nd
CWS F2	*20*	*5*	*18*
>C10-C12	5	nd	3
>C12-C16	15	5	15
CWS F3	*45*	*55*	*50*
>C16-C21	15	15	20
>C21-C35	30	40	30
CWS F4	*35*	*40*	*35*
>C35	35	40	35

The compositional data provides limited evidence of the possibility of a shift in the relative proportion of >C16 to C21 versus >C21 to C35 hydrocarbons with the CWS F3 fraction from the bioremediated versus original aged site soil that had a Mineral Oil and Grease (MOG) concentration in excess of MEF criteria.

For the soil type with an initial soil concentration of 6,900 mg/kg MOG, the toxicity test results were as follows:

Table G.12: Toxicity thresholds for former refinery site soil samples.

Organism	Endpoint	Toxicity Unit[A]	Effects Conc (% soil)	Effective MOG conc. (mg/kg)
Soil contaminated at > criterion (6,900 mg/kg MOG)				
Lettuce germination	5 day EC_{20}	**2.4**	**41%**	**2,800**
Cress germination	5 day EC_{20}	**1.0**	**100%**	**6,900**
Cress plant growth	16 day EC_{20}	<1.0	> 100%	>6,900
Barley germination	5 day EC_{20}	**2.0**	**50%**	**3,400**
Barley plant growth	17 day EC_{20}	<1.0	> 100%	>6,900
Earthworm	14 day LC_{50}	<1.0	>100%	>6,900
Soil contaminated at<> criterion (2,000 mg/kg MOG)				
Lettuce germination	5 day EC_{20}	<1.0	>100%	>2,000
Cress germination	5 day EC_{20}	<1.0	>100%	>2,000
Cress plant growth	16 day EC_{20}	<1.0	>100%	>2,000
Barley germination	5 day EC_{20}	<1.0	>100%	>2,000
Barley plant growth	17 day EC_{20}	<1.0	>100%	>2,000
Earthworm	14 day LC_{50}	<1.0	>100%	>2,000
Biotreated Soil (3,100 mg/kg MOG)				
Lettuce germination	5 day EC_{20}	**1.1**	**91%**	2,800
Cress germination	5 day EC_{20}	<1.0	>100%	> 2,800
Cress plant growth	16 day EC_{20}	<1.0	>100%	> 2,800
Barley germination	5 day EC_{20}	<1.0	>100%	> 2,800
Barley plant growth	17 day EC_{20}	<1.0	>100%	> 2,800
Earthworm	14 day LC_{50}	<1.0	>100%	> 2,800
Thermally treated Soil (<40 mg/kg MOG)				
Lettuce germination	5 day EC_{20}	<1.0	>100%	B
Cress germination	5 day EC_{20}	<1.0	>100%	B
Cress plant growth	16 day EC_{20}	**1.6**	**63%**	B
Barley germination	5 day EC_{20}	**1.4**	**71%**	B
Barley plant growth	17 day EC_{20}	<1.0	>100%	B
Earthworm	14 day LC_{50}	**1.4**	**71%**	B

Notes: A) Toxicity Unit , T.U. is defined as 1/[effects Conc (% soil)]; B) it is unlikely that the growth inhibition was attributable to the MOG content, as opposed to alteration of other soil properties during thermal treatment.

A longer term, follow-up study is presently underway. A more detailed chemical characterization of the soils is available, although the PHC constituents appear to have only been analyzed as MOG as well as individual PAHs. The lowest MOG concentration in toxicity test units associated with an effect was 2,800 mg/kg (Table G.12). It is difficult to convert this into an equivalent concentration for the PHC CWS four fractions, due to the highly disparate nature of the different underlying analytical methodologies. In fact, an assumption that MOG concentrations are directly equivalent to TPH measurements using GC-FID approaches as refined for the PHC CWS would not be justified. With this cautionary note in mind, a MOG concentration of 2,800 mg/kg would be divided among the CWS fractions – assuming a direct equivalence of the analytical techniques – as follows: F1 – nd; F2 - 504 mg/kg; F3 – 1,400 mg/kg; F4 – 980 mg/kg.

This can be compared, with some trepidation in the equivalence of the soil concentration data and toxicity endpoints, with the soil toxicity thresholds for fresh Federated Whole

Crude, as provided by Stephenson et al (1999). As shown in Figures 4.17 and 4.18, the 25th percentile for fresh Federated Whole Crude of the EC_{50} (or LC_{50}) soil concentrations for soil invertebrates or plants was 1,600 mg/kg and 5,500 mg/kg, respectively, when expressed as a nominal concentration. In general, this is within the range of thresholds for the higher concentration aged soil from the Montreal site.

G.5.0 Miscellaneous Studies

Figures G.3 through G.7 illustrate the range of toxicological responses encountered, based primarily on data from the primary peer-reviewed literature, including the previously discussed data from studies by Saterbak *et al.,* but excluding data discussed in Sections 4.2.4 to 4.2.6. The data base, which comprised more than a thousand individual toxicity endpoints, was broken down into the following subgroups for analysis:

- by type of whole product used or originally released;
- divided between soil invertebrates and plants
- further divided between fresh versus weathered product; and
- finally divided into the effects database (comprising all non-redundant LOEC, EC_x and LC_x endpoints) and the no-effects database (NOEC endpoints).

The plots show the challenges associated with the reconstruction of multi-species sensitivity curves from toxicity data that were collected for other purposes. The existing whole products database suggests the following:

> The effects and no-effects concentration distribution for soil invertebrates or plants overlapped substantially, in a way that is contrary to the underlying theoretical model for multi-species sensitivity curves.
> There was no evidence that weathered crude oil was less toxic to either soil invertebrates or plants. If anything, the existing data would suggest that fresh product tends to be less toxic to more sensitive species.
> The 25th percentile concentration for the effects endpoint data, if adjusted to reflect expected exposure concentration as opposed to nominal concentration, varied substantially, but were generally consistent with the equivalent 25th percentile estimates for the F3 and F2 distillates.

Figure G.7 shows the distribution of the available weathered and unweathered effects data for diesel or heating oil. The existing database is very limited. At face value, the data suggest that weathered diesel is substantially less toxic to plants than fresh diesel. It is important to note, however, that the diesel (nominal) exposure concentrations were expressed as TPH, generally encompassing >C9 to some upper boiling point limit depending on analytical conditions.

Fresh diesel would be roughly divisible as 50% F2 and 50% F3, as previously discussed. Weathered diesel, on the other hand, would undoubtedly exhibit a very different composition, possibly with a strong proportion of higher end F3 and lower end F4 constituents. Overall, the data do not allow a discrimination between toxicity changes

associated with compositional changes during weathering and other aspects such as the strength of soil sorption.

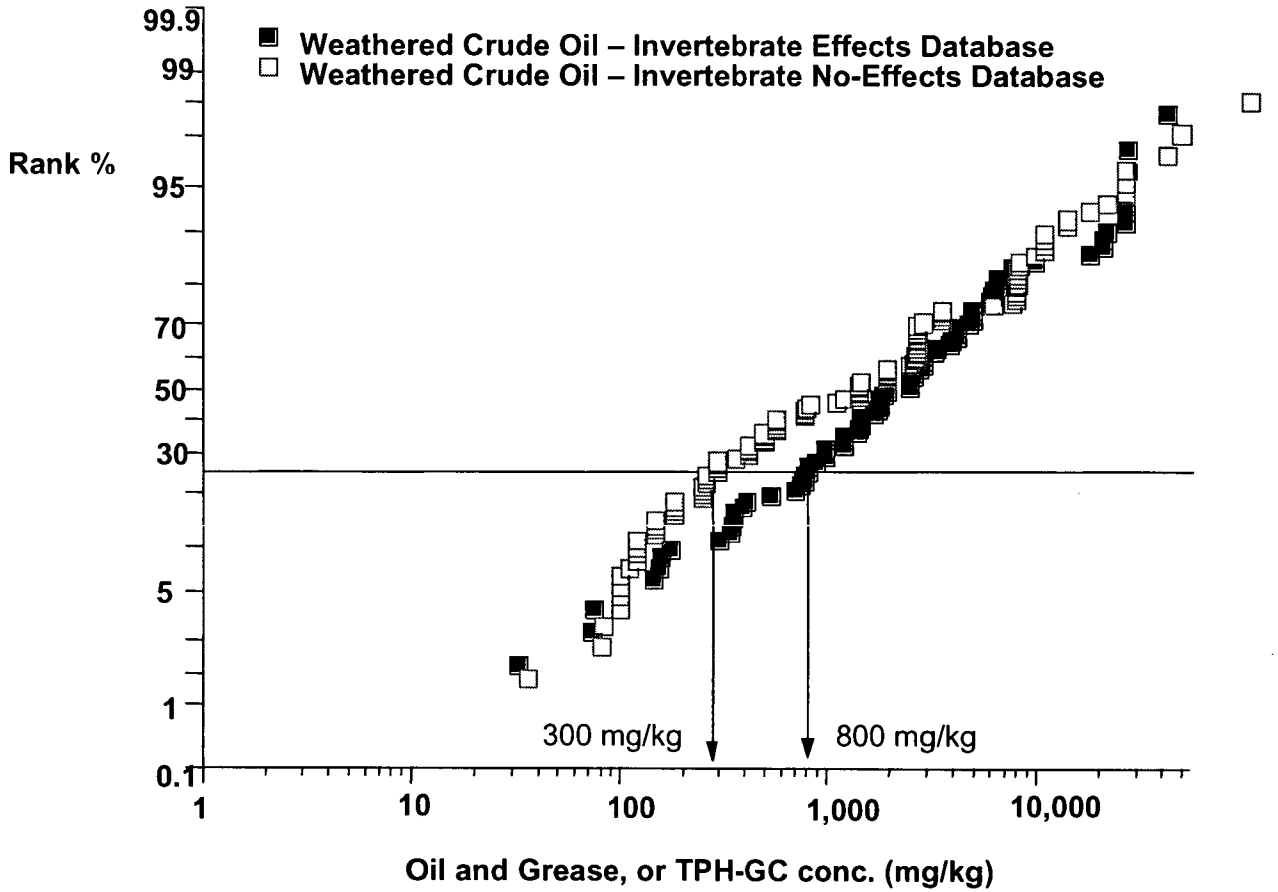


Figure G.3: Ranks data for toxicity of weathered crude oil to soil invertebrates (with comparison of effects and no-effects data distribution).

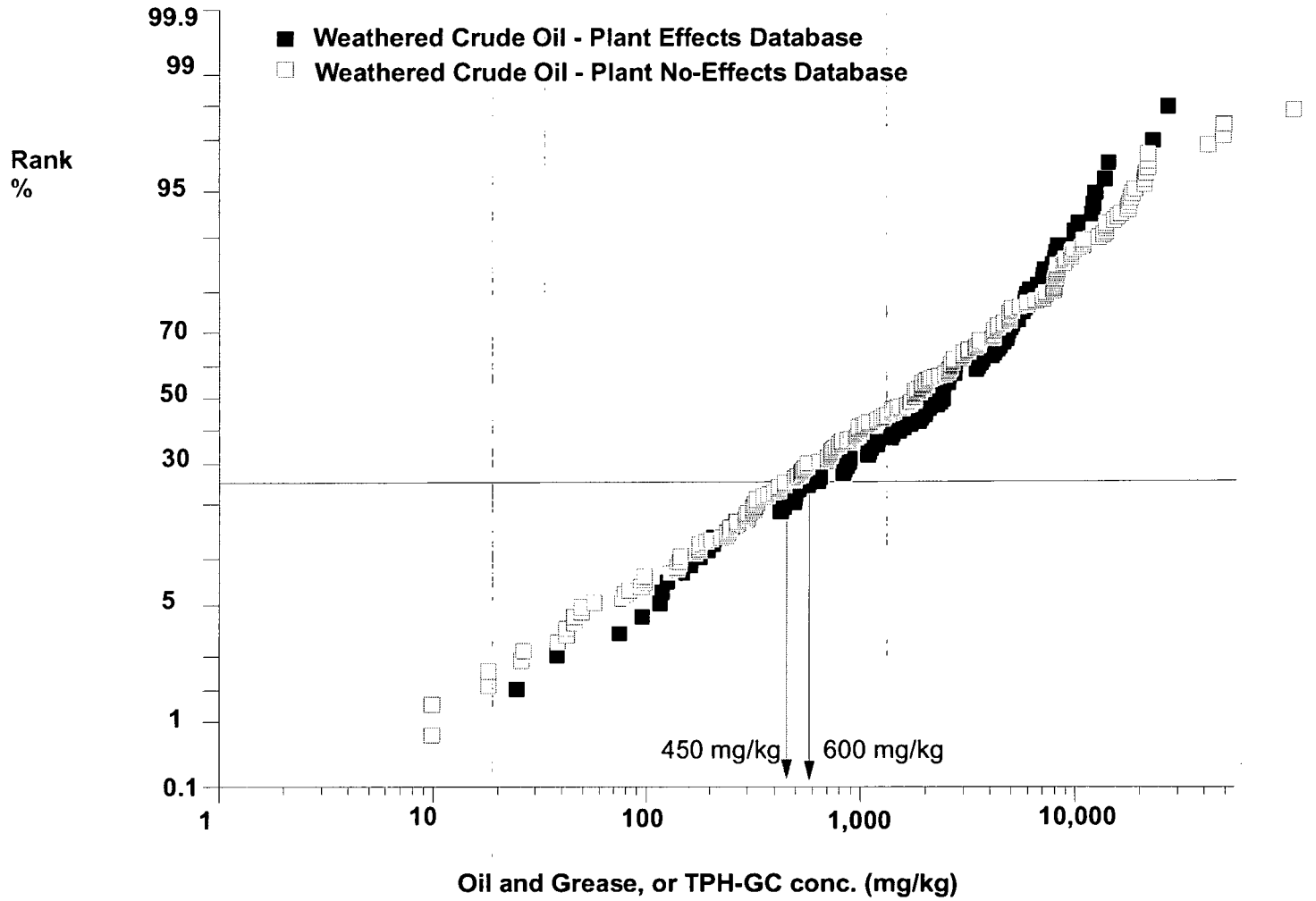


Figure G.4: Ranks data for toxicity of weathered crude oil to plants (with comparison of effects and no-effects data distribution).

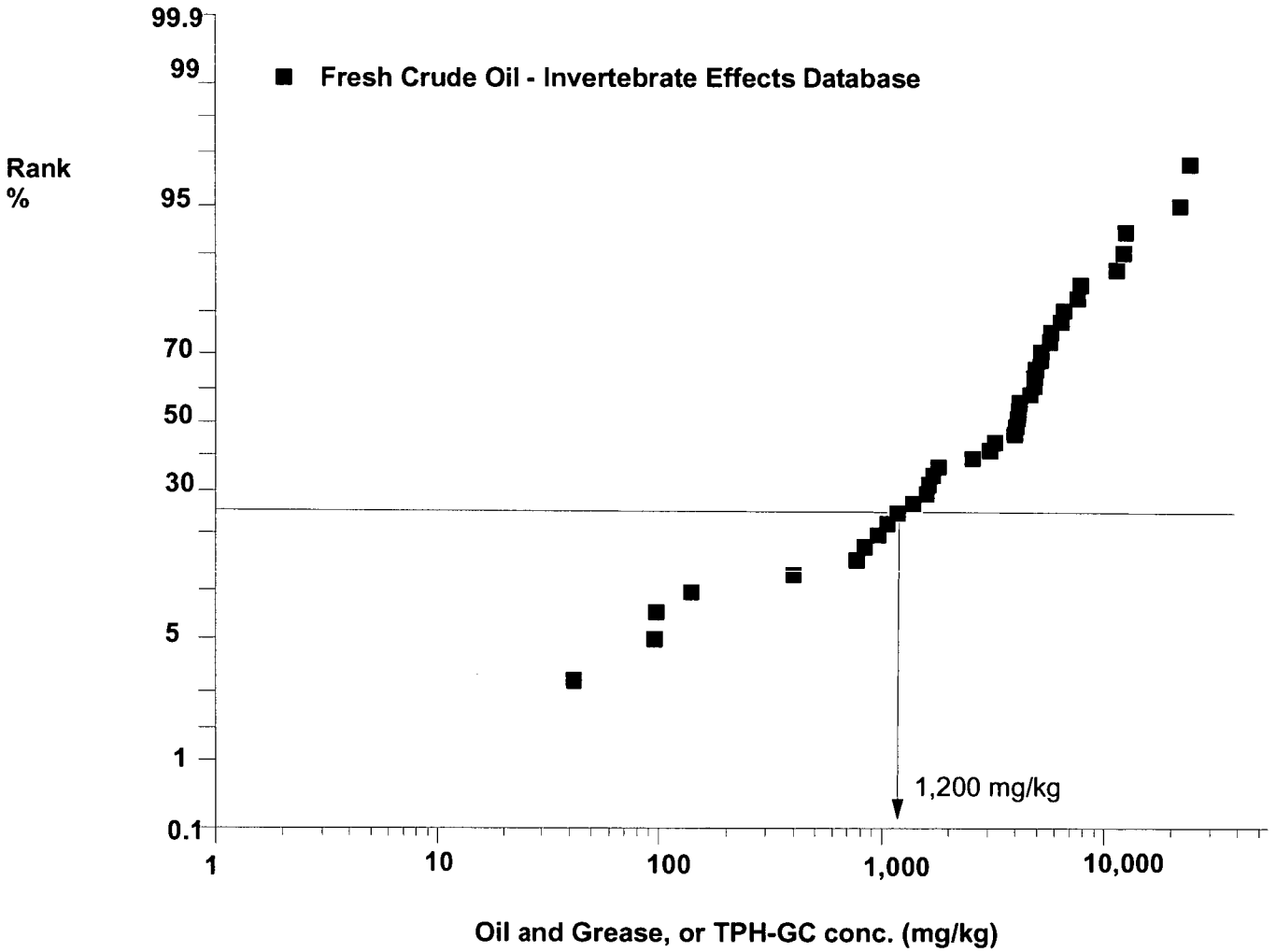


Figure G.5: Ranks data for toxicity of fresh crude oil to soil invertebrates.

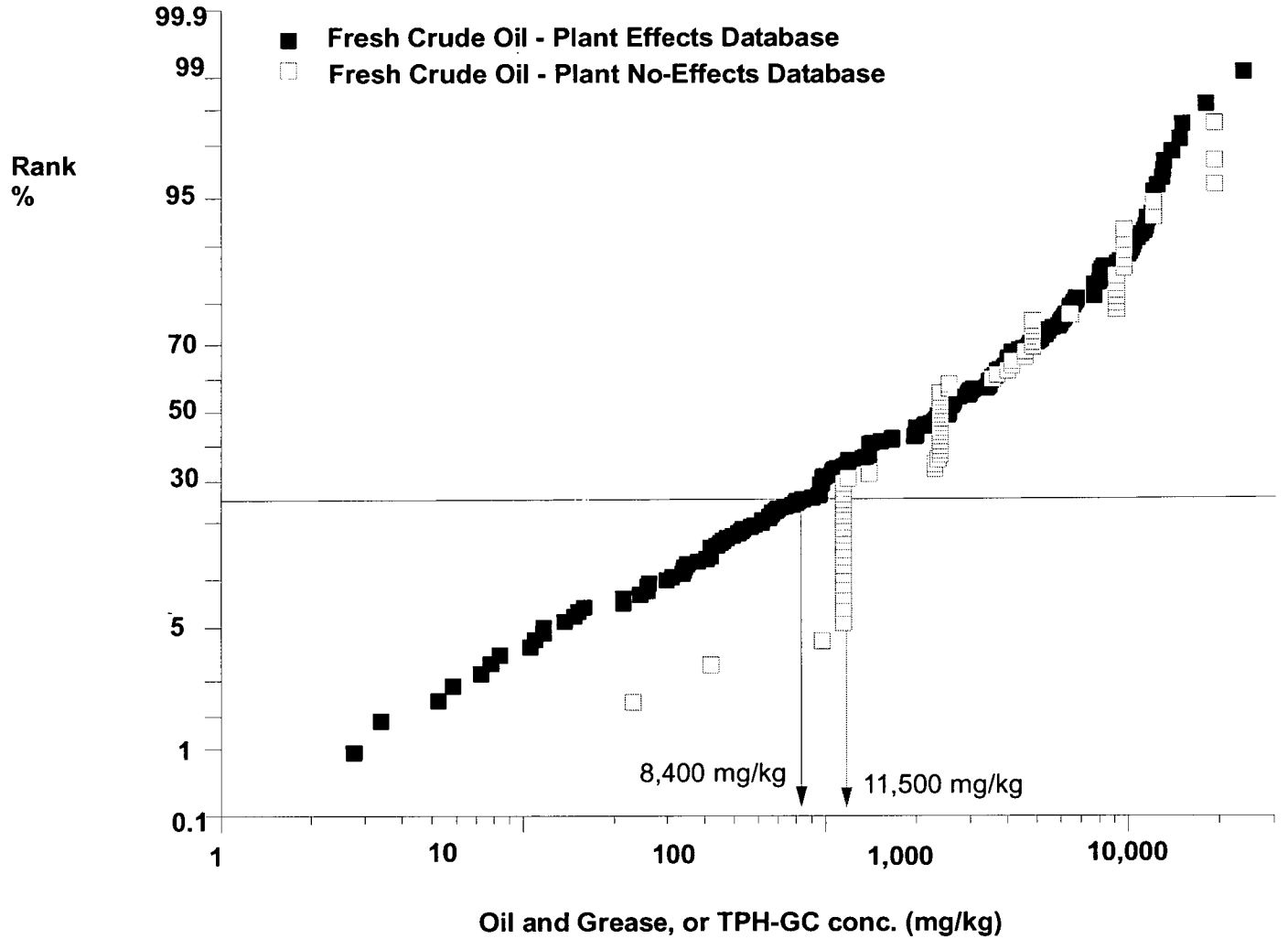


Figure G.6: Ranks data for toxicity of fresh crude oil to plants (with comparison of effects and no-effects data distribution).

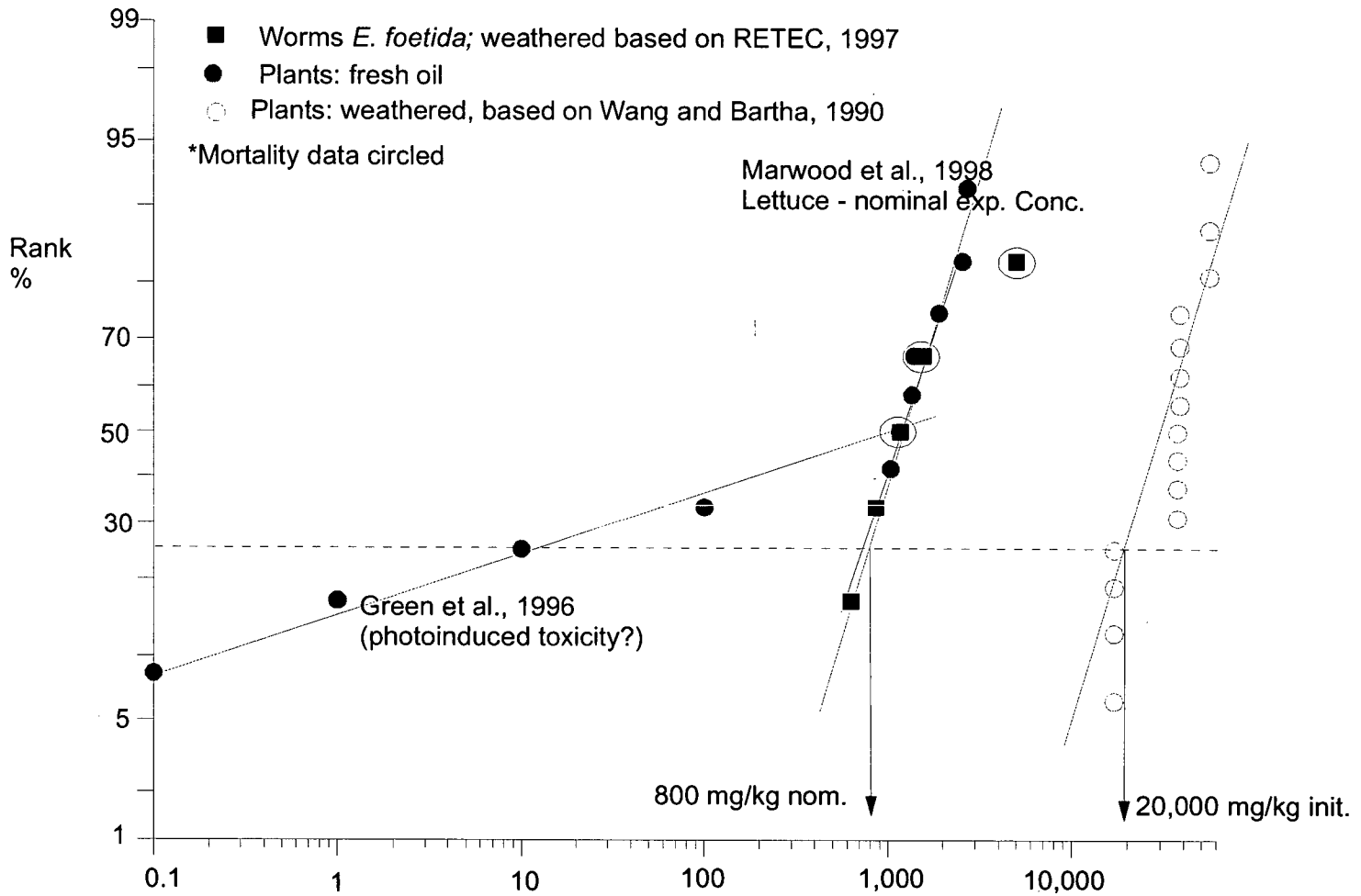


Figure G.7: Toxicity of diesel or heating oil to soil invertebrates and plants.

Appendix H: The B.C. Environment groundwater model.

H.1.0 The B.C. Environment Groundwater Model and Default Assumptions

The model presently used by the Pollution Prevention and Remediation Branch of the British Columbia Ministry of Environment, Lands and Parks (BCE) simulates contaminant partitioning from the soil to groundwater via the unsaturated zone, entry into the water table, and subsequent transport of contaminants in the saturated zone to a surface water body containing aquatic receptors. The model assumes one-dimensional groundwater flow, but may include transport mechanisms such as dispersion, biodegradation, adsorption-desorption, and dilution (between contaminated leachate and groundwater).

The CSST groundwater model includes four main components as follows:

i) Contaminant partitioning between soil particles, soil pore air, and soil pore water;

ii) Groundwater flow and contaminant leachate transport in the unsaturated zone;

iii) Mixing of unsaturated and saturated groundwater at the water table; and

iv) Groundwater flow and contaminant transport in the saturated zone to a receptor.

Numerous assumptions are incorporated into the model. They are as follows:

- the soil is physically and chemically homogeneous;
- the moisture content is uniform throughout the unsaturated zone;
- the infiltration rate is uniform throughout the unsaturated zone;
- decay of the contaminant source is not considered (i.e., infinite source mass);
- flow in the unsaturated zone is assumed to be one dimensional and downward only (vertical recharge) with dispersion, sorption-desorption, and biological degradation;
- the contaminant is not present as a free product phase;
- the maximum concentration in the leachate is equivalent to the solubility limit of the chemical in water under the defined site conditions;
- the groundwater aquifer is unconfined;
- groundwater flow is uniform and steady;

- co-solubility and oxidation/reduction effects are not considered;
- attenuation of the contaminant in the saturated zone is assumed to be one dimensional with respect to sorption-desorption, dispersion, and biological degradation;
- dispersion is assumed to occur in the longitudinal and transverse directions only and diffusion is not considered;
- mixing of the leachate with the groundwater is assumed to occur through mixing of leachate and groundwater mass fluxes; and
- dilution of the plume by groundwater recharge down-gradient of the source is not included.

The model is constructed by specifying the contaminant concentration in groundwater (saturated zone) at the source. The model then back-calculates the soil concentration at the source and forward calculates the groundwater concentration at the receptor. The model derives soil concentration standards to ensure that the contaminant concentrations in the groundwater discharging to the surface aquatic receptor are less than or equal to the Canadian Water Quality Guideline criteria for the receptor or some other suitably protective benchmark of groundwater quality.

H.2.0 Site Assumptions for Tier I Groundwater Fate Modeling

Table H.1 presents the default model input parameters adopted by CSST, based on a 'generic' site. Given the nature of Tier I guidance within Canadian jurisdictions, the default site parameters conservatively assume that conditions are optimal for the exposure of aquatic life from a mass of PHC contaminated soils on site, based on groundwater transport. No attempt was made to calibrate the model for PHCs; however, the model was originally developed for petroleum hydrocarbon spills, and there may be suitable validation studies available. The CSST default values are considered typical of the conditions for the lower Fraser River/Vancouver area of British Columbia.

Table H.1 also contains assumed generic site parameters for Tier I guidance, based on previous deliberations by the Human Health Fate and Transport Technical Advisory Committee (HHFT TAG) and the Protocol Implementation Working Group (PIWG), as well as discussions between Bright and Mah-Paulson, O'Connor Associates. The tabulated site parameter estimates were, to the extent possible, consistent with assumptions made for the derivation of human health protective PHC soil quality guidelines based on groundwater transport to potable water sources. In the case of potable water, however, it was assumed that the point of exposure - the drinking water well - was in the immediate vicinity of the contaminated soil mass.

In deriving modified estimates of site parameters, it is important to note that some of the properties are linked. The modification of one parameter in the suite must be carried out

in careful consideration of the values of the rest of the suite, otherwise the modeling predictions are invalid:

Suite 1 source soil volume			Suite 2 climatic conditions		Suite 3 subsurface environ.	
X	source length	dimension	***P***	precipitation rate	**x**	distance from source to receptor
Y	source width	dimension	**(RO + EV)**	run-off and evaporation	**n**	contaminated soil porosity
Z	source depth	dimension	**D1/2US**	days when ground surface temp is below 0° C.	**nu**	water-filled porosity
					ne	effective porosity
					foc	soil org. C. fraction
					V	Darcy velocity in saturated zone
					d	depth to unconfined aquifer
					da	depth of unconfined aquifer
					ρb	soil dry bulk density
					pH(s)	soil pH
					pH(gw)	groundwater pH

The default assumptions used herein are based on PHC-contaminated soils at a generic site with a biota-containing surface water body, or livestock watering dugout, that is within 10 m in a down-gradient direction. The site is assumed to have a 3 m unsaturated zone, which is contaminated throughout its entire depth at the source. As a worst case, the soil is assumed to have limited organic carbon content (0.5%) and the subsurface environment remains unfrozen throughout the year.

Table H.1: Default model input parameters and site-specific model calibration data.

Parameter	Units	Default CSST Value	PHC CWS Values, as recommended by PIWG and HHFT TAG[A]	
			coarse textured	fine textured
Contaminant Source Width	m	30		
Contaminant Source Depth	m	3	(3) [B]	(3) [B]
Contaminant Source Length	m	5	10 [C]	10 [C]
Distance to Receptor	m	10		
Precipitation	m/yr	1.000		
Runoff & Evaporation	m/yr	0.454	(0.72) [D]	(0.80) [D]
Precip. minus Runoff and Evap.	m/yr		0.28	0.20
Depth to Groundwater (water table)	m	3.0	(3) [E]	(3) [E]
Half-life in unsaturated zone	days	substance specific	infinite (set at 1E+09) [H]	infinite (set at 1E+09) [H]
Partition Coefficient, K_{oc}	mL/g	substance specific		
Weight fraction of organic carbon in soil, f_{oc}	[/]	0.006	0.005	0.005
H_2O-filled porosity (unsaturated)	[/]	0.1	0.119	0.168
Air filled porosity (unsaturated)	[/]	0.2	0.281	0.132
Henry's Constant = H*42.3	[/]	substance specific		
Days with surface temp. < 0 deg. C	days	0		
Darcy velocity in saturated zone	m/yr	12.6	16	1.6
Depth of unconfined aquifer	m	5	(5) [F]	(5) [F]
Total porosity (saturated)	[/]	0.3	0.4	0.3
Effective porosity (saturated)	[/]	0.2	(0.4) [G]	(0.3) [G]
Soil bulk density	g/cm^3	1.74	1.7	1.4
Maximum solubility of contaminant	mg/L	substance specific		
Half-life in saturated zone	days	substance specific	infinite (set at 1E+09) [H]	infinite (set at 1E+09) [H]

Shaded values indicate a chemical specific parameter for which CSST has not supplied default values.

Additional Notes: (A) Where no determination was made by HHFT TAG and/or PIWG, the CSST defaults were applied provided that they were reasonable estimates; (B) Not explicitly defined as part of HHFT modeling calculations; however, the model assumed intimate contact between the top of the groundwater table and the PHC contaminated soil mass. This is also consistent with CSST default assumptions; (C) Not required for HHFT modeling calculations. However, the original publication by Domenico on which the PIRI toolkit model is based makes mention of a 'width' of 10 m in the direction of groundwater flow; (D) Not set as part of human health-based calculations; however, "precip. minus runoff and evaporation" was set at 0.28 m/yr for coarse-grained soils and 0.20 m/yr for fine-grained soils; (E) 3 m based on discussions between Mah-Paulson and Bright, in recognition of the nature of the generic site scenario; (F) not defined by PIWG: Set at 5 m herein, since this was the minimum allowable distance within the BCE model; (G) For purpose of the PHC CWS, it was assumed that the effective porosity is 100% of the total porosity; (H) The issue of biodegradation in the subsurface environment was subsequently revisited. After extensive deliberations, the t1/2 for CWS F1 and F2, respectively was established as 712 d and 1,750 d for both the saturated and unsaturated zones. These were chosen as being highly conservative values.

H.3.0 Model Details

The groundwater model used for the PHC CWS Tier I calculations for ecological receptors is directly adopted from the model established by British Columbia Environment, Lands and Parks, in support of the B.C. Contaminated Sites Regulation.

BC Environment, with the assistance of Golder Associates Ltd., compiled a model in which flow is assumed to be essentially one dimensional, while still incorporating the major transport and attenuation processes affecting contaminant movement. The draft "Soil Screening Guidance, 1994" produced by the US Environment Protection Agency was used as the framework to develop the model (U.S. EPA 1994b). The mathematical code for the saturated groundwater transport is based on work by Domenico and Robbins, (Domenico and Robbins 1984). Model assumptions however, were based on work by BC Environment.

BC Environment recommended its four component model because:

- the major transport processes are represented,
- the major variables affecting each of the transport components are included, can be identified, and can be modified,
- physical and chemical affects are considered,
- model assumptions and criteria derivations are "transparent,"
- the model can be calibrated,
- the model performs with reasonable accuracy using a small set of input parameters,
- the accuracy and reliability of the model increases as site specific information increases,
- the model can be used with assumed site characteristics or use site specific data, and
- the model is scientifically based and defensible.

The BC Environment Transport Model as approved by the Contaminated Sites Soils Taskgroup (CSST) has been used to develop soil matrix standards for the protection of groundwater for both organic and inorganic contaminants. The model best simulates the transport of non-polar organic contaminants, and with modifications the model is used to simulate the transport of weakly ionizing substances. Metal transport modelling must be augmented by using an equilibrium geochemical speciation model, such as MINTEQ2.

In all transport models, the proportionment or partitioning of a chemical between soil, soil pore air, and soil pore water is critical. In the CSST approved model, the partitioning for non-polar organic contaminants is primarily a function of the organic carbon coefficient of the contaminant and the amount of organic carbon in the soil. For weakly ionizing substances, such as pentachlorophenols, partitioning in the model is additionally influenced by the pH of the soil. Partitioning of inorganics is considerably more complex, being additionally dependent on factors such as pH, sorption to clays, organic matter, iron oxides, oxidation/reduction conditions, major ion chemistry and the

chemical form of the metal. This model uses distribution coefficients (Kd) calculated as a function of pH, and as a function of an idealized soil with assigned physical and chemical characteristics. For inorganic contaminants modeling flexibility is limited in that distribution coefficients are only allowed to vary with respect to changes in soil pH. Soil pH, however, is only one of many geochemical parameters that actually can affect and change the distribution coefficient.

Attenuation within the model is essentially confined to adsorption-desorption reactions (partitioning), dilution (mixing between contaminated leachate and groundwater, biological degradation (for organics only) and dispersion.

The transport model derives soil concentration standards to ensure that the contaminant concentrations in the groundwater discharging and in contact with a receptor are less than or equal to established substance specific water quality criteria for the receptor (i.e. aquatic life) or water use (i.e. irrigation watering, livestock watering or drinking water) of concern. Thus, allowable concentrations in the groundwater at the point of contact with a receptor are based on either the aquatic life criteria, or for irrigation and livestock water uses. The respective irrigation or livestock watering criteria, presented in the CCME "Interim Canadian Environmental Quality Criteria for Contaminated Sites" (CCME 1991), or "Canadian Environmental Quality Guidelines" (CCME 1999) and/or BC Environment's "Approved and Working Criteria for Water Quality" (BC Ministry of Environment, Lands and Parks 1995b). Soil standards to protect groundwater for use as drinking water are based on the drinking water criteria presented in "Guidelines for Canadian Drinking Water Quality" (Health Canada 1993) and/or "Approved and Working Criteria for Water Quality" (BC Ministry of Environment, Lands and Parks 1995b) documents.

The Groundwater Protection Transport Model is based on assumptions generally typical of the climatic conditions of the lower Fraser River/ Vancouver area of British Columbia, and assumed groundwater characteristics typical of those found within the Fraser River sands of the Fraser River delta area. Other assumptions include:

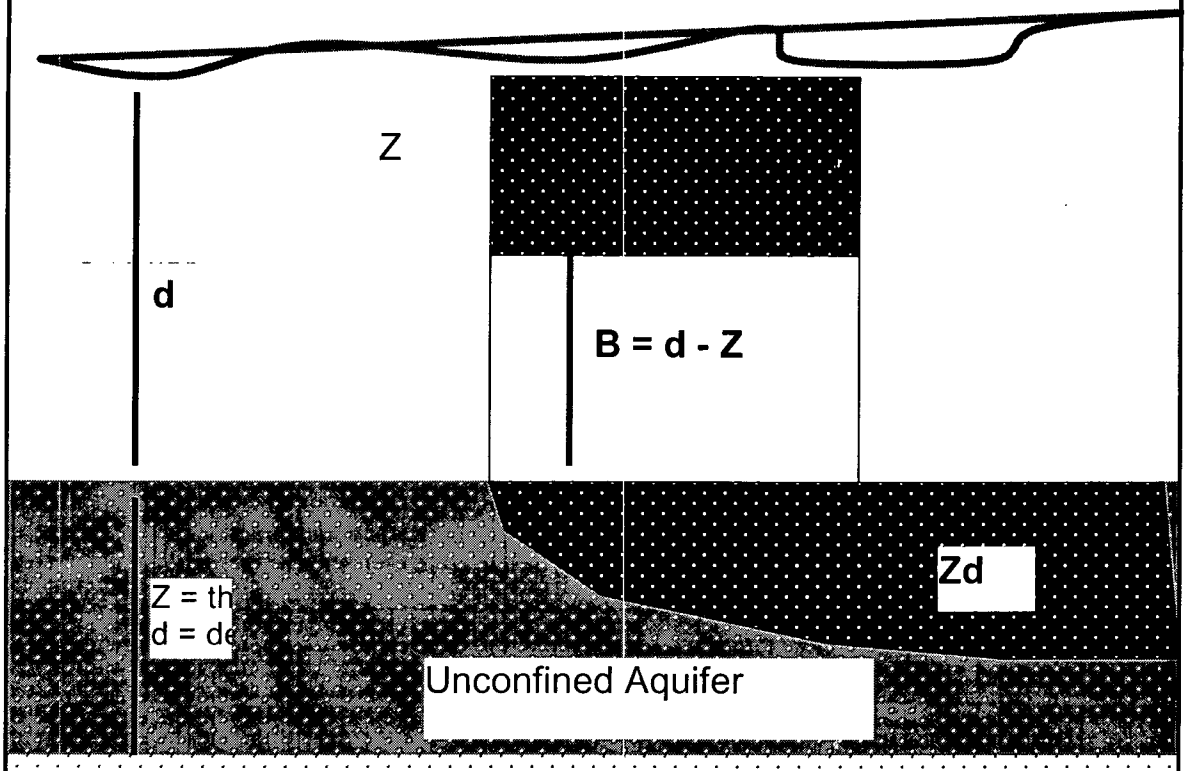
- the site is medium sized (between 1500 m^2 and 12,000 m^2),
- the total volume of contaminated soil is less than 450 cubic metres (5m x 30 m x 3 m),
- the depth to groundwater is not more than three (3) metres,
- the distance to the receptor is at least 10 metres,
- the soil is physically and chemically homogeneous,
- the organic content of the soil is at least 0.6 percent,
- the moisture content is uniform throughout the unsaturated zone,

- the porosity of the soil is 30 percent, and 10 percent of the pore volume is water filled,
- the infiltration rate is uniform throughout the unsaturated zone,
- flow in the unsaturated zone is assumed to be one dimensional and downward only, with dispersion, retardation and biological degradation,
- the contaminant is not present as a free product phase (i.e. a non-aqueous phase liquid),
- the maximum concentration in the leachate is equivalent to the solubility limit of the chemical in water under the defined site conditions,
- the groundwater aquifer is unconfined,
- the groundwater flow is uniform and steady,
- co-solubility and oxidation/reduction effects are not considered,
- attenuation in the saturated zone is assumed to be one dimensional with respect to retardation, dispersion and biodegradation,
- dispersion is assumed to occur in the longitudinal and horizontal transverse directions only, and diffusion is not considered,
- mixing of the leachate with the groundwater is assumed to occur through mixing of leachate and groundwater mass fluxes, and
- dilution by groundwater recharge down gradient of the source is not included.

Refer to Schematic drawing 1 for a typical transverse section through a contaminated source.

The mathematical equations for each of the four model components are presented below in Exhibits 1, 2, 3, 4 and 5. The soil/leachate partitioning component is presented in Exhibit 1. The flow component in the unsaturated soil zone is presented in Exhibit 2. The mixing of unsaturated and saturated zone waters is presented in Exhibit 3. The flow component in the saturated groundwater zone is presented in Exhibit 4. Conditions relating to the contaminant concentration in the saturated groundwater zone are provided in Exhibit 5.

Schematic drawing 1 – Transverse section of contaminated source in various layers of soil



Z = thickness of contaminated source
d = depth from ground surface to uncontaminated groundwater surface
b = thickness of the unsaturated zone
da = thickness of the unconfined groundwater aquifer
Zd = thickness of the mixing zone

Exhibit 6 provides definitions for parameters, and corresponding default values, used in modelling to produce matrix soil groundwater protective standards.

For each of the chemicals for which matrix soil-groundwater protection standards have been derived, the chemical characteristics used in the model are presented in Tables H.2 and H.3. Chemical characteristics provided include solubility, organic:water and other distribution coefficients, biological degradation rates, and Henry's Law constants.

Exhibit 1 - Soil/Leachate Partitioning Model

$$C_S = C_L \{Kd + (n_u + H'n_a)\} / P_b$$

Parameter	Definition (units)	Default
C_S	= soil concentration at source (mg/kg)	
C_L	= leachate concentration at source (mg/L)	calculated value
Kd	= distribution coefficient for a chemical (cm^3/g)	chemical/physical specific[1]
n_u	= water filled porosity (dimensionless)	H x 42.3[2]
H'	= dimensionless Henry's Law constant for the chemical	
H	= Henry's Law constant (atm-m^3/mol)	chemical specific
n_a	= air filled porosity (dimensionless): $n_a = n - n_u$.	0.2
P_b	= dry bulk density of soil (g/cm^3)	
n	= total porosity (dimensionless)	

Notes:
1 = see Annex A
2 = where 42.3 is a units conversion factor for 15°C
3 = based on "Fraser River sand" characteristics

Exhibit 2 - Unsaturated Groundwater Zone

$$C_Z = C_L \, exp\left[\frac{b}{2\partial_u} - \frac{b}{2\partial_u}\left\{1 + \left(\frac{4\partial_u L_{US}}{V_u}\right)\right\}^{1/2}\right]$$

Parameter	Definition (units)	Default
C_Z	= chemical concentration of the leachate at the watertable (mg/L)	
C_L	= leachate concentration at the source (mg/L)	calculated value
b	= thickness of the unsaturated zone (m): b=d-Z	0
d	= depth from surface to uncontaminated groundwater surface (m)	3
Z	= depth of contaminated soil (m)	3
∂_u	= dispersivity in the unsaturated zone (m)	0.1 x b
L_{US}	= decay constant for chemical ($seconds^{-1}$) in unsaturated zone:	calculated value
	$L_{US} = \frac{0.691}{t_{1/2US}} \times (e^{-0.07 \times d}) \times 1 - \left(\frac{D_{1/2US}}{365}\right)$	
$t_{1/2US}$	= chemical half-life in unsaturated zone	chemical specific[1]
$D_{1/2US}$	= frost free days	365
V_u	= average linear leachate velocity (m/s)	calculated value
I	= infiltration rate (m/yr): $I = P - (RO + EV)$	0.55
P	= precipitation rate (m/yr)	1
(RO + EV)	= sum of runoff rate (R0) + surface evapotranspiration rate (EV) (m/yr)	0.45
n_u	= water-filled porosity (dimensionless)	0.1
R_u	= retardation factor in unsaturated zone (dimensionless)	calculated value
P_b	= dry bulk density of soil (kg/L)	1.75 [2]
K_d	= distribution coefficient for a chemical (cm^3/g): for organics - $K_d = K_{oc} \times f_{oc}$ for metals - K_d = function of soil organic carbon, pH, redox conditions, iron oxide content, cation exchange capacity, and major ion chemistry	chemical specific[1]
K_{oc}	= organic carbon partitioning coefficient (cm^3/g)	chemical specific[1]
f_{oc}	= weight fraction of organic carbon in soil (dimensionless)	0.006

Notes:

1 = see Annex A

2 = based on "Fraser River sand" characteristics

Exhibit 3 - Mixing Zone Unsaturated/Saturated

$$C_Z = C_{gw} \{1 + (\frac{Z_d \times V}{I \times X})\}$$

Parameter	Definition (units)	Default
C_Z	= chemical concentration of the leachate at the water table (mg/L)	
C_{gw}	= chemical concentration in the groundwater at source (mg/L)	calculated value
Z_d	= average thickness of mixing zone (m)	0.5[1]
V	= Darcy velocity in groundwater (m/year)	12.6
I	= infiltration rate (m/s)	2×10^{-8}
X	= length of contaminated soils (m) for point source	5

1 = Z_d is a function of mixing zone depths available due to dispersion/diffusion and due to infiltration and underground flow rates. See Exhibit 4.

Exhibit 4 - Calculation of Average Thickness of Mixing Zone, Z_d

$$Z_d = r + s$$

Parameter	Definition (units)	Default
Z_d	= average thickness of mixing zone (m)	
r	= mixing depth available due to dispersion and diffusion (m): $r = 0.01 \times X$	calculated value
X	= length of contaminated soils (m)	5
s	= mixing depth available due to infiltration rate and groundwater flow rate (m): $s = d_a \{1 - e^{-[2.178 \times (X \times 1)/V x d a]}\}$	calculated value
d_a	= unconfined groundwater aquifer (m) (used to calculate Z_d)	5
	= infiltration rate (m/yr): $I = P - (RO + EV)$	0.55
	= precipitation rate (m/yr)	1
(RO + EV)	= sum of runoff rate (R0) + surface evapotranspiration rate (EV) (m/yr)	0.45
V	= Darcy velocity (m/yr)	12.6

Exhibit 5 - Saturated Groundwater Zone

$$C_w(x,y,z,t) = \left(\frac{C_{gw}}{4}\right) \exp\left\{\left(\frac{x}{2\partial_x}\right)\left[1-\left(1+\frac{4L_s\partial_x}{v}\right)^{1/2}\right]\right\} \operatorname{erfc}\left[\frac{x-vt\left(1+4L_s\partial_x/v\right)^{1/2}}{2(\partial_x vt)^{1/2}}\right]$$

$$\left\{\operatorname{erf}\left[\frac{(y+Y/2)}{2(\partial_y x)^{1/2}}\right] - \operatorname{erf}\left[\frac{y-Y/2}{2(\partial_y x)^{1/2}}\right]\right\}$$

$$V = Ki; \quad v = \frac{V}{n_e R_f}; \qquad R_f = 1 + \left(\frac{P_b K_d}{n}\right); \qquad K_d = K_{oc} f_{oc}$$

Parameter	Definition (units)	Default
C_w	= chemical concentration in groundwater flow at receptor (mg/L)	applicable water quality standard
x	= distance to source (m)	10
x,y,z	= Cartesian coordinates that coincide with principle directions of the dispersivity tensor (m)	x is site specific
t	= time since contaminant release (years)	100
C_{gw}	= chemical concentration in the groundwater at source (rng/L)	calculated value
$\partial_{xf}\partial_{yf}\partial_z$	= principle values of the dispersivity tensor (m): $\partial_x = 0.1_X$ $\partial_y = 0.1\partial_x$	calculated values
L_S	= decay constant (seconds^{-1}) in saturated zone: $L_S = \frac{0.691}{t_{1/2S}} \times (e^{-0.07 \times d})$	chemical/depth specific
d	= depth from surface to uncontaminated groundwater surface (m)	3
$t_{1/2s}$	= decay (biodegradation) half-life (yr)	chemical specific[1]
v	= velocity of the contaminant (m/s)	$v = V/n_eR_f$
V	= Darcy velocity or specific discharge (m/yr): $V = Ki$	12.6
K	= hydraulic conductivity (m/yr): $K = V/i$	calculated value
I	= groundwater gradient (dimensionless): $i = V/K$	calculated value
n	= porosity of contaminated soil	0.3
n_e	= effective porosity (dimensiordess)[1]	0.2
Y	= source's width (m), perpendicular to ground-water flow	30
R_f	= Retardation factor (dimensionless)	calculated value
P_b	= bulk density of soil (g/cm^3)	1.75

Exhibit 5 - Saturated Groundwater Zone (Con't.)

K_d	= distribution coefficient for chemical and soil (cm^3/g)	chemical/soil specific[1]

$$K_d = K_{oc} \times f_{oc}$$

K_{oc}	= distribution coefficient for chemicals between organic carbon and water (cm^3/g)	chemical specific[1]
f_{oc}	= weight fraction of organic carbon in soil (dimensionless)	0.006

Note: Above simplified solution based on the assumptions that there is no vertical dispersion, and effective molecular diffusion is relatively negligible,
Therefore –

$D_X = \partial_x v$ and $D_Y = \partial_x v$

D_X	= longitudinal mechanical dispersion coefficient (m^2/s)	$\partial_x v + D^*$
D_Y	= lateral mechanical dispersion coefficient (m^2/s)	$\partial_Y v + D^*$

Notes
1 = see Annex A

Exhibit 6 - Default Groundwater Model Parameters

Parameter	Definition (units)	Default
S	= maximum solubility	chemical specific[1]
n	= total porosity (dimensionless)	0.3
n_u	= water filled porosity	0.1
n_a	= air filled porosity (dimensionless):	calculated value
	$n_a = n - n_u$	0.2
P_b	= dry bulk density of soil (g/cm,)	1.75
H	= Henry's Law constant	chemical specific[1]
H'	= dimensionless Henry's Law constant	chemical specific[1]
∂_u	= dispersivity in unsaturated zone	0.1 x b
f_{oc}	= fraction of organic carbon in soil	0.006
V	= Darcy velocity in saturated zone (m/yr)	12.6
Z_d	= thickness of mixing zone (m)	0.5
K_d	= distribution coefficient for a chemical (cm^3 /g)	chemical specific[1]
Koc	= organic carbon partitioning coefficient (cm^3/g)	chemical specific[1]
∂_x	= dispersivity in x-direction	∂_x = 0.lx
∂_y	= dispersivity in y-direction	$\partial_Y = 0.1\partial_x$
d	= unconfined groundwater aquifer (m)	5
b	= thickness of the unsaturated zone	0
	note: b = d-Z	
d	= depth from surface to uncontaminated groundwater surface (m)	3
x	= distance from source to receptor (m)	10
n_e	= effective porosity (dimensionless)	0.2
$t_{1/2US}$	= decay (biodegradation) half-life at unsaturated sites	chemical specific[1]
$t_{1/2S}$	= decay (biodegradation) half-life at saturated sites	chemical specific[1]
I	= infiltration rate (m/yr)	0.55
	Note: 1 = P - (RO + EV)	(1 - 0.45)
P	= precipitation rate (m/yr) 1	
(RO-EV)	= runoff rate plus surface evapotranspiration rate (m/yr)	0.45
X	= source dimension length (m)	5
Y	= source dimension width (m)	30
Z	= source dimension thickness (rn)	3
$D_{1/2US}$	= frost free days	365

Notes
1 =reference values provided in Annex A

Table H.2: Values for BCE Groundwater Model.

Substance	pH Range	RECEPTOR CRITERIA				Solubility (mg/L)	Koc	t ½ unsat (days)	t ½ sat (days)	H' [/] =H*42.3
		AW (mg/L)	Irr (mg/L)	Lstk (mg/L)	DW (mg/L)					
Benzene		0.3	-	-	0.005	1745	83.2	183	365	2.32E-01
Ethylbenzene		0.7	-	-	0.0024	152	1,096.5	114	114	3.67E-01
Toluene		0.3	-	-	0.024	515	302.0	56	105	2.85E-01
Xylenes		-	-	-	0.3	170	389.0	183	183	2.26E-01
Benzo(a)pyrene		0.00001	-	-	0.00001	0.004	891,250	529	1059	1.02E-04
Naphthalene		0.001	-	-	-	32	1,288.2	65	129	2.60E-02
Pyrene		0.00002	-	-	-	0.17	72,443.6	1898	3796	1.04E-03
Pentachlorophenol	<6.9	0.00002	-	0.03	0.03	5000	pH*	383	767	6.01E-04
	6.9 – 7.9	0.0001	-	0.03	0.03	5000	pH*	383	767	6.01E-04
	>7.9	0.0003	-	0.03	0.03	5000	pH*	383	767	6.01E-04
Tetrachloroethylene		0.11	-	-	-	150	158.5	411	821	7.61E-01
Trichloroethylene		0.02	-	0.05	0.05	1070	1,070	411	821	8.46E-01
PCBs		0.0000001	0.0005	-	-	-	-	-	-	-
Dioxins/Furans		-	-	-	-	-	-	-	-	-
Arsenic (As+3)		0.05	0.1	0.5	0.025	pH*	Kd**	-	-	-
Cadmium (Cd+2)		0.0018	0.01	0.02	0.005	pH*	Kd**	-	-	-
Chromium (Cr+3)		-	-	-	-	pH*		-	-	-
Chromium (Cr+6)		-	-	-	-	pH*	Kd**	-	-	-
Chromium (total)		0.002	0.1	1	0.05	pH*		-	-	-
Copper (Cu+2)		0.008	0.2	0.3	1	pH*	Kd**	-	-	-
Lead (Pb+2)		0.011	0.2	0.1	0.01	pH*		-	-	-
Zinc (Zn+2)		0.03	1.0-5.0	50	5	pH*	Kd**	-	-	-

Rule: t1/2 unsaturated (organics) - Greater of the anaerobic rate high (lowest number of days) and 25% of the anaerobic rate low (highest number of days). Unless t1/2 unsaturated > t1/2 saturated, then t1/2 unsaturated equals t1/2 saturated.
Rule: t1/2 saturated (organics) – Equals to 50 percent of anaerobic rate low (highest number of days).
*pH dependent
** Kd calculated

Table H.3: Koc and Kd values for BCE Groundwater Model.

pH	Koc PCP	Kd PCP foc = 0.006	Kd As(+3)	Kd Cd	Kd Cr(+6)	Kd Cu(2+)	Kd* Pb	Kd Zn(2+)
4.5	20,303	121.82	24.3		35.0			
4.6	18,454	110.73	24.4		34.0			
4.7	16,557	99.34	24.6		33.1			
4.8	14,659	87.95	24.8		32.2			
4.9	12,810	76.86	25.0	0.8	31.4	39.8	*	1.6
5.0	11,055	66.33	25.2	0.9	30	50.1	*	1.8
5.1	9,429	56.57	25.4	1.0	29.7	63.1	*	2.0
5.2	7,956	47.73	25.6	1.1	28.9	79.4	*	2.2
5.3	6,648	39.89	25.7	1.3	28.2	100	*	2.5
5.4	5,508	33.05	25.9	1.5	27.4	126	*	3.2
5.5	4,530	27.18	26.1	1.7	26.7	158	*	4.0
5.6	3,703	22.22	26.3	2.0	26.0	219	*	5.0
5.7	3,010	18.06	26.5	2.5	25.3	302	*	6.3
5.8	2,437	14.62	26.7	3.2	24.6	417	*	8.6
5.9	1,965	11.79	26.9	4.0	24.0	575	*	11.7
6.0	1,580	9.482	27.1	5.0	23.3	794	*	15.8
6.1	1,268	7.607	27.3	7.5	22.7	1,148	*	24.0
6.2	1,015	6.090	27.5	11.2	22.1	1,660	*	36.3
6.3	811	4.868	27.7	16.8	21.5	2,399	*	55.0
6.4	648	3.887	27.9	25.1	21.0	3,467	*	83.2
6.5	517	3.100	28.1	36.9	20.4	5,012	*	126
6.6	412	2.470	28.3	54.1	1@91.91	6,310	*	191
6.7	328	1.967	28.6	79.4	19.3	7,943	*	288
6.8	261	1.566	28.8	117	18.8	10,000	*	437
6.9	208	1.246	29.0	171	18.3	12,589	*	661
7.0	165	0.991	29.2	251	17.8	15,849	*	1,000
7.1	131	0.788	29.4	355	17.4	17,783	*	1,380
7.2	104	0.626	29.6	501	16.9	19,953	*	1,905
7.3	83.0	0.498	29.9	708	16.4	22,387	*	2,630
7.4	65.9	0.396	30.1	972	16.0	25,119	*	3,631
7.5	52.4	0.314	30.3	1,334	15.6	25,119	*	5,012
7.6	41.6	0.250	30.5	1,830	15.2	25,119	*	6,310
7.7	33.1	0.198	30.8	2,512	14.8	25,119	*	7,943
7.8	26.3	0.158	31.0	3,073	14.4	25,119	*	10,000
7.9	20.9	0.125	31.2	3,758	14.0	25,119	*	12,589
8.0	16.6	0.100	31.4	4,597	13.6	25,119	*	15,849
8.1	13.2	0.079	31.7	56,234	13.3			19,953
8.2	10.5	0.063	31.9		12.9			
8.3	8.3	0.050	32.2		12.6			
8.4	6.6	0.040	32.4		12.2			
8.5	5.2	0.031	32.6		11.9			

* Copper Kd values used as surrogates for lead Kd values.

Appendix I: PHC biodegradation in the subsurface environment.

I.1.0 Literature Review of PHC Biodegradation in the Subsurface Environment

In light of the sensitivity of the groundwater modeling predictions to estimated degradation half-life, especially in the often anaerobic saturated zone, a brief literature review was carried out on PHC persistence in the subsurface environment. Table I.1 provides a summary.

It should be noted that the major portion of studies cited have very limited applicability to the generic site scenario established for the PHC CWS. Several of the cited studies are based on bench-top or other studies that are of limited relevance to the prediction of PHC fate in *in situ* subsurface soils and groundwater.

Table I.1: Brief overview of literature values for the environmental persistence of various petroleum hydrocarbon constituents.

Substance	Estimated Environ-mental Half-Life	Medium/ Conditions	Reference	Notes
MONOAROMATICS				
Benzene	10 day – 2 year	groundwater	Piet and Smeenk, 1985	
	8.6 day	soil incubations study	Tabak *et al.*, 1981	
	120 day	soil slurry	Zoetman *et al.*, 1981	Static-culture flask biodegradation test
	68 day	field soils	Baker and Mayfield, 1980	
	24-248 day	soil incubation study	Baker and Mayfield, 1980	
	7 day	surface water	Heath *et al.*, 1993	
***eip*-isopropylbenzene**	2 day	surface water	Heath *et al.*, 1993	
1,2,4-trimethyl-benzene	7 day	surface water	Heath *et al.*, 1993	
Ethylbenzene	3 day	surface water	Heath *et al.*, 1993	
	37 day	groundwater		natural soil groundwater system
Toluene	4 day	surface water	Heath *et al.*, 1993	
	37 day		Swindoll *et al.*, 1987	
	1 day	groundwater	Zoeteman *et al.*, 1981	Field observation
	37 day	groundwater	Baker and Patrick, 1985	Field observation
	8 day	groundwater	Baker *et al.*, 1987	Field observation
	126 day	groundwater, anaerobic/ methanogenic env.	Wilson *et al.*, 1986	Microcosm study

Substance	Estimated Environ-mental Half-Life	Medium/ Conditions	Reference	Notes
	9.9 day	plowed plot with sewage-sludge amended soils	Wilson *et al.*, 1997.	Field plots
	0.4 day	pasture plot with sewage sludge amended soils		
Xylenes	7 day	surface water	Heath *et al.*, 1993	
	5.8 to 7.6 day	plowed plot with sewage-sludge amended soils	Wilson *et al.*, 1997.	Field plots
	0.3 to 0.7 day	pasture plot with sewage sludge amended soils		
(*o*-xylene)	11 day	groundwater	Zoeteman *et al.*, 1981	Field observation
	126 day	Soil incubation study	Wilson *et al.*, 1982	
	32 day	shallow subsurface soils and water	Baker and Patrick, 1985	
Phenol	2.7 h to 23 day	various soil types based on biodegradation	CEPA, 1999, and references therein	
	7 day	soil; volatilization/ partitioning only	Mackay *et al.*, 1995	

Substance	Estimated Environ-mental Half-Life	Medium/ Conditions	Reference	Notes
	total biol. dissim-ilation (1-7 day)	soil at 20° C; aerobic	Prager, 1995.	Degradation slower under anaerobic conditions
	(5-19 day)	soil at 4° C; aerobic		
	3.7 day	water soluble fraction of soils	Loehr and Webster, 1997 (adapted from Dassapa and Loehr, 1991)	phenolics contaminated soils in a slurry bioreactor from a PCP treatment facility
	0.56 day	subsurface soiis	Federle, 1988	
	23 day	acidic soil (pH 4.8)	**Loehr and Matthews, 1992**	In batch microcosms at 20° C.
	4.1 day	basic soils (pH 7.8)		
***p*-Cresol**	7 day	soils	ASTDR, 1992.	
	0.5 day	acidic soils (pH 4.8)	Loehr and Matthews, 1992	In batch microcosms at 20° C.
	< 1 day	basic soils (pH 7.8)		
POLYAROMATIC HYDROCARBONS				
Acenaphthene	25-204 day	groundwater (estimated)	Howard *et al.*, 1991	
Acenaphthylene	85-120 day	groundwater (estimated)	Howard *et al.*, 1991	
Anthracene	100 day – 2.5 year	groundwater (estimated)	Howard *et al.*, 1991	
Benzo(a)anthracene	204 day – 3.73 year	groundwater (estimated)	Howard *et al.*, 1991	

Substance	Estimated Environ-mental Half-Life	Medium/ Conditions	Reference	Notes
Benzo(b)fluoranthene	1.97-3.34 year	groundwater (estimated)	Howard *et al.*, 1991	
Benzo(k)fluoranthene	5 – 11.7 year	groundwater (estimated)	Howard *et al.*, 1991	
Benzo(a)pyrene	114 day – 2.9 year	groundwater (estimated)	Howard *et al.*, 1991	
Chrysene	2.04 – 5.48 year	groundwater (estimated)	Howard *et al.*, 1991	
Fluoranthene	0.8 – 2.4 year	groundwater (estimated)	Howard *et al.*, 1991	
Fluorene	64-120 day	groundwater (estimated)	Howard *et al.*, 1991	
Naphthalene	7-14 day	soils in slurry reactor	Loehr and Webster, 1997	soils from slurry reactor treatment of PAH contaminated wood-treatment site
	1-258 day	slurry	Tabak *et al.*, 1981	Static-culture flask biodegradation test
	0.9 day	Natural soil groundwater system	Zoeteman *et al.*, 1981	
	33 day	sludge-amended soils	Wild and Jones, 1993	
	15 day	spiked soils		
	1.1 day	soil - top 1 cm	Environment Canada, 1996b	soil with 1.25% org. C
	14 day	soil - top 10 cm (based on loss through volatilization)		
	2.1- 2.2 day	soil -microbial biodegradation	Park *et al.*, 1990, as cited in Environment Canada, 1996b	0.5% org. C, pH 7.9; sandy loams

Substance	Estimated Environmental Half-Life	Medium/ Conditions	Reference	Notes
Phenanthrene	28-46 day	soils in slurry reactor	Loehr and Webster, 1997	soils from slurry reactor treatment of PAH contaminated wood-treatment site
	108 day	sludge-amended soils	Wild and Jones, 1993	
	14 day	spiked soils		
	2.5 day to 5.7 year	soils	CEPA, 1993	
	32 day – 1.1 year	groundwater (estimated)	Howard *et al.*, 1991	
Pyrene	7-14 day	soils in slurry reactor	Loehr and Webster, 1997	soils from slurry reactor treatment of PAH contaminated wood-treatment site
	43 day	soils -batch study	Symon and Sims, 1988; as cited in	In "Kidman Sandy Loam"
	30 day	soils - soil column	Loehr and Webster, 1997	
	32 day	soils -batch study	Symon and Sims, 1988; as cited in	In "Nunn Clay Loam"
	33 day	soils - soil column	Loehr and Webster, 1997	
	285 day	sludge-amended soils	Wild and Jones, 1993	
	51 day	spiked soils		
	1.15 – 10.4 year	groundwater (estimated)	Howard *et al.*, 1991	

Substance	Estimated Environ-mental Half-Life	Medium/ Conditions	Reference	Notes
2-ring PAHs 3-ring PAHs 4-ring PAHs	17-48 day 31-176 day 206-1,003 day	hydrocarbon-contaminated soils (observed range)	Loehr and Webster, 1997 (Table 2-62: adapted from US EPA data as documented in Howard *et al.*., 1991)	
2-ring PAHs 3-ring PAHs 4-ring PAHs	1,746 day 856 day 1,144 day	hydrocarbon-contaminated soils (observed range)	Loehr and Webster, 1997 (Table 2-62)	based on six years of intrinsic/passive bioremediation of soils, **following** one year of active bioremediation.
ALIPHATICS				
Octadecane (C18)	66% in 20 day	aerobic soil suspension	Haines and Alexander, 1974	1% silt-loam suspension w mineral salts
Octacosane (C28)	3.2, 108 day 3-300 day	surface water groundwater, aerobic	Matsumoto, 1983 Zoeteman *et al.*, 1980	Tama R., Tokyo, aerobic estimate from field study
Dotriacontane(C36)	0.6 to 43% over 28 day	soil, aerobic	Moucawi *et al.*, 1981	biodegradation rate dependent on soil type; France

It is evident from the tabulated values that estimates of degradation are highly variable either for a single compound, or across compounds within a narrow range of molecular weights. This is not surprising: The environmental persistence of a substance, while undoubtedly influenced by the inherent chemical properties, is likely to be more strongly influenced by site specific conditions, including microbial ecology and site-specific ecological history, microclimate, soil and groundwater properties, co-contaminants, and so on. Expected site-to-site variations notwithstanding, constituents of PHC mixtures that tend to be more persistent in the saturated zone include PAHs, alkyl-PAHs and alkyl-benzenes. In addition, it is clear from the published literature that microbial degradation of petroleum hydrocarbons occurs more rapidly in aerobic than anaerobic conditions.

In choosing biodegradation rates which are applicable to sites across Canada, and on a generic basis, worst-case estimates of degradation are appropriate: i.e.-likely underestimates of the rate at which PHCs degrade in the saturated zone.

For some of the more refractory polyaromatic compounds in the PHC CWS Fraction 2 boiling point range, aerobic degradation half-lives of up to approximately 1,750 days have been previously observed for two-ring PAHs (naphthalene) (Loehr and Webster 1997). This is based on a rather slower rate of degradation in soils passively remediated *in situ*, and following one year of active bioremediation, wherein initial loss rates were much higher. An upper estimate of around 1,750 days for the half-life of PAHs in the F2 fraction is generally consistent with estimates provided by Howard *et al.* (1991). On the other hand, the field experimental conditions used by Zoeteman *et al.* (1980) to calculate a half-life for naphthalene in groundwater of only 0.9 days were probably more representative of the 'generic' conditions of the conceptual model inherent in the PHC CWS.

For lighter PHCs in the CWS F1 fraction (C6 to nC10), estimated environmental half-lives as tabulated above ranges from 0.3 day to 2 years (for benzene; Piet and Smeenk 1985). Wilson *et al.* (1986) used soil microcosms to study the biodegration of toluene under methanogenic/anaerobic conditions. The estimated environmental half-life was 126 day.

Based on the consulted studies, conservatively low estimates of environmental biodegradation were established as follows:

1. **CWS F1: 2 years = 712 day**
2. **CWS F2: 1,750 day**

In light of the highly conservative nature of these environmental half-life estimates, it is recommended that they apply to fate calculations in both the saturated and unsaturated zone.

Plice

20

Some Effects of Crude Petroleum on Soil Fertility

M. J. PLICE[1]

THE damaging of soils by crude oil and salt water is of common occurrence in petroleum-producing regions. The present work reports a study of the mechanism of injury to soil by petroleum and presents recommendations for the reclamation of oil-injured soils. A study of the damage of soils by salt water was also made but this work will be presented at another time.

PREVIOUS WORK

The literature indicates that very little study has been made of oil damage from a field standpoint. Carr (3)[2] found that crude oil added to a sandy soil at the rate of 0.75% stimulated the growth of soybean plants. It required an increase up to 4% of oil before the plants succumbed. The damage seemed to be due, at least in part, to the inability of the plant to secure water rapidly enough from the soil to meet its needs. Nodule growth was stimulated and nodule formation occurred in plants which were injured by the oil.

Baldwin (1) found that increasing amounts of crude oil retarded nitrification in soil, but it began again in all instances within 2 weeks incubation. Bacterial counts rose with increasing amounts of oil but bacterial "types" were reduced by the larger amounts. The numbers of anaerobes were little affected by the oil increments. Results in growing corn were not striking but the yields were highest on the plots receiving the largest amount of crude oil, which was 425 cc per hill. Murphy (5) reported that nitrate formation in soil was reduced even by very small applications of oil. One per cent of oil, when mixed with the soil, practically checked nitrate formation. Oil added to the surface of the soil, at the rate of 2,500 gallons per acre, reduced a wheat stand to 23% as compared with the check plot. A similar amount added 4 inches beneath the soil surface did not cause stand reduction but, when it was mixed with the soil, germination of seed was prevented.

From 1938 to 1944, the Texas Agricultural Experiment Station conducted a study of the effect of crude petroleum on the cotton root-rot fungus. The results, according to Brooks (2), indicate that the oil had little effect on the fungus. Cotton growth was decreased at first by the heaviest application—approximately 10,000 gallons per acre. After 2 or 3 years it was noted that the soil thus treated became more mellow and friable than before. Another Texas experiment, reported by Friend (4), involved the use of "stove oil" and kerosene, in spray form, as herbicides for the control of certain soil insects. Marked stimulation in parsley growth was obtained when the oils were used at rates of 300 to 600 gallons per acre. Stimulation of certain second-growth grasses by the sprays was also noted. It was inferred that these stimulating effects might be due to bacterial decomposition of the hydrocarbons.

Some effects of petroleums and kerosenes used as sprays on vegetation have been noted by Young (8) who found that the sprays produced varying degrees of plant injury, somewhat according to the amounts of sulphonatable fractions present in the oils. The sprays which were low in such fractions caused only slight injury to plants. The damage proved to be due to two causes: (a) "suffocating effect," and (b) toxicity, as such.

In a study of soil bacteria which attack crude petroleum, Stone (7) found that such organisms appeared to be present wherever soil samples were taken. He states that there seems to be no specialized group of organisms involved and that all of the common soil forms have the ability to adapt themselves to an infinite variety of organic compounds. He found, however, that different oils vary in their degree of susceptibility to bacterial attack. In general, lighter-weight oils oxidize more readily than heavier ones and paraffinic oils more easily than asphaltic (aromatic or naphthenic) oils.

PRESENT WORK

In order to study the effect of crude petroleum on soil and on plant growth, four series of 32 plots each were laid out in the spring of 1938. Two series involved a heavy clay soil and the others a fine sandy loam. Three types of crude-oil material were used—paraffin base, asphalt base, and basic sediment. Some characteristics of the materials used are given in Table 1. Each of the materials was added, in quadruplicate replication, in the percentages by weight, of one-tenth, five-tenths, and one. These amounts were considered to constitute light, medium, and heavy additions, respectively. The soils were dry and each material was incorporated uniformly to a depth of 6 inches. Within 24 hours after treatment the soils were completely wetted by rain. One week later the following crops were planted: Darso sorghum, cotton, soybeans, and field peas. Compared with the check plots, the average crop stands resulted as follows: Light application, 86%; medium, 61%; heavy, 42%. The cotton and darso were less sensitive to the oil than the beans and peas. The yield of each of these crops was quite disproportionate to stand because the plots with the poorer stands had more moisture available per plant; the fewer the plants per plot, the larger and heavier they became.

TABLE 1.—*Characteristics of petroleum materials.*

Material	Specific gravity	Volatile 105° C %	Nitrogen %	Carbon %	Sulfur %
Paraffin base	0.81	65.6	0.01	85.1	0.07
Asphalt base	0.84	22.8	0.05	86.6	0.23
Basic sediment	0.86	37.8	0.03	87.2	0.65

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[2] *Figures in parenthesis refer to "Literature Cited" p. 416.*

In the fall of 1938 the plots were seeded to wheat, barley, and rye. Practically full stands resulted and, when harvested in the summer of 1939, no significant differences in crop yields could be detected. These results indicated that the amounts of oil materials used did not simulate the amounts which can get on land in pipeline breakages or overflows from retaining reservoirs. Consequently in the fall of 1939 all of the treatments were duplicated and the same crops grown, as before. Crop stands and yields were virtually the same as before except that the asphalt-base oil reduced stands less and the paraffin-base oil more than previously. This was especially the case on the sandy soil where no stands resulted on the medium and heavy paraffin-oil plots.

During the second season (1941) the deleterious effect of the oils diminished greatly while in the third season (1942) all of the plants on the oiled plots gave increased yields over the check plots. These increases amounted to approximately 5, 15, and 20%, respectively, from light to heavy oil application. The stimulating effect of the petroleum materials continued to about the same extent through the season of 1943 when hairy vetch, crimson clover, and hubam clover were grown.

NATURAL PIPELINE BREAKS

During the time the present study was being made observations were also made on several areas of land which had suffered some damage caused by natural, or accidental, breaks in oil lines. It was noted that the nature and extent of the damage done by the oil were influenced considerably by the moisture content of the soil when the break, or overflow, occurred. When the soil was wet the oil tended not to soak downwards but to flow over the surface and to collect in pools at depressional places. In such instances the collected oil was pumped out and mostly recovered by oil field crews. The small (usually) amounts of oil that were left gradually thickened and became partly to entirely solidified during hot, sunny weather.

On the other hand, should the soil be dry to a considerable depth, overflow oil tends rather rapidly to soak downward and saturate the soil to a greater or lesser extent depending on the amount of leakage, soil porosity, and topography. The type of oil is important, for paraffinic oils tend to penetrate soils much more readily than asphaltic oils. Observations have been made in this connection where oil has saturated an area to a depth of 4 feet for various extents up to nearly an acre. Depending on the subsequent weather, such an affected area may remain boggy and barren for several years. A protracted period of dry, hot, and windy weather will dissipate the more volatile oil fractions and the soil surface will gradually become stable enough to withstand the weight of cultivating machinery. In one instance, which was considered to be an extra-bad break, the soil was boggy and barren for 3 years. By the end of the fourth year cultivation became possible and a crop was planted at the beginning of the fifth season. From this planting approximately a half-stand was obtained. The seventh year after the break occurred the soil which had been oil-soaked was evidently somewhat more productive than the surrounding soil, as gauged by the eye.

SHALLOW VERSUS DEEP OIL PENETRATIONS

Observations of a number of pipeline breaks, most of which were deep-penetrating, led to the conclusion that the present oil study, thus far, did not simulate actual oil-break conditions. The deepest penetrations of oil into the soil of the treated plots had not been greater than 4 inches. Since all cultivations have been to a depth of 6 inches, this means that the oil aliquots added have been diluted with soil. It means, further, that the oil has been oxidized more rapidly and lost its unctuousness sooner than if the soil had been wetted by the oil to a greater depth. Consequently, in the summer of 1943, two series of plots were installed in order to study deep penetration.

The weather was hot and the soils were dry, almost to hygroscopic moisture, to a depth of 4 feet. Sufficient paraffin-base petroleum was used to saturate the soils to that depth. It was noticed that, as the oil percolated downward, there was a filtration effect; those constituents which give the crude oil its color and viscosity were filtered out in the top foot of soil. The oil fractions which penetrated deeper than this were colorless and had the approximate consistency of mixed kerosene and gasoline. The fraction which penetrated most deeply was more nearly like gasoline but did not have the characteristic odor either of kerosene or gasoline.

It was decided not to plant any crop but to let nature take its course and permit vegetation to come in as it might. One-half of the plots were given intense cultivation until the end of hot weather. By this time the gumminess of the stirred soils had decreased considerably. In the summer of 1944 the uncultivated plots were quite blackish and tarry-looking while the cultivated soils assumed a rich brownish coloration. These colors have changed very slightly to the present time—fall of 1948.

Occasional probings have shown that the deeply-oiled soil reacts to moisture quite differently than does shallow-oiled soil. The latter comes to moisture equilibrium within a week or two after a good rain and dries out relatively fast in dry weather. The former was not wetted at all by direct rainfall; instead, it was wetted from the sides and from below by moving ground water. Even though plentiful precipitation occurred during the fall and winter, it was not until late spring that the surface soil became moist. Then, after once becoming wetted, it remained so for most of the summer. This was true for both the cultivated and uncultivated, deeply-oiled soils.

Both of these soils were entirely bare for 2 full years. During the second summer (1945) the deeply-oiled plots, which were cultivated, dried out in the surface layer. During a subsequent period of dry, windy weather it was noticed that these particular soils had become subject to blowing. Examination showed that aggregation had broken down, even in the clay soil, to the extent that the soil had a "silty" feeling. Further wind damage was prevented by covering these plots with a thin layer of straw. The uncultivated, deeply-oiled soils were seemingly de-aggregated to a small extent but never to the extent of being subject to wind action.

During the third summer after installation (1946) crab and blue grama grasses began to become established on the cultivated, deeply-oiled soils. During 1947 several other grasses came in and at present (1948) these plots are completely occupied by grasses. No growth of any sort has, as yet, taken place on the *uncultivated,* deeply-oiled plots.

BIOLOGICAL ASPECT OF SOILS AFFECTED BY HYDROCARBONS

As already mentioned at the beginning it was noticed that plant growth was more luxuriant on the medium and heavy oiled plots, that is, on the plots which received the petroleum materials in the amounts of 5/10 and 1%, by weight. This extra growth was at first believed to be due almost entirely to the extra moisture in the oiled soils. Careful nitrogen determinations, however, revealed that these soils contained more nitrogen than the check-plot soils. Further, the soils which were deeply saturated with oil, in 1943, contained more nitrogen in 1948 than the shallow-treated soils just mentioned.

Previously, and in another connection, it had been observed that considerable nitrogen fixation took place when several nitrogen-free organic materials were added to the soil. These materials lowered the redox potential of the soil considerably for a period of time and it was during the time of this lowered potential that the nitrogen was fixed. A redox study of the oiled soils revealed that petroleum also lowered the potential and played a part in nitrogen fixation therein during the period of lowered potential—approximately one year. Table 2 shows the effects of the various oil treatments in increasing the nitrogen and organic matter contents of the sandy loam soil. The figures for the clay soil are practically the same as for the sandy soil.

In the above table—by "shallow-oiled plots" is meant those which were installed in the beginning and which received two oil treatments at the rates of 1/10, 5/10, and 1%, by weight, each time. The designations, *light, medium,* and *heavy,* connote these percentages, respectively. The soil samples of these plots and those of the check plots were composites from the four different replications. As described further above, the oil saturated plots are those which were soaked with oil to a depth of 4 feet. They consisted of two replications—one-half of each one being cultivated and the other remaining uncultivated. The soil samples of these plots were composites of the duplicate replications.

Nitrogen determinations involved the usual Kjeldahl method. Organic matter was determined by carbon dioxide measurement and applying the regular factor to these determinations. Carbon dioxide evolution was caused by digestion with a sulphuric-perchloric acid mixture (6). The chromic acid method of organic matter determination gives much too high results where hydrocarbons are involved.

In order to see whether the organic matter in the variously-oiled soils, as shown in Table 2 is now present as real soil humus or still as hydrocarbon material, samples of each were refluxed with tetrachlorethane and the residues from these extracts weighed. This solvent extracts hydrocarbon materials rather completely and attacks soil humus very slightly. This treatment showed that the petroleums had been practically completely "fixed" as organic matter in the shallow-oiled soils but not entirely so in the oil-saturated soils. The cultivated, oil-saturated soil still contains 3.52% extractable hydrocarbon and the uncultivated contains 6.77%. However, samples of soil from oil breaks of at least as great intensity, but of several years longer standing, show that only traces of soluble hydrocarbons are now present.

Parallel instances of nitrogen fixation and organic matter formation in soils, in huge amounts, by organisms using hydrocarbon material as their energy source, occur quite often about leaks in natural gas lines. If the ground is moist, but not too wet, soil organisms—both molds and bacteria—rapidly attack the gas and within a week the soil begins to blacken in color. This blackening is increased and extended with time. The black material, itself, which impregnates the soil seems to be composed of microbial substance and "carbonized gas" residue. It is high in humic material and nitrogen. The soil, around one such leak studied, contained 12.47% organic matter and 0.81% nitrogen. The unaffected soil, 2 feet distant, contained 0.52% organic matter and 0.03% nitrogen. Both samples were taken at a depth of 2 feet. Extraction of this black soil with the solvent showed that only 0.27% of unhumified hydrocarbon material was present.

Both bacteria and fungi are evidently active in attacking petroleum, as well as natural gas, in soil. No quantitative estimation of molds was made but qualitative tests showed that at least several distinct species were present. Bacteria can be determined readily in soil in which the oil has had time to oxidize and the soil to become friable again. In freshly oiled soils counts are difficult to make because the oil interferes with soil dispersion. In the present instance this difficulty was mostly surmounted by

TABLE 2.—*Organic matter and nitrogen contents of soils.*

Shallow-oiled plots						Check plots		Oil-saturated plots			
Light		Medium		Heavy				Cultivated		Uncultivated	
O.M. %	N %	O.M. %	N %	O.M. %	N %	O.M. %	N %	O.M. %	N %	O.M. %	N %
1.97	0.06	2.66	0.07	3.71	0.08	1.74	0.05	8.23	0.10	11.45	0.12

thoroughly triturating the soils with several volumes of sterilized ultra-clay particles obtained from Kaolin by sedimentation. This treatment reduced plasticity and adhesiveness sufficiently to permit suitable dispersion. Several dilution platings were made, using a standard Difco yeast-agar medium buffered at pH 7.0.

The purpose of making bacterial counts was to learn whether the petroleum is toxic to microbial life. In the shallow-oiled soil, using the 1% oil addition, the number of bacteria found was 7.1 million per gram. The check soil contained 7.8 million. Three months later the check soil was found to have approximately the same count as at first but the oiled soil had 87 million bacteria per gram. In the deeply-oiled, or saturated, soils, shortly after the treatments were made, the number of bacteria counted was 7.3 million per gram; the check contained 8.1 million. This shows that either the oiled soil was incompletely dispersed or that some of the organisms were killed, or made inactive by the oil. Determinations made two years later on these oil-saturated soils showed the check plot to contain 9.0 million organisms; the cultivated plots 94 million; and the uncultivated plots 110 million.

No presumption was attempted at bacterial identification. It was apparent, however, that at least 15 or 20 "types" of organisms were present, including actinomycetes and anaerobes.

In order to observe the activities of the organisms in the variously oiled soils, sterile samples of Ashby's medium were inoculated with 1.0 gram soil portions and let stand to incubate. Intensity of biologic activity was gauged by the rapidity of the onset of emulsification. That the organisms were numerous and active was shown by the advanced emulsification that took place in every flask within one week. No carbon dioxide-evolution study was made since rational correlations with organism activity cannot be made in this manner.

DISCUSSION

It is quite apparent, both by observation of natural contaminations and by experimentation, that areas of land can be injured for crop growing by crude petroleum for a greater or lesser period of time. The amount of damage done and the time which will be required for reclamation depends on the size of the area involved and the degree of saturation by the oil. Oil penetrations which do not go deeper into the soil than plow depth can usually be overcome within a year or two by cultivation—particularly if dry, sunny weather can lend a hand. The present study indicates that, in the case of deep penetrations of 1 foot or more, no attempt should be made to make cultivations until the oil has "weathered" to a depth somewhat greater than the soil will be plowed. Depending on the extent of subsequent hot and dry weather, this might not be for a period of 2 or 3 years, or even longer.

Hot, dry, and sunny weather greatly hastens the escape of the volatile fractions and, in time, removes the gumminess of the oil so that the soil will scour a plow. The processes which solidify the oil and make the soil friable again are, seemingly, mostly biological ones and involve oxidation and reduction, and dehydration. It is possible that condensation and polymerization also play a part.

After friability has been restored a crop may be planted. A decreased stand at first is almost inevitable. This decrease seems to be due mostly to hydrostatic relationships in the soil whereby the plants are unable to ramify their root systems. When the excess of oil volatiles has escaped, pure toxicity, as such, seems to play little part in decreasing seed viability. The volatile-oil fractions have high "wetting" capacity and penetrating power. If they come into contact with plant seed they enter the seed coat readily and kill the germ. That oil toxicity harms the microorganism population of the soil only slightly is seen in counts made after the soil has been properly dispersed.

SUMMARY

It is well known, in petroleum-producing regions, that crude oil can "sterilize" soils and prevent crop growth for various periods of time. The duration of the damaging effect depends largely on the degree and depth to which the soil is saturated with the oil. The damage that oil does is due mostly to the prevention of the plant from obtaining sufficient moisture and air and from ramifying its roots; very little is due to toxicity, as such. Oil-damaged soils are best reclaimed by cultivation, after the petroleum has "hardened" to the extent that the soil will scour a plow share. Depending on depth of saturation and climatic conditions this might be anywhere from 1 or 2 to several years following contamination. Crude petroleums are converted to soil organic matter by bacteria and fungi. During the conversion the organisms, which are free livers, fix fairly large amounts of atmospheric nitrogen in their substance. Later, this nitrogen becomes available for plant growth and the organic matter improves soil physical conditions.

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22

Crude Oil Hydrocarbon Bioremediation and Soil Ecotoxicity Assessment

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In this study, we determined the limits and extent of hydrocarbon biodegradation, earthworm and plant toxicity, and waste leachability of crude oil-containing soils. Three oils (heavy, medium, and light of API gravity 14, 30, and 55, respectively) were mixed into silty loamy soils containing low (0.3%) or high (4.7%) organic carbon at 4000–27 000 mg/kg TPH. Hydrocarbon bioremediation in these artificially weathered oily soils usually followed first-order removal rates in which 50–75% and 10–90% of the total petroleum hydrocarbons (TPH) were degraded in 3–4 months for the low and high organic soils, respectively. Gas chromatographic profiles (simulated boiling point distillation of saturates and aromatic compounds) showed that, after bioremediation, hydrocarbons in oily soils decreased from 70 to 90%, from 40 to 60%, and from 35 to 60% for those carbon number species in the range of C_{11}–C_{22}, C_{23}–C_{32}, and C_{35}–C_{44}, respectively. Most oily soils were initially toxic to earthworms in which few animals survived 14-day bioassays. In a solid phase Microtox test, most oily soils had EC50 values that were ≤50%. Seed germination and plant growth (21-day test, wheat and oat but not corn) were also significantly reduced (0–25% of controls) in untreated soils containing the medium and light crude oils but not the heavy oil. Bioremediated soils were neither toxic to earthworms, inhibitory in the Microtox assay, nor inhibited seed germination after 5 (high organic soil) or 10–12 (low organic soil) months of treatment. Water-soluble hydrocarbons (e.g., O&G and BTEX) could leach from pretreated soils (medium and light crude oily soils) in column or batch extraction experiments. However, after bioremediation, most of the aromatic compounds were no longer leachable from the soils. These data demonstrate that treated oily soils lose their toxicity and potential to leach significant amounts of BTEX. These nontoxic soils contain 1000–8600 mg/kg residual hydrocarbons as TPH. Furthermore, these data suggest that the remaining petroleum compounds may be bound or unavailable in that they are not (a) biodegraded further, (b) toxic to soil-dwelling species (earthworms and plants), and (c) susceptible to leaching and subsequent impact to groundwater. These findings provide a basis for a framework in which petroleum hydrocarbon-containing soils can be evaluated by ecological assessment methods such as biodegradability, ecotoxicity, and leaching potential of regulated substances.

Introduction

Bioremediation is often a cost-effective method to treat oily soils and petroleum wastes containing biodegradable hydrocarbons and indigenous microbes. This soil cleanup technology has been successfully demonstrated in laboratory and field tests for refineries (*1*–*6*), in oil and gas operations in the treatment of oily sludges, and at pipeline sites to remediate accidental crude oil spills (*7*–*9*). The land treatment process requires the management of appropriate levels (e.g., oil hydrocarbons as percentage total petroleum hydrocarbons, TPH) of applied waste to soil, aeration and mixing, nutrient fertilizer addition, pH amendment as required, and moisture control to optimize degradation by soil microorganisms. Guidance on the lab feasibility assessment, field implementation, and soil sampling strategies required to demonstrate land treatment of wastes have been developed by Huesemann (*10*, *11*) and Sims et al. (*12*). A petroleum industry review based on such land treatment practices several years ago indicated that 70–90% of oily sludge hydrocarbons were removed from surface soils having loading rates of 10 000–50 000 mg/kg oil (*1*). Loehr et al. (*13*) studied the treatability of an oily sludge in field plots in a silty loam soil and demonstrated that 60–70% of the initial O&G (20 000–55 000 mg/kg) hydrocarbons were biodegraded within 2–3 years.

There have been numerous studies and reviews in the literature documenting the ready degradability of crude oil hydrocarbons (alkanes, alkenes, aromatics, and polars) in soils, sludges, sediments, and the marine environment by naturally-occurring microbes. Experiments have shown that differences in the extent of soil hydrocarbon biodegradation may depend upon soil and crude oil types, concentration of total applied hydrocarbon, and nutrient growth stimulants (e.g., NH_3 and PO_4^{3-}) based on optimum C:N:P ratios (*14*–*20*). Research by Huesemann and Moore (*21*) on the influence of oil type on bioremediation in a sandy soil showed that a light-medium (API gravity 39 and high saturate fraction) crude oil biodegraded (O_2 uptake and reduction in oil and grease) more extensively than a heavier crude (API gravity 21). In these experiments, optimum rates of O_2 consumption and CO_2 formation were observed in the first 3–4 months. There have been few definitive studies on identifying the fraction and types of petroleum hydrocarbons that are readily degraded or recalcitrant in oily waste soil treatment systems. Recently, Huesemann and Moore (*22*) showed that 93% of the saturate and 79% of the aromatic compounds having carbon numbers in the range of C_{10}–C_{44+} were degraded in a sandy soil containing weathered Michigan (medium API gravity) crude oil with an initial concentration of 30 000 mg/kg TPH. In this same study, however, the polar fraction was resistant to microbial metabolism and did not degrade during the 5.5-month test. Experiments by Huesemann (*23*) on the limits and extent of bioremediating TPH in different oily soils showed that 90% of the alkanes and monocyclic saturates and 50–70% of aromatic compounds ($<C_{44}$) were degraded. The significance of this work is that overall bioremediation effectiveness was dependent upon hydrocarbon types present and was not affected as much by soil type, nutrient fertilizer addition, microbial populations, or treatment conditions (slurry versus static soil conditions). It was also shown that saturate and aromatic compounds with polycyclic structures were most resistant to removal by enhanced soil biotreatment

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methods. The apparent recalcitrance of petroleum hydrocarbon fractions may be due to factors such as lack of bioavailability (inaccessible because of soil sorption and uptake by soil microbes), lack of requisite oxidizing enzymes, and/or steric hindrance for enzyme attack and toxicity to soil microorganisms.

Currently, there are no universal TPH cleanup standards that have been adopted by federal or state regulatory agencies for soils contaminated with fresh or weathered crude oils. State guidelines developed mainly for oil product (e.g., gasoline, diesel, and other middle distillate fuels) spills to surface or subsurface soils have varying remediation end points such as 10–10 000 mg/kg TPH and 0.1–500 mg/kg BTEX, cleanup to background levels, or allow the use of risk-based criteria coupled to environmental fate and effects (*24*). Based on our current understanding of bioremediation of crude oil-impacted soils, it would be difficult to achieve those low cleanup levels at most sites containing varying types of residual, weathered petroleum hydrocarbons. Doyle and Sweet (*25*) have suggested that soil remediation standards should be based upon the BTEX components in crude oil and oil products (fuels)-impacted soils since these are the most mobile (leachable) hydrocarbons that could be transported to groundwater. Ecologically relevant criteria for estimating the impacts of oil hydrocarbons in soils are also important end points for risk assessment. In this respect, ecotoxicity bioassays such as seed germination and plant growth have been used for monitoring treatment effects and restoration of oiled land sites (*26–29*). Plant species have been proposed as indicators of soil quality and toxicity of leachable constituents in assessing damage and risk to impacted ecosystems (*30, 31*). There have been relatively few studies, however, describing the effects of oil hydrocarbons on soil-dwelling invertebrates such as earthworms, nematodes, other polychaetes and microarthropods (*32–34*). Earthworms have been used to evaluate the effects of chemicals and contaminated soils on animal survival, growth, and reproduction (*35–39*).

Another factor in ecorisk evaluation of oily soils is the potential for dissolution and leaching of water-soluble aromatic hydrocarbons like benzene, toluene, ethylbenzene, and xylenes (BTEX) into the vadose zone and groundwater environments. Laboratory soil microcosm experiments and field investigations in aquifers have been used to study hydrocarbon source migration from oil and fuel spills (*40–42*). Fate and transport methodologies have been developed to validate those natural attenuation factors (e.g., inherent biodegradation of hydrocarbons in groundwater, evaporation rates from spills, and soil sorption/desorption rates) governing the dissolution and dispersion of petroleum compounds into the subsurface (*40, 43–45*).

Clearly, the integration of chemical analysis, ecotoxicity, and remediation potential data is required to properly assess ecological risk in the management of crude oil-impacted soils. In the present laboratory study, we compared the biotreatability of three artificially weathered crude oils (heavy, medium, and light) in soils with high or low organic carbon content using traditional land treatment techniques. Soil samples taken before, during, or after bioremediation were evaluated for TPH content, hydrocarbon composition changes, earthworm survival, seed germination and plant growth, Microtox inhibition, and hydrocarbon and metal leaching potential. Our data demonstrate the effectiveness of bioremediation techniques in reducing hydrocarbon levels, eliminating acute soil toxicity, and reducing leaching of water-soluble aromatic compounds (BTEX).

Materials and Methods

Test Soils and Crude Oils. The effects of hydrocarbon bioremediation on soil toxicity was investigated in two soils with high (4.6%, Norwood/Baccto) and low (0.3%, Norwood) organic matter to which were added three different crude oils of API gravity (measured at 60 °C) 14 (heavy), 30 (medium), and 55 (light). The distribution (%) of saturated/aromatic/polar fractions in the heavy, medium, and light oils was 20.3/28.9/44.1, 56.4/23.7/14.7, and 86.7/6.4/0.7, respectively. Total BTEX concentrations were 1735, 15 140, and 36 100 mg/kg, respectively, in the heavy, medium, and light oils. The predominant polyaromatic hydrocarbons (PAH) naphthalene and phenanthrene were present at combined levels of 180, 460, and 960 mg/kg in the heavy, medium, and light oils, respectively. PAH with four or more rings were present at or below the quantitative detection limit (≤20 mg/kg). Metal analysis of the crude oils indicated that Ni, V, and Zn were present in the heavy and light crudes at 99, 130, and 450 mg/kg, respectively (data not shown). Most other metals (e.g., As, B, Cr, Cu, Hg, Mo, Pb, and Se) were <20 mg/kg.

The Norwood soil used in these studies was obtained from the surface (6 in. depth) of a typical agricultural horizon (cotton field) near College Station, TX, and was characterized as a silty loam containing 15% clay and 60% silt, low organic matter (0.3% organic carbon), and a pH of 8.2. The Norwood/Baccto test soil mixture consisted of 75% v/v Norwood soil and 25% Baccto topsoil, had a pH of 7.1, and had an organic carbon content of 4.65%. The Baccto topsoil was a commercially available sandy loam potting soil of low clay (4%) and silt (11%) content, low pH (4.0), and high organic matter (20.3% organic carbon) due to the presence of peat. Soil grain size analysis indicated that 99% (Norwood) and 95% (Norwood/Baccto) of the particles were ≤0.11 mm. Inorganic nitrogen and phosphorus and organic nitrogen were higher in the Norwood/Baccto (469, 473, and 2921 mg/kg, respectively) as compared to the Norwood soil (20, 315, and 517 mg/kg). The initial moisture content of both soils varied from 18 to 28%.

The pH of the six oily soils during the 12-month study did not change appreciably and varied from 6.8 to 7.5. Total heterotrophic bacteria and hydrocarbon degraders were similar and did not vary during biotreatment. Microbial enumeration of soil samples taken during the first 6 months showed that there were 10^8–10^{10} heterotrophs and 10^7–10^9 hydrocarbon degraders/g of soil. Bacteria were estimated by cell growth in MPN dilution methods using Trypticase soy broth (BBL, Becton-Dickinson) medium for heterotrophs and Bushnell-Haas (Difco) minerals containing 1% hexadecane for hydrocarbon degraders.

Oily Soil Mesocosms. Approximately 4.5 kg (5% w/w) of heavy, medium, or light crude oil was added to 95 kg wet wt of Norwood or Norwood/Baccto soils. The sieved soil (1.3 cm screen) was mixed in a cement mixer to maximize hydrocarbon distribution. The oily soil was placed onto plastic sheeting for aeration and artificial "weathering" (2–3 days) and to manually break up clumps of clay and oil. A significant fraction of the volatile hydrocarbons was lost by this procedure. We calculated, for example, that based on the total BTEX hydrocarbons applied to the soil (5% oil addition) and the BTEX level at the start of the bioremediation process, about 40–95% were "volatilized" during the "mixing and weathering" process. Fertilizer solution was added to each 95 kg of oily soil as N (100 g of NH_4NO_3) and P (40 g of K_2HPO_4) at a C:N:P ratio of 100:1:0.2 (assuming a carbon content of 80% for crude oils). Deionized water was added to soils to a moisture content of 50–80% of the field moisture capacity. The fertilizer-amended oily soils were placed (12 in. soil depth) into 128-L capacity stainless steel chambers (45 cm × 45 cm × 30 cm) fitted with plexiglass covers. The mesocosms were continuously swept over the soil surface with humidified air at a flow rate of 250 L/h to minimize moisture loss and to aerate the soil. When mesocosms were sampled for residual TPH and O&G, soil was mixed and aerated and five randomly selected 400-g portions were withdrawn. This 2-kg sample was subsampled and submitted

for O&G, TPH, and BTEX and [redacted]city tests.

Methods for Hydrocarbon Analyses. (A) Total Petroleum Hydrocarbons. Duplicate samples (40 g wet wt) of oily soils from each treatment were taken monthly for determinations of O&G and TPH. O&G content was measured gravimetrically after evaporation of the Freon 113 solvent used in the Soxhlet extraction according to Method 5520E (*46*). This analysis is similar to EPA Method 413.1 for total O&G. The Freon extract was either (a) treated with silica gel to remove polar compounds and analyzed by an infrared analyzer (Horiba Instrument Co.) according to EPA Method 418.1 as TPH-IR or (b) dried under N_2 and the residue weighed and reported as gravimetric TPH (TPH-Gr) according to Method 5520F (*46*). The calibration standard used in the TPH-IR method was 25% (v/v) *n*-hexadecane, 37.5% (v/v) isooctane, and 37.5% (v/v) chlorobenzene; absorption was measured in the IR spectral range of 3400−3500 cm^{-1}.

(B) Aromatic Hydrocarbons. Polyaromatic compounds (two-, three-, and four-ring PAH) were extracted using sonication and methylene chloride from 2 g of soil according to EPA Method 3550 and analyzed by a direct injection GC/MS determination based on EPA Method 8270 (*47*). Volatile organics such as BTEX were determined using a modification of Method 8240 (*47*) by extracting (vortex mixing) 10 g of soil with 10 mL of high-purity methanol and then analyzed by GC/MS.

(C) TCLP Organics and Metals. The extraction procedures (Method 1331) for organics (Methods 8240 and 8270) and metals (Methods 6010 and 7470) were described in the SW-846 manual (*48*) and performed by Chester Laboratories, Houston, TX. Total fixed metals in soil were determined by Methods 6010 and 7471 as given in SW-846.

(D) Group-Type Separation Analysis. In the analysis of the saturate, aromatic, and polar fractions of the whole oils, TPH extracts were dried and redissolved in cyclopentane and separated on a packed silica gel glass column. The saturates, aromatics, and polar fractions were eluted with pentane, pentane−benzene (60:40), and benzene−2-propanol (80:20), respectively. The dry weight of each fraction was obtained by evaporating the solvent at 60 °C and weighing the residue.

(E) Hydrocarbon Distribution by "Simulated Boiling Point" Gas Chromatography. A gas chromatographic simulated high-temperature distillation of hydrocarbons by carbon number was performed on methylene chloride extracts of the untreated and bioremediated oily soils using a modification of ASTM Method D-2887 (*49, 50*). Hydrocarbon fractions (saturates and aromatics) from C_{11}−C_{44} were separated, and a standard normal paraffin mixture was used for matching retention time with carbon number in the temperature-programmed column distillation.

Leaching Potential. The ready desorption and dissolution of water-soluble hydrocarbons and metals from each oily soil before and after bioremediation was determined by batch and column extraction methods. In the batch test, 20 g of soil was sequentially extracted five times with 200-mL aliquots of 0.01 M $CaSO_4$−2% sodium azide solution on a rotary platform agitator at 20 rpm for 24−48-h intervals. Sodium azide was added to the $CaSO_4$ solution to prevent microbial growth and biodegradation of the soluble hydrocarbons released from the soil. Soil slurries were centrifuged (2000 rpm, 45 min), and the combined supernatants were analyzed for O&G, TPH, BTEX, and metals (e.g., V, Ni, and Cu). These batch extraction methods were modified from the California Waste Extraction Test Procedures (*51*). In the column leaching studies, 500 g of soil was packed into a 2 in. × 6 in. glass column between 0.5 in. layers of Ottawa sand (Mallinckrodt Chem. Co.; 95% of the particles pass a no. 50 sieve). Columns were operated in an upflow direction using a syringe pulse pump flowing 2 pore vol/day of 0.01 M $CaSO_4$−2% sodium azide solution. These conditions simulated a water leaching flow rate [redacted]ugh soil of 1 ft/day. Column leachates were also analyzed for O&G, TPH, BTEX, and metals.

Ecotoxicity Bioassays. (A) Earthworm Survival Test. The common earthworm species, *Eisenia foetida*, was used to determine acute toxicity of the oily soils before, during, and after biotreatment. Animals were obtained from Carolina Biological Supply Company (Burlington, NC) and held in uncontaminated soil until testing. The assay methods were similar to those described in an EPA protocol (*52*). Ten adult animals (five replicates) were placed into 200 g (dry wt) of soil in 1-L wide-mouth jars with loose fitting lids. The LC50 for each oily soil was estimated using five concentrations of bioremediated soil (100, 50, 25, 12.5, 6.5, and 0%) prepared with control (oil-free) Norwood or Norwood/Baccto soil. The soil water content was adjusted to 12−18% for the Norwood and to 30% for the Norwood/Baccto soils. Surviving earthworms were counted after a 14-day incubation at room temperature under constant fluorescent lighting conditions. The LC50 end point was calculated using probit techniques.

(B) Microtox Solid Phase Assay. The Microtox Analyzer M500 and solid-phase test kit (Microbics Corp., Carlsbad, CA) were used to evaluate the response of the luminescent bacteria (*Photobacterium phosphoreum*) to oily soils. The test methods employed were described in the Microbics Manual (*53*). Soil dilutions were prepared (0.3 g/3 mL of Microtox diluent), incubated for 20 min with reconstituted lyophilized bacteria, and then sampled for substrate-induced (Microtox ATP reagents) photoluminescence activity. The EC50 soil dilution that inhibits 50% of the light output relative to the control (hydrocarbon-free soil) was calculated for each soil.

(C) Plant Seed Germination and Growth. The methodology used in these seed germination/plant growth studies was similar to that outlined in the OECD Guideline for Testing of Chemicals (*54*). The effects of untreated and bioremediated oily soils were determined in corn, wheat, and oat species. Corn (*Zea mays*), wheat (*Triticum aestivum*), and oat (*Avena sativa*) were purchased from Carolina Biological Supply Company (Burlington, NC), and seeds were stored at room temperature until used in germination tests.

Oily soils or oil-free (control) soils were dispensed (ca. 80 g/cell) into molded plastic trays (57 cm long × 27 cm wide × 6 cm high) containing 36 cells/tray. Seeds (5 per cell) were placed 1−1.5 cm below the soil surface in each of 20 cells (100 seeds) for each soil treatment. Seed cultures were exposed to 12-h light/dark cycles at a soil surface light intensity of 310−350 lm provided by six 34-W white fluorescent lamps. The room temperature varied from 20 to 23 °C. Soil treatments were kept moist (ca. 30% of the soil mixture holding capacity) by spraying the soil surface with unchlorinated well water.

The percent of seeds germinated before and after (at 8 and 10 months) bioremediation was determined after 21 days. Plant foliar and root dry weights were also measured from all germinated seeds. Plants from a cell were removed as a group, washed to remove soil particles, and then dried at 120 °C for 3 h. The average dry weight/plant was calculated for all plants, and incompletely germinated seeds were not included in the plant dry weight. Plant germination data (where applicable) were compared between treatments using the χ^2 test with a continuity correction or the Irwin−Fisher exact test. A sample size of 100 seeds per treatment can detect a 20% treatment effect when the control group germination rate is ≥60%. The plant dry weight data were analyzed by analysis of variance, followed by the method of least significant difference (LSD) for assessing treatment effects (*55*).

Results and Discussion

Hydrocarbon Biodegradation in Oily Soils. The initial soil concentrations of the applied hydrocarbon varied from 12 000 to 14 000 mg/kg, from 26 000 to 27 000 mg/kg and from 4000

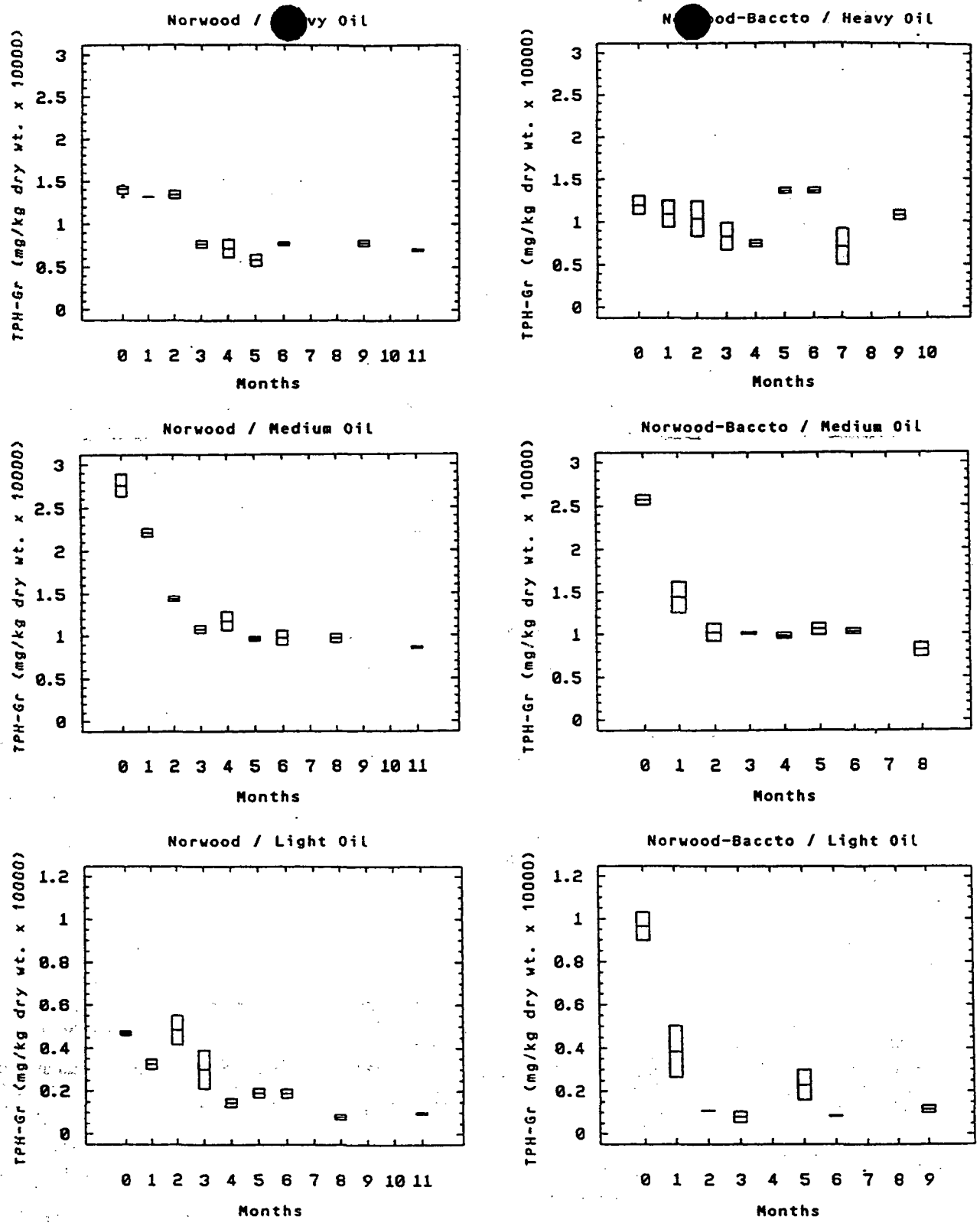

FIGURE 1. TPG-Gr analyses of oily soils during bioremediation. Values given represent the median and actual levels for duplicate soil samples at each time point.

to 9600 mg/kg TPH-Gr for the heavy, medium, and light oils, respectively. Most duplicate soil samples taken at each time point were within 10–20% of each other based on bulk hydrocarbon analysis. Profiles of the decline in oil hydrocarbons during soil bioremediation are shown in Figure 1. Table 1 is a summary of the initial and final (8–11 months) hydrocarbon levels in both soils as analyzed by TPH-Gr, TPH-IR, and O&G methods. The TPH-Gr data show that the heavy, medium, and light oils were significantly degraded in low (Norwood) and high (Norwood/Baccto) organic soils. The overall maximum decline in TPH was similar for the two soils, but different between oil types. For example, the decrease in TPH in soils with heavy, medium, or light oils was 10–50%, 65–70%, and 75–90% of the initial TPH-Gr levels after 8–11 months (see Table 3). Similar net reductions in heavy, medium, and light hydrocarbons were noted for both soils based on O&G (5 and 45%; 55 and 60%; 50 and 80%) and TPH-IR (12 and 73%; 70–80%; 95%) analyses (see Table 1).

TABLE 1. Decline in Bulk Hydrocarbon Levels in Oily Soils after Bioremediation As Measured by TPH, O&G, and TPH-IR

soil	oil type	initial concn (mg/kg)[a] TPH	O&G	TPH-IR	% degraded based on[b] TPH	O&G	TPH-IR	degradation rate (%/mo)[b,c]
Norwood	heavy	14 000	23 600	35 700	50	44	63	16
	medium	26 600	34 800	81 400	67	57	71	21, 30
	light	4 200	9 760	40 100	76	83	95	26, 48
Norwood/Baccto	heavy	11 900	37 000	64 700	10, 40	6	12, 73	12, 42
	medium	25 700	41 400	122 200	68	62	83	46, 69
	light	9 600	14 000	77 600	88	52	97	108, 126

[a] Based on dry wt of soil. [b] Calculations were the average of duplicate soil samples (±10%–20%, otherwise individual values are given) after 7–9 (Norwood/Baccto) and 8–11 (Norwood) months treatment. [c] Based on a best fit to a first-order decay curve.

TABLE 2. BTEX and Hydrocarbon Number Distribution in Oily Soils[a]

soil type	oil type	treatment	B	TEX (mg/kg)	carbon range (mg/kg) C_{11}–C_{22}	C_{23}–C_{32}	C_{33}–C_{44}
Norwood	heavy	untreated	<0.02	1.64	6010	6234	4308
		bioremediated	<0.02	<0.02	1743 (71)[b]	3615 (42)	2848 (34)
	medium	untreated	3.19	256	7269	6688	3835
		bioremediated	<0.02	2.21 (<0.02)[c]	1887 (74)	3272 (51)	2384 (38)
	light	untreated	63.7	1027	4723	477	157
		bioremediated	<0.02	56.0 (<0.02)[c]	586 (88)	185 (61)	73 (53)
Norwood/Baccto	heavy	untreated	1.77	43.4	5545	6682	5603
		bioremediated	<0.02	<0.02	1100 (80)	2653 (60)	2910 (48)
	medium	untreated	10.0	35.0	5168	4845	3335
		bioremediated	<0.02	<0.02	944 (82)	1880 (61)	1764 (47)
	light	untreated	53.0	1624	13 796	854	218
		bioremediated	0.18 (<0.02)[c]	<0.02	1308 (90)	435 (49)	82 (62)

[a] Soils extracted for BTEX or other hydrocarbons after 2 or 8–11 months bioremediation, respectively. Concentrations are mg/kg dry wt soil. [b] Number in parentheses is the percent reduction of each fraction from the untreated soil. [c] Number in parentheses is the BTEX concentration after 8–11 months.

Calculation of the TPH-Gr rates of degradation (based on best-fit first-order equation during the first 4 months) was highly variable between soils and oils. In general, degradation rates were greater in the high organic Norwood/Baccto soil for the medium (73%/month) and light (81%/month) oil and lower (13–31%/month) for the heavy oil in either soil and for the three oils in the lower organic Norwood soil (Table 1). Lowest hydrocarbon levels in all oily soils were achieved within 4 months, and further biotreatment did not significantly decrease hydrocarbons. TPH-Gr analyses from the soil with heavy crude were the most variable (Figure 1) in which concentrations of TPH-Gr (also TPH-IR, data not shown) in the Norwood/Baccto soil samples varied from 5000 to 13 500 mg/kg during the 9-month treatment. These variations were not observed with the O&G analysis (profile not shown). It is possible that compounds extracted from the high organic soil interfered with removal of polar petroleum hydrocarbons during the silica gel adsorption step for the TPH determination. Indeed, inaccuracies (up to 85% relative error) and biases in the use of silica gel for the determination of TPH in soils containing petroleum products have been discussed by George (*56*). The heavy crude oil contains a larger fraction (44%) of polar material than the medium and light oils.

Analyses of hydrocarbons (mainly saturates and aromatics extracted with CH_2Cl_2) based on a simulated gas chromatographic distillation profile in the range of C_{11}–C_{44} in untreated and bioremediated oily soils are summarized in Table 2. The extent of biodegradation of hydrocarbons was higher (70–90%) for those compounds in the C_{11}–C_{22} range and lower for those in the C_{23}–C_{33} (40–60%) and C_{34}–C_{44} (35–60%) ranges. These degradation values are consistent with the decline in the hydrocarbon concentrations observed in both oily soil types based on TPH-Gr, TPH-IR, and O&G determinations (Table 1). The data also indicate that 8–18% more hydrocarbons were degraded in the higher organic carbon soil (Norwood/Baccto mixture) as compared to the Norwood soil. Residual hydrocarbons (C_{11}–C_{44} fractions) in biotreated soils containing heavy and medium oils was 4500–8200 and 850–1825 mg/kg in the soil with light oil. These hydrocarbon concentrations are also consistent with those TPH residues (8000–10 000 mg/kg for the heavy and medium oily soils and 1000 mg/kg for the light oily soils) that remain after bioremediation (see Figure 1).

Leaching Potential of Oily Soils. It has been recognized that the predominant leachable components from petroleum-containing wastes are the more water-soluble hydrocarbons benzene, toluene, ethylbenzene, and xylenes (BTEX). Table 2 shows data on the residual BTEX components in the six oily soils before and after bioremediation. Solvent-extractable (CH_2Cl_2) B was detected (1.8–64 mg/kg) mainly from the medium and light oils. After 2 months of biotreatment, most soils contained little or no detectable B (<0.02 mg/kg). Initial TEX concentrations (35–1624 mg/kg) in the Norwood/Baccto soils were also reduced to low levels (<0.02 mg/kg) during the same period. Although residual TEX from the medium and light oils (2 and 56 mg/kg) were detected in the Norwood soil after 2 months, these hydrocarbons were below the detection level after 8–11 months. Data on batch and column leaching experiments on the oily soils are summarized in Table 3. Soluble O&G levels in aqueous (neutral pH) batch extractions were only 10–30 mg/L in the bioremediated soil after the first extraction (Table 3, Section A). Subsequent extractions reduced the O&G levels to <5–15 mg/L. No BTEX compounds (<5 μg/L) were detected in the first or subsequent O&G extracts. Soil column leaching tests (Table 3, Section B) also showed that the highest B leachate concentrations (900–10 000 μg/L) were from the soils containing medium and light crude oils and lowest in soils weathered with heavy crude. Biotreated soils had substantially reduced levels of BTEX after 10–30 column pore vol varying from <1 to 50 μg/L leachate from initial high levels of 10 000 μg/L. We also observed that no heavy metals such as V, Ni, or Cu were released (<0.4 mg/L leachate) from any oily soil during the column leaching experiment. These data indicate that

TABLE 3. Leaching Potential of [redacted]oils in Batch Extractionand Column Leaching Test[redacted]

Section A: Batch Extraction—Hydrocarbon Levels after Bioremediation[a]

soil	oil	O&G (mg/L) after extraction[b] 1	2	3	5
Norwood	heavy	15	11	7	<5
	medium	30	17	12	9
	light	12	<5	<5	<5
Norwood/Baccto	heavy	16	11	9	6
	medium	31	16	14	8
	light	<5	<5	<5	<5

Section B: Soil Column—Hydrocarbon Levels (μg/L Leachate) before and after Bioremediation[a,c]

soil	oil	B untreated	B bioremediated	TEX untreated	TEX bioremediated
Norwood	heavy	<2	<2	17	2
	medium	630	<2	5260	8
	light	4900	<2	18270	6
Norwood/Baccto	heavy	160	<2	700	<2
	medium	1660	<2	5980	48
	light	7690	<2	16980	5

[a] 8–11 months treatment. [b] TPH and BTEX concentrations in aqueous extractions were <5 mg/L and <5 μg/L, respectively. [c] Values given are the BTEX concentrations in the first 2–3 pore volumes of leachate.

TABLE 4. Earthworm (*Eisenia*) and Microtox Tests on Oily Soils

Section A: Earthworm Survival[a]

soil	oil	LC50 as % soil after bioremediation month 0	0.5	1	3	5	8	10	12
Norwood	heavy	22	26	28	100	92	100	100	—[b]
	medium	4	9	4	22	90	100	100	—
	light	1	1	1	6	30	—	66	100
Norwood/Baccto	heavy	34	27	100	100	100	100	—	—
	medium	10	4	79	100	100	100	—	—
	light	1	9	23	100	100	100	—	—

Section B: Microtox[c]

soil	oil	EC50 in percent soil after bioremediation month 0	0.5	1	3	5	8	10
Norwood	heavy	100	—	—	—	—	100	—
	medium	52	88	30	81	100	100	—
	light	36	53	49	67	68	100	100
Norwood/Baccto	heavy	7	7	100	100	100	—	—
	medium	33	92	44	100	100	—	—
	light	41	63	42	100	100	—	—

[a] Percent survival after 2 weeks incubation in dilutions of oily soil. [b] (—) not done. [c] Solid phase modification.

bioremediated oily soils will contain very low levels of leachable aromatic hydrocarbons. Oily soils of similar composition that are undergoing land treatment remediation would present a very low risk from BTEX infiltration to the subsoil and groundwater environment since it is well known also that BTEX concentrations of 10–5000 μg/L are rapidly biodegraded by naturally-occurring soil microbes (*57*). There have been reports demonstrating the low leachability of oily waste components from soil. Huddleston and Myers (*3*) showed that heavy metals and water-soluble organics leaching was <0.01 to <1% of the total metal and organic content of refinery oily waste during rainfall simulation experiments. Bioremediation studies by Huesemann and Moore (*7*) on a weathered Michigan crude oily soil also showed that no BTEX (<1 μg/L leachate) was detected in batch extractions (pH 7) of the soil. Laboratory lysimeter experiments by Dibble and Bartha (*58*) on land treatment of refinery oily sludges (5% w/w) in an acidic (pH 3.7) sandy loam showed that little or no ether-extractable (O&G determination) material was detected in column leachates of bioremediated waste. More recently, Gould and Pardus (*44*) presented a simple one-dimensional model to describe the potential for migration of organic compounds to groundwater by estimating leaching potential using soil/waste characteristics, contaminant concentrations, rainfall rates, soil hydraulic conductivity, groundwater gradients, and distance to receptor wells. These types of models would be helpful in assessing the mobility of residual hydrocarbons (e.g., BTEX) in treated and untreated oily soils.

Earthworm Survival and Microtox Assays. In estimating the environmental toxicology and efficacy of the bioremediation process on oily soils, we chose tests utilizing representative soil-dwelling species such as earthworms and plants. In the earthworm bioassay, survival of adult *Eisenia* was determined after a 2-week exposure to soil. These results shown in Table 4, Section A, indicate that all oily soils were acutely toxic to *Eisenia* in the first 2–4 weeks of the bioremediation experiment. The Norwood soils with heavy, medium, and light oils were toxic to earthworms for at least 8 months. In contrast, all animals survived in the three

TABLE 5. Effects of Oily Soil Bioremediation on Seed Germination[a]

soil	oil	TPH-Gr (mg/kg in soil)		% germination in soil					
				untreated			bioremediated		
		untreated	bioremediated	corn	wheat	oat	corn	wheat	oat
Norwood	none	ND[c]	523	90, 77[b]	90, 92[b]	89, 87[b]			
	heavy	14 000	7 000	81	89	68	87	87	95
	medium	26 600	8 600	100	81	95	85	82	95
	light	4 200	1 000	74	51[d]	19[d]	82	77	90
Norwood/Baccto	none	ND	523	93, 83[b]	92, 86[b]	70, 92[b]			
	heavy	11 900	10 800	93	86	88	73	72	88
	medium	25 700	8 200	97	25[d]	71	84	89	96
	light	9 600	1 200	4[d]	0[d]	0[d]	89	88	83

[a] Determined after 10 (Norwood) or 8 (Norwood/Baccto) months treatment. [b] Different values represent the variation in seed germination of control (no oil and untreated) soil initially and after 8–10 months. [c] Not done. [d] Values are significantly ($p < 0.01$) less than the control soil with no oil.

TABLE 6. Effects of Oily Soil Bioremediation on Plant Growth[a]

soil	oil	plant growth (mg dry wt/plant in soil)					
		untreated			bioremediated		
		corn	wheat	oat	corn	wheat	oat
Norwood	none	82.1, 68.4[b]	15.2, 18.3[b]	16.6, 14.3[b]			
	heavy	119[c]	16.7	8.2[c]	88.8	16.9	14.3
	medium	123[c]	12.1[c]	8.3[c]	91.3[c]	15.6	16.9
	light	83.7	8.3[c]	5.1[c]	68.9	10.3[c]	8.2[c]
Norwood/Baccto	none	73.4, 58.9[b]	16.3, 18.4[b]	12.5, 13.9[b]			
	heavy	135[c]	19.0	17	40.3[c]	14.5	9.5[c]
	medium	113[c]	9.4[c]	8.2[c]	98.9[c]	18.4	16.5
	light	46[c]	0[c]	0[c]	60.5	18.7	11.7

[a] Determined after 10 (Norwood) or 8 (Norwood/Baccto) months treatment. For corresponding TPH concentrations before and after bioremediation, see Figure 8. [b] Different values represent the variation in plant weight of control (no oil and untreated) soil initially and after 8–10 months. [c] Values are significantly ($p < 0.05$) less than or greater than the control soil with no oil.

Norwood/Baccto oily soils after only 3–5 months treatment. We previously showed (Figure 1) that the maximum reduction in oil hydrocarbons (TPH) was usually after 3–5 months for both soil types. In general, loss in earthworm toxicity appeared to correlate with optimum hydrocarbon biodegradation with the exception of the low organic Norwood soil. It is not known why toxicity persisted in the Norwood soils; however, it is possible that residual or uncharacterized petroleum compounds (undegraded or incompletely metabolized) contributed to the acute effects on *Eisenia* survival. In contrast, hydrocarbons may have degraded more rapidly or were sequestered (not bioavailable) in the higher organic Norwood/Baccto soil.

Results of the solid phase Microtox assay utilizing sensitivity to the luminescent microbe, *Photobacterium*, to dilutions of oily soils are shown in Table 4, Section B. The Microtox test appears to be less sensitive and more variable than the earthworm bioassay. Also, bioremediated soils lose most of their Microtox inhibiting activity after 3 months.

Seed Germination and Plant Growth. Data on the effects of heavy, medium, and light oily soils on the 21-day seed germination and plant growth bioassays before and after bioremediation are summarized in Tables 5 and 6. In the untreated soils, seed germination for corn, wheat, and oat species was inhibited (50–100%) by the presence of 25 000–26 000 and 4200–9600 mg/kg TPH, respectively, of medium and light crude oils. In contrast, seed germination in the bioremediated soils was not significantly different from control soils that contained no crude oil (Table 5). It is interesting to note that the residual TPH in which germination was not affected in both bioremediated soils varied from 7000 to 10 000, from 8200 to 8600, and from 1000 to 1200 mg/kg for the heavy, medium, and light oily soils, respectively.

Results of the effects of oily soils on plant growth (Table 6) show that, in the untreated material, heavy and medium crude oils significantly enhanced growth (mg/plant dry wt) of the corn plant by 40–70% over control plants grown in oil-free soil. The growth stimulating effect was still apparent in the bioremediated soils. This enhanced effect of crude oil hydrocarbons on plant growth has been reported in the literature. Over 75 years ago, Carr (*59*) observed that soybean yields increased at least 50% in field plots of a sandy peat soil with 7500 mg/kg oil from an accidental pipeline release. Concentrations of crude oil in soil ≥25 000 mg/kg, however, affected nodule formation and growth. Also, Baker (*60*) cited (a) studies on increased yields of saltmarsh grass exposed to soils containing a heavy crude fraction (high boiling cut) of Kuwati oil and (b) experiments by Russian workers on increased crop yields associated with a heavy polar oil fraction containing naphthenic acids. In our studies, growth yields of germinated wheat and oat seeds were significantly reduced (20–70% less) in both untreated soils containing medium and light oils. After 8–11 months bioremediation, wheat and oat growth yields were significantly improved and similar to control plants grown in oil-free soil. However, some plant growth inhibition was still apparent in both soil types with the heavy, medium, and light oils. This reduction in growth between plant species (corn, wheat, and oat) varied from 0 to 40% from the control (no oil) soils. These results indicate that undegraded petroleum compounds (other than BTEX) or metabolites may be affecting plant growth. The phytotoxicity of petroleum hydrocarbons has not been studied sufficiently in recent years. Work by Baker (*60*) and Currier and Peoples (*61*) several years ago indicated that high concentrations of light hydrocarbons (octane, decane), aromatics (BTEX), and naphtha(cyclohexanes) and phenolic-like compounds reduced respiration, transpiration, and photosynthesis in grasses (barley, mustard) and crop plants (carrot, citrus). More current experiments by Wang and Bartha (*62*) showed that soybean and rye germination and

dry wt yield in soil lysimeters contaminated with a jet fuel, heating oil, or diesel fuel (5[illegible]0–75 000 mg/kg) were significantly improved after 2–5 months biotreatment. In field plot studies of land treating heavy crude oils, Raymond et al. (*26*) observed that although 30–50% of the initial O&G levels (25 000–35 000 mg/kg) were degraded in 6 months, germination and growth of radish, beans, and turnip plants were restricted, indicating that residual hydrocarbons or metabolites were phytotoxic. Huddleston and Myers (*3*) applied a mixed oily waste (15% w/w) to field plots and showed that soils which contained 17 000–22 000 mg/kg residual hydrocarbons had no adverse effects on wheat and bermuda grass germination and growth. These latter studies suggest that hydrocarbon phytotoxicity cannot be predicted and varies widely with oil and soil type, concentration and plant species tested.

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ECOTOXICOLOGICAL AND ANALYTICAL ASSESSMENT OF HYDROCARBON-CONTAMINATED SOILS AND APPLICATION TO ECOLOGICAL RISK ASSESSMENT

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Abstract—Ecotoxicological assessments of contaminated soil aim to understand the effect of introduced chemicals on the soil flora and fauna. Ecotoxicity test methods were developed and conducted on hydrocarbon-contaminated soils (<5,000–30,000 mg/kg total petroleum hydrocarbon) and on adjacent uncontaminated control soils from eight field locations. Tests included 7-d, 14-d, and chronic survival tests and reproduction assays for the earthworm (*Eisenia fetida*) and seed germination, root length, and plant growth assays for corn, lettuce, mustard, and wheat. Species-specific responses were observed with no-observed effect concentrations (NOECs) ranging from <1 to 100% contaminated soil. The 14-d earthworm survival NOEC was equal to or greater than the reproduction NOEC values for numbers of cocoons and juveniles, which were similar to one another. Cocoon and juvenile production varied among the control soils. Germination and root length NOECs for mustard and lettuce were less than NOECs for corn and wheat. Root length NOECs were similar to or less than seed germination NOECs. Statistically significant correlations ($p < 0.05$) for earthworm survival and seed germination as a function of hydrocarbon measurements were found. The 14-d earthworm survival and the seed germination tests are recommended for use in the context of a risk-based framework for the ecological assessment of contaminated sites.

Keywords—Soil Terrestrial ecotoxicity Earthworms Petroleum hydrocarbons

INTRODUCTION

Introduction of organic or inorganic contaminants into the soil may alter the natural soil chemistry, thereby resulting in changes in micro- and macroscale biotic communities. Soil is fundamental to the diverse communities of microbes, plants, and invertebrate and vertebrate animals that comprise the terrestrial ecosystem; thus, understanding the effects and risks of contaminated soil sites in relation to ecological receptors is important. Risk-based decision criteria for contaminated sites are being more fully developed in response to increased assessment and remediation costs and in response to the uncertainties associated with adequate protection of the environment [1,2]. Risk assessment tools for terrestrial ecosystems are less well developed but are essential for the protection of the ecosystem [3,4].

A recent review of research strategies revealed a diverse range of approaches to understanding the complex nature and interaction of contaminants in the soil matrix [5]. This review presented laboratory and field studies that showed that the biological availability of chemicals to receptors, such as microbes and soil organisms, may be altered by binding to soil particles. Furthermore, the rate and extent that a chemical is released from the soil into the vapor and/or aqueous phases may change over time [5,6]. By definition, reduced availability of a chemical within the soil correlates with a lower dose and/or less exposure of the chemical to the ecological receptor. Decreased availability of a chemical may also alter its mobility and transport in the environment. Thus, the total concentration of a contaminant in soil may not give the site assessor adequate or accurate information regarding ecological risk [1,5].

Biological assays have been developed by the Organization for Economic Cooperation and Development (OECD), by the U.S. Environmental Protection Agency (U.S. EPA), and by individual researchers for use in assessing soil toxicity related to earthworms (*Eisenia fetida*) [7–9], plants [9–11], and bacteria [12]. This broad group of tests, referred to as "ecotoxicity tests" in this paper, were developed in order to quantify the toxicological impact of chemicals on ecological receptors. Ecotoxicity testing has been used in combination with contaminant concentration measurements to assess risks associated with contaminated and remediated soils and sediments in site assessments [10,13]. Ecotoxicological tests are also being used as a tool to monitor bioremediation of hydrocarbon and other wastes, both in the laboratory and in the field [9,14–16]. The use of biologically based endpoints may help appropriately define acceptable clean-up standards [5,15].

Oil production, refining, and marketing operations may result in surficial soils that are enriched with petroleum hydrocarbons. Factors influencing the bioavailability of petroleum hydrocarbons in soils and the impact of fresh and aged hydrocarbons on terrestrial receptors are both under investigation. Few studies on the toxicity of soils either spiked with hydrocarbon mixtures in the laboratory or contaminated in the field have involved the use of various bacterial, plant, and earthworm assays [9,11,16,17]. Most of these studies noted that the type of oil and soil were important in predicting toxicological responses. However, none of the studies provides

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Table 2. Ecotoxicity tests conducted on field soils

Test	Soil 2	Soil 4	Soil 6	Soil 8	Soil 9	Soil 14	Soil 17	Soil 18
Earthworm								
Avoidance	+[a]	+	+	+	−	−	+	+
7-d Survival	+	+	+	+	−	+	+	+
14-d Survival	+	+	+	+	−	+	+	+
Chronic survival	+	+	+	+	−	−	+	+
Reproduction: juveniles/adult/week	+	+	+	+	−	−	+	+
Reproduction: cocoons/adult/week	NR[b]	+	+	+	−	−	+	+
Plant								
Corn: germination and root length	DE[c]	+	+	+	+	+	+	+
Lettuce: germination and root length	DE	DE	DE	DE	DE	DE	DE	DE
Mustard: germination and root length	DE	+	+	+	+	+	+	+
Wheat: germination and root length	DE	+	+	+	+	+	+	+
Plant growth test	—[d]	+	NR	−	−	−	−	−
Rapid life-cycle *B. rapa*	NR	NR	NR	NR	−	−	NR	NR

[a] Test conducted, data reported, and data included in correlation analysis.
[b] Test conducted and data are not reported because of a failure of test method.
[c] Test conducted, data reported, and data excluded from correlation analysis.
[d] Test not conducted.

to C_{25} range was identified and quantified using a gas chromatography (GC) method developed at Shell's Westhollow Technology Center (Houston, TX, USA). In this method, the soil was extracted with pentane and the extract analyzed by GC with flame ionization detection.

A more complete speciation of the hydrocarbons, into classes including *n*- and *iso*-alkanes, aromatics, polar compounds, and asphaltenes, was also conducted by Core Laboratories (Houston, TX, USA). For these analyses, the soils were extracted with carbon disulfide (CS_2) (U.S. EPA method 3550A modified [19]), and a portion of this extract was analyzed by GC for C_5 to C_9 hydrocarbons (ASTM method D5134-90 modified [25]). The CS_2 solvent was then evaporated from the remainder of the extract, and the resulting residue was weighed to yield the gravimetric CS_2-extractable value. The residue was then dissolved in pentane and filtered (0.45 μm pore size). The pentane-insoluble fraction was quantified as the asphaltene fraction (ASTM method D3279-90 modified [26]). The pentane-soluble fraction was then loaded onto a silica gel column and eluted with pentane, to isolate the alkanes; with diethyl ether, to recover the aromatics; and with chloroform and ethanol, to isolate the polar compounds. The solvent was evaporated from each fraction, and the concentration of the hydrocarbon residue was determined gravimetrically (ASTM method D2549-91 modified [25]). The pentane-soluble residue was then redissolved in CS_2 and subjected to high-temperature simulated distillation to obtain the carbon number distribution of the various fractions (ASTM method D2887-89 modified [25]). Ring distributions of the recovered alkanes and aromatics were obtained by mass spectrometry (MS) (ASTM methods D2786-91 and D3239-91 [25]). Further analysis of the alkane fraction by GC-MS was used to determine the relative amounts of *n*- and *iso*-alkanes.

Quantification of 16 target PAH compounds in the soils was conducted by RECRA Labnet (Houston, TX, USA). The method involved extraction with dichloromethane and analysis by GC-MS (U.S. EPA method 8270B [19]). Benzene, toluene, ethylbenzene, and xylenes (BTEX) concentrations were determined by purge-and-trap GC-MS of a methanol extract of each of the soils (U.S. EPA method 8260 modified [19]).

Weathering (transformation) of the crude oil in the contaminated soils was established qualitatively by inspection of the GC chromatograms [27]. When normal (*n*)-alkanes predominate over branched (*iso*)-alkanes, the crude oil is characterized as slightly weathered. As biological transformation and volatilization occur; the *n*-alkanes decrease in abundance relative to the branched alkanes. A moderately weathered sample is described as one with dominant *iso*-alkanes but with some *n*-alkanes present. A highly weathered sample is described as one with only *iso*-alkanes (i.e., pristane and phytane) present.

Soil preparation

Before toxicity testing, deionized water was added to each control soil until it was moist, but water did not drip from the sample when it was squeezed between thumb and forefinger. The moisture content of the wetted soils was measured with a CEM Lab Wave 9000 Moisture/Solids Analyzer (CemCorp, Mathews, NC, USA). The measured value became the target moisture content for future tests for that control soil and its associated contaminated soil.

Before each test, a range of dilutions of contaminated soil was prepared by mixing a hydrocarbon-containing soil with its partner, uncontaminated (control) soil. For example, a 10% soil concentration was prepared with 10 weight% (wt%) contaminated soil mixed with 90 wt% control soil. Dilutions were calculated on a dry-weight basis and were produced by hand-mixing the soils. Immediately before each test, deionized water was added to the soil to achieve the target moisture content. Soil amounts for all assays are given on a dry-weight basis.

Earthworm assays

The earthworm avoidance, survival, and reproduction protocols were adapted from a number of sources [7,8,28,29] and from OECD 207 [30]. Table 2 lists the conducted earthworm bioassays.

Laboratory cultures of *E. fetida* were purchased from Carolina Biological Supply (Burlington, NC, USA). Cultures were established and maintained for up to a year in moist peat that had been adjusted to neutral pH. The cultures were loosely covered with plastic and were maintained at ambient temperature (23°C) under continuous light. The earthworms were fed alfalfa paste that was added to the top surface of the soil, such that alfalfa was visible at all times. The paste was prepared by adding dry alfalfa pellets to deionized water (1:3, by

For these assays, the test chambers were constructed from PVC pipes (2.5-cm internal diameter; 25-cm length for wheat and corn tests, 13-cm length for lettuce and mustard tests). The test chambers were filled with soil, and a single seed was pressed gently into the surface of the soil. The bottom of each tube was covered with four layers of gauze, which were fixed in place with silicon sealant or a tie-wrap. Thirty chambers were prepared for each soil treatment for each test species, and each set of chambers was placed in a box. The test chambers were illuminated under six 40-W fluorescent bulbs with a 16:8-h light to dark photoperiod at 23°C. At approximately 5-d intervals, water was added to the boxes up to the level of the soil in the chambers, left for 1 h, and then emptied, allowing the soils to drain to field capacity. Twice during the test, 5 ml of one-half–strength Hoagland's solution [35] was applied to the soil at the top of each chamber. Germination of the seeds was recorded daily, and the plants were harvested at day 19 (17 d after 50% seed germination in control soils). The soil core within each tube was soaked in water, and the entire root mass was then easily separated from the soil. The plants were blotted dry, and the belowground (root) and aboveground (shoot and leaves) wet weights were recorded to the nearest 0.01 g.

Rapid life-cycle *Brassica rapa* can pass through a complete life cycle, from germination to seed set, in 35 to 40 d. Wisconsin Fast Plant kits were purchased from Carolina Biological Supply. The kit method was modified to include four test chambers each of the control soils 2C, 4C, 6C, 8C, and 17C/18C and of the 100% contaminated soils 2, 4, 6, 8, 17, and 18 in addition to eight chambers for the supplied vermiculite/potting soil mixture. Ten grams of soil and three slow-release N-P-K fertilizer pellets were added to each test chamber. In each chamber, three seeds were placed in a depression and then covered with soil. Initially, the chambers were watered on top until water dripped from the wicks. To sustain moisture in the chambers, a wick extended through a hole in the bottom of each test chamber to a watering mat. The chambers were then placed 10 cm beneath six 40-W fluorescent bulbs. As the plants grew, the lights were raised. Five days a week, the capillary watering was supplemented by watering on top (2-4 ml water per chamber). On day 7, chambers containing more than one plant were thinned to one plant per chamber. If one chamber contained more than one plant and another chamber of the same soil contained no plants, a plant was transplanted from the chamber with a surplus to the chamber without a plant. On days 15 to 18, open flowers were artificially cross-pollinated using a dead bee impaled on a toothpick, provided in the test kit. On day 18, unopened buds were pinched from the plants. On day 38, the chambers were removed from the watering mat and left on a dry surface for an additional 5 d. The seeds in the pods of each plant were collected separately and counted. Aboveground wet weights of the plants were then determined, as described previously.

Data analyses

All seed germination and root length tests were subjected to an initial screening for test acceptability. Control germination must have been greater than or equal to 65% [32]. Tests conducted in both the light and dark are reported. However, only tests conducted in the dark were used in subsequent data analyses [32].

No-observed effect concentrations (NOECs) were estimated for earthworm avoidance, for earthworm survival in the 7-d, 14-d, and chronic tests, for earthworm reproduction, for seed germination, and for root length assays. In the earthworm avoidance tests, earthworms were found in one of four quadrants. Given this experimental design, the avoidance test results followed a multinomial distribution. The NOEC was determined by comparing the number of earthworms found in each of the contaminated soil quadrants with that in the control, using a one-sided z-test for proportions under normal approximation. For earthworm survival, significant differences between treatment soils and control soils were determined by pairwise contrasts using Fisher's exact test.

For earthworm reproduction, seed germination, and root length, NOECs were obtained by statistically comparing the responses in the treatment soils with those in the control soils. For the earthworm reproduction tests, the data were normalized as cocoons/adult/week and juveniles/adult/week. Soil concentrations greater than the chronic survival NOECs were excluded from the reproduction NOEC determinations. For the plant tests, percent germination and mean root length per replicate were used as response parameters. Soil concentrations with no germination were excluded from the germination NOEC determination. Root length NOEC values were calculated by excluding data from soil concentrations greater than the germination NOEC. In general, our exclusion criteria followed U.S. EPA guidelines for effluent toxicity tests [36]. Before determining the NOEC, the assumption of a normal distribution was tested using Shapiro-Wilk's test, and homogeneity of variance was tested using Bartlett's test. In order to calculate the NOEC, Dunnett's t test or Bonferroni t test for multiple comparisons was used to compare each treatment mean to control mean for data that met the parametric assumptions in tests with equal or unequal replicates, respectively. When the data did not meet the normality or equal variance assumptions, the Mann-Whitney U test was used. The analyses were performed at an $\alpha = 0.05$, using TOXSTAT and STATGRAPHICS software [37,38].

Two-way analysis of variance (ANOVA) was used to evaluate soil effects, plant species differences, and possible interactions on germination and root length. The calculated NOEC values were used in this analysis. The data set was unbalanced because of limited data for soil 2 for all species and from lettuce tests for most soils; thus, interaction effects could not be determined. Therefore, this data were eliminated from further inspection by ANOVA. Initial analysis indicated a significant interaction term between soil and plant species for germination. However, the interaction was minor, since the interaction plot showed generally similar patterns of response for each species across the different soils. Therefore, the ANOVA was rerun without the interaction term. In this reanalysis, the least significant difference was used to investigate differences between factor levels.

One-way ANOVA was used to test for effects of control soil on the production of earthworm cocoons and juveniles. Juveniles/adult/week and cocoons/adult/week were used in this analysis. Statistically significant differences ($p \leq 0.05$) were determined. The least significant difference was used to investigate differences between factor levels.

Relationships between physical–chemical parameters, hydrocarbon measurements, and physical–chemical and hydrocarbon parameters and the bioassay endpoints (average NOEC values from several tests) were evaluated with Pearson product–moment correlation coefficients using Statgraphics programs [38]. Based on an incomplete data set and because of

Table 3. Physical–chemical characterization of field soils

Physical–chemical test	Soil 2C	Soil 2	Soil 4C	Soil 4	Soil 6C	Soil 6	Soil 8C	Soil 8	Soil 9C	Soil 9	Soil 14C	Soil 14	Soil 17C/ Soil 18C	Soil 17	Soil 18
Soil category[a]	C	HC	C	HC	C	HC	C	HC	C	HC	C	HC	C	HC	HC
pH	8	8.3	7.5	7.5	7.1	7	7.8	7	8.4	6.3	8.8	6.7	7.3	6.4	6.8
EC[b] (mmhos/cm)	2.7	1.2	0.32	4.0	0.73	3.3	0.37	0.6	0.9	8.8	0.7	3.0	0.72	0.44	0.41
Texture															
Sand (%)	2	7	82	78	63	64	84	80	64	77	68	76	84	84	89
Silt (%)	48	47	2	20	16	12	9	10	13	2	13	14	2	10	4
Clay (%)	50	46	16	2	21	24	7	10	23	21	19	10	14	6	7
Soil classification[c]	SC	SC	SL	LS	SCL	SCL	LS	LS	SCL	SCL	SL	SL	LS	LS	S
Bulk density (g/cm^3)	1.6	1.6	1.6	1.6	1.5	1.5	1.7	1.6	1.6	1.4	1.5	1.5	1.7	1.7	1.7
Particle density (g/cm^3)	2.6	2.5	2.7	2.7	2.6	2.5	2.6	2.6	2.6	2.7	2.6	2.6	2.6	2.6	2.6
Porosity (%)	39	38	38	41	42	41	35	38	41	48	44	45	33	34	34
Total metals (mg/kg soil)															
Ag	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
As	6.5	7.8	0.9	2	3.4	4.7	1.2	1.2	9	9	7.5	4.6	0.9	1	0.7
Ba	580	680	24	40	59	84	42	12	140	1,800	64	107	24	13	10
Cd	2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	1	<1	<1
Cr	4	37	4	4	9	9	4	5	20	42	15	12	10	3	4
Hg	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pb	18	12	10	10	13	27	24	12	3	15	1	15	13	10	12
Se	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	0.4	0.4	0.1	0.3	0.1	0.1	0.1	0.1	<0.1
Zn	59	50	25	48	34	46	17	18	33	160	28	82	27	35	120
NO_3-N (mg/kg soil)	0.5	0.5	3.0	0.6	2.9	0.4	2.2	1.8	4.1	0.5	5.3	0.4	16	0.2	0.5
NH_4-N (mg/kg soil)	30	25	32	28	37	25	41	29	47	56	29	24	19	37	38
Total P (mg/kg soil)	270	240	150	210	270	240	190	200	410	770	420	290	210	320	350
TOC (%)	0.2	0.4	0.2	2.6	1.0	2.1	0.2	0.6	0.2	5.7	0.2	1.8	0.3	0.7	1.9
Target moisture content[d]	0.20	0.20	0.11	0.11	0.15	0.15	0.063	0.063	0.14	0.14	0.12	0.12	0.099	0.099	0.099

[a] C = uncontaminated (control) soil; HC = soil containing hydrocarbons.
[b] EC = electrical conductivity.
[c] SC = silty clay; SL = sandy loam; LS = loamy sand; SCL = sandy clay loam; S = sand.
[d] (g-water/g-dry soil). Set by laboratory personnel at project initiation.

within species. Comparisons among different growth endpoints for corn and wheat could not be made, because NOECs were lower than the lowest soil concentration tested. Differences among species were identified by comparing NOECs from the plant growth tests with the germination and root length tests (Table 8). Plant growth, germination, and root length endpoints were similar for lettuce and mustard. Although difficult to evaluate for corn and wheat, plant growth appeared more sensitive than germination and was equally or more sensitive than root length.

Assay variability

The earthworm reproduction response of juveniles/adult/week was more variable than the response of cocoons/adult/week. For control soils 4C, 6C, 8C, 17C, and 18C, coefficients of variation (CVs) were calculated using the mean and standard deviation results given in Table 5. Coefficients of variation for cocoons/adult/week ranged from 3 to 23%, whereas CVs for juveniles/adult/week ranged from 11 to 120%. Similar trends were observed for responses to the contaminated soils.

Repeated toxicity tests on a soil resulted in similar NOEC values on some soils (e.g., corn germination on soil 4) and NOEC values different by a factor of 10 on other soils (e.g., mustard root length on soil 4) (Table 7). Investigation of the total variance in the seed germination data over all soils showed that the contribution from variance from test date was small compared to the variance among replicates for most species. The mean repeatability of the germination tests over all soils for the four species ranged from 16% for corn to 40% for lettuce (Table 9). The calculated mean repeatability of 26% for wheat germination indicates that germination can differ up to 26% between two replicates within a single test date and yet not differ significantly ($p \leq 0.05$). The calculated percent repeatability for germination indicated that variability between replicates within a single test date was highest for lettuce and lowest for corn.

For the root length data, variance due to individual plants within the test chamber was greater than variance from test date or variance among replicates. Repeatability in root length ranged from 2.0 mm for lettuce to 5.2 mm for corn (Table 9). For example, the calculated mean repeatability of 4.3 mm for wheat indicates that root lengths between two replicates within a single test date can differ up to 4.3 mm and yet not differ significantly ($p \leq 0.05$). When normalized to mean root length over all control soils, percent repeatabilities were similar among species ranging from 87 to 111%. Root length percent repeatability was greater than germination percent repeatability by a factor of two to six. Thus, root length is more variable than germination among replicates for all plants.

Correlating soil and hydrocarbon parameters with toxicity

The range of responses of one endpoint across soils and of different endpoints on a single soil emphasized the need to understand the observed toxic effects in relation to measured physical–chemical parameters and hydrocarbon contents. Correlation analysis showed that several hydrocarbon and physical–chemical parameters were significantly correlated to the bioassay endpoints (Table 10). For each test endpoint, the hydrocarbon parameters were ordered based on the absolute value of the correlation coefficient. Endpoints were grouped as described below, so that the hydrocarbon parameters that were consistently at the top of the rankings could be identified.

Earthworm avoidance and survival in the 7-d, 14-d, and chronic assays were each significantly correlated with hydrocarbon measurements. The highest ranking parameters for earthworm avoidance and survival were TPH by GC, polar compounds, and *n*- and *iso*-saturates. Earthworm reproduction endpoints were most highly correlated with soil texture and metal constituents. The highest ranking hydrocarbon parameter for earthworm reproduction was gravimetric TPH. Corn and wheat germination were most highly and significantly correlated with several hydrocarbon measurements, TOC, and EC. For plant germination, the identified hydrocarbon parameters were polar compounds, asphaltenes, and TPH by GC. In general, root length endpoints correlated poorly with physical–chemical and hydrocarbon parameters. The highest ranking hydrocarbon parameters for root length endpoints were asphaltenes and total aromatics. Plots of ecotoxicity test endpoints as a function of identified hydrocarbon parameters were constructed for all described cases; two are reviewed in the Discussion (Figs. 4 and 5).

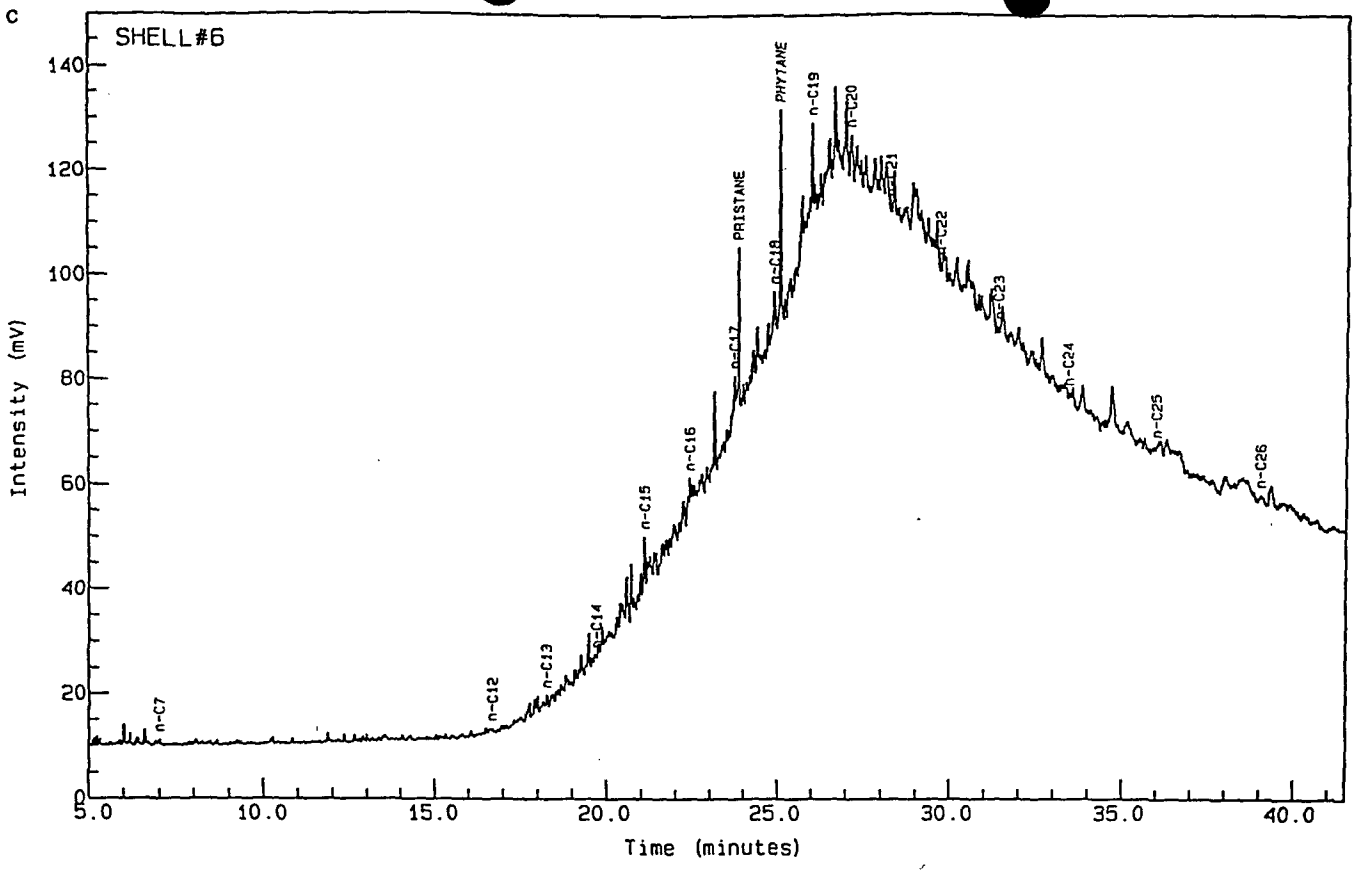
DISCUSSION

Development of earthworm testing protocols

One objective for conducting this study was to develop and refine laboratory testing procedures applicable to field soils. Earthworm survival and reproduction tests were successfully conducted on control field soils that had a range of physical–chemical characteristics. Earthworm survival tests were relatively easy to conduct and required little maintenance. The modified extraction procedure for juvenile earthworms was effective and rapid; in contrast, extracting and counting cocoons using the sieving technique were tedious and time consuming.

Reproductive responses of earthworms in the control soils varied with a mean cocoons/adult/week rate of 1.3 to 2.9. These rates, and the mean production of juveniles/cocoon, are similar to those observed by van Gestel et al. [8] and Hartenstein et al. [41]. Variability in cocoon production may depend on soil texture and other physical–chemical properties of soils [42]. It is imperative that contaminated field soils be tested with a field reference soil that has similar physical–chemical properties and that lacks contamination. Thus, contaminant constituents are diluted while the background soil properties remain constant, and poor tolerance of the species for the field soil will not be confused with the effects caused by the contaminant. Laboratory soils, such as the OECD reference soil [30], may not be appropriate controls for testing field soils, except as a control for the health of the earthworm culture [42,43].

Several protocol development issues for the earthworm assays need further attention. First, the moisture content of the soils tended to increase during testing. Presumably, additional moisture entered the system through the alfalfa paste during food application. Thus, use of a thicker paste may be desirable. Second, the feeding strategy is not yet optimized. Gibbs et al. [7] noted effects on earthworm growth and reproduction that were attributed to differences in amounts of food. It is unlikely that these factors dramatically affected our results, because excess food was always available; however, additional studies to refine the procedures are desirable.



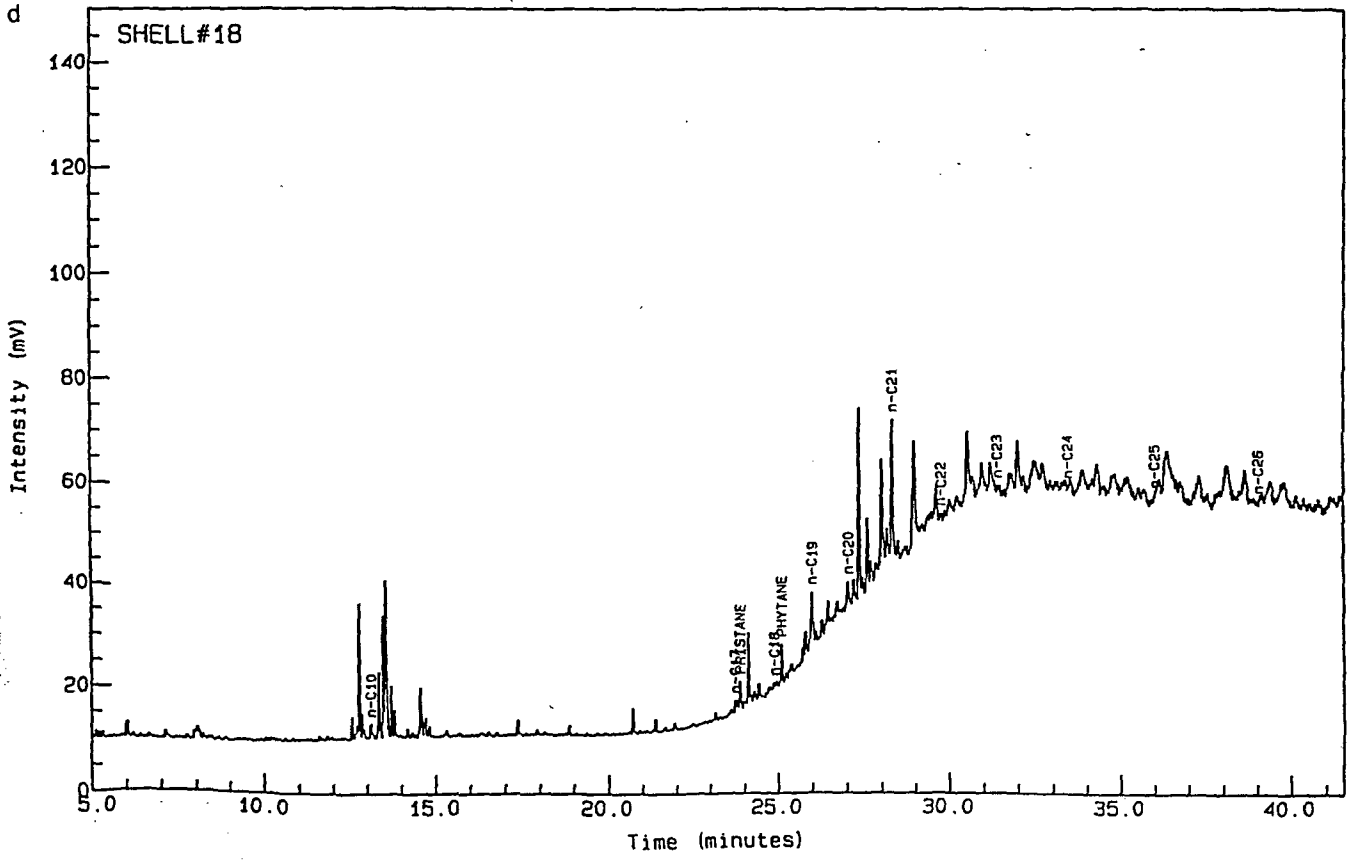


Fig. 1. Continued

Table 7. Selected corn and mustard seed germination (germ) and root length (RL) no-observed effect concentrations (NOECs)

Plant test	Test no.	NOEC (% Concentration of contaminated soil)							
		Soil 2	Soil 4	Soil 6	Soil 8	Soil 9	Soil 14	Soil 17	Soil 18
Corn germ	1	100	100	30	100	30	100	100	100
	2	100	100	100	100	30	100	100	100
	3	—	100	100	100	—	—	30	100
	4	—	—	—	—	—	—	100	—
Mustard germ	1	<10[a]	3	10	10	1	1	3	30
	2	10[a]	3	3	10	<0.3	3	10	100
	3	3[a]	10	10	10	—	—	10	100
	4	10[a]	3	—	—	—	—	—	30
Corn RL	1	100	30	<1	10	10	100	30	100
	2	100	10	100	10	<30	100	<10	100
	3	—	10	3	3	—	—	30	100
	4	—	—	—	—	—	—	10	—
Mustard RL	1	<10[a]	1	1	10	0.3	1	3	30
	2	+[b]	3	1	10	<0.3	3	10	100
	3	+[b]	10	1	10	—	—	3	100
	4	+[b]	3	—	—	—	—	—	30

[a] Test done in the light.
[b] Roots broken during extraction.

to the soil and to any contaminant the soil contained. Each chamber contained one or two plants that grew considerably more than the other seedlings, suggesting that plant growth was not independent. Also, the roots of the five plants often entangled, such that the root biomass of individual plants could not be determined. Given these observations, it was determined that too many seeds were planted in each chamber. Although labor-intensive to prepare, the plant growth test that used protocol B with the deeper test chambers largely retained the root and was successfully conducted on one soil. This assay must be tested further to determine its utility with soils of different textures. In the *B. rapa* assay, germination of seeds on the field control soils was 17 to 50%, whereas germination on the vermiculite/potting soil was 92%. If the *B. rapa* assay is to be used for assessing field soils, additional work may be needed.

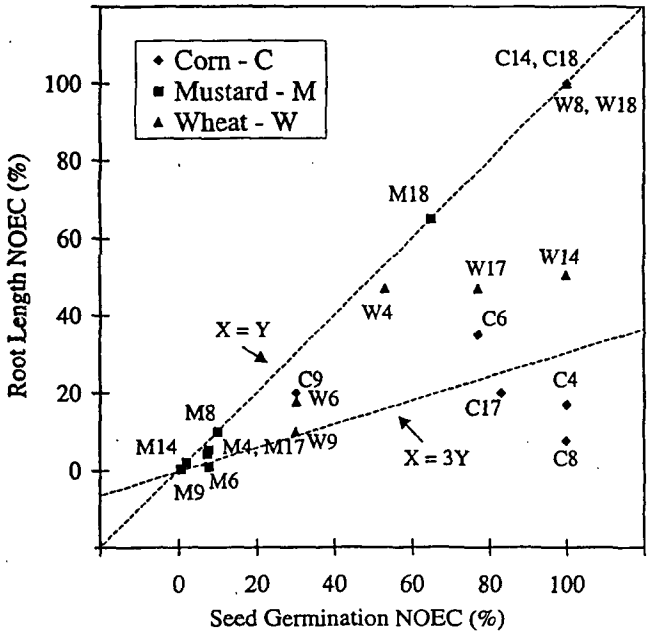


Fig. 3. Average germination and root length no-observed effect concentrations (NOECs) for corn, mustard, and wheat. For NOECs listed as "<X" in Table 7, the value, X, was used to compute the average. Individual points were labeled as follows: C# = corn test, soil #; M# = mustard test, soil #; W# = wheat test, soil #. Two lines were added to the graph: germination NOEC = root length NOEC (X = Y), and germination NOEC = 3·root length NOEC (X = 3·Y).

Assay sensitivity and endpoint similarity

A second objective of this work was to identify rapid, low-cost tests to use to screen contaminated soils for acute and chronic effects related to particular ecological receptors. To this end, the relative sensitivity of the tests and the ratios of endpoints within a species, between plant species, and between taxa are discussed by comparing NOEC values. The use of the NOEC has been criticized for a variety of reasons [44]. However, NOECs were used in this study predominately because of the lack of dose–response data. Differences in NOECs in the earthworm assays of less than a factor of 10 may be attributed to the soil dilution spacings. In the germination and root length assays, differences in NOECs of less than a factor of three may be attributed to the soil dilution spacings.

The earthworm 14-d survival test and the avoidance test, to a lesser extent, were good indicators of chronic survival. The NOECs for 14-d survival and both reproduction endpoints were identical on four of the six soils. The reproduction NOECs were lower than 14-d survival NOECs on the other

Table 8. Plant growth test no-observed effect concentrations (NOECs) for soil 4

Plant	NOEC (% Concentration of contaminated soil)				
	Total weight	Shoot weight	Root weight	Germination[a]	Root length[a]
Corn	<10	<10	<10	100	10–30
Lettuce	0.1	1	0.1	<1–3	<1–3
Mustard	1	1	10	3–10	1–10
Wheat	<10	<10	<10	30–100	10–100

[a] Germination and root length NOEC ranges for soil 4 are included for comparison.

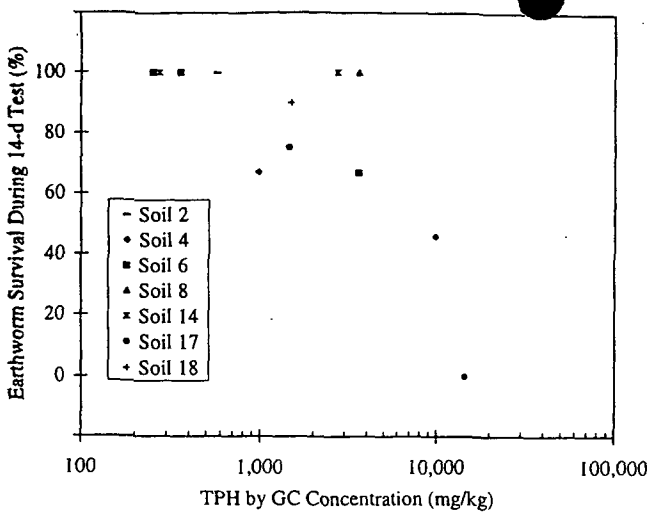


Fig. 4. Percent earthworm survival during the 14-d test (number of earthworms surviving on contaminated soil normalized to the number of earthworms surviving on the appropriate control soil) as a function of total petroleum hydrocarbon (TPH) by gas chromatography (GC) concentration for soils 2, 4, 6, 8, 14, 17, and 18. The TPH by GC concentration was determined from the measured contaminant concentration at 100% contaminated soil and the soil dilution, down to the method detection limit of 250 mg/kg soil.

One of the clearest concentration–response curves was earthworm 14-d survival as a function of TPH by GC (Fig. 4). Based on these findings, TPH by GC values of <4,000 mg/kg soil are unlikely to be acutely toxic to individual *E. fetida*. Within the TPH by GC range of 4,000 to 10,000 mg/kg soil, some mortality of individuals might be expected; and when TPH by GC values are >10,000 mg/kg soil, survival in a 14-d assay is expected to be low. Selecting TPH by GC ranges was admittedly complicated by comparison to control soil survival (as low as 83%) and by differences of up to 40% survival over a narrow TPH by GC range. The TPH by GC method measures C_6 to C_{25} hydrocarbons, which are the more volatile, soluble, and biodegradable constituents in crude oil. Thus, TPH by GC may be a good indicator of acute toxicity to *E. fetida*.

The more common hydrocarbon measurements, such as Freon-extractable TPH and O&G concentrations, did not correlate strongly with 14-d earthworm survival. Thus, quantification by these procedures may not reveal the toxic "drivers." Other hydrocarbon measures, such as polar compounds, had acceptable concentration–response relationships for 14-d and chronic earthworm survival (plots not shown).

Mustard germination correlated most strongly, although not significantly, with asphaltene concentration. Mustard seed germination was reduced at asphaltene concentrations of 200 to 1,000 mg/kg soil (Fig. 5). Wheat seed germination was reduced at asphaltene concentrations of 4,000 to 7,000 mg/kg soil. Wheat and mustard differed by an order of magnitude in their asphaltene "threshold" values; this outcome is consistent with the previous assertion that mustard is more sensitive than wheat.

Concentration–response relationships for 14-d earthworm survival and seed germination, each as functions of specific hydrocarbon parameters, were explored. For root length and earthworm reproduction, few of the correlation coefficients were significant, and even the most highly correlated parameters had poor concentration–response relationships when plotted against hydrocarbon constituents (plots not shown). Previous attempts to link earthworm and plant toxicity test endpoints to particular hydrocarbon measurements have generally been unsuccessful [46]. Our data support the hypothesis that different taxa respond differently to hydrocarbons and that a "universal" hydrocarbon parameter that can be used to predict toxic effects on soil communities has not yet been identified.

Recommendations for application of testing in a risk-based framework

Ecological risk assessments are often conducted in a tiered framework [2,4,18]. During the initial assessment and tier 1 evaluation, ecotoxicity tests, such as those described here, are generally not appropriate. A tier 1 evaluation might include a visual characterization and an assessment of the site in terms of types of vegetation. Visual differences between contaminated and uncontaminated adjacent areas may be noted.

Based on the authors' experience, the use of benchmark values for hydrocarbon-contaminated soils [18,47] at a tier 1 or 2 level should be discouraged. Presently, there are insufficient data and understanding of the impact of most hydrocarbon contaminants on soils to allow for the development of soil benchmark screening values. In the absence of terrestrial ecotoxicity data relating to individual chemicals or mixtures, numerical criteria are being adopted from aquatic data and are being estimated using equilibrium-partitioning theory [48]. Additional complexities arise because of differences in soil types and in the length of time the contaminant has been in the soil. Interspecies differences in the sensitivities of plants, microbes, and invertebrates that constitute the soil community make it difficult to develop soil-quality criteria or benchmark values that are not overly conservative.

It may be appropriate to conduct simple ecotoxicity screening tests during a tier 2 or 3 evaluation. When considering the appropriate test or suite of tests, a number of

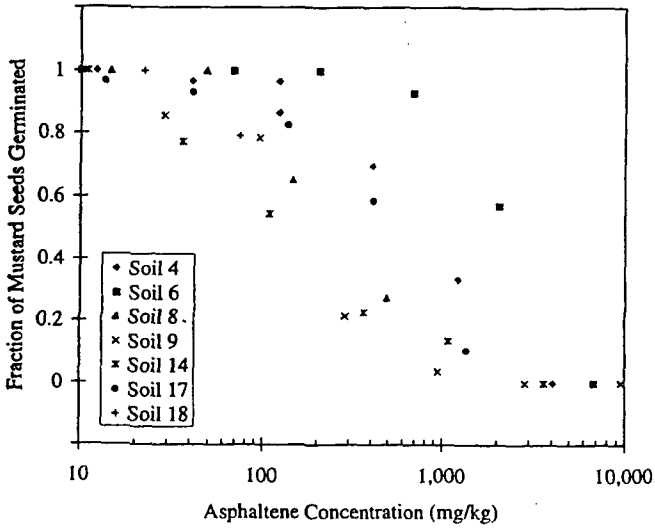


Fig. 5. Fraction of mustard seeds germinated (number of seeds germinated on contaminated soil normalized to the number of seeds germinated on the appropriate control soil) as a function of asphaltene concentration for soils 4, 6, 8, 9, 14, 17, and 18. Asphaltene concentration was determined from the measured contaminant concentration at 100% contaminated soil and the soil dilution, down to the method detection limit of 10 mg/kg soil.

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