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May 1997

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MICROBIOLOGY

Fundamentals and Applications

Ronald M. Atlas

University of Louisville

Macmillan Publishing Company
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SECTION SIX

Chapelle, 1993

GROUND-WATER MICROBIOLOGY AND GEOCHEMISTRY

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Hemming, 1988

Monitoring and Identification of Bacteria from Agricultural Environments by Gas Chromatography Fatty Acid Methyl Ester (GCFAME) Analysis

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St. Louis, MO 63198

INTRODUCTION

In many laboratories the identification and classification of microorganisms is a crucial part of significant research projects. Some of these projects include the development of biological control agents, strategies for waste treatment and pollution control, or use of organisms for mineral leaching and microbially produced substances as component materials for new products. Most diagnostic bacteriology laboratories are equipped for identification of microbial species isolated from clinical specimens and tests for pathogenicity in humans and animals. Plant pathogens are often identified within the United States by diagnostic laboratories sponsored by the Department of Agriculture and its various extension programs. These labs are frequently associated with university departments of plant pathology which provide specialized expertise in the identification of such microorganisms. It is also possible to contract with the American Type Culture Collection (ATCC) for the identification of an unknown isolate, generally with a fee of several hundred dollars per isolate.

Throughout the past decade, microbiology laboratories have been faced with both an increasing number of specimens for identification and numerous legal and regulatory issues related to their characterization in addition to their research projects of scientific inquiry. The advances in the application of recombinant DNA (rDNA) techniques have extended the possibilities for improvement in food production and disease control via biological means, as well as, improvements in pollution control and manufacturing processes based upon biological agents. The potential benefits will become a reality only when the debates along scientific, regulatory and public perception lines concerning the safety of genetically engineered microorganisms have moved from the realm of speculation and storytelling to research, demonstration and fact generation. In this light, the monitoring and identification of bacteria from agricultural as well as other natural environments is of significant importance. Monitoring, detection, dispersal, and survival studies require reproducible, and reliable identification of introduced strains, as well as a good knowledge base for naturally occurring species in the specific environment of study.

The major aspects of this particular work will be to provide, following this INTRODUCTION, 1) a BACKGROUND concerning identification and classification of bacteria from agronomic environs, general observations and problems encountered, a brief mention of the numerical methods used in microbial ecology and taxonomy, and initial information on the specific application of gas chromatography for bacterial identifications, and to provide 2) specific information on the METHODOLOGY of GCFAME as related to the Hewlett-Packard 5898A Microbial Identification System (MIS) and to provide 3) EXAMPLES of bacterial identifications which were completed in preparation for the first field test in the U.S. of a live recombinant microbe expressing genes from a different organism. This field test received the first approval granted by the U.S. Environmental Protection Agency under the Toxic Substances Control Act (TSCA) and was conducted jointly by scientists from Clemson University, South Carolina and Monsanto Co., St. Louis, Missouri.

BACKGROUND

Many researchers have attempted identification and classification of microorganisms based on their characteristics demonstrated by tests which defined biochemical, morphological, serological, and/or toxigenic parameters. Such tests are critically useful, but often assigning an organism to its proper taxon on the basis of these properties can be difficult. In addition, many of these tests are time consuming, labor intensive or require extended periods of incubation before final identification. In numerous cases, a final identification is not required, but a screen or determination of the diversity of microbial species is desired which may entail several hundred even thousands of isolates. Rapid differentiation of species is therefore a prerequisite of these studies.

Numerous problems are often encountered during attempts at identification of bacteria which have been isolated from natural habitats. Many difficulties arise either from strains that do not give "typical" results in the tests employed or from the inadequacies of existing taxonomic classifications. Microbial ecologists have therefore defined populations by their physiological features with a limited number of tests sufficient to allow numerical taxonomic procedures and determination of dominant bacterial genera. Microbiologists conducting research on environmental samples have noted the inadequacies of identification of soil and plant isolates using automated test kits and methods. Typically, the tests are rapid and for the most part excellent. The problem lies in the comparison of the unknown strain to a data base drawn from known isolates of only clinical origin with a preponderance of enteriobacterial isolate identifications. Additionally, the often encountered phenomenon of phenotypic dissonance of bacteria growing in the laboratory on media to which they have become adapted, compared with strains of the same species in the natural environment, is a very real complicating factor. Despite these drawbacks, automated identification methods provide a wealth of information about an isolate of interest. The instrumentation involved in many of these systems can be quite varied and include significant developments in computer interfacing and software, greatly reducing the tedium, labor and time required in characterizing numerous isolates. Table 1 lists a number of companies involved in the manufacturing and/or marketing of microbial identification systems which vary from relative simple growth tests to complex, technically sophisticated instrumental operation and analysis.

Cluster analysis, an important numeric and taxonomic tool, has assumed an important role in microbial ecology. Study of the distribution of microbial populations in natural habitats has relied greatly upon developments in numerical taxonomy (for further information on these statistical methods see the references by Sneath or Wishart). Numerical methods can be implemented on nonidentified isolates which have been characterized by a number of tests; in addition, species diversity indices can be generated from systematically analyzed data. Such indices can be of help in defining the stability of the microfloral ecosystem, whereas the systematic analysis treatments of the data allow the investigator to identify correlations and interrelationships amongst the bacterial groups and the types of tests used in the characterization.

Numerical taxonomy has been applied in several ways. For example, it has been used to determine characterization keys for taxonomic groups such as the *Pseudomonas* and the *Vibrio* families in order to assign diagnostic tests for specific intragroup differentiations. In addition, cluster analysis has been used to investigate the effect of specific physical environment parameters on bacterial species diversity such as in hypersaline habitats or other water quality parameters of rivers. Broad spectrum isolation and characterization of bacterial strains from the Gulf of Alaska have also been completed in an attempt to establish microbial diversity prior to impact by offshore oil drilling. Similar studies have been made in determining the bacterial diversity response to the degradation of xenobiotic compounds such as phenanthrene. This was done in order to find microbial candidates for applications in genetic engineering technology. It is also of interest to obtain qualitative and quantitative data on dominant bacterial populations associated with roots from different crop plants in order to build up a rationale for the selection of potential bacterial pesticides and/or fertilizers. Data from such studies can be analyzed by numerical methods which permit reduction in the data and permit interpretations to be more graphically presented, with interpretations more easily conveyed to the less mathematically oriented person or group.

Over the past decade, in a search for more rapid and specific methods for identification, several researchers and industrial concerns have used gas liquid chromatography (GLC), high performance liquid chromatography (HPLC) or combinations of these analytical tools for natural product separation in conjunction with mass spectrometry (MS) to determine the chemical composition and metabolic activity of bacteria, in particular, as a basis for their classification. Gas liquid chromatography is valuable in bacterial identification because it overcomes many of the problems associated with identification of large numbers of isolates. GLC analyses of the fatty acids present in the lipid fraction of cell membranes provides a specific, reproducible fingerprint or profile of a bacterial population isolated in pure culture. Increased resolution of the separation of components in a complex fatty acid mixture is possible with capillary GC columns made of flexible, fused, silicaglass or other materials introduced by several commercial companies. The analysis of fatty acid profiles is applicable to identification of yeasts and other microorganisms where currently the significant development of a data base is the primary limiting factor.

Strains of a bacterial species have been shown to provide only minor quantitative

variations in their distinctive fatty acid methyl ester (FAME) which permits grouping to various taxonomic levels in some cases as distinct as subspecies. Fingerprinting or profiling of bacterial strains has also been accomplished using electrophoretic means in addition to or separately from the chromatographic methods. Such techniques employ examination of protein patterns or endonuclease restriction digest patterns of genomic DNA prepared from bacterial cultures. These techniques can provide profiles which are strain specific, but further data base development and automation is the major focus of current research attention on these methods.

As in the use of polyacrylamide gel electrophoresis in the separation of proteins and peptides from bacterial preparations, fatty acid profiles of closely related species or genera are distinguished by qualitative differences (as in the presence or absence of fatty acid peaks in a chromatogram rather than changes in protein band patterns) or by a large quantitative difference in a specific fatty acid peak separated by gas chromatography. Databases are established for comparison with unknown isolates by repetitive determinations of reference strains within a species for GCFAME profiles. Essentially, a hypothetical mean profile is generated for each taxon, such as a particular bacterial species. The data generated by this methodology is also compatible to study by numerical analysis and various cluster methods.

METHODOLOGY

As an example of one type of sample preparation from agricultural environments, a generalized procedure for determination of bacterial root colonization is outlined. Plant root samples are analyzed by shaking free the excess adhering soil, with placement of roots in a centrifuge bottle of appropriate size containing sterile distilled water. The bottle is shaken at approximately 250 rpm for 15 minutes on a rotary shaker. After shaking, the water is removed and replaced aseptically with an equal volume of sterile distilled water, and shaken as before. This process is repeated a third time, but the water of this third wash is retained for the analysis of bacteria.

The bacterial concentration is assessed by appropriate dilution and plating onto the particular bacterial isolation growth medium required by the nature of the species being examined. For example, selective media that permit growth of selected pseudomonad species to the exclusion of all other bacteria are desirable for epidemiological studies and for identification. Numerous media have been described, but none are totally satisfactory, as a result of being too inhibitory to the desired selected isolates, or the bacteria that are cultured on them become atypical. The best approach is to use several selective media designed for the same purpose and to use a nonselective medium in parallel studies.

As inferred in the frequent appellation given a particular subgeneric group "the fluorescent pseudomonads," the singular characteristic common to this group is the production of diffusible, extracellular, water soluble, UV fluorescent pigments which can be readily detected using *Pseudomonas* Agar F (Difco). Upon this medium, following 24 hours incubation at 27°C, these pigments are visible when examined under a blacklight emitting 360nm wavelength light. Examples of more nonselective media commonly employed are nutrient agar and trypticase soy broth agar (TSBA). These will allow the growth of many, but not all bacterial genera. Environmental preparations are typically incubated at a much lower temperature than the common 37°C (body temperature) used for clinical samples. In some studies, it may be desirable to use an osmotically tempered diluent such as 0.1 M magnesium chloride or physiological saline solution rather than distilled water in the preparation of samples. Single colonies are picked and restreaked for isolation on the same or possibly a different subsequent growth medium.

It is well known that cells alter the fatty acid composition of their membrane lipids to maintain fluidity under varying environmental conditions. It is therefore essential in GCFAME identification of purified isolates to control the time and temperature of incubation and the selection of media before comparing fatty acid compositions. The conditions used to generate the database or library of known taxa must be adhered to rigorously when processing an unknown isolate. The Hewlett-Packard Co. manufactures an automated GCFAME system composed of a sophisticated chromatographic system and integrated computer system known as the HP 5898A Microbial Identification System (MIS). This system is used by the author and has been the means by which all examples, to be given herein, have been generated.

Chromatographic experience is not essential for operation of the MIS. The software of the system calibrates and monitors the instrumentation to ensure that the system is functioning properly. However, the MIS can only identify those microorganisms for which fatty acid composition profiles of a representative number of correctly named reference strains have been determined and entered in the system's library. This system is therefore heavily influenced by the taxonomy used to develop its library. More than 60 genera

are contained in the Aerobe Library Version 3.0 with other libraries under development by various investigators. Calibration standards and MIS software including programs for individual library database generation is now made available by Microbial ID, Inc., a company located in Newark, Delaware. For detailed operating instructions, researchers rely on the HP 5898A MIS Operating Manual (Part No. 1929890100) provided by Hewlett-Packard Co., Avondale, Pennsylvania.

One basic procedure for preparation of fatty acids from bacterial cells was developed at the Center for Disease Control in Atlanta, Georgia by Dr. C. W. Moss and colleagues. Dr. Lindy Miller and other scientists of the Hewlett-Packard Co. have incorporated the basic procedure in their protocol for use with the MIS system. Once strains have been isolated as distinct colonies, aerobic bacteria are further grown at 28°C on TSBA agar medium for 22-24 hours. Cells are harvested by gently scraping the agar surface with a 4mm inoculating loop. The cells, typically a heaping loopful, are placed in a 100 x 13 mm screw cap test tube. Fatty acid extracts are prepared by saponifying whole bacteria cells by addition of strong base (Reagent 1: sodium hydroxide in aqueous methanol). After saponification, the solution is acidified and the liberated fatty acids are then methylated to increase their volatility upon injection into the gas chromatograph. This is accomplished by addition of hydrochloric acid in aqueous methanol (Reagent 2). The methyl esters of the fatty acids are extracted by an equal volume mixture of hexane and methyltert butyl ether (Reagent 3). A dilute base wash (Reagent 4: 0.3 N sodium hydroxide) removes residual acid and reagent which would be damaging to the capillary column, as well as aids in preventing hydroxy fatty acid peak tailing in the separation. This procedure, schematically shown in Figure 1, is rapid, allowing 50 samples to be easily prepared in about an hour. The final organic extracts are placed individually into vials specific to the automatic sampling system of the MIS and capped to prevent evaporation or spillage. Sample vials may also be stored refrigerated for up to two weeks for later analysis.

The MIS gas chromatograph (HP 5890) is equipped with a 50m x 0.2mm methyl silicone fused silica capillary column with hydrogen used as the carrier gas for increased sensitivity,these combine for the resolution of iso and anteiso branched chain fatty acids and positional isomers of unsaturated acids. The details as to the chromatographic conditions will be left to the technical literature. Suffice it to say, the thermal gradient run requires 25 minutes per sample, which permits unattended determinations of 48 samples and standards per day. The cost is comparable to that of using one of the commercial biochemical phenotypic test kits. The first report generated by the system is the raw chromatographic plot which is the trace of the electronic signal from the flame ionization detector (FID) generated by the flame oxidations of each fatty acid peak eluting from the column during a separation. Retention time and other raw data describing the peaks is printed by an integration unit (HP 3392A) which passes the information to a computer for further processing. The second report is obtained from the computer which contains the fatty acid composition of the organisms and lists the results of the library search comparison. Data comparisons between the composition of an unknown and the means of reference strains can also be generated. Software is also available whereby researchers can build their own libraries.

EXAMPLES

The bacterial isolate selected as the field test candidate and recipient of the genetically engineered *lacZY* gene marker system developed at Monsanto Co. was arbitrarily designated a strain number of Ps. 3732RN. This isolate was isolated in 1981 from soil planted to corn at a Monsanto owned research farm, located in St. Charles County, Missouri, as a spontaneously derived rifampicin and nalidixic acid resistant (indicated by 'RN' of the strain number given) pseudomonad strain. Additional isolates for which comparative information is provided include the fluorescent pseudomonad strains designated as 1141F1, 1606F2, 701E1, and 1954D3. Strains numbered 1141F1 and 1606F2 were isolated in 1982 from root washings of soybean plants (*Glycine max* cv. *'Williams'*) grown near Sun Prairie, Wisconsin. Strains 701E1 and 1954D3 were isolated as well from healthy soybean plants from Hoopeston, Illinois and St. Charles, Missouri, respectively.

Strains were characterized by standardized micromethods combining on the order of 21 biochemical and assimilation tests for the identification of gram negative, nonfermentative bacteria such as *Pseudomonas*. Such tests were conducted using the Rapid NFT InVitro Diagnostic Test Kit (DMS Industries) and/or provided by the API20E microtube system (Analytab Products, Inc.) The API data base generated from strains predominantly of clinical origin, provides identification of bacteria based on a seven digit profile code generated from the test results for each strain examined. An "Analytical Profile Index" for comparison of profile codes is made available, updated, and maintained by the manufacturer of the test kit. The index includes an estimated frequency of occurrence for a

particular profile code. An estimated occurrence of 1/260 is interpreted to mean that if one considers randomly 260 isolates of the identified taxon (i.e. a fluorescent pseudomonad species), you have an estimated one chance out of 260 of encountering a profile similar to the profile of the strain being studied. As noted previously, the inadequacies of identification of soil and plant associated isolates using only a single method are overcome by additional tests or methods as provided here by GCFAME analysis. However, the API tests do aid greatly in the phenotypic characterization of strains. The frequency of occurrence of profiles generated for strains from these environs differs from those of the clinical environment. Table No. 2 provides the profile codes of bacterial isolates exhibiting diffusable fluorescent pigment production on *Pseudomonas* Agar F (Difco), a characteristic also of strain Ps. 3732RN, and profile occurrence among an additional 331 fluorescent isolates obtained from the rhizosphere of healthy soybean plants harvested from seven different sites of four midwestern States. The profile of Ps. 3732RN and those of additional comparison strains are provided in Table No. 3, along with its identification by the API20E methodology, the page number of a profile as found published in the "Analytical Profile Index" and the frequency of a profile occurrence as determined with this database. From this data, 3732RN is classified as an excellent fit for inclusion in those *Pseudomonas* species known collectively, as fluorescent pseudomonads.

The 1982 edition of this database indicates that the number of bacterial strains and results studied for compilation of the database was 286,870 strains of which 15,583 were of the genus *Pseudomonas* and 11,836 were within fluorescent pseudomonad groups. The API20E tests include the hydrolysis of onitropheny-ß-d-galactoside (ONPG) as indicated by the appearance of the yellow coloration of the liberated o-nitrophenyl moiety, a reaction catalyzed by the presence of the enzyme, beta-d-galactosidase. Since the seven digit profile is derived from the 21 biochemical tests, it can be determined from the profile codes provided for the soybean rhizosphere strains (Table No. 2), as well as from the API index, that fluorescent pseudomonads universally lack this enzyme. The first digit of the code represents a summary of the first three tests of this system. The ONPG test is the first test. Only positive reactions are recorded and assigned a numerical value dependent upon the order of the test within a group of 3 tests; a value of ONE is given for the first test, a value of TWO for the second test and a value of FOUR for the third test. Since no fluorescent pseudomonad profile begins with an odd number, obtainable only by being positive for the first test, the absence of beta-galactosidase is ascertained; therefore, the introduction of the *lacZ* gene from *E. coli*, which codes for this enzyme, confers a unique, readily determined phenotypic marker for fluorescent pseudomonads. Further descriptions of these strains in regard to their colony morphology, Gram stain reaction, flagellation, etc. were confirmed by the ATCC in work conducted for Monsanto Co., prior to data submission to the Environmental Protection Agency requesting permission to conduct the field test of the recombinant strain.

All strains discussed above have been examined using the Hewlett-Packard 5898A Microbial Identification System (MIS). Strains were analyzed by comparisons to two versions of the database; namely, Version 1.2 and Version 2.1. Confidence in the reliability of this relatively new instrumentation and software for identification of fluorescent pseudomonads was reinforced by its performance in the lab in the identification of well characterized reference strains of the author's collection which includes a number of strains originally obtained as reference stocks from the American Type Culture Collection (ATCC). Of 47 such pseudomonad reference strains, 41 strains (87%) were correctly identified to species or biotype. Of the six unidentified or misidentified strains, three represented species unlisted in the library data file of the system; namely, two *P. delafieldii* strains (*acidovorans* group) and one *P. methanolica* strain. In summary, 19 species were included with 17 of them correctly identified which included four biotypes of *P. fluorescens*.

The host strain and its engineered derivative, 3732RNL11, which contains the genomic insert of the *lacZ* and *lacY* genes), were identified by the GCFAME analysis and MIS database as being *P. fluorescens* biotype D (*P. chlororaphis*), which is in harmony with the previously presented API20E characterizations. The ATCC using a battery of biochemical and growth tests identified the host as *P. fluorescens* biotype E (*P. aureofaciens*). These two biotypes are very close by DNA and RNA homology, but are distinguished as to their phenazine pigment production. Biotype E (*P. aureofaciens*) synthesizes a yellow orange pigment, phenazine-1-carboxylate, whereas, *P. chlororaphis* produces the green chlororaphin or the yellow oxychlororaphin, which are derivatives of phenazine-1-carboxylate amide. The fact of the matter is that strain 3732RN appears to be an intermediate between these two taxa.

The engineered strain behaves identically as its wild type parent with the characteristic exceptions conferred on it by the expression of the *lacZY* marker system. Expression of the

lacZ gene provides within the cytoplasm of the cell the enzymatic protein product, beta-galactosidase, which functions to break the glycosidic bond of the disaccharide sugar, lactose, to form glucose and galactose. These simple sugars are then easily metabolized. The *lacY* gene product forms the lactose carrier protein or permease found as an integral membrane transport protein in the transformed strain. These genes permit its growth on lactose as a sole carbon source and provide the ability to cleave a colorless substrate, a lactose analog termed Xgal, to produce a blue colored indolyl derivative and galactose, thereby providing a selectable chromogenic marker for this type of bacteria, important in their differentiation and detection when introduced back into their native environments. GCFAME analyses can still be used to identify the strain since these genetic modifications do not effect the fatty acid profile produced. This may be of importance in monitoring the exchange of such gene elements into a different pseudomonad host since a different GCFAME profile may be found for the recipient after selection on a medium of lactose as the carbon source.

Strain 3732RNL11 has been effectively monitored or tracked using this selectable chromogenic marker system. This first in recombinant organism field tests, commenced with the introduction of this strain during the planting of winter wheat on Nov. 2, 1987 as part of an 18 month study conducted at the Edisto Research and Education Center near Blacksville, South Carolina. The Environmental Protection Agency decided to catalogue this "intermediate" strain as *P. aureofaciens* (*P. fluorescens* biotype E). Recently, this strain and its parent isolate were shown by HPLC not to produce the normal levels of phenazine-1-carboxylate typical of *P. aureofaciens* strains, thereby behaving similar to biotype D strains, thus is the nature of the intricate debates over taxonomy. The important aspect of the characterization is that both taxa related to the intermediate strain represent strains nonpathogenic to animals, plants or insect life. Additional plant pathogenicity related data was also submitted to the USDA for a concurrence on the nonpathogenic status of these strains in preparation for the field test. The identities of the engineered strain and the other selected comparison strains as determined by the software used in the MIS analysis are presented in Table 4.

Cluster analysis of strains listed in Table 4 is presented as an example of this type of numerical analysis. Figure 2 presents the dendrogram developed from using the similarity coefficients or indices found in Table 4 which were obtained by GCFAME analysis. These similarity indices are numerical values expressing how closely the composition of these strains compare with the fatty acid composition of the library match, the hypothetical mean organism for the taxon, *Pseudomonas chlororaphis*. The highest value possible is 1.0 with an index of 0.6 to 1.0 illustrative of an excellent match. Cluster analysis of this data permits a visual representation of the relatedness of these strains. It is particularly useful when working with large numbers of strains. Strains from different clusters often are chosen as representatives for these groups in subsequent tests or used to systematically identify strains closest to given "type" strains of current taxonomical classifications. It should be clear that in this example, strain No. 606F2 is significantly different from the other strains and may not actually be a *P. chlororaphis* strain. Its similarity index of 0.1 would be interpreted to mean it is of a related fluorescent pseudomonad species cluster.

Figure 3 presents the raw chromatographic trace or chromatogram of the engineered strain 3732RNL11. Retention times of fatty acid peaks are given in minutes. An instrument integrates the area under these peaks and prints this data, along with retention times, the names of identified fatty acids which typically give rise to such peaks, a value known as the equivalent chain length (ECL), and the percent of the total area identified, in a composition report (Figure 4). The equivalent chain length value or ECL is a linear interpolation of a peak's retention between two saturated straight chain fatty acid methyl ester reference peaks. This value is used in the analysis of each peak with the expected ECL values of fatty acids in a peak naming table. The software makes this comparison and prints the fatty acid name in the composition report.

For example, the peak having a retention time of 3.761 minutes in the composition report shown (Figure 4) has been named a 10 carbon chain length fatty acid possessing an hydroxyl group on the third carbon of the chain. This is a peak common but not exclusive to fluorescent pseudomonads. Peaks that do not correspond to ECL values of known fatty acids are left unnamed in the report and are not used in a library search to find matching identifications. Peak areas are modified by a quantitative response factor and normalized to 100%, the resulting weight percent (%) is listed in the report. The response factor is derived from running a quantitative calibration mix along with the bacterial samples. It corrects for long term drift and instrument to instrument variation.

The library search (Figure 4) lists the most likely matches and provides the similarity index for each. Examination of a comparison chart (Figure 5) sometimes provides a better

understanding of the quality of a match, but it must be understood as presenting only a small portion of the data upon which a match is made. All fatty acids found in the isolate's extract and the taxon matched are listed in elution order with the percentage of each acid indicated at the top of the chart. The percentage composition of the fatty acids of the isolate or bacterial sample (i.e. 3732RNL11) is indicated by an "X", whereas, the hypothetical mean organism from the database is indicated by "+". Where these values overlap directly a "*" is placed. The window indicated by the dashed line represents +/-2 standard deviations from the mean.

SUMMARY

There are always a number of precautions which apply universally in the application of methods useful for bacterial identifications and others which pertain specifically to the methods under discussion. This work has been written as an introduction to the use of GCFAME analysis for bacterial identification in agriculture and its aid in tracking or monitoring these organisms. A listing of various disadvantages and advantages of the methodologies discussed has been avoided. Significant progress is being made in this area, which will undoubtedly impact the knowledge and use of these tools. The examples have demonstrated some of the problems which arise for the environmental microbiologist and have demonstrated the use of some of the tools currently employed. They have highlighted the background of real world concerns which are increasingly influenced by the taxonomist's artificial schemes of classification and identification.

With current methods it is possible to answer many questions related to developing applications of genetically engineered microorganisms in the environment. Significant benefits to society still await the further development of better methods for using the often simple but profound microbial processes found in nature. Further environmental research should magnify the small but important microorganisms about us, for although small, they make a significant difference.

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ABOUT THE AUTHOR

Dr. Bruce C. Hemming serves as a Research Specialist in the Biological Sciences Division of Monsanto Co. As a founding member of the Plant Microbiology Group, he serves as a project leader in the development of microbiological biocontrol agents targeted towards major plant diseases and the use of recombinant microorganisms to enhance plant protection and development. Dr. Hemming was closely involved in the first U.S. environmental release

of an approved genetically-engineered microbe expressing genes of two organisms. Dr. Hemming has served as a Visiting Associate Professor in the Dept. of Biology, University of Missouri, St. Louis, teaching a graduate course in phytobacteriology. Dr. Hemming joined Monsanto in March, 1982 as a Senior Research Biologist. Prior to this appointment, Dr. Hemming worked with bacterial plant pathogens at Montana State University in the Department of Plant Pathology. He graduated with a B.S. degree (1974, cum laude) in microbiology and chemistry and an M.S. degree (1977) in biochemistry from Brigham Young University. He earned his Ph.D. degree (1982) in Plant Pathology from Montana State University following additional graduate studies in the Department of Biochemistry, University of California, Riverside.

Table No. 1

Commercial Suppliers of Microbiological Identification Systems

Access Medical Systems, Inc.
Ambis Systems
Analytab Products (API)
Analytical Measuring Systems
API Systems SA
Austin Biological Labs
Baxter Healthcare Corp.,
Microscan Division
Beckman Instruments, Inc.
Beckman Instruments, Inc./Diagnostic Systems
Becton Dickinson Diagnostic
Instrument Systems
Behringwerke AG
Buhlmann Laboratories AG
CLONATEC-BIOSOFT
Costar Corp.
Curtin Matheson Scientific, Inc.
Diagnostics Pasteur
Du Pont Diagnostics
ECO-BIO N.V.
Eldan Bio-Technologies (ETB) Ltd.
Environmental Diagnostics, Inc.
Fisher Scientific
Flow Laboratories
Flow Laboratories (INT.)S.A.
Hewlett Packard Ltd.
F. Hoffman-LaRoche & Co. AG
Mast Laboratories Ltd.
Mercia Diagnostics Ltd.
Microbial ID
Omega Diagnostics Ltd.
Organon Teknika (USA)
Organon Teknika
Pro-Lab, Inc.
Radiometer America
Roche Diagnostic Systems
Sensititre (UK) Ltd.
Vitek Systems
VWR Scientific

Table No. 2

Phenotypic Profile Codes (Api20E) obtained for 332 Soil Fluorescent Bacterial Isolates & Their Frequency

No. of Isolates presenting same the same profile	Seven Digit Profile Codes					No. of Profiles
37	2206046	← *Ps. 701E1*				1
24	2202004	*profile*				1
17	2202046					1
17	2206042					1
16	2202044	← *Ps. 1141F1 &*				1
12	2200004	*Ps. 1954D3 profiles*				1
11	0202004	2204046				2
10	0200004					1
9	2200044					1
8	(2204042)	2206044				2
7	(2206040)	2204044	← *Ps. 1606F2*			2
6	(2202040)	0000004	*profile*			2
5	(2200040)	2200046	2202000	(2202042)		4
4	0200000	2202002	(2204000)	2202006		4
3	(2204040)	(6200004)	0000000			3
2	not presented	← *see footnote*				16
1	not presented	*for Ps. 3732RN*				49

Total No. of Distinct Profiles: 92

Ps. 3732RN generated a profile of 2206006 which was only duplicated by one other isolate of this soybean rhizosphere bacterial collection

Table No. 3

Identification of Selected Strains by the Api20E Test Method and Frequency of Profile Occurrence in Database

Strain No.	7-Digit Profile	Identification	Quality of I.D.	Page of Database (2/82) Edition	Frequency in Database
3732RN	2206006	Fluorescent Ps. group	Acceptible	p. 134	1:353
701E1	2206046	Fluorescent Ps. group	Excellent	p. 134	1:1765
1141F1	2202044	Fluorescent Ps. group	Excellent	p. 133	1:260
1606F2	2204044	Fluorescent Ps. group	Excellent	p. 133	1:83
1954D3	2202044	Fluorescent Ps. group	Excellent	p. 133	1:260

Table No. 4

Identifications by GC-FAME Analysis Using Version 1.2 of the HP5898A MIS Database

Strain No.	% Area Of Fatty-acids Named	Similarity Coefficient	Identification (Version 1.2)
3732RNL11	99	0.6	*P. chlororaphis*
701E1	99	0.5	*P. chlororaphis*
1141F1	96	0.63	*P. chlororaphis*
1606F2	94	0.1	*P. chlororaphis*
1954D3	97	0.59	*P. chlororaphis*

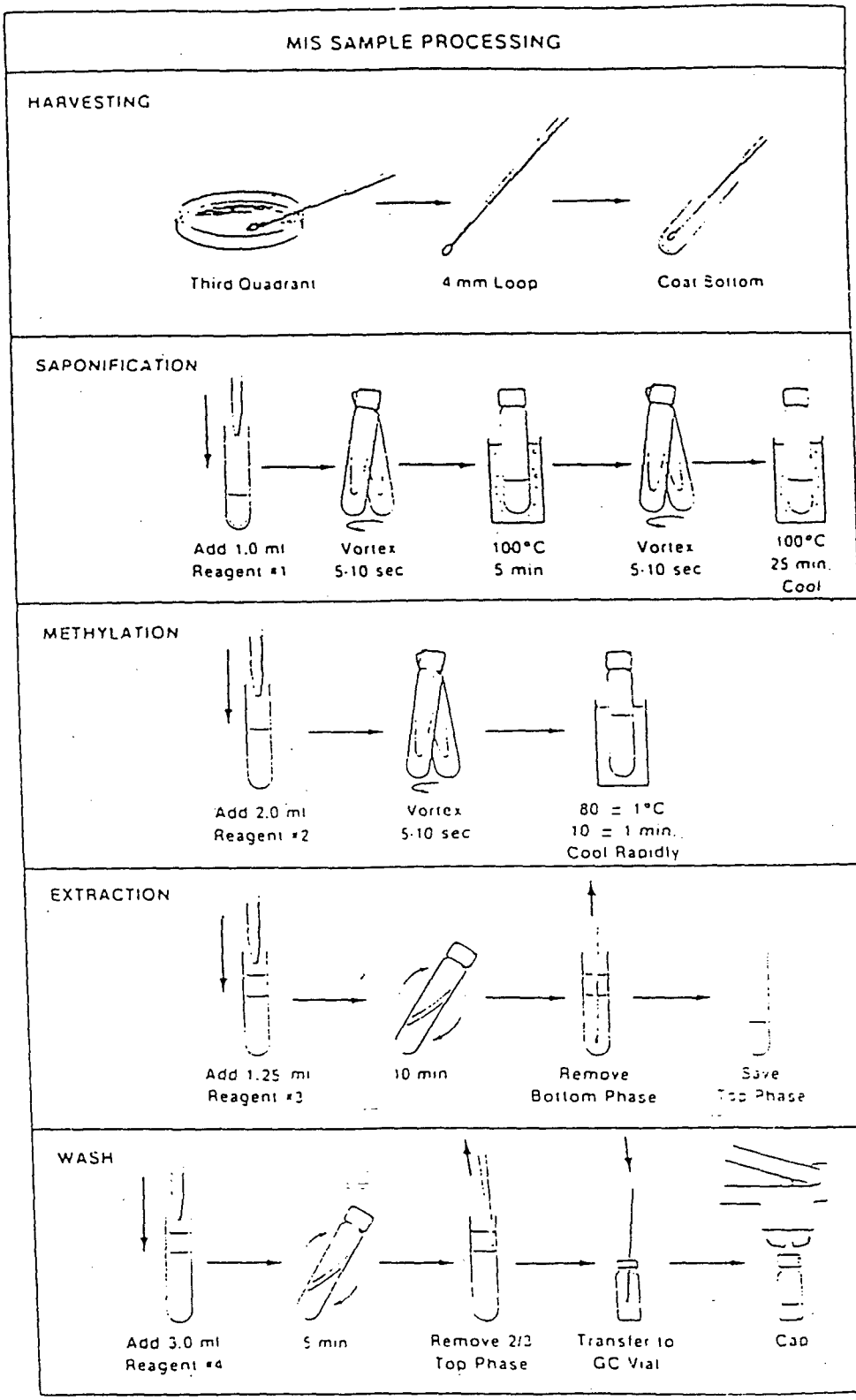
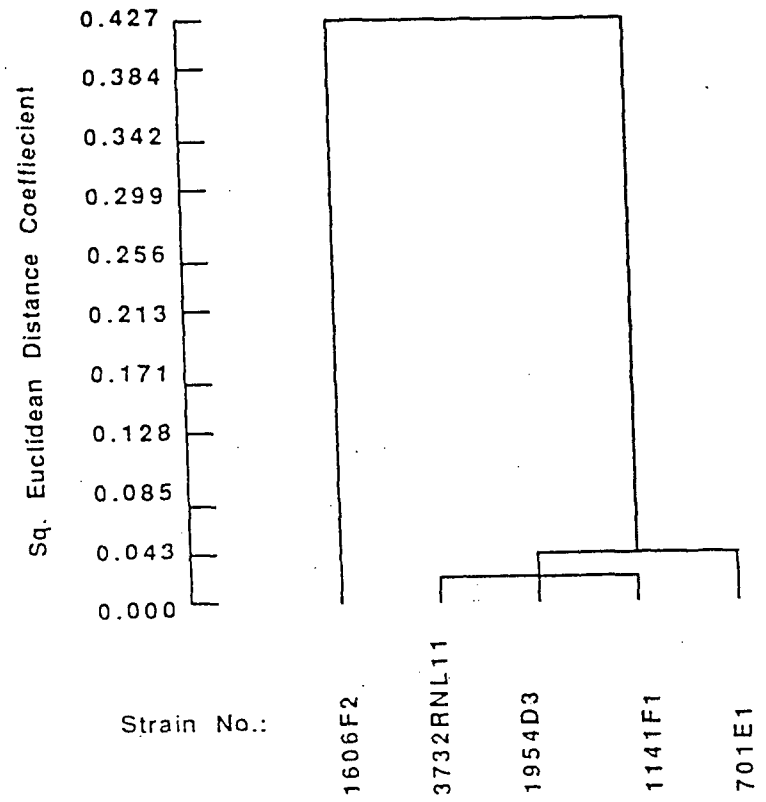


Figure 1. A schematic diagram illustrating the MIS sample processing procedure (reproduced by permission of the Hewlett-Packard Co.).



Cluster Analysis by Ward's Hierarchial Method for 5
Pseudomonas chlororaphis strains using GC-FAME Similarity Indices

Figure 2. An illustration of a dendrogram produced by cluster analysis on data (similarity coefficients) from Table 4 showing the dissimilarity of strain No. 1606F2. Dendrogram was produced using the CLUSTAN version 2 software package.

Raw Chromatographic Trace

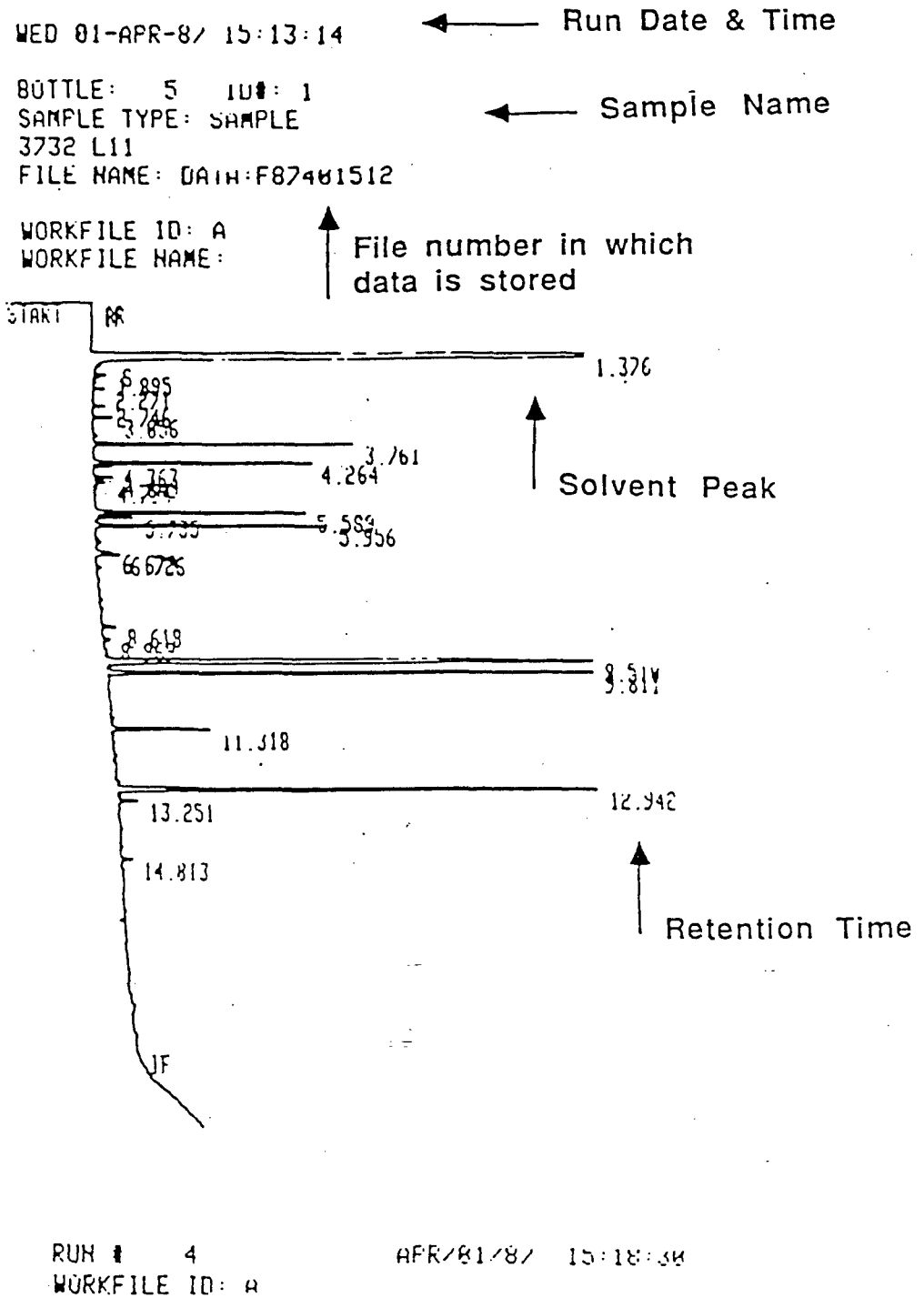


Figure 3. The GC-FAME chromatogram from a sample processed from strain No. 3732RNL11 as produced by the Hewlett-Packard 3392A integrator.

Composition & Library Search Report

HP 5898A: Microbial Identification System (Vers: 1.2) (Software s/n: 2616A100038 Computer s/n: 2510A21255)

*** SAMPLE ***

File: ORIA:F87101512
Bottle: 5
ID: 1
Name: 3732 L11

Date of report: 01-APR-87 15:12:30
Date of run: 01-APR-87 15:10:30

RT	Area	Ar/Ht	Respon	ECL	Name	Area %	Comment 1	Comment 2
1.376	39901000	0.050	. . .	7.052	SOLVENT PEAK	. . .	< min rt	
1.895	502	0.024	. . .	8.167	. . . . .	. . .	< min rt	
2.271	562	0.027	. . .	8.976	. . . . .	. . .	< min rt	
2.715	671	0.030	1.216	9.997	10:0	0.23	ECL deviates -0.002	Reference -0.011
3.056	1033	0.028	. . .	10.178	. . . . .	. . .		
3.761	14091	0.030	1.106	11.423	10:0 3OH	4.30	ECL deviates 0.000	
4.264	13431	0.034	1.072	12.002	12:0	3.97	ECL deviates 0.003	Reference 0.000
4.393	1164	0.033	1.057	12.093	11:0 ISO 3OH	0.34	ECL deviates 0.003	
4.619	1092	0.032	. . .	12.353	. . . . .	. . .		
4.794	673	0.033	1.046	12.486	unknown 12.486 . . .	0.19	ECL deviates -0.001	
5.589	13345	0.037	1.014	13.174	12:0 2OH	3.88	ECL deviates -0.004	
5.735	2457	0.036	1.010	13.264	12:1 3OH	0.69	ECL deviates -0.005	
5.956	15344	0.037	1.003	13.452	12:0 3OH	4.25	ECL deviates -0.003	
6.673	1045	0.039	0.993	13.999	14:0	0.28	ECL deviates -0.001	Reference -0.001
6.726	1749	0.040	. . .	14.031	. . . . .	. . .		
8.618	1026	0.042	. . .	15.269	. . . . .	. . .		
8.959	636	0.049	0.940	15.494	16:1 ISO I/14:0 3OH	0.17	ECL deviates 0.002	Sum In Feature 3
9.510	136630	0.043	0.932	15.816	16:1 CIS 9	35.69	ECL deviates -0.001	
9.811	97398	0.043	0.928	16.000	16:0	24.97	ECL deviates 0.000	Reference 0.000
11.318	8165	0.046	0.913	16.865	17:0 CYCLO	2.06	ECL deviates -0.003	Reference -0.004
12.942	73423	0.047	0.902	17.822	18:1 CIS 11/t 9/t 6	18.29	ECL deviates 0.000	Sum In Feature 7
13.251	1781	0.050	0.901	18.000	18:0	0.44	ECL deviates 0.000	Reference -0.003
14.813	1023	0.049	0.858	18.903	19:0 CYCLO C11-12 .	0.25	ECL deviates 0.003	Reference -0.004
*******	636	. . . . .	. . .		SUMED FEATURE 3 . .	0.17		
*******	73423	. . . . .	. . .		SUMED FEATURE 7 . .	18.29		

Solvent Ar	Total Area	Named Area	% Named	Total Amnt	Nbr Ref	Ref ECL Shift	ECL Deviation
39901000	386640	383759	98.74	362126	7	0.005	0.002

HP 5899A: MIS Aerobic Library (Vers: 1.1) (Library s/n: 2616A100038)

MOST LIKELY MATCHES	SIMILARITY	
Pseudomonas	0.622	
P. chlororaphis	0.599	(P. fluorescens Q)
P. syringae	0.510	
P. s. pisi	0.457	
P. s. savastanoi ash	0.440	
P. s. savastanoi privet	0.421	
P. lolaasii	0.475	

Figure 4. The composition and library search report for the chromatogram of Figure 3 providing fatty-acid peak names, most likely identifications and similarity indices for strain No. 3732RNL11 as produced by the Hewlett-Packard MIS instrumentation.

Comparison Chart

HP 5898A: Microbial Identification System (Vers: 1.2) (Software s/n: 2616A100038 Computer s/n: 2510A21266)

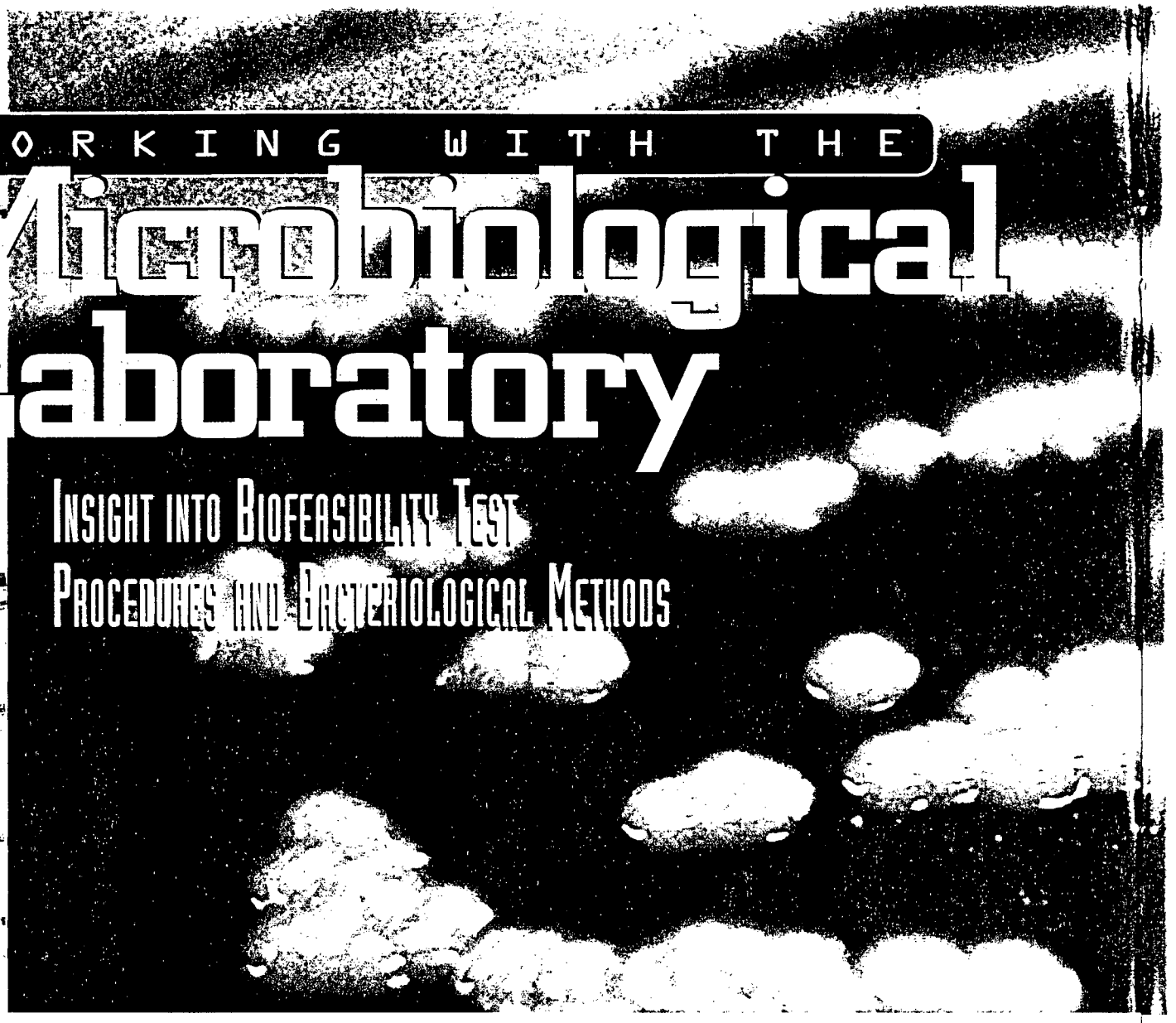
Library Comparison

File: 4DATA:F87101512 Date of report: 01-APR-87 15:19:30
Bottle: 5 Date of run: 01-APR-87 15:18:30
ID: 1
Name: 3732 L11
HP 5898A: MIS Aerobic Library (Vers: 1.1) (Library s/n: 2616A100038)
Library match: Pseudomonas chlororaphis (P. fluorescens 0)

	0 5I 10I 15I 20I 25I 30I 35I 40I 45I 50I 55I 60I 65I 70I 75I 80I
10:0	*-- . . . .
10:0 3OH	. --*-- . . . .
12:0	---+-x. . . . .
11:0 ISO 3OH	*-- . . . .
unknown 12.112	*-- . . . .
unknown 12.18E	*-- . . . .
12:0 2OH	. -x+-- . . . .
12:1 3OH	*x- . . . .
12:0 3OH	. --*-- . . . .
14:0	x+-- . . . .
unknown 14.503	*-- . . . .
15:0	*-- . . . .
16:1 CIS 9	. . . . ----------+----x------- . . . .
16:0	. . . . . x-----+----- . . . .
17:0 CYCLO	--x---+--------- . . . .
17:0	*-- . . . .
18:0	*-- . . . .
19:0 ISO	*-- . . . .
19:0 CYCLO C11-12	*-- . . . .
SUMED FEATURE 3	*-- . . . .
SUMED FEATURE 7	. . ------+--x--- . . . .

Figure 5. The comparison report for the GC-FAME profile of strain No. 3732RNL11 in contrast to the most likely library match (hypothetical mean organism), identified as *Pseudomonas chlororaphis*.

Hemming, Milke, 1996



WORKING WITH THE

Microbiological Laboratory

Insight into Biofeasibility Test Procedures and Bacteriological Methods

Although bacteria are small and simple, they have profound workings in the process of bioremediation. A microbiological laboratory that specializes in the environment can provide a high level of insight as well as significant test methodologies to evaluate and apply remediation.

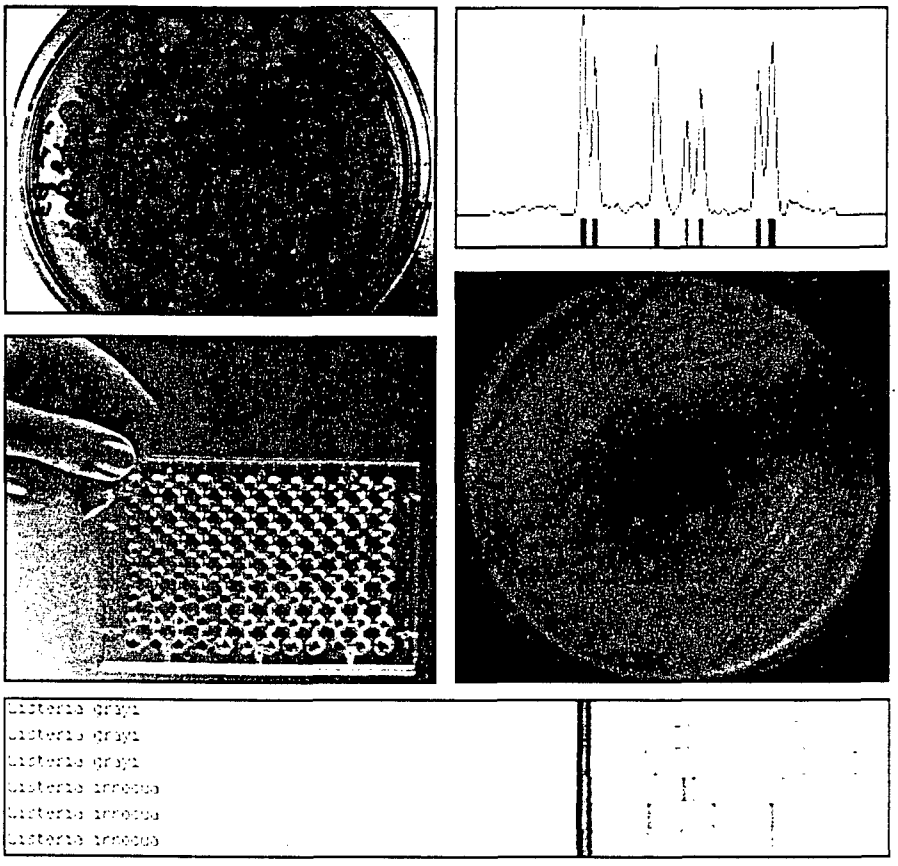
Bruce C. Hemming and Julie K. Milke

The microbiologist is as at home with bacterial organisms as the botanist is on a nature hike describing each plant species and its unique characteristics. When evaluating soil and water samples for bioremediation feasibility many people are acquainted with or use the limited biological plate counts offered by analytical chemistry laboratories. A microbiological laboratory that specializes in the environment can provide a higher level of insight and more significant test methodologies when evaluating and applying bioremediation. In general, there are three major microbiological steps in a study to determine the feasibility of bioremediation for a specific site: Establish viability by appropriate sampling; identify the microscopic players; and assess their abilities. When dealing with living organisms, close interaction with the laboratory is advisable and welcome, as environmental samples remain biologically representative for at most three or four days. On the other hand, most bacteria can be isolated and stored for years at ultra-cold temperatures. Neither you nor the microbiologist know the bacterial population levels and diversity of bacterial types in your sample until they are examined. This first examination is typically the total heterotrophic plate count (TPC). After arrival of a soil sample—typically in a 4-oz. wide-mouth jar—a portion of the sample is placed in a sterile diluent usually as a four- or five-serial, one-part to nine-part dilution scheme. From each dilution a measured quantity of liquid is placed on the surface of a Petri plate containing a standard bacterial growth medium. This is known as a "spread plate." Each spread plate is then incubated at 86° F (30° C) for 24 hours. After 24 hours the bacteria on the plate have reproduced to form colonies that can be seen with the naked eye. The colonies are counted and the results recorded, after which the

plates may be returned to the incubator for another 24 hours and counted again. This second reading is conducted by knowledgeable laboratories for two purposes. First, it is at this 48-hour point that the colonies have become differentiated, much more so than at the 24-hour reading, and each displays a distinct colony morphology in terms of color, size, shape, and texture. The observable morphology is termed a "phenotype." There is a direct correlation between the number of phenotypes present and the diversity of strains in the sample. Second, a great disparity in the magnitude of the populations at 24 and 48 hours indicates typically one of two conditions. Either the strains are of slow-growing species, or they are recovering from the previous stress under which they may have been growing at the site. The "stress" may be a result either of nutrient deprivation or toxicity toward the organisms at the site. The TPC test does not determine which of the conditions exist, only that the organisms appear to be under such stress or some combination of the two.

Results of the TPC are reported as a number of colony-forming units (CFUs) per gram in the case of soil or per milliliter in the case of a water sample. This number is the average of the number of colonies read on each plate of this dilution series, and refers to the number of carbon-using (heterotrophic) bacteria. One CFU is theoretically equal to one bacterium in the original sample, and is an indicator of how lively or viable the site bacterial populations are. To provide perspective, a rich agricultural soil may have plate counts of between 10^9 to 10^{12} CFU/g with perhaps as many as 13 or 14 different phenotypic colonies, whereas a bulk soil with little root mass to provide microbial nutrients may have plate counts closer to 10^7. Gasoline- or diesel-contaminated site plate counts generally range from 10^6 to 10^4 CFU/g and exhibit only seven or eight different types of recoverable strains, with some soils providing only two or three different bacterial strains.

A strain is a unique member of a species of bacteria. Strains within a species have different abilities. The genus *Pseudomonas* has many species, including several that fluoresce yellow-green visible light when placed under a blacklight (long UV). Strains of one such species, *Pseudomonas flourescens,* often are recognized as degraders of hydrocarbons, but each strain (in similar fashion to a member of a human family) may or may not degrade a specific hydrocarbon (i.e. play the piano). Certain species are recognized as having a greater likelihood of being degraders just as musical talent seems prevalent in some family lines. If a sample contains a fairly diverse, indigenous population, it probably contains some strains that are already successful at using the target contaminant. While each strain in a species has unique characteristics, it will have the same requirements within more narrowly defined ranges for nutrients, oxygen, and optimum growth temperature as other members of that species. Definition of the environmental parameters leads to the importance of identifying strains of the indigenous population. Bacterial species frequently have a definable habitat.

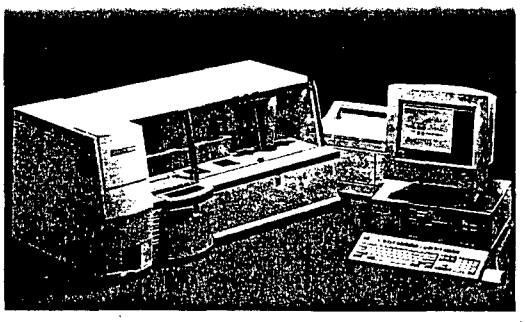


Shown are methods of characterization. Commonly performed total plate counts (upper left) show population densities; the riboprint with intensity tracing (upper right) identifies a specific strain; the 96-well microtiter plate (middle left) permits examination of a strain's metabolic activities. The RiboPrinter Microbial Characterization System (middle right) generates riboprints permitting differentiation of both species level isolates (bottom) by comparison of their riboprint patterns.

Two microbial identification systems used as a hand-in-glove combination include a fully automated gas chromatographic analytical system that identifies bacteria based on their unique fatty acid profiles, and the Biolog microplate system that uses carbon-source pattern recognition. Because no subjective tests are required in either of these methods the naming is highly objective and reproducible.

We at Microbe Inotech Laboratories Inc. in St. Louis, MO have developed several tests for determining if and how well bioremediation can occur at a site. The first test is called the endpoint assay, which will indicate if any of the indigenous or purchased strains of bacteria isolated are able to use a chosen contaminant or substrate as a carbon source. It also reveals how well this bacteria can use the carbon source compared to hundreds of other strains that have been tested. The endpoint assay uses the 96-well microtiter plate to give rapid testing with increased savings. In this test the microplate is loaded with a suspension of the isolated bacteria, the contaminant chosen, and media and water for the positive and negative controls. Each unknown and control is done in replicates of at least four wells for added accuracy. After 24 hours of incubation the plate is read in a microplate reader to determine the optical density of

each of the wells. A dye in the wells turns purple if the bacteria are using the carbon source. The higher the optical density the better the strains are at consuming the contaminant. Data are reported in an easy-to-read bar chart. Various organic compounds and products typically tested in this system are shown in Table 1, in which the reagent-grade chemical or product is prepared as aqueous solution or in an appropriate solvent. A second test, similar in design to the endpoint assay, is the hydrocarbon degradation kinetic assay used to screen and quickly characterize potential degraders for bioremedition uses. It is described in a later section.



RiboPrinter microbial characterization system.

A third analysis is called the comparative population assay. This is a most probable number (MPN) test that gives the order of magnitude of the degrader populations. The 96-well plate also is used in this test. The comparative population assay differs from the endpoint assay since a serial dilution of the soil or water sample is used directly in the plate along with the contaminant instead of the isolated strains. After 48 hours of incubation the plate is read in the microplate reader to determine the highest dilution at which growth is detected. This gives the MPN of the degrader populations. Also in the plate are positive growth control wells to provide the TPC information. Data from this test are displayed in bar chart form.

TABLE 1. ORGANIC SUBSTRATES

Acetone	Ethanol	Nitrobenzene
Aminonaphthalene	Fluorene	Phenanthrene
Benzene	Gasoline	Tetrachloroethylene
Carbon Tetrachloride	Jet Propellant No. 4	Toluene
Chloroform	Methanol	I,I,I Trichloroethane
Chrysene	Methyl Ethyl Ketone	Xylene
Crude oil	Methylene Chloride	Various Pesticides and Herbicides
1,2 Dichloroethylene	MTBE	
Diesel No. 2	Naphthalene	

One of the most frequently requested set of tests is the bioremediation feasibility study. It is a straightforward series of the analyses described above that provide an objective evaluation of a site for bioremediation.

The sample can be soil, water, or sludge. When the sample is received at the laboratory it is immediately prepared for the TPC. Over the next 48 hours the Petri plates containing dilutions of the samples are incubated for optimum bacteria growth. It is at this time that the number of different types of bacteria in the soil or water are determined by colony morphology. The next step is isolation, in which each type of bacterial colony is picked using a sterile loop, and then streaked onto a new Petri plate. These plates are then incubated for 24 hours in order to produce sufficient quantities of the strain. The isolated strains of bacteria are then harvested for processing in the endpoint assay and for identification by GC-FAME and Biolog. The endpoint assay tests the individual bacterial strains for their ability to use a specific substrate/contaminant as its only carbon source. This custom-designed test uses a negative control of water and a positive control of a nutrient broth. The growth success of the bacteria is illustrated in a bar chart report. The identification of the bacterial strains takes place while the endpoint assay is running. Two methods are employed as a cross-check for precision and to provide an exact profile of the strain. The GC-FAME method provides a profile of the fatty-acid composition of the bacteria, and the Biolog method provides a characterization of the bacteria by the carbon sources the strain can consume. Next, the raw data are compiled, and a summary table of the bacterial identifications and a bar chart of the endpoint assay raw data are created. These two items are incorporated into the full report at the conclusion of all tests.

Bacteria capable of degrading toxic organic chemicals have been isolated from a variety of environmental sites, including aquatic systems, deep wells, terrestrial subsurface sites, and fuel tanks. Procedures previously employed to determine degradative ability of isolates often required repeated enrichment and culture lasting from several weeks to months of exposure in toxic substances. Once it has been determined there are degraders present it is possible to determine how the addition of nutrients or oxygen will affect their growth rate by means of a nutrient kinetic study. The hydrocarbon degradation kinetic assay can be used to screen and quickly characterize potential degraders for bioremediation uses. Either kinetic study is similar to the endpoint assay in that it uses the 96-well microtiter plate. The kinetic plate is put into the microplate reader immediately after preparation. The optical density of the wells is then read every 10 or 15 minutes for 18 to 24 hours. Each reading is automatically plotted to create a growth curve. Comparisons of curves from wells with nutrients to the control wells gives precise information about how the addition of any substrates will affect the growth of strains from a site or innoculum mixture. Control wells consist of a series of wells with water-only as a blank; water plus the strain of interest for establishing the base-time metabolic activity; a bacterial growth medium as a positive test for strain viability; and the hydrocarbon of interest with water as another background check. The kinetic assay charts the growth behavior of the strain on the hydrocarbon present as the sole source of carbon for the microorganism. It is conducted by growing the strains to be tested overnight and suspending them in a diluent for transfer to the multi-well titer plate. The wells contain an undisclosed growth medium of mineral salts, vitamins, and buffer without a major carbon source except that introduced as a control or test hydrocarbon. The wells also contain a tetrazolium-dye redox indicator system. Bacterial growth (metabolic respiration, or oxidation of carbon sources) is monitored by tetrazolium reduction as measured at 590 nm wavelength in a microplate reader. Plots from all 96 wells can be viewed simultaneously, or plots from selected wells may be enlarged for closer examination of the growth curves.

The newest automated technology provides for molecular typing of bacteria. This type of technology can be used to track a particular organism among others and mon-

itor quality in the products of an industrial manufacturer or in the food products industry. Qualicon, a DuPont subsidiary, now provides Microbe Inotech Laboratories an instrument known as the RiboPrinter Microbial Characterization System that uses an array of patented technologies to produce a characteristic genetic fingerprint or pattern from any bacterial isolate. The technology can readily distinguish among bacterial isolates beyond the species level based on their genetic relatedness. The methodology involves a five-step process:

•*DNA Fragmentation.* DNA is extracted from bacterial cells and cut into fragments by a restriction enzyme (molecular scissors of the molecular biologist);

•*Separation and Membrane Transfer.* The DNA fragments are separated according to molecular size by gel electrophoresis and then transferred to a membrane;

•*Detection.* After hybridization with a labeled DNA probe, a chemiluminescent agent is introduced; the emission of light from the hybridized fragments is then captured by a digitizing camera and stored as image data;

•*Computer Analysis.* Using proprietary algorithms, a RiboPrint pattern for each sample is extracted from the image data; this pattern is compared to other RiboPrint patterns stored in the system to characterize and identify the sample; and

•*Final Report.* A report that characterizes and identifies the bacterium and includes its RiboPrint pattern is automatically printed.

The genetic fingerprint pattern of this system is generated from the ribosomal RNA (rRNA) operons and surrounding regions of the bacterial genome. The rRNA genes in bacteria, while highly conserved, are unique. Varying in number and position within the genome, they also vary in sequence regions within and adjacent to the operons. RiboPrint patterns explain this organism-specific information. The rRNAs are major components of ribosomes, which are responsible for protein synthesis. These operons are among the most highly conserved regions within the bacterial genomes. Thus the rRNA-based pattern is extraordinarily stable and resistant to environmental factors, such as growth media and stress. In addition, the similarity between patterns corresponds directly to the evolutionary relatedness of organisms.

Along with other technologies this allows microbiologists to utilize pathogen tracking and screening, such as examination of sludges for Salmonella or other specific organisms of interest at greatly reduced costs over manual and older methodologies. The modern life sciences laboratory with its smorgasbord of techniques and methods is a powerful aid to the informed bioremediation practitioner. Environmental microbiology is creating many options to the older microcosm approach in aiding the establishment of viability, quality control, liability reduction, isolate identification, and to strain functional characterizations such as biodegradation of specific environmental toxicants. **RM**

Bruce Hemming *is president and CEO, and* ***Julie Milke*** *is laboratory manager at Microbe Inotech Laboratories in St. Louis, MO.*

Bioremediation of Chlorinated Solvents

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American Chemical Society
September 27-29, 1993

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Volume III of III

CHARACTERIZATION OF HYDROCARBON DEGRADING BACTERIA USING A MULTI-WELL PLATE FORMAT.

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Solutions to feasibility issues of using indigenous or introduced bacterial populations for bioremediation of hydrocarbon contaminants can be assisted by bacterial identifications and characterization studies of bacteria from the contamination site. Following GC-FAME identifications of bacterial strains, functional assays for hydrocarbon degradation ability are performed in 96 well microtiter plates. Microtiter plates are used to incubate the bacteria, hydrocarbon contaminants, and media controls to determine the growth of strains on hydrocarbon contaminants such as gasoline, diesel fuel, crude oil or halogenated solvents (TCE, etc.) Aminopeptidase characterization assays have been utilized to examine the carbon and nitrogen utilization by contaminant degrading strains. Co-metabolic analyses for determination of the stimulatory or inhibitory effects of different carbon sources are completed in an automated fashion. The applicability of this format for examination of recombinant "biosensor" strains expressing metal dependent "switchable" enzymes is feasible.

Rifai, 1995

Intrinsic Bioattenuation for Subsurface Restoration

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ABSTRACT

Intrinsic bioattenuation has recently evolved as a viable remediation alternative at a number of sites where the risk of exposure to contaminants is within acceptable standards. Important mechanisms controlling the instrinsic bioattenuation include advection, dispersion, sorption, dissolution from a residual source, and abiotic and biological transformations. Because intrinsic bioattenuation is a plume management strategy, it requires characterizing and monitoring these processes. Intrinsic bioattenuation involves an assessment of risks to public health and the environment, and consequently requires prediction of the fate and transport of contaminants at the candidate sites. This paper reviews the processes controlling intrinsic bioremediation and summarizes case histories in which intrinsic bioattenuation has been observed at sites contaminated with petroleum hydrocarbons and chlorinated solvents. The key steps in evaluating natural attenuation as a remedial alternative are summarized.

INTRODUCTION

In the absence of human intervention, many contaminant plumes will develop until they reach a quasi-steady-state condition. At steady state, the contaminant plume is no longer growing in extent and may shrink somewhat over time. Major processes controlling the size of the steady-state plume include (1) release of dissolved contaminants from the source area, (2) downgradient transport of the contaminants and mixing with uncontaminated groundwater, (3) volatilization, and (4) abiotic and biologically mediated transformations of the contaminants of concern.

Intrinsic bioattenuation is a plume management strategy by which the natural assimilation processes are monitored and used to limit adverse impacts of groundwater contamination. This strategy also requires an assessment of risks to public health and other environmental receptors. A successful

implementation of intrinsic bioattenuation at a field site requires adequate site hydrogeological, chemical, and biological characterization; detailed data analysis to determine whether contaminants are being attenuated and/or removed from the aquifer; modeling of the fate and transport of the dissolved groundwater plume; and, finally, long-term monitoring to confirm and ensure protection of human health and the environment.

PROCESSES CONTROLLING THE STEADY-STATE CONTAMINANT DISTRIBUTION

Physical

The primary physical processes affecting the distribution of contaminants in groundwater include advection, dispersion, sorption, volatilization, and dissolution from residual contaminants located in the source area. Advection is the process by which contaminants are transported with the flow of groundwater. Dispersion accounts for mechanical and molecular mixing processes. Both advection and dispersion reduce contaminant concentrations but do not cause a net loss of mass of contaminants in the aquifer. Higher advection and dispersion cause more spreading and more dilution of a dissolved contaminant plume.

Sorption describes the partitioning of contaminants between the aqueous phase and the solid aquifer matrix. Sorptive processes tend to reduce the dissolved contaminant concentrations and limit the migration of the aqueous-phase plume, but they do not result in a loss of contaminant mass from the aquifer. Under steady-state conditions, sorption will not affect the final contaminant distribution; however, sorption will delay the development of a steady-state plume.

Volatilization refers to the partitioning of a contaminant between the aqueous phase in the saturated zone and the vapor phase in the unsaturated zone. While volatilization actually removes mass from the aquifer, it is not thought to be a significant attenuation mechanism except in situations where the groundwater table is less than 15 ft (4.6 m) deep and the unsaturated zone consists of relatively transmissive soils. Chiang et al. (1989) estimated that volatilization resulted in a mass loss of benzene of less than 5% at a gas plant facility in Michigan.

Dissolution from residual contaminants located in the source area is by far the most significant physical process that controls the extent of a contaminant plume. In the case of petroleum hydrocarbons, contaminants may dissolve from a lens of mobile hydrocarbons floating on the water table, or from residual hydrocarbons trapped in the soil matrix above and/or below the water table. Seasonal fluctuations in the water table can cause additional "smearing" and dissolution from residual source areas. Until sources are depleted, a contaminant plume will expand until it reaches a quasi-steady-state

Abiotic and Biologically Mediated Transformations

Aerobic and anaerobic biodegradation processes are believed to account for both contaminant concentration reduction and loss of pollutant mass from the aquifer. Abiotic transformations such as hydrolysis and dehydrohalogenation also attenuate concentrations and contaminant mass in an aquifer, but they are significant only for specific chemicals such as chlorinated solvents.

Aerobic biodegradation relies on dissolved oxygen as the electron acceptor used by the microorganisms. Petroleum hydrocarbons are generally very amenable to aerobic biodegradation in aquifers with dissolved oxygen concentrations exceeding 1 to 2 mg/L. Many shallow-water-table aquifers contain background dissolved oxygen concentrations between 1 to 12 mg/L depending on the temperature of the groundwater. While aerobic biodegradation takes place at relatively higher rates than anaerobic processes, it is often limited by the available supply of oxygen to a contaminant plume. Once the background dissolved oxygen is consumed in the center of the plume, aerobic biodegradation is limited to the edges of the contaminant plume, where the dissolved contaminants come into contact with oxygen-rich groundwaters.

Anaerobic processes refer to a variety of biodegradation mechanisms that use NO_3^-, SO_4^{2-}, Fe^{3+}, and CO_2 as terminal electron acceptors. Anaerobic biodegradation dominates the interior of a contaminant plume. Both petroleum hydrocarbons and chlorinated solvents are believed to biodegrade to varying degrees under anaerobic conditions. However, the rates of biodegradation are often slower than under aerobic conditions.

Hydrocarbon Biodegradation. Most organic compounds found in crude, refined oil and fuels are known to degrade under aerobic conditions. The aerobic biodegradation of benzene, toluene, ethylbenzene, xylenes, naphthalene, methyl-napthalenes, dibenzofuran, and fluorene has been confirmed by a large number of laboratory and field studies. Aerobic processes are relatively fast and limited by the rate at which oxygen is supplied to a contaminant plume. Because of this phenomenon, Rifai et al. (1988) modeled aerobic biodegradation as an instantaneous reaction between oxygen and the hydrocarbons.

Current research efforts have also shown that monoaromatic compounds degrade under anaerobic conditions. This biodegradation occurs with NO_3^- (Evans et al. 1991), Fe^{3+} (Lovley and Lonergan 1990), SO_4^{2-} (Edwards et al. 1991), and carbon dioxide (Grbic-Galic and Vogel 1987; Wilson et al. 1986) as electron acceptors.

Benzene has been found to be recalcitrant to anaerobic biodegradation in laboratory studies using nitrate and sulfate as electron acceptors (Kuhn and Suflita 1989a,b; Edwards et al. 1991). However, some laboratory and field studies demonstrated the degradation of all monoaromatic hydrocarbons under denitrifying, sulfate-reducing, and methanogenic conditions (Major et al. 1988; Cozzarelli et al. 1990; Vogel and Grbic-Galic 1986; Barker and Wilson 1992; Wilson et al. 1994a). The aromatic compounds may be oxidized first to phenols

mineralization. Anaerobic biodegradation of aromatic hydrocarbons is therefore associated with the production of fatty acids, methane, carbon dioxide, solubilization of iron, and reduction of nitrate and sulfate.

Adaptation of an aromatic plume to nitrate as a terminal electron acceptor seems to occur readily once oxygen is depleted. Natural biodegradation through nitrate respiration should be similar to oxidative biodegradation. Depending on its concentration, sulfate can also be an important electron acceptor. Acton and Barker (1992) demonstrated the sulfate reduction of toluene and *m*-xylene in a forced-gradient injection experiment at an active landfill in Ontario, Canada. Benzene, *o*-xylene, ethylbenzene, and 1, 2, 4- trimethylbenzene were not degraded at the site.

Chlorinated Aliphatic Hydrocarbons (CAH) Transformation. Chlorinated solvents, consisting primarily of CAHs, can be transformed by chemical and biological processes to form a variety of other CAHs (McCarty, 1994). Reduction of tetrachloroethene (PCE) and trichloroethene (TCE) to ethene has occurred at many sites, although transformations often are not complete. Freedman and Gossett (1989) provided evidence for the conversion of PCE and TCE to ethene and de Bruin et al. (1992) reported complete reduction to ethane. McCarty (1994) lists the possible transformations for a number of the predominant chlorinated solvents in groundwater (Table 1). McCarty (1994) indicates that methanogenesis is the most favorable mechanism for complete reduction of PCE and TCE to ethene.

A number of researchers have confirmed the biological transformation of CAHs at field sites. Major et al. (1991) reported evidence for bioattenuation of PCE to ethene and ethane at a chemical transfer facility in North Toronto. Fiorenza et al. (1994) presented data on the chemical and biological transformation of trichloroethane (TCA) to 1,1-dichoroethane (1, 1-DCA) and that of PCE and TCE to *cis*-dichloroethene (*c*-DCE), vinyl chloride (VC), and ethene at a manufacturing plant in Ontario. Beck (1994) reported the degradation of 1, 1, 1-TCA, PCE, and TCE to ethene and methane at the Dover Air Force Base (AFB) in Delaware. McCarty and Wilson (1992), Haston et al. (1994), Kitanidis et al. (1993), McCarty et al. (1991), and Wilson et al. (1994b) confirmed the

TABLE 1. Environmental conditions generally associated with reductive transformations of chlorinated solvents.

	Redox Environment			
Chlorinated Solvent	**All**	**Denitrification**	**Sulfate Reduction**	**Methanogenesis**
Carbon tetrachloride		CT → CF	CT → CO_2+Cl	
1,1,1-Trichloroethane	TCA → 1,1-DCE +CH_3COOH		TCA → 1,1-DCA	TCA → CO_2+Cl
Tetrachloroethylene			PCE → 1,2-DCE	PCE → ethene

intrinsic biodegradation of chlorinated solvents at the St. Joseph, Michigan, Superfund site.

In addition to biological transformations, chemical transformations of some CAHs can occur in groundwater through elimination or hydrolysis. TCA is one of the main chlorinated solvents that can be transformed chemically in groundwater under all conditions likely to be found and within a reasonable time frame (McCarty 1994). The rate of chemical transformations is usually expressed using a first-order reaction. TCA chemical transformation, for example, leads to the formation of 1,1-DCE and acetic acid with a reported average half-life of less than 1 year at a temperature of 20°C.

CASE STUDY—INTRINSIC BIOREMEDIATION OF A UST RELEASE

The underground storage tank (UST) release in Rocky Point, North Carolina, provides a representative example of a dissolved benzene, toluene, ethyl benzene, and xylenes (BTEX) plume undergoing intrinsic biodegradation using oxygen, nitrate, iron, and sulfate as terminal electron acceptors (Borden et al. 1995). The water table aquifer consists of mostly fine-grained, dark-gray or greenish-gray, micaceous, glauconitic, slightly silty, and compact quartz sand. The sand appears to be very homogeneous throughout the site with only a few exceptions. This sand is overlain by lower-permeability clays and clayey sands that form a surface confining layer throughout the site. The average groundwater velocity is approximately 30 m/y. The organic-carbon content of the sand is relatively low (0.1%), and consequently sorption is not a major attenuation mechanism for the moderately soluble BTEX fraction.

Spatial Distribution of BTEX and Indicator Parameters

Background groundwater contains moderate levels of dissolved oxygen (2 to 3 mg/L), nitrate (1 to 6 mg/L as N), and sulfate (20 to 30 mg/L). Background dissolved iron is low (< 0.5 mg/L), and the groundwater is acidic (pH < 5) with low buffering capacity (alkalinity ~ 6 mg/L as $CaCO_3$) and low levels of dissolved CO_2 (15 to 30 mg/L as C). At the upgradient edge of the BTEX plume, residual hydrocarbon is trapped below the water table in the sand aquifer. As uncontaminated groundwater enters this region, soluble hydrocarbons partition out of the nonaqueous-phase (NAPL) and into the aqueous phase. Figure 1 shows the observed variation in BTEX components, electron acceptors, and indicator parameters in a profile along the dissolved-hydrocarbon-plume centerline. Several distinct zones can be identified where different oxidation-reduction processes dominate.

At the upgradient edge of the BTEX plume, a portion of the soluble hydrocarbons released from the residual NAPL are immediately degraded using oxygen and nitrate carried into this zone by the flowing groundwater. Dissolved iron

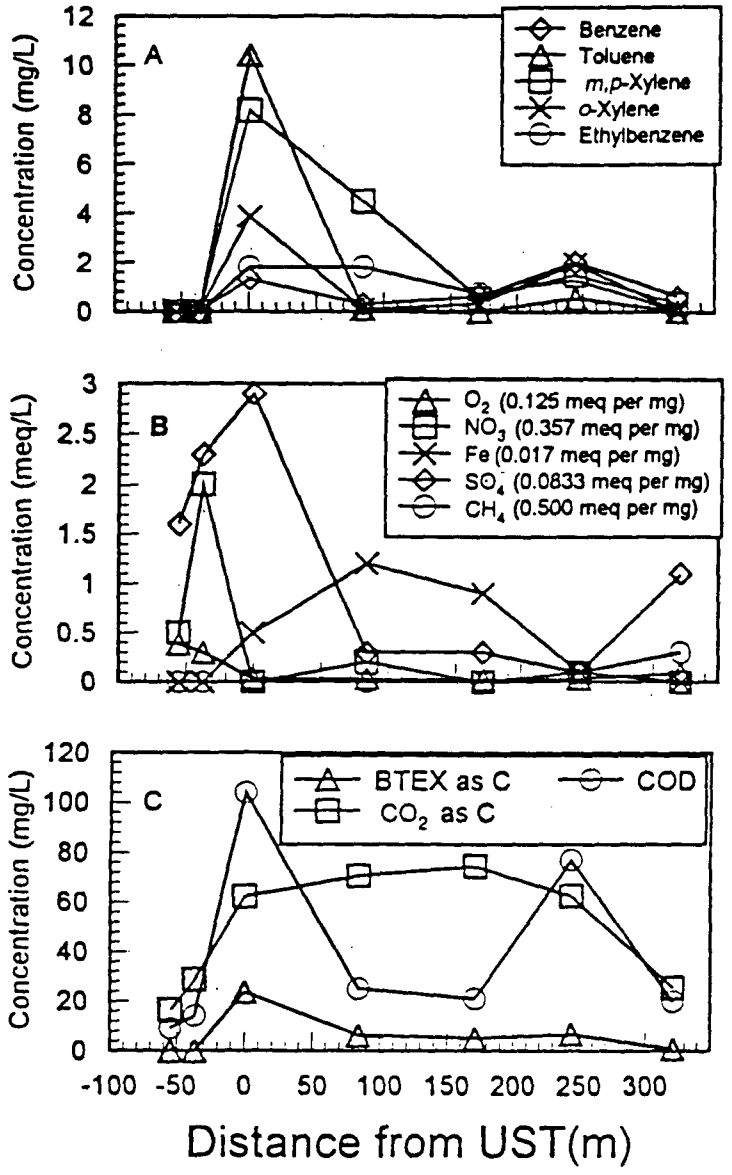

FIGURE 1. Variations in (A) BTEX components, (B) electron acceptors, and (C) indicator parameters in a profile along the plume centerline.

oxides associated with the sediment. In this region, the dominant electron acceptor is nitrate, followed by iron and oxygen. Dissolved CO_2 increases from 16 to 60 mg/L as carbon (C) because of oxidation of organic matter. The pH also rises from ~ 4.7 to 5.8 because of consumption of H^+ during iron reduction.

During transport downgradient from the source, toluene and *o*-xylene decline rapidly followed by *m*, *p*-xylene and benzene. Ethylbenzene does not decline notably with distance. This pattern is apparently due to preferential biodegradation of the *o*-xylene isomer (and toluene) by subsurface microorganisms. Sulfate decreases from 34 to 0.7 mg/L, total sulfur decreases from 37 to 5 mg/L as SO_4, and dissolved iron increases from 29 to 65 mg/L. The large decline in sulfate and increase in dissolved iron indicate that both sulfate and

sulfate is being reduced but is not being removed as ferrous sulfide (FeS) precipitates. Ion chromatographic analysis of the groundwater indicates that thiosulfate is a major component of the nonsulfate sulfur. Oxygen and nitrate are not significant electron acceptors in this portion of the plume since they were already consumed during transport through the source area.

The dissolved hydrocarbon plume becomes slightly narrower with distance downgradient. The limited spreading of the plume is apparently due to the combined effects of anaerobic biodegradation in the plume center and aerobic biodegradation at the sides of the plume. The background dissolved oxygen concentration varies from 2 to 3 mg/L, whereas in the center of the plume dissolved oxygen is below the field detection limit (0.3 mg/L). As the plume spreads in width by dispersion, oxygen in the uncontaminated groundwater mixes with BTEX, enhancing biodegradation at the plume sides. The zone of highest BTEX concentration also moves vertically downward with increasing distance downgradient. The vertical drop along the length of the plume is due to surficial groundwater recharge that both adds a layer of clean, uncontaminated water on top of the plume and enhances biodegradation by introducing oxygen and other electron acceptors with the recharge water.

Rates of Intrinsic Bioremediation

Field implementation of intrinsic bioremediation requires an accurate estimation of in situ biodegradation rates. Three different approaches were applied at the Rocky Point site to estimate intrinsic bioremediation rates: (1) comparing peak contaminant concentrations in monitoring wells versus travel time from the source (Borden et al. 1994); (2) monitoring laboratory microcosms under ambient (anaerobic) aquifer conditions (Hunt et al. 1995); and (3) monitoring in situ test chambers to determine compound loss over time (Hunt et al. 1995). The in situ test chambers were installed approximately midway down the plume in the iron-reducing zone, at the same location used to collect the sediment for the laboratory microcosms. Results from each of these approaches are compared in Table 2.

In the laboratory microcosms, a distinct order of biodegradation was observed. Toluene and *o*-xylene appeared to be the most biodegradable followed by *m*-, *p*-xylene and benzene, with ethylbenzene being the least biodegradable. This same order of disappearance is also seen in the field data. Unfortunately, the rates of biodegradation estimated from the field data are vastly different from the laboratory data. In the laboratory microcosms, the benzene, toluene, and xylene isomers were degraded from between 2,000 and 3,000 μg/L each to below detection limit in 400 days. Ethylbenzene was only slightly degraded over this period. If similar biodegradation rates were observed in the field, the benzene, toluene, and xylene plumes would completely biodegrade over 100 to 200 ft (30 to 60 m). Yet significant concentrations of these dissolved hydrocarbons persist over 1,300 ft (396 m) downgradient from the source. The cause of this discrepancy is not well understood

TABLE 2. Comparison of intrinsic bioremediation rates from field monitoring, laboratory microcosms and in situ test chambers.

Compound	Field Rate (d^{-1})	Laboratory Rate (d^{-1})	In Situ Rate (d^{-1})
Benzene	0.0002	0.024	0.004
Toluene	0.0021	0.045	0.012
Ethylbenzene	0.0015	0.002	N.S.[a]
o-Xylene	0.0021	0.056	N.S.
m-,p-Xylene	0.0013	0.02[b]	0.014

(a) Not significant at 95% level.
(b) Only *m*-xylene in laboratory microcosms.

Figures 2a and 2b show the vertical distribution of benzene, ethylbenzene, *m*-, *p*-xylene, and two trimethylbenzene isomers (mesitylene and pseudocumene) in a multilevel sampler located 800 ft (244 m) downgradient from the source near the location of the in situ test columns. The concentrations of toluene and *o*-xylene were too low to be shown on these figures. In both figures, the vertical distribution of the more recalcitrant compounds (benzene, ethylbenzene, and mesitylene) is relatively consistent. In contrast, there are large changes in the concentration of the more biodegradable compounds (*m*-, *p*-xylene and pseudocumene). This suggests that the rate of biodegradation may be significantly different between adjoining layers.

The observed differences in field and laboratory biodegradation rates could be due to changes in the activity of different layers against the pollutants. In the field, if one layer is not active against the pollutants, the vertically averaged concentration measured with long-screened wells would remain high and the apparent biodegradation rate would be low. In contrast, within in situ test columns and laboratory microcosms, groundwater is forced into contact with sediment of differing activities. This would result in a higher apparent biodegradation rate.

CASE STUDY—INTRINSIC BIOREMEDIATION OF TCE IN GROUND WATER

The groundwater at the St. Joseph, Michigan, site is contaminated with CAHs at concentrations ranging from 10 to 100 mg/L. The contaminants are divided into eastern and western plumes as the suspected sources were situated over a groundwater divide. Both plumes contain TCE; *cis*- and *trans*-1, 2-dichloroethene (*c*-DCE and *t*-DCE), 1, 1-dichloroethene (1, 1-DCE), and VC

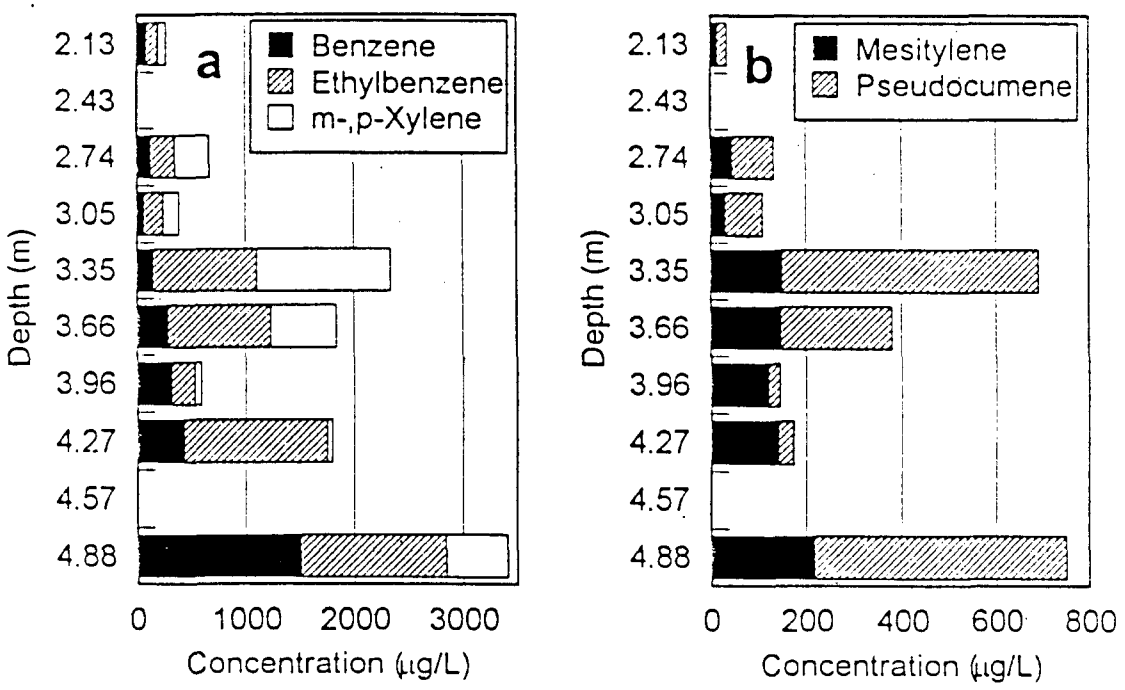

FIGURE 2. Vertical distribution of dissolved hydrocarbons in iron-reducing zone 170 m downgradient from the former UST.

et al. 1993; McCarty and Wilson 1992), confirming the natural attenuation of TCE.

McCarty and Wilson (1992) delineated contours of the chemical oxygen demand (COD)—a surrogate for the capacity of a donor to supply electrons—and correlated them with contours of chlorinated aliphatic compounds (see Figure 3a and b). The authors found a correlation between COD decrease and transformations of TCE to VC. Also shown in Figure 3a are the locations of three transects where data were collected for the detailed bioattenuation characterization. Table 3 summarizes the electrons released by TCE reduction to different products, along with the equivalent amount of COD decrease. Essentially, the reduction of 1 mole or 131 g of TCE to ethene releases six electrons, and an equivalent decrease of 48 g of COD is needed.

Table 4 summarizes the CAHs, ethene, and methane found at some of the monitoring locations. The average concentration of methane at depths of 25 m or more was 6 mg/L. This concentration of methane corresponds to an equivalent COD decrease of 24 mg/L. However, McCarty and Wilson (1992) measured COD rease, as high as 200 mg/L. They attribute this inconsistency to either dilution effects between the lagoon and the detailed characterization location, or to the presence of other electron acceptors such as nitrate and sulfate.

Apparent Degradation Constants

Wilson et al. (1994b) studied the western plume at the site to estimate the

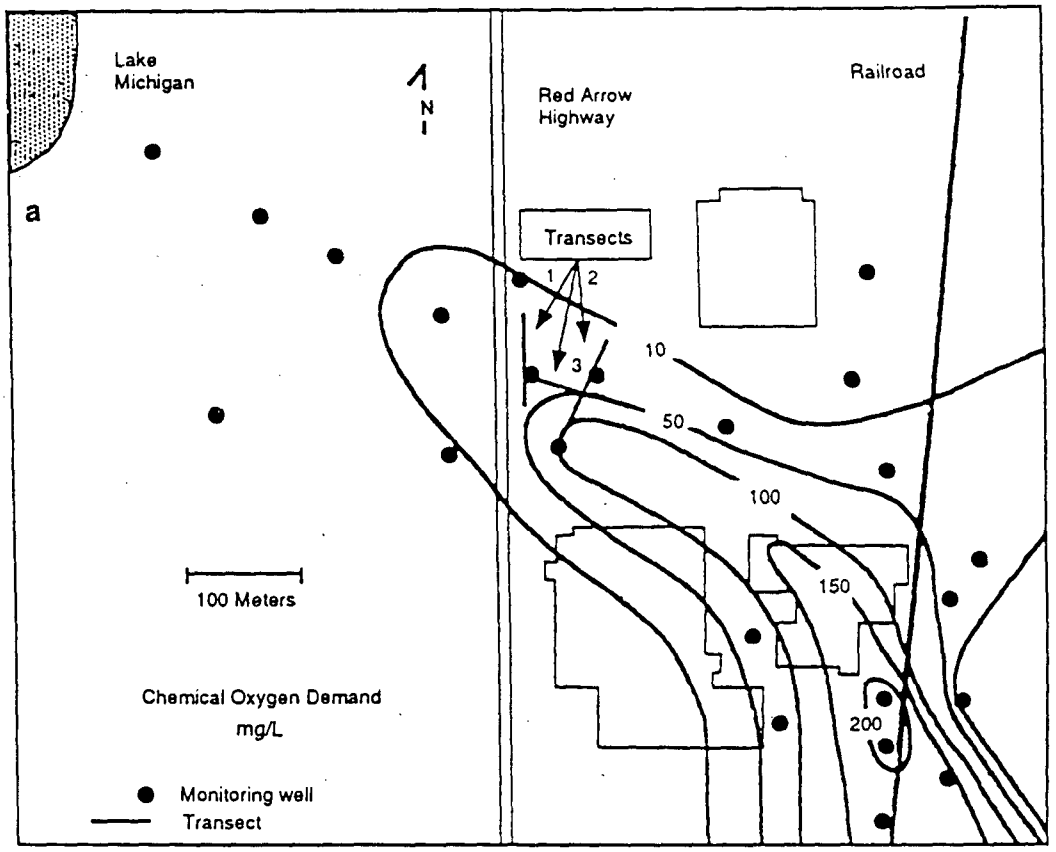

FIGURE 3a. COD contours at the St. Joseph, Michigan, NPL site.

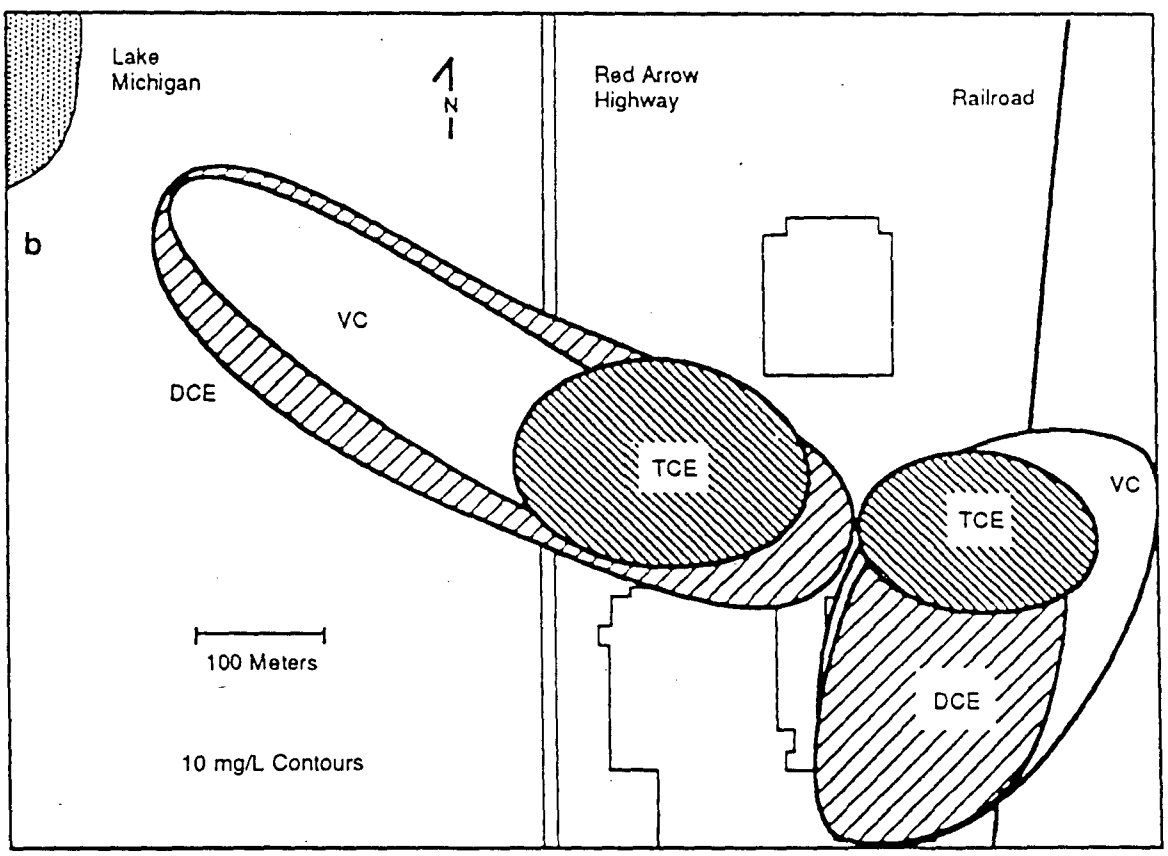

TABLE 3. Half-reactions indicating electron equivalents of change and associated equivalent COD decrease associated with change.

Transform product	Mol. Wt.	Half-Reaction	Equiv. COD decrease g COD/g product[a]
Methane	16	$CO_2+8H^++8e^- \rightarrow CH_4+2H_2O$	4
DCE	97	$CHCl=CCl_2+H^++2e^- \rightarrow CHCl=CHCl+Cl^-$	0.16
VC	62.5	$CHCl=CCl_2+2H^++4e^- \rightarrow CH_2=CHCl+2Cl^-$	0.51
Ethene	28	$CHCl=CCl_2+3H^++6e^- \rightarrow CH_2=CH_2+3Cl^-$	1.71

(a) From ($O_2+4H^+4e^- \rightarrow 2H_2O$), the half-reaction for oxygen, one electron equivalent of COD equals one-fourth mole of molecular oxygen or 8 grams, thus equiv. COD decrease = (8n/Mol. Wt), where n is the number of electrons in the half-reaction.

TABLE 4. Concentrations of CAHs, ethene, and methane found at selected sampling locations along detailed characterization transects and the equivalent COD decrease associated with the products.

Sample[a]		TCE	1,1-DCE	c-DCE	t-DCE	VC	Ethene	CH_4	Total
1-2-70	mg/L	4.03	0.09	4.14	0.81	3.19	6.62	4.61	
	Equiv. COD Decrease, mg/L	0.0	0.01	0.66	0.13	0.41	11.32	18.44	30.97
	% of Equiv. COD	0.0	0.0	2.1	0.4	1.3	36.6	59.5	
1-3-75	mg/L	12.80	0.27	16.90	0.67	56.40	2.25	6.62	
	Equiv. COD Decrease, mg/L	0.0	0.04	2.70	0.11	28.80	3.84	26.00	61.5
	% of Equiv. COD	0.0	0.1	4.4	0.2	46.8	6.2	42.2	
22-1-75	mg/L	0.44	0.09	13.40	0.21	1.46	3.15	7.43	
	Equiv. COD Decrease, mg/L	0.0	0.01	2.14	0.03	0.74	5.39	29.72	38.03
	% of Equiv. COD	0.0	0.0	5.6	0.1	1.9	14.2	78.1	
2-6-65	mg/L	0.51		4.70	0.03	2.66	4.27	11.72	
	Equiv. COD Decrease, mg/L	0.0	0.0	0.75	0.0	1.36	5.98	46.88	54.97
	% of Equiv. COD	0.0	0.0	1.4	0.0	2.5	10.9	85.3	
3-2-80	mg/L	2.53	0.01	0.90	0.03	0.27	4.87	11.59	
	Equiv. COD Decrease, mg/L	0.0	0.0	0.14	0.0	0.14	8.32	46.36	54.96
	% of Equiv. COD	0.0	0.0	0.3	0.0	0.3	15.1	84.4	

(a) First value is transect number, second value is borehole number, and third value is depth of sample below ground surface in feet.

collected in 1991 from three transects near the source of the western plume and data collected in 1992 from two additional transects were used in the analysis (see Figure 4 for locations of the transects). The mass estimates combined with the [illegible] were used to estimate the mass flux at each transect. As

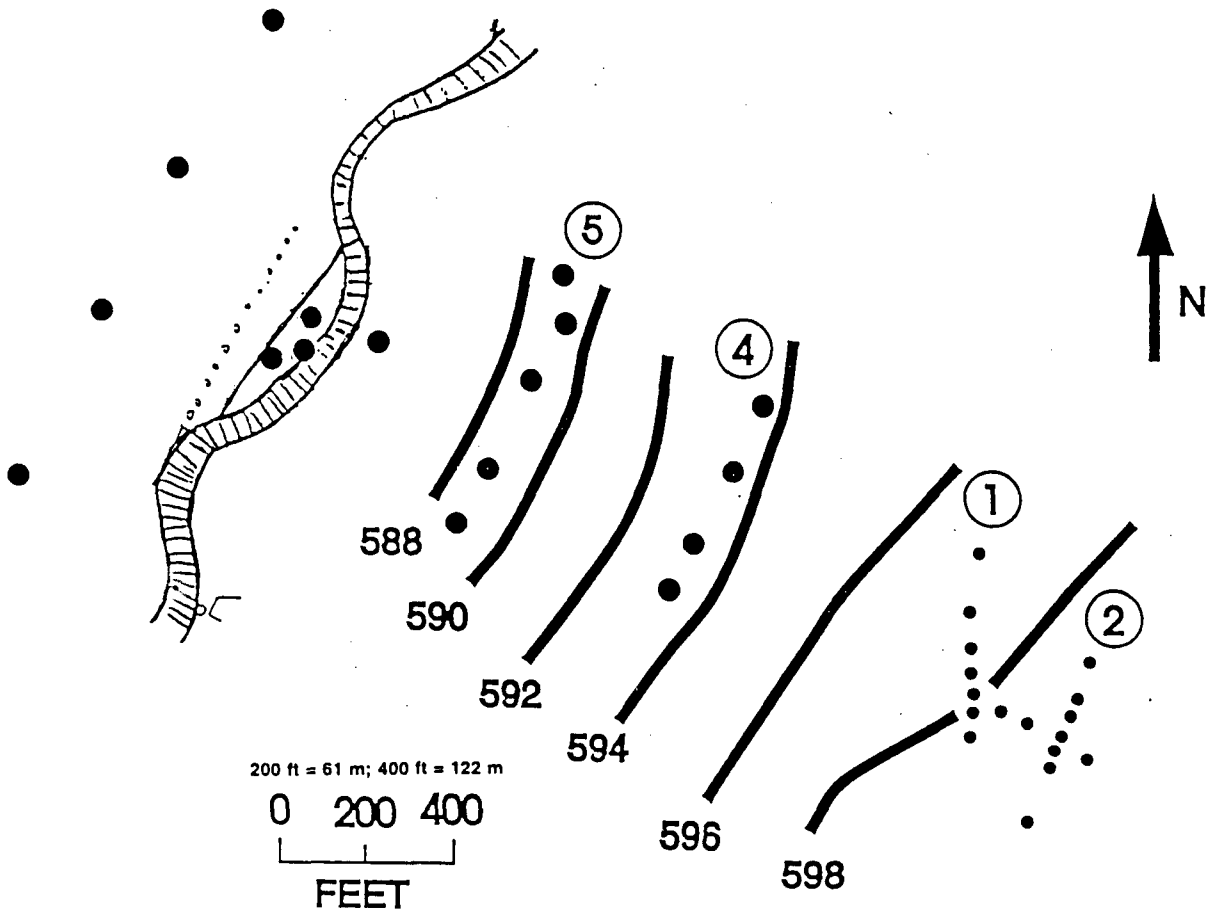

FIGURE 4. Locations of the 1991 and 1992 sampling transects at the St. Joseph, Michigan, NPL site.

would be expected, the mass fluxes decline toward the downgradient edge of the plume.

The mass per unit thickness of TCE at transects 2, 4, and 5 was used to estimate first-order degradation constants. Table 5 lists the computed apparent loss coefficients for three different estimates of the hydraulic conductivity at the site. The rate for TCE degradation ranges from 0.0048 to 0.011 wks^{-1} between the upgradient transects 2 and 4. This rate increases up to 0.023 wks^{-1} between transects 4 and Lake Michigan.

DEMONSTRATING INTRINSIC BIOREMEDIATION IN THE FIELD

Initial Monitoring to Determine Feasibility of Intrinsic Bioremediation

Extensive field monitoring is initially conducted to determine if intrinsic bioremediation is feasible as a remedial alternative at a site. Rifai (1990) and

TABLE 5. Apparent loss coefficients at St. Joseph, Michigan.

	Compound	Low Conductivity Estimate (1wk)	Avg. Conductivity Estimate (1 wk)	High Conductivity Estimate (1 wk)
Transects 2 to 4				
	TCE	0.0048	0.0074	0.011
	c-DCE	0.0064	0.0097	0.013
	t-DCE	0.0076	0.012	0.0016
	1,1-DCE	0.0066	0.010	0.0135
	VC	0.0023	0.0035	0.0047
Transects 4 to 5				
	TCE	0.016	0.025	0.033
	c-DCE	0.010	0.016	0.021
	t-DCE	0.010	0.016	0.021
	1,1-DCE	0.012	0.018	0.024
	VC	0.011	0.017	0.023
Transects 5 to Lake				
	TCE	0.011	0.018	0.023
	c-DCE	0.038	0.059	0.079
	t-DCE	0.0092	0.014	0.019
	1,1-DCE	—	—	—
	VC	0.053	0.081	0.11

and soil gas (see Table 6). These protocols were intended for UST sites and mostly focused on defining the electron acceptor distribution in the groundwater, and on quantifying the by-products of biodegradation in groundwater and soil gas. Since then, the Air Force Center for Environmental Excellence (AFCEE) has developed a detailed protocol for site characterization in support of the natural attenuation alternative at Air Force facilities (Wiedemeier et al. 1994).

At a minimum, site characterization in an intrinsic bioattenuation protocol should provide data on the location and extent of contaminant sources, the extent and distribution of dissolved contaminants, groundwater geochemical data (i.e., concentrations of electron acceptors and by-products of biodegradation mechanisms), geologic characterization data, and hydrogeologic parameters such as hydraulic conductivity, gradients, and potential migration pathways.

The site characterization data are analyzed to quantify the extent of intrinsic bioattenuation. Overall, three indicators of natural attenuation can be

TABLE 6. Proposed parameters for field measurements.

Medium	Parameter
Soil	Microbial counts/activity
	TOC[a]
	BTEX
Groundwater	Temperature
	Dissolved oxygen
	Carbon dioxide
	Conductance
	pH, TDS[b]
	Redox potential
	Ca, Mg, Na, Mn, Fe, SO_4, Cl
	Total alkalinity
	BOD[c], COD[d], TOC, BTEX
	NO_3, NO_2, NH_4, PO_4
Soil Vapor	O_2, CO_2, CH_4, H_2S

(a) TOC = total organic carbon;
(b) TDS = total dissolved solids;
(c) BOD = biological oxygen demand;
(d) COD = chemical oxygen demand.

1. Compound disappearance: one of the most convincing arguments for natural attenuation involves demonstrating the disappearance of a dissolved organic chemical at the site relative to the persistence of another "conservative" or "recalcitrant" organic (internal standard). In some cases, it is sufficient to demonstrate that the extent of migration of the organic of concern is less than that of the "conservative" tracer, and thus its transport downgradient is being limited by natural attenuation. In cases where compound disappearance cannot be related to an internal standard, it may be possible to demonstrate mass loss as a function of time for the organic of interest. Another alternative involves analyzing the peak concentrations of the organic at the different monitoring wells downgradient from the source. This analysis should demonstrate the overall decline of these concentrations as a function of time and distance.
2. Loss of electron donors: measuring dissolved oxygen concentrations and those of other electron acceptors can provide a key indicator of natural attenuation. Reduced oxygen, nitrate, and sulfate concentrations within the plume relative to their background concentrations are considered to be strong evidence of intrinsic bioattenuation. Many field studies, for instance, have correlated depressed oxygen concentrations within the center of a

3. Degradation products: the accumulation of dissolved iron and the production of carbon dioxide, hydrogen sulfide, and methane are additional indicators of biological attenuation at intrinsic bioremediation sites.

One of the interesting questions that is currently being investigated by researchers is whether it may be possible to complete a mass balance on the supply of electron donors and electron acceptors at a given field site. This question is complicated, because of sampling and field-data collection limitations. Other complicating factors involve the temporal nature of the distributions of the electron acceptors and donors.

Risk Assessment

The successful application of the natural attenuation alternative involves an exposure- and risk-assessment analysis that considers the location of receptors at a site in relation to the extent of the contaminant plume. While a detailed discussion of risk assessment is beyond the scope of this paper, it is important to note that intrinsic bioremediation will only be viable as a remedial alternative if it can be demonstrated that little risk to human health and the environment will be incurred as a consequence of this management strategy. To demonstrate the viability of intrinsic bioremediation, it may be necessary to conduct fate and transport predictions of the future conditions at contaminated sites.

Prediction of Plume Migration—Modeling Approaches

Two key questions need to be answered when determining the viability of natural attenuation as a remediation alternative, namely (1) how far the dissolved plume will migrate before it is attenuated to below a predetermined cleanup standard, and (2) how long it will take for the attenuation process to "clean up" the plume. Both questions can be readily answered using analytical and numerical models of fate and transport. Analytical models are simpler to use, but they are limited in their capabilities to simplified hydrogeologic scenarios. Numerical models are more complicated, but can be used to simulate heterogeneous systems and more complex hydrogeologic and contaminant scenarios.

Numerous fate and transport models have been developed over the years. The majority of these models simulate advection, dispersion, sorption, and some form of source representation. A smaller number of these models, however, can actually simulate complex biological and chemical transformation processes. In the analytical modeling arena, the most common method for simulating biodegradation is through the use of a first-order decay coefficient. The contaminant of concern is assumed to biodegrade exponentially, and the modeler specifies the first-order decay constant for a given site and a given contaminant. This leaves the modeler with the dilemma of selecting a first-order decay constant.

While many laboratory and field studies have developed first-order decay constants for a variety of contaminants under a number of hydrogeologic scenarios, these constants are not readily transferable to other sites. Another problem noted by Rifai (1994) is that the first-order decay model does not account for electron acceptor limitations and thus can overestimate the effect of biodegradation on a given system. Connor et al. (1994) proposed using an instantaneous reaction expression similar to that used in BIOPLUME II (Rifai et al. 1988) as an alternative to the first-order decay model. Additionally, Rifai and Hopkins (1995) have developed, through modeling with BIOPLUME II, "electron-acceptor" limited decay coefficients for scenarios with contaminant sources removed and continuous contaminant sources (Tables 7a and 7b) to provide more "applicable" decay constants.

Finally, and for sites where a long history of monitoring exists, it may be possible to estimate a first-order decay constant based on the observed mass loss in the aquifer. The dissolved concentrations for different sampling events are used to generate an estimate of the dissolved mass in the aquifer as a function of time. The resulting data allow the modeler to estimate a first-order decay constant. It should be mentioned, however, that this procedure is highly dependent on the density of the sampling network and would not be very accurate for sites with a limited number of monitoring wells.

Numerical models, as mentioned earlier, can provide more simulation capabilities than analytical models. The BIOPLUME II model (Rifai et al. 1988) allows the user to simulate a heterogeneous aquifer system with a variable flow field. The BIOPLUME II model is one of the few two-dimensional models that can simulate the transport of an electron acceptor (oxygen in this case) and its reactions with the aquifer contaminants. The model currently simulates the instantaneous reaction between oxygen and aromatic hydrocarbons. Rifai et al.

TABLE 7a. **Aerobic decay rates for removed source scenario.** [a]

	Gradient	12 mg/L	9 mg/L	6 mg/L	3 mg/L
Sand	0.01	3.8E-04	2.5E-04	1.8E-04	1.0E-04
	0.001	1.0E-06	1 0E-06	7.5E-07	7.5E-07
Silt	0.01	1.0E-05	1.0E-05	7.5E-06	5.0E-06
Clay	0.01	1.0E-05	1.0E.05	1.0E-06	1.0E-06

(a) The decay rates listed in this table were obtained through BIOPLUME II model simulations. A continuous source scenario assuming 100 mg/L was injected at a rate of 10 gal/d (38 L/d) in the sand hydrogeologic environment. A lower injection rate, 1 gal/d (3.8 L/d), was used in the silt and clay hydrogeologic environment to minimize mounding in the model. Centerline concentrations at different receptor well locations modeled for oxygen-limited

TABLE 7b. Aerobic decay rates for continuous source scenario. [b]

	Gradient	12 mg/L	9 mg/L	6 mg/L	3 mg/L
Sand	0.01	–3.2E-01	–2.1E-01	–1.3E-01	–6.8E-02
	0.001	–3.3E-02	–2.4E-02	–1.7E-02	–1.0E-02
	0.0001	–8.7E-03	–6.3E-03	–4.1E-03	–2.5E-03
Silt	0.01	–5.8E-03	–4.1E-03	–3.0E-03	–1.6E-03
	0.001	–2.8E-04	–2.4E-04	–2.1E-04	–1.8E-04
	0.0001	–2.5E-05	–2.4E-04	–2.1E-05	–2.3E-05
Clay	0.01	–4.0E-04	–3.4E-04	–3.0E-04	–2.6E-04
	0.001	–2.1E-04	–3.5E-05	–3.0E-05	–2.7E-05
	0.0001	–4.3E-06	–3.7E-06	–3.2E-06	–2.9E-06

(b) The decay rates listed in this table were obtained through BIOPLUME II model simulations. A removed source scenario assuming a plume 45 ft (14 m) and 50 ft (15 m) long with an initial concentration of 10 mg/L was simulated. Log of present mass dissolved at 1 month to 5 to 10 years was plotted over time. The decay rate is the slope of the plotted line.

(1995) are extending the BIOPLUME II model to allow the simulation of multiple electron acceptors within a contaminant plume. A number of other numerical biodegradation models exist in addition to BIOPLUME II (Table 8). The majority of these models, however, are either one dimensional or of a proprietary nature.

One of the difficulties encountered in using numerical models is determining what data are required and how to incorporate the field data into the modeling process. Most fate and transport models require an estimate of the aquifer thickness, matrix conductivity, porosity, and sorptive characteristics. Additionally, most models require some description of the hydraulic and hydrologic stresses on the system in the form of boundary conditions, or recharge and discharge specifications. One of the most complicated parameters to estimate for numerical models is the source representation because, in most cases, the history of contamination at the site is not known with any degree of certainty. Finally, biodegradation models require input on the electron acceptor availability within the aquifer.

The process of simulating natural attenuation at a site using a numerical model requires (1) calibrating the model to the hydraulics at the site so that the model can emulate the direction of flow and observed groundwater velocities in the field; and (2) calibrating the model to simulate existing contamination conditions. Once those two steps have been completed, the numerical model can be used to determine the distribution of contaminants at the site as a func-

TABLE 8. Biodegradation models (from Bedient et al. 1994).

Name	Description	Author(s)
—	1-D, aerobic, microcolony, Monod	Molz et al. (1986)
BIOPLUME	1-D, aerobic, Monod	Borden and Bedient (1986)
—	1-D, analytical first order	Domenico (1987)
BIO1D	1-D, aerobic and anaerobic, Monod	Srinivasan and Mercer (1988)
—	1-D, cometabolic, Monod	Semprini and McCarty (1991)
—	1-D, aerobic anaerobic, nutrient limitations, microcolony, Monod	
—	1-D, aerobic, cometabolic, multiple substrates, fermentative, Monod	Celia et al. (1989)
BIOPLUME II	2-D, aerobic, instantaneous	Rifai et al. (1988)
—	2-D, Monod	MacQuarrie et al. (1990)
BIOPLUS	2-D, aerobic, Monod	Wheeler et al. (1987)
ULTRA	2-D, first order	Tucker et al. (1986)
—	2-D, denitrification	Kinzelbach et al. (1991)
—	2-D, Monod, biofilm	Odencrantz et al. (1990)

One of the problems faced in modeling intrinsic bioattenuation of organic chemicals at sites is the fact that the observed data usually incorporate the effects of advection, dispersion, sorption and biodegradation. Therefore, it may be difficult to estimate the advective and dispersive components independently from these data. A possible solution is to use a "conservative tracer" or an "internal standard" in the calibration of the numerical model that does not sorb or biodegrade. For example, when simulating gasoline spills, it may be possible to use methyl terbutyl ether (MTBE) concentrations in the calibration process if the data exist. (MTBE does not sorb or biodegrade and thus would reflect the advective and dispersive characteristics of the aquifer). The biodegradation and sorption of the aromatic hydrocarbons within the gasoline plume can be readily estimated by comparing the BTEX plume to the MTBE plume. Wiedemeier et al. (1995a,b) have also suggested the use of tetramethylbenzene as a more recalcitrant internal standard at fuel-spill sites.

SUMMARY OF INTRINSIC BIOREMEDIATION FIELD SITES

Over the past decade, a large number of sites undergoing intrinsic bioremediation have been studied in detail. Some of the major characteristics of selected sites are provided in Table 9. Upgradient background concentrations of oxygen, nitrate, and sulfate provide an indication of the concentrations potentially available for biodegradation. Elevated concentrations of Fe^{2+} and CH_4 in the plume reflect the importance of iron reduction and methanogenic fermentation. At many sites, significant concentrations of iron, nitrate, and sul

TABLE 9. Characteristics of intrinsic bioremediation field sites.

			Background			Plume	
Site	Aquifer Type	pH	O_2 (mg/L)	NO_3-N (mg/L)	SO_4 (mg/L)	Fe^{2+} (mg/L)	CH_4 (mg/L)
Borden, Ontario (Barker et al. 1987)	glaciolacustrine, medium to fine sand						
Borden, Ontario (Barbaro et al. 1992)	glaciolacustrine, medium to fine sand	7.4	<0.07	<0.05	220		
Rocky Point, NC (Borden et al. 1995)	marine, fine sand	4.7	2.5	6	30	102	0.4
Kalkaska, MI (Chiang et al. 1989)	medium-coarse sand, gravel interbeds	5.5-7.0	9	0.8	1-6		
Columbus, MS (MacIntyre et al. 1993)	fluvial, hetero-geneous sands and clays		2.6-3.8				
Sleeping Bear, MI (Wilson et al. 1994a)	glacial outwash, coarse sand/gravel	6.4	2.4	15	20	17-28	24-30
Eglin AFB, FL (Wilson et al. 1994a)	sands and silty peats	5.6-6.7				8.0	17
Hill AFB-1, UT (Wiedemeier et al. 1994)	thin channel sands in deltaic deposits	~7	6	8	100	50	2
Patrick AFB, FL (Wiedemeier et al. 1994)	fine to coarse marine sand with shell fragments	~7	3.7	0.3	86	1.9	14.6
Fairfax, VA (Buscheck et al. 1993)		5	2.5-4			43	
Sampson Co., NC (Borden personal communication 1995)	clayey and silty sands	4-5	8	17	8	0.4	<0.01
Traverse City (Wilson et al. 1990)	glaciolacustrine, medium sand with gravel	7	9	3	10	12	17
Broward Co., FL (Caldwell et al. 1992)		7.2	2-3	0.3	<5	1.8	
Pensacola, FL (Godsy et al. 1992; Bekins et al. 1993)	poorly sorted fine to coarse deltaic sands	6.9	0.04	2	6	33	13
Bemidji, MN (Baedecker et al. 1993)	glacial outwash, coarse sand with silt layers	7.6	7.7	0.001	2	16	12
Galloway, NJ (Cozzarelli and Baedecker 1992)	fine to coarse sand, perched water table on clay lens	4.7	6	9	24	37	0.007
Perth, Australia (Thierrin et al. 1993)	medium to fine aeolian sand	5.8	0.4	0.1	20-100	1.4	
Manufacturing Plant (Davis et al. 1994)	glacial silty sand over bedrock	6.9	1.5	<0.005			
Cliffs-Dow (Klecka et al. 1990)	coarse sand and gravels	6.1	1.2	1.7	48		
Hill AFB-2, UT (Dupont et al. 1994)			4	6.9			

fermentation has been documented at several sites, it appears to be less important than iron and sulfate reduction.

Biodegradation results from field and laboratory studies are reported in Table 10. Laboratory results are reported only if the laboratory study was designed to simulate field conditions. Effective decay rates have been estimated in the field using several approaches. The most reliable approach is to calculate a mass balance for a known mass of contaminant injected into an aquifer, using a dense network of monitoring points. This approach is feasible only when a pulse of contaminant is injected. For continuous sources at steady state, the degradation rates may be calculated from the change in total mass flux across several lines of monitoring wells. Both the mass balance and mass flux approaches are expensive to implement because of the high number of monitoring points required. At most field sites, the only feasible approach is to estimate the degradation rate from a plot of peak contaminant concentration versus travel time from the source. This general approach has been modified by normalizing the contaminant concentrations to an internal standard that is poorly biodegradable, has similar sorption and volatilization properties as the contaminant, and is present in the waste source. Ideally, the internal-standard approach should correct for changes in concentration due to dilution.

There is a wide range in reported biodegradation rates. Reported first-order degradation rates for benzene range from nondetectable to approximately 1% per day, with an average of approximately 0.2% per day. Degradation rates for other hydrocarbons are typically somewhat higher, but in the same general range. Higher biodegradation rates occur most frequently at sites containing higher concentrations of sulfate in the background water and higher concentrations of dissolved iron in the plume. Where high concentrations of methane are observed, biodegradation rates are often lower.

SUMMARY

Past research has shown that intrinsic bioremediation can control the migration of dissolved hydrocarbon plumes. Field biodegradation rates are often lower than would be expected based on laboratory results, but are often sufficient to contain the contaminant plumes within reasonable transport distances. Fewer data are available on chlorinated hydrocarbon plumes, but ongoing studies suggest that intrinsic bioremediation may also be technically feasible at these sites. At many sites intrinsic bioremediation alone may be the best alternative available for risk management.

Intrinsic bioremediation will be the preferred alternative when the costs of conventional remediation are high, the problem compounds are easily biodegradable, aquifer conditions are appropriate, there are no nearby groundwater receptors, and/or there is a well-defined surface-water discharge. Intrinsic bioremediation alone may not be the best alternative when the costs

TABLE 10. Biodegradation results from field and laboratory studies at intrinsic bioremediation sites.

Site	Contaminant	V (m/d)	Field Results	Laboratory Results
Borden, Ontario (Barker et al. 1987)	BTX stock solution injected into uncontaminated aquifer	0.09	Zero-order decay rates from mass balance method: benz. = 30 mg d^{-1}; tol. = 37 mg d^{-1}; *m*-xyl. = 47 mg d^{-1}; *p*-xyl. = 55 mg d^{-1}; *o*-xyl. = 33 mg d^{-1}.	Zero-order decay rates (per 1,800 L) from aerobic microcosms: benz. = 58 d^{-1} tol. = 61 mg d^{-1}; *m*-xyl. = 50 mg d^{-1}; *p*-xyl. = 65 mg d^{-1}; *o*-xyl. = 54 mg d^{-1}.
Borden, Ontario (Barbaro et al. 1992)	stock solution contacted with gasoline then injected into leachate plume	0.09	% loss over 4 m travel.	
Rocky Point, NC (Borden et al. 1995)	residual gasoline from UST	0.08	Rates from conc. vs. travel time: benz. = 0.0002 d^{-1}; tol. = 0.0021 d^{-1}; e-benz. = 0.0015 d^{-1}; *m,p*-xyl. = 0.0013 d^{-1}; *o*-xyl. = 0.0021 d^{-1}.	Rates from Fe/SO_4 reducing microcosms: benz. = 0.024 d^{-1}; tol. = 0.045 d^{-1}; e-benz. = 0.002 d^{-1}; *m,p*-xyl. = 0.02 d^{-1}; *o*-xyl. = 0.056 d^{-1}.
Kalkaska, MI (Chiang et al. 1989)	natural gas condensate–BTEX	0.2	Rates from mass balance: benz. = 0.0095 d^{-1}.	Rates from aerobic microcosms: BTX = 0.01 to 0.1 d^{-1}.
Columbus, MS (MacIntyre et al. 1993)	stock solution of benzene, *p*-xylene, naphthalene, *o*-dichlorobenzene		Tritium used as nonreactive tracer. Mineralization proven using ^{14}C -*p*-xyl. Rates from mass balance: benz. = 0.0070 d^{-1}; *p*-xyl. = 0.0107 d^{-1}; naphthalene = 0.0064 d^{-1}; *o*-DCB = 0.0046 d^{-1}.	
Sleeping Bear, MI (Wilson et al. 1994b; Schafer, 1994)	residual gasoline from UST release–BTEX	0-0.4	Rates from conc. vs. travel time using 2,3-dimethylpentane as an internal standard: benz. = N.S.; tol. = 0.02 - 0.07 d^{-1}; e-benz.. = 0.03 - 0.011 d^{-1}; *m*-xyl. = 0.004 - 0.014 d^{-1}; *p*-xyl. = 0.002 - 0.010 d^{-1}; *o*-xyl. = 0.004 - 0.011 d^{-1}.	Rates from methanogenic microcosms: benz. = N.S.; tol. = 0.007 - 0.04 d^{-1}; e-benz. = N.S.; *m/p*-xyl. = N.S.; *o*-xyl. = N.S. 12 to 16 mg/L CH_4 produced in lab microcosms.
Indian River, FL (Kemblowski et al. 1987)	gasoline from UST–BTEX	0.06	Conc. vs. travel time: benz. = 0.0085 d^{-1}.	1st-order rates from aerobic microcosms: benz. = 0.02 to 0.2 d^{-1}.

TABLE 10. (continued).

Site	Contaminant	V (m/d)	Field Results	Laboratory Results
Morgan Hill, CA (Kemblowski et al. 1987)	gasoline–BTEX	0.05	Rates from conc. vs. travel time: benz. = 0.0035 d^{-1}.	
Eglin AFB, FL (Wilson et al. 1994a)	JP-4 from POL depot	1.3	Rates from conc. vs. travel time using 1,2,4-trimethylbenzene as internal standard: benz.= B.D.; tol. = 0.05 to 0.013 d^{-1}; e-benz. = 0.03 to 0.05 d^{-1}; *m*-xyl. = 0.02 to 0.1 d^{-1}; *p*-xyl. = 0.02 to 0.08 d^{-1}; *o*-xyl. = 0.21 d^{-1}.	
Hill AFB, UT (Wiedemeier et al. 1994)	JP-4 from POL depot	0.5	Rates from conc. vs. travel time using total trimethyl-benzene as internal standard: benz. = 0.03 to 0.09 d^{-1}; e-benz. = 0.01 to 0.08 d^{-1}; *p*-xyl. = 0.01 to 0.03 d^{-1}; *m*-xyl. = 0 to 0.03 d^{-1}; *o*-xyl. = 0 to 0.02 d^{-1}. Toluene rate not calculable.	
Patrick AFB, FL (Wiedemeier et al. 1994)	700 gal (2,650 L) unleaded gasoline from UST	0.13	Rates from conc. vs. travel time using total methane as internal standard: benz. = 0 to 0.004 d^{-1}; tol. = 0.0006 to 0.004 d^{-1}; e-benz. = 0.0001 to 0.004 d^{-1}; *p*-xyl. = 0.001 to 0.003 d^{-1}; *m*-xyl. = 0.001 to 0.004 d^{-1}; *o*-xyl. = 0.004 to 0.02 d^{-1}.	
Fairfax, VA (Buscheck et al. 1993)		0.015	Rates from conc. vs. travel time: benz. = 0.00055 d^{-1}; tol. = 0.00045 d^{-1}; e-benz. = 0.00045 d^{-1}; *m,p,o*-xyl. = 0.00040 d^{-1}.	
San Francisco, CA (Buscheck et al. 1993)		0.03	Rates from conc. vs. travel time: benz. = 0.0028 d^{-1}; tol. = 0.0022 d^{-1};	

TABLE 10. (continued).

Site	Contaminant	V (m/d)	Field Results	Laboratory Results
Alameda County, CA (Buscheck et al. 1993)	gasoline–BTEX	0.01	Rates from conc. vs. travel time: benz. = 0.0020 d^{-1}; tol. = 0.0017 d^{-1}; e-benz. = 0.0020 d^{-1}; *m,p,o*-xyl. = 0.0017 d^{-1}.	
Elko County, NV (Buscheck et al. 1993)	gasoline–BTEX	0.04	Rates from conc. vs. travel time: benz. = 0.001 d^{-1}.	
Sampson Co., NC (Borden, personal communication 1995)	gasoline from UST–BTEX/MTBE	0.04	High nitrate concentrations in groundwater may enhance biodegradation 1st-order rates from mass flux: MTBE = 0.0006 d^{-1}; benz. = 0.0006 d^{-1}; tol. = 0.0021 d^{-1}; e-benz. = 0.0023 d^{-1}; *m,p*-xyl. = 0.0016 d^{-1}; *o*-xyl. = 0.0009 d^{-1}.	Toluene and ethylbenzene rapidly degraded in denitrifying microcosms after a 56-d lag period.
Traverse City (Wilson et al. 1990)	aviation gasoline from UST–BTEX	1.5	Rates from conc. vs. travel time: benz. = 0.001 d^{-1}; tol. = 0.2 d^{-1}; *m,p,o*-xyl. = 0.004 d^{-1}.	Anaerobic microcosm rates: benz. = 0.07 d^{-1}; tol. = 0.04 d^{-1}; *m,p*-xyl. = 0.06 d^{-1}; *o*-xyl. = 0.07 d^{-1}. Methane produced in microcosms.
Broward Co., FL (Caldwell et al. 1992)	gasoline from UST–BTEX and MTBE	0.1	Anaerobic decay rate from matching BIOPLUME for total BTEX = 0.00012 d^{-1}. Aerobic decay will increase net biodegradation.	
Pensacola, FL (Bekins et al. 1993)	creosote–phenols	0.3 to 1.2	Selected phenols were completely degraded over a 100-d travel time through methanogenic aquifer.	Selected phenols were completely degraded over 100 to 200 d in methanogenic microcosms.
Bemidji, MN (Baedecker et al. 1993)	crude oil–BTEX	0.25	tol. and *o*-xyl. depleted over 20 m (200 d travel time); benz. and e-benz. depleted over 100 m. Downgradient migration was limited by mixing with uncontaminated water.	98% benz. loss in 125 d and 99% tol. loss in 45 d in anaerobic microcosms.

TABLE 10. (continued).

Site	Contaminant	V (m/d)	Field Results	Laboratory Results
Perth, Australia (Thierrin et al. 1993)	gasoline from UST– BTEX	0.4	Rates from conc. vs. travel time: benz. = N.S.; tol. = 0.006 d^{-1}; e-benz. = 0.003 d^{-1}; *m,p*-xyl. = 0.004 d^{-1}; *o*-xyl. = 0.006 d^{-1}; naphthalene = 0.004 d^{-1}. Field (plume scale) rates closely match rates from tracer test using deuterated compounds.	Anaerobic columns with 14 mg/L SO_4 benz. = N.S. tol. = 2.3 d^{-1} e-benz. = N.S. *o*-xyl. = N.S.
Manufacturing Plant (Davis et al. 1994)	benzene only	0.16	BIO1D match to field data showed benzene decay rate > 0.01 d^{-1}.	Over 90% benzene loss over 77 d in methanogenic and sulfate-reducing microcosms.
Cliffs-Dow (Klecka et al. 1990)	charcoal wastes, phenols, naphthalene	0.2 to 0.46	All organics degraded within 100 m of source.	All organics degraded in aerobic microcosms within 30 to 60 d.
Hill AFB-2, UT (Dupont et al. 1994)	18,000 gal (68,137 L) UST	0.14	Rates from mass balance: 1st order for TPH = 0.005 d^{-1}. Zero order for: benz. = 0.02 kg/d; e-benz. = 0.06 kg/d; *p*-xyl. = 0.06 kg/d.	
Gas Plant (Piontek et al. 1994)	NAPL released from natural gas plant–BTEX		105 reduction in BTEX over 100 m.	
Picatinny Arsenal, NJ (Martin and Imbrigiotta 1994)	TCE, 1,1,1-trichloroethane and metals from plating wastewater	0.3 to 1.0	Spatial distribution of TCE, DCE, and VC indicate reductive dechlorination.	Anaerobic microcosms: TCE = 0.0001 to 0.003 d^{-1}.
St. Joseph, MI (Wilson et al. 1994b)	TCE from lagoons/dry wells	0.1	Rates from mass flux: TCE = 0.001 to 0.003 d^{-1}.	
Finger Lakes, NY (Major et al. 1994)	TCE, acetone, methanol		Spatial distribution of TCE, DCE, VC, and ethene were indicative of reductive dechlorination.	

(a) benz. = benzene, tol. = toluene, e-benz. = ethylbenzene, xyl. = xylenes, TPH = total petroleum hydrocarbons, N.S. = not significant, POL = petroleum, oil, and lubricants.

of poorly degradable compounds. Norris et al. (1994) argue that, at some sites, it may be more cost effective to implement some low-level activities (e.g., limited air sparging or venting) than to rely on intrinsic bioremediation as the only management technique. If these limited remediation activities can shorten the monitoring period by several years, they may more than pay for themselves in reduced long-term monitoring costs.

ACKNOWLEDGMENTS

Portions of the research described in this article were supported by the American Petroleum Institute under Grant No. GW-25A-0400-38. The opinions, findings, and conclusion expressed are those of the authors and do not necessarily represent those of the American Petroleum Institute.

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EPA/600/SV-95/001 September 1995

EPA

Project Summary

Natural Bioattenuation of Trichloroethene at the St. Joseph, Michigan Superfund Site

James W. Weaver, John T. Wilson, and Don H. Kampbell

Data from the St. Joseph, Michigan, Superfund Site were used in a peer-reviewed video entitled "Natural Bioattenuation of Trichloroethene at the St. Joseph, Michigan Superfund Site." Computer visualizations of the data set show how trichloroethene, or TCE, can degrade under natural conditions. The purpose of the tape is to present sampling results from the site to a technical audience. Although the visualizations show the general distribution of chemicals at the site, it is not possible to determine the precise concentrations from the tape. Thus the data set itself is available in a companion document. The following text is an amplified version of the narration on the video.

This Project Summary was developed by the National Risk Management Research Laboratory's Subsurface Protection and Remediation Division, Ada, OK, to announce key findings of the research project that is documented in a video of the same title (see video ordering information at back).

Site History

The site is located four miles south of St. Joseph and one-half mile east of Lake Michigan (Figure 1). Since the 1940s, the site has supported auto-parts manufacturing, including a foundry, as well as machining and painting operations. Because of past activities, ground water at the site is contaminated with industrial wastes that include trichloroethene (TCE). A plume of contamination reaches from its source near the industry, toward Lake Michigan to the west (*Tiedeman and Gorelick*, 1993).

The aquifer is primarily composed of medium, fine, and very fine sands that are of glacial origin. The base of the aquifer is defined by a clay layer that lies between 21 and 29 meters below the ground surface. Since the ground water flows toward Lake Michigan, the contamination underlies residential and shoreline property. This water eventually discharges directly into the lake.

Although the TCE contamination is moving toward the lake, evidence indicates that the contaminants are degrading naturally along the way (*McCarty and Wilson*, 1992). Reduction in concentration alone does not necessarily indicate bioattenuation, because concentrations can decline from the effects of advection, dispersion and sorption. Rather, bioattenuation of TCE is indicated here by the presence of daughter products and certain geochemical conditions.

Degradation of TCE

Chlorinated organic compounds such as TCE can be biodegraded in the subsurface, but not because the microorganisms oxidize these compounds as a food source. On the contrary, the degradation of TCE under anaerobic conditions occurs through a reductive transformation where the TCE molecule serves as an electron acceptor. In a loose analogy, we could say that the microorganisms "breathe" TCE. For this type of degradation to occur, another organic

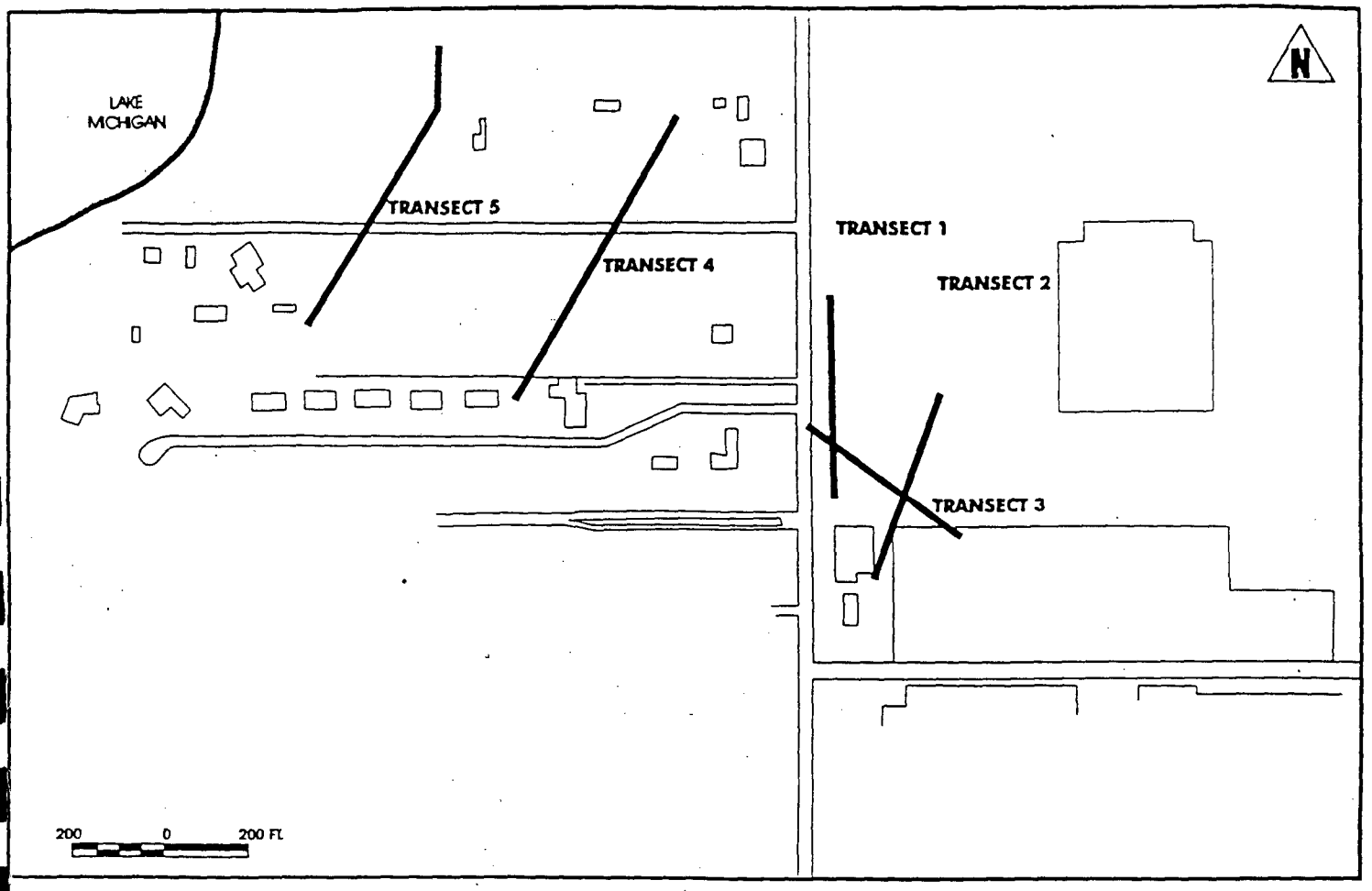

Figure 1. Site plan showing the location of the sampling transects.

ompound must be present to serve as an xidizable carbon source, or "food" for the microorganisms. Under this condition, and in the absence of oxygen, TCE can be ansformed through a series of intermediate emical compounds to ethene. The intermediates are hazardous, and therefore incomplete degradation of TCE is potentially desirable.

TCE may undergo a reductive transformation in an anaerobic environment. An enzyme or cofactor catalyzes the duction of TCE (HC_2Cl_3), resulting in the ss of one chlorine atom:

$$H^{\cdot} + HC_2Cl_3 = H_2C_2Cl_2 + Cl^{\cdot} \quad (1)$$

Three isomers of dicholoroethene, or DCE ($H_2C_2Cl_2$), can result: 1,1-DCE; cis-1,2 DCE and trans-1,2 DCE. Of these, cis-DCE is ually produced in the greatest abundance. e presence of the DCE isomers is significant, because these chemicals have arely been used on a large scale for dustrial purposes. Therefore their sence is an indication of transformations ccurring in the subsurface.

With the loss of another chlorine atom from a DCE isomer, vinyl chloride (H_3C_2Cl) is produced:

$$H^{\cdot} + H_2C_2Cl_2 = H_3C_2Cl + Cl^{\cdot} \quad (2)$$

The production of vinyl chloride is undesirable because it is a known carcinogen. However, ethene, which is not a compound of regulatory concern, can result from the loss of the chlorine atom from the vinyl chloride:

$$H^{\cdot} + H_3C_2Cl = H_4C_2 + Cl^{\cdot} \quad (3)$$

For further information on TCE biodegradation see McCarty and Semprini, 1994, and Semprini et al. 1995.

Field Evidence for TCE Bioattenuation

At a field site, natural bioattenuation of TCE is indicated

- by the presence and degradation of an oxidizable substrate;
- by the absence of oxygen and the presence of strongly reducing conditions (i.e., the abundance of methane);
- by the presence of the intermediate products (the DCE isomers and vinyl chloride); and,
- by the presence of ethene, the end product.

Specific site conditions determine the rate at which the transformations occur and the likelihood of producing a harmless end product. Each site must be evaluated individually for its potential to degrade TCE. There are sites where TCE either does not degrade or is only partially degraded. Thus the results from St. Joseph show the possilbilty of degradation of TCE, but do not indicate that degradation will occur at all sites.

Representation of the Data

In the visualizations, each data set is displayed as a set of colored cubes that

surround the borings. Each boring appears as an elongated, colored stack of cubes. This approach was taken so that the data was not smoothed, interpolated, nor extrapolated. The representations of the data, therefore, show the variation in concentration that occurs over small intervals at the site, and the irregularity of the distributions. The top of each set of cubes roughly corresponds to the water table; and the bottom corresponds to the clay layer that forms the base of the aquifer.

Narration on the tape makes it clear that the views have been exaggerated in the vertical direction in order to better illustrate the distribution of the chemicals over the thickness of the aquifer. The lengths of the borings were indicated by noting that each cube in the on-shore borings is 1.5 meters tall, and that the borings contain from five to eleven cubes. Thus the borings represent aquifer thicknesses varying from 7.5 to 16.5 meters. This scale is also noted by the distance (16.5 meters) between the top of the bluff and the shore line. The exaggerated vertical distances contrast with the distance across the site from the industry's parking lot to the shore of Lake Michigan (730 meters); and the width of the contaminant plume (110 meters). These features of the visualizations indicate that the views emphasize vertical variations in the contaminant distribution. In actuality the contaminant plume is a long and thin object.

The color scale that is used to indicate concentration ranges from blue to red, indicating low to high concentrations, respectively. A logarithmic scale was used to discriminate between concentrations that range over six orders of magnitude.

The St. Joseph Data Set

Data were collected at St. Joseph in sets of borings that form transects across the site. The borings were made with a 1.5 meter long slotted auger from which water samples were taken. A gas chromatograph was used to detect the pollutants as the borings were made. These procedures assured that the transects crossed the entire width of the contaminant plume.

Data were collected from the site in 1991 along transects near the source region, and in 1992 along two transects lying between the source and the lake (*Semprini et al.*, 1994). In August 1994, a set of samples were taken from a barge anchored in Lake Michigan. These samples determined the contaminant concentrations in the ground water immediately before it discharges into the lake.

Features of the St. Joseph Data Set

In the vicinity of the plume, dissolved oxygen is depleted from the ground water, even though the ground water is oxygen-rich outside the contaminated zone. The ground water is depleted of oxygen near the bottom of the aquifer. Oxygen at intermediate and high concentrations, from two to ten milligrams per liter, is found in some locations near the water table. The methane data show a pattern that is almost exactly opposite that of the dissolved oxygen. Methane concentrations are highest near the bottom of the aquifer and are lowest near the water table. This distribution shows that the aerobic and anaerobic zones in the aquifer are clearly separated.

At St. Joseph, there is a decrease of COD from the source area to the lake. This is indicative of anaerobic degradation of the oxidizable carbon source, which remains to be specifically identified.

The highest TCE concentration at the site is 89,000 micrograms per liter and is found near the source area. The contaminants tend to move toward the lake in the deeper part of the aquifer, as noted by the absence of TCE near the water table. By the time TCE reaches the lake, however, the concentrations are reduced to levels that are mostly undetectable. There are a few TCE concentrations of one to two micrograms per liter in the lake transect. These concentrations are below the EPA drinking water standard of 5 micrograms per liter.

The pattern of declining concentration as the chemicals flow toward the lake is repeated in both the DCE and vinyl chloride data sets. Dechlorination of TCE usually produces the cis-DCE isomer in the greatest abundance. At St. Joseph, for example, the trans-DCE and the 1,1-DCE concentrations are generally lower than the cis-DCE concentrations by at least a factor of 10. The transformation of TCE to DCE may occur under sulfate reducing conditions and sulfate concentrations should be measured.

The maximum cis-DCE concentration is 128,000 micrograms per liter, occurring near the bottom of the aquifer in the source region. cis-DCE concentrations decline toward the lake and the compound is undetectable in the lake transect. Because the cis-DCE is the dominant isomer at St. Joseph, the trans-DCE and 1,1-DCE data sets are not shown in the video tape.

The vinyl chloride distribution follows the general pattern of highest concentrations near the bottom of the aquifer and declining concentrations toward the lake. No vinyl chloride concentrations above the drinking water standard of two micrograms per liter were detected from samples taken in the lake.

The presence of ethene is evidence for the complete dechlorination of the TCE. Ethene is present throughout the contaminant plume; its distribution follows the pattern of the other degradation products.

Summary

In summary, the intermediate products of TCE bioattenuation are found in oxygen depleted portions of the aquifer that are also rich in methane. Ethene is found in significant concentration, indicating some of the TCE is degraded to a compound that is not of regulatory concern. The concentrations of TCE and the degradation products significantly decline toward the lake. The off-shore data show that only minute concentrations of these chemicals exist in the ground water that discharges into the lake.

Analysis of data from the St. Joseph, Michigan Superfund site indicates that natural bioattenuation of TCE is occurring as the contaminants flow toward Lake Michigan. Depletion of oxygen, the presence of methane and the appearance of degradation products indicate that the reduction in TCE concentrations is not solely due to volatilization or dilution. Rather, they are indicative of microbial processes helping to reduce the contaminant concentrations below EPA drinking water standards before the water is discharged into Lake Michigan. Continued monitoring of the site is necessary to demonstrate that contaminant levels remain below accepted standards and that the flux of chemicals into the lake remains low.

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The video, entitled "Natural Bioattenuation of Trichloroethene at the St. Joseph, Michigan Superfund Site" (EPA/600/V-95/001), will be available upon request from:

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TECHNICAL PROTOCOL FOR EVALUATING NATURAL ATTENUATION OF CHLORINATED SOLVENTS IN GROUNDWATER

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September 1996

for

Air Force Center for Environmental Excellence
Technology Transfer Division
Brooks Air Force Base
San Antonio, Texas

*This United States Air Force guidance was developed in cooperation with United States Environmental Protection Agency (USEPA) researchers but was not issued by the USEPA and does not represent USEPA guidance.

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ACKNOWLEDGMENTS

The authors would like to thank Dr. Robert Hinchee, Doug Downey, and Dr. Guy Sewell for their contributions and their extensive and helpful reviews of this manuscript. Thanks also to Leigh Alvarado Benson, R. Todd Herrington, Robert Nagel, Peter Guest, Mark Vesseley, John Hicks, and Saskia Hoffer for their efforts at making this project a success!

List of Acronyms and Abbreviations

AAR	American Association of Railroads
AFB	Air Force Base
AFCEE	Air Force Center for Environmental Excellence
ASTM	American Society for Testing and Materials
bgs	below ground surface
BRA	baseline risk assessment
BRAC	Base Realignment and Closure
BTEX	benzene, toluene, ethylbenzene, xylenes
CAP	corrective action plan
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
cfm	cubic feet per minute
CFR	Code of Federal Regulations
COPC	chemical of potential concern
CPT	cone penetrometer testing
CSM	conceptual site model
DAF	dilution/attenuation factor
DERP	Defense Environmental Restoration Program
DO	dissolved oxygen
DOD	Department of Defense
DQO	data quality objective
EE/CA	engineering evaluation/cost analysis
FS	feasibility study
gpd	gallons per day
$\Delta G_r°$	standard (Gibbs) free energy
HDPE	high-density polyethylene
HSSM	Hydrocarbon Screening Spill Model
HSWA	Hazardous and Solid Waste Amendments of 1984
ID	inside-diameter
IDW	investigation derived waste
IRP	Installation Restoration Program
L	liter
LEL	lower explosive limit
LNAPL	light nonaqueous-phase liquid

LTM	long-term monitoring
LTMP	long-term monitoring plan
LUFT	leaking underground fuel tank
MAP	management action plan
MCL	maximum contaminant level
MDL	method detection limit
µg	microgram
µg/kg	microgram per kilogram
µg/L	microgram per liter
mg	milligram
mg/kg	milligrams per kilogram
mg/L	milligrams per liter
mg/m^3	milligrams per cubic meter
mm Hg	millimeters of mercury
MOC	method of characteristics
MOGAS	motor gasoline
NAPL	nonaqueous-phase liquid
NCP	National Contingency Plan
NFRAP	no further response action plan
NOAA	National Oceanographic and Atmospheric Administration
NOEL	no-observed-effect level
NPL	National Priorities List
OD	outside-diameter
OSHA	Occupational Safety and Health Administration
OSWER	Office of Solid Waste and Emergency Response
PAH	polycyclic aromatic hydrocarbon
PEL	permissible exposure limit
POA	point-of-action
POC	point-of-compliance
POL	petroleum, oil, and lubricant
ppmv	parts per million per volume
psi	pounds per square foot
PVC	polyvinyl chloride
QA	quality assurance
QC	quality control
RAP	remedial action plan
RBCA	risk-based corrective action
RBSL	risk-based screening level
redox	reduction/oxidation
RFI	RCRA facility investigation

RI	remedial investigation
RME	reasonable maximum exposure
RPM	remedial project manager
SAP	sampling and analysis plan
SARA	Superfund Amendments and Reauthorization Act
scfm	standard cubic feet per minute
SPCC	spill prevention, control, and countermeasures
SSL	soil screening level
SSTL	site-specific target level
SVE	soil vapor extraction
SVOC	semivolatile organic compound
TC	toxicity characteristic
TCLP	toxicity-characteristic leaching procedure
TMB	trimethylbenzene
TOC	total organic carbon
TPH	total petroleum hydrocarbons
TRPH	total recoverable petroleum hydrocarbons
TVH	total volatile hydrocarbons
TVPH	total volatile petroleum hydrocarbons
TWA	time-weighted-average
UCL	upper confidence limit
US	United States
USGS	US Geological Survey
UST	underground storage tank
VOCs	volatile organic compounds

Definitions

Aerobe: bacteria that use oxygen as an electron acceptor.

Anabolism: The process whereby energy is used to build organic compounds such as enzymes and nucleic acids that are necessary for life functions. In essence, energy is derived from catabolism, stored in high-energy intermediate compounds such as adenosine triphosphate (ATP), guanosine triphosphate (GTP) and acetyl-coenzyme A, and used in anabolic reactions that allow a cell to grow (Chapelle, 1993).

Anthropogenic: Man-made.

Catabolism: The process whereby energy is extracted from organic compounds by breaking them down into their component parts.

Cometabolism: The process in which a compound is fortuitously degraded by an enzyme or cofactor produced during microbial metabolism of another compound.

Daughter Product: A compound that results directly from the biodegradation of another. For example *cis*-1,2-dichloroethene (*cis*-1,2-DCE)is commonly a daughter product of trichloroethene (TCE).

Dehydrohalogenation: Elimination of HX resulting in formation of an alkene.

Diffusion: The process whereby molecules move from a region of higher concentration to a region of lower concentration as a result of Brownian motion.

Dihaloelimination: Reductive elimination of two halide substituents resulting in formation of an alkene.

Dispersivity: A property that quantifies mechanical dispersion in a medium.

Effective Porosity: The percentage of void volume that contributes to percolation; roughly equivalent to the specific yield.

Electron Acceptor: A compound capable of accepting electrons during oxidation-reduction reactions. Microorganisms obtain energy by transferring electrons from electron donors such as organic compounds (or sometimes reduced inorganic compounds such as sulfide) to an electron acceptor. Electron acceptors are compounds that are relatively oxidized and include oxygen, nitrate, iron (III), manganese (IV), sulfate, carbon dioxide, or in some cases the chlorinated aliphatic hydrocarbons such as perchloroethene (PCE), TCE, DCE, and vinyl chloride (VC).

Electron Donor: A compound capable of supplying (giving up) electrons during oxidation-reduction reactions. Microorganisms obtain energy by transferring electrons from electron donors such as organic compounds (or sometimes reduced inorganic compounds such as sulfide) to an electron acceptor. Electron donors are compounds that are relatively reduced and include fuel hydrocarbons and native organic carbon.

Electrophile: A reactive species that accepts an electron pair.

Elimination: Reaction where two groups such as chlorine and hydrogen are lost from adjacent carbon atoms and a double bond is formed in their place.

Epoxidation: A reaction wherein an oxygen molecule is inserted in a carbon-carbon double bond and an epoxide is formed.

Facultative Anaerobes: microorganisms that use (and prefer) oxygen when it is available, but can also use alternate electron acceptors such as nitrate under anaerobic conditions when necessary.

Fermentation: Microbial metabolism in which....

Heterotroph: Organism that uses organic carbon as an external energy source and as a carbon source.

Hydraulic Conductivity: The relative ability of a unit cube of soil, sediment, or rock to transmit water.

Hydraulic Head: The height above a datum plane of the surface of a column of water. In the groundwater environment, it is composed dominantly of elevation head and pressure head.

Hydraulic Gradient: The maximum change in head per unit distance.

Hydrogenolysis: A reductive reaction in which a carbon-halogen bond is broken, and hydrogen replaces the halogen substituent.

Hydroxylation: Addition of a hydroxyl group to a chlorinated aliphatic hydrocarbon.

Lithotroph: Organism that uses inorganic carbon such as carbon dioxide or bicarbonate as a carbon source and an external source of energy.

Mechanical Dispersion:

Metabolic Byproduct: A product of the reaction between an electron donor and an electron acceptor. Metabolic byproducts include volatile fatty acids, daughter products of chlorinated aliphatic hydrocarbons, methane, and chloride.

SECTION 1

INTRODUCTION

Over the past several years remediation by natural attenuation has become increasingly accepted as a remedial alternative for organic compounds dissolved in groundwater. The United States Environmental Protection Agency (USEPA) Office of Research and Development (ORD) and the USEPA Office of Solid Waste and Emergency Response (OSWER) define natural attenuation as:

> *The biodegradation, dispersion, dilution, sorption, volatilization, and/or chemical and biochemical stabilization of contaminants to effectively reduce contaminant toxicity, mobility, or volume to levels that are protective of human health and the ecosystem.*

In practice, natural attenuation also is referred to by several other names, such as intrinsic remediation, intrinsic bioremediation, or passive bioremediation. The goal of any site characterization effort is to understand the fate and transport of the contaminants of concern over time in order to assess any current or potential threat to human health or the environment. Natural attenuation processes, such as biodegradation, can often be dominant factors in the fate and transport of contaminants. Thus, consideration and quantification of natural attenuation is essential to a more thorough understanding of contaminant fate and transport.

The intent of this document is to present a technical protocol for data collection and analysis in support of natural attenuation with long-term monitoring (LTM) for restoration of groundwater contaminated with chlorinated solvents and groundwater contaminated with mixtures of fuels and chlorinated aliphatic hydrocarbons. Specifically, this protocol is designed to evaluate the fate in groundwater of chlorinated aliphatic hydrocarbons and/or fuel hydrocarbons that have regulatory standards. In some cases, the information collected using this protocol will show that natural degradation processes will reduce the concentrations of these contaminants below risk-based corrective action criteria or regulatory standards before potential receptor exposure pathways are completed. The evaluation should include consideration of existing exposure pathways, as well as exposure pathways arising from potential future use of the groundwater.

Natural attenuation in groundwater systems results from the integration of several subsurface attenuation mechanisms that are classified as either destructive or nondestructive. Biodegradation is the most important destructive attenuation mechanism, although abiotic destruction of some compounds does occur. Nondestructive attenuation mechanisms include sorption, dispersion, dilution from recharge, and volatilization. Figure 1.1 shows the significant fate and transport mechanisms that influence contaminant migration in the subsurface. The natural attenuation of fuel hydrocarbons is described in the *Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater*, recently published by the Air Force Center for Environmental Excellence (AFCEE) (Wiedemeier *et al.*, 1995d). This document differs from the technical protocol for intrinsic remediation of fuel hydrocarbons because it focuses on the individual processes of chlorinated aliphatic hydrocarbon biodegradation which are fundamentally different from the processes involved in the biodegradation of fuel hydrocarbons.

For example, biodegradation of fuel hydrocarbons, especially benzene, toluene, ethylbenzene, and xylenes (BTEX), is mainly limited by electron acceptor availability, and generally will proceed until all of the contaminants biochemically accessible to the microbes are destroyed. In the experience of the authors, there appears to be an inexhaustible supply of electron acceptors in most, if not all, hydrogeologic environments. On the other hand, the more highly chlorinated solvents such as perchloroethene (PCE) and trichloroethene (TCE) typically are biodegraded under natural conditions via reductive dechlorination, a process that requires both electron acceptors (the chlorinated aliphatic hydrocarbons) and an adequate supply of electron donors. Electron donors include fuel hydrocarbons or other types of anthropogenic carbon (e.g., landfill leachate) or natural organic carbon. If the subsurface environment is depleted of electron donors before the chlorinated aliphatic hydrocarbons are removed, reductive dechlorination will cease, and natural attenuation may no longer be protective of human health and the environment. This is the most significant difference between the processes of fuel hydrocarbon and chlorinated aliphatic hydrocarbon biodegradation.

For this reason, it is more difficult to predict the long-term behavior of chlorinated aliphatic hydrocarbon plumes than fuel hydrocarbon plumes. Thus, it is important to have a good understanding of the important natural attenuation mechanisms. In addition to having a better understanding of the processes of advection, dispersion, dilution from recharge, and sorption, it is necessary to better quantify biodegradation. This requires an understanding of the interactions between chlorinated aliphatic hydrocarbons, anthropogenic or natural carbon, and inorganic electron acceptors at the site. Detailed site characterization is required to adequately document and understand these processes.

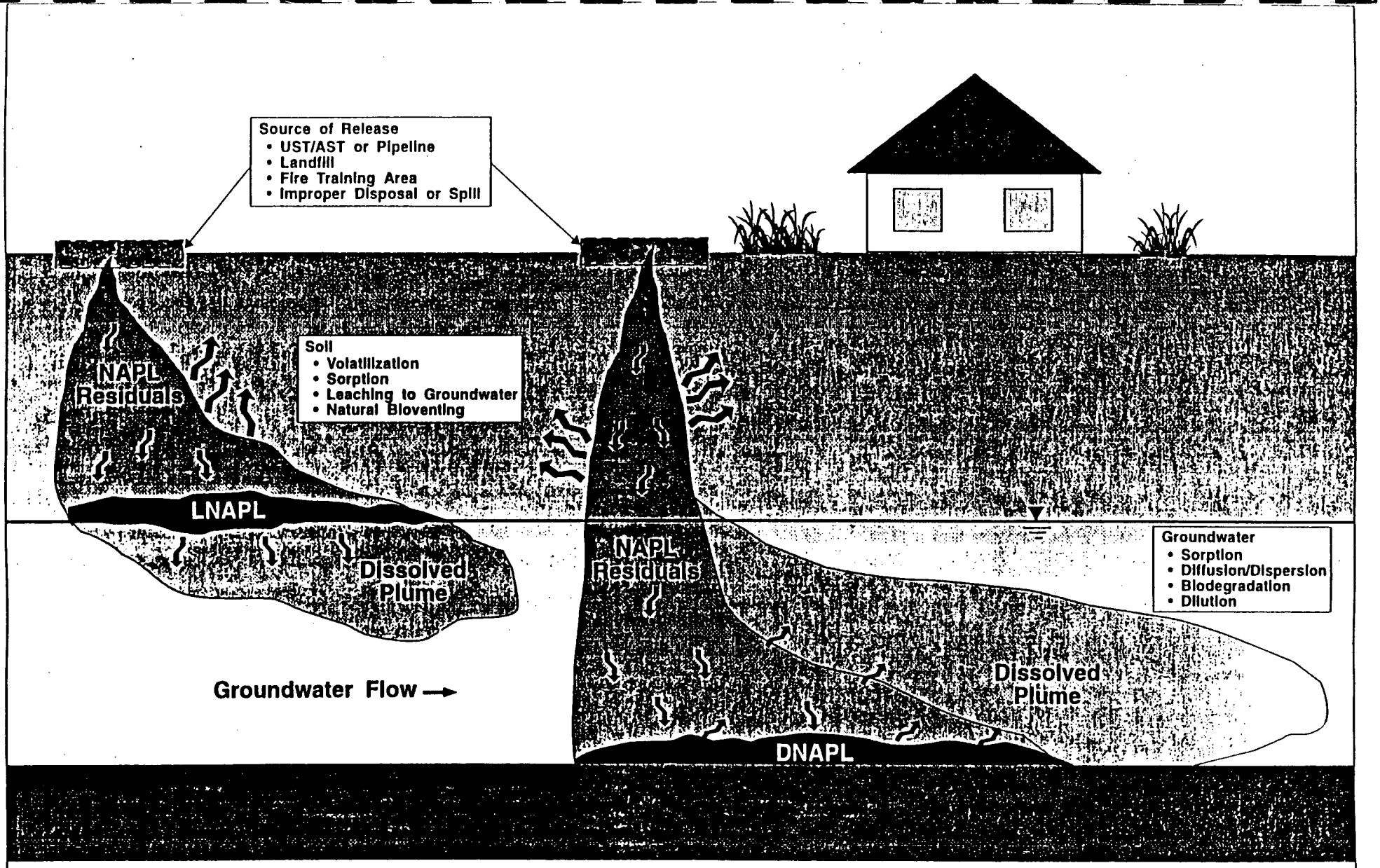

Figure 1.1
Significant Chemical Fate and Transport Mechanisms in the Subsurface

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Based on experience at over 40 Air Force sites, the cost to fully implement this protocol ranges from $100,000 to $175,000, depending on site conditions. These costs are relevant only for typical sites at Air Force bases; other sites may cost more or less. These costs include site characterization (with monitoring well installation), chemical analyses, numerical modeling, report preparation including comparative analysis of remedial options, and regulatory negotiations. The additional chemical analyses required to implement this protocol typically increase analytical costs by 10 to 15 percent over the analytical costs of a conventional remedial investigation.

The intended audience for this document is United States Air Force personnel and their contractors, scientists, consultants, regulatory personnel, and others charged with remediating groundwater contaminated with chlorinated aliphatic hydrocarbons or mixtures of fuel hydrocarbons and chlorinated aliphatic hydrocarbons. This protocol is intended to be used within the established regulatory framework. It is not the intent of this document to prescribe a course of action, including site characterization, in support of all possible remedial technologies. Instead, this protocol is another tool, similar to the AFCEE - Technology Transfer Division protocols for bioventing (Hinchee *et al.*, 1992) or bioslurping (Battelle, 1995) that allow practitioners to adequately evaluate these alternatives in subsequent feasibility studies. It is not the intent of this document to replace existing USEPA or state-specific guidance on conducting remedial investigations.

The AFCEE Remediation Matrix - Hierarchy of Preferred Alternatives identifies natural attenuation as the first option to be evaluated for remediation of contaminated groundwater at Air Force sites. This matrix implies only that natural attenuation should be evaluated prior to proceeding (if necessary) to more costly solutions (e.g., groundwater extraction and treatment or another engineered solution), not that natural attenuation be selected as a presumptive remedy. The USEPA has not identified natural attenuation as a presumptive remedy at the time of this writing.

Chlorinated solvents are released into the subsurface under two possible scenarios 1) As relatively pure solvents that are more dense than water; or 2) as mixtures of fuel hydrocarbons and chlorinated aliphatic hydrocarbons which, depending on the relative proportion of each, may be more or less dense that water. These products commonly are referred to as "nonaqueous-phase liquids," or NAPLs. If the NAPL is more dense than water the material is referred to as a "dense nonaqueous-phase liquid," or DNAPL. If the NAPL is less dense than water the material is referred to as a "light nonaqueous-phase liquid," or LNAPL. Contaminant sources generally consist of hydrocarbons present as mobile NAPL (NAPL occurring at sufficiently high saturations to drain under the influence of gravity into a well) and residual NAPL (NAPL occurring at immobile, residual saturations that are unable to drain into a well by gravity). In general, the

greatest mass of contaminant is associated with these NAPL source areas, not with the aqueous phase. As groundwater or recharge moves through the NAPL source areas, soluble constituents partition into the water to generate a plume of dissolved contamination. After further releases have been stopped, these NAPL source areas tend to slowly weather away as the soluble components, such as BTEX or TCE, are depleted. In cases where mobile NAPL removal is feasible, it is desirable to remove product and decrease the time required for complete remediation of the site. However, at many sites mobile NAPL removal is not feasible with available technology. In fact, the quantity of mobile NAPL recovered by commonly used recovery techniques is a trivial fraction of the total NAPL available to contaminate groundwater. Frequently less than 10 percent of the total NAPL mass in a spill can be recovered by mobile NAPL recovery.

In comparison to conventional engineered remediation technologies, natural attenuation is advantageous because:

- During natural attenuation, contaminants are ultimately transformed to innocuous byproducts (e.g., carbon dioxide, ethene, and water), not just transferred to another phase or location within the environment;
- Natural attenuation is nonintrusive and allows continuing use of infrastructure during remediation;
- Engineered remedial technologies can pose greater risk to potential receptors than natural attenuation when contaminants are transferred into the atmosphere during remediation activities;
- Natural attenuation is less costly than currently available remedial technologies such as groundwater extraction for *ex situ* treatment;
- Natural attenuation is not subject to limitations imposed by the use of mechanized remediation equipment (e.g., no equipment downtime); and
- Those compounds that are the most mobile and toxic generally are the most susceptible to biodegradation.

Natural attenuation has the following potential limitations:

- Natural attenuation is subject to natural and anthropogenic changes in local hydrogeologic conditions, including changes in groundwater velocity, pH, electron acceptor concentrations, electron donor concentrations, and potential future releases;
- Aquifer heterogeneity may complicate site characterization, as it will with any remedial technology;
- Time frames for complete remediation may be relatively long; and
- Intermediate products of biodegradation (e.g., vinyl chloride) can be more toxic than the original contaminant.

This document describes (1) those processes that bring about natural attenuation, (2) the site characterization activities that may be performed to conduct a full-scale evaluation of natural attenuation, (3) natural attenuation modeling using analytical or numerical solute fate and transport models, and (4) the post-modeling activities that should be completed to ensure successful support and verification of remediation by natural attenuation. The objective of the work described herein is to quantify and provide defensible data in support of natural attenuation at sites where naturally occurring subsurface attenuation processes are capable of reducing dissolved chlorinated aliphatic hydrocarbon and/or fuel hydrocarbon concentrations to acceptable levels. A comment made by a member of the regulatory community summarizes what is required to successfully implement natural attenuation:

> *A regulator looks for the data necessary to determine that a proposed treatment technology, if properly installed and operated, will reduce the contaminant concentrations in the soil and water to legally mandated limits. In this sense the use of biological treatment systems calls for the same level of investigation, demonstration of effectiveness, and monitoring as any conventional* [remediation] *system* (National Research Council, 1993).

To support remediation by natural attenuation, the proponent must scientifically demonstrate that attenuation of site contaminants is occurring at rates sufficient to be protective of human health and the environment. Three lines of evidence can be used to support natural attenuation of chlorinated aliphatic hydrocarbons, including:

1) Observed reductions in contaminant concentrations along the flow path downgradient from the source of contamination.

2) Documented loss of contaminant mass at the field scale using

   a) Chemical and geochemical analytical data including;
      - decreasing parent compound concentrations
      - increasing daughter compound concentrations
      - depletion of electron acceptors and donors
      - increasing metabolic byproduct concentrations

   b) A conservative tracer and a rigorous estimate of residence time along the flow path to document contaminant mass reduction and to calculate biological decay rates at the field scale.

3) Microbiological laboratory data that support the occurrence of biodegradation and give rates of biodegradation.

At a minimum, the investigator must obtain the first two lines of evidence or the first and third lines of evidence. The second and third lines of evidence are crucial to the natural attenuation demonstration because they provide biodegradation rate constants. These rate constants are used in conjunction with the other fate and transport parameters to predict contaminant concentrations and to assess risk at downgradient points of compliance.

The first line of evidence is simply an observed reduction in the concentration of released contaminants downgradient from the NAPL source area along the groundwater flow path. This line of evidence does not prove that contaminants are being destroyed because the reduction in contaminant concentration could be the result of advection, dispersion, dilution from recharge, sorption, and volatilization with no loss of contaminant mass (i.e., the majority of apparent contaminant loss could be due to dilution). Conversely, an increase in the concentrations of some contaminants, most notably degradation products such as VC, also could be indicative of natural attenuation.

In order to support remediation by natural attenuation at most sites, the investigator will have to show that contaminant mass is being destroyed via biodegradation. This is done using either, or both, of the second or third lines of evidence. The second line of evidence relies on chemical and physical data to show that contaminant mass is being destroyed via biodegradation, not just being diluted or sorbed to the aquifer matrix. The second line of evidence is divided into two components:

- Using chemical analytical data in mass balance calculations to show that decreases in contaminant and electron acceptor/donor concentrations can be directly correlated to increases in metabolic end products/daughter compounds. This evidence can be used to show that electron acceptor/donor concentrations in groundwater are sufficient to facilitate degradation of dissolved contaminants. Solute fate and transport models can be used to aid mass balance calculations and to collate and present information on degradation.
- Using measured concentrations of contaminants and/or biologically recalcitrant tracers in conjunction with aquifer hydrogeologic parameters such as seepage velocity and dilution to show that a reduction in contaminant mass is occurring at the site and to calculate biodegradation rate constants.

The third line of evidence, microbiological laboratory data, can be used to show that indigenous biota are capable of degrading site contaminants at a particular rate. Because it is

SECTION 2

PROTOCOL FOR IMPLEMENTING NATURAL ATTENUATION

The primary objective of the natural attenuation investigation is to determine whether natural processes of contaminant degradation will reduce contaminant concentrations in groundwater to below regulatory standards before potential receptor exposure pathways are completed. Further, natural attenuation should be evaluated to determine if it can meet all appropriate federal and state remediation objectives for a given site. This requires that projections of the potential extent and concentrations of the contaminant plume in time and space be made. These projections should be based on historic variations in, and the current extent and concentrations of, the contaminant plume, in conjunction with measured rates of contaminant attenuation. Because of the inherent uncertainty associated with such predictions, it is the responsibility of the proponent of natural attenuation to provide sufficient evidence to demonstrate that the mechanisms of natural attenuation will reduce contaminant concentrations to acceptable levels before potential receptors are reached. This requires the use of solute fate and transport models with conservative input parameters and numerous sensitivity analyses so that consideration is given to all plausible contaminant migration scenarios. When possible, both historical data and modeling should be used to provide information that collectively and consistently confirms the natural reduction and removal of the dissolved contaminant plume.

Figure 2.1 outlines the steps involved in a natural attenuation demonstration and shows the important regulatory decision points for implementing natural attenuation. The key steps outlined in this figure include:

1) Review available site data and develop preliminary conceptual model;
2) Screen the site and assess the potential for natural attenuation;
3) If natural attenuation is selected as potentially appropriate, perform site characterization to support natural attenuation;
4) Refine conceptual model based on site characterization data, complete pre-modeling calculations, and document indicators of natural attenuation;
5) Simulate natural attenuation using analytical or numerical solute fate and transport models that allow incorporation of a biodegradation term, as necessary;

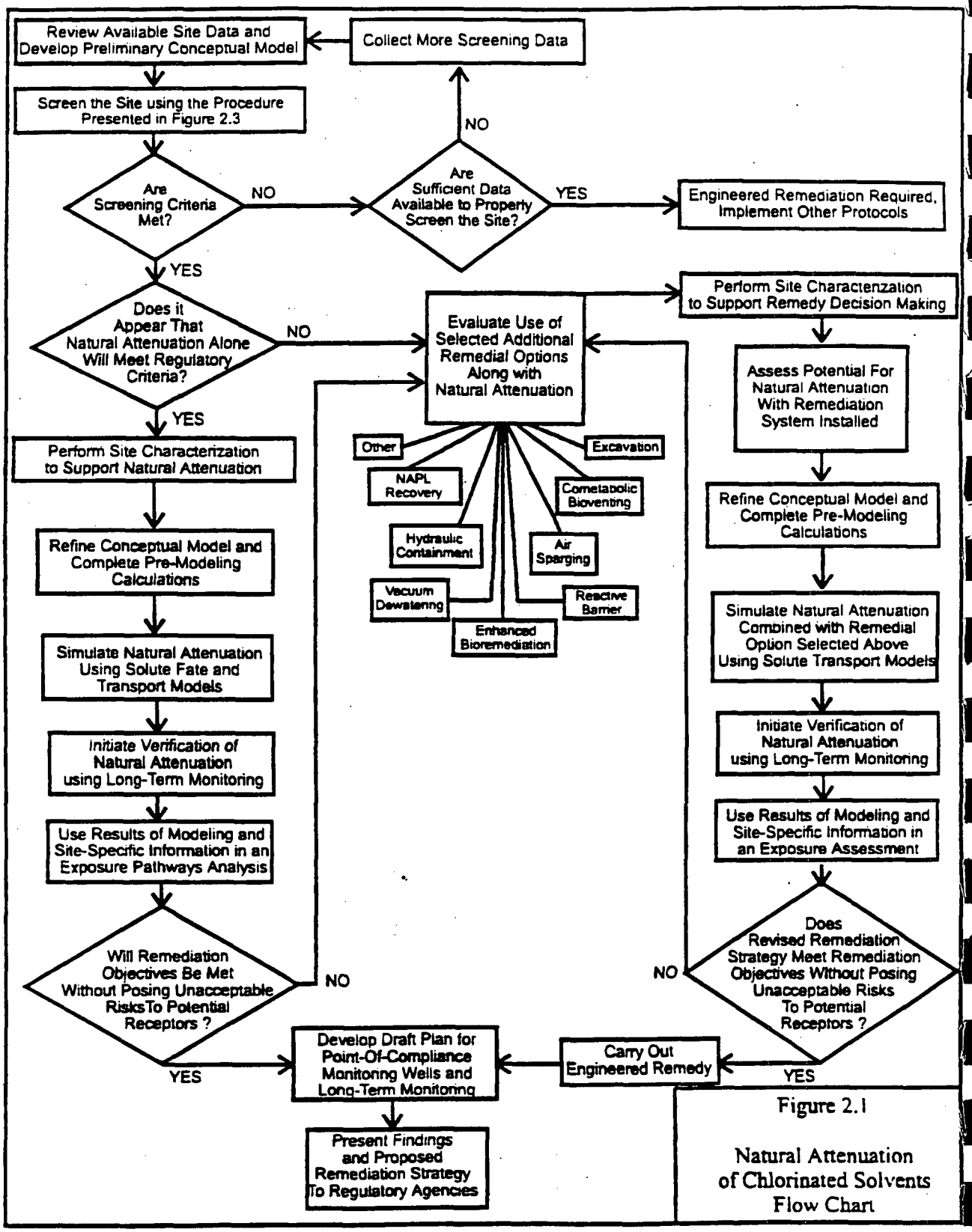

Figure 2.1

Natural Attenuation of Chlorinated Solvents Flow Chart

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6) Identify potential receptors and exposure points and conduct an exposure pathways analysis;

7) Evaluate practicability and potential efficiency of supplemental source removal;

8) If natural attenuation with or without source removal is acceptable, prepare LTM plan; and

9) Present findings to regulatory agencies and obtain approval for the natural attenuation with LTM option.

The following sections describe each of these steps in more detail.

2.1 REVIEW AVAILABLE SITE DATA AND DEVELOP PRELIMINARY CONCEPTUAL MODEL

The first step in the natural attenuation investigation is to review available site-specific data. Once this is done it is possible to use the initial site screening processes presented in Section 2.2 to determine if natural attenuation is a viable remedial option. A thorough review of these data also allows development of a preliminary conceptual model. The preliminary conceptual model will help identify any shortcomings in the data and will facilitate placement of additional data collection points in the most scientifically advantageous and cost-effective manner possible.

When available, information to be obtained during data review includes:

- Nature, extent, and magnitude of contamination:
  - Nature and history of the contaminant release:
    - --Catastrophic or gradual release of NAPL ?
    - --More than one source area possible or present ?
    - --Divergent or coalescing plumes ?
  - Three-dimensional distribution of mobile and residual NAPL and dissolved contaminants. The distribution of mobile and residual NAPL will be used to define the dissolved plume source area.
  - Groundwater and soil chemical data.
  - Historical water quality data showing variations in contaminant concentrations.
  - Chemical and physical characteristics of the contaminants.
  - Potential for biodegradation of the contaminants.
- Geologic and hydrogeologic data (in three dimensions, if feasible):
  - Lithology and stratigraphic relationships.
  - Grain-size distribution (sand *vs.* silt *vs.* clay).
  - Aquifer hydraulic conductivity.

  - Groundwater flow gradients and potentiometric or water table surface maps (over several seasons, if possible).
  - Preferential flow paths.
  - Interactions between groundwater and surface water and rates of infiltration/recharge.
- Locations of potential receptor exposure points:
  - Groundwater wells.
  - Downgradient and crossgradient groundwater discharge points.

In some cases, few or no site-specific data are available. If this is the case, all future site characterization activities should include collecting the data necessary to screen the site for potential natural attenuation. The additional costs incurred by such data collection are greatly outweighed by the cost savings that will be realized if natural attenuation is selected. Moreover, much of the data collected in support of natural attenuation can be used to design and support other remedial measures.

Available site characterization data should be used to develop a conceptual model for the site. The conceptual model is a three-dimensional representation of the NAPL source area, groundwater flow, and solute transport system based on available geological, biological, geochemical, hydrological, climatological, and analytical data for the site. This type of conceptual model differs from the conceptual site models commonly used by risk assessors that qualitatively consider the location of contaminant sources, release mechanisms, transport pathways, exposure points, and receptors. However, the groundwater system conceptual model facilitates identification of these risk-assessment elements for the exposure pathways analysis. After development, the conceptual model can be used to help determine optimal placement of additional data collection points, as necessary, to aid in the natural attenuation investigation and to develop the solute fate and transport model. Contracting and management controls must be flexible enough to allow for the potential for revisions to the conceptual model and thus the data collection effort.

Successful conceptual model development involves:

- Definition of the problem to be solved (generally the nature, magnitude, and extent of existing and future contamination).
- Integration and presentation of available data, including:
  - Local geologic and topographic maps,
  - Geologic data,
  - Hydraulic data,

- Biological data,
- Geochemical data, and
- Contaminant concentration and distribution data.

- Determination of additional data requirements, including:
  - Borehole locations and monitoring well spacing,
  - A sampling and analysis plan (SAP), and
  - Any data requirements listed in Section 2.1 that have not been adequately addressed.

Table 2.1 contains the recommended soil and groundwater analytical protocol for natural attenuation of chlorinated aliphatic hydrocarbons and/or fuel hydrocarbons. Any plan to collect additional groundwater and soil quality data should include the analytes listed in this table.

2.2 INITIAL SITE SCREENING

After reviewing available site data and developing a preliminary conceptual model, an assessment of the potential for natural attenuation must be made. As stated previously, existing data can be useful to determine if natural attenuation might be sufficient to prevent a dissolved contaminant plume from completing receptor exposure pathways, or from reaching a predetermined point of compliance (POC), in concentrations above applicable federal, state, or risk-based standards. Determining the likelihood of exposure pathway completion is an important component of the natural attenuation investigation. This is achieved by estimating the migration and future extent of the plume based on (1) contaminant properties, including volatility, sorptive properties, and biodegradability; (2) aquifer properties, including hydraulic gradient, hydraulic conductivity, porosity and total organic carbon (TOC) concentrations, and (3) the location of the plume and contaminant source relative to potential receptor exposure points (i.e., the distance between the leading edge of the plume and the potential receptor exposure points). These parameters (estimated or actual) are used in this section to make a preliminary assessment of the effectiveness of natural attenuation in reducing contaminant concentrations.

Table 2.1A. Soil, Soil Gas, and Groundwater Analytical Protocol/ Standard*

Matrix	Analysis	Method/Reference	Comments	Data Use	Recommended Frequency of Analysis	Sample Volume, Sample Container, Sample Preservation	Field or Fixed-Base Laboratory
Soil	Aromatic and chlorinated hydrocarbons (benzene, toluene, ethylbenzene, and xylene [BTEX]; chlorinated compounds)	SW8260A	Handbook method	Data are used to determine the extent of soil contamination, the contaminant mass present, and the need for source removal	Each soil sampling round	Sample volume approximately 100 ml; use teflon-lined cap on an undisturbed sample or completely filled glass container; cool to 4°C	Fixed-base
Soil	Total organic carbon (TOC)	SW9060 modified for soil samples	Procedure must be accurate over the range of 0.01–5 percent TOC	The rate of migration of petroleum contaminants in groundwater is dependent upon the amount of TOC in the aquifer matrix.	At initial sampling	Collect 100 g of soil in a glass container with Teflon-lined cap; cool to 4°C	Fixed-base
Soil Gas	O_2, CO_2	Field Soil Gas Analyzer		Useful for determining bioactvity in vadose zone.	At initial sampling and respiration testing	Reusable 3-liter Tedlar bags.	Field
Soil Gas	Fuel and Chlorinated VOCs	EPA Method TO-14		Useful for determining chlorinated and BTEX compounds in soil	At initial sampling	1-liter Summa Canister	Fixed-base

Table 2.1.A. (Continued)

Matrix	Analysis	Method/Reference	Comments	Data Use	Recommended Frequency of Analysis	Sample Volume, Sample Container, Sample Preservation	Field or Fixed-Base Laboratory
Water	Aromatic and chlorinated hydrocarbons (BTEX, trimethylbenzene isomers, chlorinated compounds)	SW8260A	Handbook method; analysis may be extended to higher molecular weight alkyl benzenes	Method of analysis for BTEX and chlorinated solvents/byproducts, which are the primary target analytes for monitoring natural attenuation; method can be extended to higher molecular weight alkyl-benzenes; trimethylben-zenes are used to monitor plume dilution if degradation is primarily anaerobic.	Each sampling round	Collect water samples in a 40 mL VOA vial; cool to 4°C; add hydrochloric acid to pH 2	Fixed-base
Water	Polycyclic aromatic hydrocarbons (PAHs) (optional, intended for diesel and other heavy oils)	GC/mass spectroscopy method SW8270B; high-performance liquid chromatography method SW8310	Analysis needed only when required for regulatory compliance.	PAHs are components of fuel and are typically analyzed for regulatory compliance. These compounds also are a potential carbon source.	As required by regulations	Collect 1 L of water in a glass container; cool to 4°C	Fixed-base

Table 2.1.A. (Continued)

Matrix	Analysis	Method/Reference	Comments	Data Use	Recommended Frequency of Analysis	Sample Volume, Sample Container, Sample Preservation	Field or Fixed-Base Laboratory
Water	Oxygen	Dissolved oxygen meter	Refer to method A4500 for a comparable laboratory procedure.	Concentrations less than 1 mg/L generally indicate an anaerobic pathway	Each sampling round	Measure dissolved oxygen onsite using a flow-through cell	Field
Water	Nitrate	IC method E300	Method E300 is a Handbook method.	Substrate for microbial respiration if oxygen is depleted	Each sampling round	Collect at least 40 mL of water in a glass or plastic container; add H_2SO_4 to pH less than 2, cool to 4°C	Fixed-base
Water	Iron (II) (Fe^{2+})	Colorimetric Hach Method # 8146	Filter if turbid.	May indicate an anaerobic degradation process due to depletion of oxygen, nitrate, and manganese	Each sampling round	Collect 100 mL of water in a glass container and analyze as soon as possible	Field
Water	Sulfate (SO_4^{2-})	IC method E300	Method E300 is a Handbook method, if this method is used for sulfate analysis, do not use the field method.	Substrate for anaerobic microbial respiration	Each sampling round	Collect at least 40 mL of water in a glass or plastic container; cool to 4°C	Fixed-base
Water	Sulfate (SO_4^{2-})	Hach method # 8051	Colorimetric, if this method is used for sulfate analysis, do not use the fixed-base laboratory method.	Same as above	Each sampling round	Collect at least 40 mL of water in a glass or plastic container; cool to 4°C	Field
Water	Methane, ethane, and ethene	Kampbell *et al.*, 1989 or SW3810 Modified	Method published by researchers at the US Environmental Protection Agency. Limited to few commercial labs.	The presence of CH_4 suggests BTEX degradation via methanogenesis. Ethane and ethene data are used where chlorinated solvents are suspected of undergoing biological transformation.	Each sampling round	Collect water samples in 50 mL glass serum bottles with butyl gray/Teflon-lined caps; add H_2SO_4 to pH less than 2, cool to 4°C	Fixed-base

Table 2.1.A. (Continued)

Matrix	Analysis	Method/Reference	Comments	Data Use	Recommended Frequency of Analysis	Sample Volume, Sample Container, Sample Preservation	Field or Fixed-Base Laboratory
Water	Alkalinity	Hach alkalinity test kit model AL AP MG-L	Phenolphthalein method	General water quality parameter used (1) as a marker to verify that all site samples are obtained from the same groundwater system; (2) to measure the buffering capacity of groundwater; and (3) to estimate the amount of carbon dioxide produced.	Each sampling round	Collect 100 mL of water in glass container	Field
Water	Oxidation-reduction potential (ORP)	A2580B	Measurements made with electrodes; results are displayed on a meter; protect samples from exposure to oxygen. Report results against a silver/silver chloride reference electrode	The ORP of groundwater influences and is influenced by the nature of the biologically mediated degradation of contaminants; the ORP of groundwater may range from more than 800 mV to less than -400 mV.	Each sampling round	Collect 100–250 mL of water in a glass container, filling container from bottom; analyze immediately	Field
Water	pH	Field probe with direct reading meter.	Field	Aerobic and anaerobic processes are pH-sensitive	Each sampling round	Collect 100–250 mL of water in a glass or plastic container; analyze immediately	Field
Water	Temperature	Field probe with direct reading meter.	Field only	Well development	Each sampling round	Not Applicable	Field
Water	Conductivity	E120.1/SW9050, direct reading meter	Protocols/Handbook methods	General water quality parameter used as a marker to verify that site samples are obtained from the same groundwater system	Each sampling round	Collect 100–250 mL of water in a glass or plastic container	Field

Table 2.1.A. (Concluded)

Matrix	Analysis	Method/Reference	Comments	Data Use	Recommended Frequency of Analysis	Sample Volume, Sample Container, Sample Preservation	Field or Fixed-Base Laboratory
Water	Chloride	Mercuric nitrate titration A4500-Cl^- C	Ion chromatography (IC) method E300 or method SW9050 may also be used	General water quality parameter used as a marker to verify that site samples are obtained from the same groundwater system. Final product of chlorinated solvent reduction.	Each sampling round	Collect 250 mL of water in a glass container	Fixed-base
Water	Chloride (optional, see data use)	Hach Chloride test kit model 8-P	Silver nitrate titration	As above, and to guide selection of additional data points in real time while in the field.	Each sampling round	Collect 100 mL of water in a glass container	Field
Water	Total Organic Carbon	SW9060	Laboratory	Used to classify plume and to determine if cometabolism is possible in the absence of anthropogenic carbon	Each sampling round	Collect 100 mL of water in a glass container, cool	Laboratory

Table 2.1.B. Soil and Groundwater Analytical Protocol/ Special Analyses*

Matrix	Analysis	Method/Reference	Comments	Data Use	Recommended Frequency of Analysis	Sample Volume, Container, and Preservation	Field or Fixed-Base Laboratory
Soil	Biologically Available Iron (III)	Under development	HCL extraction followed by quantification of released iron (III)	To predict the possible extent of iron reduction in an aquifer	One round of sampling in five borings, five cores from each boring	Minimum 1inch diameter core samples collected into plastic liner. Cap and prevent aeration	Laboratory
Water	Nutritional quality of native organic matter	Under Development	Spectrophotometric method	Used to determine the extent of reductive dechlorination allowed by the supply of electron donor	One round of sampling in two to five wells	1,000 mL in amber glass container	Laboratory
Water	Hydrogen (H_2)	Equilibration with gas in the field. Determined with a reducing gas detector.	Specialized analysis	Determine terminal electron accepting process. Predicts the possibility for reductive dechlorination.	One round of sampling	Sampled at well head requires the production of 100mL per minute of water for 30 minutes	Field
Water	Oxygenates (including MTBE, ethers, acetic acid, methanol, and acetone)	SW8260/8015	Laboratory	Contaminant or electron donors for dechlorination of solvents.	At least one sampling round or as determined by regulators	Collect 1 L of water in a glass container, preserve with HCL	Laboratory

NOTES:

* Analyses other than those listed in this table may be required for regulatory compliance.

1. "Hach" refers to the Hach Company catalog, 1990.
2. "A" refers to *Standard Methods for the Examination of Water and Wastewater*, 18th edition, 1992.
3. "E" refers to *Methods for Chemical Analysis of Water and Wastes*, USEPA, 1983.
4. "Protocols" refers to the AFCEE *Environmental Chemistry Function Installation Restoration Program Analytical Protocols*, 11 June 1992.
5. "Handbook" refers to the AFCEE *Handbook to Support the Installation Restoration Program (IRP) Remedial Investigations and Feasibility Studies (RI/FS)*, September 1993.
6. "SW" refers to the *Test Methods for Evaluating Solid Waste, Physical, and Chemical Methods*, SW-846, USEPA, 3rd edition, 1986.
7. "ASTM" refers to the *American Society for Testing and Materials*.
8. "LUFT" refers to the State of California *Leaking Underground Fuel Tank Field Manual*, 1988 edition.

If, after completing the steps outlined in this section, it appears that natural attenuation will be a significant factor in contaminant removal, detailed site characterization activities in support of this remedial option should be performed. If exposure pathways have already been completed and contaminant concentrations exceed regulatory levels, or if such completion is likely, other remedial measures should be considered, possibly in conjunction with natural attenuation. Even so, the collection of data in support of the natural attenuation option can be integrated into a comprehensive remedial strategy and may help reduce the cost and duration of engineered remedial measures such as intensive source removal operations or pump-and-treat technologies.

2.2.1 Overview of Chlorinated Aliphatic Hydrocarbon Biodegradation

Because biodegradation is the most important destructive process acting to reduce contaminant concentrations in groundwater, an accurate estimate of the potential for natural biodegradation is important to consider when determining whether groundwater contamination presents a substantial threat to human health and the environment. This information also will be useful when selecting the remedial alternative that will be most cost effective at eliminating or abating these threats should natural attenuation alone not prove to be sufficient.

Over the past two decades, numerous laboratory and field studies have demonstrated that subsurface microorganisms can degrade a variety of hydrocarbons and chlorinated solvents (e.g., Bouwer *et al.*, 1981; Miller and Guengerich, 1982; Wilson and Wilson, 1985; Nelson *et al.*, 1986; Bouwer and Wright, 1988; Lee, 1988; Little *et al.*, 1988; Mayer *et al.*, 1988; Arciero *et al.*, 1989; Cline and Delfino, 1989; Freedman and Gossett, 1989; Folsom *et al.*, 1990; Harker and Kim, 1990; Alvarez-Cohen and McCarty, 1991a, 1991b; DeStefano *et al.*, 1991; Henry, 1991; McCarty *et al.*, 1992; Hartmans and de Bont, 1992; McCarty and Semprini, 1994; Vogel, 1994). Whereas fuel hydrocarbons are biodegraded through use as a primary substrate (electron donor), chlorinated aliphatic hydrocarbons may undergo biodegradation through three different pathways: use as an electron acceptor; use as an electron donor; or through cometabolism, where degradation of the chlorinated organic is fortuitous, and there is no benefit to the microorganism. At a given site, one or all of these processes may be operating, although at many sites the use of chlorinated aliphatic hydrocarbons as electron acceptors appears to be most important under natural conditions. In this case biodegradation of chlorinated aliphatic hydrocarbons will be an electron-donor-limited process. Conversely, biodegradation of fuel hydrocarbons is an electron-acceptor-limited process.

In a pristine aquifer, native organic carbon is used as an electron donor, and dissolved oxygen (DO) is used first as the prime electron acceptor. Where anthropogenic carbon (e.g., as fuel hydrocarbons) is present, it also will be used as an electron donor. After the DO is consumed,

anaerobic microorganisms typically use additional electron acceptors (as available) in the following order of preference: nitrate, ferric iron oxyhydroxide, sulfate, and finally carbon dioxide. Evaluation of the distribution of these electron acceptors can provide evidence of where and how chlorinated aliphatic hydrocarbon biodegradation is occurring. In addition, because chlorinated aliphatic hydrocarbons may be used as electron acceptors or electron donors (in competition with other acceptors or donors), isopleth maps showing the distribution of these compounds and their daughter products can provide evidence of the mechanisms of biodegradation working at a site. As with BTEX, the driving force behind oxidation-reduction reactions resulting in chlorinated aliphatic hydrocarbon degradation is electron transfer. Although thermodynamically favorable, most of the reactions involved in chlorinated aliphatic hydrocarbon reduction and oxidation do not proceed abiotically. Microorganisms are capable of carrying out the reactions, but they will facilitate only those oxidation-reduction reactions that have a net yield of energy.

2.2.1.1 Mechanisms of Chlorinated Aliphatic Hydrocarbon Biodegradation

2.2.1.1.1 Electron Acceptor Reactions (Reductive Dehalogenation)

The most important process for the natural biodegradation of the more highly chlorinated solvents is reductive dechlorination. During this process, the chlorinated hydrocarbon is used as an electron acceptor, not as a source of carbon, and a chlorine atom is removed and replaced with a hydrogen atom. Figure 2.2 illustrates the transformation of chlorinated ethenes via reductive dechlorination. In general, reductive dechlorination occurs by sequential dechlorination from PCE to TCE to DCE to VC to ethene. Depending upon environmental conditions, this sequence may be interrupted, with other processes then acting upon the products. During reductive dechlorination, all three isomers of DCE can theoretically be produced; however, Bouwer (1994) reports that under the influence of biodegradation, *cis*-1,2-DCE is a more common intermediate than *trans*-1,2-DCE, and that 1,1-DCE is the least prevalent of the three DCE isomers when they are present as daughter products. Reductive dechlorination of chlorinated solvent compounds is associated with the accumulation of daughter products and an increase in the concentration of chloride ions.

Reductive dechlorination affects each of the chlorinated ethenes differently. Of these compounds, PCE is the most susceptible to reductive dechlorination because it is the most oxidized. Conversely, VC is the least susceptible to reductive dechlorination because

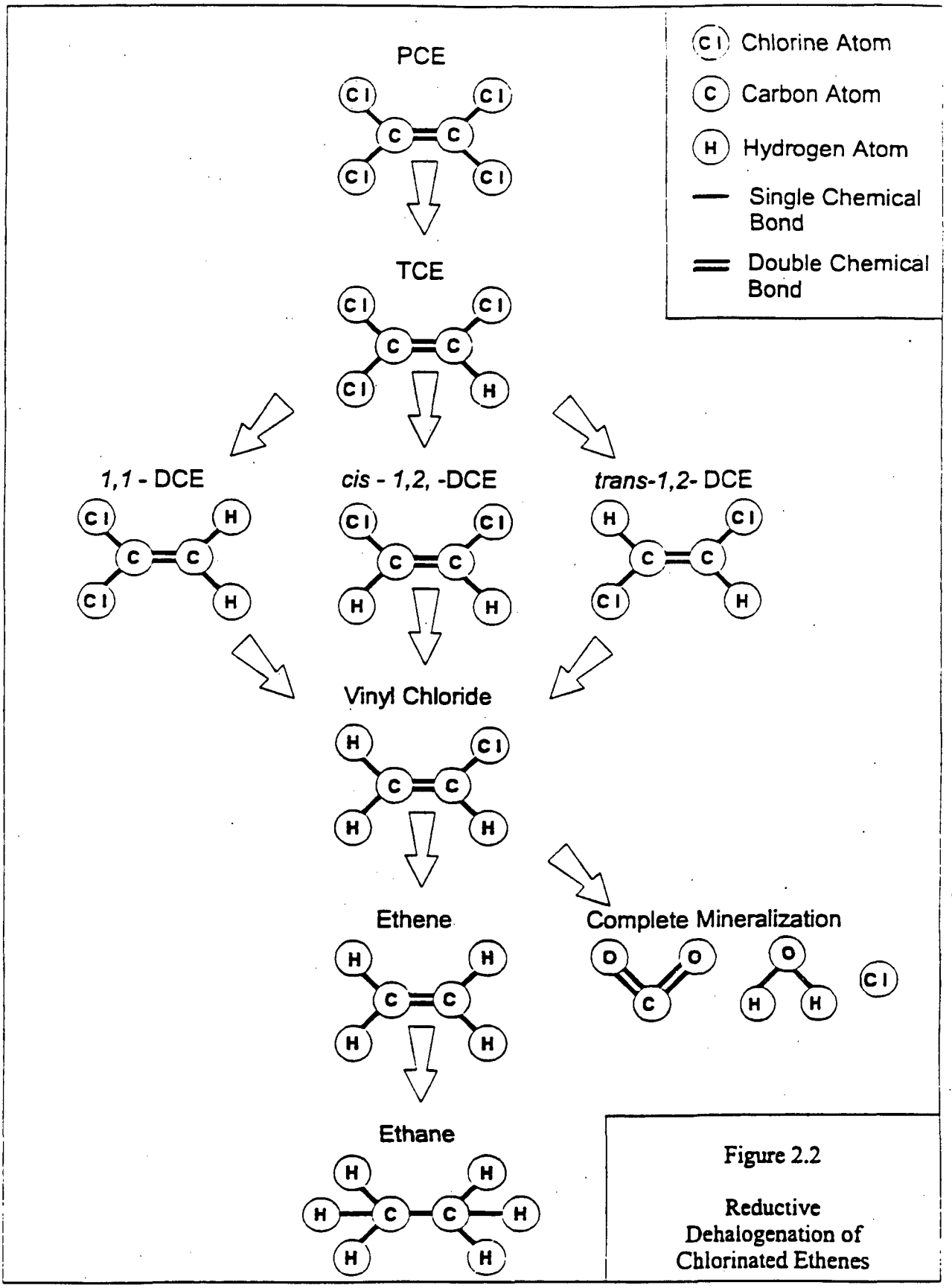

Figure 2.2

Reductive Dehalogenation of Chlorinated Ethenes

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it is the least oxidized of these compounds. As a result, the rate of reductive dechlorination decreases as the degree of chlorination decreases (Vogel and McCarty, 1985; Bouwer, 1994). Murray and Richardson (1993) have postulated that this rate decrease may explain the accumulation of VC in PCE and TCE plumes that are undergoing reductive dechlorination. Reductive dechlorination has been demonstrated under nitrate- and iron-reducing conditions, but the most rapid biodegradation rates, affecting the widest range of chlorinated aliphatic hydrocarbons, occur under sulfate-reducing and methanogenic conditions (Bouwer, 1994). Because chlorinated aliphatic hydrocarbon compounds are used as electron acceptors during reductive dechlorination, there must be an appropriate source of carbon for microbial growth in order for this process to occur (Bouwer, 1994). Potential carbon sources include natural organic matter, fuel hydrocarbons, or other anthropogenic organic compounds such as those found in landfill leachate.

2.2.1.1.2 Electron Donor Reactions

Murray and Richardson (1993) write that microorganisms are generally believed to be incapable of growth using PCE and TCE as a primary substrate (i.e., electron donor). However, under aerobic and some anaerobic conditions, the less oxidized chlorinated aliphatic hydrocarbons (e.g., VC) can be used as the primary substrate in biologically mediated oxidation-reduction reactions (McCarty and Semprini, 1994). In this type of reaction, the facilitating microorganism obtains energy and organic carbon from the degraded chlorinated aliphatic hydrocarbon. In contrast to reactions in which the chlorinated aliphatic hydrocarbon is used as an electron acceptor, only the least oxidized chlorinated aliphatic hydrocarbons can be used as electron donors in biologically mediated oxidation-reduction reactions. McCarty and Semprini (1994) describe investigations in which VC and 1,2-dichloroethane (DCA) were shown to serve as primary substrates under aerobic conditions. These authors also document that dichloromethane has the potential to function as a primary substrate under either aerobic or anaerobic environments. In addition, Bradley and Chapelle (1996) show evidence of mineralization of VC under iron-reducing conditions so long as there is sufficient bioavailable iron (III). Aerobic metabolism of VC may be characterized by a loss of VC mass and a decreasing molar ratio of VC to other chlorinated aliphatic hydrocarbon compounds.

2.2.1.1.3 Cometabolism

When a chlorinated aliphatic hydrocarbon is biodegraded via cometabolism, the degradation is catalyzed by an enzyme or cofactor that is fortuitously produced by the organisms for other purposes. The organism receives no known benefit from the degradation of the chlorinated

aliphatic hydrocarbon. Rather, the cometabolic degradation of the chlorinated aliphatic hydrocarbon may in fact be harmful to the microorganism responsible for the production of the enzyme or cofactor (McCarty and Semprini, 1994). Cometabolism is best documented in aerobic environments, although it potentially could occur under anaerobic conditions. It has been reported that under aerobic conditions chlorinated ethenes, with the exception of PCE, are susceptible to cometabolic degradation (Murray and Richardson, 1993; Vogel, 1994; McCarty and Semprini, 1994). Vogel (1994) further elaborates that the rate of cometabolism increases as the degree of dechlorination decreases. During cometabolism, the chlorinated alkene is indirectly transformed by bacteria as they use BTEX or another substrate to meet their energy requirements. Therefore, the chlorinated alkene does not enhance the degradation of BTEX or other carbon sources, nor will its cometabolism interfere with the use of electron acceptors involved in the oxidation of those carbon sources.

2.2.1.2 Behavior of Chlorinated Solvent Plumes

Chlorinated solvent plumes can exhibit three types of behavior depending on the amount of solvent, the amount of biologically available organic carbon in the aquifer, the distribution and concentration of natural electron acceptors, and the types of electron acceptors being used. Individual plumes may exhibit all three types of behavior in different portions of the plume. The different types of plume behavior are summarized below.

2.2.1.2.1 Type 1 Behavior

Type 1 behavior occurs where the primary substrate is anthropogenic carbon (e.g., BTEX or landfill leachate), and microbial degradation of this anthropogenic carbon drives reductive dechlorination. When evaluating natural attenuation of a plume exhibiting type 1 behavior the following questions must be answered:

1) Is the electron donor supply adequate to allow microbial reduction of the chlorinated organic compounds? In other words, will the microorganisms "strangle" before they "starve" [i.e., will they run out of chlorinated aliphatic hydrocarbons used as electron acceptors before they run out of anthropogenic carbon used as the primary substrate?
2) What is the role of competing electron acceptors (e.g., dissolved oxygen, nitrate, iron (III) and sulfate)?
3) Is VC oxidized, or is it reduced?

Appendices B and C discuss what these questions mean and how they are answered. Type 1 behavior results in the rapid and extensive degradation of the more highly-chlorinated solvents such as PCE, TCE, and DCE.

2.2.1.2.2 Type 2 Behavior

Type 2 behavior dominates in areas that are characterized by relatively high concentrations of biologically available native organic carbon. Microbial utilization of this natural carbon source drives reductive dechlorination (i.e., it is the primary substrate for microorganism growth). When evaluating natural attenuation of a type 2 chlorinated solvent plume, the same questions as those posed in the description of type 1 behavior must be answered. Type 2 behavior generally results in slower biodegradation of the highly chlorinated solvents than Type 1 behavior, but under the right conditions (e.g., areas with high natural organic carbon contents), this type of behavior also can result in rapid degradation of these compounds.

2.2.1.2.3 Type 3 Behavior

Type 3 behavior dominates in areas that are characterized by low concentrations of native and/or anthropogenic carbon, and concentrations of dissolved oxygen that are greater than 1.0 mg/L. Under these aerobic conditions reductive dechlorination will not occur. The most significant natural attenuation mechanisms for PCE, TCE, and DCE will be advection, dispersion, and sorption. However, VC can be rapidly oxidized under these conditions, and cometabolism generally occurs under aerobic conditions.

2.2.1.2.4 Mixed Behavior

As mentioned above, a single chlorinated solvent plume can exhibit all three types of behavior in different portions of the plume. This can be beneficial for natural biodegradation of chlorinated aliphatic hydrocarbon plumes. For example, Wiedemeier *et al.* (1996a) describe a plume at Plattsburgh AFB, New York that exhibits Type 1 behavior in the source area and Type 3 behavior downgradient from the source. The most fortuitous scenario involves a plume in which PCE, TCE, and DCE are reductively dechlorinated with accumulation of VC near the source area (Type 1 or Type 2 behavior), then VC is oxidized (Type 3 behavior), either aerobically or via iron reduction further downgradient. Vinyl chloride is oxidized to carbon dioxide in this type of plume and does not accumulate. The following sequence of reactions occurs in a plume that exhibits this type of mixed behavior.

$$\text{PCE} \rightarrow \text{TCE} \rightarrow \text{DCE} \rightarrow \text{VC} \rightarrow \text{Carbon Dioxide}$$

In general, TCE, DCE, and VC may attenuate at approximately the same rate, and thus these reactions may be confused with simple dilution. Note that no ethene is produced during this reaction. Vinyl chloride is removed from the system much faster under these conditions than it is under VC-reducing conditions.

A less desirable scenario, but one in which all contaminants may be entirely biodegraded, involves a plume in which all chlorinated aliphatic hydrocarbons are reductively dechlorinated via Type 1 or Type 2 behavior. Vinyl chloride is reduced to ethene, which may be further reduced to ethane or methane. The following sequence of reactions occur in this type of plume.

$$\text{PCE} \rightarrow \text{TCE} \rightarrow \text{DCE} \rightarrow \text{VC} \rightarrow \text{Ethene} \rightarrow \text{Ethane}$$

This sequence has been investigated by Freedman and Gossett (1989). In this type of plume, VC degrades more slowly than TCE, and thus tends to accumulate.

2.2.2 Screening Process

Based on the experience of the authors, it is estimated that for 80 percent of fuel-hydrocarbon spills at federal facilities, natural attenuation will be protective of human health and the environment. For spills of chlorinated aliphatic hydrocarbons at federal facilities however, natural attenuation alone may be protective of human health and the environment for approximately 20 percent of spills. With this in mind, it is easy to understand why an accurate assessment of the potential for natural biodegradation of chlorinated compounds should be made before investing in a detailed study of natural attenuation. The screening process presented in this section is outlined in Figure 2.3. This approach should allow the investigator to determine if natural attenuation is likely to be a viable remedial alternative before additional time and money are expended. The data required to make the preliminary assessment of natural attenuation also can be used to aid the design of an engineered remedial solution should the screening process suggest that natural attenuation is not feasible.

The following information is required for the screening process:

- The chemical and geochemical data presented in Table 2.2 for a minimum of six (6) samples. Figure 2.4 shows the schematic locations of these data collection points

  Note: if other contaminants are suspected, then data on the concentrations and distribution of these compounds also should be obtained

- Locations of source(s) and receptor exposure points.

- An estimate of the transport velocity and direction of groundwater flow

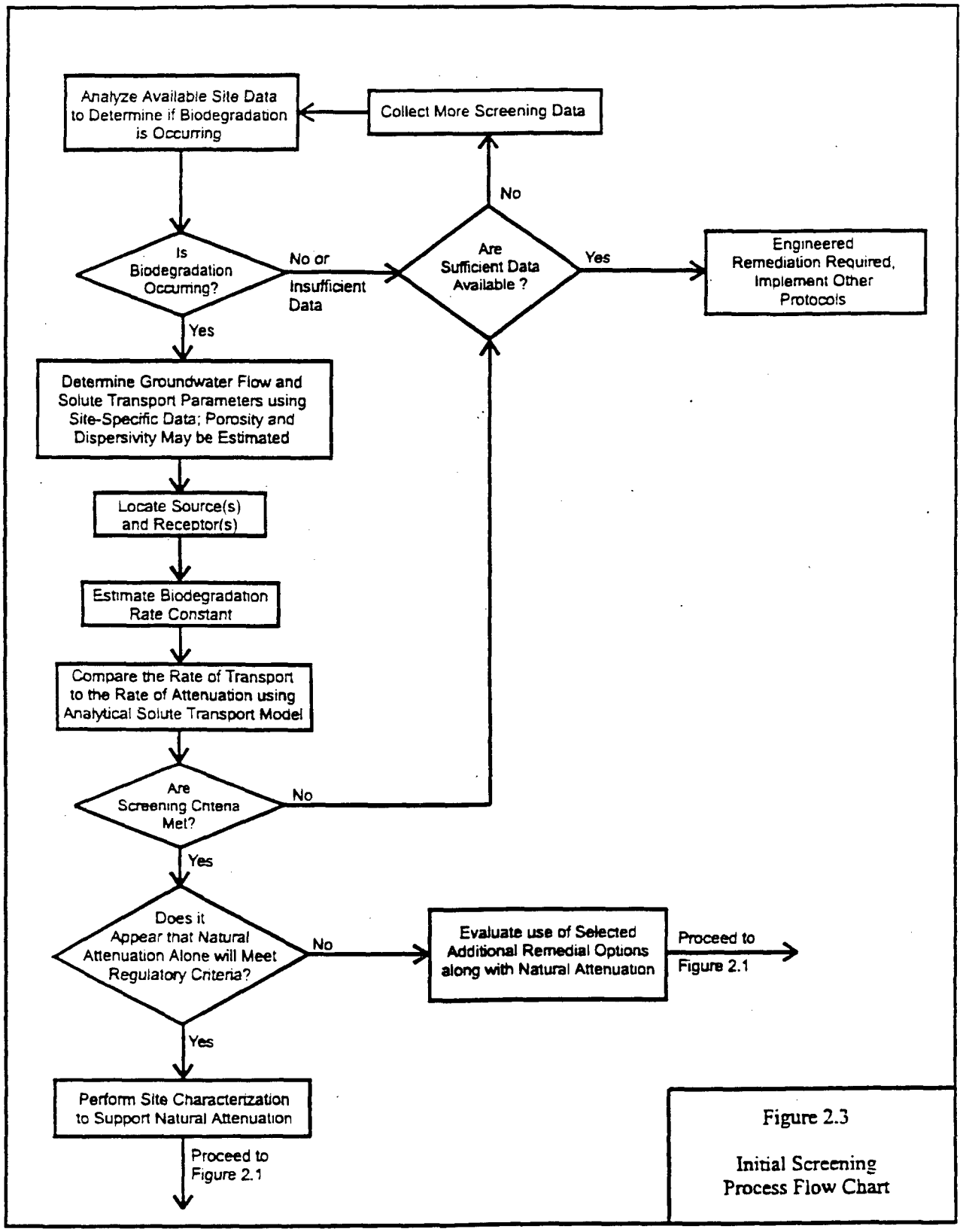

Figure 2.3

Initial Screening Process Flow Chart

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Table 2.2

Analytical Parameters and Weighting for Preliminary Screening

Analysis	Concentration in Most Contaminated Zone	Interpretation	Value
Oxygen*	<0.5 mg/L	Tolerated, suppresses the reductive pathway at higher concentrations	3
Oxygen*	>1 mg/L	VC may be oxidized aerobically	-3
Nitrate*	<1 mg/L	At higher concentrations may compete with reductive pathway	2
Iron II*	>1 mg/L	Reductive pathway possible	3
Sulfate*	<20 mg/L	At higher concentrations may compete with reductive pathway	2
Sulfide*	>1 mg/L	Reductive pathway possible	3
Methane*	<0.5 mg/L >0.5 mg/L	VC oxidizes Ultimate reductive daughter product, VC Accumulates	0 3
Oxidation Reduction Potential* (ORP)	<50 millivolts (mV) <-100mV	Reductive pathway possible Reductive pathway likely	1 2
pH*	5 < pH < 9 5 > pH >9	Optimal range for reductive pathway Outside optimal range for reductive pathway	0 -2
TOC	> 20 mg/L	Carbon and energy source; drives dechlorination; can be natural or anthropogenic	2
Temperature*	> 20°C	At T >20°C biochemical process is accelerated	1
Carbon Dioxide	>2x background	Ultimate oxidative daughter product	1
Alkalinity	>2x background	Results from interaction of carbon dioxide with aquifer minerals	1
Chloride*	>2x background	Daughter product of organic chlorine	2
Hydrogen	>1 nM	Reductive pathway possible, VC may accumulate	3
Hydrogen	<1 nM	VC oxidized	0
Volatile Fatty Acids	> 0.1 mg/L	Intermediates resulting from biodegradation of aromatic compounds; carbon and energy source	2
BTEX*	> 0.1 mg/L	Carbon and energy source; drives dechlorination	2
PCE*		Material released	0
TCE*		Material released Daughter product of PCE	0 2a/
DCE*		Material released Daughter product of TCE. If cis is greater than 80% of total DCE it is likely a daughter product of TCE	0 2a/
VC*		Material released Daughter product of DCE	0 2a/
Ethene/Ethane	>0.01mg/L >0.1 mg/L	Daughter product of VC/ethene	2 3
Chloroethane*		Daughter product of VC under reducing conditions	2
1,1,1-Trichloroethane*		Material released	0
1,2-dichlorobenzene*		Material released	0
1,3-dichlorobenzene*		material released	0
1,4-dichlorobenzene*		material released	0
chlorobenzene*		Material released or daughter product of dichlorobenzene	2a/
1,1-DCE*		Daughter product of TCE or chemical reaction of 1,1,1-TCA	2a/

* Required analysis.

a/ Points awarded only if it can be shown that the compound is a daughter product (i.e., not a constituent of the source NAPL).

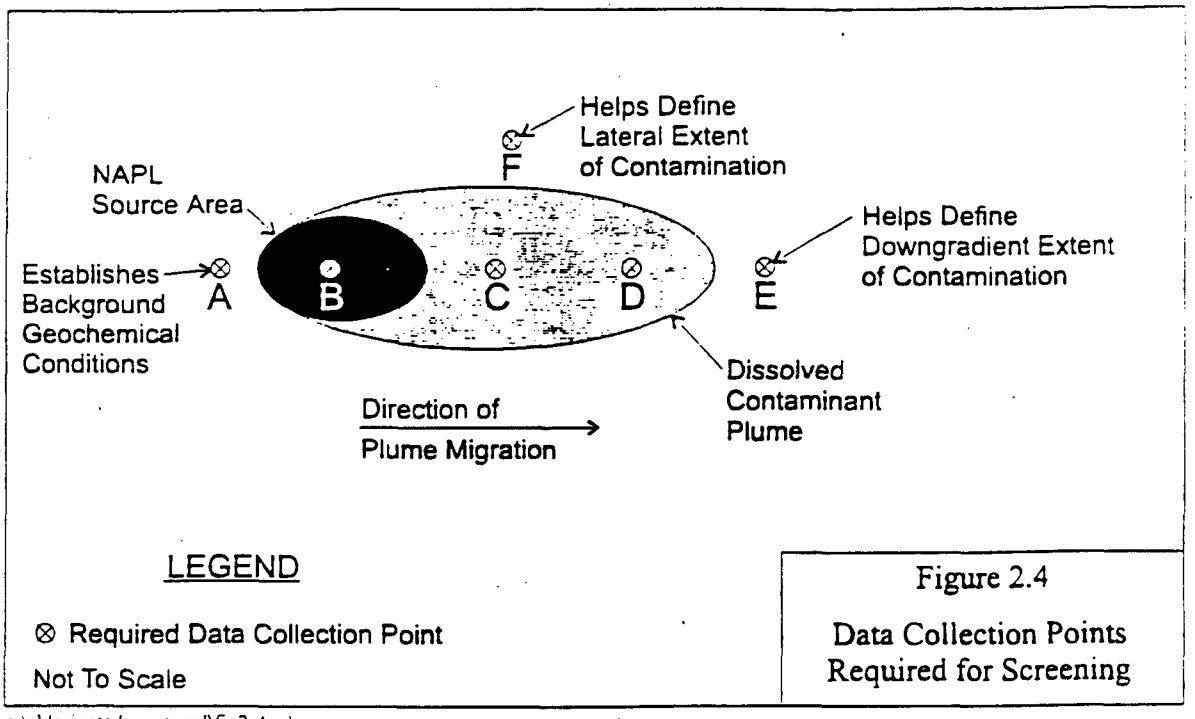

Figure 2.4

Data Collection Points Required for Screening

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Once these data have been collected, the screening process can be undertaken. The following steps summarize the screening processes:

1) Determine if biodegradation is occurring using geochemical data

   If biodegradation is occurring, proceed to step 2. If it is not, assess the amount and types of data available. If data are insufficient to determine if biodegradation is occurring, collect supplemental data.

2) Determine groundwater flow and solute transport parameters.

   Dispersivity and porosity may be estimated but the hydraulic conductivity and the groundwater gradient and flow direction may not. The investigator should use the highest hydraulic conductivity measured at the site during the preliminary screening because solute plumes tend to follow the path of least resistance (i.e., highest hydraulic conductivity). This will give the "worst-case" estimate of the solute migration distance over a given period of time.

3) Locate source(s) and receptor exposure points.

4) Estimate the biodegradation rate constant.

   Biodegradation rate constants can be estimated using a conservative tracer found commingled with the contaminant plume, as described in Appendix C and by Wiedemeier *et al.* (1996b). When dealing with a plume that contains only chlorinated solvents, this procedure can be modified to use chloride as a tracer. Rate constants derived from microcosm studies can also be used. If it is not possible to estimate the biodegradation rate using these procedures, then use a range of accepted literature

values for biodegradation of the contaminants of concern. Appendix C presents a range of biodegradation rate constants for various compounds.

5) Compare the rate of transport to the rate of attenuation.
   Use analytical solutions or a screening model such as BIOSCREEN.
6) Determine if screening criteria are met.

Step 1: Determine if Biodegradation is Occurring

The first step in the screening process is to sample at least six (6) wells that are representative of the contaminant flow system (Figure 2.4) and analyze them for the parameters listed in Table 2.2 (see also Section 2.3.2). These samples should include (1) a sample from the most contaminated portion of the aquifer (generally in the area where NAPL currently is present or was present in the past); (2) samples collected downgradient from the NAPL source area but still in the dissolved contaminant plume; (3) samples collected downgradient from the dissolved contaminant plume; and (4) samples collected from upgradient and lateral locations that are not impacted by the plume.

The sample collected in the NAPL source area allows determination of the dominant terminal electron-accepting processes operating at the site. In conjunction with the sample collected in the NAPL source zone, samples collected in the dissolved plume downgradient from the NAPL source zone allow the investigator to determine if the plume is degrading with distance along the flow path and to determine the distribution of electron acceptors and donors and metabolic byproducts along the flow path. The sample collected downgradient from the dissolved plume aids in plume delineation and allows the investigator to determine if metabolic byproducts are present in an area of groundwater that has been remediated. The upgradient and lateral samples allow delineation of the plume and determination of background concentrations of the electron acceptors and donors.

After these samples have been analyzed for the parameters listed in Table 2.2, the investigator should analyze the data to determine if biodegradation is occurring. The right-hand column of Table 2.2 contains scoring values that can be used as a test to assess the likelihood that biodegradation is occurring. This method relies on the fact that biodegradation will cause predictable changes in groundwater chemistry. For example, if the dissolved oxygen concentration in the area of the plume with the highest contaminant concentration is less than 0.5 milligrams per liter (mg/L), 3 points are awarded. Table 2.3 summarizes the range of possible scores and gives an interpretation for each score. If the score totals 15 or more points, it is likely that biodegradation is occurring, and the investigator can proceed to Step 2.

Table 2.3
Interpretation of Points Awarded During Screening Step 1

Score	Interpretation
0 to 5	Inadequate evidence for biodegradation of chlorinated organics
6 to 14	Limited evidence for biodegradation of chlorinated organics
15 to 20	Adequate evidence for biodegradation of chlorinated organics
> 20	Strong evidence for biodegradation of chlorinated organics

The following two examples illustrate how step 1 of the screening process is implemented. The site used in the first example is a former fire training area contaminated with chlorinated solvents mixed with fuel hydrocarbons. The presence of the fuel hydrocarbons appears to reduce the ORP of the groundwater to the extent that reductive dechlorination is favorable. The second example contains data from a dry cleaning site contaminated only with chlorinated solvents. This site was contaminated with spent cleaning solvents that were dumped into a shallow dry well situated just above a well-oxygenated, unconfined aquifer with low organic carbon concentrations.

Example 1: Strong Evidence for Biodegradation of Chlorinated Organics

Analyte	Concentration in Most Contaminated Zone	Points Awarded
Dissolved Oxygen	0.1 mg/L	3
Nitrate	0.3 mg/L	2
Iron (II)	10 mg/L	3
Sulfate	2 mg/L	2
Methane	5 mg/L	3
ORP	-190 mV	2
Chloride	3 times background	2
PCE (released)	1,000 µg/L	0
TCE (none released)	1,200 µg/L	2
cis-DCE (none released)	500 µg/L	2
VC (none released)	50 µg/L	2
	Total Points Awarded	23 Points

In this example the investigator can infer that biodegradation is likely occurring and may proceed to Step 2.

Example 2: Biodegradation Unlikely

Analyte	Concentration in Most Contaminated Zone	Points Awarded
Dissolved Oxygen	3 mg/L	-3
Nitrate	0.3 mg/L	2
Iron (II)	Not Detected (ND)	0
Sulfate	10 mg/L	2
Methane	ND	0
ORP	100 mV	0
Chloride	background	0
TCE (released)	1,200 µg/L	0
cis-DCE (none released)	ND	0
VC (none released)	ND	0
	Total Points Awarded	1 Point

In this example the investigator can infer that biodegradation is probably not occurring or is occurring too slowly to be a viable remedial option. In this case, the investigator should not proceed to Step 2 and will likely have to implement an engineered remediation system.

Step 2: Determine Groundwater Flow and Solute Transport Parameters

After it has been shown that biodegradation is occurring, it is important to quantify groundwater flow and solute transport parameters. This will make it possible to use a solute transport model to quantitatively estimate the concentration of the plume and its direction and rate of travel. To use an analytical model it is necessary to know the hydraulic gradient and hydraulic conductivity for the site and to have estimates of porosity and dispersivity. It also is helpful to know the coefficient of retardation. Quantification of these parameters is discussed in detail in Appendix B.

In order to make the modeling as accurate as possible, the investigator must have site-specific hydraulic gradient and hydraulic conductivity data. To determine the groundwater flow and solute transport direction, it is necessary to have at least three accurately surveyed wells at the site. The porosity and dispersivity are generally estimated using accepted literature values for the types of sediments found at the site. If the investigator has total organic carbon data for soil, it is possible to estimate the coefficient of retardation; otherwise it is best to assume that the solute transport and groundwater velocities are the same.

Step 3: Locate Sources and Receptor Exposure Points

To determine the length of flow for the predictive modeling to be conducted in Step 5, it is important to know the distance between the source of contamination, the toe of the dissolved plume, and any potential downgradient or cross-gradient receptor exposure points.

Step 4: Estimate the Biodegradation Rate

Biodegradation is the most important process that degrades contaminants in the subsurface; therefore, the biodegradation rate is one of the most important model input parameters. Biodegradation of chlorinated aliphatic hydrocarbons can commonly be represented as a first-order rate constant. It is generally best to use site-specific biodegradation rates. Calculation of site-specific biodegradation rates is discussed in Appendix C. If it is not possible to determine site-specific biodegradation rates, then it will be necessary to use literature values for the biodegradation rate of the contaminant of interest. A useful approach is to start with average values, and then to vary the model input to predict "best-case" and "worst-case" scenarios. Estimated biodegradation rates can be used only after it has been shown that biodegradation is occurring (see Step 1).

Step 5: Compare the Rate of Transport to the Rate of Attenuation

At this early stage in the natural attenuation demonstration, comparison of the rate of solute transport to the rate of attenuation is best accomplished using an analytical model. Several analytical models are available, but the BIOSCREEN model is probably the simplest to use. This model is non-proprietary and is available from the Robert S. Kerr Research Center's home page on the Internet (www.epa.gov/ada/kerrlab.html). The BIOSCREEN model is based on Domenico's (1987) solution to the advection-dispersion equation, and allows use of either a first-order biodegradation rate or an instantaneous reaction between contaminants and electron acceptors to simulate the effects of biodegradation. To model transport of chlorinated aliphatic hydrocarbons using BIOSCREEN, only the first-order decay rate option should be used. BIOCHLOR, a similar model, is under development by the Technology Transfer Division of AFCEE. This model will likely use the same analytical solution as BIOSCREEN, but will be geared toward evaluating transport of chlorinated compounds under the influence of biodegradation.

The primary purpose of comparing the rate of transport to the rate of attenuation is to determine if the residence time along the flow path is adequate to be protective of human health and the environment (i.e., to qualitatively estimate if the contaminant is attenuating at a rate fast enough to allow degradation of the contaminant to acceptable concentrations before receptors are exposed). It is important to perform a sensitivity analysis to help evaluate the confidence in the

preliminary screening modeling effort. If modeling shows that receptors will not be exposed to contaminants at concentrations above risk-based corrective action criteria, then the screening criteria are met, and the investigator can proceed with the natural attenuation evaluation.

Step 6: Determine if Screening Criteria are Met

Before proceeding with the full-scale natural attenuation evaluation, the investigator should ensure that the answers to all of the following questions are yes:

- Has the plume moved a shorter distance than expected based on the known (or estimated) time since the contaminant release and the contaminant velocity, as calculated from site-specific measurements of hydraulic conductivity and hydraulic gradient, and estimates of effective porosity and contaminant retardation?
- Is it likely that the contaminant mass is attenuating at rates sufficient to be protective of human health and the environment at potential exposure points (e.g., at a point of discharge to a sensitive environmental resource)?
- Does it appear that the plume is going to attenuate to concentrations less than federal, state, or risk-based guidelines before reaching potential receptors?

If the answer to each of these questions is yes, then the investigator can proceed with the full-scale natural attenuation demonstration.

2.3 COLLECT ADDITIONAL SITE CHARACTERIZATION DATA IN SUPPORT OF NATURAL ATTENUATION AS REQUIRED

Detailed site characterization is necessary to document the potential for natural attenuation to meet cleanup objectives. As discussed in Section 2.1, review of existing site characterization data is particularly useful before initiating site characterization activities. Such review should allow identification of data gaps and guide the most effective placement of additional data collection points.

There are two goals during the site characterization phase of a natural attenuation investigation. The first is to collect the data needed to determine if natural mechanisms of contaminant attenuation are occurring at rates sufficient to protect human health and the environment. The second is to provide sufficient site-specific data to allow prediction of the future extent and concentrations of a contaminant plume through solute fate and transport modeling. It is the responsibility of the proponent to "make the case" for natural attenuation. Thus, detailed site characterization is required to achieve these goals and to support this remedial

option. Adequate site characterization in support of natural attenuation requires that the following site-specific parameters be determined:

- Extent and types of soil and groundwater contamination.
- Location and extent of contaminant source area(s) (i.e., areas containing mobile or residual NAPL).
- The potential for a continuing source due to leaking tanks or pipelines, or other site activity.
- Aquifer geochemical parameters.
- Regional hydrogeology, including:
  - Drinking water aquifers, and
  - Regional confining units.
- Local and site-specific hydrogeology, including:
  - Local drinking water aquifers,
  - Location of industrial, agricultural, and domestic water wells,
  - Patterns of aquifer use (current and future),
  - Lithology,
  - Site stratigraphy, including identification of transmissive and nontransmissive units,
  - Grain-size distribution (sand *vs.* silt *vs.* clay),
  - Aquifer hydraulic conductivity,
  - Groundwater hydraulic information,
  - Preferential flow paths,
  - Locations and types of surface water bodies, and
  - Areas of local groundwater recharge and discharge.
- Identification of current and future potential exposure pathways, receptors, and exposure points.

The following sections describe the methodologies that should be implemented to allow successful site characterization in support of natural attenuation.

2.3.1 Soil Characterization

In order to adequately define the subsurface hydrogeologic system and to determine the amount and three-dimensional distribution of mobile and residual NAPL that can act as a continuing source of groundwater contamination, extensive soil characterization must be

completed. As appropriate, soil gas data may be collected and analyzed to better characterize soil contamination. Depending on the status of the site, this work may have been completed during previous remedial investigation work. The results of soils characterization will be used as input into a solute fate and transport model to help define a contaminant source term and to support the natural attenuation investigation.

The purpose of soil sampling is to determine the subsurface distribution of hydrostratigraphic units and the distribution of mobile and residual NAPL. These objectives can be achieved through the use of conventional soil borings or direct-push methods (e.g., Geoprobe® or cone penetrometer testing), and through collection of soil gas samples. All soil samples should be collected, described, analyzed, and disposed of in accordance with local, state, and federal guidance. Appendix A contains suggested procedures for soil sample collection. These procedures may require modification to comply with local, state, and federal regulations or to accommodate site-specific conditions.

The analytical protocol to be used for soil and soil gas sample analyses is presented in Table 2.1. This analytical protocol includes all of the parameters necessary to document natural attenuation, including the effects of sorption and biodegradation. Each analyte is discussed separately below.

- **Volatile Organic Compounds**: Knowledge of the location, distribution, concentration, and total mass of contaminants of regulatory concern sorbed to soils or present as mobile or immobile NAPL is required to calculate contaminant partitioning from NAPL into groundwater.
- **Total Organic Carbon**: Knowledge of the TOC content of the aquifer matrix is important for sorption and solute-retardation calculations. TOC samples should be collected from a background location in the stratigraphic horizon(s) where most contaminant transport is expected to occur.
- **Oxygen and Carbon Dioxide**: Oxygen and carbon dioxide soil gas measurements can be used to identify areas in the unsaturated zone where biodegradation is occurring. This can be a useful and relatively inexpensive way to track contamination and degradation in the subsurface.
- **Fuel and Chlorinated Volatile Organic Compounds**: Knowledge of the distribution of contaminants in soil gas can be used as a cost-effective way to estimate the extent of soil contamination.

2.3.2 Groundwater Characterization

To adequately determine the amount and three-dimensional distribution of dissolved contamination and to document the occurrence of natural attenuation, groundwater samples must be collected and analyzed. Biodegradation of organic compounds, whether natural or anthropogenic, brings about measurable changes in the chemistry of groundwater in the affected area. By measuring these changes, it is possible to document and quantitatively evaluate the importance of natural attenuation at a site.

Groundwater sampling is conducted to determine the concentrations and distribution of contaminants, daughter products, and groundwater geochemical parameters. Groundwater samples may be obtained from monitoring wells or with point-source sampling devices such as a Geoprobe®, Hydropunch®, or cone penetrometer. All groundwater samples should be collected, handled, and disposed of in accordance with local, state, and federal guidelines. Appendix A contains suggested procedures for groundwater sample collection. These procedures may need to be modified to comply with local, state, and federal regulations or to accommodate site-specific conditions.

The analytical protocol for groundwater sample analysis is presented in Table 2.1. This analytical protocol includes all of the parameters necessary to delineate dissolved contamination and to document natural attenuation, including the effects of sorption and biodegradation. Data obtained from the analysis of groundwater for these analytes is used to scientifically document natural attenuation and can be used as input into a solute fate and transport model. The following paragraphs describe each groundwater analytical parameter and the use of each analyte in the natural attenuation demonstration.

2.3.2.1 Volatile and Semivolatile Organic Compounds

These analytes are used to determine the type, concentration, and distribution of contaminants and daughter products in the aquifer. At a minimum, the volatile organic compound (VOC) analysis (Method SW8260a) should be used, with the addition of the trimethylbenzene isomers if fuel hydrocarbons are present or suspected. The combined dissolved concentrations of BTEX and trimethylbenzenes should not be greater than about 30 mg/L for a JP-4 spill (Smith *et al.*, 1981) or about 135 mg/L for a gasoline spill (Cline *et al.*, 1991; American Petroleum Institute, 1985). If these compounds are found in higher concentrations, sampling errors such as emulsification of LNAPL in the groundwater sample likely have occurred and should be investigated.

Maximum concentrations of chlorinated solvents dissolved in groundwater from neat solvents should not exceed their solubilities in water. Appendix B contains solubilities for common contaminants. If contaminants are found in concentrations greater than their solubilities, then sampling errors such as emulsification of NAPL in the groundwater sample have likely occurred and should be investigated.

2.3.2.2 Dissolved Oxygen

Dissolved oxygen is the most thermodynamically favored electron acceptor used by microbes for the biodegradation of organic carbon, whether natural or anthropogenic. Anaerobic bacteria generally cannot function at dissolved oxygen concentrations greater than about 0.5 mg/L and hence reductive dechlorination will not occur. This is why it is important to have a source of carbon in the aquifer that can be used by aerobic microorganisms as a primary substrate. During aerobic respiration, dissolved oxygen concentrations decrease. After depletion of dissolved oxygen, anaerobic microbes will use nitrate as an electron acceptor, followed by iron (III), then sulfate, and finally carbon dioxide (methanogenesis). Each sequential reaction drives the ORP of the groundwater downward into the range within which reductive dechlorination can occur. Reductive dechlorination is most effective in the ORP range corresponding to sulfate reduction and methanogenesis, but dechlorination of PCE and TCE also may occur in the ORP range associated with denitrification or iron (III) reduction. Because reductive dechlorination is most effective in the sulfate-reduction and methanogenesis ORP range, competitive exclusion between sulfate reducers, methanogens, and reductive dechlorinators can occur.

Dissolved oxygen measurements should be taken during well purging and immediately before and after sample acquisition using a direct-reading meter. Because most well purging techniques can allow aeration of collected groundwater samples, it is important to minimize the potential for aeration as described in Appendix A.

2.3.2.3 Nitrate

After dissolved oxygen has been depleted in the microbiological treatment zone, nitrate may be used as an electron acceptor for anaerobic biodegradation of organic carbon via denitrification. In order for reductive dechlorination to occur, nitrate concentrations in the contaminated portion of the aquifer must be less than 1.0 mg/L.

2.3.2.4 Iron (II)

In some cases iron (III) is used as an electron acceptor during anaerobic biodegradation of organic carbon. During this process, iron (III) is reduced to iron (II), which may be soluble in water. Iron (II) concentrations can thus be used as an indicator of anaerobic degradation of fuel compounds and VC.

2.3.2.5 Sulfate

After dissolved oxygen and nitrate have been depleted in the microbiological treatment zone, sulfate may be used as an electron acceptor for anaerobic biodegradation. This process is termed sulfate reduction and results in the production of sulfide.

2.3.2.6 Methane

During methanogenesis acetate is split to form carbon dioxide and methane, or carbon dioxide is used as an electron acceptor, and is reduced to methane. Methanogenesis generally occurs after oxygen, nitrate, and sulfate have been depleted in the treatment zone. The presence of methane in groundwater is indicative of strongly reducing conditions. Because methane is not present in fuel, the presence of methane above background concentrations in groundwater in contact with fuels is indicative of microbial degradation of fuel hydrocarbons. Methane also is associated with spills of pure chlorinated solvents. It is not known if the methane comes from chlorinated solvent carbon or from native dissolved organic carbon.

2.3.2.7 Alkalinity

The total alkalinity of a groundwater system is indicative of a water's capacity to neutralize acid. Alkalinity is defined as the net concentration of strong base in excess of strong acid with a pure carbon dioxide-water system as the point of reference (Domenico and Schwartz, 1990). Alkalinity results from the presence of hydroxides, carbonates, and bicarbonates of elements such as calcium, magnesium, sodium, potassium, or ammonia. These species result from the dissolution of rock (especially carbonate rocks), the transfer of carbon dioxide from the atmosphere, and respiration of microorganisms. Alkalinity is important in the maintenance of groundwater pH because it buffers the groundwater system against acids generated during both aerobic and anaerobic biodegradation. In the experience of the authors, biodegradation of organic compounds rarely, if ever, generates enough acid to impact the alkalinity of groundwater.

2.3.2.8 Oxidation-Reduction Potential

The ORP of groundwater (Eh) is a measure of electron activity and is an indicator of the relative tendency of a solution to accept or transfer electrons. Oxidation-reduction reactions in groundwater containing organic compounds (natural or anthropogenic) are usually biologically mediated, and therefore, the ORP of a groundwater system depends upon and influences rates of biodegradation. Knowledge of the ORP of groundwater also is important because some biological processes operate only within a prescribed range of ORP conditions. The ORP of groundwater generally ranges from -400 millivolts (mV) to 800 mV.

ORP measurements can be used to provide real-time data on the location of the contaminant plume, especially in areas undergoing anaerobic biodegradation. Mapping the ORP of the groundwater while in the field helps the field scientist to determine the approximate location of the contaminant plume. To map the ORP of the groundwater while in the field, it is important to have at least one ORP measurement (preferably more) from a well located upgradient from the plume. ORP measurements should be taken during well purging and immediately before and after sample acquisition using a direct-reading meter. Because most well purging techniques can allow aeration of collected groundwater samples (which can affect ORP measurements), it is important to minimize potential aeration by following the steps outlined in Appendix A.

2.3.2.9 Dissolved Hydrogen

Concentrations of dissolved hydrogen can also be used to evaluate redox processes in groundwater systems (Lovley and Goodwin, 1988; Lovley et al., 1994; Chapelle et al., 1995). H_2 is continuously produced in anoxic groundwater systems by fermentative microorganisms that decompose natural and anthropogenic organic matter. This H_2 is then consumed by respiratory microorganisms that use nitrate, Fe(III), sulfate, or CO_2 as terminal electron acceptors. This continuous cycling of H_2 is called *interspecies hydrogen transfer*. Significantly, nitrate-, Fe(III)-, sulfate- and CO_2-reducing (methanogenic) microorganisms exhibit different efficiencies in utilizing the H_2 that is being continually produced. Nitrate reducers are highly efficient H_2 utilizers and maintain very low steady-state H_2 concentrations. Fe(III) reducers are slightly less efficient and thus maintain somewhat higher H_2 concentrations. Sulfate reducers an methanogenic bacteria are progressively less efficient and maintain even higher H_2 concentrations. Because each terminal electron accepting process has a characteristic H_2 concentration associated with it, H_2 concentrations can be an indicator of predominant redox processes. These characteristic ranges are given in Table 2.4. An analytical protocol for quantifying H_2 concentrations in ground water is given in Appendix II.

Table 2.4

Range of Hydrogen Concentrations for a Given Terminal Electron-Accepting Process

Terminal Electron Accepting Process	Hydrogen (H_2) Concentration (nanomoles per liter)
Denitrification	< 0.1
Iron (III) Reduction	0.2 to 0.8
Sulfate Reduction	1 to 4
Methanogenesis	5-20

In practice, it is preferable to interpret H_2 concentrations in the context of electron acceptor (oxygen, nitrate, Fe(III), sulfate) availability and the presence of the final products (Fe(II), hydrogen sulfide, methane) of microbial metabolism (Chapelle *et al.*, 1995). For example, if sulfate concentrations in ground water are less than 0.5 mg/L, methane concentrations are greater than 0.5 mg/L, and H_2 concentrations are in the 5-20 nM range, it can be concluded with a high degree of certainty that methanogenesis is the predominant redox process in the aquifer. Similar logic can be applied to identifying denitrification (presence of nitrate, H_2<0.1 nM), Fe(III) reduction (production of Fe(II), H_2 0.2 to 0.8 nM), and sulfate reduction (presence of sulfate, production of sulfide, H_2 1-4 nM).

2.3.2.10 pH, Temperature, and Conductivity

Because the pH, temperature, and conductivity of a groundwater sample can change significantly within a short time following sample acquisition, these parameters must be measured in the field in unfiltered, unpreserved, "fresh" water collected by the same technique as the samples taken for dissolved oxygen and ORP analyses. The measurements should be made in a clean glass container separate from those intended for laboratory analysis, and the measured values should be recorded in the groundwater sampling record.

The pH of groundwater has an effect on the presence and activity of microbial populations in groundwater. This is especially true for methanogens. Microbes capable of degrading chlorinated aliphatic hydrocarbons and petroleum hydrocarbon compounds generally prefer pH values varying from 6 to 8 standard units.

Groundwater temperature directly affects the solubility of oxygen and other geochemical species. The solubility of dissolved oxygen is temperature-dependent, with oxygen being more soluble in cold water than in warm water. Groundwater temperature also affects the metabolic

activity of bacteria. Rates of hydrocarbon biodegradation roughly double for every 10°C increase in temperature ("Q"$_{10}$ rule) over the temperature range between 5 and 25°C.

Conductivity is a measure of the ability of a solution to conduct electricity. The conductivity of groundwater is directly related to the concentration of ions in solution; conductivity increases as ion concentration increases. Conductivity measurements are used to ensure that groundwater samples collected at a site are representative of the water comprising the saturated zone in which the dissolved contamination is present. If the conductivities of samples taken from different sampling points are radically different, the waters may be from different hydrogeologic zones and they should not be compared to evaluate contaminant attenuation. This is particularly true when the conductivity of the contaminated water sample is high and the conductivity of the clean sample is low.

2.3.2.11 Chloride

Elemental chlorine is the most abundant of the halogens. Although chlorine can occur in oxidation states ranging from Cl^- to Cl^{+7}, the chloride form (Cl^-) is the only form of major significance in natural waters (Hem, 1985). Chloride forms ion pairs or complex ions with some of the cations present in natural waters, but these complexes are not strong enough to be of significance in the chemistry of fresh water (Hem, 1985). The chemical behavior of chloride is neutral. Chloride ions generally do not enter into oxidation-reduction reactions, form no important solute complexes with other ions unless the chloride concentration is extremely high, do not form salts of low solubility, are not significantly adsorbed on mineral surfaces, and play few vital biochemical roles (Hem, 1985). Thus, physical processes control the migration of chloride ions in the subsurface. Kaufman and Orlob (1956) conducted tracer experiments in groundwater, and found that chloride moved through most of the soils tested more conservatively (i.e., with less retardation and loss) than any of the other tracers tested.

During biodegradation of chlorinated hydrocarbons dissolved in groundwater, chloride is released into the groundwater. This results in chloride concentrations in groundwater in the contaminant plume that are elevated relative to background concentrations. Because of the neutral chemical behavior of chloride, it can be used as a conservative tracer to estimate biodegradation rates, as discussed in Appendix C.

2.3.3 Aquifer Parameter Estimation

Estimates of aquifer parameters are necessary to accurately evaluate contaminant fate and transport.

2.3.3.1 Hydraulic Conductivity

Hydraulic conductivity is a measure of an aquifer's ability to transmit water, and is perhaps the most important aquifer parameter governing fluid flow in the subsurface. The velocity of groundwater and dissolved contamination is directly related to the hydraulic conductivity of the saturated zone. In addition, subsurface variations in hydraulic conductivity directly influence contaminant fate and transport by providing preferential paths for contaminant migration. Estimates of hydraulic conductivity are used to determine residence times for contaminants and tracers, and to determine the seepage velocity of groundwater.

The most common methods used to quantify hydraulic conductivity are aquifer pumping tests and slug tests (Appendix A). Another method that may be used to determine hydraulic conductivity is the borehole dilution test. One drawback to these methods is that they average hydraulic properties over the screened interval. To help alleviate this potential problem, the screened interval of the test wells should be selected after consideration is given to subsurface stratigraphy. Information about subsurface stratigraphy should come from geologic logs for continuous cores or from cone penetrometer tests. The rate of filling of a Hydropunch can be used to determine local hydraulic conductivity at the same time the water sample is collected. An alternate method to delineate zones with high hydraulic conductivity is to use pressure dissipation data from cone penetrometer tests.

2.3.3.1.1 Pumping Tests

Pumping tests generally give the most reliable information on hydraulic conductivity, but are difficult to conduct in contaminated areas because the water produced during the test generally must be contained and treated. In addition, a minimum 4-inch-diameter well is generally required to complete pumping tests in highly transmissive aquifers because the 2-inch submersible pumps available today are not capable of producing a flow rate large enough for meaningful pumping tests. In areas with fairly uniform aquifer materials, pumping tests can be completed in uncontaminated areas, and the results can be used to estimate hydraulic conductivity in the contaminated area. Pumping tests should be conducted in wells that are screened in the most transmissive zones in the aquifer. If pumping tests are conducted in wells with more than fifteen feet of screen, a down-hole flowmeter test can be used to determine the interval actually contributing to flow.

2.3.3.1.2 Slug Tests

Slug tests are a commonly used alternative to pumping tests. One commonly cited drawback to slug testing is that this method generally gives hydraulic conductivity information only for the area immediately surrounding the monitoring well. Slug tests do, however, have two distinct advantages over pumping tests: they can be conducted in 2-inch monitoring wells, and they produce no water. If slug tests are going to be relied upon to provide information on the three-dimensional distribution of hydraulic conductivity in an aquifer, multiple slug tests must be performed. It is not advisable to rely on data from one slug test in one monitoring well. Because of this, slug tests should be conducted at several monitoring wells at the site. Like pumping tests, slug tests ideally should be conducted in wells that are narrowly screened in the most transmissive zones in the aquifer.

2.3.3.1.3 Downhole Flowmeter

Borehole flowmeter tests are conducted to investigate the relative vertical distribution of horizontal hydraulic conductivity in the screened interval of a well or the uncased portion of a borehole. These tests can be done to identify any preferential flow pathways within the portion of an aquifer intersecting the test well screen or the open borehole. The work of Molz and Young (1993), Molz *et al.* (1994) , Young and Pearson (1995), and Young (1995) describes the means by which these tests may be conducted and interpreted.

In general , measurements of ambient groundwater flow rates are collected at several regularly spaced locations along the screened interval of a well. Next, the well is pumped at a steady rate, and the measurements are repeated. The test data may be analyzed using the methods described by Molz and Young (1993) and Molz *et al.* (1994) to define the relative distribution of horizontal hydraulic conductivity within the screened interval of the test well. Estimates of bulk hydraulic conductivity from previous aquifer tests can be used to estimate the absolute hydraulic conductivity distribution at the test well.

Using flowmeter test data, one may be able to more thoroughly quantify the three-dimensional hydraulic conductivity distribution at a site. This is important for defining contaminant migration pathways and understanding solute transport at sites with heterogeneous aquifers. Even at sites where the hydrogeology appears relatively homogeneous, such data may point out previously undetected zones or layers of higher hydraulic conductivity that control contaminant migration. In addition, groundwater velocities calculated from hydraulic conductivity data may be used to evaluate site data or for simple transport calculations. In these cases, it is also important to have

the best estimate possible of hydraulic conductivity for those units in which the contaminants are migrating.

2.3.3.2 Hydraulic Gradient

The horizontal hydraulic gradient is the change in hydraulic head (feet of water) divided by the distance of groundwater flow between head measurement points. To accurately determine the hydraulic gradient, it is necessary to measure groundwater levels in all monitoring wells and piezometers at a site. Because hydraulic gradients can change over a short distance within an aquifer, it is essential to have as much site-specific groundwater elevation information as possible so that accurate hydraulic gradient calculations can be made. In addition, seasonal variations in groundwater flow direction can have a profound influence on contaminant transport. Sites in upland areas are less likely to be affected by seasonal variations in groundwater flow direction than low-elevation sites situated near surface water bodies such as rivers and lakes.

To determine the effect of seasonal variations in groundwater flow direction on contaminant transport, quarterly groundwater level measurements should be taken over a period of at least 1 year. For many sites, these data may already exist. If hydraulic gradient data over a 1-year period are not available, natural attenuation can still be implemented pending an analysis of seasonal variation in groundwater flow direction.

2.3.3.3 Processes Causing an Apparent Reduction in Total Contaminant Mass

Several processes cause reductions in contaminant concentrations and apparent reductions in the total mass of contaminant in a system. Processes causing apparent reductions in contaminant mass include dilution, sorption, and hydrodynamic dispersion. In order to determine the mass of contaminant removed from the system it is necessary to correct observed concentrations for the effects of these processes. This is done by incorporating independent assessments of these processes into the comprehensive solute transport model. The following sections give a brief overview of the processes that result in apparent contaminant reduction. Appendix B describes these processes in detail.

Dilution results in a reduction in contaminant concentrations and an apparent reduction in the total mass of contaminant in a system due to the introduction of additional water to the system. The two most common causes of dilution (real or apparent) are infiltration and sampling from monitoring wells screened over large vertical intervals. Infiltration can cause an apparent reduction in contaminant mass by mixing unaffected waters with the contaminant plume, thereby causing dilution. Monitoring wells screened over large vertical distances may dilute groundwater

samples by mixing water from clean aquifer zones with contaminated water during sampling. To avoid potential dilution during sampling, monitoring wells should be screened over relatively small vertical intervals (less than 5 feet). Nested wells should be used to define the vertical extent of contamination in the saturated zone. Appendix C contains example calculations showing of how to correct for the effects of dilution.

The retardation of organic solutes caused by sorption is an important consideration when simulating the effects of natural attenuation over time. Sorption of a contaminant to the aquifer matrix results in an apparent decrease in contaminant mass because dissolved contamination is removed from the aqueous phase. The processes of contaminant sorption and retardation are discussed in Appendix B.

The dispersion of organic solutes in an aquifer is another important consideration when simulating natural attenuation. The dispersion of a contaminant into relatively pristine portions of the aquifer allows the solute plume to mix with uncontaminated groundwater containing higher concentrations of electron acceptors. Dispersion occurs vertically as well as parallel and perpendicular to the direction of groundwater flow.

To accurately determine the mass of contaminant transformed to innocuous byproducts, it is important to correct measured contaminant concentrations for those processes that cause an apparent reduction in contaminant mass. This is accomplished by normalizing the measured concentration of each of the contaminants to the concentration of a tracer that is biologically recalcitrant. Because chloride is produced during the biodegradation of chlorinated solvents, this analyte can be used as a tracer. For chlorinated solvents undergoing reductive dechlorination, it is also possible to use the carbon component of the total chlorinated contaminants as a tracer because carbon is not removed as the parent solvent is systematically dechlorinated. Trimethylbenzene and tetramethylbenzene are two chemicals found in fuel hydrocarbon plumes that also may be useful as tracers. These compounds are difficult to biologically degrade under anaerobic conditions, and frequently persist in groundwater longer than BTEX. Depending on the composition of the fuel that was released, other tracers may be used.

2.3.4 Optional Confirmation of Biological Activity

Extensive evidence can be found in the literature showing that biodegradation of chlorinated solvents and fuel hydrocarbons frequently occurs under natural conditions. Many references from the large body of literature in support of natural attenuation are listed in Section 3 and discussed in Appendix B. The most common technique used to show explicitly that microorganisms capable of degrading contaminants present at a site is the microcosm study.

If additional evidence (beyond contaminant and geochemical data and supporting calculations) supporting natural attenuation is required, a microcosm study using site-specific aquifer materials and contaminants can be undertaken.

If properly designed, implemented, and interpreted, microcosm studies can provide very convincing documentation of the occurrence of biodegradation. Such studies are the only line of evidence that allows an unequivocal mass-balance determination based on the biodegradation of environmental contaminants. The results of a well-designed microcosm study will be easy for decision makers with nontechnical backgrounds to interpret. Results of such studies are strongly influenced by the nature of the geological material submitted for study, the physical properties of the microcosm, the sampling strategy, and the duration of the study. Because microcosm studies are time-consuming and expensive, they should be undertaken only at sites where there is considerable uncertainty concerning the biodegradation of contaminants.

Biodegradation rate constants determined by microcosm studies often are higher than rates achieved in the field. The collection of material for the microcosm study, the procedures used to set up and analyze the microcosm, and the interpretation of the results of the microcosm study are presented in Appendix C.

2.4 REFINE CONCEPTUAL MODEL, COMPLETE PRE-MODELING CALCULATIONS, AND DOCUMENT INDICATORS OF NATURAL ATTENUATION

Site investigation data should first be used to refine the conceptual model and quantify groundwater flow, sorption, dilution, and biodegradation. The results of these calculations are used to scientifically document the occurrence and rates of natural attenuation and to help simulate natural attenuation over time. It is the responsibility of the proponent to "make the case" for natural attenuation. This being the case, all available data must be integrated in such a way that the evidence is sufficient to support the conclusion that natural attenuation is occurring.

2.4.1 Conceptual Model Refinement

Conceptual model refinement involves integrating newly gathered site characterization data to refine the preliminary conceptual model that was developed on the basis of previously collected site-specific data. During conceptual model refinement, all available site-specific data should be integrated to develop an accurate three-dimensional representation of the hydrogeologic and contaminant transport system. This refined conceptual model can then be used for contaminant fate and transport modeling. Conceptual model refinement consists of several steps, including preparation of geologic logs, hydrogeologic sections, potentiometric surface/water table maps,

contaminant and daughter product contour (isopleth) maps, and electron acceptor and metabolic byproduct contour (isopleth) maps.

2.4.1.1 Geologic Logs

Geologic logs of all subsurface materials encountered during the soil boring phase of the field work should be constructed. Descriptions of the aquifer matrix should include relative density, color, major textural constituents, minor constituents, porosity, relative moisture content, plasticity of fines, cohesiveness, grain size, structure or stratification, relative permeability, and any other significant observations such as visible contaminants or contaminant odor. It is also important to correlate the results of VOC screening using soil sample headspace vapor analysis with depth intervals of geologic materials. The depth of lithologic contacts and/or significant textural changes should be recorded to the nearest 0.1 foot. This resolution is necessary because preferential flow and contaminant transport paths may be limited to thin stratigraphic units.

2.4.1.2 Cone Penetrometer Logs

Cone penetrometer logs express stratigraphic information as the ratio of sleeve friction to tip pressure. Cone penetrometer logs also may contain fluid resistivity data and estimates of aquifer hydraulic conductivity. To provide meaningful data, the cone penetrometer must be capable of providing stratigraphic resolution on the order of 3 inches. To provide accurate stratigraphic information, cone penetrometer logs must be correlated with continuous subsurface cores. At a minimum, there must be one correlation for every hydrostratigraphic unit found at the site. Cone penetrometer logs, along with geologic boring logs, can be used to complete the hydrogeologic sections discussed in Section 2.4.1.3.

2.4.1.3 Hydrogeologic Sections

Hydrogeologic sections should be prepared from boring logs and/or CPT data. A minimum of two hydrogeologic sections are required; one parallel to the direction of groundwater flow and one perpendicular to the direction of groundwater flow. Hydraulic head data including potentiometric surface and/or water table elevation data should be plotted on the hydrogeologic section. These sections are useful in locating potential preferential contaminant migration paths and in simulating contaminant transport using solute fate and transport models.

2.4.1.4 Potentiometric Surface or Water Table Map(s)

A potentiometric surface or water table map is a two-dimensional graphic representation of equipotential lines shown in plan view. These maps should be prepared from water level measurements and surveyor's data. Because groundwater flows from areas of higher hydraulic head to areas of lower hydraulic head, such maps are used to estimate the probable direction of plume migration and to calculate hydraulic gradients. These maps should be prepared using water levels measured in wells screened in the same relative position within the same hydrogeologic unit. To determine vertical hydraulic gradients, separate potentiometric maps should be developed for different horizons in the aquifer to document vertical variations in groundwater flow. Flow nets should also be constructed to document vertical variations in groundwater flow. To document seasonal variations in groundwater flow, separate potentiometric surface or water table maps should be prepared for quarterly water level measurements taken over a period of at least 1 year. In areas with mobile LNAPL, a correction must be made for the water table deflection caused by the LNAPL. This correction and potentiometric surface map preparation are discussed in Appendix C.

2.4.1.5 Contaminant and Daughter Product Contour Maps

Contaminant and daughter product contour maps should be prepared for all contaminants present at the site for each discrete sampling event. Such maps allow interpretation of data on the distribution and the relative transport and degradation rates of contaminants in the subsurface. In addition, contaminant contour maps are necessary so that contaminant concentrations can be gridded and used for input into a numerical model. Detection of daughter products not present in the released NAPL (e.g., *cis*-1,2-DCE, VC, or ethene) provides evidence of reductive dechlorination.

If mobile and residual NAPLs are present at the site, a contour map showing the thickness and vertical and horizontal distribution of each should be prepared. These maps will allow interpretation of the distribution and the relative transport rate of NAPLs in the subsurface. In addition, these maps will aid in partitioning calculations and solute fate and transport model development. It is important to note that, because of the differences between the magnitude of capillary suction in the aquifer matrix and the different surface tension properties of fuel and water, LNAPL thickness observations made at monitoring points may not provide an accurate estimate of the actual volume of mobile and residual LNAPL in the aquifer. To accurately determine the distribution of NAPLs, it is necessary to take continuous soil cores or, if confident that chlorinated solvents present as NAPL are commingled with fuels, to use cone penetrometer

testing coupled with laser-induced fluorescence. Appendix C discusses the relationship between actual and apparent NAPL thickness.

2.4.1.6 Electron Acceptor, Metabolic Byproduct, and Alkalinity Contour Maps

Contour maps should be prepared for electron acceptors consumed (dissolved oxygen, nitrate, and sulfate) and metabolic byproducts produced [iron (II), chloride, and methane] during biodegradation. In addition, a contour map should be prepared for alkalinity and ORP. The electron acceptor, metabolic byproduct, alkalinity, and ORP contour maps provide evidence of the occurrence of biodegradation at a site.

Contour maps should be prepared for electron acceptors, including dissolved oxygen, nitrate, and sulfate. During aerobic biodegradation, dissolved oxygen concentrations will decrease to levels below background concentrations. Similarly, during anaerobic degradation, the concentrations of nitrate and sulfate will be seen to decrease to levels below background. The electron acceptor contour maps allow interpretation of data on the distribution of the electron acceptors and the relative transport and degradation rates of contaminants in the subsurface. Thus, electron acceptor contour maps provide visual evidence of biodegradation and a visual indication of the relationship between the contaminant plume and the various electron acceptors.

Contour maps should be prepared for the metabolic byproducts iron (II), chloride, and methane. During anaerobic degradation, the concentrations of these parameters will be seen to increase to levels above background. These maps allow interpretation of data on the distribution of metabolic byproducts resulting from the microbial degradation of fuel hydrocarbons and the relative transport and degradation rates of contaminants in the subsurface. Thus, metabolic byproduct contour maps provide visual evidence of biodegradation and a visual indication of the relationship between the contaminant plume and the various metabolic byproducts.

A contour map should be prepared for total alkalinity (as $CaCO_3$). Respiration of dissolved oxygen, nitrate, iron (III), and sulfate tends to increase the total alkalinity of groundwater. Thus, the total alkalinity inside the contaminant plume generally increases to levels above background. This map will allow visual interpretation of alkalinity data by showing the relationship between the contaminant plume and alkalinity.

2.4.2 Pre-Modeling Calculations

Several calculations must be made prior to implementation of the solute fate and transport model. These calculations include sorption and retardation calculations, NAPL/water partitioning calculations, groundwater flow velocity calculations, and biodegradation rate-constant

calculations. Each of these calculations is discussed in the following sections. The specifics of each calculation are presented in the appendices referenced below.

2.4.2.1 Analysis of Contaminant, Daughter Product, Electron Acceptor, Metabolic Byproduct, and Total Alkalinity Data

The extent and distribution (vertical and horizontal) of contamination, daughter product, and electron acceptor and metabolic byproduct concentrations are of paramount importance in documenting the occurrence of biodegradation and in solute fate and transport model implementation.

Comparison of contaminant, electron acceptor, electron donor, and metabolic byproduct distributions can help identify significant trends in site biodegradation. Dissolved oxygen concentrations below background in an area with organic contamination are indicative of aerobic biodegradation of organic carbon. Similarly, nitrate and sulfate concentrations below background in an area with contamination are indicative of anaerobic biodegradation of organic carbon. Likewise, elevated concentrations of the metabolic byproducts iron (II), chloride, and methane in areas with contamination are indicative of biodegradation of organic carbon. In addition, elevated concentrations of total alkalinity (as $CaCO_3$) in areas with contamination are indicative of biodegradation of organic compounds via aerobic respiration, denitrification, iron (III) reduction, and sulfate reduction. If these trends can be documented, it is possible to quantify the relative importance of each biodegradation mechanism, as described in Appendices B and C. The contour maps described in Section 2.4.1 can be used to provide graphical evidence of these relationships.

Detection of daughter products not present in the released NAPL (e.g., *cis*-1,2-DCE, VC, or ethene) provides evidence of reductive dechlorination. The contour maps described in Section 2.4.1 in conjunction with NAPL analyses can be used to show that reductive dechlorination is occurring.

2.4.2.2 Sorption and Retardation Calculations

Contaminant sorption and retardation calculations should be made based on the TOC content of the aquifer matrix and the organic carbon partitioning coefficient (K_{oc}) for each contaminant. The average TOC concentration from the most transmissive zone in the aquifer should be used for retardation calculations. A sensitivity analysis should also be performed during modeling using a range of TOC concentrations, including the lowest TOC concentration measured at the site. Sorption and retardation calculations should be completed for all contaminants and any tracers. Sorption and retardation calculations are described in Appendix C.

2.4.2.3 NAPL/Water Partitioning Calculations

If NAPL remains at the site, partitioning calculations should be made to account for the partitioning from this phase into groundwater. Several models for NAPL/water partitioning have been proposed in recent years, including those by Hunt *et al.* (1988), Bruce *et al.* (1991), Cline *et al.* (1991), and Johnson and Pankow (1992). Because the models presented by Cline *et al.* (1991) and Bruce *et al.* (1991) represent equilibrium partitioning, they are the most conservative models. Equilibrium partitioning is conservative because it predicts the maximum dissolved concentration when NAPL in contact with water is allowed to reach equilibrium. The results of these equilibrium partitioning calculations can be used in a solute fate and transport model to simulate a continuing source of contamination. The theory behind fuel/water partitioning calculations is presented in Appendix B, and example calculations are presented in Appendix C.

2.4.2.4 Groundwater Flow Velocity Calculations

The average linear groundwater flow velocity of the most transmissive aquifer zone containing contamination should be calculated to check the accuracy of the solute fate and transport model and to allow calculation of first-order biodegradation rate constants. An example of a groundwater flow velocity calculation is given in Appendix C.

2.4.2.5 Biodegradation Rate-Constant Calculations

Biodegradation rate constants are necessary to accurately simulate the fate and transport of contaminants dissolved in groundwater. In many cases, biodegradation of contaminants can be approximated using first-order kinetics. In order to calculate first-order biodegradation rate constants, the apparent degradation rate must be normalized for the effects of dilution, sorption, and volatilization. Two methods for determining first-order rate constants are described in Appendix C. One method involves the use of a biologically recalcitrant compound found in the dissolved contaminant plume that can be used as a conservative tracer. The other method, proposed by Buscheck and Alcantar (1995) involves interpretation of a steady-state contaminant plume and is based on the one-dimensional steady-state analytical solution to the advection-dispersion equation presented by Bear (1979).

2.5 SIMULATE NATURAL ATTENUATION USING SOLUTE FATE AND TRANSPORT MODELS

Simulating natural attenuation allows prediction of the migration and attenuation of the contaminant plume through time. Natural attenuation modeling is a tool that allows site-specific

data to be used to predict the fate and transport of solutes under governing physical, chemical, and biological processes. Hence, the results of the modeling effort are not in themselves sufficient proof that natural attenuation is occurring at a given site. The results of the modeling effort are only as good as the original data input into the model; therefore, an investment in thorough site characterization will improve the validity of the modeling results. In some cases, straightforward analytical models of solute transport are adequate to simulate natural attenuation.

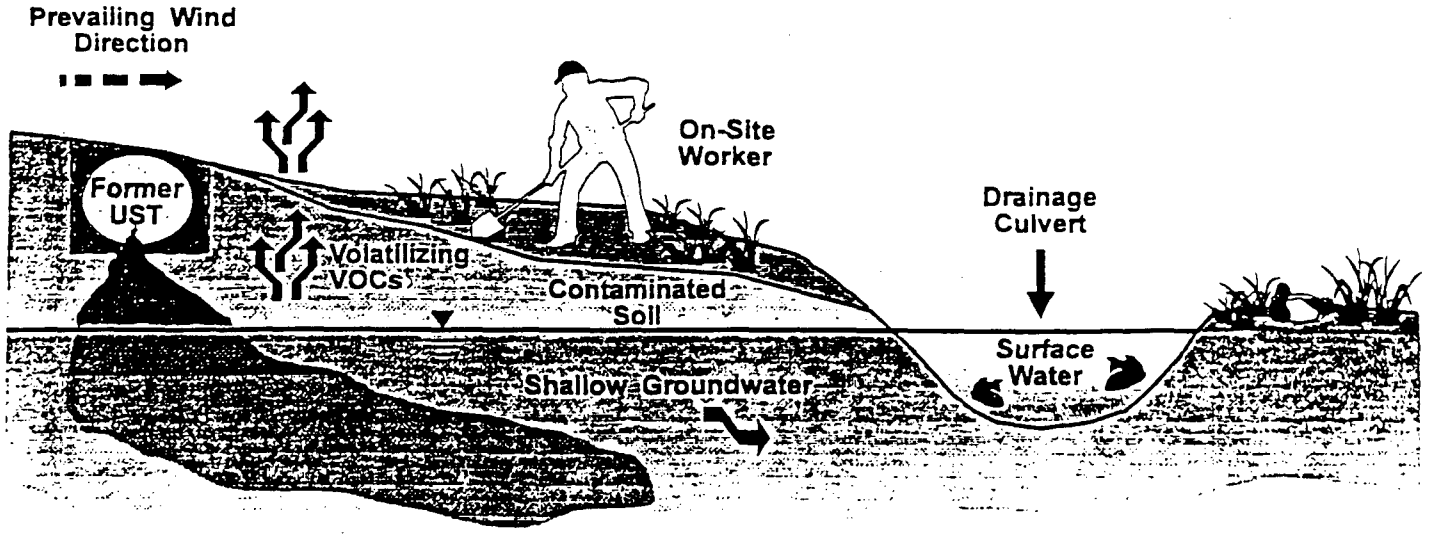
Several well-documented and widely accepted solute fate and transport models are available for simulating the fate and transport of contaminants under the influence of advection, dispersion, sorption, and biodegradation. Solute fate and transport modeling is described in Appendix D.

2.6 CONDUCT A RECEPTOR EXPOSURE PATHWAYS ANALYSIS

After the rates of natural attenuation have been documented, and predictions of the future extent and concentrations of the contaminant plume have been made using the appropriate solute fate and transport model, the proponent of natural attenuation should combine all available data and information to negotiate for implementation of this remedial option. Supporting the natural attenuation option generally will involve performing a receptor exposure pathways analysis. This analysis includes identifying potential human and ecological receptors and points of exposure under current and future land and groundwater use scenarios. Figure 2.5 presents some of the potential migration pathways, exposure routes, and potential receptors for contaminants associated with fuels and chlorinated solvents. The results of solute fate and transport modeling are central to the exposure pathways analysis. If conservative model input parameters are used, the solute fate and transport model should give conservative estimates of contaminant plume migration. From this information, the potential for impacts on human health and the environment from contamination present at the site can be assessed.

2.7 EVALUATE SUPPLEMENTAL SOURCE REMOVAL OPTIONS

Source removal or reduction may be necessary to reduce plume expansion if the exposure pathways analysis suggests that one or more exposure pathways may be completed before natural attenuation can reduce chemical concentrations below federal, state, or risk-based levels of concern. Further, some regulators may require source removal in conjunction with natural attenuation. Several technologies suitable for source reduction or removal are listed on Figure 2.1. Other technologies also may be used as dictated by site conditions and local regulatory requirements. The authors' experience suggests that source removal can be very effective at limiting plume migration and decreasing the remediation time frame, especially at sites



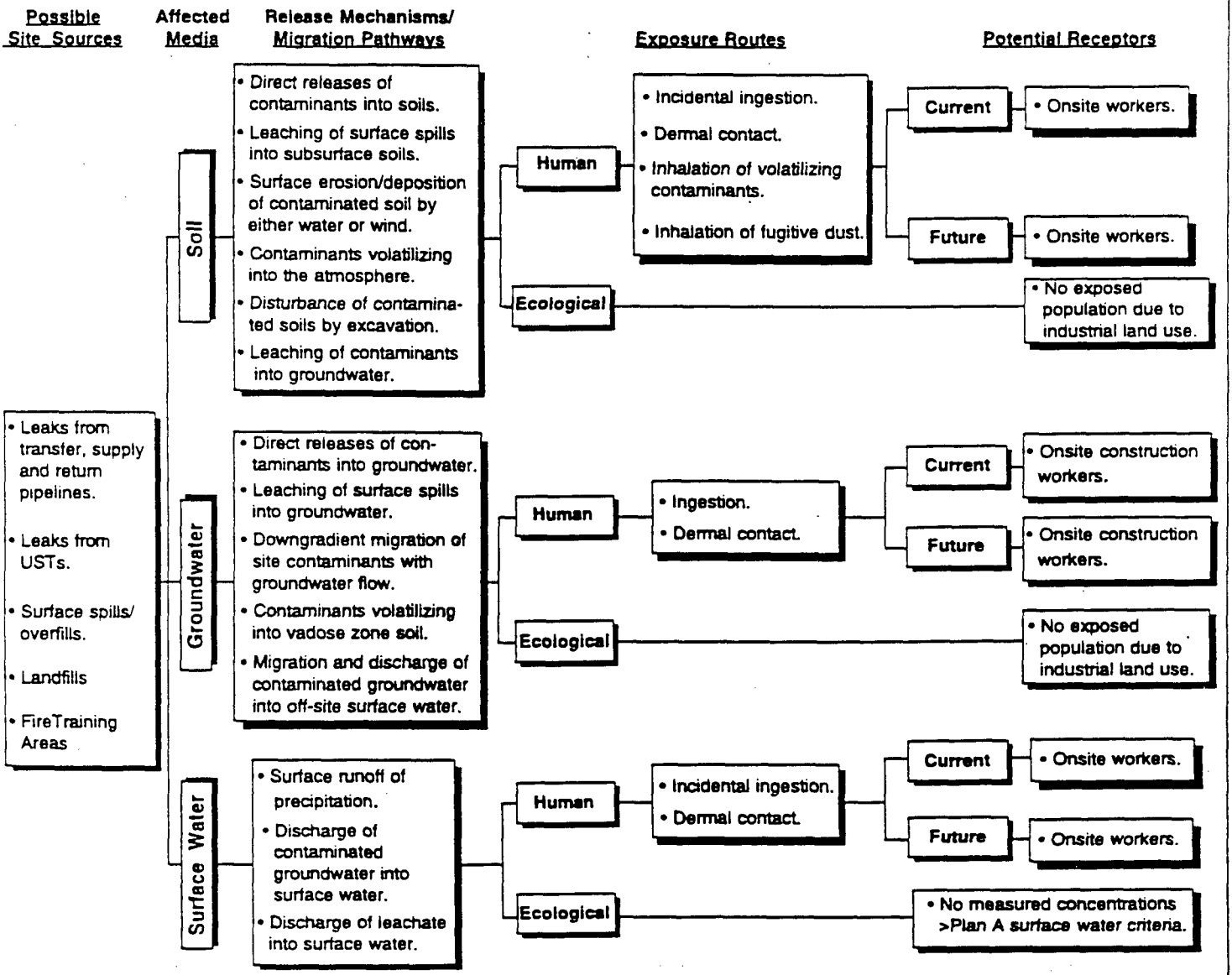


Figure 2.5
Example Migration Pathways and Exposure Routes for Potential Receptors of Fuel Hydrocarbons and Chlorinated Solvents

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where biodegradation is contributing to natural attenuation of a dissolved contaminant plume. If a solute fate and transport model has been prepared for a site, the impact of source removal can readily be evaluated by modifying the contaminant source term; this will allow for a reevaluation of the exposure pathways analysis.

2.8 PREPARE LONG-TERM MONITORING PLAN

Groundwater flow rates at many Air Force sites studied to date are such that many years will be required before contaminated groundwater could potentially reach the Air Force installation boundary. Thus, there frequently is sufficient time and space for natural attenuation alone to reduce contaminant concentrations in groundwater to acceptable levels. Experience at 40 Air Force sites contaminated with fuel hydrocarbons evaluated using the protocol presented by Wiedemeier *et al.* (1995d) suggests that many fuel hydrocarbon plumes are relatively stable, or are moving slowly with respect to groundwater flow. This information is complemented by data collected by Lawrence Livermore National Laboratories in a study of over 1,100 leaking underground fuel tank sites performed for the California State Water Resources Control Board (Rice *et al.*, 1995). These examples demonstrate the efficacy of using long-term monitoring to track plume migration and to validate or refine modeling results. There is not a large enough database available at this time to assess the stability of chlorinated solvent plumes, but it is the experience of the authors that chlorinated solvent plumes are likely to migrate further downgradient than fuel hydrocarbon plumes before reaching steady-state equilibrium or before receding.

The long-term monitoring plan consists of locating groundwater monitoring wells and developing a groundwater sampling and analysis strategy. This plan is used to monitor plume migration over time and to verify that natural attenuation is occurring at rates sufficient to protect potential downgradient receptors. The long-term monitoring plan should be developed based on site characterization data, the results of solute fate and transport modeling, and the results of the receptor exposure pathways analysis.

The long-term monitoring plan includes two types of monitoring wells. Long-term monitoring wells are intended to determine if the behavior of the plume is changing. Point-of-compliance (or point-of-action) wells are intended to detect movements of the plume outside the negotiated perimeter of containment, and to trigger an action to manage the risk associated with such expansion. Figure 2.6 depicts 1) an upgradient well in unimpacted groundwater; 2) a well in the NAPL source area; 3) a well downgradient of the NAPL source area in a zone of anaerobic treatment; 4) a well in the zone of aerobic treatment, along the periphery of the plume; 5) a well located downgradient from the plume where contaminant concentrations are below regulatory

acceptance levels and soluble electron acceptors are depleted with respect to unimpacted groundwater; and 6) three point-of-compliance wells.

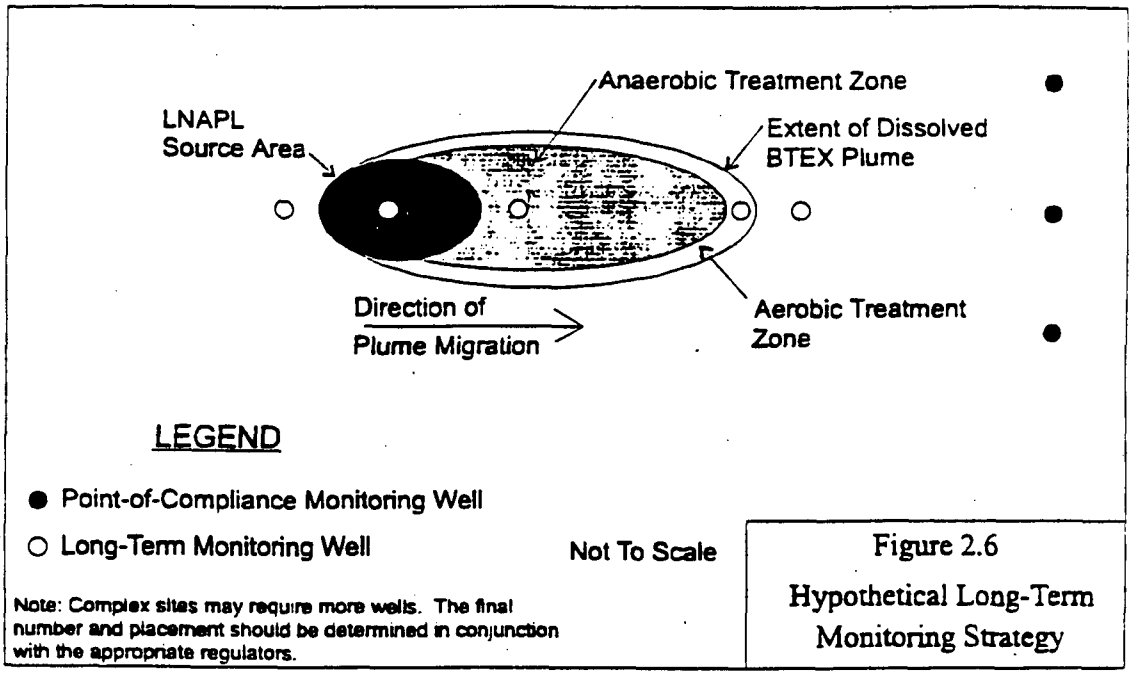

Figure 2.6
Hypothetical Long-Term Monitoring Strategy

Although the final number and placement of long-term monitoring and point-of-compliance/action wells should be determined through regulatory negotiation, the locations of long-term monitoring wells should be based on the behavior of the plume as revealed during the initial site characterization and on regulatory considerations. Point-of-compliance wells are placed 500 feet downgradient from the leading edge of the plume or the distance traveled by the groundwater in 2 years, whichever is greater. If the property line is less than 500 feet downgradient, the point-of-compliance wells often are placed near and upgradient from the property line. The final number and location of point-of-compliance monitoring wells also will depend on regulatory considerations. Local practice may be more stringent than this recommendation.

The results of a solute fate and transport model can be used to help site the long-term monitoring and point-of-compliance wells. In order to provide a valid monitoring system, all monitoring wells must be screened in the same hydrogeologic unit as the contaminant plume. This generally requires detailed stratigraphic correlation. To facilitate accurate stratigraphic correlation, detailed visual descriptions of all subsurface materials encountered during borehole drilling or cone penetrometer testing should be prepared prior to monitoring well installation.

A groundwater sampling and analysis plan should be prepared in conjunction with point-of-compliance and long-term monitoring well placement. For long-term monitoring wells, groundwater analyses should include VOCs, dissolved oxygen, nitrate, iron (II), sulfate, and methane. For point-of-compliance wells, groundwater analyses should be limited to determining VOC and dissolved oxygen concentrations. Any state-specific analytical requirements also should be addressed in the sampling and analysis plan to ensure that all data required for regulatory decision making are collected. Water level and LNAPL thickness measurements must be made during each sampling event. Except at sites with very low hydraulic conductivity and gradients, quarterly sampling of long-term monitoring wells is recommended during the first year to help determine the direction of plume migration and to determine baseline data. Based on the results of the first year's sampling, the sampling frequency may be reduced to annual sampling in the quarter showing the greatest extent of the plume. Sampling frequency is dependent on the final placement of the point-of-compliance monitoring wells and groundwater flow velocity. The final sampling frequency should be determined in collaboration with regulators.

2.9 CONDUCT REGULATORY NEGOTIATIONS

The purpose of regulatory negotiations is to provide scientific documentation that supports natural attenuation as the most appropriate remedial option for a given site. All available site-specific data and information developed during the site characterization, conceptual model development, pre-modeling calculations, biodegradation rate calculation, groundwater modeling, model documentation, and LTM plan preparation phases of the natural attenuation investigation should be presented in a consistent and complementary manner at the regulatory negotiations. Of particular interest to the regulators will be proof that natural attenuation is occurring at rates sufficient meet regulatory compliance levels at the POC and to protect human health and the environment. The regulators must be presented with a "weight-of-evidence" argument in support of this remedial option. For this reason, all model assumptions should be conservative, and all available evidence in support of natural attenuation must be presented at the regulatory negotiations.

A comprehensive LTM and contingency plan also should be presented to demonstrate a commitment to proving the effectiveness of natural attenuation as a remedial option. Because LTM and contingency plans are very site-specific, they should be addressed in the individual reports generated using this protocol. See Sections 6 and 7 of the two case studies presented in Appendices E and F for examples of such plans.

SECTION 3

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APPENDIX A

FIELD INVESTIGATION METHODOLOGIES

NOTE: THIS APPENDIX IS IN EARLY DRAFT STAGE. MANY OF THE SECTIONS REQUIRE ADDITIONAL TEXT - COMMENTS WILL BE APPRECIATED

TABLE OF CONTENTS - APPENDIX A

FIGURES

SECTION A-1

INTRODUCTION

Detailed site characterization is an important aspect of the remediation by natural attenuation demonstration. Typically, it is necessary to collect additional site-specific data in order to successfully complete the demonstration. This appendix presents an overview of field techniques that can be used to collect the data used to support natural attenuation. Selection of locations for field investigation activities and analytical protocols used for soil and water samples are discussed in Section 2 of the protocol document.

This appendix consists of six sections, including this introduction. Section A-2 discusses subsurface investigation methodologies. Section A-3 discusses soil characterization methodologies. Section A-4 discusses groundwater characterization methodologies. Section A-5 discusses surface water and sediment characterization methodologies. Section A-6 discusses sample handling procedures. Section A-7 discusses aquifer characterization methodologies.

SECTION A-2

SUBSURFACE INVESTIGATION METHODOLOGIES

2.1 TRADITIONAL DRILLING TECHNIQUES

A.2.1.1 Hollow Stem Auger

Drilling in unconsolidated soils is generally accomplished using the hollow-stem auger method. If subsurface conditions are such that the planned drilling technique does not produce acceptable results (e.g., unstable borehole walls or poor soil sample recovery), another technique deemed more appropriate for the type of soils present should be used. Any alternate soil sampling procedure used must be approved by the field scientist and should be appropriate for the subsurface lithologies present at the site.

Continuous soil samples should be obtained using a CME® split-barrel, continuous sampling device or another similar method judged acceptable by the field scientist. Samples must be collected continuously over the full depth of the soil borehole.

A.2.1.2 Rotary

A.2.1.3 Air Percussion

A.2.1.4 Chain Tool

A.2.2 CONE PENETROMETER

CPT is increasingly being used for successful site characterization. CPT is accomplished using a cone penetrometer truck, which consists of an instrumented probe that is forced into the ground using a hydraulic load frame mounted on a heavy truck, with the weight of the truck providing the necessary reaction mass. The penetrometer equipment is generally mounted inside an 18-foot van body attached to a 10-wheel truck chassis with a turbo-charged diesel engine. Ballast in the form of metal weights and a steel water tank that can hold approximately 5,000 pounds of water, are added to the truck to achieve an overall push capability of approximately 45,000 pounds. This push capacity may be limited in tight soils by the structural bending capacity of the 1.405-inch outside-diameter (OD) push rods, rather than by the weight of the truck. Penetration force is supplied by a pair of large hydraulic cylinders bolted to the truck frame.

The penetrometer probe generally has a 1.405-inch-OD, 60-degree conical tip, and a 1.405-inch-OD by 5.27-inch-long friction sleeve. Inside the probe, two load cells independently measure the vertical resistance against the conical tip and the side friction along the sleeve. Each load cell is a cylinder of uniform cross section inside the probe which is instrumented with four strain gauges in a full-bridge circuit. Forces are sensed by the load cells, and the data are transmitted from the probe assembly via a cable running through the push tubes. The analog data are digitized, recorded, and plotted by computer in the penetrometer truck. Penetration, dissipation, and resistivity data are used to determine site stratigraphy.

A.2.3 GEOPROBE

A.2.4 HAND AUGER

A.2.5 HAND DRIVEN

SECTION A-3

SOIL CHARACTERIZATION METHODOLOGIES

A.3.1 SAMPLE ACQUISITION

A.3.2 PHYSICAL DESCRIPTION

A.3.3 FIELD SCREENING

PID, UV Lamp,

A.3.4 FIXED-BASE LABORATORY ANALYSES

The analytical protocol to be used for soil sample analysis is presented in Table 2.1. This analytical protocol includes all of the parameters necessary to document intrinsic remediation of fuel hydrocarbons, including the effects of sorption and both aerobic and anaerobic biodegradation of fuel hydrocarbons. The protocol document describes each soil analytical parameter and the use of each analyte in the intrinsic remediation demonstration.

SECTION A-4

GROUNDWATER CHARACTERIZATION METHODOLOGIES

This section describes the scope of work required to collect groundwater quality samples to support the intrinsic remediation demonstration. In order to maintain a high degree of quality control during groundwater sampling, the procedures described in the following sections should be followed.

Groundwater sampling should be conducted only by qualified scientists and technicians trained in the conduct of well sampling, sampling documentation, and chain-of-custody procedures. In addition, sampling personnel should thoroughly review this protocol document and the site-specific work plan prior to sample acquisition and have a copy of the work plan available onsite for reference. Detailed groundwater sampling and sample handling procedures are presented in following sections. Samples should be collected in accordance with local, state, and federal requirements.

Rapid and inexpensive survey techniques such as Geoprobe or CPT are appropriate for the initial site characterization and plume definition of the intrinsic remediation demonstration. Conventional monitoring wells will be required for long-term monitoring (LTM) and point-of-compliance (POC) groundwater sampling.

A.4.1 CONDUITS FOR GROUNDWATER EXTRACTION

A.4.1.1 Monitoring Wells

Groundwater monitoring wells should be located based on the distribution of contaminants in each plume. At a minimum, one monitoring well should be placed upgradient of the contaminant plume, two wells should be placed within the plume, and three wells should be placed various distances downgradient of the plume. The number of wells should be related to site conditions and the size of the spill. To define the three-

dimensional extent of contamination and to determine the three-dimensional hydraulic relationships within the saturated zone, it is best to use nested wells with a maximum screened interval of 5 feet. Screening a larger area of the saturated zone will result in averaging of contaminant concentrations and hydraulic properties. To ensure well integrity, nested well pairs generally should be completed in separate boreholes. Detailed well installation procedures are described in the following paragraphs. Of course, local protocols, regulations, and site conditions should dictate actual well completion details.

Upon completion of drilling to the proper boring termination depth, the monitoring well casing can be installed. Blank well casing should be constructed of Schedule 40 polyvinyl chloride (PVC) with an inside diameter (ID) of 2 inches when installing wells in boreholes, and Schedule 40 PVC with an ID of 0.5 or 1.5 inches when installing wells in CPT holes. All well casing sections should be flush-threaded; glued joints should not be used. The casing at each well should be fitted with a threaded bottom plug and a top cap constructed of the same type of material as the well casing. The top should be vented to maintain ambient atmospheric pressure within the well casing. Site conditions and local, state, and federal requirements should ultimately dictate well completion details and materials.

The field scientist should verify and record the boring depth, the lengths of all casing and screen sections, and the depth to the top of all well completion materials placed in the annulus between the casing and borehole wall. All lengths and depths should be measured to the nearest 0.1 foot.

Well screens should be constructed of Schedule 40 PVC with an ID of 2 inches when installing wells in boreholes, and Schedule 40 PVC with an ID of 0.5 or 1.5 inches when installing wells in CPT holes. The screens should be factory slotted with 0.010-inch openings. Wells generally should be installed in nested pairs with a maximum 5-foot screened interval. Screening a larger section of the saturated zone will result in averaging of contaminant concentrations and hydraulic properties. It is usually desirable to screen at least one well so that seasonal fluctuations of the water table can be measured. The positioning of well screens should be selected by the field scientist after consideration is given to the geometry and hydraulic characteristics of the stratum in which the well will be screened. Wells should be screened so that the vertical distribution of contaminants and hydraulic gradients can be delineated. To ensure well integrity, nested well pairs generally

should be completed in separate boreholes. Site conditions and local, state, and federal requirements should ultimately dictate well completion details and materials.

A.4.1.2 Monitoring Points

Groundwater monitoring points are installed by pushing 0.5-inch ID PVC through the inside of the CPT pushrods. As the pushrod descends, new PVC casing is continuously attached until the desired depth is reached and a fully cased monitoring point is created.

Groundwater monitoring points are similar to monitoring wells in that they consist of Schedule 40 PVC slotted screen and solid riser. Groundwater monitoring points differ from monitoring wells in that they are completed in holes created using CPT (or Geoprobe®) equipment. Because of the extremely small to nonexistent annular space between the PVC monitoring point completion materials and the hole created using the CPT, common monitoring well completion components including the gravel pack, bentonite seal, and Portland cement/sodium bentonite seal are not used. Because these components are missing, groundwater monitoring points should be installed only in shallow aquifers where installation of such devices will not result in the cross-contamination of adjacent water-bearing strata. Groundwater monitoring points are best utilized in shallow unconfined aquifers where such contamination is not a potential problem.

Groundwater monitoring points should be located based on the distribution of contaminants in each plume. At a minimum, one monitoring point should be placed upgradient of the contaminant plume, two points should be placed within the plume, and three points should be placed various distances downgradient of the plume. The number of points should be related to site conditions and the size of the spill. Each monitoring point should consist of a pair of nested monitoring points: a shallow point intended to sample the shallow portion of the aquifer and a deep point intended to sample the groundwater at some depth below the water table. The shallow screened interval generally should extend from 1 foot above the water table to no more than 5 feet below the water table. The deep screened interval should have between 3 and 6 feet of screen. The deep points should be placed based on contaminant distribution. Such short screened intervals, with between 3 and 6 feet of screen each, help mitigate the dilution of water samples from potential vertical mixing of contaminated and uncontaminated groundwater in the monitoring point casing In addition, short screened intervals used in nested pairs give important information on the nature of vertical hydraulic gradients in the area.

All necessary digging, coring, drilling, and groundwater monitoring point installation permits should be obtained prior to mobilizing to the field. In addition, all utility lines should be located and proposed drilling locations cleared prior to any intrusive activities.

Monitoring point screens are constructed of flush-threaded, Schedule 40 PVC with an ID of 0.5 inch. The screens should be factory slotted with 0.01-inch openings. The positions of the screens should be selected by the field hydrogeologist after consideration is given to the geometry and hydraulic characteristics of the stratum in which the monitoring point will be screened.

Blank monitoring point casing should be constructed of Schedule 40 PVC with an ID of 0.5 inch. All monitoring point casing sections should be flush-threaded; glued joints should not be used. The casing at each monitoring point should be fitted with a bottom cap and a top cap constructed of PVC. The top cap should be vented to maintain ambient atmospheric pressure within the monitoring point casing.

The field hydrogeologist should verify and record the total depth of the monitoring point, the lengths of all casing sections, and the depth to the top of all monitoring point completion materials. All lengths and depths are to be measured to the nearest 0.1 foot.

A.4.1.3 Grab Sampling (Hydropunch, Geoprobe, Cone Penetrometer, Manual Methods)

A.4.1.3.1 Hydropunch Sampling

The HydroPunch II® sampling device is designed to be pushed or driven to the desired sample depth, either from the ground surface or from the bottom of a drilled borehole. The HydroPunch® utilizes an air-tight and water-tight sealed intake screen and sample chamber that is isolated from the surrounding environment as the tool is advanced. The surface of the HydroPunch® is designed to prevent the downward transport of contamination as the tool is advanced; it cleans itself as the soil particles are displaced to the side. The tight seal created as the soil is displaced and compacted allows the collection of a discrete sample from a specific depth.

The HydroPunch® can be used to sample both groundwater and floating LNAPL. Groundwater samples should be collected from the groundwater table to below visibly impacted groundwater at 5-foot intervals using the HydroPunch® sampling apparatus.

When performing a groundwater investigation exclusively with the HydroPunch® sampling device, samples should be taken in an upgradient (background) area, within the defined mobile LNAPL plume, in the area immediately downgradient of the mobile LNAPL plume, within the dissolved BTEX plume, and immediately downgradient of the dissolved BTEX plume. HydroPunch® provides up to 1.2 liters of sample volume. This should be sufficient for the water quality analyses detailed in Table 2.1. Should the sample volume prove to be insufficient, the analytical protocol should be modified based on sample yield at each depth interval.

The sampling depth and interval generally should be specified prior to driving the HydroPunch® into the ground. The field scientist should verify the sampling depth by measuring the length of each HydroPunch® sampling rod prior to insertion into the ground. After insertion, the drive rods or hammer are retracted to pull the cone out of the body of the HydroPunch® device, permitting groundwater to enter. A minimum of 6 inches of the body of the device must be in the driven hole to provide a good annular seal.

After allowing for adequate fill time, the HydroPunch® sampling device is pulled to the surface, unthreaded from the upper subassembly, and replaced with the thread retainer. The sample is then transferred directly into the analyte-appropriate sample container. The water should be carefully poured down the inner walls of the sample bottle to minimize aeration of the sample. Unless other instructions are given by the analytical laboratory, sample containers should be completely filled so that no air space remains in the container.

A.4.1.3.2 Geoprobe Sampling

This section describes the scope of work required for collecting groundwater quality samples using the Geoprobe® sampling apparatus. In order to maintain a high degree of quality control during the sampling event, the procedures described in the following sections should be followed.

The sampling depth and interval should be determined prior to driving the Geoprobe® sampling rods into the ground. The field scientist should verify the sampling depth by measuring the length of each Geoprobe® sampling rod prior to insertion into the ground.

The Geoprobe® sampling point should be purged prior to sample acquisition. Groundwater should be pumped through the same dedicated Teflon®-lined polyethylene tubing that will be used for sample acquisition. The sampling point should be purged until

pH, temperature, specific conductivity, dissolved oxygen, and redox potential readings have stabilized.

A peristaltic pump should be used to extract groundwater samples from the Geoprobe® sampling point. Prior to sample collection, groundwater should be purged until dissolved oxygen, temperature, pH, specific conductivity, and redox readings have stabilized. The sample is collected at the discharge end of the HDPE tubing directly into the appropriate sample container. The water should be carefully directed down the inner walls of the sample bottle to minimize aeration of the sample.

A.4.2 MEASUREMENT OF STATIC FLUID LEVELS

A.4.1.3.3 Water Level and Total Depth Measurements

Prior to removing any water from the well the static water level should be measured. An electric water level probe should be used to measure the depth to groundwater below the datum to the nearest 0.01 foot. After measuring the static water level, the water level probe should be slowly lowered to the bottom of the well, and the total well depth should be measured to the nearest 0.01 foot. Based on these measurements the volume of water to be purged from the well can be calculated. If mobile LNAPL is encountered, the LNAPL thickness should be determined, and attempts should be made to sample both the groundwater below the LNAPL layer and the fluid making up the LNAPL.

Prior to removing any water from the Geoprobe® sampling device, the static water should be measured. Several commercially available water-level probes are capable of recording water levels through the center of the hollow Geoprobe® rods. The depth to water should be determined to the nearest 0.1 foot. The sampling depth also should be measured (to the nearest 0.1 foot) by noting the depth to which the Geoprobe® tool was driven.

Prior to removing any water from the HydroPunch® sampling device, the static water should be measured. Hollow, high-density polyethylene (HDPE) tubing connected to a manometer will be inserted into the hollow HydroPunch® until the manometer indicates that groundwater has been reached. The HDPE attached to the manometer will then be marked at the level of the ground surface and removed. The depth to water will be determined by placing a tape measure next to the HDPE tubing and measuring the length

from the base of the tubing to the ground level mark to the nearest 0.01 foot. The sampling depth is measured (to the nearest 0.1 foot) by noting the depth to which the HydroPunch® tool was driven.

Special care should be taken to prevent contamination of the groundwater and extracted samples. The two primary ways that sample contamination can occur are through contact with improperly cleaned equipment and by cross contamination through insufficient cleaning of equipment between wells. To prevent such contamination, new HDPE tubing must be used for each water level measurement. If the water level probe and cable are used to determine static water levels and well total depths, they should be thoroughly cleaned between uses at different sampling locations. In addition to the use of properly cleaned equipment, a clean pair of new, disposable nitrile gloves will be worn each time a different well is sampled.

A.4.1.3.4 Mobile LNAPL Thickness Measurements

At sites where phase-separated hydrocarbons are present in the groundwater system, it is important to accurately measure the thickness of floating hydrocarbons. Accurate measurement of hydrocarbon thickness allows for estimation of the amount and distribution of the hydrocarbon and correction of measured groundwater elevations. There are three methods that can be used to determine the thickness of mobile LNAPL in a well, including use of an interface probe, a bailer, or tape and paste. Interface probes generally operate on either tight refraction sensors or density float switches to detect hydrocarbons and the hydrocarbon/water interface. The depth to mobile LNAPL and depth to water should be measured to the nearest 0.01 foot. The thickness of phase-separated hydrocarbons should also be measured to the nearest 0.01 foot. Three consecutive measurements should be made to ensure the accuracy of the measuring instrument. A clear bailer can be slowly lowered into the well until it intersects the fluid but is not totally immersed. The bailer is then retrieved, and the floating LNAPL can be visually observed and measured with an engineer's tape. The third method for measurement of floating hydrocarbon thickness is hydrocarbon paste and an engineer's tape. The paste, when applied to the tape, changes color when it intersects the hydrocarbon and the hydrocarbon/water interface. Measurements of the mobile LNAPL thickness can be made directly from the engineer's tape. It is extremely important to remember to thoroughly decontaminate all equipment between well measurement events to prevent cross contamination of wells.

Measurements of mobile LNAPL thickness made in monitoring wells provide only an estimate of the actual thickness of NAPL at that location. Actual mobile and residual LNAPL thicknesses can only be obtained from continuous soil cores. Correcting apparent mobile LNAPL thickness as measured in monitoring wells to true thickness is discussed in Appendix C.

A.4.3 METHODS FOR GROUNDWATER EXTRACTION

Because most well purging techniques can allow aeration of collected groundwater samples, it is important to minimize the potential for aeration by taking the following precautions:

1) Use a peristaltic pump, bladder pump, or similar low-flow and low-disturbance device to purge the well. To prevent downhole aeration of the sample in wells screened across the water table, well drawdown should not exceed about 5 percent of the height of the standing column of water in the well. The pump tubing should be immersed alongside the dissolved oxygen probe beneath the water level in the sampling container (Figure A.4.1). This will minimize aeration and keep water flowing past the dissolved oxygen probe's sampling membrane. If bubbles are observed in the tubing during purging, the flow rate of the peristaltic pump must be slowed. If bubbles are still apparent, the tubing should be checked for holes and replaced.

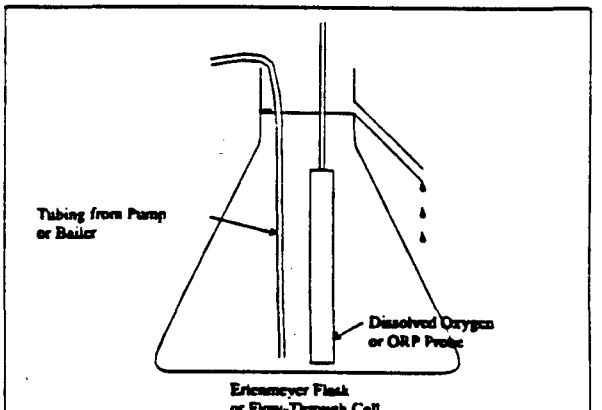

Figure A.4.1

Diagram Showing the Suggested Procedure for Dissolved Oxygen and ORP Sampling

2) When using a bailer, the bailer should be slowly immersed in the standing column of water in the well to minimize aeration. After sample collection, the water should be drained from the bottom of the bailer through tubing into the sampling container. The tubing used for this operation should be immersed alongside the dissolved oxygen probe beneath the water level in the sampling container (Figure A.4.1). This will minimize aeration and keep water flowing past the dissolved oxygen probe's sampling membrane.

3) Downhole dissolved oxygen probes can be used for dissolved oxygen analyses, but such probes must be thoroughly decontaminated between wells. In some cases decontamination procedures can be harmful to the dissolved oxygen probe.

A.4.3.1 Peristaltic Pumps

A.4.3.2 Other Pumps

A.4.3.3 Bailers

A.4.4 ANALYTICAL PROCEDURES

Laboratory analyses should be performed on all soil and groundwater samples using the analytical procedures listed in Table 2.1. Prior to sampling, arrangements should be made with the analytical laboratory to provide a sufficient number of appropriate sample containers for the samples to be collected. All containers, preservatives, and shipping requirements should be consistent with the analytical protocol. The field scientist must specify the necessary quality control samples and notify the laboratory so that they can prepare these bottles. For samples requiring chemical preservation, preservatives should be added to containers by the laboratory prior to shipping. Shipping containers, ice chests with adequate padding, and cooling media should be sent by the laboratory to the site.

A.4.4.1 Standard Well Head Analyses

A.4.4.1.1 Temperature

A.4.4.1.2 pH

A.4.4.1.3 Conductivity

A.4.4.2 Dissolved Hydrogen Analysis

Dissolved hydrogen (H_2) concentrations can be an indicator of microbially mediated redox processes in ground-water systems (Lovley and Goodwin, 1988; Lovley et al., 1994; Chapelle et al., 1995). H_2 is continuously produced in anoxic ground-water systems by fermentative microorganisms. This H_2 is then consumed by respiratory microorganisms that use nitrate, Fe(III), sulfate, or CO_2 as terminal electron acceptors. This continuous cycling of H_2 is called interspecies hydrogen transfer. Significantly, nitrate-, Fe(III)-, sulfate- and CO_2-reducing (methanogenic) microorganisms exhibit different efficiencies in utilizing H_2. Nitrate reducers are highly efficient H_2 utilizers and maintain very low (<0.1 nM) H_2 concentrations. Fe(III) reducers are slightly less efficient and thus maintain somewhat higher (0.2-0.8 nM) H_2 concentrations. Sulfate reducers an methanogenic bacteria are progressively less efficient and maintain even higher H_2 concentrations (1-4 nM for sulfate reducers and 5-20 nM for methanogens). Because each terminal electron accepting process has a characteristic H_2 concentration associated with it, H_2 concentrations can be an indicator of redox processes in ground-water systems.

Oxidation-reduction potential (ORP) measurements are based on the concept of thermodynamic equilibrium and, within the constraints of that assumption, can be used to evaluate redox processes in ground-water systems. The H_2 method is based on the ecological concept of interspecies hydrogen transfer by microorganisms and, within the constraints of that assumption, can also be used to evaluate redox processes. These methods, therefore, are fundamentally different. A direct comparison of these methods (Chapelle et al., 1996) has shown that ORP measurements were effective in delineating oxic from anoxic ground water, but that ORP measurements could not distinguish between nitrate-reducing, Fe(III)-reducing, sulfate-reducing, or methanogenic zones in an

aquifer. In contrast, the H_2 method could readily distinguish between different anaerobic zones. For those sites where distinguishing between different anaerobic processes is important information, H_2 measurements are an available technology for making such distinctions.

A.4.4.2.1 Sampling Method

Hydrogen is highly volatile, and this chemical property can be used to measure H_2 concentrations in ground water. The principle is to continuously pump ground water through a gas-samping bulb that contains a 20-ml nitrogen bubble. The H_2 partitions between the gas and liquid phases. As water flushes through the bulb, the concentrations of H_2 in the nitrogen bubble come into equilibrium with concentrations of H_2 in the ground water. The nitrogen bubble is then analyzed for H_2 and the concentration of H_2 in the ground water is calculated using the Ideal Gas Law and Henry's Law. This method is referred to as the "bubble strip" method (Chapelle et al., ;1995), because the nitrogen bubble "strips" H_2 out of the water.

The procedure for the "bubble strip" method is as follows: Place the intake hose of a peristaltic pump, a Bennett positive displacement pump, or a bladder pump (note, electrical submersible pumps may produce hydrogen and should not be used for measuring H_2 concentrations in ground water) into the PVC or other non-metal sampling well (note, metal well screens or casing can produce hydrogen and interfere with H_2 measurements in ground water. Position the intake at the depth of the screened interval. Attach a glass, 250-ml gas-sampling bulb (Figure A.4.2) to the outflow end of the hose. Turn on the pump and adjust the flow rate to between 400 and 700 mL/min. Briefly hold the outlet end of the sampling bulb in the upright position to remove any gas bubbles from the bulb. Place the bulb in a horizontal position and inject 20 mL of hydrogen-free N_2 gas through the septum (Figure A.4.2). Allow the N_2 bubble to come into equilibrium with the flowing ground water. This equilibration process takes approximately 20 minutes. After 20 minutes remove 3-5 mL of the gas bubble using a 10 mL glass syringe with attached mini-inert valve. Close the valve to seal the sample. Wait an additional 5 minutes and remove another 3-5 mL from the N_2 bubble. Close the valve to seal the sample. Analyze both samples on the hydrogen detector. If the H_2 concentrations of the duplicate samples do not agree within 10 percent, the well should be resampled.

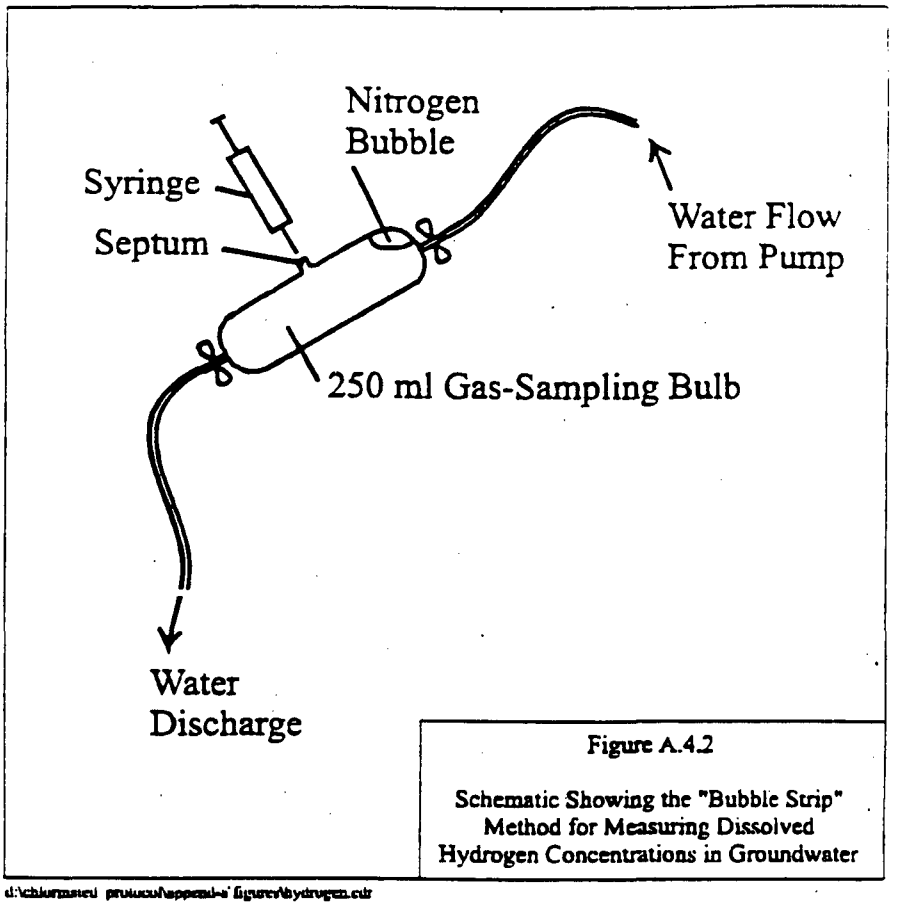

Figure A.4.2

Schematic Showing the "Bubble Strip" Method for Measuring Dissolved Hydrogen Concentrations in Groundwater

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A.4.4.2.2 Analytical Method

Concentrations of H_2 in the nitrogen bubble are determined by gas chromatography (GC) with reduction gas detection (Trace Analytical, Menlo Park, CA). In this analysis, a gaseous sample is injected into the stream of a carrier gas such as N_2. The sample is transported by the carrier through a separation column where the components of the sample are separated based on variations in their efficiency of transport through the column matrix. The column is packed with CarboSieve II which separates chemical species primarily on the basis of molecular size. The separated components elute from the column and pass through a heated bed of HgO where the reduced gases (primarily H_2 and CO) are oxidized and Hg vapor is released. The concentration of Hg vapor released is directly proportional to the concentration of reduced gases present in the sample and is detected by means of an ultraviolet photometer. Because chlorinated solvents can destroy the HgO bed, the column is backflushed immediately after the H_2 peak is quantified.

The concentration of H_2 dissolved in the ground water can be calculated from the equilibrated concentration in the nitrogen gas bubble as follows:

1) Prepare a calibration curve for H_2 using a 100 ppm Scotty II standard gas mixture. The calibration curve should range from 0.1 to 10.0 µL/L (ppm).
2) Analyze the gas sample taken from the gas-sampling bulb. Obtain results (C_B) in units of µL/L (ppm) in the gas phase.
3) Calculate aqueous concentration of H_2 (C_w in nanomoles per liter (nM)) in equilibrium with the equilibrated bubble gas (C_B, µL/L (ppm)) sample using the conversion factor:

$$C_W = 0.81 C_B \qquad \text{eq. A.4.1}$$

This conversion factor is derived from the Ideal Gas Law and Henry's Law as follows:

$$PV = nRT \qquad \text{eq. A.4.2}$$

Rearrange to give:

$$\frac{n}{V} = \frac{P}{RT} \qquad \text{eq. A.4.3}$$

Where n = the quantity of gas in moles
V = the volume the gas occupies in Liters
P = the partial pressure of the gas in atm
T = the temperature in °K
R = the gas constant (R = 0.08205 atm L $mole^{-1}$ $°K^{-1}$

Thus the concentration of a pure gas at atmospheric pressure and room temperature is 40.9 mmoles/L. For a 100 ppm standard (ie. 100 µL/L), the H_2 concentration in molar units is:

$$(40.9 mmoles / L_{H_2})(10^4 L_{H_2} / L_{gas})(10^6 nmoles / mmole) = 4090 nmoles / L_{gas} \qquad \text{eq. A.4.4}$$

The dissolved H_2 concentration in the aqueous phase is given by Henry's Law:

$$C_w = \frac{C_h}{H_{H_2}} \qquad \text{eq. A.4.5}$$

$$Conversion factor = \frac{40.9 nmoles\, L^{-1}\, ppm^{-1})}{50.4} = 0.81 \qquad \text{eq. A.4.6}$$

Where C_w = the dissolved H_2 concentration in nmoles/L
C_h = the equilibrated bubble H_2 concentration in nmoles/L
H_{H_2} = the dimensionless Henry's Law coefficient for the distribution of H_2 between the gaseous and dissolved phases (H_{H_2} = 50.4).

The conversion factor between gas concentration units of µL/L quantified by the reduction gas detector and dissolved H_2 concentration (nmoles/L) is given by the equation:

4) Identify the predominant terminal electron accepting process for the water sample using the characteristic ranges presented in Table 2.4

A.4.4.3 Field Analytical Laboratory Analyses

A.4.4.4 Fixed-Base Laboratory Analyses

SECTION A-5

SURFACE WATER AND SEDIMENT CHARACTERIZATION METHODOLOGIES

At sites where surface water bodies are affected (or potentially affected) by contamination, surface water and sediment sample collection and analysis may be required as a component of the remediation by natural attenuation demonstration.

A.5.1 Surface Water Sample Collection

A.5.2 Sediment Sample Collection

SECTION A-6

SAMPLE HANDLING

This section describes the handling of soil and groundwater samples from the time of sampling until the samples arrive at the laboratory.

A.6.1 SAMPLE PRESERVATION, CONTAINERS, AND LABELS

The analytical laboratory should add any necessary chemical preservatives prior to shipping the containers to the site. Samples should be properly prepared for transportation to the analytical laboratory by placing the samples in a cooler containing ice to maintain a shipping temperature of approximately 4 degrees centigrade (°C).

Sample containers and appropriate container lids should be provided by the analytical laboratory. The sample containers should be filled in accordance with accepted procedures for the sample matrix and the type of analysis to be conducted. Container lids should be tightly closed. The sample label should be firmly attached to the container side, and the following information legibly and indelibly written on the label:

- Facility name;
- Sample identification;
- Sample type (groundwater, surface water, etc.);
- Sampling date;
- Sampling time;
- Preservatives added; and
- Sample collector's initials.

A.6.2 SAMPLE SHIPMENT

After the samples are sealed and labeled, they should be packaged for transport to the analytical laboratory. The packaged samples should be delivered to the analytical laboratory shortly after sample acquisition using an overnight delivery service. The following packaging and labeling procedures are to be followed:

- Abide by all US Department of Transportation (DOT) shipping regulations;
- Package samples so that they will not leak, spill, or vaporize from their containers;
- Label shipping container with
  - Sample collector's name, address, and telephone number;
  - Laboratory's name, address, and telephone number;
  - Description of sample;
  - Quantity of sample; and
  - Date of shipment.

A.6.3 CHAIN-OF-CUSTODY CONTROL

After the samples are collected, chain-of-custody procedures must be followed to establish a written record of sample handling and movement between the sampling site and the analytical laboratory. Each shipping container should have a chain-of-custody form completed in triplicate by the sampling personnel. One copy of this form should be kept by the sampling contractor after sample delivery to the analytical laboratory; the other two copies should be retained at the laboratory. One of the laboratory copies will become a part of the permanent record for the sample and will be returned with the sample analytical results. The chain-of-custody form should contain the following information:

- Unique sample identification number;
- Sample collector's printed name and signature;
- Date and time of collection;
- Sample location;
- Sample matrix;
- Sample size and container;
- Chemical preservatives added;
- Analyses requested;
- Signatures of individuals involved in the chain of possession; and
- Inclusive dates of possession.

The chain-of-custody documentation should be placed inside the shipping container so that it will be immediately apparent to the laboratory personnel receiving the container, but cannot be damaged or lost during transport. The shipping container is to be sealed so that it will be obvious if the seal has been tampered with or broken.

A.6.4 SAMPLING RECORDS

In order to provide complete documentation of the sampling event, detailed records are to be maintained by the field scientist. At a minimum, these records must include the following information:

- Sample location (facility name);
- Sample identification;
- Sample location map or detailed sketch;
- Date and time of sampling;
- Sampling method;
- Field observations of
  - Sample appearance,
  - Sample odor;
- Weather conditions;
- Water level prior to purging (groundwater samples);
- Total well depth (groundwater samples);
- Purge volume (groundwater samples);
- Water level after purging (groundwater samples);
- Well condition (groundwater samples);
- Sample depth;
- Sampler's identification;
- Field measurements of pH, temperature, specific conductivity, dissolved oxygen concentration, and redox potential (groundwater samples); and
- Any other relevant information.

SECTION A-7

AQUIFER CHARACTERIZATION METHODOLOGIES

Adequate characterization of the groundwater flow and contaminant transport system is an important component of the natural attenuation demonstration. The following sections describe methodologies that are recommended to characterize the hydrogeologic system.

A.7.1 HYDRAULIC CONDUCTIVITY

Hydraulic conductivity is a measure of an aquifer's capacity to transmit water and governs groundwater flow and contaminant transport in the subsurface. Methods for determining hydraulic conductivity in the field can include slug tests, pumping tests, and downhole flowmeter measurements. The method selected for a given site will depend on the dimensions, locations, and screened intervals of site wells and monitoring points; site stratigraphy; equipment availability; budget; and waste handling requirements.

A.7.1.1 Slug Tests

A slug test is a single-well hydraulic test used to determine the hydraulic conductivity of an aquifer in the immediate vicinity of the well. Because hydraulic conductivity varies spatially within and between aquifers and because slug test results reflect aquifer conditions only in the immediate vicinity of the tested well, slug tests should be conducted in as many wells as possible at a site. Slug tests can be used for both confined and unconfined aquifers that have transmissivities of less than approximately 7,000 square feet per day (ft^2/day). Slug tests are accomplished by removing a solid slug (rising head) or introducing a solid slug (falling head), and then allowing the water level to stabilize while taking water level measurements at closely spaced time intervals. The method presented herein discusses the use of falling head and rising head slug tests in sequence. The analysis of slug test data is discussed in Appendix C.

Slug testing should not proceed until water level measurements show that static water level equilibrium has been achieved. Unvented wells should be uncapped at least 24 hours prior to initiating the test in order to allow the static water level to come to equilibrium. The protective casing should remain locked during this time to prevent vandalism. During the slug test, the water level change should be influenced only by the introduction or removal of the slug volume. Other factors, such as inadequate well development or extended pumping, may lead to inaccurate results. It is the field scientist's responsibility to decide when static equilibrium has been reached in the well.

The following equipment is needed to conduct a slug test:

- Teflon®, PVC, or metal slug
- Nylon or polypropylene rope
- Electric water level indicator
- Pressure transducer/sensor
- Field logbook/forms
- Automatic data recorder (such as the Hermit Environmental Data Logger®, In-Situ, Inc. Model SE1000B, or equal)

The falling head test is the first step in the two-step slug-testing procedure. The following steps describe the recommended falling head slug test procedure:

1. Decontaminate all downhole equipment.
2. Record pre-test information including: well number, personnel, climatic data, ground surface elevation, measuring point elevation, equipment identifications, and date.
3. Measure and record the static water level in the well to the nearest 0.01 foot.
4. Lower the decontaminated pressure transducer into the well and allow the displaced water to return to within 0.01 foot of the original static level.
5. Lower the decontaminated slug into the well to just above the water surface in the well.
6. Start the data logger and quickly lower the slug below the water table being careful not to disturb the pressure transducer. Follow the owner's manual for proper operation of the data logger.
7. Terminate data recording when the water level has recovered at least 80 percent from the initial slug displacement.

Immediately following completion of the falling head test, the rising head test is performed. The following steps describe the rising head slug test procedure:

1. Measure the static water level in the well to the nearest 0.01 foot to ensure that it has returned to the static water level.
2. Initiate data recording and quickly withdraw the slug from the well. Follow the owner's manual for proper operation of the data logger.
3. Terminate data recording when the water level has recovered at least 80 percent from the initial slug displacement.

It is advisable to produce hard copies or backup electronic copies of the data logger output (drawdown vs. time) daily and before transporting the logger from the field site.

A.7.1.2 Pump Tests

A pumping test involves pumping one well at a constant rate for a specified length of time and collecting periodic water level measurements in both the pumped well and nearby observation wells in order to determine aquifer hydraulic characteristics representative of a large area. As a rule, pumping tests provide more representative measurements of hydraulic parameters; however, they require a greater commitment of resources (time, money, and equipment) that cannot be afforded by all projects. In addition, for pumping test results to be representative, site hydrogeologic conditions should not change appreciably over short distances. This section outlines methods that can be used for conducting pump tests in both confined and unconfined aquifers. For a more detailed discussion of how to conduct a pumping test, the reader is referred to the work of Dawson and Istok (1991), Kruseman and de Ridder (1991), and Driscoll (1986).

The interpretation of aquifer pumping test data is not unique. Similar sets of data can be obtained from various combinations of geologic conditions. The interpretation of pumping test data is discussed in Appendix C of this protocol document.

A.7.1.2.1 Pumping Test Design

Prior to performing an aquifer pumping test, all available site and regional hydrogeologic information should be assembled and evaluated. Such data should include groundwater flow direction, hydraulic gradients, other geohydraulic properties, site stratigraphy, well construction details, regional water level trends, and the performance of other pumping wells in the vicinity of the test area. This information is used to select test duration, proposed pumping rates, and pumping well and equipment dimensions.

The precise location of an aquifer test is chosen to be representative of the area under study. In addition, the location is selected on the basis of numerous other criteria, including:

- Size of the investigation area;
- Uniformity and homogeneity of the aquifer;
- Distribution of contaminant sources and dissolved contaminant plumes;
- Location of known or suspected recharge or barrier boundary conditions;
- Availability of pumping and/or observation wells of appropriate dimension and screened at the desired depth; and
- Requirements for handling discharge.

The dimensions and screened interval of the pumping well must be appropriate for the tested aquifer. For example, the diameter of the well must be sufficient to accommodate pumping equipment capable of sustaining the desired flow rate at the given water depth. In addition, if testing a confined aquifer that is relatively thin, the pumping well should be screened for the entire thickness of the aquifer. For an unconfined aquifer, the wells should be screened in the bottom one-third or two-thirds of the saturated zone.

Any number of observation wells may be used. The number chosen is contingent upon both cost and the need to obtain the maximum amount of accurate and reliable data. If three or more observation wells are to be installed, and there is a known boundary condition, the wells should be placed along a radial line extending from the pumping well toward the boundary, with one well placed perpendicular to the line of observation wells to determine whether radial anisotropy exists within the aquifer. If two observation wells are to be installed, they should be placed in a triangular pattern, non-equidistant from the pumping well. Observation wells should be located at distances and depths appropriate for the planned method for analysis of the aquifer test data. Observation well spacing should be determined based upon expected drawdown conditions that are the result of the geohydraulic properties studies, proposed pumping test duration, and proposed pumping rate. Preliminary pumping results should also be used (if available). Not all projects can afford the luxury of preliminary testing.

The equipment needed to perform aquifer pumping tests includes:

- Pumps
- Gate valve
- Electrical generator
- Flow meter with totalizer
- Water level indicators
- Pressure gauge
- Field logbook/forms
- Pressure transducers and data recorder
- Engineer's tape calibrated to 0.01 ft
- 5-gallon pail
- Conductivity meter, pH meter, and thermometer
- Barometer
- Semi-log and log-log graph paper
- Portable computer
- Field printer for data
- Type matching curves
- Meter and stopwatch for discharge measurement
- Hose or pipe for transfer of water
- Adequately sized tank for storing contaminated water

Pumping equipment should conform to the size of the well and be capable of delivering the estimated range of pumping rates. The selection of flow meter, gate valve, and water transfer lines should be based on anticipated rates of water discharge. Both the discharge rate and test duration should be considered when selecting a tank for storing discharge water if the water cannot be released directly released to the ground, sanitary sewer, storm sewer, or nearby water treatment facility.

In areas of severe winter climates, where the frost line may extend to depths of several feet, pumping tests should be avoided during cold weather months where the water table is less than 12 feet from the surface. Under certain conditions, the frozen soil acts as a confining stratum, and combined with leaky aquifer and delayed storage characteristics, test results may be unreliable.

A.7.1.2.2 Preparation for Testing

Barometric changes may affect water levels in wells, particularly in semiconfined and confined aquifers. A change in barometric pressure may cause a change in the water level. Therefore, for at least 24 hours prior to performing a pumping test, barometric pressure and water levels in the test well, observation wells, and a well beyond the influence of the pumping well should be measured hourly to establish trends in groundwater level fluctuation. If a trend is apparent, the barometric pressure should be used to develop curves depicting the change in water level versus time. These curves should be used to correct the water levels observed during the pumping test. Groundwater levels in the background well as well as barometric pressures should continue to be recorded throughout the duration of the test.

Test wells should undergo preliminary pumping or step drawdown tests prior to the actual test. This will enable fines to be flushed from the adjacent formation near the well and a steady flow rate to be established. The preliminary pumping should determine the maximum drawdown in the well and the proper pumping rate should be determined by step drawdown testing. The aquifer should then be given time to recover before the actual pumping test begins (as a rule-of-thumb, one day).

A record should be maintained in the field logbook of the times of pumping and discharge of other wells in the area, and if their radii of influence intersect the cone of depression of the test well. All measurements and observations should be recorded in a field notebook or on an Aquifer Test Data Form. If data loggers with transducers are used, field measurements should be performed in case of data logger malfunction.

A.7.1.2.2 Conducting the Pumping Test

Immediately prior to starting the pump, the water levels should be measured and recorded for all wells to determine the static water levels upon which all drawdowns will be based. Data loggers should be reset for each well to a starting water level of 0.0 foot.

Water pumped from an unconfined aquifer during a pumping test should be disposed of in such a manner as not to allow the aquifer to be recharged by infiltration during the test. This means that the water must be piped away from the well and associated observation wells. Recharge could adversely affect the results. Also, if contaminated water is pumped during the test, the water must be stored and treated or disposed of according to the project work plan for the study. The discharge water may be temporarily stored in drums, a lined, bermed area, or tanks. If necessary, it should be transported and staged in a designated secure area.

The discharge rate should be measured frequently throughout the test and controlled to maintain it as constant as possible, after the initial excess discharge has been stabilized. This can be achieved by using a control valve.

The pitch or rhythm of the pump or generators provides a check on performance. If there is a sudden change in pitch, the discharge should be checked immediately and proper adjustments to the control valve or the engine speed should be made, if necessary. Do not allow the pump to

1. Water level, organic liquid (NAPL) interfaces (if present), and total depth (TD) will be measured prior to test initiation.

2. Depending on site conditions, flowmeter measurements using the 0.5-inch-ID probe will be obtained at 1- to 3-foot intervals starting at TD and proceeding up the well under static (ambient) conditions.

3. A short-term, single-well pumping test will be conducted in the test well to stress the aquifer. Drawdown will be measured and recorded using an electronic datalogger with a pressure transducer. The groundwater extraction rate will be monitored and adjusted, as necessary, to maintain constant flow. Groundwater will be contained for disposal by site personnel. It is estimated that extraction rates may range from less than 1 L/min to approximately 10 L/min, and that the test duration may range from 1 to 4 hours.

4. Upon stabilization of the flow rate, the profile of vertical flow will be obtained using the 1.0-inch-ID probe at the same elevations occupied during the ambient profile.

5. Data collected during the tests will be analyzed to estimate relative distribution of flow into the wells and the relative hydraulic conductivity distribution at each location.

All downhole test equipment will be properly decontaminated between tests at different monitoring wells.

APPENDIX B

IMPORTANT PROCESSES AFFECTING THE FATE AND TRANSPORT OF ORGANIC COMPOUNDS IN THE SUBSURFACE

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FIGURES

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SECTION B-1

INTRODUCTION

B.1.1 FATE AND TRANSPORT MECHANISMS

This appendix presents an overview of the important processes affecting the fate and transport of chlorinated solvents and fuel hydrocarbons dissolved in groundwater. The environmental fate and transport of a contaminant is controlled by the compound's physical and chemical properties and the nature of the subsurface media through which the compound is migrating. Several processes are known to cause a reduction in the concentration and/or mass of a contaminant dissolved in groundwater. Those processes that result only in the reduction of a contaminant's concentration but not of the total contaminant mass in the system are termed nondestructive. Those processes that result degradation of contaminants are referred to as destructive. Nondestructive processes include advection, hydrodynamic dispersion (mechanical dispersion and diffusion), sorption, dilution, and volatilization. Destructive processes include biodegradation and abiotic degradation mechanisms. Biodegradation may be the dominant destructive attenuation mechanism acting on a contaminant, depending upon the type of contaminant and the availability of electron donors or carbon sources. Abiotic degradation processes are also known to degrade chlorinated solvents; where biodegradation is not occurring, these may be the only destructive processes operating. However, the rates of abiotic processes are generally slow relative to biodegradation rates.

Remediation by natural attenuation results from the integration of all the subsurface attenuation mechanisms (both nondestructive and destructive) operating at a given site. Table B.1.1 summarizes the processes that affect fate and transport of chlorinated solvents and fuel hydrocarbons dissolved in groundwater. Important factors to consider include:

- The compound's soil/water distribution coefficient (K_d);
- The compound's organic carbon/water partition coefficient (K_{oc});

Table B.1.1
Summary of Important Processes Affecting Solute Fate and Transport

Process	Description	Dependencies	Effect
Advection	Movement of solute by bulk groundwater movement.	Dependent on aquifer properties, mainly hydraulic conductivity and effective porosity, and hydraulic gradient. Independent of contaminant properties.	Main mechanism driving contaminant movement in the subsurface.
Dispersion	Fluid mixing due to groundwater movement and aquifer heterogeneities.	Dependent on aquifer properties and scale of observation. Independent of contaminant properties.	Causes longitudinal, transverse, and vertical spreading of the plume. Reduces solute concentration.
Diffusion	Spreading and dilution of contaminant due to molecular diffusion.	Dependent on contaminant properties and concentration gradients. Described by Fick's Laws.	Diffusion of contaminant from areas of relatively high concentration to areas of relatively low concentration. Generally unimportant relative to dispersion at most groundwater flow velocities.
Sorption	Reaction between aquifer matrix and solute whereby relatively hydrophobic organic compounds become sorbed to organic carbon or clay minerals.	Dependent on aquifer matrix properties (organic carbon and clay mineral content, bulk density, specific surface area, and porosity) and contaminant properties (solubility, hydrophobicity, octanol-water partitioning coefficient).	Tends to reduce apparent solute transport velocity and remove solutes from the groundwater via sorption to the aquifer matrix.
Recharge (Simple Dilution)	Movement of water across the water table into the saturated zone.	Dependent on aquifer matrix properties, depth to groundwater, surface water interactions, and climate.	Causes dilution of the contaminant plume and may replenish electron acceptor concentrations, especially dissolved oxygen.
Volatilization	Volatilization of contaminants dissolved in groundwater into the vapor phase (soil gas).	Dependent on the chemical's vapor pressure and Henry's Law constant.	Removes contaminants from groundwater and transfers them to soil gas.
Biodegradation	Microbially mediated oxidation-reduction reactions that degrade contaminants.	Dependent on groundwater geochemistry, microbial population and contaminant properties. Biodegradation can occur under aerobic and/or anaerobic conditions.	May ultimately result in complete degradation of contaminants. Typically the most important process acting to truly reduce contaminant mass.
Abiotic Degradation	Chemical transformations that degrade contaminants without microbial facilitation; only halogenated compounds are subject to these mechanisms in the groundwater environment.	Dependent on contaminant properties and groundwater geochemistry.	Can result in partial or complete degradation of contaminants. Rates typically much slower than for biodegradation.
Partitioning from NAPL	Partitioning from NAPL into groundwater. NAPL plumes, whether mobile or residual, tend to act as a continuing source of groundwater contamination.	Dependent on aquifer matrix and contaminant properties. as well as groundwater mass flux through or past NAPL plume.	Dissolution of contaminants from NAPL represents the primary source of dissolved contamination in groundwater.

- The compound's octanol/water partition coefficient (K_{ow});
- The compound's water solubility;
- The compound's vapor pressure;
- The compound's Henry's Law constant (air/water partition coefficient, H);
- Indigenous bacterial population;
- Hydraulic conductivity of aquifer materials;
- Porosity of aquifer materials;
- Total organic carbon content of aquifer materials;
- Bulk density of aquifer materials;
- Aquifer heterogeneity; and
- Ambient groundwater geochemistry.

Nondestructive attenuation mechanisms are discussed in Section B-2. Biodegradation is discussed in Section B-3. Abiotic degradation mechanisms are discussed in Section B-4. It is important to separate nondestructive from destructive attenuation mechanisms during the natural attenuation demonstration. The methods for correcting apparent attenuation caused by nondestructive attenuation mechanisms are discussed in Appendix C.

B.1.2 MATHEMATICAL DESCRIPTION OF SOLUTE FATE AND TRANSPORT

The partial differential equation describing contaminant migration and attenuation in the saturated zone includes terms for advection, dispersion, sorption, and degradation. In one dimension, the partial differential equation describing solute transport in the saturated zone is:

$$\frac{\partial C}{\partial t} = \frac{D_x}{R}\frac{\partial^2 C}{\partial x^2} - \frac{v_x}{R}\frac{\partial C}{\partial x} \pm \underline{Q}_s \qquad \text{eq. B.1.1}$$

Where: C = solute concentration [M]
t = time [T]
D_x = hydrodynamic dispersion [L^2/T]
R = coefficient of retardation [dimensionless]
x = distance along flow path [L]
v_x = transport velocity in x direction [L/T]
$\underline{Q}_s$ = general source or sink term for reactions involving the production or loss of solute (e.g., biodegradation) [$M/L^3/T$]

The degradation of organic contaminants commonly can be approximated using first-order kinetics. In one dimension, the partial differential equation describing solute transport with first-order decay in the saturated zone is given by:

$$\frac{\partial C}{\partial t} = \frac{D_x}{R}\frac{\partial^2 C}{\partial x^2} - \frac{v_x}{R}\frac{\partial C}{\partial x} - \lambda C \qquad \text{eq. B.1.2}$$

Where: C = concentration [M/L^3]
t = time [T]
D_x = hydrodynamic dispersion [L^2/T]
x = distance along flow path [L]
R = coefficient of retardation [dimensionless]
v_x = transport velocity in x direction [L/T]
λ = first-order decay rate [T^{-1}]

These equations serve to illustrate how the processes of advection, dispersion, sorption, and biotic and abiotic degradation are integrated to describe the fate and transport of solutes in the saturated zone. These relationships were derived using the continuity (conservation of mass) equation, which states that the rate of change of contaminant mass within a unit volume of porous media is equal to the flux of contaminant into the unit volume minus the flux out of the unit volume (Freeze and Cherry, 1979). Processes governing flux into the unit volume include advection and hydrodynamic dispersion (including mechanical dispersion and diffusion). Processes governing flux out of the unit volume include advection, hydrodynamic dispersion, dilution, sorption, and chemical reactions (most notably biodegradation). The change in solute concentration may therefore be stated mathematically as:

Change in Solute Concentration = Flux In - Flux Out ± Reactions

The following sections describe the most significant reactions affecting this mass balance (and therefore the fate and transport) of organic contaminants in the subsurface. Methods for evaluating the flux through the system will be discussed in Appendix C.

SECTION B-2

NONDESTRUCTIVE ATTENUATION MECHANISMS

B.2.1 ADVECTION

Advective transport is the transport of solutes by the bulk movement of groundwater. Advection is the most important process driving dissolved contaminant migration in the subsurface. The linear groundwater velocity in the direction parallel to groundwater flow caused by advection is given by:

$$v_x = -\frac{K}{n_e}\frac{dH}{dL} \qquad \text{eq. B.2.1}$$

Where: v_x = average linear velocity [L/T]
K = hydraulic conductivity [L/T]
n_e = effective porosity [L^3/L^3]
dH/dL = hydraulic gradient [L/L]

Solute transport by advection alone yields a sharp solute concentration front. Immediately ahead of the front, the solute concentration is equal to the background concentration (generally zero). At and behind the advancing solute front, the concentration is equal to the initial contaminant concentration at the point of release. This is referred to as plug flow and is illustrated in Figures B.2.1, B.2.2, and B.2.3. In reality, the advancing front spreads out due to the processes of dispersion and diffusion, as discussed in Section B-3, and is retarded by sorption and biodegradation, as discussed in Sections B-4 and B-5, respectively.

The one-dimensional advective transport component of the advection-dispersion equation is given by:

$$\frac{\partial C}{\partial t} = -v_x \frac{\partial C}{\partial x} \qquad \text{eq. B.2.2}$$

Where: v_x = average linear velocity [L/T]
C = contaminant concentration [M/L^3]
t = time [T]
x = distance along flow path [L]

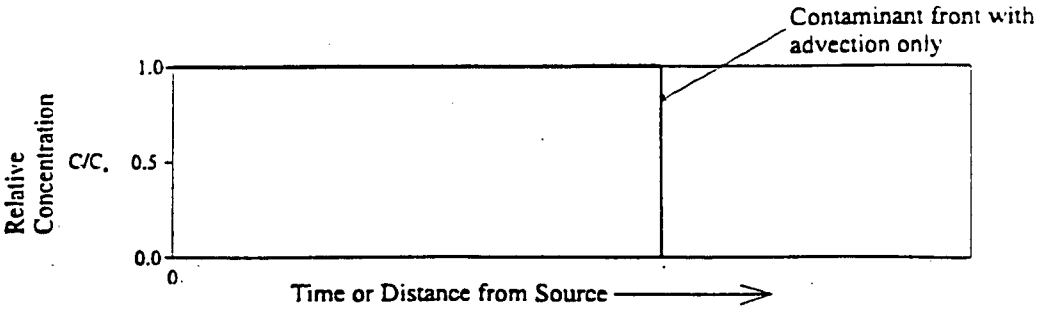

Figure B.2.1 Breakthrough curve in one dimension showing plug flow with continuous source resulting from advection only.

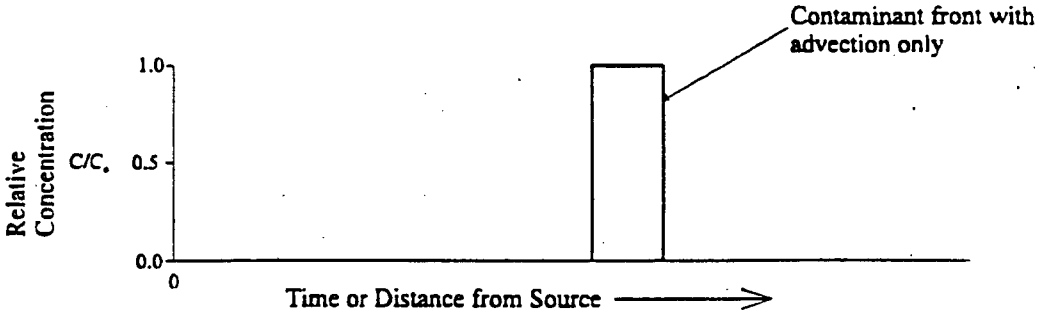

Figure B.2.2 Breakthrough curve in one dimension showing plug flow with instantaneous source resulting from advection only.

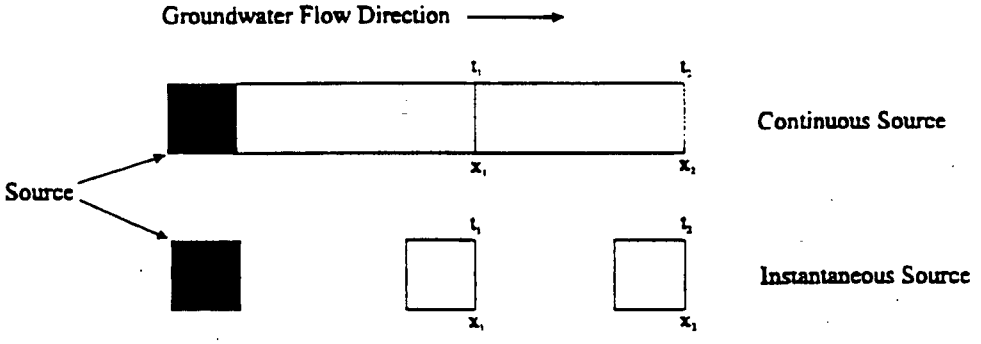

Figure B.2.3 Plume migration in two dimensions (plan view) showing plume migration resulting from advective flow only with continuous and instantaneous sources.

Equation B.2.2 considers only advective transport of the solute. In some cases this may be a fair approximation for simulating solute migration because advective transport is the main force behind contaminant migration. However, because of dispersion, diffusion, sorption, and biodegradation, this equation generally must be combined with the other components of the modified advection-dispersion equation (equation B.1.1) to obtain an accurate mathematical description of solute transport.

B.2.2 HYDRODYNAMIC DISPERSION

Hydrodynamic dispersion is the process whereby a contaminant plume spreads out in directions that are longitudinal and transverse to the direction of plume migration. Dispersion of organic solutes in an aquifer is an important consideration when modeling remediation by natural attenuation. Dispersion of a contaminant dilutes the concentrations of the contaminant, and introduces the contaminant into relatively pristine portions of the aquifer where it may admix with more electron acceptors crossgradient to the direction of groundwater flow. Two very different processes cause hydrodynamic dispersion; mechanical dispersion and molecular diffusion. The variable describing hydrodynamic dispersion, D, is the sum of mechanical dispersion and molecular diffusion. Mechanical dispersion is the dominant mechanism causing hydrodynamic dispersion at normal groundwater velocities. At extremely low groundwater velocities, molecular diffusion can become the dominant mechanism of hydrodynamic dispersion. Molecular diffusion is generally ignored for most groundwater studies. The following sections describe these processes and how they are incorporated into the modified advection-dispersion equation (Equation B.1.1).

B.2.2.1 Mechanical Dispersion

As defined by Domenico and Schwartz (1990), mechanical dispersion is mixing that occurs as a result of local variations in velocity around some mean velocity of flow. With time, a given volume of solute will gradually become more dispersed as different portions of the mass are transported at the differing velocities. In general, the main cause of variations of both rate and direction of transport velocities is the heterogeneity of the porous aquifer medium. These heterogeneities are present at scales ranging from microscopic (e.g., pore to pore) to macroscopic (e.g., well to well) to megascopic (e.g., a regional aquifer system).

Three processes are responsible for mechanical dispersion on the microscopic scale (Figure B.2.4). The first process is the variation in flow velocity through pores of various sizes.

As groundwater flows through a porous medium, it flows more slowly through large pores than through smaller pores. The second cause of mechanical dispersion is tortuosity, or flow path length. As groundwater flows through a porous medium, some of the groundwater follows less tortuous (shorter) paths, while some of the groundwater takes more tortuous (longer) paths. The longer the flow path, the slower the average linear velocity of the groundwater and the dissolved contaminant. The final process causing mechanical dispersion is variable friction within an individual pore. Groundwater traveling close to the center of a pore experiences less friction than groundwater traveling next to a mineral grain, and therefore moves faster. These processes cause some of the contaminated groundwater to move faster than the average linear velocity of the groundwater and some to move slower. This variation in average velocity of the solute causes dispersion of the contaminant.

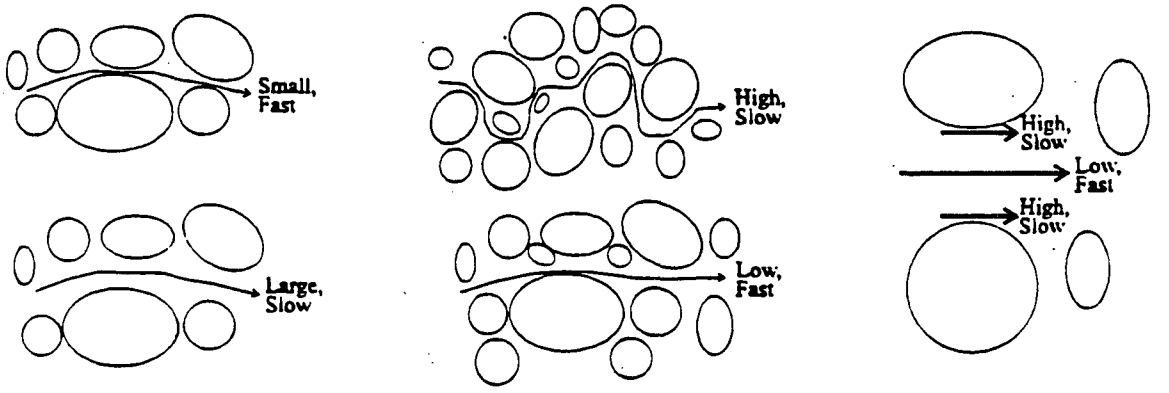

Figure B.2.4 Physical processes causing mechanical dispersion at the microscopic scale.

Heterogeneity at the macroscopic and megascopic scales also creates variability in groundwater and solute velocities, therefore producing dispersion on a larger scale. Geologic features that contribute to dispersion at the macroscopic scale include stratification characteristics such as changing unit geometry, discontinuous units, and contrasting lithologies, and permeability characteristics such as nonuniform permeability, directional permeability, and trending permeability (Domenico and Schwartz, 1990). Even in aquifer material that appears to be homogeneous, relatively small changes in the fraction of fine sediment can change hydraulic conductivity characteristics enough to produce significant variations in fluid and solute velocities and thus introduce dispersion. Larger geological features will introduce dispersion at the megascopic scale. At this scale, structural features such as faults, dipping strata, folds, or

contacts will create inhomogeneity, as will stratigraphic features such as bedding or other depositional structures.

As a result of dispersion, the solute front travels at a rate that is faster than would be predicted based solely on the average linear velocity of the groundwater. The overall result of dispersion is spreading and mixing of the contaminant plume with uncontaminated groundwater. Figures B.2.5 and B.2.6 illustrate the effects of hydrodynamic dispersion on an advancing solute front. The component of hydrodynamic dispersion contributed by mechanical dispersion is given by the relationship:

$$\text{Mechanical Dispersion} = \alpha_x v_x \qquad \text{eq. B.2.3}$$

Where: v_x = average linear groundwater velocity [L/T]
α_x = dispersivity [L]

Mechanical dispersion has two components, longitudinal dispersion and transverse (both horizontal and vertical) dispersion. Longitudinal dispersion is the spreading of a solute in a direction parallel to the direction of groundwater flow. On the microscopic scale, longitudinal dispersion occurs because of velocity changes due variations in pore size, friction in the pore throat, and tortuosity. Transverse dispersion is the spreading of a solute in directions perpendicular to the direction of groundwater flow. Transverse dispersion on the microscopic scale is caused by the tortuosity of the porous medium, which causes flow paths to branch out from the centerline of the contaminant plume.

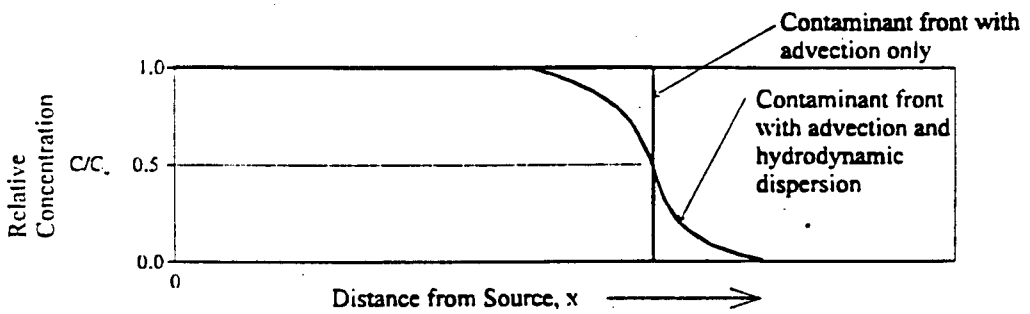

Figure B.2.5 Breakthrough curve in one dimension showing plug flow with continuous source resulting from advection only and the combined processes of advection and hydrodynamic dispersion.

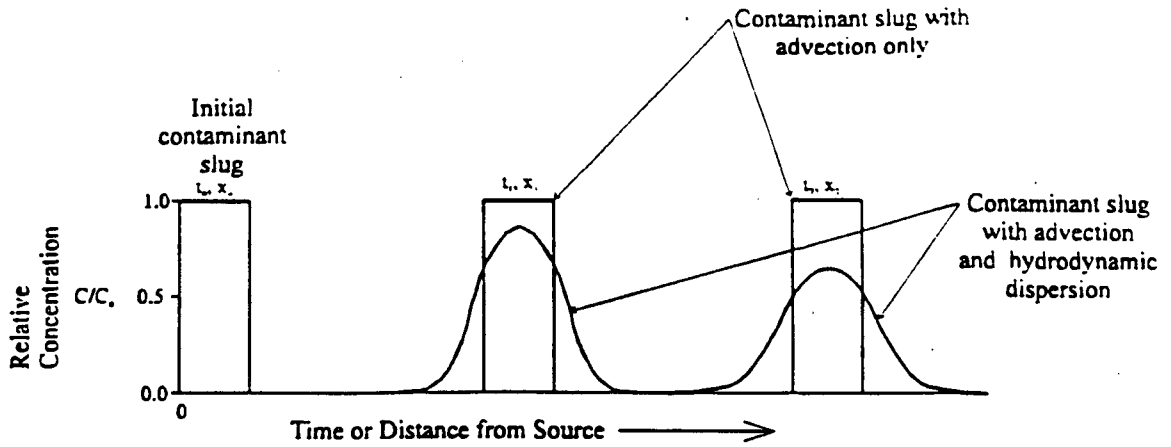

Figure B.2.6 Breakthrough curve in one dimension showing plug flow with instantaneous source resulting from advection only and the combined processes of advection and hydrodynamic dispersion.

B.2.2.2 Molecular Diffusion

Molecular diffusion occurs when concentration gradients cause solutes to migrate from zones of higher concentration to zones of lower concentration, even in the absence of groundwater flow. Molecular diffusion is only important at low groundwater velocities, and therefore can be ignored in areas with high groundwater velocities (Davis *et al.*, 1993).

The molecular diffusion of a solute in groundwater is described by Fick's Laws. Fick's First Law applies to the diffusive flux of a dissolved contaminant under steady-state conditions and, for the one-dimensional case, is given by:

$$F = -D\frac{dC}{dx} \qquad \text{eq. B.2.4}$$

Where: F = mass flux of solute per unit area of time [M/T]
D = diffusion coefficient (L^2/T)
C = solute concentration (M/L^3)
$\frac{dC}{dx}$ = concentration gradient ($M/L^3/L$)

For systems where the dissolved contaminant concentrations are changing with time, Fick's Second Law must be applied. The one-dimensional expression of Fick's Second Law is:

$$\frac{dC}{dt} = D\frac{d^2C}{dx^2} \qquad \text{eq. B.2.5}$$

Where: $\frac{dC}{dt}$ = change in concentration with time [M/T]

The process of diffusion is slower in porous media than in open water because the ions must follow more tortuous flow paths (Fetter, 1988). To account for this, an effective diffusion coefficient, D*, is used.

The effective diffusion coefficient is expressed quantitatively as (Fetter, 1988):

$$D^* = wD \qquad \text{eq. B.2.6}$$

Where: w = empirical coefficient determined by laboratory experiments [dimensionless]

The value of w generally ranges from 0.01 to 0.5 (Fetter, 1988).

B.2.2.3 Equation of Hydrodynamic Dispersion

Hydrodynamic dispersion, D, has two components, mechanical dispersion and molecular diffusion. For one-dimensional flow, hydrodynamic dispersion is represented by the following equation (Freeze and Cherry, 1979):

$$D_x = \alpha_x v_x + D^* \qquad \text{eq. D.2.7}$$

Where: D_x = longitudinal coefficient of hydrodynamic dispersion in the x direction [L^2/T]
α_x = longitudinal dispersivity [L]
v_x = average linear groundwater velocity [L/T]
D^* = effective molecular diffusion [L^2/T]

Dispersivity is a parameter that is characteristic of the porous medium through which the contaminant migrates. Dispersivity represents the spreading of a contaminant over a given length of flow, and therefore has units of length. It is now commonly accepted (on the basis of empirical evidence) that as the scale of the plume or the system being studied increases, the dispersivity will also increase. Therefore, dispersivity is scale-dependent, but at a given scale, data compiled by Gelhar *et al.* (1985 and 1992) show that dispersivity may vary over three orders of magnitude. The data of Gelhar *et al.* (1992) are presented on Figure B.2.7.

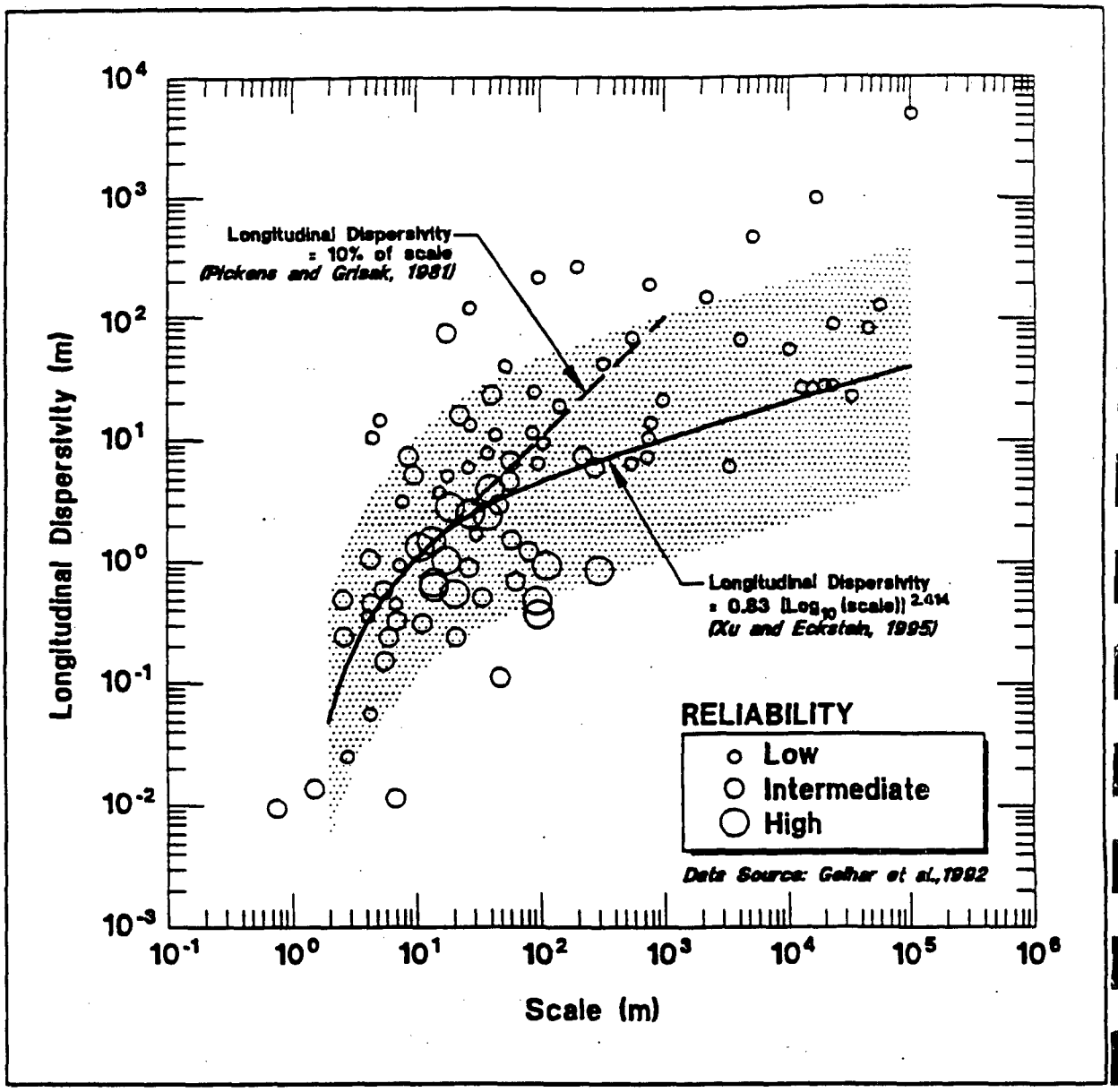

Figure B.2.1
Relationship Between
Dispersivity and

Source: Newell *et al.*, 1996

Several approaches can be used to estimate longitudinal dispersivity, α_x., on the field scale (i.e., macroscopic to megascopic scales). One technique involves conducting a tracer test. Although this is potentially the most reliable method, time and monetary constraints can be prohibitive. Another method commonly used to estimate dispersivity when implementing a solute transport model is to start with a longitudinal dispersivity of 0.1 times the plume length (Lallemand-Barres and Peaudecerf, 1978; Pickens and Grisak, 1981; Spitz and Moreno, 1996). This assumes that dispersivity varies linearly with scale. However, Xu and Eckstein (1995) evaluated the same data presented by Gelhar *et al.* (1992) and, by using a weighted least-squares method, developed the following relationship for estimating dispersivity:

$$\alpha_x = 0.83(Log_{10} L_p)^{2.414} \qquad \text{eq. B.2.8}$$

Where: α_X = longitudinal dispersivity [L]
L_p = plume length [L]

Both relationships are shown on Figure B.2.7. In either case, the value derived for dispersivity will be an estimate at best, given the great variability in dispersivity for a given plume length. However, for modeling studies, an initial estimate is needed, and these relationships provide good starting points for a modeling study.

In addition to estimating longitudinal dispersivity, it may be necessary to estimate the transverse and vertical dispersivities (α_T. and α_z., respectively) for a given site. Several empirical relationships between longitudinal dispersivity and transverse and vertical dispersivity have been described. Commonly, α_T is estimated as $0.1\alpha_x$. (based on data from Gelhar *et al.*, 1992), or as $0.33\alpha_x$. (ASTM, 1995; US EPA, 1986). Vertical dispersivity (α_z) may be estimated as $0.05\alpha_x$. (ASTM, 1995), or as $0.025\alpha_x$. to $0.1\alpha_x$. (US EPA, 1986).

Some solute transport modelers will start with an accepted literature value for the types of materials found in the aquifer matrix. After selecting initial dispersivity values, the contaminant transport model is calibrated by adjusting the dispersivities (along with other transport parameters, as necessary) within the range of accepted literature values until the modeled and observed contaminant distribution patterns match (Anderson, 1979). This is a two-step process. The first step is to calibrate the flow model to the hydraulic conditions present at the site. After the groundwater flow model is calibrated to the hydraulics of the system, the contaminant transport model is calibrated by trial and error using various values for dispersivity. There is no unique solution because several hydraulic parameters, including hydraulic conductivity, effective porosity, and dispersivity, are variable within the flow system (Anderson, 1979; Davis *et al.*,

1993), and other transport parameters such as retardation and biodegradation may not be well-defined.

B.2.2.4 One-Dimensional Advection-Dispersion Equation

The advection-dispersion equation is obtained by adding hydrodynamic dispersion to equation B.2.2. In one dimension, the advection-dispersion equation is given by:

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} \qquad \text{eq. B.2.9}$$

Where: v_x = average linear velocity [L/T]
C = contaminant concentration [M/L^3]
D_x = hydrodynamic dispersion [L^2/T]
t = time [T]
x = distance along flow path [L]

This equation considers both advection and hydrodynamic dispersion. Because of sorption and biodegradation, this equation generally must be combined with the other components of the modified advection-dispersion equation presented as equation B.1.1 to obtain an accurate mathematical description of solute transport.

B.2.3 SORPTION

Many organic contaminants, including chlorinated solvents and BTEX, are removed from solution by sorption onto the aquifer matrix. Sorption is the process whereby dissolved contaminants partition from the groundwater and adhere to the particles comprising the aquifer matrix. Sorption of dissolved contamination onto the aquifer matrix results in slowing (retardation) of the contaminant relative to the average advective groundwater flow velocity and a reduction in dissolved BTEX concentrations in groundwater. Sorption can also influence the relative importance of volatilization and biodegradation (Lyman *et al.*, 1992). Figures B.2.8 and B.2.9 illustrate the effects of sorption on an advancing solute front.

Keep in mind that sorption is a reversible reaction and that at a given solute concentrations, some portion of the solute is partitioning to the aquifer matrix and some portion is also desorbing and reentering solution. As solute concentrations change, the relative amounts of contaminant that are sorbing and desorbing will change. For example, as solute concentrations decrease

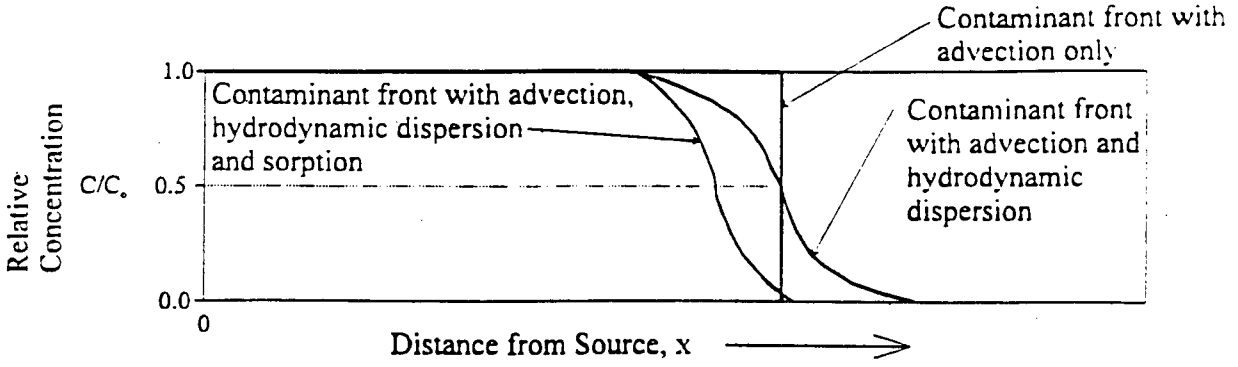

Figure B.2.9 Breakthrough curve in one dimension showing plug flow with continuous source resulting from advection only; the combined processes of advection and hydrodynamic dispersion; and the combined processes of advection, hydrodynamic dispersion, and sorption.

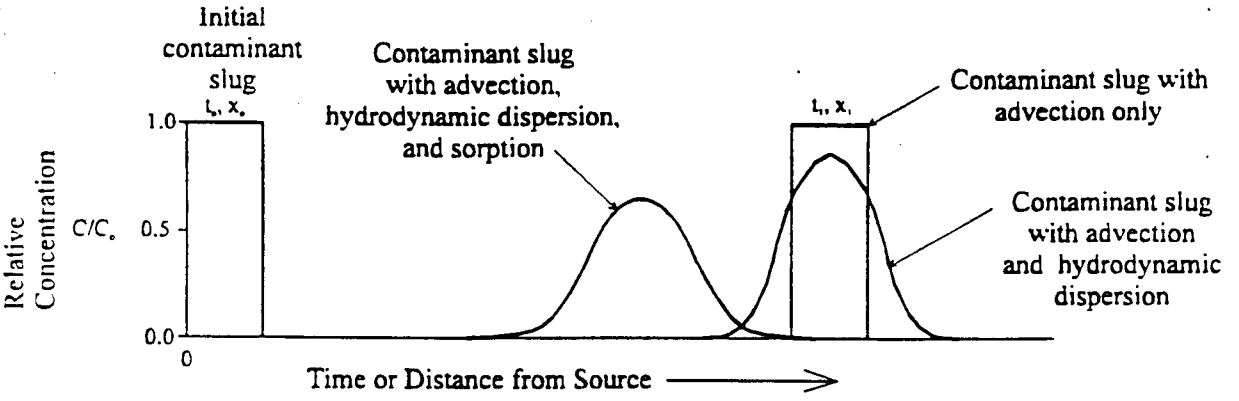

Figure B.2.9 Breakthrough curve in one dimension showing plug flow with instantaneous source resulting from advection only; the combined processes of advection and hydrodynamic dispersion; and the combined processes of advection, hydrodynamic dispersion, and sorption.

(perhaps due to plume migration or solute biodegradation and dilution), the amount of contaminant reentering solution will likely increase. The affinity of a given compound for the aquifer matrix will not be sufficient to permanently isolate it from groundwater, although for some compounds, the rates of desorption may be so slow that the loss of mass may be considered permanent for the time scale of interest. Sorption therefore does not permanently remove solute mass from groundwater; it merely retards migration. It is this slowing of contaminant migration that must be understood in order to effectively predict the fate of a dissolved contaminant.

This section provides information on how retardation coefficients are determined in the laboratory. It is not the intent of this document to instruct people in how to perform these

experiments; this information is provided for informational purposes only. Linear isotherms and previously determined soil sorption coefficients (K_{oc}) are generally used to estimate sorption and retardation.

B.2.3.1 Mechanisms of Sorption

Sorption of dissolved contaminants is a complex phenomenon caused by several mechanisms, including London-van der Waals forces, Coulomb forces, hydrogen bonding, ligand exchange, chemisorption (covalent bonding between chemical and aquifer matrix), dipole-dipole forces, dipole-induced dipole forces, and hydrophobic forces. Because of their nonpolar molecular structure, hydrocarbons most commonly exhibit sorption through the process of hydrophobic bonding. When the surfaces comprising the aquifer matrix are less polar than the water molecule, as is generally the case, there is a strong tendency for the nonpolar contaminant molecules to partition from the groundwater and sorb to the aquifer matrix. This phenomenon is referred to as hydrophobic bonding and is an important factor controlling the fate of many organic pollutants in soils (Devinny *et al.*, 1990). Two components of an aquifer have the greatest effect on sorption: organic matter and clay minerals. In most aquifers, the organic fraction tends to control the sorption of organic contaminants.

B.2.3.2 Sorption Models and Isotherms

Regardless of the sorption mechanism, it is possible to determine the amount of sorption to be expected when a given dissolved contaminant interacts with the materials comprising the aquifer matrix. Bench-scale experiments are performed by mixing water-contaminant solutions of various concentrations with aquifer materials containing various amounts of organic carbon and clay minerals. The solutions are then sealed with no headspace and left until equilibrium between the various phases is reached. The amount of contaminant left in solution is then measured.

Both environmental conservative isotherms (ECI) and constant soil to solution isotherms (CSI) can be generated. The ECI study uses the same water concentration but changes the soil to water ratio. In CSI isotherm studies the concentration of contaminant in water is varied while the amount of water and sediment is constant. In some instances, actual contaminated water from the site is added. Typically the samples are continually rotated and concentrations measured with time to document equilibrium. True equilibrium may require hundreds of hours of incubation but 80 to 90 percent of equilibrium may be achieved in one or two days.

The results are commonly expressed as a plot of the concentration of chemical sorbed (µg/g) versus the concentration remaining in solution (µg/L). The relationship between the concentration of chemical sorbed (C_a) and the concentration remaining in solution (C_l) at equilibrium is referred to as the sorption isotherm because the experiments are performed at constant temperature.

Sorption isotherms generally exhibit one of three characteristic shapes depending on the sorption mechanism. These isotherms are referred to as the Langmuir isotherm, the Freundlich isotherm, and the linear isotherm (a special case of the Freundlich isotherm). Each of these sorption isotherms, and related equations, are discussed in the following sections.

B.2.3.2.1 Langmuir Sorption Model

The Langmuir model describes sorption in solute transport systems wherein the sorbed concentration increases linearly with increasing solute concentration at low concentrations and approaches a constant value at high concentrations. The sorbed concentration approaches a constant value because there are a limited number of sites on the aquifer matrix available for contaminant sorption. This relationship is illustrated in Figure B.4.3. The Langmuir equation is described mathematically as (Devinney *et al.*, 1990):

$$C_a = \frac{KC_l b}{1 + KC_l} \qquad \text{eq. B.2.10}$$

Where:
- C_a = sorbed contaminant concentration (mass contaminant/mass soil)
- K = equilibrium constant for the sorption reaction (µg/g)
- C_l = dissolved contaminant concentration (µg/ml)
- b = number of sorption sites (maximum amount of sorbed contaminant)

The Langmuir model is appropriate for highly specific sorption mechanisms where there are a limited number of sorption sites. This model predicts a rapid increase in the amount of sorbed contaminant as contaminant concentrations increase in a previously pristine area. As sorption sites become filled, the amount of sorbed contaminant reaches a maximum level equal to the number of sorption sites, b.

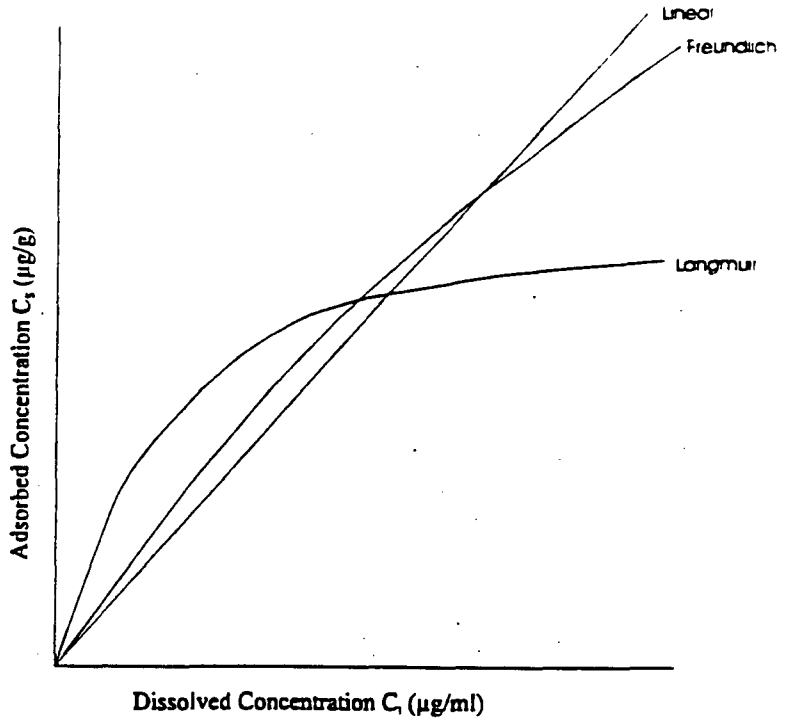

Figure B.2.10 Characteristic adsorption isotherm shapes.

B.2.3.2.2 Freundlich Sorption Model

The Langmuir isotherm model can be modified if the number of sorption sites is large (assumed infinite) relative to the number of contaminant molecules. This is generally a valid assumption for dilute solutions (e.g., downgradient from a petroleum hydrocarbon spill in the dissolved BTEX plume) where the number of unoccupied sorption sites is large relative to contaminant concentrations. The Freundlich model is expressed mathematically as (Devinny *et al.*, 1990):

$$C_a = K_d C_l^{1/n} \qquad \text{eq. B.2.11}$$

Where: K_d = distribution coefficient
C_a = sorbed contaminant concentration (mass contaminant/mass soil, µg/g)
C_l = dissolved concentration (mass contaminant/volume solution, (µg/ml)
n = chemical-specific coefficient

The value of n in this equation is a chemical-specific quantity that is determined experimentally. Values of 1/n typically range from 0.7 to 1.1, but may be as low as 0.3 and as high as 1.7 (Lyman *et al.* 1992).

The simplest expression of equilibrium sorption is the linear sorption isotherm, a special form of the Freundlich isotherm that occurs when the value of n is 1. The linear isotherm is valid for a

dissolved species that is present at a concentration less than one half of its solubility (Lyman *et al.*, 1992). This is a valid assumption for BTEX compounds partitioning from fuel mixtures into groundwater. Dissolved BTEX concentrations resulting from this type of partitioning are significantly less than the pure compound's solubility in pure water. The linear sorption isotherm is expressed as (Jury *et al.*, 1991):

$$C_a = K_d C_l \qquad \text{eq. B.2.12}$$

Where: K_d = distribution coefficient (slope of the isotherm, ml/g).
C_a = sorbed contaminant concentration (mass contaminant/mass soil, µg/g)
C_l = dissolved contaminant concentration (mass contaminant/volume solution, µg/ml)

The slope of the linear isotherm is the distribution coefficient, K_d.

B.2.3.3 Distribution Coefficient

The most commonly used method for expressing the distribution of an organic compound between the aquifer matrix and the aqueous phase is the distribution coefficient, K_d, which is defined as the ratio of the sorbed contaminant concentration to the dissolved contaminant concentration:

$$K_d = \frac{C_a}{C_l} \qquad \text{eq. B.2.13}$$

Where: K_d = distribution coefficient (slope of the sorption isotherm, ml/g).
C_a = sorbed concentration (mass contaminant/mass soil or µg/g)
C_l = dissolved concentration (mass contaminant/volume solution or µg/ml)

The transport and partitioning of a contaminant is strongly dependent on the chemical's soil/water distribution coefficient and water solubility. The distribution coefficient is a measure of the sorption/desorption potential and characterizes the tendency of an organic compound to be sorbed to the aquifer matrix. The higher the distribution coefficient, the greater the potential for sorption to the aquifer matrix. The distribution coefficient is the slope of the sorption isotherm at the contaminant concentration of interest. The greater the amount of sorption, the greater the value of K_d. For systems described by a linear isotherm, K_d is a constant. In general terms, the distribution coefficient is controlled by the hydrophobicity of the contaminant and the total surface area of the aquifer matrix available for sorption. Thus, the distribution coefficient for a single

compound will vary with the composition of the aquifer matrix. Because of their extremely high specific surface areas (ratio of surface area to volume), the organic carbon and clay mineral fractions of the aquifer matrix generally present the majority of sorption sites in an aquifer.

Based on the research efforts of Ciccioli *et al.* (1980), Rodgers *et al.* (1980), Karickhoff *et al.* (1979), and Shwarzenbach and Westall (1981), it appears that the primary adsorptive surface for organic chemicals is the organic fraction of the aquifer matrix. However, there is a "critical level of organic matter" below which sorption onto mineral surfaces is the dominant sorption mechanism (McCarty *et al.*, 1981). The critical level of organic matter, below which sorption appears to be dominated by mineral-solute interactions, and above which sorption is dominated by organic carbon-solute interactions, is given by (McCarty *et al.*, 1981)

$$f_{oc_c} = \frac{A_s}{200} \frac{1}{K_{ow}^{0.84}} \qquad \text{eq. B.2.14}$$

Where: f_{oc_c} = critical level of organic matter (mass fraction)
A_s = surface area of mineralogical component of the aquifer matrix
K_{ow} = octanol-water partitioning coefficient

From this relationship it is apparent that the total organic carbon content of the aquifer matrix is less important for solutes with low octanol-water partitioning coefficients (K_{ow}). Also apparent is the fact that the critical level of organic matter increases as the surface area of the mineralogic fraction of the aquifer matrix increases. The surface area of the mineralogic component of the aquifer matrix is most strongly influenced by the amount of clay. For compounds with low K_{ow} values in materials with a high clay content, sorption to mineral surfaces could be an important factor causing retardation of the chemical.

Several researchers have found that if the distribution coefficient is normalized relative to the aquifer matrix total organic carbon content, much of the variation in observed K_d values between different soils is eliminated (Dragun, 1988). Distribution coefficients normalized to total organic carbon content are expressed as K_{oc}. The following equation gives the expression relating K_d to K_{oc}:

$$K_{oc} = \frac{K_d}{f_{oc}} \qquad \text{eq. B.2.15}$$

Where: K_{oc} = soil sorption coefficient normalized for total organic carbon content
K_d = distribution coefficient
f_{oc} = fraction total organic carbon (mg organic carbon/mg soil)

In areas with high clay concentrations and low total organic carbon concentrations, the clay minerals become the dominant sorption sites. Under these conditions, the use of K_{oc} to compute K_d might result in underestimating the importance of sorption in retardation calculations, a source of error that will make retardation calculations based on the total organic carbon content of the aquifer matrix more conservative. In fact, aquifers that have a high enough hydraulic conductivity to spread hydrocarbon contamination generally have low clay content. In these cases, the contribution of sorption to mineral surfaces is generally trivial.

Earlier investigations reported distribution coefficients normalized to total organic matter content (K_{om}). The relationship between f_{om} and f_{oc} is nearly constant and, assuming that the organic matter contains approximately 58 percent carbon (Lyman *et al.*, 1992):

$$K_{oc} = 1.724 K_{om} \qquad \text{eq. B.2.16}$$

B.2.3.4 Coefficient of Retardation

As mentioned earlier, sorption tends to slow the transport velocity of contaminants dissolved in groundwater. The coefficient of retardation, R, is used to estimate the retarded contaminant velocity. The coefficient of retardation for linear sorption is determined from the distribution coefficient using the relationship:

$$R = 1 + \frac{\rho_b K_d}{n} \qquad \text{eq. B.2.17}$$

Where: R = coefficient of retardation [dimensionless]
ρ_b = bulk density of aquifer [M/L^3]
K_d = distribution coefficient [L^3/M]
n = porosity [L^3/L^3]

The retarded contaminant transport velocity, v_c, is given by:

$$v_c = \frac{v_x}{R} \qquad \text{eq. B.2.18}$$

Where: v_c = retarded contaminant transport velocity [L/T]
v_x = advective groundwater velocity [L/T]
R = coefficient of retardation [dimensionless]

Two methods used to quantify the distribution coefficient and amount of sorption (and thus retardation) for a given aquifer/contaminant system are presented below. The first method involves estimating the distribution coefficient by using K_{oc} for the contaminants and the fraction of organic carbon comprising the aquifer matrix. The second method involves conducting batch or column tests to determine the distribution coefficient. Because numerous authors have conducted experiments to determine K_{oc} values for common contaminants, literature values are reliable, and it generally is not necessary to conduct laboratory tests.

B.2.3.4.1 Determining the Coefficient of Retardation using K_{oc}

Batch and column tests have been performed for a wide range of contaminant types and concentrations and aquifer conditions. Numerous studies have been performed using the results of these tests to determine if relationships exist that are capable of predicting the sorption characteristics of a chemical based on easily measured parameters. The results of these studies indicate that the amount of sorption is strongly dependent on the amount of organic carbon present in the aquifer matrix and the degree of hydrophobicity exhibited by the contaminant (Bailey and White, 1970; Karickhoff *et al.*, 1979; Kenaga and Goring, 1980; Brown and Flagg, 1981; Schwarzenbach and Westall, 1981; Hassett *et al.*, 1983; Chiou *et al.*, 1983). These researchers observed that the distribution coefficient, K_d, was proportional to the organic carbon fraction of the aquifer times a proportionality constant. This proportionality constant, K_{oc}, is defined as given by equation B.2.15. In effect, equation B.2.15 normalizes the distribution coefficient to the amount of organic carbon in the aquifer matrix. Because it is normalized to organic carbon, values of K_{oc} are dependent only on the properties of the compound (not on the type of soil). Values of K_{oc} have been determined for a wide range of chemicals. Table B.2.1 lists K_{oc} values for selected chlorinated compounds, and Table B.2.2 lists K_{oc} values for BTEX and trimethylbenzene.

By knowing the value of K_{oc} for a contaminant and the fraction of organic carbon present in the aquifer, the distribution coefficient can be determined by using the relationship:

$$K_d = K_{oc} f_{oc} \qquad \text{eq. B.2.19}$$

When using the method presented in this section to predict sorption of the BTEX compounds, total organic carbon concentrations obtained from the most transmissive aquifer zone should be averaged and used for predicting sorption. This is because the majority of dissolved contaminant transport occurs in the most transmissive portions of the aquifer. In addition, because the most

transmissive aquifer zones generally have the lowest total organic carbon concentrations, the use of this value will give a conservative prediction of contaminant sorption and retardation.

Table B.2.1
Values of Aqueous Solubility and K_{oc} for selected chlorinated compounds

Compound	Solubility (mg/L)	K_{OC} (L/Kg)
Tetrachloroethene	150[a]	263[a]
Tetrachloroethene		359[b]
Tetrachloroethene	1,503[c]	209 - 238[c]
Trichloroethene	1,100[a]	107[a]
Trichloroethene		137[b]
Trichloroethene	1,100[c]	87 - 150[c]
1,1-Dichloroethene	2,250[a]	64.6[a]
1,1-Dichloroethene		80.2[b]
1,1-Dichloroethene	2,500[d]	150[d]
cis-1,2-Dichloroethene		80.2[b]
cis-1,2-Dichloroethene	3,500[c]	49[c]
trans-1,2-Dichloroethene	6,300[a]	58.9[a]
trans-1,2-Dichloroethene		80.2[b]
trans-1,2-Dichloroethene	6,300[c]	36[c]
Vinyl Chloride	1,100[a]	2.45[a]
Vinyl Chloride	2,763[d]	0.4 - 56[d]
1,1,1-Trichloroethane	1,495[c]	183[c]
1,1,2-Trichloroethane	4,420[e]	70[e]
1,1-Dichloroethane	5,060[d]	40[d]
1,2-Dichloroethane	8,520[c]	33 to 152[c]
Chloroethane	5,710[e]	33 to 143[e]
Hexachlorobenzene	0.006[f]	--
1,2-Dichlorobenzene	156[c]	272 - 1480[c]
1,3-Dichlorobenzene	111[g]	293 to 31,600[g]
1,4-Dichlorobenzene	74 to 87[d]	273 to 1833[d]
Chlorobenzene	472[d]	83 to 389[d]
Carbon Tetrachloride	805[g]	110[g]
Chloroform	7,950[c]	<34[c]
Methylene Chloride	13,000[c]	48[c]

[a] From Knox *et al.*, 1993
[b] From Jeng *et al.*, 1992; Temperature = 20°C
[c] From Howard, 1990; Temperature = 25°C
[d] From Howard, 1989; Temperature = 25°C
[e] From Howard, 1989; Temperature = 20°C
[f] ATSDR, 1990; Temperature = 20°C
[g] From Howard, 1990; Temperature = 20°C

Table B.2.2
Values of Aqueous Solubility and K_{oc} for BTEX and Trimethylbenzene Isomers

Compound	Solubility (mg/L)	K_{OC} (L/Kg)
Benzene	1750[a]	87.1[a]
Benzene		83[b]
Benzene	1780[c]	190[c,d,f]
Benzene	1780[c]	62[c,e,f]
Benzene	1780[h]	72[h,i]
Benzene*	1780[h]	79[h,i,*]
Benzene	1780[c,h]	89[k]
Toluene	515[a]	151[a]
Toluene		303[b]
Toluene	537[c]	380[c,d,f]
Toluene	537[c]	110[c,e,f]
Toluene*	537[c]	190[k,*]
Ethylbenzene	152[a]	158.5[a]
Ethylbenzene		519[b]
Ethylbenzene	167[c]	680[c,d,f]
Ethylbenzene	167[c]	200[c,e,f]
Ethylbenzene	140[h]	501[h,i]
Ethylbenzene*	140[h]	468[h,j]
Ethylbenzene	167[c]	398[k]
o-xylene	152[a]	128.8[a]
o-xylene		519[b]
o-xylene*	152[a]	422[k,*]
m-xylene	158[a]	
m-xylene		519[b]
m-xylene	162[c]	720[c,d,f]
m-xylene	162[c]	210[c,e,f]
m-xylene*	162[c]	405.37[k,*]
p-xylene	198[a]	204[a]
p-xylene		519[b]
p-xylene*	198[a]	357[k,*]
1,2,3-trimethylbenzene*	75	884[b,*]
1,2,4-trimethylbenzene	59[l]	884[b]
1,2,4-trimethylbenzene*	59[l]	772[k,*]
1,3,5-trimethylbenzene*	72.60[g]	676[k,*]

[a] From Knox *et al.*, 1993
[b] From Jeng *et al.*, 1992; Temperature = 20°C
[c] From Lyman *et al.*, 1992; Temperature = 25°C
[d] Estimated from K_{ow}
[e] Estimated from solubility
[f] Estimate from solubility generally considered more reliable
[g] From Lyman *et al.*, 1992; Temperature = 20°C
[h] From Fetter, 1993
[i] Average of 12 equations used to estimate K_{oc} from K_{ow} or K_{om}
[j] Average of 5 equations used to estimate K_{oc} from Solubility
[k] Average using equations from Kanaga and Goring (1980), Means *et al.* (1980), and Hassett *et al.* (1983) to estimate K_{oc} from solubility
[l] From Sutton and Calder (1975)
[*] Recommended value

B.2.3.4.2 Determining the Coefficient of Retardation using Laboratory Tests

The distribution coefficient may be quantified in the laboratory using batch or column tests Batch tests are easier to perform than column tests. Although more difficult to perform, column tests generally produce a more accurate representation of field conditions than batch tests because continuous flow is involved. Knox *et al.* (1993) suggest using batch tests as a preliminary screening tool, followed by column studies to confirm the results of batch testing. The authors of this document feel that batch tests, if conducted properly, will yield sufficiently accurate results for fate and transport modeling purposes provided that sensitivity analyses for retardation are conducted during the modeling.

Batch testing involves adding uncontaminated aquifer material to a number of vessels, adding solutions prepared using uncontaminated groundwater from the site mixed with various amounts of contaminants to produce varying solute concentrations, sealing the vessel and shaking it until equilibrium is reached, analyzing the solute concentration remaining in solution, and calculating the amount of contaminant sorbed to the aquifer matrix using mass balance calculations. A plot of the concentration of contaminant sorbed versus dissolved equilibrium concentration is then made using the data for each reaction vessel. The slope of the line formed by connecting each data point is the distribution coefficient. The temperature should be held constant during the batch test, and should approximate that of the aquifer system through which solute transport is taking place.

Table B.2.3 contains data from a hypothetical batch test. These data are plotted (Figure B.2.11) to obtain an isotherm unique to the aquifer conditions at the site. A regression analysis can then be performed on these data to determine the distribution coefficient. For linear isotherms, the distribution coefficient is simply the slope of the isotherm. In this example, K_d = 0.0146 L/g. Batch-testing procedures are described in detail by Roy *et al.* (1992).

Column testing involves placing uncontaminated aquifer matrix material in a laboratory column and passing solutions through the column. Solutions are prepared by mixing uncontaminated groundwater from the site with the contaminants of interest and a conservative tracer. Flow rate and time are accounted for and samples are periodically taken from the effluent end of the column and analyzed to determine contaminant and tracer concentrations. Breakthrough curves are prepared for the contaminants by plotting chemical concentration versus time (or relative concentration versus number of pore volumes). The simplest way to determine the coefficient of retardation (or the distribution coefficient) from the breakthrough curves is to determine the time

required for the effluent concentration to equal 0.5 of the influent concentration. This value can be used to determine average velocity of the center of mass of the contaminant. The retardation factor is determined by dividing the average flow velocity through the column by the velocity of the center of mass of the contaminant. The value thus obtained is the retardation factor. The coefficient of retardation also can be determined by curve fitting using the CXTFIT model of Parker and van Genuchten (1984). Breakthrough curves also can be made for the conservative tracer. These curves can be used to determine the coefficient of dispersion by curve fitting using the model of Parker and van Genuchten (1984).

Table B.2.3
Data from Hypothetical Batch Test Experiment

Initial Concentration (µg/L)	Equilibrium Concentration (µg/L)	Weight of Solid Matrix (g)	Sorbed Concentration* (µg/g)
250	77.3	20.42	1.69
500	150.57	20.42	3.42
1000	297.04	20.42	6.89
1500	510.1	20.42	9.70
2000	603.05	20.42	13.68
3800	1198.7	20.42	25.48
6000	2300.5	20.42	36.23
9000	3560.7	20.42	53.27

*Adsorbed Concentration = ((Initial Concentration-Equilibrium Concentration)*Volume of Solution)/Weight of Solid Matrix

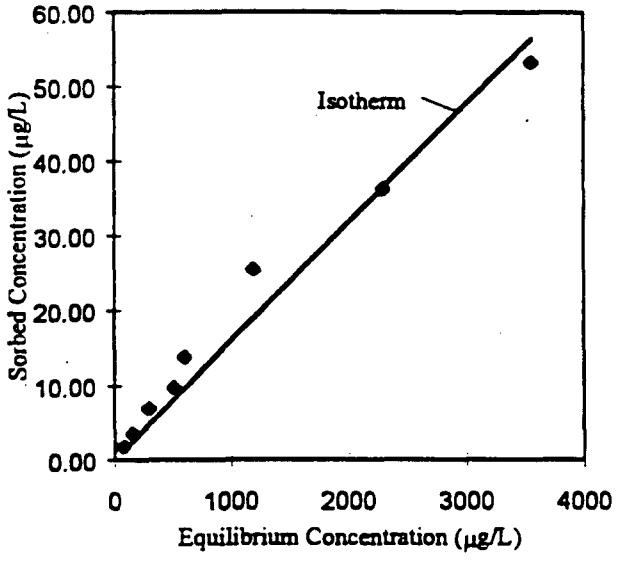

Figure B.2.11 Plot of sorbed concentration vs. equilibrium concentration.

When using the method presented in this section to predict sorption of the BTEX compounds, aquifer samples should be obtained from the most transmissive aquifer zone. This is because the majority of dissolved contaminant transport occurs in the most transmissive portions of the aquifer. In addition, because the most transmissive aquifer zones generally have the lowest organic carbon concentrations, the use of these materials will give a conservative prediction of contaminant sorption and retardation.

B.2.3.5 One-Dimensional Advection-Dispersion Equation with Retardation

The advection-dispersion equation is obtained by adding hydrodynamic dispersion to equation B.2.2. In one dimension, the advection-dispersion equation is given by:

$$R\frac{\partial C}{\partial t} = D_x\frac{\partial^2 C}{\partial x^2} - v_x\frac{\partial C}{\partial x} \qquad \text{eq. B.2.20}$$

Where: v_x = average linear velocity groundwater velocity [L/T]
R = coefficient of retardation [dimensionless]
C = contaminant concentration [M/L^3]
D_x = hydrodynamic dispersion [L^2/T]
t = time [T]
x = distance along flow path [L]

This equation considers advection, hydrodynamic dispersion, and sorption (retardation). Because of biodegradation, this equation generally must be combined with the other components of the modified advection-dispersion equation, presented as equation B.1.1, to obtain an accurate mathematical description of solute transport.

B.2.4 VOLATILIZATION

While not a destructive attenuation mechanism, volatilization does remove contaminants from the groundwater system. In general, factors affecting the volatilization of contaminants from groundwater into soil gas include the contaminant concentration, the change in contaminant concentration with depth, the Henry's Law constant and diffusion coefficient of the compound, mass transport coefficients for the contaminant in both water and soil gas, sorption, and the temperature of the water (Larson and Weber, 1994).

Partitioning of a contaminant between the liquid phase and the gaseous phase is governed by Henry's Law. Thus, the Henry's Law constant of a chemical determines the tendency of a contaminant to volatilize from groundwater into the soil gas. Henry's Law states that the

concentration of a contaminant in the gaseous phase is directly proportional to the compound's concentration in the liquid phase and is a constant characteristic of the compound. Stated mathematically, Henry's Law is given by (Lyman *et al.*, 1992):

$$C_a = HC_l \qquad \text{eq. B.2.21}$$

Where: H = Henry's Law Constant (atm m^3/mol)
C_a = concentration in air (atm)
C_l = concentration in water (mol/m^3)

Henry's Law constants for chlorinated and petroleum hydrocarbons range over several orders of magnitude. For petroleum hydrocarbons, Henry's Law constants (H) for the saturated aliphatics range from 1 to 10 atm m^3/mol @ 25°C, for the unsaturated and cyclo-aliphatics H range from 0.1 to 1 atm m^3/mol @ 25°C, and for the light aromatics (e.g., BTEX) H ranges from 0.007 to 0.02 atm m^3/mol @ 25°C (Lyman *et al.*, 1992). Values of Henry's Law constants for selected chlorinated solvents and the BTEX compounds are given in Table B.2.4. As indicated on the table, values of H for chlorinated compounds also vary over several orders of magnitude, although most are similar to those for BTEX compounds.

The physiochemical properties of chlorinated solvents and the BTEX compounds give them low Henry's Law constants, with the exception of vinyl chloride. Because of the small surface area of the groundwater flow system exposed to soil gas, volatilization of chlorinated solvents and BTEX compounds from groundwater is a relatively slow process that, in the interest of being conservative, generally can be neglected when modeling biodegradation. Chiang *et al.* (1989) demonstrated that less than 5 percent of the mass of dissolved BTEX is lost to volatilization in the saturated groundwater environment. Moreover, Rivett (1995) observed that for plumes more than about 1 meter below the air-water interface, little, if any, solvent concentrations will be detectable in soil gas due to the downward groundwater velocity in the vicinity of the water table. This suggests that for portions of plumes more than 1 meter below the water table, very little, if any, mass will be lost due to volatilization. In addition, vapor transport across the capillary fringe can be very slow (McCarthy and Johnson, 1993), thus further limiting mass transfer rates. Because of this, the impact of volatilization on dissolved contaminant reduction can generally be neglected, except possibly in the case of vinyl chloride. However, Rivett's (1995) findings should be kept in mind even when considering volatilization as a mechanism for removal of vinyl chloride from groundwater.

Table B.2.4
Henry's Law Constants and Vapor Pressures for
Common Fuel Hydrocarbons and Chlorinated Solvents

Compound	Vapor Pressure (mmHg @ 25°C)	Henry's Law Constant (atm-m^3/mol)
Benzene	95	0.0054
Ethylbenzene	10	0.0066
Toluene	28.4	0.0067
o-Xylene	10	0.00527
m-Xylene	10	0.007
p-Xylene	10	0.0071
1,2,3-Trimethylbenzene		0.00318
1,2,4-Trimethylbenzene		0.007
1,3,5-Trimethylbenzene		0.006
1,2,4,5-Tetramethylbenzene		0.0249
Tetrachloroethene	14	0.0153
Trichloroethene	57.8	0.0091
1,1-Dichloroethene	591	0.018
cis-1,2-Dichloroethene	200	0.0037
trans-1,2-Dichloroethene	265	0.0072
Vinyl Chloride	2,580	1.22
1,1,1-Trichloroethane	123.7	0.008
1,1,2-Trichloroethane	30.3	0.0012
1,1-Dichloroethane	227	0.0059
1,2-Dichloroethane	78.7	0.00098
Chloroethane	766	0.0085
Hexachlorobenzene	0.0000109	0.00068
1,2-Dichlorobenzene	1.47	0.0012
1,3-Dichlorobenzene	2.3	0.0018
1,4-Dichlorobenzene	1.76	0.0015
Chlorobenzene	11.9	0.0035
Carbon Tetrachloride	113.8	0.0304
Chloroform	246	0.00435
Methylene Chloride	434.9	0.00268

B.2.5 RECHARGE

Groundwater recharge can be defined as the entry into the saturated zone of water made available at the water-table surface (Freeze and Cherry, 1979). In recharge areas, flow near the water table is generally downward. Recharge defined in this manner may therefore include not only precipitation that infiltrates through the vadose zone, but water entering the groundwater system due to discharge from surface water bodies (i.e., streams and lakes). Where a surface water body is in contact with or is part of the groundwater system, the definition of recharge above is stretched slightly. However, such bodies are often referred to as recharging lakes or

streams. Recharge of a water table aquifer has two effects on the natural attenuation of a dissolved contaminant plume. Additional water entering the system due to infiltration of precipitation or from surface water will contribute to dilution of the plume, and the influx of relatively fresh, electron-acceptor-charged water will alter geochemical processes and in some cases facilitate additional biodegradation.

Recharge from infiltrating precipitation is the result of a complex series of processes in the unsaturated zone. Description of these processes is beyond the scope of this discussion; however, it is worth noting that the infiltration of precipitation through the vadose zone brings the water into contact with the soil and thus may allow dissolution of additional electron acceptors and possibly organic soil matter (a potential source of electron donors). Infiltration therefore provides fluxes of water, inorganic species, and possibly organic species into the groundwater. Recharge from surface water bodies occurs when the hydraulic head of the body is greater than that of the adjacent groundwater. The surface water may be a connected part of the groundwater system, or it may be perched above the water table. In either case, the water entering the groundwater system will not only aid in dilution of a contaminant plume but it may also add electron acceptors and possibly electron donors to the groundwater.

An influx of electron acceptors will tend to increase the overall electron-accepting capacity within the contaminant plume. In addition to the inorganic electron acceptors that may be dissolved in the recharge (e.g., dissolved oxygen, nitrate, or sulfate), the introduction of water with different geochemical properties may foster geochemical changes in the aquifer. For example, iron (II) will be oxidized back to iron (III). Vroblesky and Chapelle (1994) present data from a site where a major rainfall event introduced sufficient dissolved oxygen into the contaminated zone to cause reprecipitation of iron (III) onto mineral grains. This reprecipitation made iron (III) available for reduction by microorganisms, thus resulting in a shift from methanogenesis back to iron (III) reduction (Vroblesky and Chapelle, 1994). Such a shift may be beneficial for biodegradation of compounds used as electron donors, such as fuel hydrocarbons or vinyl chloride. However, these shifts can also make conditions less favorable for reductive dehalogenation.

Evaluating the effects of recharge is typically difficult. The effects of dilution might be estimated if one has a detailed water budget for the system in question, but if a plume has a significant vertical extent, it cannot be known with any certainty what proportion of the plume mass is being diluted by the recharge. Moreover, because dispersivity, sorption, and biodegradation are often not well-quantified, separating out the effects of dilution may be very difficult indeed. Where recharge enters from precipitation, the effects of the addition of electron

acceptors may be qualitatively apparent due to elevated electron acceptor concentrations or differing patterns in electron acceptor consumption or byproduct formation in the area of the recharge. However, the effects of short-term variations in such a system (which are likely due to the intermittent nature of precipitation events in most climates) may not be easily understood. Where recharge enters from surface water, the influx of mass and electron acceptors is more steady over time. Quantifying the effects of dilution may be less uncertain, and the effects of electron acceptor replenishment may be more easily identified (though not necessarily quantified).

SECTION B-3

DESTRUCTIVE ATTENUATION MECHANISMS - BIOLOGICAL

Many anthropogenic organic compounds, especially chlorinated solvents, can be degraded by both biological and abiotic mechanisms. Biological degradation mechanisms are discussed in this section; abiotic degradation mechanisms are discussed in Section B.4. Table B.3.1 summarizes the various biotic and abiotic mechanisms that result in the degradation of anthropogenic organic compounds. Biological degradation mechanisms tend to dominate in most groundwater systems, depending on the type of contaminant and the groundwater chemistry.

Table B.3.1
Biologic and Abiotic Degradation Mechanisms for Various Anthropogenic Organic Compounds

Compound	Degradation Mechanism
PCE	Reductive dechlorination, cometabolism
TCE	Reductive dechlorination, cometabolism
DCE	Reductive dechlorination, direct biological oxidation
VC	Reductive dechlorination, direct biological oxidation
TCA	Reductive dechlorination, hydrolysis, dehydrohalogenation
DCA	Reductive dechlorination, direct biological oxidation
CA	Hydrolysis
Carbon Tetrachloride	Reductive dechlorination, cometabolism, abiotic(?)
Chloroform	Cometabolism
Methylene Chloride	Direct biological oxidation
Chlorobenzenes	Direct biological oxidation, reductive dechlorination, cometabolism
Benzene	Direct biological oxidation
Toluene	Direct biological oxidation
Ethylbenzene	Direct biological oxidation
Xylenes	Direct biological oxidation

Many organic contaminants are biodegraded by microorganisms indigenous to the subsurface environment. During biodegradation, dissolved contaminants are ultimately transformed into innocuous byproducts such as carbon dioxide, chloride, methane, and water. In some cases, intermediate products of these transformations may be more hazardous than the original

compound; however, they may also be more easily degraded. Biodegradation of organic compounds dissolved in groundwater results in a reduction in contaminant concentration (and mass) and slowing (retardation) of the contaminant relative to the average advective groundwater flow velocity. Figures B.3.1 and B.3.2 illustrate the effects of biodegradation on an advancing solute front.

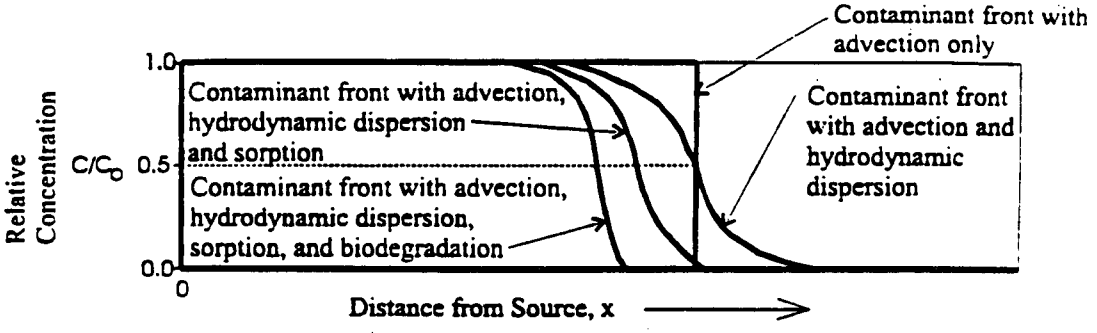

Figure B.3.1 Breakthrough Curve in One Dimension Showing Plug Flow with Continuous Source Resulting from Advection Only; the Combined Processes of Advection and Hydrodynamic Dispersion; the Combined Processes of Advection, Hydrodynamic Dispersion, and Sorption; and the Combined Processes of Advection, Hydrodynamic Dispersion, Sorption, and Biodegradation

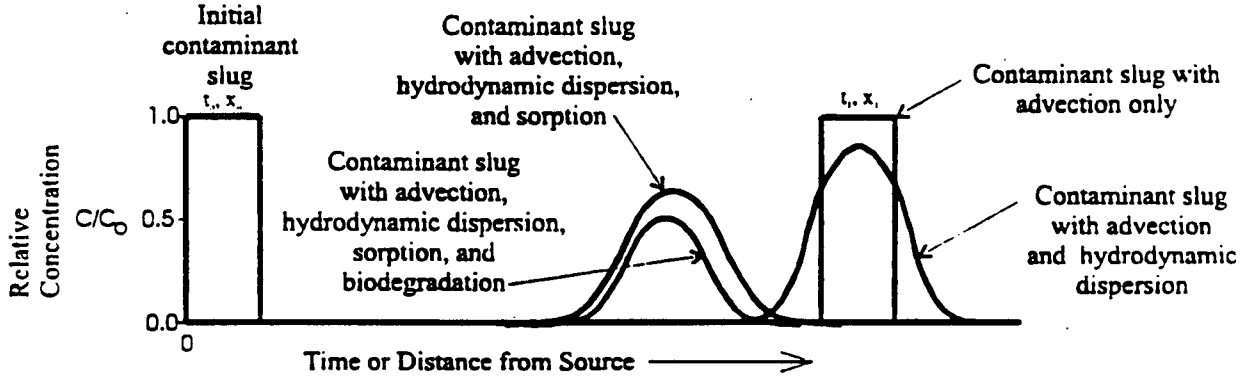

Figure B.3.2 Breakthrough Curve in One Dimension Showing Plug Flow with Instantaneous Source Resulting from Advection Only; the Combined Processes of Advection and Hydrodynamic Dispersion; the Combined Processes of Advection, Hydrodynamic Dispersion, and Sorption; and the Combined Processes of Advection, Hydrodynamic Dispersion, Sorption, and Biodegradation

B.3.1 OVERVIEW OF BIODEGRADATION

As recently as 1975 the scientific literature reported the subsurface/aquifer environment as devoid of significant biological activity. It is now known that soils and shallow sediments contain a large variety of microorganisms, ranging from simple prokaryotic bacteria and cyanobacteria to

more complex eukaryotic algae, fungi, and protozoa. Over the past two decades, numerous laboratory and field studies have shown that microorganisms indigenous to the subsurface environment can degrade a variety of organic compounds, including components of gasoline, kerosene, diesel, jet fuel, chlorinated ethenes, chlorinated ethanes, the chlorobenzenes, and many other compounds (e.g., for fuels see Jamison *et al.*, 1975; Atlas, 1981, 1984, and 1988; Young, 1984; Bartha, 1986; B. H. Wilson *et al.*, 1986 and 1990; Barker *et al.*, 1987; Baedecker *et al.*, 1988; Lee, 1988; Chiang *et al.*, 1989; Cozzarelli *et al.*, 1990; Leahy and Colewell, 1990; Alvarez and Vogel, 1991; Evans *et al.*, 1991a and 1991b; Edwards *et al.*, 1992; Edwards and Grbic-Galic, 1992; Thierrin *et al.*, 1992; Malone *et al.*, 1993; Davis *et al.*, 1994a and 1994b; and Lovley *et al.*, 1995; and for chlorinated solvents see Brunner and Leisinger, 1978; Brunner *et al.*, 1980; Rittman and McCarty, 1980; Bouwer *et al.*, 1981; Miller and Guengerich, 1982; Roberts *et al.*, 1982; Bouwer and McCarty, 1983; Stucki *et al.*, 1983; Reineke and Knackmuss, 1984; Wilson and Wilson, 1985; Fogel *et al.*, 1986; Egli *et al.*, 1987; Vogel and McCarty, 1987; Vogel *et al.*, 1987; Bouwer and Wright, 1988; Little *et al.*, 1988; Freedman and Gossett, 1989; Sewell and Gibson, 1991; Chapelle, 1993; DeBruin *et al.*, 1992; Ramanand *et al.*, 1993; Vogel, 1994; Suflita and Townsend, 1995; Adriaens and Vogel, 1995; Bradley and Chapelle, 1996; Gossett and Zinder, 1996; Spain, 1996). Table B.3.2 presents a partial list of microorganisms known to degrade anthropogenic organic compounds.

Although we now recognize the ubiquitous nature and significance of subsurface microorganisms, the study of the microbial ecology and physiology of the subsurface, below the rhizosphere, is still in its infancy. However, great progress has been made at least in identifying, if not fully understanding, the numerous and diverse types of microbially-mediated contaminant transformations that can occur in the subsurface.

Chemothrophic organisms, such as humans and most microorganisms, obtain energy for growth and activity from physiologically coupling oxidation and reduction reactions and harvesting the potential/chemical energy that is available. Under aerobic conditions (in the presence of molecular oxygen) humans and many bacteria couple the oxidation of organic compounds (food) to the reduction of oxygen (from the air). However in the absence of oxygen (anaerobic conditions), microorganisms may use other compounds as electron acceptors. Anaerobic microorganisms can obtain energy from a variety of electron donors and acceptors. During reductive dechlorination, the chlorinated compound acts as the electron acceptor resulting in the removal of a chloride atom and the addition of a proton in a two electron transfer. This process must be linked to the oxidation of an electron donor. In some cases, the chlorinated aromatics can serve as both an electron donor and an electron acceptor (Tiedje and Stevens,

1988), but with chloroethenes another source of reducing equivalents (electron donor) generally must be supplied. Some chlorinated ethenes and ethanes may serve as electron donors or substrates, such as vinyl chloride, 1,2-dichloroethane, and dichloromethane (McCarty and Semprini, 1994; Bradley and Chapelle, 1996).

Table B.3.2

Some Microorganisms Capable of Degrading Organic Compounds
(Modified from Riser-Roberts, 1992).

Contaminant	Microorganisms	Comments/ Biodegradability
Benzene	*Pseudomonas putida, P. rhodochrous, P. aeruginosa, Acinetobacter sp., Methylosinus trichosporium* OB3b, *Nocardia sp., methanogens, anaerobes*	Moderate to High
Toluene	*Methylosinus trichosporium* OB3b, *Bacillus sp., Pseudomonas sp., P. putida, Cunninghamella elegans, P. aeruginosa, P. mildenberger, P. aeruginosa, Achromobacter sp., methanogens, anaerobes*	High
Ethylbenzene	*Pseudomonas putida*	High
Xylenes	*Pseudomonas putida, methanogens, anaerobes*	High
Jet Fuels	*Cladosporium, Hormodendrum*	High
Kerosene	*Torulopsis, Candidatropicalis, Corynebacterium hydrocarboclastus, Candidaparapsilosis, C. guilliermondii, C. lipolytica, Trichosporon sp., Rhohosporidium toruloides, Cladosporium resinae*	High
Chlorinated Ethenes	*Dehalobacter restrictus, Dehalospirillum multivorans, Enterobacter agglomerans, Dehalococcus entheogenes* strain 195,*Desulfitobacterium sp.* strain PCE1, *Pseudomonas putida* (multiple strains), *P. cepacia* G4, *P. mendocina, Desulfobacterium sp., Methanobacterium sp., Methanosarcina sp.* strain DCM, *Alcaligenes eutrophus* JMP 134, *Methylosinus trichosporium OB3b, Escherichia coli, Nitorsomonas europaea, Methylocystis parvus* OBBP, *Mycobacterium sp., Rhodococcus erythopolis*	Moderate
Chlorinated Ethanes	*Desulfobacterium sp., Methanobacterium sp., Pseudomonas putida, Clostridium sp., C. sp.* strain TCAIIB,	Moderate
Chlorinated Methanes	*Acetobacterium woodii, Desulfobacterium sp., Methanobacterium sp., Pseudomonas sp.* strain KC, *Escherichia coli* K-12, *Clostridium sp., Methanosarcina sp., Hyphomicrobium sp.* strain DM2,	Moderate
Chlorobenzenes	*Alcaligenes sp.* (multiple strains), *Pseudomonas sp.*(multiple strains), *P. putida, Staphylococcus epidermis*	Moderate to high

The introduction of oxidizable soluble organic contaminants into ground water initiates a series of complex and poorly understood responses by subsurface microorganisms. Field and laboratory research suggests that multiple, physiologically-defined-communities develop which are spatially and temporally separate. These communities are most likely ecologically defined by the flux of

biologically available electron donors and acceptors. The biological processes of these communities are potentially useful as natural attenuation mechanisms, as the basis of new bioremediation technologies, and as indicators of the extent and severity of the release

As electron acceptors and nutrients are depleted by microbial activity during biodegradation of contaminants, the pH and redox potential of contaminated aquifers decreases. This results in a succession of bacterial types adapted to specific redox regimes and electron acceptors. Metabolic byproducts of contaminant biodegradation also exert selective forces, either by presenting different carbon sources or by further modifying the physical/chemical environment of the aquifer. Like organic and inorganic colloids, microorganisms possess complex surface chemistry, and can themselves serve as mobile and immobile reactive sites for contaminants.

Under anaerobic conditions most organic compounds are degraded by groups of interacting microorganisms referred to as a consortium. In the consortium, individual types of organisms carry out different specialized reactions which, when combined, can lead to the complete mineralization of a particular compound. The metabolic interaction between organisms can be complex and may be so tightly linked under a given set of conditions that stable consortia can be mistakenly identified as a single species. There seems to be several advantages to the consortial system, including: 1) This system allows for the creation of microenvironments where certain types of organisms can survive in otherwise hostile conditions; 2) Reactions that are thermodynamically unfavorable can be driven by favorable reactions when they are metabolically linked within the consortium; and, 3) This system takes advantage of the diverse metabolic capabilities of microorganisms by allowing for the formation and enrichment of associations that can utilize an introduced substrate faster than a single species could evolve a novel complex enzyme pathway to degrade the same compound.

It appears that subsurface microbial communities contain the metabolic diversity required to utilize a wide variety of organic contaminants as a primary growth substrate in the presence of electron acceptors such as oxygen. Some pollutants, especially the highly oxidized chlorinated hydrocarbons, are not amenable to use as a primary growth substrate. Instead, these compounds are used as electron acceptors in reactions that rely on another source of carbon as a primary substrate or are degraded fortuitously via cometabolism. Thus, biodegradation of organic compounds in groundwater occurs via three mechanisms:

- Use of the organic compound as the primary growth substrate;
- Use of the organic compound as an electron acceptor; and
- Cometabolism.

The first two biodegradation mechanisms involve the microbial transfer of electrons from electron donors (primary growth substrate) to electron acceptors. This process can occur under aerobic or anaerobic conditions. Electron donors include natural organic material, fuel hydrocarbons, chlorobenzenes, and the less oxidized chlorinated ethenes and ethanes Electron acceptors are elements or compounds that occur in relatively oxidized states. The most common naturally occurring electron acceptors in groundwater include dissolved oxygen, nitrate, manganese (IV), iron (III), sulfate, and carbon dioxide. In addition, the more oxidized chlorinated solvents such as PCE, TCE, DCE, TCA, DCA, and polychlorinated benzenes can act as electron acceptors under favorable conditions. Under aerobic conditions, dissolved oxygen is used as the terminal electron acceptor during aerobic respiration. Under anaerobic conditions, the electron acceptors listed above are used during denitrification, manganese (IV) reduction, iron (III) reduction, sulfate reduction, methanogenesis, or reductive dechlorination. Chapelle (1993) and Atlas (1988) discuss terminal electron accepting processes in detail.

Electron transfer results in oxidation of the electron donor and reduction of the electron acceptor and the production of usable energy. The energy produced by these reactions is quantified by the Gibb's free energy of the reaction (ΔG_r) which is given by:

$$\Delta G^\circ_r = \sum \Delta G^\circ_{f,\ products} - \sum \Delta G^\circ_{f,\ reactants} \qquad \text{eq. B.3.1}$$

Where: ΔG_r = Gibb's Free Energy of the Reaction at Standard State
$\Delta G_{f,\ products}$ = Gibb's Free Energy of Formation for Products at Standard State
$\Delta G_{f,\ reactants}$ = Gibb's Free Energy of Formation for the Reactants at Standard State

The ΔG_r defines the maximum useful energy change for a chemical reaction at a constant temperature and pressure. Table B.3.3 presents select electron acceptor and electron donor half-cell reactions and the calculated ΔG_r values for each of these reactions. Table B.3.4 gives the Gibbs free energy of formation (ΔG_f) for species used in these half-cell reactions. Table B.3.5 presents coupled oxidation-reduction reactions that result in biodegradation of select organic contaminants. In general, those reactions that yield the most energy tend to take precedence over less energy-yielding reactions (Stumm and Morgan, 1981; Godsey, 1994). Figure B.3.3 illustrates the expected sequence of microbially mediated redox reactions based on ΔG_r.

The third biodegradation mechanism is cometabolism. During cometabolism the compound being degraded does not serve as an electron donor or an electron acceptor. Instead, degradation is brought about by a fortuitous reaction wherein an enzyme produced during an unrelated reaction degrades the organic compound.

Table B.3.3
Electron Donor and Electron Acceptor Half Cell Reactions

HALF-CELL REACTIONS	ΔG°, (kcal/equiv)*	ΔG°, (kJ/equiv)*	E° (V)	Eh (V)	pe	Conditions for Eh and pe §
ELECTRON-ACCEPTOR (REDUCTION) HALF CELL REACTIONS						
$5e^- + 6H^+ + NO_3^- \Rightarrow 0.5N_2 + 3H_2O$ *Denitrification*	-28.7	-120.	+1.24	+0.708	+12.0	pH = 7 $\Sigma[N]=10^{-3}$
$4e^- + 4H^+ + O_2 \Rightarrow 2H_2O$ *Aerobic Respiration*	-28.3	-119.	+1.23	+0.805	+13.6	pH = 7 $P_{O_2}=0.21$ atm
$2e^- + 4H^+ + \underline{MnO_2} \Rightarrow Mn^{2+} + 2H_2O$ *Pyrolusite Dissolution/Reduction*	-28.3	-119	+1.23	+0.550	+9.27	pH = 7 $\Sigma[Mn]=10^{-3}$
$CO_2 + e^- + H^+ + \underline{MnOOH} \Rightarrow MnCO_3 + H_2O$ *a Manganite Carbonation/Reduction*	-23.1	-96.8	+1.00	+0.408	+6.90	pH = 8 $P_{CO_2}=10^{-2}$
$e^- + H^+ + MnO_2 \Rightarrow \underline{MnOOH}$ *Pyrolusite Hydrolysis/Reduction*	-22.1	-92.5	+0.959	+0.545	+9.21	pH = 7
$e^- + 3H^+ + \underline{Fe(OH)_{3\,amph}} \Rightarrow Fe^{2+} + 2H_2O$ *Amorphous "Goethite" Dissolution/Reduction*	-21.5	-89.9	+0.932	+0.163	+2.75	pH = 6 $\Sigma[Fe]=10^{-3}$
$8e^- + 10H^+ + NO_3^- \Rightarrow NH_4^+ + 3H_2O$ *Nitrate Reduction*	-20.3	-84.9	+0.879	+0.362	+6.12	pH = 7
$2e^- + 2H^+ + NO_3^- \Rightarrow NO_2^- + H_2O$ *Nitrate Reduction*	-18.9	-78.9	+0.819	+0.404	+6.82	pH = 7
$e^- + 3H^+ + \underline{FeOOH} \Rightarrow Fe^{2+} + 2H_2O$ *"Ferric oxyhydroxide" Dissolution/Reduction*	-15.0	-62.9	+0.652	-0.118	-1.99	pH = 6 $\Sigma[Fe]=10^{-3}$
$e^- + 3H^+ + \underline{Fe(OH)_{3\,cryst}} \Rightarrow Fe^{2+} + 3H_2O$ *Crystallized "Goethite" Dissolution/Reduction*	-11.8	-49.2	+0.510	-0.259	-4.38	pH = 6 $\Sigma[Fe]=10^{-3}$
$e^- + H^+ + CO_{2g} + \underline{Fe(OH)_{3\,amph}} \Rightarrow \underline{FeCO_3} + 2H_2O$ *Amorphous "Goethite" Carbonation/Reduction*	-11.0	-46.2	+0.479	-0.113	-1.90	pH = 8 $P_{CO_2}=10^{-2}$ atm
$8e^- + 9H^+ + SO_4^{2-} \Rightarrow HS^- + 4H_2O$ *Sulfate Reduction*	-5.74	-24.0	+0.249	-0.278	-4.70	pH = 8
$8e^- + 10H^+ + SO_4^{2-} \Rightarrow H_2S^{aq} + 4H_2O$ *Sulfate Reduction*	-6.93	-28.9	+0.301	-0.143	-2.42	pH = 6
$8e^- + 8H^+ + CO_{2g} \Rightarrow CH_{4g} + 2H_2O$ *Methanogenesis*	-3.91	-16.4	+0.169	-0.259	-4.39	pH = 7 $P_{CO_2}=10^{-2}$ $P_{CH_4}=10^{0}$
$C_2Cl_4 + H^+ + 2e^- \Rightarrow C_2HCl_3 + Cl^-$ *PCE Reductive Dechlorination*	-14.79	-61.9	+0.642	+0.553	+9.35	pH = 7 $[Cl^-]=10^{-4}$
$C_2HCl_3 + H^+ + 2e^- \Rightarrow C_2H_2Cl_2 + Cl^-$ *TCE Reductive Dechlorination*	-14.50	-60.7	+0.629	+0.540	+9.13	pH = 7 $[Cl^-]=10^{-4}$
$C_2H_2Cl_2 + H^+ + 2e^- \Rightarrow C_2H_3Cl + Cl^-$ *c-DCE Reductive Dechlorination*	-12.12	-50.7	+0.526	+0.437	+7.39	pH = 7 $[Cl^-]=10^{-4}$
$C_2H_3Cl + H^+ + 2e^- \Rightarrow C_2H_4 + Cl^-$ *VC Reductive Dechlorination*	-13.73	-57.4	+0.595	+0.506	+8.55	pH = 7 $[Cl^-]=10^{-4}$
$C_2H_2Cl_4 + H^+ + 2e^- \Rightarrow C_2H_3Cl_3 + Cl^-$ *PCA Reductive Dechlorination*	-13.64	-57.0	+0.591	+0.502	+8.49	pH = 7 $[Cl^-]=10^{-4}$
$C_2H_3Cl_3 + H^+ + 2e^- \Rightarrow C_2H_4Cl_2 + Cl^-$ *TCA Reductive Dechlorination*	-18.26	-76.3	+0.791	+0.702	+11.9	pH = 7 $[Cl^-]=10^{-4}$
$C_2H_4Cl_2 + H^+ + 2e^- \Rightarrow C_2H_5Cl + Cl^-$ *DCA Reductive Dechlorination*	-17.34	-72.5	+0.751	+0.662	+11.2	pH = 7 $[Cl^-]=10^{-4}$
$C_6Cl_6 + H^+ + 2e^- \Rightarrow C_6HCl_5 + Cl^-$ *Hexachlorobenzene Reductive Dechlorination*	-13.91	-58.1	+0.602	+0.513	+8.67	pH = 7 $[Cl^-]=10^{-4}$
$C_6HCl_5 + H^+ + 2e^- \Rightarrow C_6H_2Cl_4 + Cl^-$ *Pentachlorobenzene Reductive Dechlorination*	-11.53	-48.2	+0.500	+0.411	+6.95	pH = 7 $[Cl^-]=10^{-4}$
$C_6H_2Cl_4 + H^+ + 2e^- \Rightarrow C_6H_3Cl_3 + Cl^-$ *Tetrachlorobenzene Reductive Dechlorination*	-8.45	-35.3	+0.366	+0.277	+4.68	pH = 7 $[Cl^-]=10^{-4}$
$C_6H_3Cl_3 + H^+ + 2e^- \Rightarrow C_6H_4Cl_2 + Cl^-$ *Trichlorobenzene Reductive Dechlorination*	-3.94	-16.5	-0.171	+0.082	+1.39	pH = 7 $[Cl^-]=10^{-4}$

HALF-CELL REACTIONS	ΔG°, (kcal equiv)*	ΔG°, (kJ equiv)*	E° (V)	Eh (V)	pe	Conditions for Eh and pe §
ELECTRON-DONOR (OXIDATION) HALF CELL REACTIONS						
$12H_2O + C_6H_6 \Rightarrow 6CO_2 + 30H^+ + 30e^-$ *Benzene Oxidation*	+2.83	+11.8	-0.122	+0.316	+5.34	pH = 7 $P_{CO_2}=10^{-2}$
$14H_2O + C_6H_5CH_3 \Rightarrow 7CO_2 + 36H^+ + 36e^-$ *Toluene Oxidation*	+2.96	+12.4	-0.128	+0.309	+5.22	pH = 7 $P_{CO_2}=10^{-2}$
$16H_2O + C_6H_5C_2H_5 \Rightarrow 8CO_2 + 42H^+ + 42e^-$ *Ethylbenzene Oxidation*	+2.96	+12.4	-0.128	+0.309	+5.21	pH = 7 $P_{CO_2}=10^{-2}$
$20H_2O + C_{10}H_8 \Rightarrow 10CO_2 + 48H^+ + 48e^-$ *Naphthalene Oxidation*	+2.98	+12.5	-0.130[a]	+0.309	+5.22	pH = 7 $P_{CO_2}=10^{-2}$
$18H_2O + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 48H^+ + 48e^-$ *1,3,5-Trimethylbenzene Oxidation*	+3.07	+12.8	-0.133[a]	+0.303	+5.12	pH = 7 $P_{CO_2}=10^{-2}$
$18H_2O + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 48H^+ + 48e^-$ *1,2,4-Trimethylbenzene Oxidation*	+3.07	+12.9	-0.134[a]	+0.302	+5.11	pH = 7 $P_{CO_2}=10^{-2}$
$4H_2O + C_2H_3Cl \Rightarrow 2CO_2 + 11H^+ + 10e^- + Cl^-$ *Vinyl Chloride Oxidation*	-0.55	-2.30	+0.024[a]	-0.455	-7.69	pH = 7 $P_{CO_2}=10^{-2}$
$12H_2O + C_6H_2Cl_4 \Rightarrow 6CO_2 + 26H^+ + 25e^- + 4Cl^-$ *Tetrachlorobenzene Oxidation*	-0.66	-2.74	+0.028	-0.431	-7.28	pH = 7 $P_{CO_2}=10^{-2}$
$12H_2O + C_6H_3Cl_3 \Rightarrow 6CO_2 + 27H^+ + 26e^- + 3Cl^-$ *Trichlorobenzene Oxidation*	+0.42	+1.77	-0.018	-0.475	-8.02	pH = 7 $P_{CO_2}=10^{-2}$
$12H_2O + C_6H_4Cl_2 \Rightarrow 6CO_2 + 28H^+ + 27e^- + 2Cl^-$ *Dichlorobenzene Oxidation*	+1.39	+5.81	-0.060	-0.516	-8.72	pH = 7 $P_{CO_2}=10^{-2}$
$12H_2O + C_6H_5Cl \Rightarrow 6CO_2 + 29H^+ + 28e^- + Cl^-$ *Chlorobenzene Oxidation*	+2.21	+9.26	-0.096[a]	+0.358	+6.05	pH = 7 $P_{CO_2}=10^{-2}$

NOTES:

* = ΔG°_r for half cell reaction as shown divided by the number of electrons involved in reaction.

§ = Conditions assumed for the calculation of Eh and pe (pe = Eh/0.05916). Where two dissolved species are involved, other than those mentioned in this column, their activities are taken as equal. Note, this does not affect the free energy values listed.

[a] = E° calculated using the following equation; $E^{\circ} = \Delta G^{\circ}_r(J/nF) * 1.0365 \times 10^{-5}$ (VF/J) from Stumm and Morgan, 1981

Table B.3.4
Gibbs Free Energy of Formation for Species used in Half Cell Reactions and Coupled Oxidation-Reduction Reactions

Species	State	$\Delta G^{\circ}_{f298.15}$ (kcal/mole)	Source
e^-	i	0	std
H^+	i	0	std
O_2	g	0	std
H_2O	l	-56.687	Dean (1972)
Carbon Species			
CO_2	g	-94.26	Dean (1972)
CH_2O, formaldehyde	aq	-31.02	Dean (1972)
C_6H_6, benzene	l	+29.72	Dean (1972)
CH_4, methane	g	-12.15	Dean (1972)
$C_6H_5CH_3$, toluene	l	+27.19	Dean (1972)
$C_6H_5C_2H_5$, ethylbenzene	l	+28.61	Dean (1972)
$C_6H_4(CH_3)_2$, o-xylene	l	+26.37	Dean (1972)
$C_6H_4(CH_3)_2$, m-xylene	l	+25.73	Dean (1972)
$C_6H_4(CH_3)_2$, p-xylene	l	+26.31	Dean (1972)
C_2Cl_4, PCE	l	+1.1	CRC Handbook (1990)
C_2HCl_3, TCE	l	+2.9	CRC Handbook (1990)
$C_2H_2Cl_2$ 1,1-dichloroethene	l	+5.85	Dean (1972)
$C_2H_2Cl_2$ cis-1,2-dichloroethene	l	5.27	CRC Handbook (1990)
$C_2H_2Cl_2$ trans-1,2-dichloroethene	l	+6.52	CRC Handbook (1990)
C_2H_4 Ethene	g aq, m=1	+16.28 +19.43	CRC Handbook (1990)
C_2H_6 Ethane	g aq, m=1	-7.68 -4.09	CRC Handbook (1990)
HCl hydrochloric acid	aq, m=1	-31.372	CRC Handbook (1990)a
$C_2H_2Cl_4$, 1,1,2,2-PCA	l	-22.73	Dean (1972)
$C_2H_3Cl_3$, 1,1,2-TCA	g	-18.54	Dean (1972)
$C_2H_4Cl_2$, 1,2-DCA	g	-17.68	Dean (1972)
C_2H_5Cl, Chloroethane	g	-14.47	Dean (1972)
$C_{10}H_8$, naphthalene	l	+48.05	Dean (1972)
$C_6H_3(CH_3)_3$, 1,3,5-TMB	l	+24.83	Dean (1972)
$C_6H_3(CH_3)_3$, 1,2,4-TMB	l	+24.46	Dean (1972)
C_2H_3Cl, Vinyl chloride	g	+12.4	Dean (1972)
C_6Cl_6, Hexachlorobenzene	l	+0.502	Dolfing (1992)
C_6HCl_5, Pentachlorobenzene	l	+3.16	Dolfing (1992)
$C_6H_2Cl_4$, 1,2,4,5-Tetrachlorobenzene	l	+5.26	Dolfing (1992)
$C_6H_3Cl_3$, 1,2,4-Trichlorobenzene	l	+9.31	Dolfing (1992)
$C_6H_4Cl_2$, 1,4-Dichlorobenzene	l	+14.28	Dolfing (1992)
C_6H_5Cl, chlorobenzene	l	+21.32	Dean (1972)
$C_{14}H_{10}$, phenanthrene	l	+64.12	Dean (1972)

Table B.3.4 - Con't

Gibbs Free Energy of Formation for Species used in Half Cell Reactions
Coupled Oxidation-Reduction Reactions

Species	State	$\Delta G^{\circ}_{f298.15}$ (kcal/mole)	Source
Nitrogen Species			
NO_3^-	l	-26.61	Dean (1972)
N_2	g	0	std
NO_2^-	l	-7.7	Dean (1972)
NH_4^+	aq	-18.97	Dean (1972)
Sulfur Species			
SO_4^{2-}	i	-177.97	Dean (1972)
H_2S	aq	-6.66	Dean (1972)
H_2S	g	-7.9	Dean (1972)
HS^-	i	+2.88	Dean (1972)
Iron Species			
Fe^{2+}	i	-18.85	Dean (1972)
Fe^{3+}	i	-1.1	Dean (1972)
Fe_2O_3, hematite	c	-177.4	Dean (1972)
FeOOH, ferric oxyhydroxide	c	-117.2	Naumov *et al.* (1974)
$Fe(OH)_3$, goethite	a	-167.416	Langmuir and Whittemore (1971)
$Fe(OH)_3$, goethite	c	-177.148	Langmuir and Whittemore (1971)
$FeCO_3$, siderite	c	-159.35	Dean (1972)
Manganese Species			
Mn^{2+}	i	-54.5	Dean (1972)
MnO_2, pyrolusite	c	-111.18	Stumm and Morgan (1981)
MnOOH, manganite	c	-133.29	Stumm and Morgan (1981)
$MnCO_3$, rhodochrosite	p	-194	Dean (1972)
Chloride Species			
Cl^-	aq	-31.37	Dean (1972)

NOTES:

c = crystallized solid l = liquid g = gaseous aq = undissociated aqueous species
a = amorphous solid (may be partially crystallized - dependent on methods of preparation)
p = freshly precipitated solid
i = dissociated, aqueous ionic species (concentration = 1 m)
std = accepted by convention
Wherever possible multiple sources were consulted to eliminate the possibility of typographical error.

Table B.3.5

Coupled Oxidation-Reduction Reactions

Coupled Benzene Oxidation Reactions	ΔG°, (kcal/ mole)	ΔG°, (kJ/ mole)	Stoichiometric Mass Ratio of Electron Acceptor or Metabolic Byproduct to Primary Substrate	Mass of Primary Substrate Utilized per mass of Electron Acceptor Utilized or Metabolic Byproduct Produced
$7.5O_2 + C_6H_6 \Rightarrow 6CO_{2g} + 3H_2O$ *Benzene oxidation /aerobic respiration*	-765.34	-3202	3.07:1	0.326:1
$6NO_3^- + 6H^+ + C_6H_6 \Rightarrow 6CO_{2g} + 6H_2O + 3N_{2g}$ *Benzene oxidation / denitrification*	-775.75	-3245	4.77:1	0.210:1
$30H^+ + 15\underline{MnO_2} + C_6H_6 \Rightarrow 6CO_{2g} + 15Mn^{2+} + 18H_2O$ *Benzene oxidation / manganese reduction*	-765.45	-3202	10.56:1	0.095:1
$3.75\ NO_3^- + C_6H_6 + 7.5\ H^+ + 0.75\ H_2O \Rightarrow 6\ CO_2 + 3.75\ NH_4^+$ *Benzene oxidation / nitrate reduction*	-524.1	-2193	2.98:1	0.336:1
$60H^+ + 30\underline{Fe(OH)_{3,a}} + C_6H_6 \Rightarrow 6CO_2 + 30Fe^{2+} + 78H_2O$ *Benzene oxidation / iron reduction*	-560.10	-2343	21.5:1	0.047:1
$7.5H^+ + 3.75SO_4^{2-} + C_6H_6 \Rightarrow 6CO_{2g} + 3.75H_2S^\circ + 3H_2O$ *Benzene oxidation / sulfate reduction*	-122.93	-514.3	4.61:1	0.217:1
$4.5H_2O + C_6H_6 \Rightarrow 2.25CO_{2g} + 3.75CH_4$ *Benzene oxidation / methanogenesis*	-32.40	-135.6	0.77:1	1.30:1
$15\ C_2H_2Cl_4 + C_6H_6 + 12\ H_2O\ 6\ CO_2 + 15\ C_2H_3Cl_3 + 15\ H^+ + 15\ Cl^-$ *Benzene oxidation / PCA reduction*	-374.56	-1570	31.9:1	0.03:1
$15\ C_2H_3Cl_3 + C_6H_6 + 12\ H_2O\ 6\ CO_2 + 15\ C_2H_4Cl_2 + 15\ H^+ + 15\ Cl^-$ *Benzene oxidation / TCA reduction*	-377.86	-1580	25.4:1	0.04:1
$15\ C_2H_4Cl_2 + C_6H_6 + 12\ H_2O\ 6\ CO_2 + 15\ C_2H_3Cl + 15\ H^+ + 15\ Cl^-$ *Benzene oxidation / DCA reduction*	-337.96	-1410	18.8:1	0.05:1
$15C_2Cl_4 + 12H_2O + C_6H_6 \Rightarrow 15C_2HCl_3 + 6CO_2 + 15H^+ + 15Cl^-$ *Benzene oxidation/ Tetrachloroethylene reductive dehalogenation*	-358.59	-1500	31.8:1	0.03:1
$15C_2HCl_3 + 12H_2O + C_6H_6 \Rightarrow 15C_2H_2Cl_2 + 6CO_2 + 15H^+ + 15Cl^-$ *Benzene oxidation/ Trichloroethylene reductive dehalogenation*	-350.04	-1465	25.2:1	0.04:1
$15C_2H_2Cl_2 + 12H_2O + C_6H_6 \Rightarrow 15C_2H_3Cl + 6CO_2 + 15H^+ + 15Cl^-$ *Benzene oxidation/ cis-Dichloroethylene reductive dehalogenation*	-278.64	-1166	18.6:1	0.05:1
$15C_2H_3Cl + 12H_2O + C_6H_6 \Rightarrow 15C_2H_4 + 6CO_2 + 15H^+ + 15Cl^-$ *Benzene oxidation/ Vinyl chloride reductive dehalogenation*	-327.37	-1370	11.9:1	0.08:1

Table B.3.5 - Con't

Coupled Oxidation-Reduction Reactions

Coupled Toluene Oxidation Reactions	ΔG°, (kcal/ mole)	ΔG°, (kJ/ mole)	Stoichiometric Mass Ratio of Electron Acceptor or Metabolic Byproduct to Primary Substrate	Mass of Primary Substrate Utilized per mass of Electron Acceptor Utilized or Metabolic Byproduct Produced
$9O_2 + C_6H_5CH_3 \Rightarrow 7CO_{2(g)} + 4H_2O$ *Toluene oxidation /aerobic respiration*	-913.76	-3823	3.13:1	0.32:1
$7.2NO_3^- + 7.2H^+ + C_6H_5CH_3 \Rightarrow 7CO_{2(g)} + 7.6H_2O + 3.6N_{2(g)}$ *Toluene oxidation / denitrification*	-926.31	-3875	4.85:1	0.21:1
$36H^+ + 18\underline{MnO_2} + C_6H_5CH_3 \Rightarrow 7CO_{2(g)} + 18Mn^{2+} + 22H_2O$ *Toluene oxidation / manganese reduction*	-913.89	-3824	10.74:1	0.09:1
$72H^+ + 36\underline{Fe(OH)_{3(s)}} + C_6H_5CH_3 \Rightarrow 7CO_2 + 36Fe^{2+} + 94H_2O$ *Toluene oxidation / iron reduction*	-667.21	-2792	21.86:1	0.05:1
$9H^+ + 4.5SO_4^{2-} + C_6H_5CH_3 \Rightarrow 7CO_{2(g)} + 4.5H_2S^{\circ} + 4H_2O$ *Toluene oxidation / sulfate reduction*	-142.86	-597.7	4.7:1	0.21:1
$5H_2O + C_6H_5CH_3 \Rightarrow 2.5CO_{2(g)} + 4.5CH_4$ *Toluene oxidation / methanogenesis*	-34.08	-142.6	0.78:1	1.28:1
$18\ C_2H_2Cl_4 + C_6H_5CH_3 + 14\ H_2O \rightarrow 7\ CO_2 + 18\ C_2H_3Cl_3 + 18H^+ + 18Cl^-$ *Toluene oxidation / PCA reduction*	-1383	-5781	32.5:1	0.03:1
$18\ C_2H_3Cl_3 + C_6H_5CH_3 + 14\ H_2O \rightarrow 7\ CO_2 + 18\ C_2H_4Cl_2 + 18H^+ + 18Cl^-$ *Toluene oxidation / TCA reduction*	-1391	-5814	25.8:1	0.04:1
$18\ C_2H_4Cl_2 + C_6H_5CH_3 + 14\ H_2O \rightarrow 7\ CO_2 + 18\ C_2H_3Cl + 18\ H^+ + 18\ Cl^-$ *Toluene oxidation / DCA reduction*	-1343	-5614	19.2:1	0.05:1
$18C_2Cl_4 + 14H_2O + C_6H_5CH_3 \Rightarrow 18C_2HCl_3 + 7CO_2 + 18H^+ + 18Cl^-$ *Toluene oxidation/ Tetrachloroethylene reductive dehalogenation*	-425.66	-1781	32.4:1	0.03:1
$18C_2HCl_3 + 14H_2O + C_6H_5CH_3 \Rightarrow 18C_2H_2Cl_2 + 7CO_2 + 18H^+ + 18Cl^-$ *Toluene oxidation/ Trichloroethylene reductive dehalogenation*	-415.40	-1738	25.7:1	0.04:1
$18C_2H_2Cl_2 + 14H_2O + C_6H_5CH_3 \Rightarrow 18C_2H_3Cl + 7CO_2 + 18H^+ + 18Cl^-$ *Toluene oxidation/ cis-Dichloroethylene reductive dehalogenation*	-329.72	-1380	18.9:1	0.05:1
$18C_2H_3Cl + 14H_2O + C_6H_5CH_3 \Rightarrow 18C_2H_4 + 7CO_2 + 18H^+ + 18Cl^-$ *Toluene oxidation/ Vinyl chloride reductive dehalogenation*	-388.22	-1624	12.1:1	0.08:1

Table B.3.5 - Con't

Coupled Oxidation-Reduction Reactions

Coupled Ethylbenzene Oxidation reactions	ΔG°, kcal/ mole	ΔG°, kJ/ mole	Stoichiometric Mass Ratio of Electron Acceptor or Metabolic Byproduct to Primary Substrate	Mass of Primary Substrate Utilized per mass of Electron Acceptor Utilized or Metabolic Byproduct Produced
$10.5O_2 + C_6H_5C_2H_5 \Rightarrow 8CO_{2g} + 5H_2O$ *Ethylbenzene oxidation /aerobic respiration*	-1066.13	-4461	3.17:1	
$8.4NO_3^- + 8.4H^+ + C_6H_5C_2H_5 \Rightarrow 8CO_{2g} + 9.2H_2O + 4.2N_{2g}$ *Ethylbenzene oxidation / denitrification*	-1080.76	-4522	4.92:1	
$46H^+ + 22MnO_2 + C_6H_5C_2H_5 \Rightarrow 8CO_{2g} + 22Mn^{2+} + 28H_2O$ *Ethylbenzene oxidation / manganese reduction*	-1066.27	-4461	11.39:1	
$84H^+ + 42Fe(OH)_{3s} + C_6H_5C_2H_5 \Rightarrow 8CO_2 + 42Fe^{2+} + 110H_2O$ *Ethylbenzene oxidation / iron reduction*	-778.48	-3257	22.0:1	
$10.5H^+ + 5.25SO_4^{2-} + C_6H_5C_2H_5 \Rightarrow 8CO_{2g} + 5.25H_2S^* + 5H_2O$ *Ethylbenzene oxidation / sulfate reduction*	-166.75	-697.7	4.75:1	
$5.5H_2O + C_6H_5C_2H_5 \Rightarrow 2.75CO_{2g} + 5.25CH_4$ *Ethylbenzene oxidation / methanogenesis*	-39.83	-166.7	0.79:1	
$21C_2Cl_4 + 16H_2O + C_6H_5C_2H_5 \Rightarrow 21C_2HCl_3 + 8CO_2 + 21H^+ + 21Cl^-$ *Ethylbenzene oxidation/ Tetrachloroethylene reductive dehalogenation*	-496.67	-2078	32.8:1	
$21C_2HCl_3 + 16H_2O + C_6H_5C_2H_5 \Rightarrow 21C_2H_2Cl_2 + 8CO_2 + 21H^+ + 21Cl^-$ *Ethylbenzene oxidation/ Trichloroethylene reductive dehalogenation*	-484.70	-2028	26.0:1	
$21C_2H_2Cl_2 + 16H_2O + C_6H_5C_2H_5 \Rightarrow 21C_2H_3Cl + 8CO_2 + 21H^+ + 21Cl^-$ *Ethylbenzene oxidation/ cis-Dichloroethylene reductive dehalogenation*	-384.74	-1610	19.2:1	
$21C_2H_3Cl + 16H_2O + C_6H_5C_2H_5 \Rightarrow 21C_2H_4 + 8CO_2 + 21H^+ + 21Cl^-$ *Ethylbenzene oxidation/ Vinyl chloride reductive dehalogenation*	-452.99	-1895	12.3:1	

Table B.3.5 - Con't

Coupled Oxidation-Reduction Reactions

Coupled m-Xylene Oxidation Reactions	ΔG°, (kcal/ mole)	ΔG°, (kJ/ mole)	Stoichiometric Mass Ratio of Electron Acceptor or Metabolic Byproduct to Primary Substrate	Mass of Primary Substrate Utilized per mass of Electron Acceptor Utilized or Metabolic Byproduct Produced
$10.5O_2 + C_6H_4(CH_3)_2 \Rightarrow 8CO_{2,g} + 5H_2O$ *m-Xylene oxidation /aerobic respiration*	-1063.25	-4448	3.17:1	
$8.4NO_3^- + 8.4H^+ + C_6H_4(CH_3)_2 \Rightarrow 8CO_{2,g} + 9.2H_2O + 4.2N_{2,g}$ *m-Xylene oxidation / denitrification*	-1077.81	-4509	4.92:1	
$46H^+ + 22MnO_2 + C_6H_4(CH_3)_2 \Rightarrow 8CO_{2,g} + 22Mn^{2+} + 28H_2O$ *m-Xylene oxidation / manganese reduction*	-1063.39	-4449	11.39:1	
$84H^+ + 42Fe(OH)_{3,s} + C_6H_4(CH_3)_2 \Rightarrow 8CO_2 + 42Fe^{2+} + 110H_2O$ *m-Xylene oxidation / iron reduction*	-775.61	-3245	22:1	
$10.5H^+ + 5.25SO_4^{2-} + C_6H_4(CH_3)_2 \Rightarrow 8CO_{2,g} + 5.25H_2S^* + 5H_2O$ *m-Xylene oxidation / sulfate reduction*	-163.87	-685.6	4.75:1	
$5.5H_2O + C_6H_4(CH_3)_2 \Rightarrow 2.75CO_{2,g} + 5.25CH_4$ *m-Xylene oxidation / methanogenesis*	-36.95	-154.6	0.79:1 *	
$21C_2Cl_4 + 16H_2O + C_6H_4(CH_3)_2 \Rightarrow 21C_2HCl_3 + 8CO_2 + 21H^+ + 21Cl^-$ *m-Xylene oxidation/ Tetrachloroethylene reductive dehalogenation*	-493.79	-2066	32.8:1	
$21C_2HCl_3 + 16H_2O + C_6H_4(CH_3)_2 \Rightarrow 21C_2H_2Cl_2 + 8CO_2 + 21H^+ + 21Cl^-$ *m-Xylene oxidation/ Trichloroethylene reductive dehalogenation*	-481.82	-2016	26.0:1	
$21C_2H_2Cl_2 + 16H_2O + C_6H_4(CH_3)_2 \Rightarrow 21C_2H_3Cl + 8CO_2 + 21H^+ + 21Cl^-$ *m-Xylene oxidation/ cis-Dichloroethylene reductive dehalogenation*	-381.86	-1598	19.2:1	
$21C_2H_3Cl + 16H_2O + C_6H_4(CH_3)_2 \Rightarrow 21C_2H_4 + 8CO_2 + 21H^+ + 21Cl^-$ *m-Xylene oxidation/ Vinyl chloride reductive dehalogenation*	-450.11	-1883	12.3:1	

Table B.3.5 - Con't

Coupled Oxidation-Reduction Reactions

Coupled Naphthalene Oxidation Reactions	ΔG^{o}_{r} (kcal/ mole)	ΔG^{o}_{r} (kJ/ mole)	Stoichiometric Mass Ratio of Electron Acceptor or Metabolic Byproduct to Primary Substrate	Mass of Primary Substrate Utilized per mass of Electron Acceptor Utilized or Metabolic Byproduct Produced
$12O_2 + C_{10}H_8 \Rightarrow 10CO_2 + 4H_2O$ *Naphthalene oxidation /aerobic respiration*	-1217.40	-5094	3.00:1	
$9.6NO_3^- + 9.6H^+ + C_{10}H_8 \Rightarrow 10CO_2 + 8.8H_2O + 4.8N_{2g}$ *Naphthalene oxidation / denitrification*	-1234.04	-5163	4.65:1	
$24MnO_2 + 48H^+ + C_{10}H_8 \Rightarrow 10CO_2 + 24Mn^{2+} + 28H_2O$ *Naphthalene oxidation / manganese reduction*	-1217.57	-5094	16.31:1	
$48Fe(OH)_{3s} + 96H^+ + C_{10}H_8 \Rightarrow 10CO_2 + 48Fe^{2+} + 124H_2O$ *Naphthalene oxidation / iron reduction*	-932.64	-3902	40.13:1	
$6SO_4^{2-} + 12H^+ + C_{10}H_8 \Rightarrow 10CO_2 + 6H_2S^{o} + 4H_2O$ *Naphthalene oxidation / sulfate reduction*	-196.98	-824.2	4.50:1	
$8H_2O + C_{10}H_8 \Rightarrow 4CO_2 + 6CH_4$ *Naphthalene oxidation / methanogenesis*	-44.49	-186.1	1.13:1	
$24C_2Cl_4 + 20H_2O + C_{10}H_8 \Rightarrow 24C_2HCl_3 + 10CO_2 + 24H^+ + 24Cl^-$ *Naphthalene oxidation/ Tetrachloroethylene reductive dehalogenation*	-566.59	-2371	31.1:1	
$24C_2HCl_3 + 20H_2O + C_{10}H_8 \Rightarrow 24C_2H_2Cl_2 + 10CO_2 + 24H^+ + 24Cl^-$ *Naphthalene oxidation/ Trichloroethylene reductive dehalogenation*	-552.91	-2313	24.6:1	
$24C_2H_2Cl_2 + 20H_2O + C_{10}H_8 \Rightarrow 24C_2H_3Cl + 10CO_2 + 24H^+ + 24Cl^-$ *Naphthalene oxidation/ cis-Dichloroethylene reductive dehalogenation*	-438.67	-1835	18.2:1	
$24C_2H_3Cl + 20H_2O + C_{10}H_8 \Rightarrow 24C_2H_4 + 10CO_2 + 24H^+ + 24Cl^-$ *Naphthalene oxidation/ Vinyl chloride reductive dehalogenation*	-516.67	-2162	11.6:1	

Table B.3.5 - Con't

Coupled Oxidation-Reduction Reactions

Coupled 1,3,5-Trimethylbenzene Oxidation Reactions	ΔG°, (kcal/ mole)	ΔG°, (kJ/ mole)	Stoichiometric Mass Ratio of Electron Acceptor or Metabolic Byproduct to Primary Substrate	Mass of Primary Substrate Utilized per mass of Electron Acceptor Utilized or Metabolic Byproduct Produced
$12O_2 + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 6H_2O$ *1,3,5-Trimethylbenzene oxidation /aerobic respiration*	-1213.29	-5076	3.20:1	
$9.6NO_3^- + 9.6H^+ + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 10.8H_2O + 4.8N_{2g}$ *1,3,5-Trimethylbenzene oxidation / denitrification*	-1229.93	-5146	4.96:1	
$24MnO_2 + 48H^+ + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 30H_2O + 24Mn^{2+}$ *1,3,5-Trimethylbenzene oxidation / manganese reduction*	-1213.46	-5077	17.40:1	
$48Fe(OH)_{3a} + 96H^+ + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 48Fe^{2+} + 126H_2O$ *1,3,5-Trimethylbenzene oxidation / iron reduction*	-928.53	-3885	42.80:1	
$6SO_4^{2-} + 12H^+ + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 6H_2O + 6H_2S^o$ *1,3,5-Trimethylbenzene oxidation / sulfate reduction*	-192.87	-807.0	4.80:1	
$6H_2O + C_6H_3(CH_3)_3 \Rightarrow 3CO_2 + 6CH_4$ *1,3,5-Trimethylbenzene oxidation / methanogenesis*	-40.39	-169.0	0.90:1	
$24C_2Cl_4 + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_2HCl_3 + 9CO_2 + 24H^+ + 24Cl^-$ *1,3,5-Trimethylbenzene oxidation/ Tetrachloroethylene reductive dehalogenation*	-562.48	-2353	33.2:1	
$24C_2HCl_3 + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_2H_2Cl_2 + 9CO_2 + 24H^+ + 24Cl^-$ *1,3,5-Trimethylbenzene oxidation/ Trichloroethylene reductive dehalogenation*	-548.80	-2296	26.3:1	
$24C_2H_2Cl_2 + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_2H_3Cl + 9CO_2 + 24H^+ + 24Cl^-$ *1,3,5-Trimethylbenzene oxidation/ cis-Dichloroethylene reductive dehalogenation*	-434.56	-1818	19.4:1	
$24C_2H_3Cl + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_2H_4 + 9CO_2 + 24H^+ + 24Cl^-$ *1,3,5-Trimethylbenzene oxidation/ Vinyl chloride reductive dehalogenation*	-512.56	-2145	12.4:1	

Table B.3.5 - Con't

Coupled Oxidation-Reduction Reactions

Coupled 1,2,4-Trimethylbenzene Oxidation Reactions	ΔG°, (kcal/ mole)	ΔG°, (kJ/ mole)	Stoichiometric Mass Ratio of Electron Acceptor or Metabolic Byproduct to Primary Substrate	Mass of Primary Substrate Utilized per mass of Electron Acceptor Utilized or Metabolic Byproduct Produced
$12O_2 + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 6H_2O$ *1,2,4-Trimethylbenzene oxidation /aerobic respiration*	-1212.92	-5075	3.20:1	
$9.6NO_3^- + 9.6H^+ + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 10.8H_2O + 4.8N_{2g}$ *1,2,4-Trimethylbenzene oxidation / denitrification*	-1229.56	-5144	4.96:1	
$24\underline{MnO_2} + 48H^+ + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 30H_2O + 24Mn^{2+}$ *1,2,4-Trimethylbenzene oxidation / manganese reduction*	-1213.09	-5076	17.4:1	
$48\underline{Fe(OH)}_{3a} + 96H^+ + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 48Fe^{2+} + 126H_2O$ *1,2,4-Trimethylbenzene oxidation / iron reduction*	-928.16	-3883	42.8:1	
$6SO_4^{2-} + 12H^+ + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 6H_2O + 6H_2S$ *1,2,4-Trimethylbenzene oxidation / sulfate reduction*	-192.50	-805.4	4.80:1	
$6H_2O + C_6H_3(CH_3)_3 \Rightarrow 3CO_2 + 6CH_4$ *1,2,4-Trimethylbenzene oxidation / methanogenesis*	-40.02	-167.4	0.90:1	
$24C_2Cl_4 + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_2HCl_3 + 9CO_2 + 24H^+ + 24Cl^-$ *1,2,4-Trimethylbenzene oxidation/ Tetrachloroethylene reductive dehalogenation*	-562.11	-2352	33.2:1	
$24C_2HCl_3 + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_2H_2Cl_2 + 9CO_2 + 24H^+ + 24Cl^-$ *1,2,4-Trimethylbenzene oxidation/ Trichloroethylene reductive dehalogenation*	-548.43	-2295	26.3:1	
$24C_2H_2Cl_2 + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_2H_3Cl + 9CO_2 + 24H^+ + 24Cl^-$ *1,2,4-Trimethylbenzene oxidation/ cis-Dichloroethylene reductive dehalogenation*	-434.19	-1817	19.4:1	
$24C_2H_3Cl + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_2H_4 + 9CO_2 + 24H^+ + 24Cl^-$ *1,2,4-Trimethylbenzene oxidation/ Vinyl chloride reductive dehalogenation*	-512.19	-2143	12.4:1	

Table B.3.5 - Con't

Coupled Oxidation-Reduction Reactions

Coupled Chlorobenzene Oxidation Reactions	ΔG°, (kcal/ mole)	ΔG°, (kJ/ mole)	Stoichiometric Mass Ratio of Electron Acceptor or Metabolic Byproduct to Primary Substrate	Mass of Primary Substrate Utilized per mass of Electron Acceptor Utilized or Metabolic Byproduct Produced
$7O_2 + C_6H_5Cl \Rightarrow 6CO_2 + H^+ + 2H_2O + Cl^-$ *Chlorobenzene oxidation /aerobic respiration*	-731.62	-3061	2.00:1	
$5.6NO_3^- + 4.6H^+ + C_6H_5Cl \Rightarrow 6CO_2 + 4.8H_2O + 2.8N_{2g} + Cl^-$ *Chlorobenzene oxidation / denitrification*	-741.33	-3102	3.10:1	
$14\underline{MnO_2} + 27H^+ + C_6H_5Cl \Rightarrow 6CO_2 + 16H_2O + 14Mn^{2+} + Cl^-$ *Chlorobenzene oxidation / manganese reduction*	-731.72	-3062	10.9:1	
$28\underline{Fe(OH)_{3s}} + 55H^+ + C_6H_5Cl \Rightarrow 6CO_2 + 72H_2O + 28Fe^{2+} + Cl^-$ *Chlorobenzene oxidation / iron reduction*	-565.51	-2366	26.8:1	
$3.5SO_4^{2-} + 6H^+ + C_6H_5Cl \Rightarrow 6CO_2 + 2H_2O + 3.5H_2S^\circ + Cl^-$ *Chlorobenzene oxidation / sulfate reduction*	-136.38	-570.6	3.00:1	
$5H_2O + C_6H_5Cl \Rightarrow 2.5CO_2 + 3.5CH_4 + H^+ + Cl^-$ *Chlorobenzene oxidation / methanogenesis*	-47.43	-198.4	0.80:1	
$14C_2Cl_4 + 12H_2O + C_6H_5Cl \Rightarrow 14C_2HCl_3 + 6CO_2 + 15H^+ + 15Cl^-$ *Chlorobenzene oxidation/ Tetrachloroethylene reductive dehalogenation*	-351.99	-1473	20.7:1	
$14C_2HCl_3 + 12H_2O + C_6H_5Cl \Rightarrow 14C_2H_2Cl_2 + 6CO_2 + 15H^+ + 15Cl^-$ *Chlorobenzene oxidation/ Trichloroethylene reductive dehalogenation*	-344.01	-1439	16.4:1	
$14C_2H_2Cl_2 + 12H_2O + C_6H_5Cl \Rightarrow 14C_2H_3Cl + 6CO_2 + 15H^+ + 15Cl^-$ *Chlorobenzene oxidation/ cis-Dichloroethylene reductive dehalogenation*	-277.37	-1161	12.1:1	
$14C_2H_3Cl + 12H_2O + C_6H_5Cl \Rightarrow 14C_2H_4 + 6CO_2 + 15H^+ + 15Cl^-$ *Chlorobenzene oxidation/ Vinyl chloride reductive dehalogenation*	-322.87	-1351	7.75:1	

Table B.3.5 - Con't

Coupled Oxidation-Reduction Reactions

Coupled Vinyl Chloride Oxidation Reactions	ΔG°, (kcal/ mole)	ΔG°, (kJ/ mole)	Stoichiometric Mass Ratio of Electron Acceptor or Metabolic Byproduct to Primary Substrate	Mass of Primary Substrate Utilized per mass of Electron Acceptor Utilized or Metabolic Byproduct Produced
$2.5O_2 + C_2H_3Cl \Rightarrow 2CO_2 + H_2O + H^+ + Cl^-$ *Vinyl Chloride oxidation /aerobic respiration*	-288.98	-1209	1.29:1	
$2NO_3^- + H^+ C_2H_3Cl \Rightarrow 2CO_2 + 2H_2O + Cl^- + N_{2g}$ *Vinyl Chloride oxidation / denitrification*	-292.44	-1224	2.00:1	
$5\underline{MnO_2} + 9H^+ + C_2H_3Cl \Rightarrow 2CO_2 + 6H_2O + 5Mn^{2+} + Cl^-$ *Vinyl Chloride oxidation / manganese reduction*	-289.01	-1209	7.02:1	
$10\underline{Fe(OH)_{3s}} + 19H^+ + C_6H_3(CH_3)_3 \Rightarrow 2CO_2 + 10Fe^{2+} + 26H_2O + Cl^-$ *Vinyl Chloride oxidation / iron reduction*	-229.65	-960.9	17.3:1	
$1.25SO_4^{2-} + 1.5H^+ + C_2H_3Cl \Rightarrow 2CO_2 + H_2O + 1.25H_2S^o + Cl^-$ *Vinyl Chloride oxidation / sulfate reduction*	-76.40	-319.7	1.94:1	
$1.5H_2O + C_2H_3Cl \Rightarrow .75CO_2 + 1.25CH_4 + H^+ + Cl^-$ *Vinyl Chloride oxidation / methanogenesis*	-44.62	-186.7	0.44:1	
$5C_2Cl_4 + 4H_2O + C_2H_3Cl \Rightarrow 5C_2HCl_3 + 2CO_2 + 6H^+ + 6Cl^-$ *Vinyl Chloride oxidation/ Tetrachloroethylene reductive dehalogenation*	-153.39	-641.8	13.4:1	
$5C_2HCl_3 + 4H_2O + C_2H_3Cl \Rightarrow 5C_2H_2Cl_2 + 2CO_2 + 6H^+ + 6Cl^-$ *Vinyl Chloride oxidation/ Trichloroethylene reductive dehalogenation*	-150.54	-629.9	10.6:1	
$5C_2H_2Cl_2 + 4H_2O + C_2H_3Cl \Rightarrow 5C_2H_3Cl + 2CO_2 + 6H^+ + 6Cl^-$ *Vinyl Chloride oxidation/ cis-Dichloroethylene reductive dehalogenation*	-126.74	-530.3	7.82:1	

Process	ΔG_r^{o*}
Aerobic Respiration	-3202
↓	
Denitrification	-3245
↓	
Manganese (IV) Reduction	-3202
↓	
Iron (III) Reduction	-2343
↓	
PCE Reduction	-1500
↓	
TCE Reduction	-1465
↓	
cis-1,2-DCE Reduction	-1166
↓	
Sulfate Reduction	-514
↓	
Methanogenesis	-136

Figure B.3.3

Expected Sequence of Microbially Mediated Redox Reactions and Gibb's Free Energy of the Reaction

* For Benzene Oxidation, kJ/mole

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As discussed in sections B.3.2, B.3.3, and B.3.4, biodegradation causes measurable changes in groundwater chemistry. Table B.3.6 summarizes these trends. During aerobic respiration, oxygen is reduced to water, and dissolved oxygen concentrations decrease. In anaerobic systems where nitrate is the electron acceptor, the nitrate is reduced to NO_2^-, N_2O, NO, NH^{4-}, or N_2 via denitrification, and nitrate concentrations decrease. In anaerobic systems where iron (III) is the electron acceptor, it is reduced to iron (II) via iron (III) reduction, and iron (II) concentrations increase. In anaerobic systems where sulfate is the electron acceptor, it is reduced to H_2S via sulfate reduction, and sulfate concentrations decrease. During aerobic respiration, denitrification, iron (III) reduction, and sulfate reduction, total alkalinity will increase. In anaerobic systems where CO_2 is used as an electron acceptor, it is reduced by methanogenic bacteria during methanogenesis, and CH_4 is produced. In anaerobic systems where contaminants are being used as electron acceptors they are reduced to less chlorinated daughter products; in such a system, parent compound concentrations will decrease and daughter product concentrations will increase at first and then decrease as the daughter product is used as an electron acceptor or is oxidized.

Table B.3.6

Trends in Contaminant, Electron Acceptor, Metabolic Byproduct and Total Alkalinity Concentrations During Biodegradation

Analyte	Terminal Electron Accepting Process	Trend in Analyte Concentration During Biodegradation
Fuel Hydrocarbons	Aerobic Respiration, Denitrification, Manganese (IV) Reduction, Iron (III) Reduction, Methanogenesis	Decreases
Highly Chlorinated Solvents and Daughter Products	Reductive Dechlorination	Parent Compound Concentration Decreases, Daughter Products Increase Initially and Then May Decrease
Lightly Chlorinated Solvents	Aerobic Respiration, Denitrification, Manganese (IV) Reduction, Iron (III) Reduction (Direct Oxidation)	Compound Concentration Decreases
Dissolved Oxygen	Aerobic Respiration	Decreases
Nitrate	Denitrification	Decreases
Manganese (II)	Manganese (IV) Reduction	Increases
Iron (II)	Iron (III) Reduction	Increases
Sulfate	Sulfate Reduction	Decreases
Methane	Methanogenesis	Increases
Chloride	Reductive Dechlorination or Direct Oxidation of Chlorinated Compound	Increases
ORP	Aerobic Respiration, Denitrification, Manganese (IV) Reduction, Iron (III) Reduction, Methanogenesis	Decreases
Alkalinity	Aerobic Respiration, Denitrification, Iron (III) Reduction, and Sulfate Reduction	Increases

As each subsequent electron acceptor is utilized, the groundwater becomes more reducing and the redox potential of the water decreases. Figure B.3.4 shows the typical ORP conditions for groundwater when different electron acceptors are used. The main force driving this change in

ORP is microbially mediated oxidation-reduction reactions. ORP can be used as a crude indicator of which oxidation-reduction reactions may be operating at a site. The ORP determined in the field using a probe is termed Eh. Eh can be expressed as pE, which is the hypothetical measure of the electron activity associated with a specific Eh. High pE means that the solution or redox couple has a relatively high oxidizing potential.

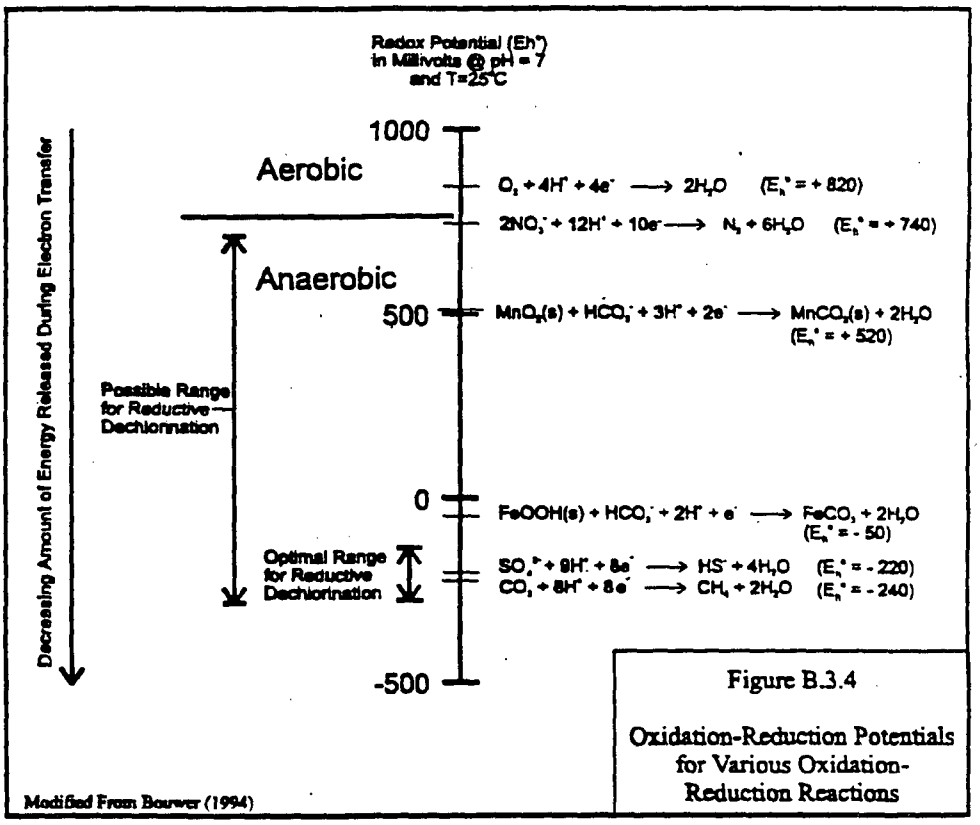


Figure B.3.4

Oxidation-Reduction Potentials for Various Oxidation-Reduction Reactions

B.3.2 BIODEGRADATION OF ORGANIC COMPOUNDS VIA USE AS A PRIMARY GROWTH SUBSTRATE

Many organic compounds including natural organic carbon, fuel hydrocarbons, and the less oxidized chlorinated compounds such as vinyl chloride can be used as a primary growth substrate (electron donor) for microbial metabolism. The following sections describe biodegradation of organic compounds through use as a primary substrate under both aerobic and anaerobic conditions.

B.3.2.1 Aerobic Biodegradation of Primary Substrates

Biodegradation of organic compounds is often an aerobic process that occurs when indigenous populations of microorganisms are supplied with the oxygen and nutrients necessary to utilize

organic carbon as an energy source. The biodegradation of fuel hydrocarbons occurs rapidly under aerobic conditions and is discussed in Wiedemeier *et al.* (1995). Some pollutants, especially the highly oxidized chlorinated hydrocarbons (i.e., those containing more chlorine substituents), are biologically recalcitrant under aerobic conditions. However, some of the less chlorinated ethenes and ethanes such as DCE, VC, and 1,2-DCA, and many of the chlorinated benzenes can be utilized as primary substrates and oxidized under aerobic conditions. During aerobic biodegradation (oxidation) of chlorinated solvents, the facilitating microorganism obtains energy and organic carbon from the degraded solvent.

Of the chlorinated ethenes, vinyl chloride is the most susceptible to aerobic biodegradation, and PCE the least. Of the chlorinated ethanes, 1,2-DCA is the most susceptible to aerobic biodegradation (CA is more likely to abiotically hydrolyze to ethanol), while TCA, PCA, and HCA are less so. Chlorinated benzenes with up to 4 chlorine atoms (i.e., chlorobenzene, dichlorobenzene, trichlorobenzene, and tetrachlorobenzene) also have been shown to be readily biodegradable under aerobic conditions (Spain, 1996). Pentachlorobenzene and hexachlorobenzene are unlikely to be oxidized by microbial activity.

B.3.2.1.1 Aerobic Oxidation of Petroleum Hydrocarbons

Fuel hydrocarbons are rapidly biodegraded when they are utilized as the primary electron donor for microbial metabolism under aerobic conditions. Biodegradation of fuel hydrocarbons occurs naturally when sufficient oxygen (or other electron acceptors) and nutrients are available in the groundwater. The rate of natural biodegradation is generally limited by the lack of oxygen or other electron acceptors rather than by the lack of nutrients such as nitrogen or phosphorus. The rate of natural aerobic biodegradation in unsaturated soil and shallow aquifers is largely dependent upon the rate at which oxygen enters the contaminated media. Biodegradation of fuel hydrocarbons is discussed by Wiedemeier *et al.* (1995).

B.3.2.1.2 Aerobic Oxidation of Chlorinated Ethenes

In general, the highly chlorinated ethenes (e.g., PCE, TCE, and probably DCE) are not likely to serve as electron donors or substrates for microbial degradation reactions. This is because the highly chlorinated compounds tend to be much more oxidized than many compounds present in a natural groundwater system.. Several microbes or microbial enrichments have been shown to be capable of TCE oxidation (Fogel *et al.*, 1986; Nelson et al., 1986; Little et al., 1988); however, as

noted by Vogel (1994), no strong evidence for the oxidation of halogenated solvents has been derived from actual hazardous waste sites.

Hartmans et al. (1985) and Hartmans and de Bont (1992) show that vinyl chloride can be used as a primary substrate under aerobic conditions, with vinyl chloride apparently being directly mineralized to carbon dioxide and water. This has also been reported by Davis and Carpenter (1990). Aerobic biodegradation is relatively rapid relative to other mechanisms of vinyl chloride degradation, especially reductive dehalogenation.

B.3.2.1.3 Aerobic Oxidation of Chlorinated Ethanes

Of the chlorinated ethanes, only 1,2-dichloroethane has been shown to be aerobically mineralized/oxidized. Stucki *et al.* (1983) and Janssen *et al.* (1985) show that 1,2-DCA can be used as a primary substrate under aerobic conditions. In this case, the bacteria transform 1,2-DCA to chloroethanol, which is then mineralized to carbon dioxide.

B.3.2.1.4 Aerobic Oxidation of Chlorobenzenes

Chlorobenzene and polychlorinated benzenes (up to and including tetrachlorobenzene) have been shown to be biodegradable under aerobic conditions. Several studies have shown that bacteria are able to utilize chlorobenzene (Reineke and Knackmuss, 1984), 1,4-DCB(Reineke and Knackmuss, 1984; Schraa *et al.*, 1986; Spain and Nishino, 1987), 1,3-DCB (de Bont *et al.*, 1986), 1,2-DCB (Haigler *et al.*, 1988), 1,2,4-TCB (van der Meer *et al.*, 1987; Sander *et al.*, 1991), and 1,2,4,5-TeCB (Sander *et al.*, 1991) as primary growth substrates in aerobic systems. Nishino *et al.* (1994) note that aerobic bacteria able to grow on chlorobenzene have been detected at a variety of chlorobenzene-contaminated sites, but not at uncontaminated sites. Spain (1996) notes that this provides strong evidence that the bacteria are selected for their ability to derive carbon and energy from chlorobenzene degradation *in situ*.

The pathways for all of these reactions are similar, and are also similar to that of benzene (Chapelle, 1993; Spain, 1996). In general, the aerobic biodegradation involves hydroxylation of the chlorinated benzene to a chlorocatechol, followed by *ortho* cleavage of the benzene ring. This produces a muconic acid, which is dechlorinated, and the non-chlorinated intermediates are then metabolized. The only significant difference between this process and aerobic benzene degradation is the elimination of chlorine at some point in the pathway (Chapelle, 1993).

B.3.2.2 Anaerobic Biodegradation of Primary Substrates

Rapid depletion of dissolved oxygen caused by microbial respiration results in the establishment of anaerobic conditions in areas with high organic carbon concentrations. Certain requirements must be met in order for anaerobic (anoxic) bacteria to degrade organic compounds, including: absence of dissolved oxygen; availability of carbon sources (natural or anthropogenic), electron acceptors, and essential nutrients; and proper ranges of pH, temperature, salinity, and redox potential. When oxygen is absent, nitrate, manganese (IV), iron (III), sulfate, and carbon dioxide can serve as terminal electron acceptors during oxidation of organic carbon. While there is a large body of evidence for anaerobic mineralization (oxidation) of fuel hydrocarbons, there is very little evidence of such transformations involving chlorinated compounds.

B.3.2.2.1 Anaerobic Oxidation of Petroleum Hydrocarbons

Biodegradation of fuel hydrocarbons will occur under anaerobic conditions in most, if not all, groundwater environments via denitrification, manganese (IV) reduction, iron (III) reduction, sulfate reduction, and methanogenesis. Biodegradation of fuel hydrocarbons is discussed by Wiedemeier *et al.* (1995), and many primary references are cited therein.

B.3.2.2.2 Anaerobic Oxidation of Chlorinated Ethenes

In general, due to the oxidized nature of polychlorinated ethenes, they are unlikely to undergo oxidation in groundwater systems. However, Bradley and Chapelle (1996) show that VC (with only one chlorine substituent) can be directly oxidized to carbon dioxide and water via iron (III) reduction. Reduction of vinyl chloride concentrations in microcosms amended with iron (III)-EDTA closely matched the production of carbon dioxide. Slight mineralization was also noted in unamended microcosms. The rate of this reaction apparently depends on the bioavailability of the iron (III). At this time, it is not known if other workers have demonstrated other anaerobic mineralization reactions involving chlorinated ethenes.

B.3.2.2.3 Anaerobic Oxidation of Chlorinated Ethanes

During preparation of this protocol, no evidence of anaerobic oxidation of chlorinated ethanes was found; this does not necessarily indicate that such reactions have not been described. However, the lack of discussion of such transformations in surveys of chlorinated hydrocarbon biodegradation (e.g., Vogel et al., 1987; Semprini and McCarty, 1994; Vogel, 1994, Adriaens and Vogel, 1995; Spain, 1996) suggests that there has indeed been little, if any, work on this subject.

B.3.2.2.4 Anaerobic Oxidation of Chlorobenzenes

While aerobic mineralization of chlorobenzenes is similar to that of benzene, similar activity under anaerobic conditions has not been documented. As discussed above, there is little, if any, discussion of this topic in the literature.

B.3.3 BIODEGRADATION OF ORGANIC COMPOUNDS VIA USE AS AN ELECTRON ACCEPTOR (REDUCTIVE DECHLORINATION)

Anaerobically, biodegradation of chlorinated solvents most often proceeds through a process called reductive dechlorination. During this process, the halogenated hydrocarbon is used as an electron acceptor, not as a source of carbon, and a halogen atom is removed and replaced with a hydrogen atom. As an example, *Dehalobacter restrictus* was shown by Holliger (1992) to use tetrachloroethene as an electron acceptor during reductive dechlorination to produce *cis-1,2*-dichloroethene. Because chlorinated compounds are used as electron acceptors during reductive dechlorination, there must be an appropriate source of carbon for microbial growth in order for reductive dehalogenation to occur (Baek and Jaffe, 1989; Freedman and Gossett, 1989; Fathepure and Boyd, 1988; Bouwer, 1994). Potential carbon sources can include low molecular weight organic compounds (lactate, acetate, methanol, glucose, etc.), fuel hydrocarbons, or naturally occurring organic matter. Biotic transformations of chlorinated solvents under anaerobic conditions generally are reductions that involve either hydrogenolysis or dihaloelimination (McCarty and Semprini, 1994). Hydrogenolysis occurs when a chlorine atom is replaced with hydrogen. Dihaloelimination occurs when two adjacent chlorine atoms are removed and a double bond is formed between the respective carbon atoms. The most important process for the natural biodegradation of the more highly chlorinated solvents is reductive dechlorination (hydrogenolysis). Bouwer *et al.* (1981) were the first to show that halogenated aliphatic hydrocarbons could be biologically transformed under anaerobic conditions in the subsurface environment. Since that time, numerous investigators have shown that chlorinated compounds can degrade via reductive dechlorination under anaerobic conditions.

Higher ratios of chlorine to carbon represent higher oxidation levels; highly chlorinated compounds are more oxidized than lesser chlorinated compounds and thus are less susceptible to oxidation. Thus, highly chlorinated compounds such as PCE, TCE, TCA, or HCB are more likely to undergo reductive reactions than oxidative reactions. During these reductive reactions, electrons are transferred to the chlorinated compound, and a chlorine atom is replaced with a hydrogen atom. As an example, consider the reductive dechlorination of PCE to TCE and then TCE to DCE, and finally DCE to VC. Because of the relatively low oxidation state of VC, this

compound more commonly undergoes aerobic biodegradation as a primary substrate than reductive dechlorination.

Reductive dechlorination processes result in the formation of intermediates which are more reduced than the parent compound. These intermediates are often more susceptible to aerobic or anaerobic oxidative bacterial metabolism, than to further reductive anaerobic processes. Following anaerobic biotransformation with an oxidative biotransformation would facilitate the removal of these products. This type of reductive/oxidative coupling can be employed for other highly oxidized compounds such as pentachlorophenol (PCP) or hexachlorobenzene (HCB). Actual mechanisms of reductive dehalogenation are still unclear (Adriaens and Vogel, 1995). In addition, other factors that will influence the process include the type of electron donor and the presence of competing electron acceptors (Adriaens and Vogel, 1995; Suflita and Townsend, 1995), temperature, and substrate availability.

One or more of the following generally is observed at a site where reductive dechlorination is ongoing:

1) Ethene is being produced (even low concentrations are indicative of biodegradation);
2) Methane is being produced;
3) Iron II is being produced;
4) Hydrogen concentrations are between 1-4 nM; and
5) Dissolved oxygen concentrations are low.

B.3.3.1 Reductive Dechlorination of Chlorinated Ethenes

PCE and TCE have been shown to undergo reductive dechlorination in a variety of anaerobic systems from different environments, with various electron donors/carbon sources (Table B.3.7) (Wilson, 1988; Sewell et al., 1991; Roberts et al, 1982). This is particularly true if the subsurface also contains other anthropogenic organic compounds that can serve as electron donors and whose utilization by subsurface bacteria will deplete any available oxygen. In general, reductive dechlorination of chlorinated ethenes occurs by sequential dechlorination from PCE to TCE to DCE to VC to ethene. Depending upon environmental conditions, this sequence may be interrupted, with other processes then acting upon the products. With sufficient quantities of electron donors, the final end-product of anaerobic reductive dehalogenation can be ethene (Freedman and Gossett, 1989). Reductive dehalogenation of chlorinated solvent compounds is associated with the accumulation of daughter products and an increase in chloride.

Table B.3.7

Sources, Donors, Acceptors, and Products of Reported Reductive Dechlorinating Laboratory Systems

Reference	Source	Donor	Acceptor-Product
Bouwer & McCarty,1983	Digester	Organic Material	PCE-TCE
Vogel & McCarty, 1985	Bioreactor	Acetate	PCE-VC, CO_2
Kleopfer *et al.*, 1985	Soil	Soybean Meal	TCE-DCE
Barrio-Lage *et al.*, 1987	Swamp Muck Soil	Organic Material Methanol (?)	PCE-VC PCE-VC
Fathepure *et al.*, 1987	Methanosarcina DCB-1	Methanol 3CB[a],Pyruvate,RF[b]	PCE-TCE PCE-TCE
Baek & Jaffe, 1989	Digester	Formate Methanol	TCE-VC,CA[c] TCE-VC,CA
Freedman & Gossett, 1989	Digester	Methanol Glucose H2 Formate Acetate	PCE-VC, Ethene PCE-VC, Ethene PCE-VC, Ethene PCE-VC, Ethene PCE-VC, Ethene
Scholz-Muramatsu *et al.*, 1990	Bioreactor	Benzoate	PCE-DCE
Gibson & Sewell, 1990	Aquifer	VFA[d]	PCE-DCE
Sewell & Gibson, 1990	Aquifer	Toluene	PCE-DCE
Sewell *et al.*, 1991	Aquifer Landfill	VFA VFA	PCE-DCE PCE-VC
Lyon *et al.*, 1995	Aquifer	Native Organic Matter	PCE-DCE

a 3 Chlorobenzoate
b Rumen Fluid
c Chloroethane
d Volatile Fatty Acid

Studies have shown that TCE can be anaerobically reduced to either 1,1-DCE, *cis*-1,2-DCE, or *trans*-1,2-DCE, all of which can be further transformed to vinyl chloride (Miller and Guengerich, 1982; Wilson and Wilson, 1985; Mayer *et al.*, 1988; Nelson, *et al.*, 1986; Henson *et al.*, 1989; Tsien *et al.*, 1989; Henry, 1991; McCarty, 1994; Wilson *et al.*, 1994). During reductive dehalogenation, all three isomers of DCE can theoretically be produced; however, Bouwer (1994) reports that *cis-1,2*-DCE is a more common intermediate than *trans-1,2*-DCE and that *1,1*-DCE is the least prevalent intermediate of the three DCE isomers. Vinyl chloride produced from dehalogenation of DCE may be subsequently reduced to innocuous products such as ethane or carbon dioxide. The removal of vinyl chloride occurs more readily under aerobic

conditions, such as those encountered at the edge of the plume. Vinyl chloride may also be used as a primary substrate by aerobic organisms, as previously discussed.

Reductive dehalogenation affects each of the chlorinated ethenes differently. PCE is the most susceptible of these compounds to reductive dehalogenation because it is also the most oxidized Conversely, VC is the least susceptible to reductive dehalogenation because it is already the least oxidized of these compounds. The rate of reductive dehalogenation also has been observed to decrease as the degree of chlorination decreases (Vogel and McCarty, 1985; Bouwer, 1994). Murray and Richardson (1993) have postulated that this rate decrease may explain the accumulation of VC in biodegrading PCE and TCE plumes. Although reductive dehalogenation may occur under nitrate- and sulfate-reducing conditions (Vogel *et al.*, 1987), the most rapid biodegradation rates, affecting the widest range of CAHs, occurs under methanogenic conditions (Bouwer, 1994).

Reductive biotransformation of chloroethenes in contaminated aquifers holds great promise as active (bioremediation) and passive (intrinsic) remedial technologies, but there are several potential problems: 1.) The acclimation period may be long, requiring a long start-up or residence times under field conditions. 2.) We have an incomplete, at best, understanding of the ecology and physiology of the organisms involved. This makes accurate projections of the extent and rates of transformation difficult. 3.) The process proceeds through the formation of more mobile or toxic chlorinated intermediate products (dichloroethenes and vinyl chloride) which can be more harmful than the original contaminants. Only if the process can be driven to non-chlorinated end products (ethene) or linked to anaerobic or aerobic oxidative degradation of less chlorinated treatment for vinyl chloride (and possibly DCE) will in-situ reductive dechlorination be a feasible treatment technology for risk reduction. 4.) the subsurface microbial population responsible for degradation requires exposure to the electron donor and the chloroethenes at appropriate concentration and geochemical parameters for the activity to occur. This limitation may be site specific and dependent on the environmental conditions present in the aquifer.

Some of the problems/limitations associated with reductive biotransformations (especially the production of hazardous/toxic daughter products) can be mitigated if it is possible to link oxidative transformations of the less chlorinated daughters with reductive transformation of PCE and/or TCE. In the subsurface these processes would have to occur at different ORP levels or in different redox zones. These conditions could occur if the contaminates migrated from highly reducing zones to less reducing or aerobic zones in an aquifer, or if injection/extraction processes were used to alter geochemical conditions of the ground water.

Ethene is an environmentally acceptable end product of reductive dechlorination because it is only slightly soluble in water and presents no significant health hazard at environmental concentrations. Ethene can be further metabolized by many gaseous alkane oxidizing bacteria in aerobic environments to carbon dioxide and cell material or may be oxidatively catabolized with alternative electron acceptors.

B.3.3.2 Reductive Dechlorination of Chlorinated Ethanes

As with the ethenes, chlorinated ethanes will also undergo reductive dehalogenation in the subsurface via use as electron acceptors. Dechlorination of TCA has been described by Vogel and McCarty (1987) and Cox *et al.* (1995), but this pathway is complicated by the abiotic reactions that can affect TCA and its byproducts (Vogel, 1994).

B.3.3.3 Reductive Dechlorination of Chlorobenzenes

For the highly chlorinated benzenes (e.g., hexachlorobenzene and pentachlorobenzene, as well as tetrachlorobenzene, and trichlorobenzene), reductive dechlorination is the most likely biodegradation mechanism (Ramanand *et al.*, 1993; Suflita and Townsend, 1995). As discussed by Suflita and Townsend (1995), reductive dehalogenation of aromatic compounds has been observed in a variety of anaerobic habitats, including aquifer materials, marine and freshwater sediments, sewage sludges, and soil samples; however, isolation of specific microbes capable of these reactions has been difficult. As with the chlorinated ethenes and ethanes, the chlorobenzenes are most likely acting as electron acceptors as other sources of carbon and energy are being utilized by microbes or microbial consortia (Suflita and Townsend, 1995). Evidence has been presented suggesting that oxidation of hydrogen using halogenated aromatics as electron acceptors may yield more energy than if more commonly available electron acceptors were used (Dolfing and Harrison, 1992).

As discussed previously, the actual mechanisms of reductive dehalogenation are not well understood. Further, reductive dehalogenation of chlorinated benzenes has not been as well-documented as for other chlorinated solvents. However, reductive dechlorination of chlorobenzenes has been documented more frequently in the past several years (e.g., Bosma *et al.*, 1988; Fathepure *et al.*, 1988; Fathepure and Vogel, 1991; Holliger *et al.*, 1992; Ramanand *et al.*, 1993). As with other chlorinated solvents, the reductive dehalogenation of chlorobenzenes is affected by the degree of chlorination of the compound. The more chlorinated aromatic compounds are typically more amenable to this reaction (Suflita and Townsend, 1995; Adriaens

and Vogel, 1995), but as they are dechlorinated, the daughter products will become more resistant to further dehalogenation reactions (Fathepure *et al.*, 1988; Bosma *et al.*, 01988; Holliger *et al.*, 1992). The reductive dechlorination of chlorobenzenes is also analogous to the biodegradation reactions involving chlorinated ethenes and ethanes in that such degradation will make them more amenable to aerobic biodegradation (Schraa, *et al.*, 1986; Spain and Nishino, 1987; Ramanand *et al.*, 1993)

B.3.4 BIODEGRADATION OF ORGANIC COMPOUNDS VIA COMETABOLISM

When a chlorinated solvent is biodegraded through cometabolism, it serves as neither an electron acceptor nor a primary substrate in a biologically mediated redox reaction. Instead, the degradation of the compound is catalyzed by an enzyme cofactor that is fortuitously produced by organisms for other purposes. The best-documented cometabolism reactions involve catabolic oxygenases that catalyze the initial step in oxidation of their respective primary or growth substrate (BTEX or other organic compounds). These oxygenases are typically nonspecific and therefore fortuitously initiate oxidation of a variety of compounds, including many of the CAHs (McCarty and Semprini, 1994). The organism receives no known benefit from the degradation of the chlorinated solvent; in some cases the cometabolic degradation of the solvent may in fact be harmful to the microorganism responsible for the production of the enzyme or cofactor (McCarty and Semprini, 1994). Chlorinated solvents are usually only partially transformed during cometabolic processes, with additional biotic or abiotic degradation generally required to complete the transformation (McCarty and Semprini, 1994).

Cometabolism is best documented in for CAHs aerobic environments; evidence of cometabolism of chlorobenzenes is scant, as is evidence of anaerobic cometabolism. In an aerobic environment many chlorinated organic compounds can only be degraded via cometabolism. It has been reported that under aerobic conditions chlorinated ethenes, with the exception of PCE, are susceptible to cometabolic degradation (Murray and Richardson, 1993; Vogel, 1994; McCarty and Semprini, 1994; Adriaens and Vogel, 1995). Vogel (1994) further elaborates that the oxidation rate increases as the degree of chlorination decreases. Aerobic cometabolism of ethenes may be characterized by a loss of contaminant mass, the presence of intermediate degradation products (e.g., chlorinated oxides, aldehydes, ethanols, and epoxides), and the presence of other products such as chloride, carbon dioxide, carbon monoxide, and a variety of organic acids (Miller and Guengerich, 1982; McCarty and Semprini, 1994).

Several groups of aerobic bacteria currently recognized as being capable of transforming TCE and other CAHs via cometabolism; these groups include:

- Methane Oxidizers (Methanotrophs) (Fogel *et al.*, 1986; Little *et al.*, 1989, Mayer *et al.*, 1988; Oldenhuis *et al.*, 1989; Tsien *et al.*, 1989; Henry and Grbic-Galic, 1990; Alvarez-Cohen and McCarty, 1991a,b; Henry and Grbic-Galic, 1991a,b; Lanzarone and McCarty, 1990; Oldenhuis *et al.*, 1991);
- Propane Oxidizers (Wackett *et al.*, 1989);
- Ethene Oxidizers (Henry, 1991);
- Toluene, Phenol, or Cresol Oxidizers (Nelson *et al.*, 1986, 1987, 1988; Wackett and Gibson, 1988; Folsom *et al.*, 1990; Harker and Kim, 1990);
- Ammonia Oxidizers (Arciero *et al.*, 1989; Vannelli *et al.*, 1990);
- Isoprene Oxidizers (Ewers *et al.*, 1991); and
- Vinyl Chloride Oxidizers (Hartmans and de Bont, 1992).

These bacteria all have catabolic oxygenases that catalyze the initial step in oxidation of their respective primary or growth substrates and have the potential for initiating the oxidation of CAHs.

Aerobic cometabolism is not nearly as important a degradation mechanism for chlorinated solvents in the saturated zone as reductive dehalogenation. Due to the need for a substrate that may be present in limited concentrations, rates of cometabolism are often slow enough that this process may not be detectable unless the system is stimulated with additional substrate mass. For a discussion of this topic, see McCarty and Semprini (1994) and many of the references contained therein.

B.3.5 ONE-DIMENSIONAL ADVECTION-DISPERSION EQUATION WITH RETARDATION AND BIODEGRADATION

The advection-dispersion equation is obtained by adding a biodegradation term to equation B.4.11. In one dimension, this is expressed as:

$$\frac{\partial C}{\partial t} = \frac{D_x}{R}\frac{\partial^2 C}{\partial x^2} - \frac{v_x}{R}\frac{\partial C}{\partial x} - \lambda C \qquad \text{eq. B.3.1}$$

Where: v_x = average linear groundwater velocity [L/T]
R = coefficient of retardation
C = contaminant concentration [M/L^3]
D_x = hydrodynamic dispersion [L^2/T]
t = time [T]
x = distance along flow path [L]
λ = first-order biodegradation decay rate [T^{-1}]

This equation considers advection, hydrodynamic dispersion, sorption (retardation), and biodegradation. First-order rate constants are appropriate for iron (III)-reducing, sulfate-reducing, and methanogenic conditions. They are not appropriate under aerobic or denitrifying conditions.

SECTION B-4

DESTRUCTIVE ATTENUATION MECHANISMS - ABIOTIC

Chlorinated solvents dissolved in groundwater may also be degraded by abiotic mechanisms, although the reactions are typically not complete and often result in the formation of an intermediate that may be at least as toxic as the original contaminant. The most common reactions affecting chlorinated compounds are hydrolysis (a substitution reaction) and dehydrohalogenation (an elimination reaction). Other possible reactions include oxidation and reduction reactions. Butler and Barker (1996) note that no abiotic oxidation reactions involving typical halogenated solvents have been reported in the literature. They also note that reduction reactions (which include hydrogenolysis and dihaloelimination) are commonly microbially mediated, although some abiotic reduction reactions have been observed.

As Butler and Barker (1996) note, attributing changes in either the presence or absence of halogenated solvents or the concentrations of halogenated solvents to abiotic processes is usually difficult. For example, microbial activity is generally required to produce reducing conditions that favor reductive dehalogenation. If such activity is taking place, chlorinated solvents may be undergoing both biotic and abiotic degradation, and discerning the relative contribution of each mechanism on the field scale, if possible, would be very difficult. As another example, Butler and Barker (1996) note that to substantiate that hydrolysis is occurring, the presence of non-halogenated breakdown products such as acids and alcohols should be established. In general, these products are more easily biodegraded that their parent compounds and can be difficult to detect. Field evidence of this nature has yet to be collected to demonstrate hydrolysis of halogenated solvents (Butler and Barker, 1996).

Given the difficulties of demonstrating abiotic degradation on the field scale, it may not be practical to demonstrate that such processes are occurring and to quantitatively evaluate the contributions of those reactions (i.e., separately from biotic processes). If biodegradation is occurring at a site, the loss of contaminant mass due to that process may dwarf the mass lost to abiotic reactions, ruling out a cost-effective evaluation of abiotic degradation. However, while the rates of abiotic degradation may be slow relative to biotic mechanisms, the contribution of these mechanisms may still play a significant role in natural attenuation, depending on site conditions (e.g., a site with a slow solute transport velocity or a long distance to the nearest

receptor). Vogel (1994) describes data patterns that may result from varying combinations of biotic and abiotic degradation of chlorinated solvents. Moreover, because some of the byproducts of these reactions are chlorinated compounds that may be more easily or less easily degraded than the parent, the contributions of abiotic mechanisms may need to be considered when evaluating analytical data from a site.

B.4.1 HYDROLYSIS AND DEHYDROHALOGENATION

As discussed by Butler and Barker (1996), hydrolysis and dehydrohalogenation reactions are the most thoroughly studied abiotic attenuation mechanisms. In general, the rates of these reactions are often quite slow within the range of normal groundwater temperatures, with half-lives of days to centuries (Vogel *et al.*, 1987; Vogel, 1994). Therefore, most information about the rates of these reactions is extrapolated from experiments run at higher temperatures so that the experiments could be performed within a practical time frame.

B.4.1.2 Hydrolysis

Hydrolysis is a substitution reaction in which an organic molecule reacts with water or a component ion of water, and a halogen substituent is replaced with a hydroxyl (OH^-) group. The hydroxyl substitution typically occurs at the halogenated carbon. This leads initially to the production of alcohols. If the alcohols are halogenated, additional hydrolysis to acids or diols may occur. Also, the addition of a hydroxyl group to a parent molecule may make the daughter product more susceptible to biodegradation, as well as more soluble (Neely, 1985). Non-alcohol products have also been reported by Vogel *et al.* (1987) and Jeffers *et al.* (1989), but they are apparently products of competing dehydrohalogenation reactions.

The likelihood that a halogenated solvent will undergo hydrolysis depends in part on the number of halogen substituents. More halogen substituents on a compound will decrease the chance for hydrolysis reactions to occur (Vogel *et al.*, 1987), and will therefore decrease the rate of the reaction. In addition, bromine substituents are more susceptible to hydrolysis than chlorine substituents (Vogel *et al.*, 1987). Locations of the halogen substituent on the carbon chain may also have some effect on the rate of reaction. The rate also may increase with increasing pH; however, a rate dependence upon pH is typically not observed below a pH of 11 (Mabey and Mill, 1978; Vogel and Reinhard, 1986). Rates of hydrolysis may also be increased by the presence of clays, which can act as catalysts (Vogel *et al.*, 1987). Hydrolysis rates can generally be described using first-order kinetics, particularly in solutions in which water is the dominant nucleophile

Table B.4.1
Approximate Half-Lives of Abiotic Hydrolysis and
Dehydrohalogenation Reactions involving Chlorinated Solvents

Compound	Half-Life (years)	Products
Chloromethane	no data	
Methylene Chloride (Dichloromethane)	704[a/]	
Trichloromethane (Chloroform)	3500[a], 1800[b]	
Carbon Tetrachloride	41[b]	
Chloroethane	0.12[c]	ethanol
1,1-Dichloroethane	61[b]	
1,2-Dichloroethane	72[b]	
1,1,1-Trichloroethane	1.7[a], 1.1[b] 2.5[d]	acetic acid 1,1-DCE
1,1,2-Trichloroethane	140[b], 170[a]	1,1-DCE
1,1,1,2-Tetrachloroethane	47[b], 380[a]	TCE
1,1,2,2-Tetrachloroethane	0.3[e] 0.4[b], 0.8[a]	1,1,2-TCA TCE
Tetrachloroethene	0.7[f]*, 1.3 x 10[6 b]	
Trichloroethene	0.7[f]*, 1.3 x 10[6 b]	
1,1-Dichloroethene	1.2 x 10[8 b]	
1,2-Dichloroethene	2.1 x 10[10 b]	

[a] From Mabey and Mill, 1978
[b] From Jeffers *et al.*, 1989
[c] From Vogel *et al.*, 1987
[d] From Vogel and McCarty, 1987
[e] From Cooper *et al.*, 1987
[f] From Dilling *et al.*, 1975
* Butler and Barker (1996) indicate that these values may reflect experimental difficulties and that the longer half-life [as calculated by Jeffers et al. (1989)] should be used.

conditions, monohalogenated aliphatics apparently do not undergo dehydrohalogenation, and these reactions are apparently not likely to occur (March, 1985; Vogel *et al.*, 1987). However, Jeffers *et al.* (1989) report on the dehydrohalogenation of CA to VC. Polychlorinated alkanes have been observed to undergo dehydrohalogenation under normal conditions and extremely basic conditions (Vogel *et al.*, 1987). As with hydrolysis, bromine substituents are more reactive with respect to dehydrohalogenation.

Dehydrohalogenation rates may also be approximated using pseudo-first-order kinetics. Once again, this is not truly a first-order reaction, but such approximations have been used in the literature to quantify the reaction rates. The rates will not only depend upon the number and types of halogen substituent, but also on the hydroxide ion concentration. Under normal pH

conditions (i.e., near a pH of 7), interaction with water (acting as a weak base) may become more important (Vogel *et al.*, 1987). Transformation rates for dehydrohalogenation reactions is presented in Table B.4.1. 1,1,1-TCA is also known to undergo dehydrohalogenation (Vogel and McCarty, 1987). In this case, TCA is transformed to 1,1-DCE, which is then reductively dehalogenated to VC. The VC is then either reductively dehalogenated to ethene or consumed as a substrate in an aerobic reaction and converted to CO_2. In a laboratory study, Vogel and McCarty (1987) reported that the abiotic conversion of 1,1,1-TCA to 1,1-DCE has a rate constant of about 0.04 $year^{-1}$. It was noted that this result was longer than indicated in previous studies, but that experimental methods differed. Jeffers *et al.* (1989) reported on several other dehydrohalogenation reactions; in addition to 1,1,1-TCA and 1,1,2-TCA both degrading to 1,1-DCE, the tetrachloroethanes and pentachloroethanes degrade to TCE and PCE, respectively. Rates of these reactions are included in Table B.4.1. As noted previously, Jeffers *et al.* (1989) also report that CA may degrade to VC, but no information on rates was encountered during the literature search for this Appendix.

B.4.2 REDUCTION REACTIONS

Two abiotic reductive dechlorination reactions that may operate in the subsurface are hydrogenolysis and dihaloelimination. Hydrogenolysis is the simple replacement of a chlorine (or another halogen) by a hydrogen, while dihaloelimination is the removal of two chlorines (or other halogens) accompanied by the formation of a double carbon-carbon bond. Butler and Barker (1996) review work by Criddle *et al.* (1986), Jafvert and Wolfe (1987), Reinhard *et al.* (1990), and Acton (1990) and this review suggests that while these reactions are thermodynamically possible under reducing conditions, they often do not take place in the absence of biological activity, even if such activity is only indirectly responsible for the reaction. While not involved in a manner similar to that for cometabolism, microbes may produce reductants that facilitate such reactions in conjunction with minerals in the aquifer matrix, as has been suggested by work utilizing aquifer material from the Borden test site (Reinhard *et al.*, 1990). Moreover, the reducing conditions necessary to produce such reactions are most often created as a result of microbial activity. It is therefore not clear if some of these reactions are truly abiotic, or if because of their reliance on microbial activity to produce reducing conditions or reactants, they should be considered to be a form of cometabolism.

In some cases, truly abiotic reductive dechlorination has been observed; however, the conditions that favor such reactions may not occur naturally. For example, Gillham and O'Hannesin (1994) describe reductive dehalogenation of chlorinated aliphatics using zero-valent

APPENDIX C

DATA INTERPRETATION AND CALCULATIONS

NOTE: THIS APPENDIX IS IN EARLY DRAFT STAGE. MANY OF THE SECTIONS REQUIRE ADDITIONAL TEXT OR FORMATTING - COMMENTS WILL BE APPRECIATED

FIGURES

C.2.3.2 Preparation of Potentiometric Surface Maps

A potentiometric surface map is a two-dimensional graphical representation of equipotential lines shown in plan view. Water table elevation maps are potentiometric surface maps drawn for water table (unconfined) aquifers. Potentiometric surface maps for water table aquifers show where planes of equal potential intersect the water table. A potentiometric surface map should be prepared from water level measurements and surveyor's data. These maps are used to estimate the direction of plume migration and to calculate hydraulic gradients. To document seasonal variations in groundwater flow, separate potentiometric surface maps should be prepared using quarterly water level measurements taken over a period of at least 1 year.

The data used to develop the potentiometric surface map should be water level elevation data (elevation relative to mean sea level) from piezometers/wells screened in the same relative position within the same hydrogeologic unit. For example, wells that are screened at the water table can be used for the same potentiometric surface map. Wells screened in different hydrogeologic units or at different relative positions within the same water table aquifer cannot be used to prepare a potentiometric surface map. Where possible, a potentiometric surface map should be prepared for each hydrogeologic unit at the site. In recharge areas, wells screened at various elevations cannot all be used to prepare the same potentiometric surface map because of strong downward vertical gradients. Likewise, wells screened at various elevations in discharge areas such as near streams, lakes, or springs, should not all be used because of the strong upward vertical gradients.

When preparing a potentiometric surface map, the locations of system boundaries should be kept in mind; particularly the site features that tend to offset the shape of the contours on the map. Such features include topographic divides, surface water bodies, and pumping wells.

In addition to, and separately from, preparation of a potentiometric surface map, water level measurements from wells screened at different depths can be used to determine any vertical hydraulic gradients. It is important to have a good understanding of vertical hydraulic gradients because they may have a profound influence on contaminant migration.

In areas with measurable mobile LNAPL, a correction must be made for the water table deflection caused by the LNAPL. The following relationship, based on Archimedes' Principle, provides a correction factor that allows the water table elevation to be adjusted for the effect of floating LNAPL.

$$CDTW = MDTW - \frac{\rho_{lnapl}}{\rho_w}(PT) \qquad \text{eq. C.2.1}$$

Where: $CDTW$ = corrected depth to water [L]
$MDTW$ = measured depth to water [L]
ρ_{lnapl} = density of the LNAPL [M/L^3]
ρ_w = density of the water, generally 1.0 [M/L^3]
PT = measured LNAPL thickness [L]

Using the corrected depth to water, the corrected groundwater elevation, CGWE, is given by:

$$CGWE = \text{Datum Elevation} - CDTW \qquad \text{eq. C.2.2}$$

Corrected groundwater elevations should be used for potentiometric surface map preparation. Figure C.2.2 is an example of a groundwater elevation map for an unconfined aquifer. Water table elevation data used to prepare this map were taken from wells screened across the water table.

C.2.3.3 Preparation of Flow Nets

Where an adequate three-dimensional database is available, flow nets can be constructed to facilitate the interpretation of the total hydraulic head distribution in the aquifer. This will help determine potential solute migration pathways. The simplest groundwater flow system is one that is homogeneous and isotropic. This type of hydrogeologic setting serves as a simple basis for describing the basic rules of flow net construction, despite the fact that homogeneous, isotropic media rarely occur in nature. Regardless of the type of geologic media, the basic rules of flow net construction must be applied, and necessary modifications must be made throughout the procedure to account for aquifer heterogeneity or anisotropic conditions. Water level data for flow net construction should come from multiple sets of nested wells (two or more wells at the same location) at various depths in the aquifer. The fundamental rules of flow net construction and the important properties of flow nets are summarized as follows:

- Flow lines and equipotential lines intersect at 90-degree angles if the permeability is isotropic;
- The geometric figures formed by the intersection of flow lines and equipotential lines must approximate squares or rectangles;
- Equipotential lines must meet impermeable boundaries at right angles (impermeable boundaries are flow lines); and

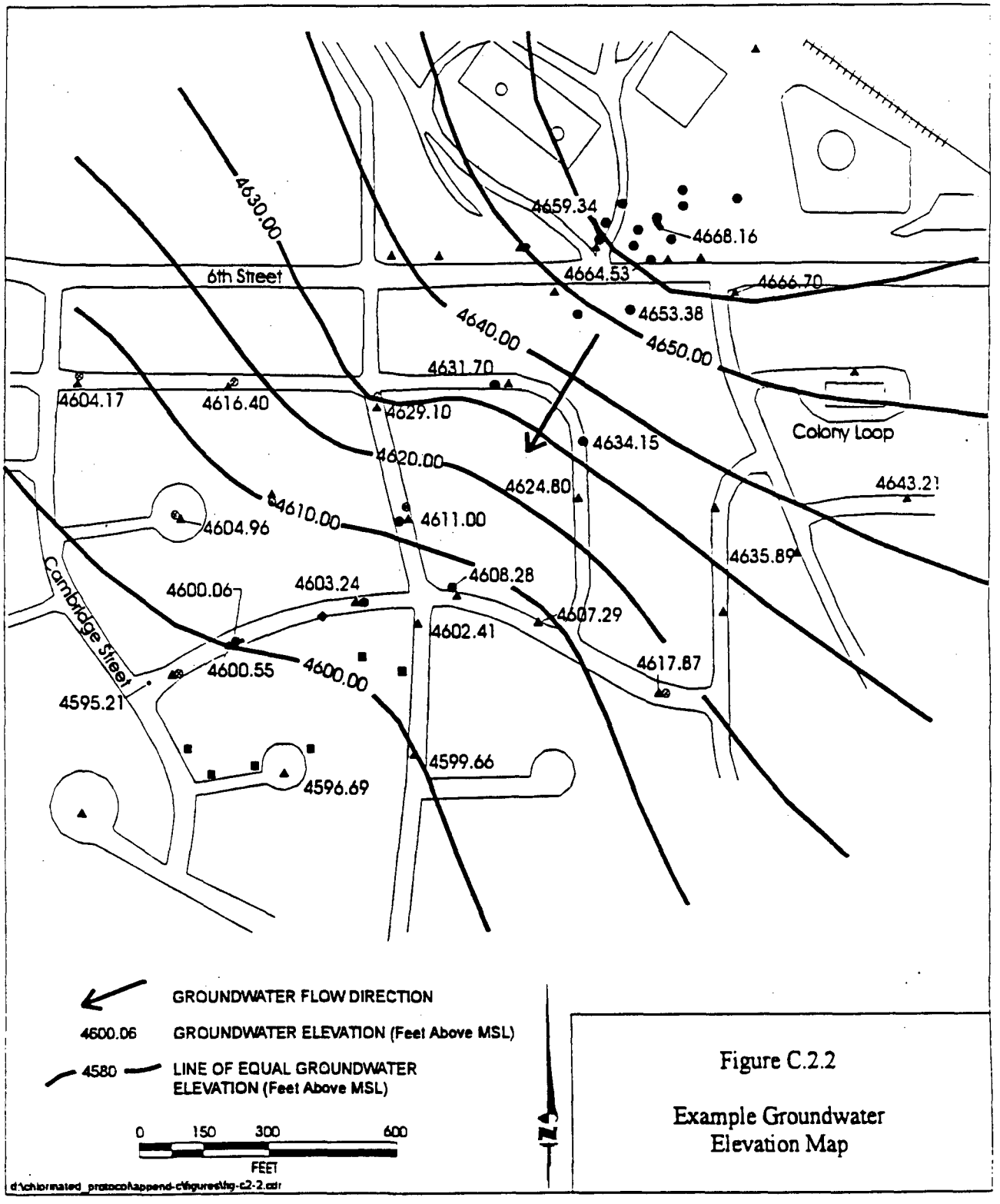


Figure C.2.2

Example Groundwater Elevation Map

- Equipotential lines must be parallel to constant-head boundaries (constant-head boundaries are equipotential lines).

Trial-and-error sketching is generally used to construct a flow net. Flow net sketching can be sufficiently accurate if constructed according to the basic rules outlined above. A relatively small number of flow lines (three to five) generally are sufficient to adequately characterize flow conditions. Flow nets should be superimposed on the hydrogeologic sections. Figure C.2.3 is an example of a completed flow net. This figure shows groundwater flow patterns in both recharge and discharge areas.

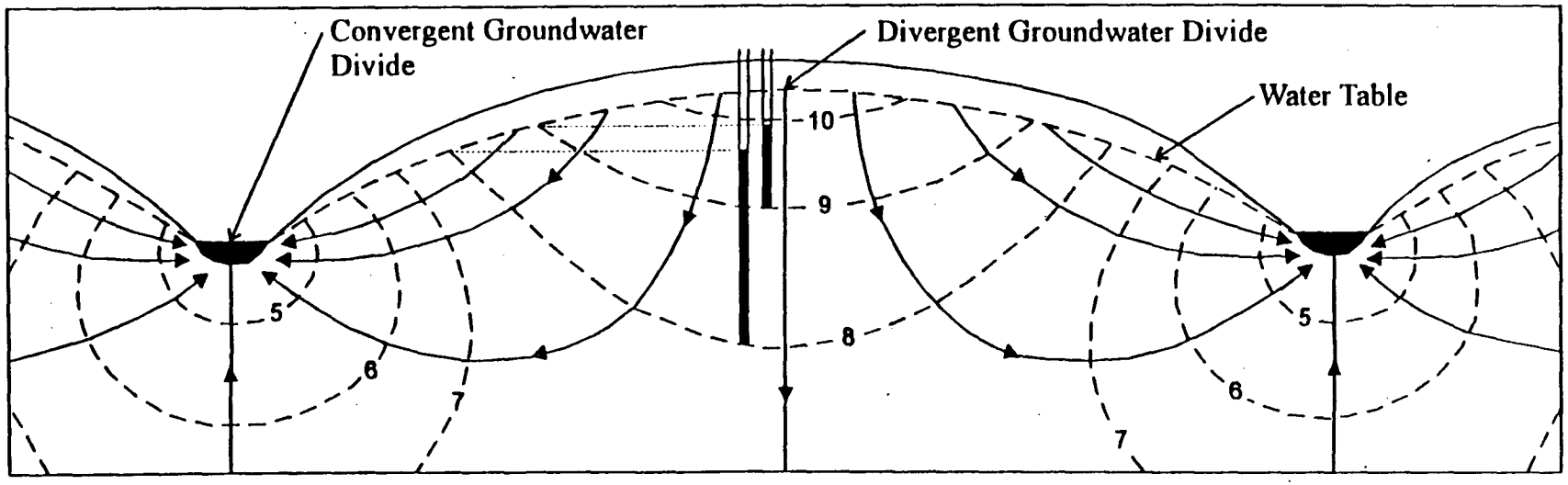
C.2.3.4 Preparation of Contaminant Isopach Maps

If NAPL is present at the site, isopach maps showing the thickness and distribution of NAPL should be prepared. Two maps should be prepared: one for mobile NAPL, and one for residual NAPL. Such isopach maps allow estimation of the distribution of NAPL in the subsurface and aid in fate and transport model development by identifying the boundary of the NAPL. Because of the differences between the magnitude of capillary suction in the aquifer matrix and the different surface tension properties of fuel and water, LNAPL thickness observations made in monitoring points are only an estimate of the actual volume of mobile LNAPL in the aquifer. To determine the actual NAPL thickness it is necessary to collect and visually analyze soil samples. LNAPL thickness data also should be used to correct for water table deflections caused by the mobile LNAPL. This process is described in Section C.2.2.3.2.

Isopach maps are prepared by first plotting the measured NAPL thickness on a base map prepared using surveyor's data. Lines of equal NAPL thickness (isopachs) are then drawn and labeled. Each data point must be honored during contouring. Figure C.2.4 is an example of a completed isopach map. This figure also contains an example of an isopleth map.

C.2.3.4.1 Relationship Between Apparent and Actual LNAPL Thickness

It is well documented that LNAPL thickness measurements taken in groundwater monitoring wells are not indicative of actual LNAPL thicknesses in the formation (de Pastrovich *et al.*, 1979; Blake and Hall, 1984; Hall *et al.*, 1984; Hampton and Miller, 1988; Hughes *et al.*, 1988; Abdul *et al.*, 1989; Testa and Paczkowski, 1989; Farr *et al.*, 1990; Kemblowski and Chiang, 1990; Lehnard and Parker, 1990; Mercer and Cohen, 1990; Ballestero *et al.*, 1994; Huntley *et al.*, 1994a and 1994b). These authors note that the measured thickness of LNAPL in a monitoring well is



Flow Line

Equipotential Line

10 Total Head (meters)

Modified from Hubbert (1940)

d:\chlorinated_protocol\append-c\figures\fig-c2-3.cdr

Figure C.2.3

Example Flow Net

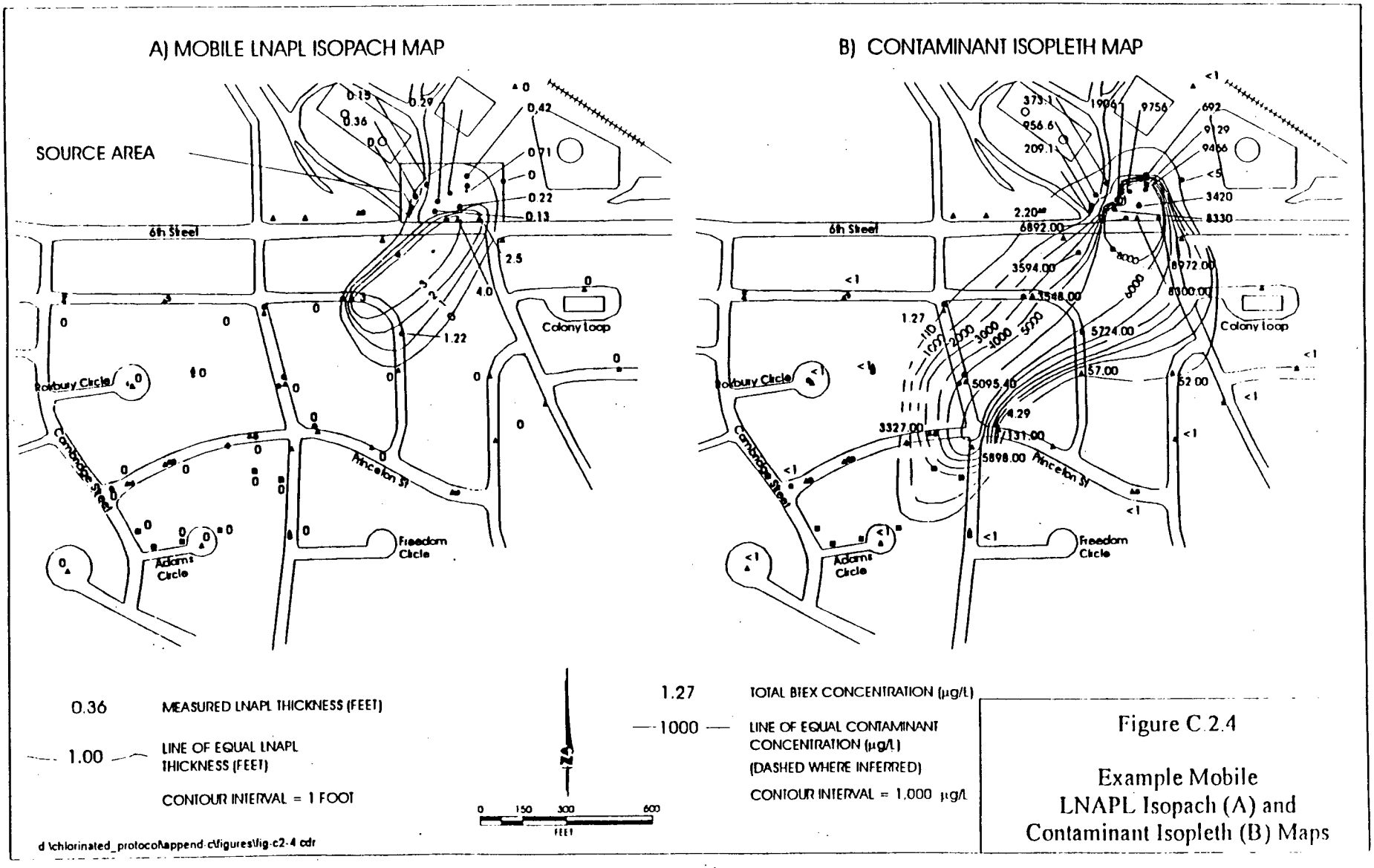


Figure C.2.4

Example Mobile LNAPL Isopach (A) and Contaminant Isopleth (B) Maps

greater that the true LNAPL thickness in the aquifer and, according Mercer and Cohen (1990), measured LNAPL thickness in wells is typically 2 to 10 times greater than the actual LNAPL thickness in the formation. The difference between actual and measured LNAPL thickness occurs because mobile LNAPL floating on the water table flows into the well (if the top of well screen is above the base of the LNAPL) and depresses the water table. Figure C.2.5 is a schematic that illustrates this relationship. The equation for correcting depth to groundwater caused by LNAPL in the well is given in Section C.2.2.3.1. Empirical relationships relating measured LNAPL thickness to actual LNAPL thickness are presented below. Also presented below are test methods that can be used to determine actual LNAPL thickness.

C.2.3.4.1.1 Empirical Relationships

There are several empirical methods available to estimate the actual thickness of mobile LNAPL in the subsurface based on LNAPL thicknesses measured in a groundwater monitoring well. Such empirical relationships are, at best, approximations because many factors influence the relationship between measured and apparent LNAPL thickness, including (Mercer and Cohen, 1990):

- Capillary fringe height depends on grain size and is hysteretic with fluid level fluctuations.
- LNAPL can become trapped below the water table as the water table rises and falls.
- The thickness of LNAPL is ambiguous because the interval of soil containing mobile LNAPL is not 100-percent saturated with LNAPL.

Some empirical methods for determining actual LNAPL thickness are described below.

Method of de Pastrovich *et al.* (1979)

Hampton and Miller (1988) conducted laboratory experiments to examine the relationship between the actual thickness of LNAPL in a formation, h_f, and that measured in a monitoring well, h_m. Based on their research, Hampton and Miller (1988) suggest using the following relationship (developed by de Pastrovich *et al.* in 1979) to estimate LNAPL thickness:

$$h_f \approx \frac{h_m(\rho_w - \rho_{inapl})}{\rho_{inapl}} \qquad \text{eq. C.2.3}$$

Where: h_f = actual thickness of LNAPL in formation
h_m = measured LNAPL thickness in well
ρ_w = density of water (1.0 gm/cm^3 for pure water)
ρ_{inapl} = density of LNAPL (See Table C.3.9)

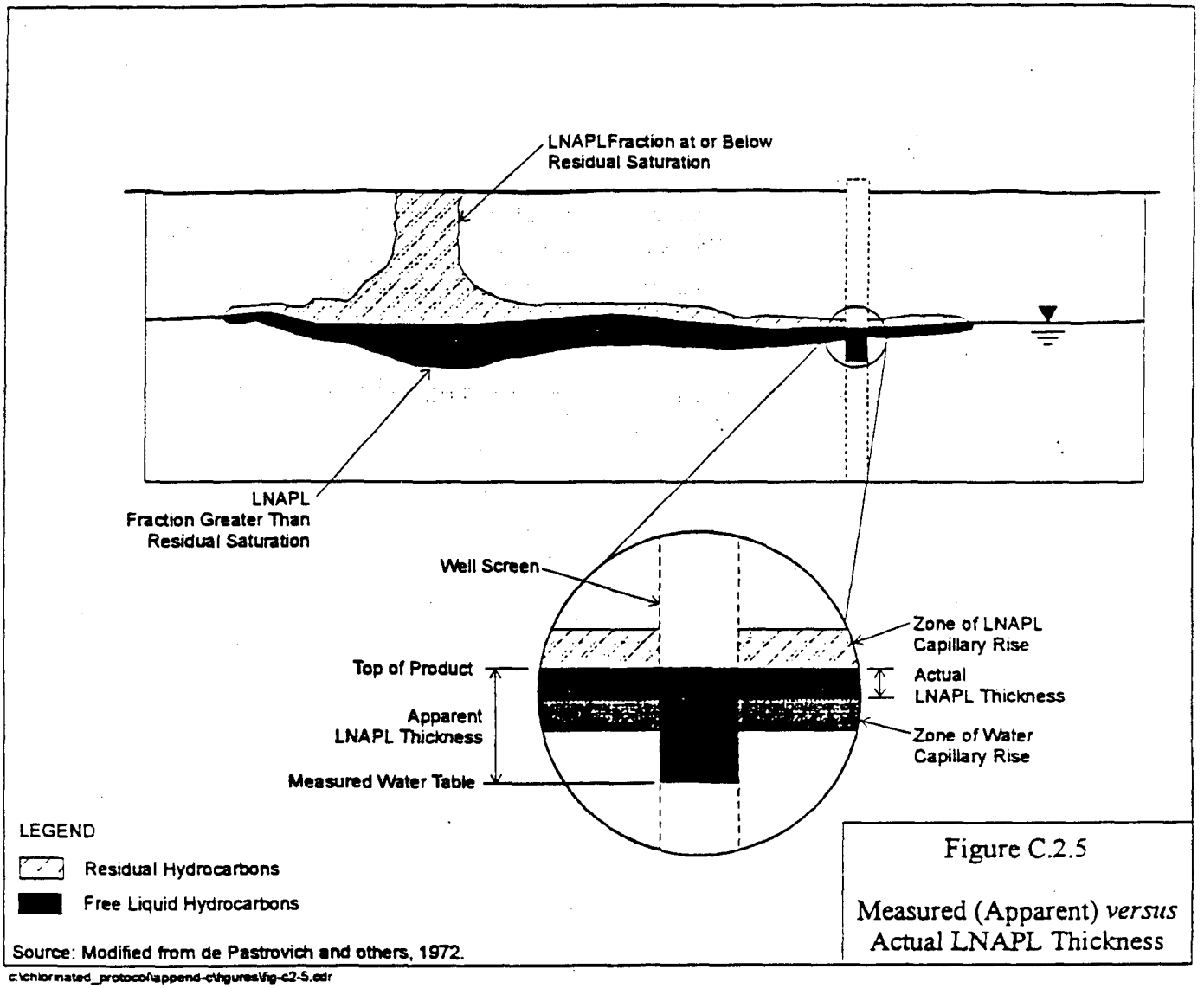


Figure C.2.5

Measured (Apparent) *versus* Actual LNAPL Thickness

Method of Kemblowski and Chiang (1990)

Another empirical relationship was proposed by Kemblowski and Chiang (1990) to estimate actual LNAPL thickness based on measured LNAPL thickness. This relationship is given by:

$$h_o = H_o - 2.2h_{aw}^c\Big|_{dr} \qquad \text{eq. C.2.4}$$

Where: h_o = equivalent thickness of LNAPL in the formation (volume of oil per unit area of aquifer, divided by porosity).

H_o = measured LNAPL thickness in well

$h_{aw}^c\Big|_{dr}$ = capillary height of air-water interface assuming water is being displaced by oil (typical values are given in Table C.2.1)

This method assumes equilibrium conditions, water drainage, and oil imbibition.

Table C.2.1

Typical values for $h_{aw}^c\Big|_{dr}$ (Bear, 1972)

Aquifer Matrix	$h_{aw}^c\Big\|_{dr}$ (cm)	$h_{aw}^c\Big\|_{dr}$ (ft)
Coarse Sand	2-5	0.066-0.16
Sand	12-35	0.39-1.15
Fine Sand	35-70	1.14-2.30
Silt	70-150	2.30-4.92
Clay	>200-400	>6.56-13.12

Method of Lehnard and Parker (1990)

Another empirical relationship was proposed by Lehnard and Parker (1990) to estimate actual LNAPL thickness based on measured LNAPL thickness. This relationship is given by:

$$D_o = \frac{\rho_{ro}\beta_{ao}H_o}{\beta_{ao}\rho_{ro} - \beta_{ow}(1-\rho_{ro})} \qquad \text{eq. C.2.5}$$

Where: D_o = actual thickness of LNAPL in formation

H_o = measured LNAPL thickness in well

ρ_{ro} = specific gravity of LNAPL (density of oil/density of water)

$\beta_{ao} = \frac{\sigma_{aw}}{\sigma_{ao}}$ = Air-oil scaling factor

$\beta_{ow} = \frac{\sigma_{aw}}{\sigma_{ow}}$ = Oil-water scaling factor

σ_{aw} = surface tension of uncontaminated water (72.75 dynes/cm @ 20°C)

σ_{ao} = surface tension of LNAPL [25 dynes/cm @ 20°C for JP-4, Table C.2.2]

$\sigma_{ow} = \sigma_{aw} - \sigma_{ao}$ = interfacial tension between water and LNAPL (47.75dynes/cm @ 20°C)

It is important to note that this method includes the capillary thickness of the hydrocarbon, and is therefore likely to be an overestimate.

Table C.2.2

Surface Tensions for Various Compounds

Compound	Surface Tension @ 20°C (dyne/cm)
JP-4	25[a/]
Gasoline	19-23[a/]
Pure Water	72.75[b/]

a/ Martel (1987).
b/ CRC Handbook (1956).

C.2.3.4.1.2 LNAPL Baildown Test

The LNAPL baildown test is applicable in areas where the hydrocarbon/water interface is below the potentiometric surface, and the recharge rate of hydrocarbon into the well is slow (Hughes *et al.*, 1988).

Baildown Test Procedure (From Hughes *et al.*, 1988):

1) Gauge the well and calculate the corrected potentiometric surface elevation using equations C.2.1 and C.2.2.

2) Rapidly bail the hydrocarbon from the well.

3) Gauge the well again, and if the thickness of the hydrocarbon is acceptable (0.1 to 1 foot), calculate the potentiometric surface elevation. The potentiometric surface elevation thus calculated should be within 0.005 foot of the value calculated in step 1. If it is, then continue to step 4; if it is not, repeat steps 2 and 3.

4) Record the top of the LNAPL surface in the well as it recharges until the well is fully recharged.

5) Plot the elevation of the top of LNAPL in the well *vs.* time since bailing ceased.

6) The true thickness of the mobile LNAPL layer (T_f) is the distance from the inflection point to the top of the hydrocarbon under static conditions (Figure C.2.6). Thus, T_f is picked directly off the plot. Table C.2.3 is an example of the results of this procedure.

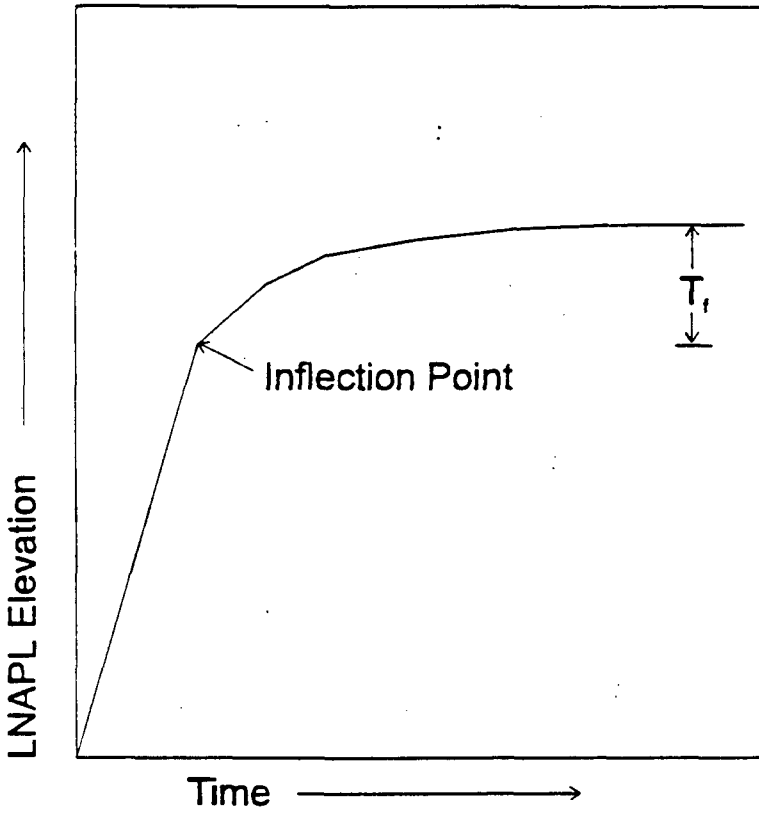


Figure C.2.6

Type Curve for LNAPL Baildown Test

Table C.2.3
Results of Example Baildown Test
(Modified from Hughes *et al.*, 1988)

Well	T_w (ft)[a/]	T_f (ft)	Exaggeration (T_w/T_f)
ROW-143	4.97	0.61	8.1:1
ROW-189	12.5	0.29	43.0:1
ROW-129	0.94	0.0[b/]	N/A

a/ T_w = LNAPL thickness initially measured in the well
b/ Capillary oil only

Hughes *et al.* (1988) also present a recharge method that involves pumping the mobile LNAPL until steady-state conditions are achieved, and then letting the well fully recharge.

C.2.3.5 Preparation of Contaminant and Daughter Product Isopleth Maps

Isopleth maps should be prepared for all chlorinated solvents of concern and their daughter products and for total BTEX if present. For example, if trichloroethene and BTEX were released (as is typical for fire training areas), then maps of dissolved trichloroethene, dichloroethene, vinyl chloride, ethene, and total BTEX concentrations should be prepared. Isopleth maps allow interpretation of data on the distribution and the relative transport and degradation rates of contaminants in the subsurface. In addition, contaminant isopleth maps allow contaminant concentrations to be gridded and used for input into a solute transport model.

Isopleth maps are prepared by first plotting the concentration of the contaminant on a base map prepared using surveyor's data. Lines of equal contaminant concentration (isopleths) are then drawn and labeled. It is important to ensure that each data point is honored during contouring, unless some data are suspect. Figures C.2.4, C.2.7, and C.2.8 contain examples of contaminant isopleth maps.

Dissolved BTEX concentrations are determined through groundwater sampling and laboratory analysis. From these data, isopleth maps for each of the BTEX compounds and for total dissolved BTEX should be made. Dissolved BTEX concentrations are transferred to the fate and transport model grid cells by overlaying the isopleth map onto the model grid.

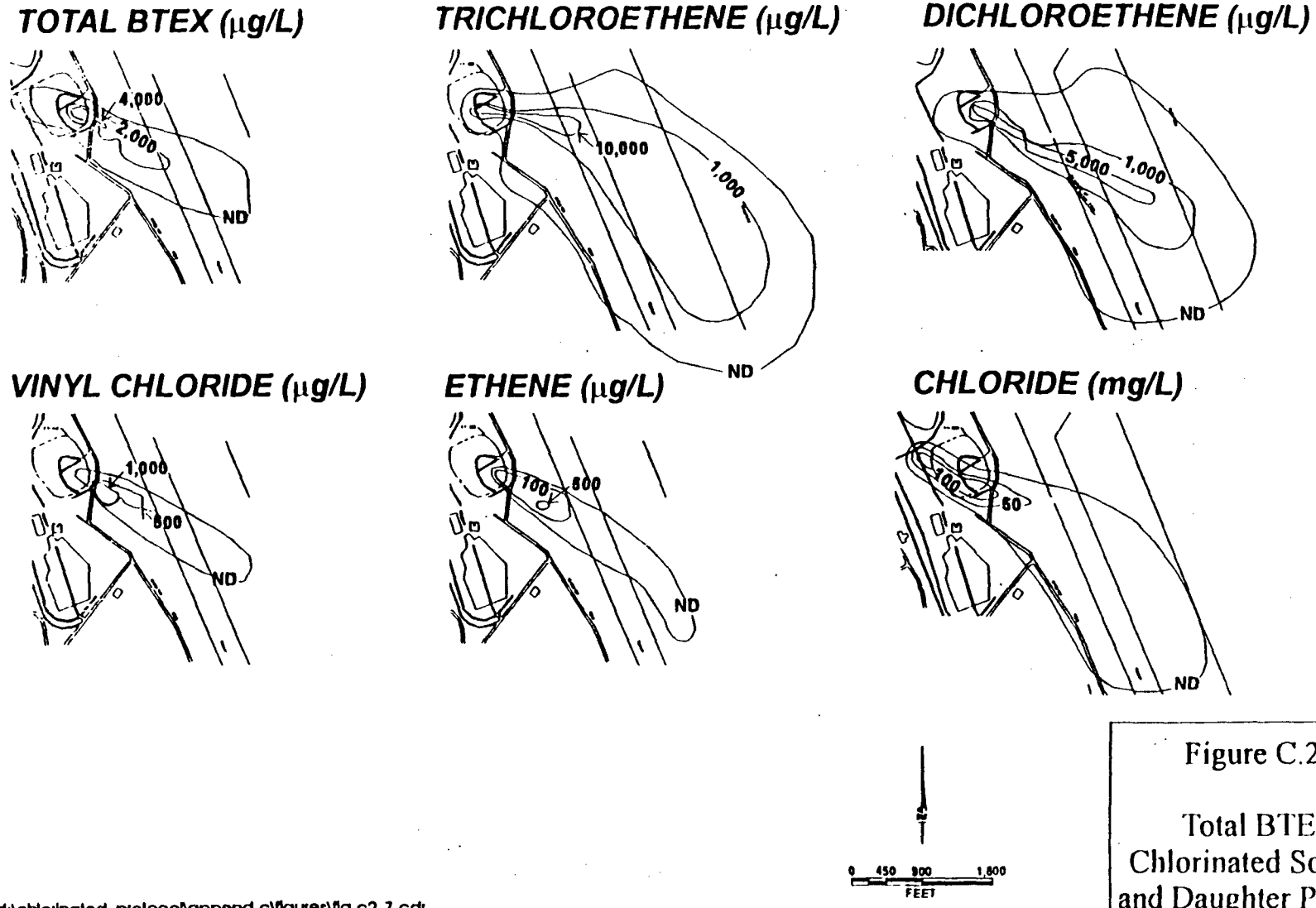


Figure C.2.7

Total BTEX, Chlorinated Solvents and Daughter Products

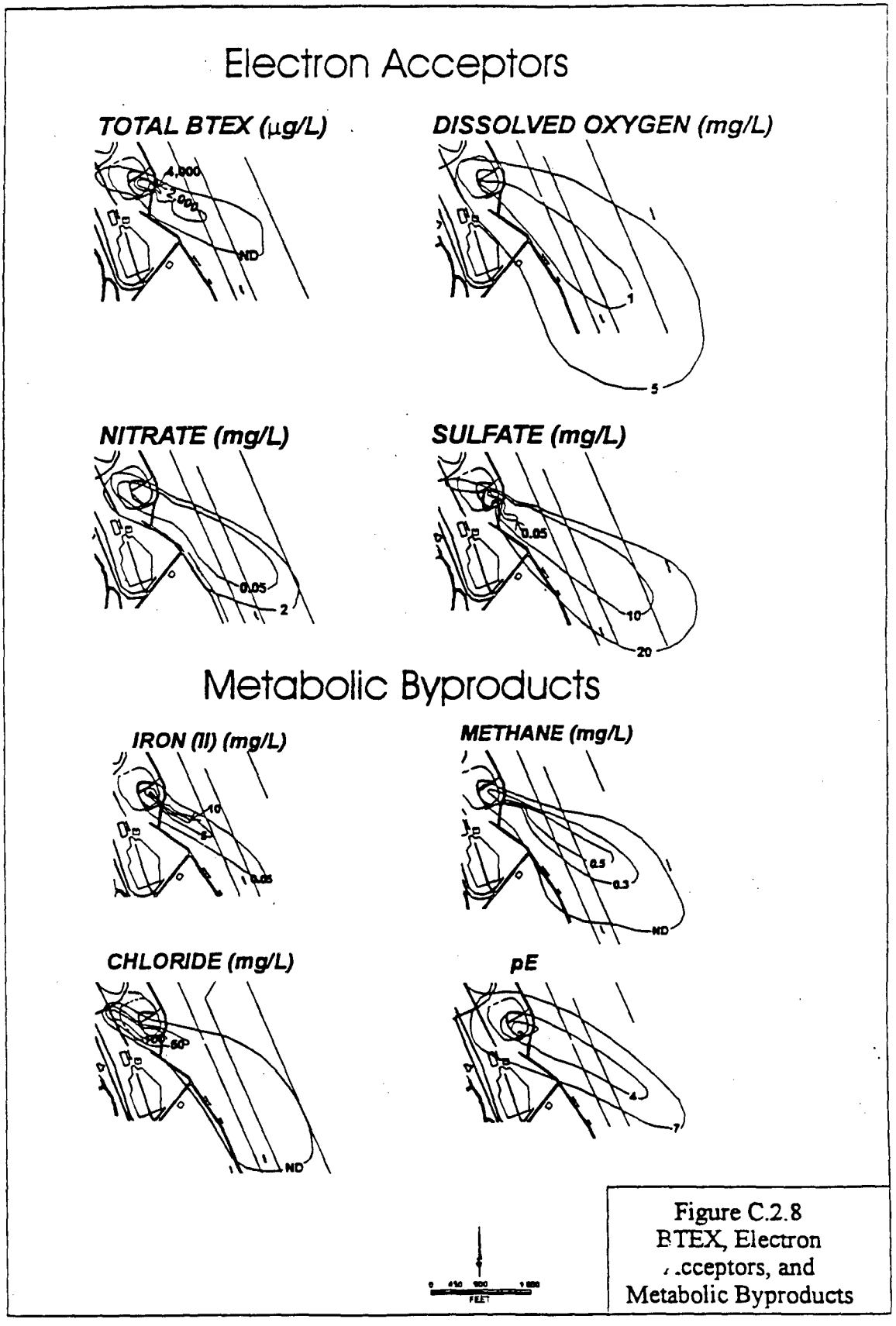


Figure C.2.8
BTEX, Electron Acceptors, and Metabolic Byproducts

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C.2.3.6 Preparation of Electron Donor, Inorganic Electron Acceptor, and Metabolic Byproduct Contour (Isopleth) Maps

Isopleth maps should be prepared for any organic compound that can be used as an electron donor. Examples of such compounds include natural organic carbon, petroleum hydrocarbons, (e.g., BTEX, napthalene, landfill leachate, etc.). These maps are used to provide visible evidence that biodegradation could occur or is occurring. Isopleth maps also should be prepared for dissolved oxygen, nitrate, manganese (II), iron (II), sulfate, methane, and chloride. These maps are used to provide visible evidence that biodegradation is occurring. The electron acceptor and metabolic byproduct isopleth maps can be used to determine the relative importance of each of the terminal electron-accepting processes (TEAPs).

Isopleth maps are prepared by first plotting the concentration of the electron donor, electron acceptor, or metabolic byproduct on a base map prepared using surveyor's data. Lines of equal concentration (isopleths) are then drawn and labeled. It is important to ensure that each data point is honored during contouring, unless some data are suspect.

C.2.3.6.1 Inorganic Electron Acceptor Isopleth Maps

Electron acceptor isopleth maps allow interpretation of data on the distribution of dissolved oxygen, nitrate, and sulfate in the subsurface. Isopleth maps for these compounds provide a visual indication of the relationship between the contaminant plume and the electron acceptors and the relative importance of each TEAP. Dissolved oxygen concentrations below background levels in areas with high organic carbon concentrations are indicative of aerobic respiration. Nitrate concentrations below background in areas with high organic carbon concentrations are indicative of denitrification. Sulfate concentrations below background in areas with high organic carbon concentrations are indicative of sulfate reduction.

Figure C.2.7 gives examples of completed isopleth maps for dissolved oxygen, nitrate, and sulfate. This figure also contains the total BTEX (electron donor) isopleth map for the same period. Comparison of the total BTEX isopleth map and the electron acceptor isopleth maps shows that there is a strong correlation between areas with elevated organic carbon and depleted electron acceptor concentrations. The strong correlation indicates that the electron acceptor demand exerted during the metabolism of BTEX has resulted in the depletion of soluble inorganic electron acceptors. These relationships provide strong evidence that biodegradation is occurring via the processes of aerobic respiration, denitrification, and sulfate reduction.

C.2.3.6.2 Metabolic Byproduct Isopleth Maps

Metabolic byproduct maps should be prepared for manganese (II), iron (II), methane, and chloride. The manganese (II) map is prepared in lieu of an electron acceptor isopleth map for manganese (IV) because the amount of bioavailable amorphous or poorly crystalline manganese (IV) in an aquifer matrix is extremely hard to quantify. The iron (II) map is prepared in lieu of an electron acceptor isopleth map for iron (III) because the amount of bioavailable amorphous or poorly crystalline iron (III) in an aquifer matrix is extremely hard to quantify. Iron (II) concentrations above background levels in areas with BTEX contamination are indicative of anaerobic iron (III) reduction. Methane concentrations above background levels in areas with BTEX contamination are indicative of methanogenesis, another anaerobic process. Biodegradation of chlorinated solvents tends to increase the chloride concentration found in groundwater. Thus, chloride concentrations inside the contaminant plume generally increase to concentrations above background. This map will allow visual interpretation of chloride data by showing the relationship between the contaminant plume and chloride. During biodegradation, the oxidation-reduction potential of groundwater is lowered. Thus, the oxidation-reduction potential (or pE) inside the contaminant plume generally decreases to levels below background.

Figure C.2.8 gives examples of completed isopleth maps for iron (II), methane, chloride, and pE. This figure also contains the total BTEX (electron donor) isopleth map for the same period. Comparison of the total BTEX isopleth map and the metabolic byproduct isopleth maps and comparison of Figures C.2.7 and C.2.8 shows that there is a strong correlation between areas with elevated organic carbon and elevated metabolic byproduct concentrations. These relationships provide strong evidence that biodegradation is occurring via the processes of iron (III) reduction, methanogenesis, and reductive dechlorination.

SECTION C-3

NATURAL ATTENUATION CALCULATIONS

Several calculations using site-specific data must be made in order to document the occurrence of natural attenuation and successfully implement the natural attenuation alternative. The following sections describe these calculations.

C.3.1 CALCULATING HYDRAULIC PARAMETERS

Hydraulic parameters necessary for adequate site characterization and model implementation include hydraulic conductivity, transmissivity, hydraulic gradient, linear groundwater flow velocity, hydrodynamic dispersion, and retarded solute transport velocity. Calculations for these parameters are discussed in the following sections.

C.3.1.1 Hydraulic Conductivity

Hydraulic conductivity, K, is a measure of an aquifer's ability to transmit water and is perhaps the most important variable governing fluid flow in the subsurface. Hydraulic conductivity has the units of length over time [L/T]. Observed values of hydraulic conductivity range over 12 orders of magnitude, from $3x10^{-12}$ to 3 cm/sec ($3x10^{-9}$ to $3x10^{3}$ m/day) (Table C.3.1). In general terms, the hydraulic conductivity for unconsolidated sediments tends to increase with increasing grain size and sorting. The velocity of groundwater and dissolved contaminants is directly related to the hydraulic conductivity of the saturated zone. Subsurface variations in hydraulic conductivity directly influence contaminant fate and transport by providing preferential pathways for contaminant migration. The most common methods used to quantify hydraulic conductivity in the subsurface are aquifer pumping tests and slug tests. The quantitative analysis of pumping and slug test data is beyond the scope of this document. For information on the quantitative analysis of these data, the reader is referred to the works of Kruseman and de Ridder (1991) and Dawson and Istok (1991).

Table C.3.1

Representative Values of Hydraulic Conductivity for Various Sediments and Rocks
(From Domenico and Schwartz, 1990)

Material	Hydraulic Conductivity (m/day)	Hydraulic Conductivity (cm/sec)
UNCONSOLIDATED SEDIMENT		
Glacial till	$9x10^{-8}$ - $2x10^{-1}$	$1x10^{-10}$ - $2x10^{-3}$
Clay	$9x10^{-7}$ - $4x10^{-4}$	$1x10^{-9}$ - $5x10^{-7}$
Silt	$9x10^{-5}$ - 2	$1x10^{-7}$ - $2x10^{-3}$
Fine sand	$2x10^{-2}$ - $2x10^{1}$	$2x10^{-5}$ - $2x10^{-2}$
Medium sand	$8x10^{-2}$ - $5x10^{1}$	$9x10^{-5}$ - $6x10^{-2}$
Coarse sand	$8x10^{-2}$ - $5x10^{2}$	$9x10^{-5}$ - $6x10^{-1}$
Gravel	$3x10^{1}$ - $3x10^{3}$	$3x10^{-2}$ - 3
SEDIMENTARY ROCK		
Karstic limestone	$9x10^{-2}$ - $2x10^{3}$	$1x10^{-3}$ - 2
Limestone and dolomite	$9x10^{-5}$ - $5x10^{-1}$	$1x10^{-7}$ - $6x10^{-3}$
Sandstone	$3x10^{-5}$ - $5x10^{-1}$	$3x10^{-8}$ - $6x10^{-3}$
Siltstone	$9x10^{-7}$ - $1x10^{-3}$	$1x10^{-9}$ - $1x10^{-5}$
Shale	$9x10^{-9}$ - $2x10^{-4}$	$1x10^{-11}$ - $2x10^{-7}$
CRYSTALLINE ROCK		
Vesicular basalt	$3x10^{-2}$ - $2x10^{3}$	$4x10^{-5}$ - 2
Basalt	$2x10^{-6}$ - $3x10^{-2}$	$2x10^{-9}$ - $4x10^{-5}$
Fractured igneous and metamorphic	$7x10^{-4}$ - $3x10^{1}$	$8x10^{-7}$ - $3x10^{-2}$
Unfractured igneous and metamorphic	$3x10^{-9}$ - $2x10^{-5}$	$3x10^{-12}$ - $2x10^{-8}$

C.3.1.1.1 Hydraulic Conductivity from Pumping Tests

Pumping tests generally provide the most reliable information about aquifer hydraulic conductivity. Pumping test data for geohydraulic characteristics are most commonly interpreted by graphic techniques. The analytical method used for interpretation of the data will depend upon the physical characteristics of the aquifer and test wells. The assumptions inherent in the analytical method used to calculate aquifer characteristics should be evaluated to ensure acceptance of the method for the subsurface conditions present at the site under investigation.

The interpretation of aquifer pumping test data is not unique. Similar sets of data can be obtained from various combinations of geologic conditions. Field data of drawdown *vs.* time and/or distance are plotted on graph paper either by hand or using programs such as AQTESOLV® or a spreadsheet program. There are numerous methods of interpreting pumping test data. The method to be used for each pumping test should be selected based on site-specific

conditions (aquifer conditions, test conditions, assumptions made, etc.). Most hydrogeology text books contain pumping test evaluation techniques. Two publications dealing with pump test analysis are recommended (Kruseman and de Ridder, 1991 and Dawson and Istok, 1991).

C.3.1.1.2 Hydraulic Conductivity from Slug Tests

Slug tests are a commonly used alternative to pumping tests that are relatively easy to conduct. The biggest advantage of slug tests is that no contaminated water is produced during the test. During pumping tests at fuel-hydrocarbon-contaminated sites, large volumes of contaminated water that must be treated typically are produced. One commonly cited drawback to slug testing is that this method generally gives hydraulic conductivity information only for the area immediately surrounding the monitoring well. If slug tests are going to be relied upon to provide information on the three-dimensional distribution of hydraulic conductivity in an aquifer, multiple slug tests must be performed, both within the same well and at several monitoring wells at the site. It is not advisable to rely on data from one slug test in a single monitoring well. Data obtained during slug testing are generally analyzed using the method of Hvorslev (1951) for confined aquifers or the method of Bouwer and Rice (1976) and Bouwer (1989) for unconfined conditions.

C.3.1.2 Transmissivity

The transmissivity, T, of an aquifer is the product of the aquifer's hydraulic conductivity, K, and the saturated thickness, b:

$$T = Kb \qquad \text{eq. C.3.1}$$

For a confined aquifer, b is the thickness of the aquifer between confining units. For unconfined aquifers, b is the saturated thickness of the aquifer measured from the water table to the underlying confining layer. Transmissivity has the units of length squared over time [L^2/T].

C.3.1.3 Hydraulic Head and Gradient

Determining the magnitude of hydraulic gradients is important because gradients influence the direction and rate of contaminant migration. Hydraulic head, H, and specifically, variations in hydraulic head within an aquifer, is the driving force behind groundwater movement and solute

migration. The total hydraulic head at one location in a system is the sum of the elevation head, pressure head, and velocity head (Figure C.3.1):

$$H = h_z + h_p + h_v \qquad \text{eq. C.3.2}$$

Where: H = total hydraulic head [L]
h_z = elevation head = z = elevation relative to the reference plane [L]
h_p = pressure head [L]
h_v = velocity head [L]

Pressure head is given by:

$$h_p = \frac{p}{\rho g}$$

Where: p = fluid pressure
ρ = density
g = acceleration due to gravity

Velocity head is given by:

$$h_v = \frac{v^2}{2g}$$

Where: v = groundwater velocity
g = acceleration due to gravity

Because h_v is generally assumed to be zero for most groundwater flow, the relationship for total head is generally written:

$$H = z + \frac{p}{\rho g} \qquad \text{eq. C.3.3}$$

Thus, the total hydraulic head at a point measured by a piezometer is the sum of the elevation at the base of the piezometer plus the length of the water column in the piezometer. The total hydraulic head in a piezometer is determined by measuring the depth from a surveyed reference point (datum) to the surface of the standing water. The elevation of the water surface is the total hydraulic head in the piezometer. This total head is the total head at the base of the piezometer, not the water table elevation, unless the piezometer terminates immediately below the water table

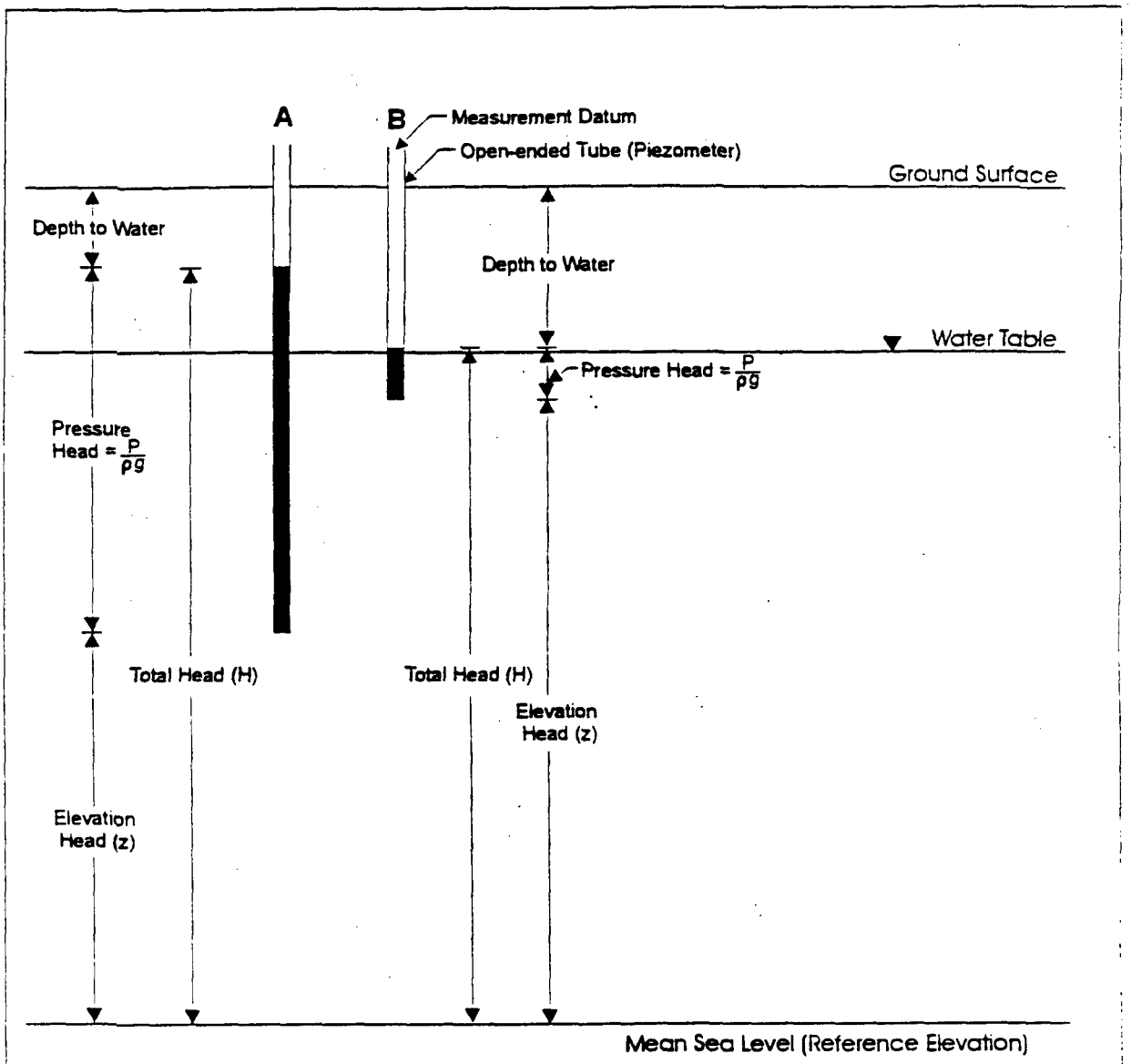


Figure C.3.1

Hydraulic Head

or is a well screened across the water table. Figure C.3.1 shows a pair of nested piezometers that illustrate the relationships between total hydraulic head, pressure head, and elevation head. Because groundwater flows from areas with high total head (point A, Figure C.3.1) to areas with lower total head (point B), this figure depicts a water table aquifer with a strong upward vertical gradient. This figure illustrates how nested piezometers (or wells) are used to determine the importance of vertical gradients at a site. This figure also illustrates the importance of using wells screened in the same portion of the aquifer (preferably across the water table) when preparing potentiometric surface maps.

The hydraulic gradient (dH/dL) is a dimensionless number that is the change in hydraulic head (dH) between two points divided by the length of groundwater flow between these same two points, parallel to the direction of groundwater flow, and is given by:

$$\text{Hydraulic Gradient} = \frac{dH}{dL} \qquad \text{eq. C.3.4}$$

Where: dH = change in total hydraulic head between two points [L]
dL = distance between the two points used for head measurement [L]

In a system where flow is not occurring, the total hydraulic head, H, is the same everywhere in the system and the hydraulic gradient is zero. To accurately determine the hydraulic gradient, it is necessary to measure groundwater levels in all monitoring wells at the site. Because hydraulic gradients can change over a short distance within an aquifer, it is essential to have as much site-specific groundwater elevation information as possible so that accurate hydraulic gradient calculations can be made. In addition, seasonal variations in groundwater flow direction can have a profound influence on contaminant transport. To determine the effect of seasonal variations in groundwater flow direction on contaminant transport, quarterly groundwater level measurements should be taken over a period of at least 1 year.

The hydraulic gradient must be determined parallel to the direction of groundwater flow. Unless two monitoring wells screened in the same relative location within the same hydrogeologic unit are located along a line parallel to the direction of groundwater flow, the potentiometric surface map is generally used to determine the hydraulic gradient. To determine the hydraulic gradient, an engineer's scale is used to draw a line perpendicular to the equal-potential lines on the potentiometric surface map (i.e., parallel to the direction of groundwater flow). Measure the distance between the two equal-potential lines, making note of the groundwater potential at each equal-potential line. Subtract the larger potential from the smaller potential, and divide this number by the distance between the two equal potential lines, being sure to use consistent units.

The number generated will be a negative number because water flows from areas of higher potential to areas of lower potential.

Example C.3.1: Hydraulic Gradient Calculation

Given the water table elevation map shown in Figure C.3.2, calculate the hydraulic gradient between points A and B. Assume that all wells are screened across the water table.

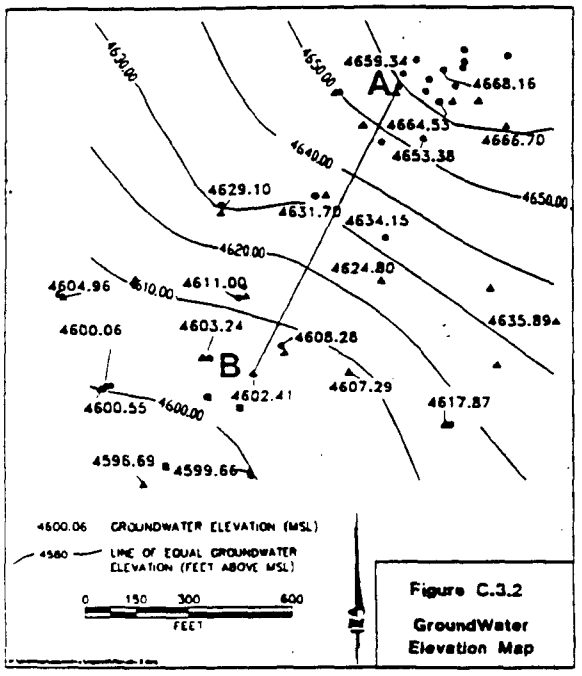


Figure C.3.2
GroundWater Elevation Map

Solution:

The hydraulic gradient is given by dH/dL. The line connecting points A and B is parallel to the direction of groundwater flow. The water table elevation is 4659.34 ft msl at point A and 4602.41 ft msl at point B. Therefore, because groundwater flows from areas of high head to areas of lower head:

$$dH = 4602.41 - 4659.34 = -56.93\,feet$$

The distance between the two points A and B is 936 feet. Therefore:

$$dL = 936\,feet$$

$$\text{and } \frac{dH}{dL} = \frac{-56.93\,ft}{936\,ft} = -0.06\frac{ft}{ft} = -0.06\frac{m}{m}$$

C.3.1.4 Total Porosity (n) and Effective Porosity (n_e)

Total porosity (n) is the volume of voids in a unit volume of aquifer. Specific retention is the amount of water (volumetric) that is retained against the force of gravity after a unit volume of an unconfined aquifer is drained. Storativity is defined as the volume of water that a confined aquifer takes into or releases from storage per unit surface area of the aquifer per unit change in total hydraulic head. Effective porosity, n_e, is the total porosity of the aquifer minus the specific retention (unconfined) or storativity (confined) of the aquifer:

$$n_e = n - S \qquad \text{eq. C.3.5}$$

Where: n_e = effective porosity [dimensionless]
n = total porosity [dimensionless]
S = specific retention (unconfined) or storativity (confined) [dimensionless]

Effective porosity can be estimated using the results of a tracer test. Although this is potentially the most accurate method, time and monetary constraints can be prohibitive. For this reason, the most common technique is to use an accepted literature value for the types of materials making up the aquifer matrix, and then to calibrate a contaminant transport model by adjusting the value of effective porosity (in conjunction with other input parameters such as transmissivity) within the range of accepted literature values until the modeled and observed contaminant distribution patterns match. Because aquifer materials can have a range of effective porosity, sensitivity analyses should be performed to determine the effect of varying the effective porosity on numerical model results. Values of effective porosity chosen for the sensitivity analyses should vary over the accepted range for the aquifer matrix material. Table C.3.2 presents accepted literature values for total porosity and effective porosity. Contaminant transport model sensitivity analysis is discussed in Appendix D.

Table C.3.2

Representative Values of Dry Bulk Density, Total Porosity, and Effective Porosity for Common Aquifer Matrix Materials (After Walton, 1988 and Domenico and Schwartz, 1990))

Aquifer Matrix	Dry Bulk Density (gm/cm^3)	Total Porosity	Effective Porosity
Clay	1.00-2.40	0.34-0.60	0.01-0.2
Peat	—	—	0.3-0.5
Glacial Sediments	1.15-2.10	—	0.05-0.2
Sandy Clay	—	—	0.03-0.2
Silt	—	0.34-0.61	0.01-0.3
Loess	0.75-1.60	—	0.15-0.35
Fine Sand	1.37-1.81	0.26-0.53	0.1-0.3
Medium Sand	1.37-1.81	—	0.15-0.3
Coarse Sand	1.37-1.81	0.31-0.46	0.2-0.35
Gravely Sand	1.37-1.81	—	0.2-0.35
Fine Gravel	1.36-2.19	0.25-0.38	0.2-0.35
Medium Gravel	1.36-2.19	—	0.15-0.25
Coarse Gravel	1.36-2.19	0.24-0.36	0.1-0.25
Sandstone	1.60-2.68	0.05-0.30	0.1-0.4
Siltstone	—	0.21-0.41	0.01-0.35
Shale	1.54-3.17	0.0-0.10	—
Limestone	1.74-2.79	0.0-50	0.01-0.24
Granite	2.24-2.46	—	—
Basalt	2.00-2.70	0.03-0.35	—
Volcanic Tuff	—	—	0.02-0.35

C.3.1.5 Linear Groundwater Flow Velocity (Seepage or Advective Velocity)

The average linear groundwater flow velocity (seepage velocity) in one dimension in the direction parallel to groundwater flow in a saturated porous medium is given by:

$$v_x = -\frac{K}{n_e}\frac{dH}{dL} \qquad \text{eq. C.3.6}$$

Where: v_x= average linear groundwater velocity parallel to groundwater flow direction (seepage velocity) [L/T]

K = hydraulic conductivity [L/T]

n_e = effective porosity [L^3/L^3]

$\frac{dH}{dL}$ = hydraulic gradient [L/L]

The average linear groundwater flow velocity should be calculated to estimate groundwater flow and solute transport velocity, to check the accuracy of groundwater models, and to calculate first-order biodegradation rate constants.

Example C.3.2: Linear Groundwater Flow Velocity Calculation

Calculate the linear groundwater flow velocity in a medium-grained sandy aquifer. The hydraulic gradient as determined from the potentiometric surface map in the previous example is -0.06 m/m. The hydraulic conductivity is 1.7×10^{-1} m/day as determined by pumping tests.

Solution:

Because the effective porosity of this sediment is not known, it is necessary to estimate this parameter. From Table C.3.2, the effective porosity for a medium-grained sand is approximately 23 percent.

$$v_x = -\frac{K}{n_e}\frac{dH}{dL} = -\frac{(0.17\frac{m}{day})(-0.06\frac{m}{m})}{0.23} = 0.044\frac{m}{day}$$

C.3.1.6 Coefficient of Retardation and Retarded Contaminant Transport Velocity

When the average linear velocity of a dissolved contaminant is less than the average linear velocity of the groundwater, the contaminant is said to be "retarded." The difference between the

velocity of the groundwater and that of the contaminant is caused by sorption and is described by the coefficient of retardation, R, which is defined as:

$$R = \frac{v_x}{v_c} \qquad \text{eq. C.3.7}$$

Where: R = coefficient of retardation
v_x = average linear groundwater velocity parallel to groundwater flow
v_c = average velocity of contaminant parallel to groundwater flow

The ratio v_x/v_c describes the relative velocity between the groundwater and the dissolved contaminant. When $K_d = 0$ (no sorption), the transport velocities of the groundwater and the solute are equal ($v_x = v_c$). If it can be assumed that sorption is adequately described by the distribution coefficient (valid when $f_{oc} > 0.001$), the coefficient of retardation for a dissolved contaminant (for saturated flow) is given by:

$$R = 1 + \frac{\rho_b K_d}{n} \qquad \text{eq. C.3.8}$$

Where: R = coefficient of retardation
ρ_b = bulk density (Section C.3.1.6.1)
K_d = distribution coefficient (Section C.3.1.6.2)
n = total porosity

This relationship expresses the coefficient of retardation in terms of the bulk density and effective porosity of the aquifer matrix and the distribution coefficient for the contaminant. Substitution of this equation into equation C.3.7 gives:

$$\frac{v_x}{v_c} = 1 + \frac{\rho_b K_d}{n} \qquad \text{eq. C.3.9}$$

Solving for the contaminant velocity, v_c, gives:

$$v_c = \frac{v_x}{1 + \frac{\rho_b K_d}{n}} \qquad \text{eq. C.3.10}$$

Retardation of a contaminant relative to the advective transport velocity of the groundwater flow system has important implications for natural attenuation. If retardation is occurring, dissolved oxygen and other electron acceptors traveling at the advective transport velocity of the groundwater sweep over the contaminant plume from the upgradient margin. This results in

greater availability of electron acceptors within the plume for biodegradation of fuel hydrocarbons. In addition, adsorption of a contaminant to the aquifer matrix results in dilution of the dissolved contaminant plume.

C.3.1.6.1 Bulk Density

The bulk density of a soil, ρ_b, as used in most groundwater models, expresses the ratio of the mass of dried soil to its total volume (solids and pores together).

$$\rho_b = \frac{M_s}{V_T} = \frac{M_s}{(V_s + V_a + V_w)} \qquad \text{eq. C.3.11}$$

Where: ρ_b = bulk density
M_s = mass of solid in the system
V_T = total volume in the system
V_s = volume of solid in the system
V_a = volume of air (or gas) in the system
V_w = volume of water (or liquid) in the system

Bulk density is related to particle density by:

$$\rho_b = (1-n)\rho_s \qquad \text{eq. C.3.12}$$

Where: ρ_b = bulk density
n = total porosity
ρ_s = density of grains comprising the aquifer

The bulk density is always less than the particle density, ρ_s; for example, if pores constitute half the volume, then ρ_b is half of ρ_s. The bulk density of a soil is affected by the structure of the soil (looseness and degree of compaction), as well as by its swelling and shrinking characteristics, both of which depend on clay content and soil moisture. Even in extremely compacted soil, the bulk density remains appreciably lower than the particle density. This is because the particles can never interlock perfectly, and the soil remains a porous body, never completely impervious. In sandy soils, ρ_b can be as high as 1.81 gm/cm^3. In aggregated loams and clayey soils, ρ_b can be as low as 1.1 gm/cm^3. Table C.3.2 contains representative values of dry bulk density for common sediments and rocks.

C.3.1.6.2 Distribution Coefficient and Total Organic Carbon Content

The distribution coefficient is described in Section B.4.3. Recall equation B.4.10, which gives the relationship between f_{oc} and K_{oc}:

$$K_d = K_{oc} f_{oc} \qquad \text{eq. C.3.13}$$

Where: K_d = distribution coefficient [L^3/M]
K_{oc} = soil adsorption coefficient for soil organic carbon content [L^3/M]
f_{oc} = fraction soil organic carbon (mg organic carbon/mg soil) [M/M]

Representative K_{OC} values are given in Table B.4.1. The fraction of soil organic carbon must be determined from site-specific data. Representative values of total organic carbon (TOC) in common sediments are given in Table C.3.3. Because most solute transport occurs in the most transmissive aquifer zones, it is imperative that soil samples collected for total organic carbon analyses come from these zones in background areas. To be conservative, the average of all total organic carbon concentrations from sediments in the most transmissive aquifer zone should be used for retardation calculations.

Example C.3.3: Retarded Solute Transport Velocity Calculation

For groundwater flow and solute transport occurring in a shallow, saturated, well-sorted, fine-grained, sandy aquifer, with a total organic carbon content of 0.7 percent, a hydraulic gradient of -0.015 m/m, and an hydraulic conductivity of 25 m/day, calculate the retarded contaminant velocity for trichloroethene.

Solution:

Because the total porosity, effective porosity, and the bulk density are not given, values of these parameters are obtained from Table C.3.2. The median values for total porosity, effective porosity, and bulk density are approximately 0.4, 0.2, and 1.6 kg/L respectively.

The first step is to calculate the average linear groundwater velocity, v_x.

$$v_x = -\frac{\left(25\frac{m}{day}\right)\left(-0.015\frac{m}{m}\right)}{0.2} = 1.9\frac{m}{day}$$

Table C.3.3

Representative Values of Total Organic Carbon for Common Sediments

Texture	Depositional Environment	Fraction Organic Carbon	Site Name
medium sand	fluvial-deltaic	0.00053 - 0.0012	Hill AFB, Utah
fine sand		0.0006 - 0.0015	Bolling AFB, D.C.
fine to coarse sand	back-barrier (marine)	0.00026 - 0.007	Patrick AFB, Florida
organic silt and peat	glacial (lacustrine)	0.10 - 0.25	Elmendorf AFB, Alaska
silty sand	glaciofluvial	0.0007 - 0.008	Elmendorf AFB, Alaska
silt with sand, gravel and clay (glacial till)	glacial moraine	0.0017 - 0.0019	Elmendorf AFB, Alaska
medium sand to gravel	glaciofluvial	0.00125	Elmendorf AFB, Alaska
loess (silt)	eolian	0.00058 - 0.0016	Offutt AFB, Nebraska
fine - medium sand	glaciofluvial or glaciolacustrine	< 0.0006 - 0.0061	Truax Field, Madison Wisconsin
fine to medium sand	glaciofluvial	0.00021 - 0.019	King Salmon AFB, Fire Training Area, Alaska
			Dover AFB, Delaware
fine to coarse sand	glaciofluvial	0.00029 - 0.073	Battle Creek ANGB, Michigan
sand	fluvial	0.0057	Oconee River, Georgia[a/]
coarse silt	fluvial	0.029	Oconee River, Georgia[a/]
medium silt	fluvial	0.020	Oconee River, Georgia[a/]
fine silt	fluvial	0.0226	Oconee River, Georgia[a/]
silt	lacustrine	0.0011	Wildwood, Ontario[b/]
fine sand	glaciofluvial	0.00023 - 0.0012	Various sites in Ontario[b/]
medium sand to gravel	glaciofluvial	0.00017 - 0.00065	Various sites in Ontario[b/]

a/ Karickhoff, 1981
b/ Domenico and Schwartz (1990)

The next step is to determine the distribution coefficient, K_d. Values of K_{oc} for chlorinated solvents and BTEX are obtained from Tables B.2.1 and B.2.2, respectively, and are listed in Table C.3.4.

For trichloroethene the most conservative (i.e., that value giving the highest solute velocity) is K_{oc} = 87 L/kg, and (using equation C.3.13):

$$K_d = \left(87\frac{L}{kg}\right)(0.007) = 0.61\frac{L}{kg}$$

The retarded contaminant velocity is given by (equation C.3.10):

$$v_c = \frac{1.9\frac{m}{day}}{1+\frac{\left(1.6\frac{kg}{L}\right)\left(0.61\frac{L}{kg}\right)}{0.4}} = 0.55\frac{m}{day}$$

This example illustrates that contaminant sorption to total organic carbon can have a profound influence on contaminant transport by significantly slowing the rate of dissolved contaminant migration.

Table C.3.4

Example Retardation Calculations for Select Compounds

Compound	K_{oc} L/kg	Fraction Organic Carbon	Distribution Coefficient (L/kg)	Bulk Density (kg/L)	Total Porosity	Coefficient of Retardation	Advective Groundwater Velocity (m/day)	Contaminant Velocity (m/day)
Benzene	79	0.007	0.553	1.60	0.40	3.21	1.90	0.59
Toluene	190	0.007	1.33	1.60	0.40	6.32	1.90	0.30
Ethylbenzene	468	0.007	3.276	1.60	0.40	14.10	1.90	0.13
m-xylene	405	0.007	2.835	1.60	0.40	12.34	1.90	0.15
Tetrachloroethene	209	0.007	1.463	1.60	0.40	6.85	1.90	0.28
Trichloroethene	87	0.007	0.609	1.60	0.40	3.44	1.90	0.55
cis-1,2-Dichloroethene	49	0.007	0.343	1.60	0.40	2.37	1.90	0.80
Vinyl Chloride	2.5	0.007	0.0175	1.60	0.40	1.07	1.90	1.78
1,3,5-trimethylbenzene	676	0.007	4.732	1.60	0.40	19.93	1.90	0.10

C.3.2 CONTAMINANT SOURCE TERM CALCULATIONS

THIS SECTION NEED TO BE UPDATED FOR CHLORINATED SOLVENTS BUT MOST OF THE RELATIONSHIPS STILL APPLY

NAPLs present in the subsurface can represent a continuing source of groundwater contamination. Sorption of contaminants onto the aquifer matrix occurs when NAPL enters the subsurface. When sufficient quantities of NAPL are present, the unsaturated zone may initially be saturated with NAPL, but after a period of time the NAPL will drain from the pores under the influence of gravity, leaving a thin coating of NAPL. Depending on the surface area of the materials comprising the subsurface, the surface tension of the NAPL, and the porosity and permeability of the subsurface materials, some NAPL also may be held between the grains by capillarity. NAPL adhering to the grains of the aquifer matrix or retained by capillarity is herein referred to as residual NAPL. If the NAPL is mobile within and among the pores of the aquifer matrix, as is generally the case near the water table, the NAPL is referred to as mobile NAPL.

If contaminant concentrations in the residual and mobile LNAPL are not decreasing over time, or if they are decreasing very slowly, extremely long times will be required for natural attenuation of the dissolved contaminant plume. This will likely make natural attenuation unattractive to regulators and will reduce the chance of implementation. In order for natural attenuation to be a viable remedial option, the source of continuing groundwater contamination must be decreasing over time (decaying), either by natural weathering processes or via engineered remedial solutions such as mobile LNAPL recovery, bioventing, or bioslurping. Because natural weathering processes can be fairly slow, especially in static systems where the groundwater elevation does not fluctuate significantly, it will generally be necessary to implement engineered remedial solutions to remove the LNAPL. However, in cases where the LNAPL has been in the ground for a long period of time, it may be weathered to the point that it no longer acts as a source of significant groundwater contamination (Section C.3.2.3). Because of their physical and chemical properties, the BTEX compounds are generally the first to be removed from the LNAPL via natural weathering processes. Wiedemeier *et al.* (1993) used mass fraction BTEX analyses from mobile LNAPL at a jet fuel spill site in Colorado to show that the weathered LNAPL was not capable of producing dissolved BTEX concentrations above regulatory groundwater quality standards.

To determine how long it will take for a dissolved contaminant plume to disappear, it is necessary to estimate how fast the contaminant source (LNAPL) is being removed. Source removal rates can be estimated where bioventing is being used to remediate residual LNAPL by collecting soil samples in the source area at the start of remedial activities. After the system has been operating for a period of time, soil samples are collected from approximately the same location(s). Comparison of BTEX concentrations in samples collected from the same location makes it possible to determine when the source area has been remediated. This approach has been used successfully at several Air Force bases where pilot-scale bioventing systems had been installed and where 1-year sampling data were available. Experience with the bioventing initiative shows that at most of the 105 sites where data are available, 99 percent of the BTEX mass in the subsurface vadose zone is remediated in 1 year. In areas with mobile LNAPL it is much more difficult to estimate cleanup times, so conservative estimates should be made based on LNAPL removal rates. Predicting the cleanup time for sites with mobile LNAPL is especially difficult because residual LNAPL will remain after the recoverable mobile LNAPL has been removed. One remedial technology that has shown promise for both residual and mobile LNAPL is bioslurping. Bioslurping removes mobile LNAPL via suction lift. During bioslurping operations, a vacuum is induced in the unsaturated zone. This vacuum draws oxygen from uncontaminated

areas into the area contaminated with residual LNAPL and extracts soil gas into which VOCs have volatilized. A properly installed bioslurping system thus acts as a mobile LNAPL recovery system, a bioventing system, and a soil vapor extraction system.

The work of Smith *et al.* (1981) and Cline *et al.* (1991) shows that the aromatic hydrocarbons, and in particular, BTEX, constitute by far the greatest mass of compounds that partition from fuels into groundwater. Smith *et al.* (1981) list 40 compounds that have equilibrium concentrations in a JP-4 jet fuel/water mixture of greater that 0.01 mg/L. The work of Smith *et al.* (1981) shows that the major water-soluble aromatic components (compounds found in concentrations greater than about 1 percent of the total mass of dissolved constituents) of jet fuel are BTEX, the trimethylbenzenes, naphthalene, and the methylnaphthalenes. Table C.3.5 shows the relative concentrations of these compounds in JP-4. In a 1:10 fuel:water mix, BTEX makes up approximately 82 percent, or 22.61 mg/L, of the total dissolved concentration of 27.63 mg/L for the 1:10 fuel to water mixture. The trimethylbenzene isomers have a combined concentration of 0.87 mg/L (approximately 3 percent of total concentration). Smith *et al.* (1981) also used fuel:water ratios of 1:100, 1:1,000, and 1:10,000. As the ratio of water increased, the total dissolved concentration of the 40 water soluble fuel components decreased, to a minimum value of 4.58 mg/L for the 1:10,000 JP-4 to water mixture (Table C.3.5). Based on this information, the highest reasonable concentration of total fuel hydrocarbons dissolved in groundwater in contact with JP-4 should be about 28 mg/L, and the highest equilibrium total BTEX concentration should be about 23 mg/L. If concentrations higher than this are reported by the analytical laboratory, emulsification of LNAPL in the sample should be suspected.

Table C.3.5

Dissolved Concentrations (in Water) of Water-Soluble Components Present in JP-4[a/]

Compound	Fuel to Water Ratio			
	1:10	1:100	1:1,000	1:10,000
Benzene (mg/L)	9.82	6.99	1.55	0.07
Toluene (mg/L)	8.49	7.79	3.71	0.70
Ethylbenzene (mg/L)	0.67	0.64	0.59	0.17
Xylenes (mg/L)	3.63	3.49	3.33	0.92
Trimethylbenzenes (mg/L)	0.87	0.79	1.13	0.54
Naphthalene (mg/L)	0.39	0.31	0.41	0.10
Methylnaphthalenes (mg/L)	0.24	0.17	0.32	0.16
All Others (mg/L)	3.52	2.83	2.85	1.92
Total (mg/L)	27.63	23.01	13.89	4.58
Total BTEX (mg/L)	22.61	18.90	9.18	1.86
Percent Total BTEX	82	82	66	41

a/ Modified from Smith *et al.*, 1981

Table C.3.6 summarizes the work conducted by Cline *et al.* (1991) on 31 gasoline samples The compounds listed in this table represent the major water-soluble components in gasoline (compounds found in concentrations greater than about 1 percent of the total gas chromatography/flame ionization detector peak area for all compounds detected in the aqueous phase), which are BTEX, n-propylbenzene, 3- and 4-ethyltoluene, and 1,2,3-trimethylbenzene. Based on the information presented in Table C.3.6, the highest reasonable concentration of total fuel hydrocarbons dissolved in groundwater in contact with gasoline should be about 135 mg/L, and the highest equilibrium total BTEX concentration should be about 132 mg/L. If concentrations higher than this are reported by the analytical laboratory, emulsification of LNAPL in the sample should be suspected.

There are two methods that can be used to determine the concentration of contaminants dissolved in groundwater beneath NAPL and thus quantify the contaminant source loading. The first method involves directly measuring the concentration of dissolved contaminants in groundwater near the NAPL plume. The second method involves the use of partitioning calculations. The following sections describe each approach.

Table C.3.6

Weight Percent Water-Soluble Components in Gasoline and Their Concentrations in Water in Contact with Gasoline

Compound	Gasoline Composition[a/] (Weight Percent)	Dissolved Concentration[a/] (mg/L)	Gasoline Composition[b/] (Weight Percent)	Dissolved Concentration[b/] (mg/L)
benzene	1.73	42.6	1.94	58.7
toluene	9.51	69.4	4.73	33.4
ethylbenzene	1.61	3.2	2.0	4.3
m- and *p*-xylene	5.95	11.4	–	–
o-xylene	2.33	5.6	2.27	6.9
m-xylene	–	–	5.66	11.0
p-xylene	–	–	1.72	4.4
n-propylbenzene	0.57	0.4	–	–
3-,4-ethyltoluene	2.20	1.7	–	–
1,2,3-trimethylbenzene	0.8	0.7	–	–
1,2,4-trimethylbenzene	–	–	3.26	1.1
Total	24.7	135	21.58	119.8
Total BTEX		132.2		118.7
Percent Total BTEX		98		99

a/ Cline *et al.* (1991)

b/ American Petroleum Institute (1985) average of 24 analyses from nine fuel:water solutions (1:10 fuel:water)

C.3.2.1 Direct Measurement of Dissolved Contaminant Concentrations in Groundwater in Contact with NAPL

Two methods can be used to determine the dissolved concentration of contaminants in groundwater near a NAPL plume. The first method involves collecting groundwater samples from near a NAPL lens in monitoring wells. The second method involves collecting samples of mixed NAPL and water from monitoring wells.

C.3.2.1.1 Collecting Groundwater Samples From Near the NAPL

This method involves carefully sampling groundwater beneath a floating LNAPL lens or near a DNAPL lens. One way of collecting a groundwater sample from beneath a lens of floating LNAPL involves using a peristaltic pump. The depth to the base of the mobile LNAPL is measured, a length of high-density polyethylene (HDPE) tubing that will reach 1 to 2 feet beneath the LNAPL is lowered into the well, and the sample is collected. Another useful technique for obtaining such a sample where the depth to groundwater is too deep to allow use of a peristaltic pump is to use a Grundfos® pump. If a Grundfos® pump is used to collect a water sample from beneath LNAPL, it is imperative that the pump be thoroughly cleaned after each use, and that good sampling logic be used (e.g., sample less contaminated wells first). Also, dedicated bladder pumps that are being used for long-term monitoring (LTM) in wells with LNAPL can be used to collect water samples from beneath the LNAPL.

C.3.2.1.2 Collecting Mixed Groundwater/NAPL Samples

This method involves collecting a sample of groundwater and floating LNAPL from a monitoring well, placing the sample in a sealed container used for volatile organics analysis being careful to ensure there is no headspace, allowing the sample to reach equilibrium, and submitting the water beneath the floating NAPL to a qualified laboratory for analysis. A disposable bailer generally works best for collection of this type of sample. Smith *et al.* (1981) has information on how to conduct such a test. Two or three samples should be collected from different monitoring wells containing LNAPL at the site. This test should only be done when it is not possible to collect a discrete sample from beneath the LNAPL.

C.3.2.2 Partitioning Calculations

LNAPL present at a site represents a continuing source of contamination because chlorinated solvents, BTEX, and other compounds will partition from the LNAPL into the groundwater. In such cases, it is generally necessary to estimate the dissolved concentration of contaminants expected in groundwater near the LNAPL. Partitioning calculations can be performed for sites with NAPL to quantify contaminant loading from the NAPL into the groundwater. Such calculations allow estimation of the impact of continuing sources of contamination on dissolved contaminant concentrations. The results of partitioning calculations may show that even if the NAPL is allowed to remain in the ground, dissolved contaminant concentrations will remain below regulatory guidelines. This is especially true when weathered NAPLs with initially low contaminant concentrations, such as jet fuels (Jet A, JP-4, *etc.*) are present. Partitioning calculations made by Wiedemeier *et al.* (1993) showed that NAPL present in the subsurface at a fueling facility near Denver, Colorado was incapable of producing dissolved contaminant concentrations in groundwater above regulatory standards. Partitioning calculations should be confirmed with a LTM program.

If partitioning calculations suggest that partitioning from the NAPL could increase dissolved contaminant concentrations in groundwater to above regulatory guidelines at a point of compliance, then this continuing source of groundwater contamination should be remediated. Residual NAPL contamination in the unsaturated zone is generally best remediated using bioventing, a technique that introduces air (oxygen) into the subsurface, thus stimulating aerobic biodegradation of fuel hydrocarbons. When found in the saturated zone, residual LNAPL is extremely difficult to remove. Maximum contaminant concentrations resulting from such partitioning will occur when the groundwater and NAPL reach equilibrium. Assuming that equilibrium is reached gives the most conservative modeling results. Alternate, less conservative models for partitioning from NAPL into the aqueous phase are given by Hunt *et al.* (1988) and Johnson and Pankow (1992). These models are described below.

C.3.2.2.1 Equilibrium Partitioning of Contaminants from Mobile LNAPL into Groundwater

The fuel-water partitioning coefficient, K_{fw}, is defined as the ratio of the concentration of a compound in the fuel to the compound's equilibrium concentration in water in contact with the fuel:

$$K_{fw} = \frac{C_f}{C_w} \qquad \text{eq. C.3.14}$$

Where: K_{fw} = fuel-water partitioning coefficient [dimensionless]
C_f = concentration of the compound in the fuel [M/L^3]
C_w = concentration of the compound dissolved in groundwater [M/L^3]

Table C.3.7 lists values of K_{fw} for BTEX and trimethylbenzenes (TMB) in jet fuel and gasoline. The relationships relating K_{fw} to the aqueous solubility of a pure compound in pure water, S, presented in Table C.3.8 can be used to estimate K_{fw} for compounds not listed in this table.

Table C.3.7

Fuel-Water Partitioning Coefficients (K_{fw}) for Those Compounds Most Commonly found in the Aqueous Phase in Water in Contact with Jet Fuel or Gasoline

Compound	K_{fw} [a] (JP-4 Jet Fuel)	K_{fw} [b] (Gasoline)	K_{fw} [c] (Gasoline)
Benzene	2,455	231	350
Toluene	2,754	895	1,250
Ethylbenzene	4,786	3,411	4,500
o-xylene	7,079	3,162	3,630
m-xylene	3,715	3,539	4,350
p-xylene	7,586	2,961	4,350
1,2,3-Trimethylbenzene	NA	NA	13,800
1,2,4-Trimethylbenzene	8,913	12,270	NA
1,3,5-Trimethylbenzene	NA	6,493	NA

a/ From experiments conducted by Smith *et al.*, 1981 (For JP-4)
b/ Model of Bruce *et al.*, 1991 (for gasoline)
c/ Model of Cline *et al.*, 1991 (for gasoline)
NA = not analyzed

Table C.3.8

Relationships Relating Fuel-Water Partitioning Coefficients (K_{fw}) to Pure Aqueous-Phase Solubility

LNAPL Type	Relationship Relating S to K_{fw} [a]	Reference
JP-4	$\log K_{fw} = -0.797 \log S + 1.681$	Smith *et al.*, 1981
JP-5	$\log K_{fw} = -0.746 \log S + 1.757$	Smith *et al.*, 1981
JP-8	$\log K_{fw} = -0.864 \log S + 1.508$	Smith *et al.*, 1981
Gasoline	$\log K_{fw} = -1.15 \log S + 6.099$	Bruce *et al.*, 1991
Gasoline	$\log K_{fw} = -1.00 \log S + 0.85$	Cline *et al.*, 1991

a/ Determined using linear regression on data for dissolved compound concentrations in a fuel-water mix.

Using the definition of K_{fw} presented above, the maximum (equilibrium) total dissolved BTEX concentration resulting from the partitioning of BTEX from NAPL into groundwater is given by:

$$C_w = \frac{C_f}{K_{fw}} \qquad \text{eq. C.3.15}$$

This relationship predicts the concentration of dissolved BTEX in the groundwater if the LNAPL is allowed to remain in contact with the groundwater long enough so that equilibrium between the two phases is reached.

To complete partitioning calculations, samples of the mobile LNAPL must be collected and analyzed to determine the type of fuel and the mass fraction of BTEX present in the fuel. From the mass fraction BTEX data, the concentration of each BTEX compound in the fuel on a volumetric basis, C_f, can be calculated by using the relationship:

$$C_f = F_f \rho_f \qquad \text{eq. C.3.16}$$

Where: ρ_f = Density of fuel (Table C.3.9)
F_f = Mass fraction of compound in the fuel

Using mass fraction BTEX data from the LNAPL analyses, and the fuel-water partitioning coefficients presented in Table C.3.7, the maximum dissolved benzene, toluene, ethylbenzene, and total xylene concentrations expected in groundwater caused by the partitioning of these compounds from the LNAPL can be calculated using equation C.3.15.

Table C.3.9

Density of Common Liquids

Type of Liquid	Density (gm/cm^3)	Density (gm/m^3 = mg/L)
Miscellaneous Liquids:		
Water	1.0	1,000,000
Gasoline	0.68-0.76	680,000 - 760,000
Jet Fuel	0.74-0.85	740,000 - 850,000
JP-4	0.75	750,000
Kerosene	0.78-0.82	780,000 - 820,000
Fuel Oil and Diesel Oil:	0.82-0.95	820,000 - 950,000
BTEX and TMB		
Benzene	0.868	868,000
Toluene	0.8669	866,900
Ethylbenzene	0.8669	866,900
o-xylene	0.8802	880,200
m-xylene	0.8642	864,200
p-xylene	0.8610	861,000
1,2,3-trimethylbenzene	0.88	880,000
1,2,4-trimethylbenzene	0.88	880,000
1,3,5-trimethylbenzene	0.87	870,000
1,2,4,5-tetramethylbenzene	0.84	840,000

Example C.3.4: Equilibrium Partitioning Calculation

Mass fraction BTEX data from a sample of JP-4 LNAPL collected at a site with up to 3 feet of mobile LNAPL floating on the water table indicate that the mass fractions of benzene, toluene, ethylbenzene, and xylene are 0.000001, 0.00002, 0.0047, and 0.0009, respectively. Calculate the concentration of BTEX dissolved in groundwater in contact with the LNAPL that would be expected under equilibrium conditions.

Solution:

The first step is to determine the concentration of each compound in the LNAPL. From Table C.3.9, the density of JP-4 jet fuel is 750,000 mg/L. The concentration of each compound is calculated using equation C.3.16. The results of this calculation are listed in Table C.3.10. The next step is to use the fuel-water partitioning coefficient (Table C.3.7) for each compound and the concentration of each compound in the fuel to determine the equilibrium concentration in the groundwater using equation C.3.15. The results of this calculation are listed in Table C.3.10.

Table C.3.10

Solution to Example C.3.4

Compound	Concentration in LNAPL (C_f, mg/L)	Fuel-Water Partitioning Coefficient (K_{fw})[a/]	Concentration in Water (µg/L)
benzene	0.75	2,455	0.31
toluene	15	2,754	5.45
ethylbenzene	3,525	4,786	736.5
xylene	675	6,126[b/]	110.2

a/ From Table C.3.7.
b/ Average of all isomers.

C.3.2.2.2 Nonequilibrium Partitioning of Contaminants from NAPL into Groundwater

The steady-state, two-dimensional dissolution of contaminants from a pool of NAPL floating on the water table into groundwater (assumed to be a semi-infinite medium) can be described by the steady-state, two-dimensional, advection-dispersion equation (Hunt *et al.*, 1988):

$$v_x \frac{\partial C}{\partial x} = D_z \frac{\partial^2 C}{\partial z^2} \qquad x,z > 0 \qquad \text{eq. C.3.17}$$

Where: C = contaminant concentration dissolved in water
v_x = average linear groundwater velocity
D_z = vertical dispersion coefficient

If it is assumed that:

- The time required for total NAPL dissolution is exceedingly long in comparison to the contact time between the NAPL pool and the flowing groundwater
- The NAPL pool is wide compared to the horizontal transverse mixing process
- The NAPL pool can be approximated as a rectangle
- The NAPL lens width does not affect the dissolution rate
- The elevation of the NAPL lens is taken as z=0, with z measured positively upward.
- The boundary conditions are:

$$C(x, z = \infty) = 0$$
$$C(x, z = 0) = C_e \qquad 0 \le x \le L$$
$$C(x = 0, z) = 0$$

Where: C = contaminant concentration dissolved in water
C_e = Effective water solubility
L = Horizontal length of NAPL pool,

then the rate of dissolution of constituents from an LNAPL lens into groundwater flowing beneath the lens can be calculated as two-dimensional, steady-state dissolution, and the surface area averaged mass transfer rate, M_a, is calculated as (Johnson and Pankow, 1992; Hunt *et al.*, 1988):

$$M_a = C_e n_e \sqrt{\frac{4 D_z v_x}{\pi L}} \qquad \text{eq. C.3.18}$$

Where: n_e = effective porosity
L = length of NAPL lens parallel to groundwater flow direction
v_x = Average linear groundwater flow velocity
C_e = Effective water solubility (proportional to a compound's pure phase solubility and mole fraction in the NAPL)
D_z = Vertical dispersion coefficient

The vertical dispersion coefficient, D_z, results from a combination of molecular diffusion and mechanical dispersion and is defined as (Johnson and Pankow, 1992):

$$D_z = D_e + v_x \alpha_z \qquad \text{eq. C.3.19}$$

Where: D_e = effective molecular diffusivity (corrected for porosity and tortuosity)
α_z = vertical dispersivity (typically 0.01 of longitudinal dispersivity)
v_x = average linear groundwater flow velocity

A typical value of D_e for a nonpolar organic compound is 1 x 10^{-5} cm^2/sec (Sellers and Schreiber, 1992).

"At very low flow velocities where molecular diffusion dominates, the average concentration decreases with increasing flow velocity because of decreasing contact time. At higher groundwater flow velocities where dispersion dominates over diffusion, average percent solubility becomes independent of velocity. This is because the transverse dispersion coefficient is proportional to flow velocity, and D_z/v is constant. At typical groundwater flow velocities, an effluent concentration far less than the solubility limit is expected. For example, for a flow velocity of 1 m/day and $\alpha_z = 10^{-4}$ m, less than 1 percent of solubility is predicted, and considerable pumping would be required to remove the contaminant. The analysis predicts a constant contaminant concentration dissolved in the extracted water as long as the separate phase covers the boundary" (Hunt *et al.*, 1988, pp. 1253 and 1254).

LNAPL dissolution is modeled in Bioplume II simulations using one injection well in each cell containing mobile LNAPL. The injection rate for each well, Q_i, is given by:

$$Q_i = \frac{AM_a}{C_e} \qquad \text{eq. C.3.20}$$

Where: Q_i = injection rate
A = cell area
M_a = average mass transfer rate
C_e = effective water solubility

A similar approach can be used for residual LNAPL. In this case it will be necessary to use BTEX data collected from cores. When this method is used, the mass of residual LNAPL in contact with the groundwater must be determined.

C.3.2.3 Natural attenuation of Contaminant Sources

The concentration of petroleum hydrocarbons in groundwater in contact with fuel spills is controlled by the concentration of the particular hydrocarbon in the oily phase hydrocarbon. Raoult's Law predicts that the equilibrium concentration would be water solubility of that particular hydrocarbon, multiplied by its mole fraction in the oily phase material. When wells that have been installed across LNAPL spills are monitored for several years, frequently the concentrations of BTEX are seen to decline by several orders of magnitude. This is largely due to natural attenuation of the LNAPL itself, supported by natural weathering processes, including diffusion of oxygen through the vadose zone. Apparently, BTEX is degraded first, leaving a

residual of branched and normal alkanes. As a result, hydrocarbon contamination (i.e., BTEX) disappears from the groundwater, although considerable quantities of total petroleum hydrocarbons (TPH) may remain in the aquifer. The effect is well illustrated in the following case study.

In 1988, at least 1,200 gallons of unleaded gasoline was inadvertently pumped from an underground storage tank onto the land surface at the petroleum, oil, and lubricants (POL) facility at Eglin AFB, Florida. The fuel flowed overland toward a small creek 160 feet from the spill, then infiltrated until it reached the water table. When sampled in 1993, the spill remained as LNAPL in a smear zone extending from the point of release to the point of discharge of groundwater to a wetland (Figure C.3.3).

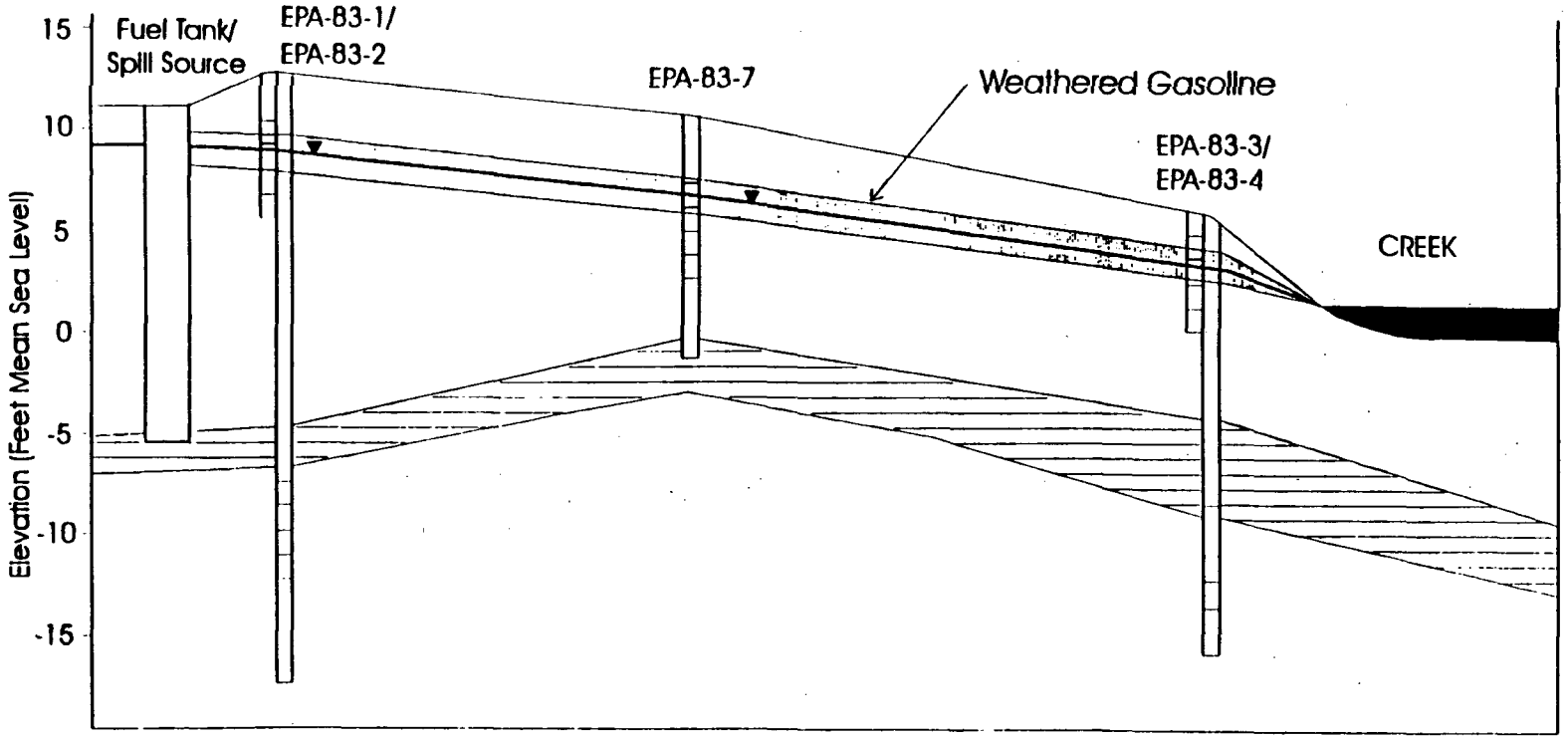
Core samples were collected across the water table at (1) the location of the original spill, (2) a location intermediate between the spill and the creek, and (3) the bank of the creek (Figure C.3.3). Core samples were analyzed for TPH and BTEX. Wells were installed in the boreholes used to acquire the cores and were screened across the interval containing TPH.

Cline *et al.* (1991) examined the variation in fuel to water partition coefficients for 31 gasoline samples. Their estimates of K_{fw} for various gasoline components are presented in Table C.3.7. TPH- and BTEX-concentration data in core samples from the spill at Eglin AFB are presented in Table C.3.11. Assuming the specific gravity of gasoline is 0.74, the following relationship was used to estimate C_f for a given BTEX compound (e.g., benzene) in a given core sample.

$$C_f = \frac{Benzene(mg/kg)}{TPH(mg/kg)} x \frac{0.74(kg)TPH}{1.0(l)TPH} x \frac{10^6(mg)TPH}{1.0(kg)TPH}$$

The concentrations of BTEX in groundwater in contact with that particular core material were predicted by dividing C_f by K_{fw} from Table C.3.7. Table C.3.12 compares the predictions to the actual measured concentrations of BTEX in groundwater from monitoring wells screened across the depth interval from which the core samples were acquired.

The gasoline near the receptor, and half way between the source and the receptor, was so weathered that no BTEX was detectable at concentrations greater than 0.01 mg/kg, although considerable quantities of TPH remained (Table C.3.11). Duplicate samples at the TPH maximum near the source were weathered, but appreciable concentrations of BTEX remained, and the pattern of weathering varied between the cores.



LEGEND

Poorly to moderately sorted, yellowish-brown to reddish-brown, silty, fine grained sands that coarsen downward into moderately sorted medium- to coarse-grained sands.

Silty and Sandy Peat

Groundwater level in September 1993.

40 30 20 0 40

FEET

VERTICAL EXAGGERATION = 5 TIMES

c:\protocol\append-c\figures\fig-c3-3.cdr

Figure C.3.3

Cross Section of a Gasoline Spill at the POL, Eglin AFB

Table C.3.11

Concentrations of TPH and BTEX in Core Material from a Gasoline Spill

Depth (feet)	TPH	Benzene	Toluene	Ethyl-benzene	p-Xylene	m-Xylene	o-Xylene
	mg/kg						
Adjacent to the Spill (EPA-83-2)							
3.0-3.4	2140	2.66	5.68	4.01	10.6	21.2	17.2
3.0-3.5	1550	0.165	18.2	2.05	41.7	69.1	59.2
On Half of the Way to the Creek (EPA-83-7)							
4.0-5.0	1170	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
6.0-7.0	5310	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Adjacent to the Creek (EPA-83-4)							
1.5-2.0	1210	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
2.0-2.5	1970	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
2.3-3.0	7090	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

Groundwater in contact with the weathered gasoline near the spill contained BTEX concentrations that were either in good agreement with those predicted from analysis of the cores, or were somewhat lower than those predicted by core analysis. A comparison of water sample results from September 1993 and October 1994 suggest that natural attenuation is continuing in the spill area. Despite high concentrations of TPH, the residual gasoline was so highly weathered that it could not support groundwater concentrations of BTEX that exceeded regulatory standards downgradient from the spill.

Extrapolation to Other Sites

The sensitivity of this comparison depends on the amount of TPH in the soil, and how extensively the TPH is weathered. To predict benzene concentrations near regulatory standards may require TPH concentrations as high as 5,000 to 10,000 mg/kg. It also depends on the detection limit for benzene in core material. If extracts are analyzed by gas chromatography (GC) using a flame ionization detector, alkanes in the window for BTEX will give false positives at the detection limit required. To avoid false positives in this case study, the concentration of BTEX in core samples were quantified by GC/mass spectral analysis.

Table C.3.12.

Comparison of BTEX in Groundwater to Predictions Based on the BTEX Content of the Weathered Residual Gasoline.

Sample Interval (ft bgs)		Benzene	Toluene	Ethyl-benzene	p-Xylene	m-Xylene	o-Xylene
		µg/L					
Well EPA 83-2, Near the Gasoline Spill							
3.0-3.4	prediction	2600	1600	310	840	1700	1600
3.0-3.5	prediction	230	7000	217	4600	7600	7800
	measured 09/93	300	1400	350	540		410
	measured 10/94	46	75	13	93	179	219
Well EPA 83-7, 70 feet Downgradient (One Half of the Distance to the Receptor)							
4.0-5.0	prediction	<18	<5	<1.4	<1.5	<1.5	<1.7
6.0-7.0	prediction	<4	<1	<0.3	<0.3	<0.3	<0.4
	measured 09/93	2.2	4.3	36	36		26
	measured 10/94	1.9	1.0	<1	<1	<1	<1
Well EPA 83-4, 150 feet Downgradient, Adjacent to the Receptor							
1.5-2.0	prediction	<17	<5	<1.4	<1.4	<1.4	<1.7
2.0-2.5	prediction	<11	<3	<0.8	<0.9	<0.9	<1.0
2.3-3.0	prediction	<3	<0.8	<0.2	<0.2	<0.2	<0.3
	measured 09/93	<1	<1	<1	<1	<1	<1
	measured 10/94	<1	1.4	<1	<1	<1	<1

C.3.3 CONFIRMING AND QUANTIFYING BIODEGRADATION

Chemical evidence of two types can be used to document the occurrence of biodegradation. The first type of evidence is graphical and is provided by the electron acceptor and metabolic byproduct maps discussed in Section C-2. The second line of evidence involves using a conservative tracer.

C.3.3.1 Isopleth maps

The extent and distribution of contamination relative to electron acceptors and metabolic byproducts can be used to qualitatively document the occurrence of biodegradation. Depleted dissolved oxygen concentrations in areas with fuel hydrocarbon contamination indicates that an active zone of aerobic hydrocarbon biodegradation is present. Depleted nitrate and sulfate concentrations in areas with fuel hydrocarbon contamination indicate that an active zone of anaerobic hydrocarbon biodegradation is present and that denitrification and sulfate reduction are occurring. Elevated iron (II) and methane concentrations in areas with fuel hydrocarbon contamination indicate that an active zone of anaerobic hydrocarbon biodegradation is present and that iron reduction and methanogenesis are occurring. Isopleth maps of contaminants, electron

acceptors, and metabolic byproducts can be used as evidence that biodegradation of fuel hydrocarbons is occurring. Figures C.2.7 and C.2.8 show how these maps can be used to support the occurrence of biodegradation. Figure C.2.7 shows that areas with depleted dissolved oxygen, nitrate, and sulfate correspond with areas having elevated BTEX concentrations. Figure C.2.8 shows that areas with elevated iron (II) and elevated methane concentrations also coincide with areas having elevated BTEX concentrations. These figures suggest that aerobic respiration, denitrification, iron reduction, sulfate reduction, and methanogenesis are all occurring at the example site.

C.3.3.2 Data Set Normalization

In order to ensure that at least a portion of observed decreases in contaminant concentrations with distance downgradient along the plume can be attributed to biodegradation, measured contaminant concentrations must be normalized for the effects of dispersion, dilution, and sorption. A convenient way to do this is to use compounds or elements associated with the contaminant plume that are relatively unaffected or predictably affected by biologic processes occuring within the aquifer. At sites where comingled fuel hydrocarbon and chlorinated solvent plumes are present, the trimethylbenzene isomers, which can be biologically recalcitrant under some geochemical conditions have proven useful when estimating biodegradation rates for BTEX and chlorinated solvents. At sites where TMB data are not available, the chloride produced as a result of biodegradation or the carbon nucleus of the chlorinated compound can be used as a tracer.

Measured tracer and contaminant concentrations from a minimum of two points along a flow path can be used to estimate the amount of contaminant remaining at each point if biodegradation had been the only attenuation process operating to reduce contaminant concentrations. To accomplish this, it is assumed that the fraction of contaminant remaining as a result of all attenuation processes is equivalent to the fraction of contaminant remaining as a result of non-destructive attenuation mechanisms only, multiplied by the fraction of contaminant remaining as a result of biodegradation. The fraction of contaminant remaining as a result of all attenuation processes can be computed from the measured contaminant concentrations at two adjacent points. The fraction of contaminant remaining as a result of non-destructive attenuation mechanisms only, can be estimated from the tracer concentrations at the same two points, because an ideal tracer is affected by non-destructive attenuation mechanisms to the same degree as the contaminant of interest and is not affected by biologic processes. The following equation uses these assumptions

to solve for the estimated downgradient contaminant concentration if biodegradation had been the only attenuation process operating between two points (i and i-1) along the flow path:

$$C_{i,corr} = C_{i-1,corr}\left(\frac{C_i}{C_{i-1}}\right)\left(\frac{T_{i-1}}{T_i}\right) \qquad \text{eq. C.3.21}$$

where: $C_{i,corr}$=corrected contaminant concentration at point i

$C_{i-1,corr}$=corrected contaminant concentration at point i-1. (If point i-1 is the first or most upgradient point, $C_{i-1,corr}$ is equivalent to the oberved contaminant concentration.)

C_i=observed contaminant concentration at point i

C_{i-1}=observed contaminant concentration at point i-1

T_i=observed tracer concentration at point i

T_{i-1}=observed tracer concentration at point i-1

This equation can be used to estimate the theoretical contaminant concentration resulting from biodegradation alone for every point along a flow path on the basis of the measured contaminant concentration at the origin and the contaminant/tracer ratios between consecutive points along the flow path. This series of normalized concentrations can then be used to estimate a first-order rate of biodegradation as described in Section C.3.3.3.1.1. If, rather than for a series of points, an estimate of the biodegradation rates between only two points (A and B) is desired equation C.3.21 simplifies to:

$$C_{B,corr} = C_B\left(\frac{T_A}{T_B}\right) \qquad \text{eq. C.3.22}$$

C.3.3.2.1 Normalization Using Organic Compounds as Tracers

A convenient way of estimating biodegradation rate constants is to use compounds present in the dissolved contaminant plume that that are biologically recalcitrant. One such compound that is useful in some, but not all, groundwater environments is TMB. The three isomers of this compound (*1,2,3*-TMB, *1,2,4*-TMB, and *1,3,5*-TMB) are generally present in sufficient quantities in fuel mixtures to be readily detectable when dissolved in groundwater. In addition, the TMB isomers are fairly recalcitrant to biodegradation under anaerobic conditions; however, the TMB isomers do not make good tracers under aerobic conditions (because they are readily biodegraded in aerobic environments). The degree of recalcitrance of TMB is site-specific, and the use of this

compound as a tracer must be evaluated on a case-by-case basis. Nevertheless, if any TMB mass is lost to biodegradation, equation C.3.21 will be conservative because the calculated mass losses and the attenuation rate constants calculated on the basis of those losses will be lower than the actual losses and attenuation rates (see also Section C.3.3.2.4.1). Another compound of potential use as a conservative tracer is tetramethylbenzene; however, detectable dissolved tetramethylbenzene concentrations are generally less common than detectable dissolved TMB concentrations.

An ideal tracer would have Henry's Law and soil sorption coefficients identical to the contaminant of interest; however, TMB is more hydrophobic than BTEX, chlorinated ethenes, and chlorinated ethanes, resulting in a higher soil sorption coefficient. This causes preferential sorption of TMB, and an increase in the coefficient of retardation for dissolved TMB in the aquifer. Therefore, for these compounds it is advisable to modify equation C.3.21, to account for the difference in contaminant and tracer velocity resulting from the higher soil sorption and consequent retardation of TMB. Without this modification, using TMB as a tracer can be so conservative that estimated biodegradation rates can be negative.

When the tracer migrates at a velocity that is significantly slower than the compound of interest, it is more important to evaluate contaminant and tracer concentrations after equal travel times rather than equal travel distances, as assumed in equation C.3.21. The equal time assumption ensures that both the contaminant and tracer are more equally affected by dilution/dispersion and sorption, which are the two dominant non-destructive attenuation mechanisms in most systems. The ratio of tracer velocity to contaminant velocity can be used to switch from equal travel distances to equal travel times as follows:

$$\frac{V_t}{V_c} = \left(\frac{V_{gw}}{R_t}\right) / \left(\frac{V_{gw}}{R_c}\right) = \frac{R_c}{R_t} \qquad \text{eq. C.3.23}$$

Where: V_t=Velocity of tracer
V_c=Velocity of contaminant
V_{gw}=Velocity of groundwater
R_t=Coefficient of retardation for the tracer
R_c=Coefficient of retardation for the contaminant

The fraction of tracer lost over the time required for the contaminant to travel between points *i*-1

and i is represented by the expression $R_c/R_t(1-T_i/T_{i-1})$ which is the product of the fraction of tracer lost between travel points and the ratio of retardation factors. Therefore, the fraction of tracer remaining is $1-R_c/R_t(1-T_i/T_{i-1})$. As discussed earlier in this section, the fraction of contaminant remaining after biodegradation is equivalent to the fraction of contaminant remaining as a result of all attenuation processes divided by the fraction of tracer remaining as a result of only non-destructive attenuation processes. Therefore, the corrected concentration at point i can be represented by the following equation:

$$C_{i,corr} = C_{i-1,corr}\left(\frac{C_i}{C_{i-1}}\right)\left(\frac{1}{\left(1-\frac{R_c}{R_t}\left(1-\frac{T_i}{T_{i-1}}\right)\right)}\right) \qquad \text{eq. C.3.24}$$

where: $C_{i,corr}$=corrected contaminant concentration at point i

$C_{i-1,corr}$=corrected contaminant concentration at point i-1. (If point i-1 is the first or most upgradient point, $C_{i-1,corr}$ is equivalent to the oberved contaminant concentration.)

C_i=observed contaminant concentration at point i

C_{i-1}=observed contaminant concentration at point i-1

T_i=observed tracer concentration at point i

T_{i-1}=observed tracer concentration at point i-1

Note: This assumes that $R_t/R_c + T_i/T_{i-1} > 1$.

When R_c is equivalent to R_t, this equation reduces to equation C.3.21.

C.3.3.2.2 Normalization Using Inorganics as Tracers

Inorganic compounds also can serve as tracers for the contaminant of interest as long as their presence is in some was associated (either directly or indirectly) with the dissolved contaminant plume. In chlorinated solvent plumes, chloride can serve as a useful tracer because elevated chloride concentrations are associated with biologic degradation of chlorinated solvents, specifically the process of reductive dechlorination. Because chloride is a chemically neutral compound, chloride is not particularly suceptible to biologic reactions or sorption. The avoidance of reactions is advantageous; however, the lack of sorption makes chloride less conservative as a tracer, therefore leading to calculation of biodegradation rates that may be greater than are

actually occurring. In addition, because chloride is produced during biodegradation of the chlorinated compounds it is important to take into account chloride produced along the flow path when using chloride as a tracer. The amount of chloride produced during the various reactions can be calculated in two ways, depending on whether one assumes that the chlorinated compound is fully converted to ethene or carbon dioxide and water in one step, or if one assumes that the reactions proceed stepwise from PCE to TCE to DCE to VC and finally to either ethene or carbon dioxide and water.

C.3.3.2.2.1 Stepwise Reaction

As PCE is reduced to TCE, 1 mole of chloride is produced:

$$C_2Cl_4 \rightarrow C_2Cl_3H + Cl^-$$

On a mass basis, the ratio of chloride produced to PCE degraded is given by:

Molecular weights:	PCE	2(12.011) + 4(35.453) = 165.83 gm
	Chloride	1(35.453) = 35.453 gm

Mass Ratio of Chloride to PCE = 35.453:165.83 = 0.21:1

The amount of chloride produced between two points, A and B (point B located downgradient from point A) by the conversion of PCE to TCE is given by:

$$Cl^-_{PCE\text{-}TCE} = 0.21(PCE_A - PCE_B) \qquad \text{eq. C.3.25}$$

Similarly, as TCE is reduced to DCE, 1 mole of chloride is produced:

$$C_2Cl_3H \rightarrow C_2Cl_2H_2 + Cl^-$$

On a mass basis, the ratio of chloride produced to TCE degraded is given by:

Molecular weights:	TCE	2(12.011) + 3(35.453) +1(1.01) = 131.39 gm
	Chloride	1(35.453) = 35.453 gm

Mass Ratio of Chloride to TCE = 35.453:131.39 = 0.27:1

The amount of chloride produced between two points, A and B (point B located downgradient from point A) by the conversion of TCE to DCE is given by:

$$Cl^-_{TCE\text{-}DCE} = 0.27(TCE_A - TCE_B) \qquad \text{eq. C.3.26}$$

Likewise, as DCE is reduced to VC, 1 molde of chloride is produced:

$$C_2Cl_2H_2 \rightarrow C_2ClH_3 + Cl^-$$

On a mass basis, the ratio of chloride produced to DCE degraded is given by:

Molecular weights: DCE 2(12.011) + 2(35.453) + 2(1.01) = 96.95 gm
Chloride 1(35.453) = 35.453 gm

Mass Ratio of Chloride to DCE = 35.453:96.95 = 0.37:1

The amount of chloride produced between two points, A and B (point B located downgradient from point A) by the conversion of DCE to VC is given by:

$$Cl^-_{DCE\text{-}VC} = 0.37(DCE_A - DCE_B) \qquad \text{eq. C.3.27}$$

As VC is reduced to either ethene or $CO_2 + H_2O$, 1 mole of chloride is produced. For example, the degradation to ethene can be represented as:

$$C_2ClH_3 \rightarrow C_2H_4 + Cl^-$$

On a mass basis, the ratio of chloride produced to VC degraded is given by:

Molecular weights: VC 2(12.011) + 1(35.453) +3(1.01) = 62.51 gm
Chloride 1(35.453) = 35.453 gm

Mass Ratio of Chloride to VC = 35.453:62.51 = 0.57:1

The amount of chloride produced between two points, A and B (point B located downgradient from point A) by the conversion of VC to ethene is given by:

$$Cl^-_{VC\text{-}Ethene} = 0.57(VC_A - VC_B) \qquad \text{eq. C.3.28}$$

The total amount of chloride produced between the two points is given by:

$$Cl^-_{Total} = Cl^-_{PCE\text{-}TCE} + Cl^-_{TCE\text{-}DCE} + Cl^-_{DCE\text{-}VC} + Cl^-_{VC\text{-}Ethene} \qquad \text{eq. C.3.29}$$

or,

$$Cl^-_{Total} = 0.21(PCE_A - PCE_B) + 0.27(TCE_A - TCE_B) + 0.37(DCE_A - DCE_B) + 0.57(VC_A - VC_B) \qquad \text{eq. C.3.30}$$

C.3.3.2.2.2 Complete Reaction

If one assumes that the given compound is fully converted to ethene or CO_2 and water between the two points the approach is more conservative than the stepwise reaction approach described above. This is because when we assume that all of the chlorine on a compound is stripped between the two points then Cl-Total is overestimated and the corrected CB (**what is CB??**) will be larger, implying less mass loss of CAHs. The following relationships should be used when assuming a complete reaction:

As PCE is reduced to ethene, 4 moles of chloride are produced:

$$C_2Cl_4 \rightarrow C_2H_4 + 4Cl^-$$

On a mass basis, the ratio of chloride produced to PCE degraded is given by:

Molecular weights: PCE 2(12.011) + 4(35.453) = 165.83 gm
Chloride 4(35.453) = 141.81 gm

Mass Ratio of Chloride to PCE = 141.81:165.83 = 0.86:1

The amount of chloride produced between two points, A and B (point B located downgradient from point A) by the conversion of PCE to ethene is then given by:

$$Cl^-_{PCE\text{-}Ethene} = 0.86(PCE_A - PCE_B) \qquad \text{eq. C.3.31}$$

Similarly, as TCE is reduced to ethene, 3 moles of chloride are produced:

$$C_2Cl_3H \rightarrow C_2H_4 + 3Cl^-$$

On a mass basis, the ratio of chloride produced to TCE degraded is given by:

Molecular weights: TCE 2(12.011) + 3(35.453) + 1(1.01)= 131.39 gm
Chloride 3(35.453) = 106.36 gm

Mass Ratio of Chloride to TCE = 106.36:131.39 = 0.81:1

The amount of chloride produced between two points, A and B (point B located downgradient from point A) by the conversion of TCE to ethene is then given by:

$$Cl^-_{TCE\text{-}Ethene} = 0.81(TCE_A - TCE_B) \qquad \text{eq. C.3.32}$$

Likewise, as DCE is reduced to ethene, 2 moles of chloride are produced:

$$C_2Cl_2H_2 \rightarrow C_2H_4 + 2Cl^-$$

On a mass basis, the ratio of chloride produced to DCE degraded is given by:

Molecular weights: DCE 2(12.011) + 2(35.453) + 2(1.01)= 96.95 gm
Chloride 2(35.453) = 70.9 gm

Mass Ratio of Chloride to DCE = 70.9:96.95 = 0.73:1

The amount of chloride produced between two points, A and B (point B located downgradient from point A) by the conversion of DCE to ethene is then given by:

$$Cl^-_{DCE\text{-}Ethene} = 0.73(DCE_A - DCE_B) \qquad \text{eq. C.3.33}$$

As VC is reduced to ethene, 1 mole of chloride is produced

$$C_2ClH_3 \rightarrow C_2H_4 + Cl^-$$

On a mass basis, the ratio of chloride produced to VC degraded is given by:

Molecular weights: VC 2(12.011) + 1(35.453) + 3(1.01)= 62.51 gm
Chloride 1(35.453) = 35.453 gm

Mass Ratio of Chloride to VC = 35.453:62.51 = 0.57:1

The amount of chloride produced between two points, A and B (point B located downgradient from point A) by the conversion of VC to ethene is then given by:

$$Cl^-_{VC\text{-}Ethene} = 0.57(VC_A - VC_B) \qquad \text{eq. C.3.34}$$

The total amount of chloride produced between the two points is given by:

$$Cl^-_{Total} = Cl^-_{PCE\text{-}Ethene} + Cl^-_{TCE\text{-}Ethene} + Cl^-_{DCE\text{-}Ethene} + Cl^-_{VC\text{-}Ethene} \qquad \text{eq. C.3.35}$$

or,

$$Cl^-_{Total} = 0.86(PCE_A - PCE_B) + 0.81(TCE_A - TCE_B) + 0.73(DCE_A - DCE_B) + 0.57(VC_A - VC_B) \qquad \text{eq. C.3.36}$$

C.3.3.2.2.3 Chloride Tracer Calculation

Once the total amount of chloride produced has been determined, the relationship that can be used to calculate the corrected contaminant concentration for a series of points is:

$$C_{i,corr} = C_{i-1,corr}\left(\frac{C_i}{C_{i-1}}\right)\left(\frac{\left(Cl^-_{i-1} + Cl^-_{Total}\right)}{\left(Cl^-_i\right)}\right) \qquad \text{eq C.3.37}$$

Where $C_{i,corr}$ = corrected concentration of compound of interest at point i assuming no dilution, dispersion, or sorption.
$C_{i-1,corr}$ = corrected concentration of compound of interest at point i-1
C_i = measured concentration of compound of interest at point i
C_{i-1} = measured concentration of compound of interest at point i-1
Cl^-_{Total} = total amount of chloride produced between points i and i-1
Cl^-_i = measured concentration of chloride at point i
Cl^-_{i-1} = measured concentration of chloride at point i-1

As before, this equation can be simplified if the correction is desired for two points (A and B) rather than for a series of points:

$$C_{B,corr} = C_B\left(\frac{\left(Cl^-_A + Cl^-_{Total}\right)}{\left(Cl^-_B\right)}\right) \qquad \text{eq. C.3.38}$$

C.3.3.2.3 Normalization Using Submolecular Units as Tracers

A third tracer method that can be used with chlorinated solvent plumes involves tracking the carbon core of the chlorinated compounds in relation to chlorine. During reductive dechlorination the source chlorinated solvent undergoes successive transformations involving the replacement of a chlorine atom by a hydrogen atom; however, the carbon core of both the parent and daughter compound remain unchanged (i.e., no carbon bonds are broken). The carbon core is subject to the same non-destructive attenuation mechanisms that act on the larger chlorinated molecule, but it is unaffected by biologically mediated reductive dechlorination. For this reason, tracking the carbon core of dissolved chlorinated solvents can serve as a theroetically perfect "tracer" for biodegradation via reductive dechlorination. The following discussion focuses on the application of this technique to chlorinated ethenes; however, this technique can be applied to any chain of chlorinated compounds and daughter products (such as chlorinated ethanes or chlorinated benzenes) that can be reductively dechlorinated.

In order to use the carbon core of the chlorinated source and daughter compounds as a "tracer" for reductive dechlorination, "equivalents" for the dissolved mass of carbon and chlorine must be calculated for each point along a flow path. The "equivalents" are calculated by first converting contaminant concentrations into molar concentrations. For chlorinated ethenes, the carbon equivalent is calculated by multiplying the number of carbon atoms per molecule of

chlorinated ethene (2) by the sum of the molar concentrations for PCE, TCE, DCE, VC, and ethene:

$$Ceq_i = 2\,(M_{PCE,i} + M_{TCE,i} + M_{DCE,i} + M_{VC,i} + M_{Ethene,i}) \qquad \text{eq. C.3.39}$$

Where: Ceq_i = carbon equivalent at point i
$M_{PCE,i}$ = molar concentration of PCE at point i
$M_{TCE,i}$ = molar concentration of TCE at point i
$M_{DCE,i}$ = molar concentration of DCE at point i
$M_{VC,i}$ = molar concentration of VC at point i
$M_{Ethene,i}$ = molar concentration of ethene at point i

The chlorine "equivalent" is defined as the sum of the products of molar concentration and chlorine atoms per molecule for each source and daughter compound. For the chlorinated ethenes, the number of chlorine atoms per molecule are 4 for PCE, 3 for TCE, 2 for DCE, 1 for VC, and 0 for ethene:

$$Cleq_i = (M_{PCE,i}*4) + (M_{TCE,i}*3) + (M_{DCE,i}*2) + M_{VC,i} \qquad \text{eq. C.3.40}$$

Where: $Cleq_i$ = chlorine equivalent at point i

Using equation C.3.21 substituting Ceq for tracer concentrations and Cleq for observed contaminant concentrations, yields the theoretical total CAH concentrations at downgradient locations if reductive dechlorination had been the only natural attenuation process operating along the flow path. The same process can be used to determine the theoretical chlorine equivalents. The normalized CAH concentrations are useful for comparison to other techniques; the normalized chlorine equivalents simplify visualization of the reductive dechlorination rate. Either the normalized total CAH concentrations or normalized chlorine equivalents can be used to calculate identical first-order rates for dechlorination.

Example C.3.5: Normalizing Total CAH Data Along a Flow Path

Given the observed concentrations of PCE, TCE, DCE, VC, ethene, TMB, Chloride, and dissolved oxygen provided in Table C.3.? for five points (A through E) that form a line parallel to the direction of groundwater flow, calculate normalized data sets for total CAH using the TMB, chloride, and carbon core methods to normalize for non-destructive attenuation processes.

Table C.3.?

To be provided in future revisions

Solution:

To be provided in future revisions.

C.3.3.3 Calculating Biodegradation Rates

Several methodologies, including first- and second-order approximations, may be used to estimate the rate of biodegradation of chlorinated compounds when they are being used to oxidize other organic compounds. Use of the first-order approximation can be appropriate to estimate biodegradation rates for chlorinated compounds where the rate of biodegradation is assumed to be controlled solely by the concentration of the contaminant. However, the use of a first-order approximation may not be appropriate when more than one substrate is limiting microbial degradation rates or when microbial mass is increasing or decreasing. In such cases a second- or higher-order approximation may provide a better estimate of biodegradation rates.

C.3.3.2.2 First-Order Decay

As with a large number of processes, the change in a solute's concentration in groundwater over time often can be described using a first-order rate constant. A first-order approximation, if appropriate, has the advantage of being easy to calculate and simplifying fate and transport modeling of complex phenomenon. In one dimension, first order decay is described by the following ordinary differential equation:

$$\frac{dC}{dt} = kt \qquad \text{eq. C.3.41}$$

Where: C = concentration at time t [M/L^3]
k = overall attenuation rate (first-order rate constant) [1/T]

Solving this differential equation yields:

$$C = C_o e^{-kt} \qquad \text{eq. C.3.42}$$

The overall attenuation rate groups all processes acting to reduce contaminant concentrations and includes advection, dispersion, dilution from recharge, sorption, and biodegradation. To

determine the portion of the overall attenuation that can be attributed to biodegradation, these effects must be accounted for, and subtracted from the total attenuation rate. Two methods for determining first-order biodegradation rates at the field scale are presented herein. The first method involves the use of a normalized data set to compute a decay rate. The second method was derived by Buscheck and Alcantar (1995) and is valid for steady-state plumes. Wiedemeier *et al.* (1995a) compare the use of these two methods with respect to BTEX biodegradation. Table C.3.15 lists representative first-order decay rate constants for chlorinated compounds.

Table C.3.15

Representative First-Order Rate Constants

Reference	Anaerobic Decay Rate (week^{-1})
To be provided in future revisions	

C.3.3.2.4.1 Use of a Normalized Data Set

In order to ensure that observed decreases in contaminant concentrations can be attributed to biodegradation, measured contaminant concentrations must be corrected for the effects of advection, dispersion, dilution from recharge, and sorption, as described in Section C.3.3.2 using equation C.3.21. The corrected concentration of a compound is the concentration that would be expected at one point (B) located downgradient from another point (A) if the processes of dispersion, dilution from recharge, volatilization, and sorption had not been occurring between points A and B.

The biodegradation rate can be estimated between any two points (A and B) of a normalized data set (where point A is upgradient of point B) by substituting the normalized concentration at point A, $C_{A,corr}$, for C_0, and the normalized concentration at point B, $C_{B,corr}$, for C in equation C.3.42. The resulting relationship is expressed as:

$$C_{B,corr} = C_{A,corr} e^{-\lambda t} \qquad \text{eq. C.3.43}$$

Where: $C_{B,corr}$ = normalized contaminant concentration at downgradient point B (from eq. C.3.22)

$C_{A,corr}$ = normalized contaminant concentration at upgradient point A (from eq. C.3.22). Note that if point A if the first point in the normalized data set, then $C_A = C_{A,corr}$

λ = first-order biological decay rate (first-order rate constant) [1/T]

t = time of contaminant travel between points A and B

The rate constant in this equation is no longer the total attenuation rate, k, but is the biological decay rate, λ, because the effects of advection, dispersion, dilution from recharge, and sorption have been removed (Section C.3.3.2). This relationship can be used to calculate the first-order biological decay rate constant between two points by solving equation C.3.43 for λ:

$$\lambda = -\frac{\ln\left(\frac{C_{B,corr}}{C_{A,corr}}\right)}{t} \qquad \text{eq. C.3.44}$$

The travel time, t, between two points is given by:

$$t = \frac{x}{v_c} \qquad \text{eq. C.3.45}$$

Where: x = distance between two points [L]
v_c = retarded solute velocity [L/T]

The simplest way to determine the first-order rate constant from an entire set of normalized data is to make a log-linear plot of normalized contaminant concentrations versus travel time. If the data plot along a straight line, the relationship is first order and an exponential regression analysis can be performed. The exponential regression analysis gives the equation of the line of best fit for the data being regressed from a log-linear plot and has the general form:

$$y = be^{mx} \qquad \text{eq. C.3.46}$$

Where: y = y axis value
b = y intercept
m = slope of regression line
x = x-axis value

When using normalized data, x is the downgradient contaminant travel time and m is the biodegradation rate constant, λ. The correlation coefficient, R^2, is a measure of how well the regression relationship approximates the data. Values of R^2 can range from 0 to 1; the closer R^2 is to 1, the more accurate the equation describing the trend in the data. Values of R^2 greater than 0.80 are generally considered good; R^2 values greater than 0.90 are considered excellent. Several commonly available spreadsheets can be used to facilitate the exponential regression analysis. The following example illustrates the use of this technique.

Example C.3.6: First-Order Decay Rate Constant Calculation Using Normalized Data Set

Calculate first-order decay rate constants for total CAHs using each of the normalized data sets computed for example C.3.5. The site site has an average gradient of ???, an average hydraulic conductivity of ???, an assumed effective porosity of ???, an average organic carbon content of ???, and an estimated soil/water partitioning coefficient for CAH of ???.

Solution:

The solution will be completed in future revisions.

An accurate first-order biological decay rate can be calculated only if it can be shown that biodegradation is a first-order process. Normalized contaminant concentrations must first be plotted on log-linear paper to ensure that biodegradation is a first order process.

The next step is to determine the retarded solute transport velocity at the site in the area where contaminant and tracer concentration data are available. Using the data presented above, the average retarded contaminant velocity at the site is ?? m/day (eq. B.2.1). Using this information it is possible to determine the residence time of the solute between two points using equation C.?. Dissolved oxygen was observed in points D and E used in this example; therefore, anaerobic processes are prevalent only between points A, B, and C.

C.3.3.2.2.2 Method of Buscheck and Alcantar (1995)

Buscheck and Alcantar (1995) derive a relationship that allows calculation of first-order decay rate constants for steady-state plumes. This method involves coupling the regression of contaminant concentration (plotted on a logarithmic scale) versus distance downgradient (plotted on a linear scale) to an analytical solution for one-dimensional, steady-state, contaminant transport that includes advection, dispersion, sorption, and biodegradation. For a steady-state plume, the first-order decay rate is given by (Buscheck and Alcantar, 1995):

$$\lambda = \frac{v_c}{4\alpha_x}\left(\left[1+2\alpha_x\left(\frac{k}{v_x}\right)\right]^2 - 1\right) \qquad \text{eq. C.3.47}$$

Where: λ = first-order biological decay rate
v_c = retarded contaminant velocity in the x-direction
α_x = dispersivity
k/v_x = slope of line formed by making a log-linear plot of contaminant concentration versus distance downgradient along flow path

Example C.3.7: **First-Order Rate Constant Calculation Using Method of Buscheck and Alcantar (1995)**

Calculate first-order decay rate constant for total CAH, TCE, and DCE using the data provided for example C.3.5. The site site has an average gradient of ???, an average hydraulic conductivity of ???, an assumed effective porosity of ???, an average organic carbon content of ???, an estimated longitudinal dispersivity of ??, and an estimated soil/water partitioning coefficient for CAH of ???.

Solution:

The solution will be completed in future revisions.

The first step is to confirm that the contaminant plume has reached a steady-state configuration. This is done by analyzing historical data to make sure the plume is no longer migrating downgradient and contaminant concentrations are not changing significantly through time. This is generally the case for older spills where the source has not been removed. The next step is to make a log-linear plot of contaminant concentration versus distance downgradient. Using linear regression, the ratio k/v is determined and entered into equation C.3.37. When using the method of Buscheck and Alcantar (1995), y in the regression analysis is the contaminant concentration, x is the distance downgradient from point (A), and m is the ratio k/v. The value of k/v determined from the regression analysis is entered into equation C.3.?? and the biodegradation rate constant, λ, is calculated. Use of two methods to determine first-order decay rate constants at the field scale is a good check on the accuracy of the calculations.

C.3.3.2.2.3 Comparison of First-Order Methods

To be provided in future revisions.

C.3.3.2.3 Second-Order Decay

Although a first-order rate assumption may provide a reasonable approximation of how chlorinated compounds are degrading in groundwater systems, this approach may neglect the importance of the electron donor-electron acceptor redox couples when more than one substrate is limiting microbial degradation rates. Intuitively, a second-order approximation makes sense in terms of how these types of degradation reactions occur: if insufficient electron acceptor mass is available to oxidize the electron donor mass, the reaction will stall (i.e., the system will strangle); if insufficient electron donor mass is available, degradation will cease (i.e., the system will starve). For example, reductive dechlorination depends not only on the concentration of the chlorinated

compound, but also on the concentration of primary substrate (e.g., BTEX, native organic carbon). This can be expressed as:

$$\frac{-d[B]}{dt} = k[B][A] \qquad \text{eq. C.3.48}$$

where k is a second-order rate constant [M/T], [B] is the concentration of chlorinated solvent, [A] is the concentration of primary substrate, and the disappearance (or degradation) of B is first-order in both [B] and [A]. The linear form of this second-order equation is:

$$\frac{1}{[A]_o + [B]_o} \ln\left[\frac{[A]_o[B]}{[B]_o[A]}\right] = kt \qquad \text{eq. C.3.49}$$

where $[A]_o$ = initial concentration of electron donor (µg/L);

[A] = measured concentration of electron donor (µg/L);

$[B]_o$ = initial stoichiometry-normalized concentration of electron acceptor (µg/L);

[B] = measured stoichiometry-normalized concentration of electron acceptors (µg/L); and

k = second-order degradation rate constant (L/µg-day).

The reason that stoichiometry-normalized electron acceptor concentrations were used to develop second-order reaction rate constants was to develop a weighted estimate of oxidizing potential. Stoichiometry normalization is unnecessary if only a single electron acceptor is being considered.

If the objective of the second-order approximation is to estimate the rate of chlorinated degradation in the presence of petroleum hydrocarbons, no significant concentration correction for the effects of nondestructive attenuation processes is necessary, because these non-destructive attenuation processes will have the same general concentration-reducing effects on anthropogenic organic electron acceptors (CAH) and anthropogenic organic electron donors (BTEX). In contrast, if the objective of the second-order approximation was to estimate the rate of degradation of anthropogenic electron donors (BTEX) in the presence of only natural electron acceptors (i.e., the common inorganic electron acceptors), the concentration-reducing effects of nondestructive attenuation processes on the BTEX compounds would have to be considered.

The simplest way to determine the second-order rate constant is to make a linear plot of the function $\frac{1}{[A]_o + [B]_o} \ln\left[\frac{[A]_o[B]}{[B]_o[A]}\right]$ versus travel time. If the data plot along a straight line through the origin, the relationship can be approximated by second order and a linear regression analysis can be performed. The linear regression analysis gives the equation of the line of best fit for the data being regressed from a log-linear plot and has the general form:

$$y = mx + b \qquad \text{eq. C.3.50}$$

Where: y = y axis value
b = y intercept
m = slope of regression line
x = x-axis value

When using normalized data, x is the downgradient contaminant travel time and m is the biodegradation rate constant, λ. The correlation coefficient, R^2, is a measure of how well the regression relationship approximates the data. Values of R^2 can range from 0 to 1; the closer R^2 is to 1, the more accurate the equation describing the trend in the data. Values of R^2 greater than 0.80 are generally considered good; R^2 values greater than 0.90 are considered excellent. Several commonly available spreadsheets can be used to facilitate the linear regression analysis.

The estimated second-order rate constant can be used to estimate the changing degradation rates for redox reactions as a function of distance from the source and/or time as follows:

$$\text{degradation rate } (\mu g/L\text{-day}) = k[B][A] \qquad \text{eq. C.3.51}$$

The following example illustrates the use of this technique.

Example C.3.7: Second-Order Rate Constant Calculation

Calculate the second-order decay rate constant for total CAH using the data provided for example C.3.5. The site site has an average gradient of ???, an average hydraulic conductivity of ???, an assumed effective porosity of ???, an average organic carbon content of ???, an estimated longitudinal dispersivity of ??, and an estimated soil/water partitioning coefficient for CAH of ???.

Solution:

The solution will be completed in future revisions.

C.3.3.3 Mass Balance Calculations

NEEDS TO BE UPDATED FOR CHLORINATED SOLVENTS

Based on the stoichiometric relationships presented in Appendix B, mass balance calculations can be completed for each of the electron acceptors. The results of the mass balance calculations give an indication of the intrinsic capacity of the groundwater to degrade BTEX. The following sections give examples of these mass balance calculations using the data provided in Table C.3.14.

C.3.3.3.1 Chloride

From a mass balance standpoint, the total mass of chlorinated solvents biodegraded to produce an increase in chloride concentration can be determined using the relationships presented in ??. Specifically,

NEED ORGANIC CARBON, ETC. CALCS

C.3.4 DESIGN, IMPLEMENTATION, AND INTERPRETATION OF MICROCOSM STUDIES

C.3.4.1 Overview

If properly designed, implemented, and interpreted, microcosm studies can provide very convincing documentation of the occurrence of intrinsic bioremediation. They are the only "line of evidence" that allows an unequivocal mass balance on the biodegradation of environmental contaminants. If the microcosm study is properly designed, it will be easy for decision makers with non-technical backgrounds to interpret. The results of a microcosm study are strongly influenced by the nature of the geological material submitted to study, by the physical properties of the microcosm, by the sampling strategy, and the duration of the study. In addition, microcosm studies are time consuming and expensive. A microcosm study should only be undertaken at sites where there is considerable uncertainty concerning the biodegradation of fuel hydrocarbons based on soil and groundwater samples alone.

Material for a microcosm study should not be selected until the geochemical behavior of the site is well understood. Contaminant plumes may consume oxygen, nitrate, sulfate, and produce iron II, manganese II, or methane. These processes usually operate concurrently in different parts of the plume. Regions where each process prevails may be separated in directions parallel to groundwater flow by hundreds of meters, in directions perpendicular to groundwater flow by tens

of meters, and vertically by only a few meters. Rate constants and constraints for petroleum hydrocarbon biodegradation will be influenced by the prevailing geochemistry. Material from microcosms must be acquired for depth intervals and locations that have been predetermined to be representative of the prevailing geochemical milieu in the plume.

Hydrocarbon biodegradation supported by oxygen and nitrate can not be adequately represented in microcosm. In the field, organisms that use oxygen or nitrate proliferate until they become limited by the supply of electron acceptor. After that time, the rate of hydrocarbon degradation is controlled by the supply of electron acceptor through diffusion or hydrodynamic dispersion. Microcosms have been used successfully to simulate sulfate-reducing, iron-reducing, and methanogenic regions of plumes. Oxygen is toxic to sulfate-reducing and methanogenic microorganisms. Material should be collected and secured in a manner that precludes oxygenation of the sample.

Batch microcosms that are sacrificed for each analysis usually give more interpretable results than column microcosms or batch microcosms that are sampled repetitively. For statistical reasons, at least three microcosms should be sampled at each time interval. If one assumes a first order rate law, and no lag, a geometrical time interval for sampling should be the most efficient. An example would be sampling after 0 weeks, 2 weeks, 1 month, 2 months, 4 months, and 8 months. As a practical matter, long lags frequently occur, and the rate of bioremediation after the lag is rapid. A simple linear time scale is most likely to give interpretable results.

The batch microcosms should have approximately the same ratio of solids to water as the original material. Most of the microbes are attached to solids. If a microcosm has an excess of water, and the contaminant is mostly in the aqueous phase, the microbes must process a great deal more contaminant to produce the same relative change in the contaminant concentration. The kinetics at field scale would be underestimated.

Microcosms are inherently time consuming. At field scale, the residence time of a plume may be several years to decades. Slow rates of transformation may have a considerable environmental significance. A microcosm study that lasts only a few weeks or months may not have the resolution to detect slow changes that are still of environmental significance. Further, microcosms often show a pattern of sequential utilization, with toluene and the xylenes degrading first, and benzene and ethylbenzene degrading at a later time. Degradation of benzene or ethylbenzene may be delayed by as much as a year.

As a practical matter, batch microcosms with an optimal solids to water ratio, sampled every 2 months in triplicate for up to 18 months, can resolve biodegradation from abiotic losses with a rate detection limit of 0.001 to 0.0005 per day.. Many plumes show significant attenuation of contamination at field-calibrated rates that are slower than the detection limit of today's microcosm technology. The most appropriate use of microcosms is to document that contaminant attenuation is largely a biological process. Rate constants for modeling purposes are more appropriately acquired from field-scale studies.

Microcosm studies are often used to provide a third line of evidence. The potential for biodegradation of the contaminants of interest can be confirmed by the use of microcosms, through comparison of removals in the living treatments with removals in the controls. Microcosm studies also permit an absolute mass balance determination based on biodegradation of the contaminants of interest. Further, the appearance of daughter products in the microcosms can be used to confirm biodegradation of the parent compound.

C.3.4.2 When to Use Microcosms

There are two fundamentally different applications of microcosms. They are frequently used in a qualitative way to illustrate the important processes that control the fate of organic contaminants. They are also used to estimate rate constants for biotransformation of contaminants that can be used in a site-specific transport and fate model of a plume of contaminated ground water. This paper only discusses microcosms for the second application.

Microcosms should be used when there is no other way to obtain a rate constant for attenuation of contaminants, in particular, when it is impossible to estimate the rate of attenuation from data from monitoring wells in the plume of concern. There are situations where it is impossible to compare concentrations in monitoring wells along a flow path due to legal or physical impediments. In many landscapes, the direction of ground-water flow (and water table elevations in monitoring wells) can vary over short periods of time due to tidal influences or changes in barometric pressure. The direction of ground-water flow may also be affected by changes in the stage of a nearby river or pumping wells in the vicinity. These changes in ground-water flow direction do not allow simple snap-shot comparisons of concentrations in monitoring wells because of uncertainties in identifying the flow path. Rate constants from microcosms can be used with average flow conditions to estimate attenuation at some point of discharge or point of compliance.

C.3.4.3 Application of Microcosms

The primary objective of microcosm studies is to obtain rate constants applicable to average flow conditions. These average condition can be determined by continuous monitoring of water table elevations in the aquifer being evaluated. The product of the microcosm study and the continuous monitoring of water table elevations will be a yearly or seasonal estimate of the extent of attenuation along average flow paths. Removals seen at field scale can be attributed to biological activity. If removals in the microcosms duplicate removal at field scale, the rate constant can be used for risk assessment purposes.

C.3.4.4 Selecting Material for Study

Prior to choosing material for microcosm studies, the location of major conduits of ground-water flow should be identified and the geochemical regions along the flow path should be determined. The important geochemical regions for natural attenuation of chlorinated aliphatic hydrocarbons are regions that are actively methanogenic; regions that exhibit sulfate reduction and iron reduction concomitantly; and regions that exhibit iron reduction alone. The pattern of biodegradation of chlorinated solvents varies in different regions. Vinyl chloride tends to accumulate during reductive dechlorination of trichloroethylene (TCE) or tetrachloroethylene (PCE) in methanogenic regions (1,2); it does not accumulate to the same extent in regions exhibiting iron reduction and sulfate reduction (3). In regions showing iron reduction alone, vinyl chloride is consumed but dechlorination of PCE, TCE, or dichloroethylene (DCE) may not occur (4). Core material from each geochemical region in major flow paths represented by the plume must be acquired, and the hydraulic conductivity of each depth at which core material is acquired must be measured. If possible, the microcosms should be constructed with the most transmissive material in the flow path.

Several characteristics of ground water from the same interval used to collect the core material should be determined. These characteristics include temperature, redox potential, pH, and concentrations of oxygen, sulfate, sulfide, nitrate, ferrous iron, chloride, methane, ethane, ethene, total organic carbon, and alkalinity. The concentrations of compounds of regulatory concern and any breakdown products for each site must be determined. The ground water should be analyzed for methane to determine if methanogenic conditions exist and for ethane and ethene as daughter products. A comparison of the ground-water chemistry from the interval where the cores were acquired to that in neighboring monitoring wells will demonstrate if the collected cores are representative of that section of the contaminant plume.

Reductive dechlorination of chlorinated solvents requires an electron donor to allow the process to proceed. The electron donor could be soil organic matter, low molecular weight organic compounds (lactate, acetate, methanol, glucose, etc.), H_2, or a co-contaminant such as landfill leachate or petroleum compounds (5,6,7). In many instances, the actual electron donor(s) may not be identified.

Several characteristics of the core material should also be evaluated. The initial concentration of the contaminated material (μg/kg) should be identified prior to construction of the microcosms. Also, it is necessary to know if the contamination is present as a nonaqueous phase liquid (NAPL) or in solution. A total petroleum hydrocarbon (TPH) analysis will determine if any hydrocarbon-based oily materials are present. The water-filled porosity is a parameter generally used to extrapolate rates to the field. It can be calculated by comparing wet and dry weights of the aquifer material.

To insure sample integrity and stability during acquisition, it is important to quickly transfer the aquifer material into a jar, exclude air by adding ground water, and seal the jar without headspace. The material should be cooled during transportation to the laboratory. Incubate the core material at the ambient ground-water temperature in the dark before the construction of microcosms.

At least one microcosm study per geochemical region should be completed. If the plume is over one kilometer in length, several microcosm studies per geochemical region may need to be constructed.

C.3.4.5 Geochemical Characterization of the Site

The geochemistry of the subsurface affects behavior of organic and inorganic contaminants, inorganic minerals, and microbial populations. Major geochemical parameters that characterize the subsurface encompasses (1) pH; (2) redox potential, Eh; (3) alkalinity; (4) physical and chemical characterization of the solids; (5) temperature; (6) dissolved constituents, including electron acceptors; and (7) microbial processes. The most important of these in relation to biological processes are redox potential, alkalinity, concentration of electron acceptor, and chemical nature of the solids.

Alkalinity Field indications of biologically active portions of a plume may be identified by increased alkalinity, compared to background wells, from carbon dioxide due to biodegradation of the pollutants. Increases in both alkalinity and pH have been measured in portions of an aquifer contaminated by gasoline undergoing active utilization of the gasoline

components (8). Alkalinity can be one of the parameters used when identifying where to collect biologically active core material.

pH Bacteria generally prefer a neutral or slightly alkaline pH level with an optimum pH range for most microorganisms between 6.0 and 8.0; however, many microorganisms can tolerate a pH range of 5.0 to 9.0. Most ground waters in uncontaminated aquifers are within these ranges. Natural pH values may be as low as 4.0 or 5.0 in aquifers with active oxidation of sulfides, and pH values as high as 9.0 may be found in carbonate-buffered systems (9). However, pH values as low as 3.0 have been measured for ground waters contaminated with municipal waste leachates which often contain elevated concentrations of organic acids (10). In ground waters contaminated with sludges from cement manufacturing, pH values as high as 11.0 have been measured (9).

Redox The oxidation/reduction (redox) potential (Eh) of ground water is a measure of electron activity that indicates the relative ability of a solution to accept or transfer electrons. Most redox reactions in the subsurface are microbially catalyzed during metabolism of native organic matter or contaminants. The only elements that are predominant participants in aquatic redox processes are carbon, nitrogen, oxygen, sulfur, iron, and manganese (11). The principal oxidizing agents in ground water are oxygen, nitrate, sulfate, manganese (IV), and iron (III). Biological reactions in the subsurface both influence and are affected by the redox potential and the available electron acceptors. The redox potential changes with the predominant electron acceptor, with reducing conditions increasing through the sequence oxygen, nitrate, iron, sulfate, and carbonate. The redox potential decreases in each sequence, with methanogenic (carbonate as the electron acceptor) conditions being most reducing. The interpretation of redox potentials in ground waters is difficult (12). The potential obtained in ground waters is a mixed potential that reflects the potential of many reactions and cannot be used for quantitative interpretation (11). The approximate location of the contaminant plume can be identified in the field by measurement of the redox potential of the ground water.

To overcome the limitations imposed by traditional redox measurements, recent work has focused on the measurement of molecular hydrogen to accurately describe the predominant *in situ* redox reactions (13, 14, 15). The evidence suggests that concentrations of H_2 in ground water can be correlated with specific microbial processes, and these concentrations can be used to identify zones of methanogenesis, sulfate reduction, and iron reduction in the subsurface (3).

Electron acceptors Measurement of the available electron acceptors is critical in identifying the predominant microbial and geochemical processes occurring *in situ* at the time of sample

The extent of attenuation from well to well listed in Table 5, and the travel time between wells in a segment (Figure 4) were used to calculate first-order rate constants for each segment (Table 6). Travel time between monitoring wells was calculated from site-specific estimates of hydraulic conductivity and from the hydraulic gradient. In the area sampled for the microcosm study, the estimated Darcy flow was 2.0 feet per year. With an estimated porosity in this particular glacial till of 0.1, this corresponds to a plume velocity of 20 feet per year.

C.3.4.9 Summary

Table 7 compares the first-order rate constants estimated from the microcosm studies to the rate constants estimated at field scale. The agreement between the independent estimates of rate is good; indicating that the rates can appropriately be used in a risk assessment. The rates of biodegradation documented in the microcosm study could easily account for the disappearance of trichloroethylene, benzene, and toluene observed at field scale. The rates estimated from the microcosm study are several-fold higher than the rates estimated at field scale. This may reflect an underestimation of the true rate in the field. The estimates of plume velocity assumed that the aquifer was homogeneous. No attempt was made in this study to correct the estimate of plume velocity for the influence of preferential flow paths. Preferential flow paths with a higher hydraulic conductivity than average would result in a faster velocity of the plume, thus a lower residence time and faster rate of removal at field scale.

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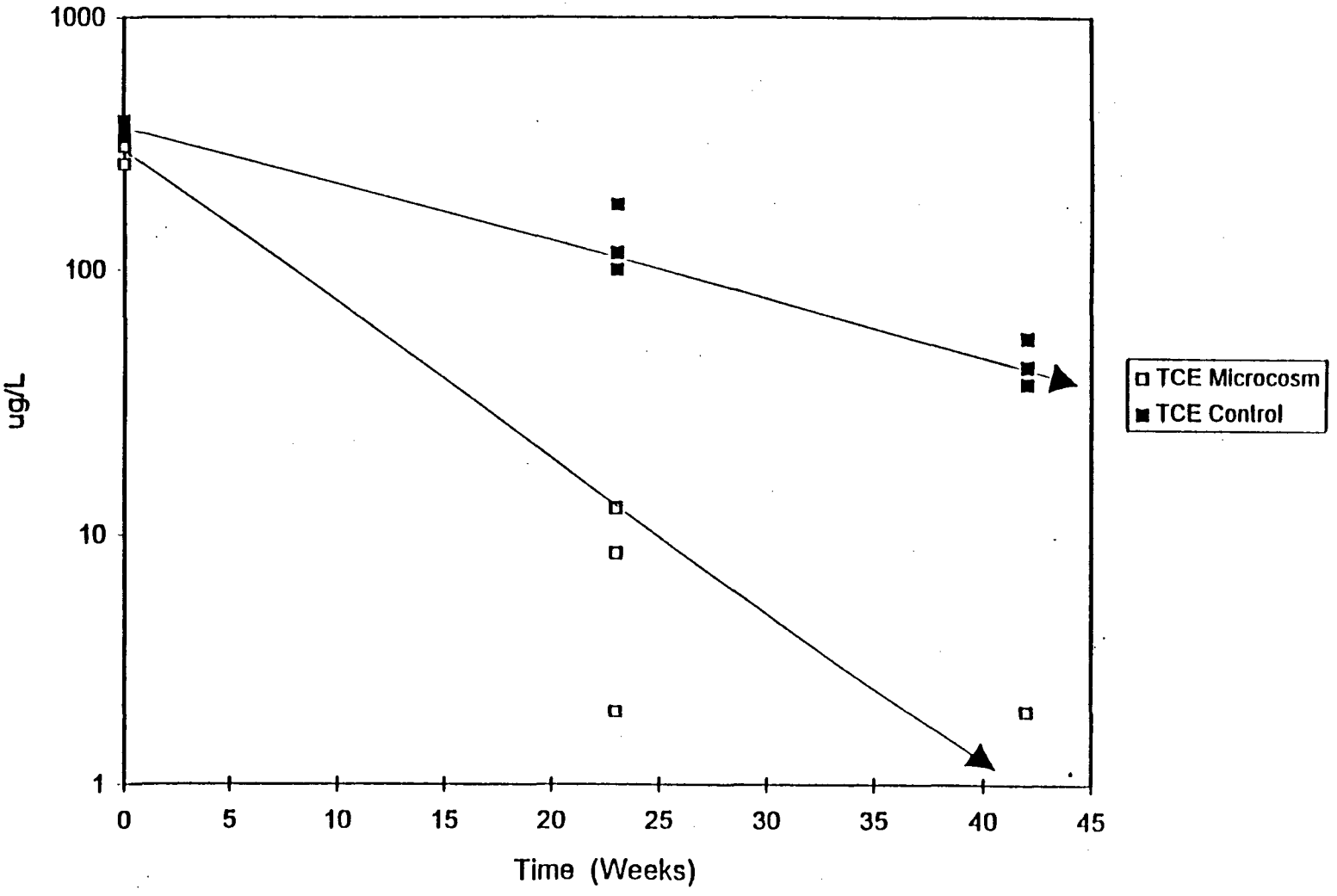

Figure 1. TCE Concentrations in the Tibbetts Road Microcosm Study.

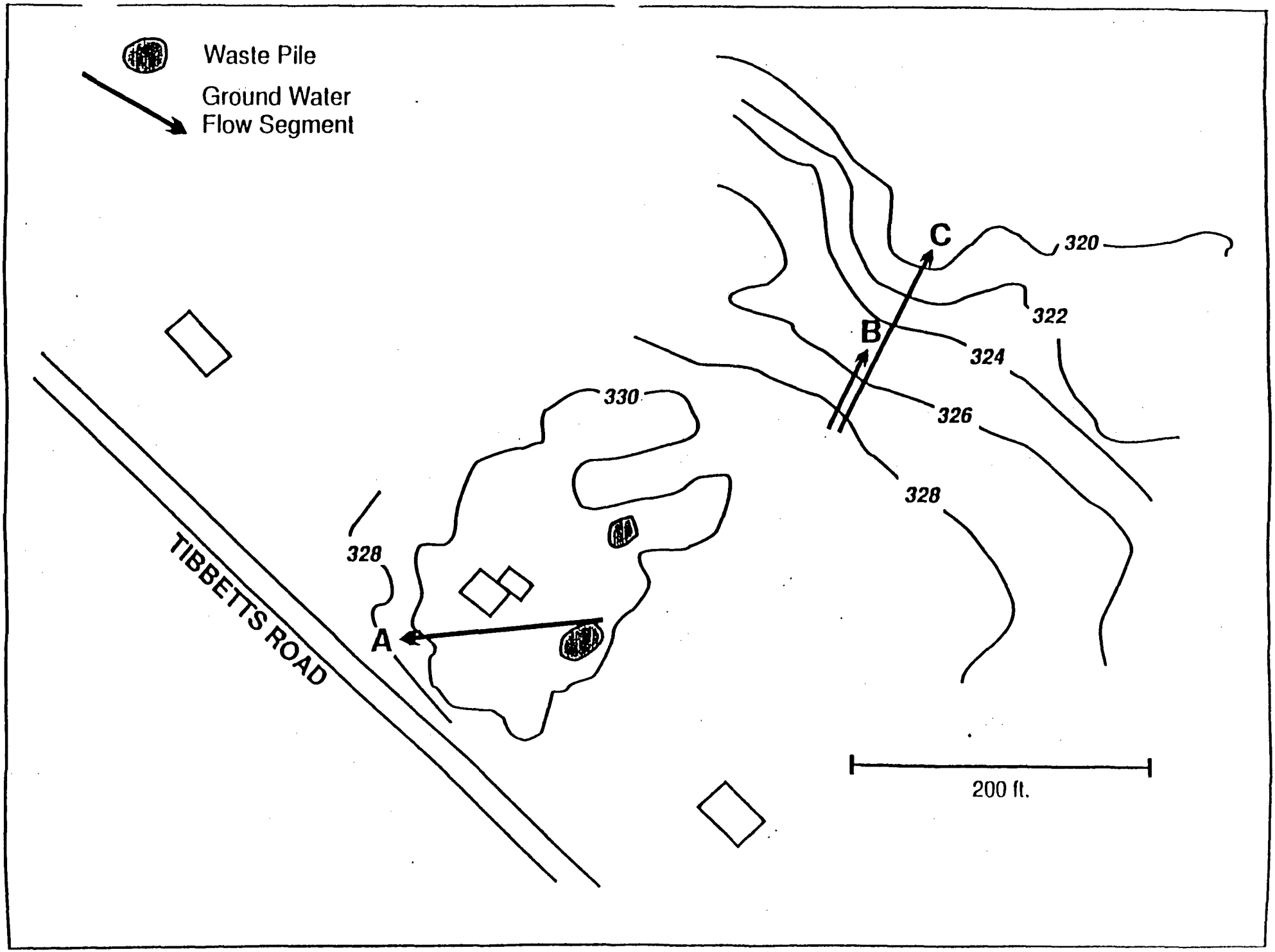
Waste Pile
Ground Water
Flow Segment
C
B
A
320
322
324
326
328
330
328
TIBBETTS ROAD
200 ft.

Table 1. Geochemical Parameters

Analysis	Range	Interpretation
Redox Potential	<50 millivolt against Ag/AgCl	Reductive pathway possible
Sulfate	<20 mg/liter	Competes at higher concentrations with reductive pathway
Nitrate	<1 mg/liter	Competes at higher concentrations with reductive pathway
Oxygen	<0.5 mg/liter	Tolerated, toxic to reductive pathway at higher concentrations
Oxygen	>1 mg/liter	Vinyl chloride oxidized
Iron II	>1 mg/liter	Reductive pathway possible
Sulfide	>1 mg/liter	Reductive pathway possible
Hydrogen	>1 nMolar	Reductive pathway possible, vinyl chloride may accumulate
Hydrogen	<1 nMolar	Vinyl chloride oxidized
pH	5 < pH < 9	Tolerated range

Table 2. Contaminants and Daughter Products

Analysis	Interpretation
PCE	Material spilled
TCE	Material spilled or daughter product of perchloroethylene
1,1,1-Trichloroethane	Material spilled
cis-DCE	Daughter product of trichloroethylene
trans-DCE	Daughter product of trichloroethylene
Vinyl Chloride	Daughter product of dichloroethylenes
Ethene	Daughter product of vinyl chloride
Ethane	Daughter product of ethene
Methane	Ultimate reductive daughter product
Chloride	Daughter product of organic chlorine
Carbon Dioxide	Ultimate oxidative daughter product
Alkalinity	Results from interaction of carbon dioxide with aquifer minerals

Table 3. Concentrations of TCE, Benzene, and Toluene in the Tibbetts Road Microcosms

Compound	Time Zero Microcosms	Time Zero Controls	Week 23 Microcosms	Week 23 Controls	Week 42 Microcosms	Week 42 Controls
TCE	328	337	1	180	2	36.3
	261	394	12.5	116	2	54.5
	309	367	8.46	99.9	2	42.3
Mean ± Standard Deviation	299 ± 34.5	366 ± 28.5	7.32 ± 5.83	132 ± 42.4	2.0 ± 0.0	44.4 ± 9.27
Benzene	366	396	201	236	11.1	146
	280	462	276	180	20.5	105
	340	433	22.8	152	11.6	139
Mean ± Standard Deviation	329 ± 44.1	430 ± 33.1	167 ± 130	189 ± 42.8	14.4 ± 5.29	130 ± 21.9
Toluene	443	460	228	254	2	136
	342	557	304	185	2.5	92
	411	502	19.9	157	16.6	115
Mean ± Standard Deviation	399 ± 51.6	506 ± 48.6	184 ± 147	199 ± 49.9	7.03 ± 8.29	114 ± 22.0

Table 4. First-order Rate Constants for Removal TCE, Benzene, and Toluene in the Tibbetts Road Microcosms.

Parameter	Living Microcosms	Autoclaved Controls	Removal Above Controls
	First-order Rate of Removal (per year)		
TCE	6.31	2.62	3.69
95% Confidence Interval	± 2.50	± 0.50	± 2.31
Minimum Rate Significant at 95% Confidence			1.38
Benzene	3.87	1.51	2.36
95% Confidence Interval	± 1.96	± 0.44	± 1.83
Minimum Rate Significant at 95% Confidence			0.53
Toluene	5.49	1.86	3.63
95% Confidence Interval	± 2.87	± 0.45	± 2.64
Minimum Rate Significant at 95% Confidence			0.99

Table 5. Concentration of Contaminants and Metabolic By-products in Monitoring Wells along Segments in the Plume used to Estimate Field-scale Rate Constants.

Parameter	Segment A		Segment B		Segment C	
Monitoring well	80S	79S	70S	52S	70S	53S
	Upgradient	Down-gradient	Up Gradient	Down Gradient	Up Gradient	Down Gradient
	(ug/liter)					
TCE	200	13.7	710	67	710	3.1
cis-DCE	740	10.9	220	270	220	2.9
trans-DCE	0.41	<1	0.8	0.3	0.8	<1
1,1-DCE	0.99	<1	<1	1.6	<1	<1
Vinyl Chloride	<1	<1	<1	<1	<1	<1
Ethene	<4	<4	7	<4	7	<4
Benzene	510	2.5	493	420	493	<1
Toluene	10000	<1	3850	900	3850	<1
o-Xylene	1400	8.4	240	71	240	<1
m-Xylene	2500	<1	360	59	360	<1
p-Xylene	1400	22	1100	320	1100	<1
Ethylbenzene	1300	0.7	760	310	760	<1
Methane	353	77	8	3	8	<2
Iron						27000

APPENDIX D

MODELING THE FATE AND TRANSPORT OF CONTAMINANTS DISSOLVED IN GROUNDWATER

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FIGURES

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SECTION D-1

INTRODUCTION

A solute fate and transport model (possibly coupled with a groundwater flow model) provides the user with a tool that is useful for many aspects of an evaluation of natural attenuation. Prediction of the migration and degradation of a dissolved contaminant plume using a solute transport model is often an important component of the natural attenuation demonstration. This is the most common use of models for this type of study. However, models can also be used to synthesize, interpret, and present available data and in turn, guide any additional data collection that must be performed in order to support remediation by natural attenuation. Some models can also be used to evaluate the effects of other remedial actions (e.g., source removal, source reduction, pump-and-treat, or hydraulic containment) on their own or in conjunction with natural attenuation.

A model, whether it is used for solute fate and transport, groundwater flow, or both, consists of several components. As enumerated by Spitz and Moreno (1996), these components are:

- the natural system for which the model is designed;
- a conceptual model as an idealized representation of the natural system;
- a mathematical model representing controlling mechanisms in mathematical terms;
- solution of the mathematical model;
- calibration of the solution by adjusting simulated to observed responses of the natural system;
- validation of the accuracy of the model predictions; and
- simulations based on the calibrated solution of the conceptual model.

In general, any modeling effort will contain some or all of these components, depending on the type of study, the available data, and the type of model being used. For example, sufficient data commonly are not available for the validation of a transport model, so that step may be eliminated from that study. Material in this appendix will briefly focus on some of these topics, with the intent to provide a limited understanding of these concepts in the context of their application to a demonstration of remediation by natural attenuation.

In order for a model to adequately predict the fate and transport of a dissolved contaminant plume, it must be capable of modeling solute transport under the influence of advection, dispersion, sorption, and biodegradation. In many cases, the model must also be able to simulate the groundwater flow field in which contaminants are transported. Models used to simulate groundwater flow and solute transport can be classified according to the mathematical technique used to solve the governing partial differential equations. Analytical solutions and numerical solutions are the two mathematical techniques used to solve the advective-dispersive transport equation. The following sections describe the mathematical relationships that describe one-, two-, and three-dimensional solute transport and the numerical techniques used to solve these relationships. Also included is a discussion of the merits of analytical and numerical models and some suggestions regarding model selection. Finally, consideration is given to whether or not a model is necessary to successfully implement remediation by natural attenuation at a given site.

D.1.1 MATHEMATICAL EXPRESSIONS USED TO DESCRIBE SOLUTE TRANSPORT AND REMEDIATION BY NATURAL ATTENUATION

The mathematical relationships that describe groundwater flow and solute transport are based on the equation of continuity and Darcy's Law. Combination of these relationships for transient conditions yields a parabolic partial differential equation. Combination of these relationships for steady-state conditions yields an elliptical partial differential equation. The following sections present the one-, two-, and three-dimensional partial differential equations that describe solute transport by the processes of advection, dispersion, sorption, and biodegradation. Several texts derive these equations (Bear, 1972 and 1979; Domenico and Schwartz, 1990; Bedient *et al.*, 1994; Segol, 1994). No discussion of groundwater flow equations will be presented here. This information can be found in the aforementioned texts, as well as those by Strack (1989) and Spitz and Moreno (1996).

D.1.1.1 One-Dimensional Reactive Solute Transport

The one-dimensional partial differential equation describing transient solute transport with first-order decay of the solute is given by:

$$\frac{\partial C}{\partial t} = \frac{D_x}{R}\frac{\partial^2 C}{\partial x^2} - \frac{v_x}{R}\frac{\partial C}{\partial x} - \lambda C \qquad \text{eq. D.1.1}$$

Where: C = solute concentration
t = time

D_x = hydrodynamic dispersion along flow path
x = distance along flow path
v_x = groundwater seepage velocity in x direction
R = coefficient of retardation
λ = first-order decay rate constant

This is a parabolic partial differential equation. The decay rate may be used to simulate any process that is observed to be reducing solute concentrations in a manner that approximates first-order decay, such as biodegradation, radioactive decay, or hydrolysis). Under steady-state conditions, the change in contaminant concentration with respect to time becomes zero, leaving the elliptical partial differential equation:

$$0 = \frac{D_x}{R}\frac{\partial^2 C}{\partial x^2} - \frac{v_x}{R}\frac{\partial C}{\partial x} - \lambda C \qquad \text{eq. D.1.2}$$

D.1.1.2 Two-Dimensional Reactive Solute Transport

The two-dimensional partial differential equation describing transient solute transport with first-order biodegradation in the saturated zone is given by:

$$\frac{\partial C}{\partial t} = \frac{D_x}{R}\frac{\partial^2 C}{\partial x^2} + \frac{D_y}{R}\frac{\partial^2 C}{\partial y^2} - \frac{v_x}{R}\frac{\partial C}{\partial x} - \lambda C \qquad \text{eq. D.1.3}$$

Where: C = solute concentration
t = time
D_x = hydrodynamic dispersion along flow path
D_y = hydrodynamic dispersion transverse to flow path
x = distance along flow path
y = distance transverse to flow path
v_x = groundwater seepage velocity in x direction
R = coefficient of retardation
λ = first-order decay rate constant

This is a parabolic partial differential equation. Under steady-state conditions, the change in contaminant concentration with respect to time becomes zero, leaving the elliptical partial differential equation:

$$0 = \frac{D_x}{R}\frac{\partial^2 C}{\partial x^2} + \frac{D_y}{R}\frac{\partial^2 C}{\partial y^2} - \frac{v_x}{R}\frac{\partial C}{\partial x} - \lambda C \qquad \text{eq. D.1.4}$$

D.1.1.3 Three-Dimensional Reactive Solute Transport

The three-dimensional partial differential equation describing transient solute transport with first-order biodegradation in the saturated zone is given by:

$$\frac{\partial C}{\partial t} = \frac{D_x}{R}\frac{\partial^2 C}{\partial x^2} + \frac{D_y}{R}\frac{\partial^2 C}{\partial y^2} + \frac{D_z}{R}\frac{\partial^2 C}{\partial z^2} - \frac{v_x}{R}\frac{\partial C}{\partial x} - \lambda C \qquad \text{eq. D.1.5}$$

Where: C = solute concentration
t = time
D_x = hydrodynamic dispersion along flow path
D_y = hydrodynamic dispersion transverse to flow path
D_z = vertical hydrodynamic dispersion
x = distance along flow path
y = distance transverse to flow path
z = vertical distance transverse to flow path
v_x = groundwater seepage velocity in x direction
R = coefficient of retardation
λ = first-order decay rate constant

This is a parabolic partial differential equation. Under steady-state conditions, the change in contaminant concentration with respect to time becomes zero, leaving the elliptical partial differential equation:

$$0 = \frac{D_x}{R}\frac{\partial^2 C}{\partial x^2} + \frac{D_y}{R}\frac{\partial^2 C}{\partial y^2} + \frac{D_z}{R}\frac{\partial^2 C}{\partial z^2} - \frac{v_x}{R}\frac{\partial C}{\partial x} - \lambda C \qquad \text{eq. D.1.6}$$

D.1.2 ANALYTICAL VERSUS NUMERICAL MODELS AND MODEL SELECTION

Partial differential equations that describe groundwater flow and/or solute transport can be solved analytically or numerically. The type of model selected to simulate site conditions will depend on the results of data review and conceptual model development. Analytical methods (models) provide exact, closed-form solutions, and numerical methods (models) provide approximate solutions. Analytical models are the simplest to set up and solve, allowing the user to evaluate many scenarios in a relatively short time. Numerical methods are more efficient for those systems that are too complex for analytical methods. Analytical models are restricted in the nature of the problems for which they can be used, and for some transport problems they may become so complex and unwieldy that the use of numerical methods may be more efficient. As suggested, numerical methods can be used for more complex systems. Theoretically there are no limits on the characteristics of the hydrogeological system and the properties of the solute(s) that

can be simulated using a numerical model code. There are, however, practical limits on the ways in which the system and any reactions within it can be represented.

Groundwater flow and solute transport modeling is both an art and a science. The "art" involves the ability to select the most reasonable set of assumptions that will yield a model that is not too complex to be solved by available mathematical techniques, yet is sufficiently detailed to accurately represent the system being modeled. A balance between simplifying assumptions and actual subsurface conditions must be reached to allow successful simulation of groundwater flow and/or contaminant fate and transport. Such a balance will depend on the nature of the hydrogeologic system being simulated, the available data, and the intended use of the model results. As an example, a simple analytical model will, in many cases, provide the appropriate information with much less effort than would be required to produce a numerical model. Spitz and Moreno (1996) note that:

> *Whenever possible, the model user should give preference to analytical solutions over numerical modeling. A large number of groundwater problems can be greatly simplified and solved analytically without substantial loss of accuracy. There is no systematic approach for simplifying a given groundwater problem and for selecting the appropriate analytical solution. In fact, it depends entirely on the capability of the model user to visualize the investigated problem and to judge professionally if a chosen analytical method is consistent with the hydrogeological controls. If the deviation between reality and the conceptual model is recognized and its impact properly estimated, analytical solutions can be beneficial.*

In addition to arguing for the use of analytical models where appropriate, his passage also illustrates the balance that must be achieved between the "art" of selecting a solution method and adequately representing the system in a simple and straightforward manner and the science of evaluating and utilizing the site data to produce a model with results that are defensible and consistent with the available data.

Subsurface groundwater flow and/or contaminant transport models incorporate a number of theoretical assumptions about the natural processes governing the transport and fate of contaminants. All modeling involves simplifying assumptions concerning parameters of the physical and chemical system that is being simulated. These parameters will influence the type and complexity of the equations that are used in the model to represent the system mathematically. Relatively simple analytical models may be useful to define the possible magnitude of a contaminant problem. Analytical models provide exact solutions, but employ

simplifying assumptions to provide tractable solutions. If limited data are available, or the hydrogeologic conditions are simple, an analytical model can be selected to simulate contaminant fate and transport. If an analytical model is selected to perform the modeling, basic source, aquifer hydraulic, and chemical parameters are entered into the model. The basic parameters typically include groundwater seepage velocity, hydraulic conductivity, saturated thickness of the aquifer, porosity, source area configuration and contaminant concentrations, leakage rates, dispersion coefficients, retardation values, and decay rates.

Analytical solutions provide exact, closed-form solutions to the governing advection-dispersion equation by making significant simplifying assumptions. The more closely the actual system approximates these assumptions, the more accurate the analytical model will be in predicting solute fate and transport. Analytical solutions are continuous in time and space and provide information on the temporal and spatial distribution of hydraulic head or solute concentrations for the governing initial and boundary conditions. The main advantage of analytical solutions is that they are simple to use and they provide a good first approximation of solute transport in relatively simple hydrogeologic settings. Analytical solutions are generally limited to steady, uniform flow or radial flow, and should not be used for groundwater flow or solute transport problems in strongly anisotropic or heterogeneous media. In some cases, such as where potential receptors are a great distance away, or where the aquifer is extremely homogeneous and isotropic, an analytical solution may adequately describe contaminant fate and transport. At a minimum, analytical models are useful for conceptual model development and can aid in siting additional data collection points. The analytical solutions of the advective-dispersive equation presented herein give solute concentration as a function of time and distance from the source of contamination. Analytical solutions are sometimes used to verify the accuracy of numerical solutions. This is done by applying both the exact analytical solution and the numerical solution to the same groundwater flow system and comparing the results. Several well-documented and widely accepted analytical models are available for modeling the fate and transport of fuel hydrocarbons under the influences of advection, dispersion, sorption, and biodegradation. Several analytical solute transport models are described in Section D-3.

Analytical models are used to estimate the impacts of contamination on a site given the qualifying assumptions used to develop the model. Analytical models are best utilized for order-of-magnitude results because a number of potentially important processes are treated in the model in an approximate manner, or are ignored completely. For example, analytical models may include terms describing a variety of chemical and hydrological processes, but usually are not capable of incorporating subsurface heterogeneity. Because of the nature of the simplifying

assumptions, analytical models may overestimate or underestimate the spread of contamination. By making assumptions that will ensure the model will overpredict contaminant concentrations and travel distances (or at least not underpredict them), the model predictions will be conservative. The more conservative a model is, the more confidence there should be that potential receptors will not be impacted by site contamination. This will aid in implementation of remediation by natural attenuation.

Numerical solutions provide approximate solutions to the advection-dispersion equation. Numerical models are less burdened by simplifying assumptions and are capable of addressing more complicated problems. Unlike analytical models, numerical models allow subsurface heterogenieties and varying aquifer parameters to be simulated, as well as transient simulations (i.e., one or more properties or conditions change over time), if the requisite data are available. In numerical models, the continuous problem domain is replaced by a discretized domain. The resolution of the results provided by a model depends on the degree of discretization (in the model) of the groundwater system under investigation. Many of the assumptions required for the analytical solutions are not necessary when numerical techniques are used to solve the governing solute transport equation. However, a greater amount of site-specific data is needed to implement a numerical model, and the solutions are inexact numerical approximations. Numerical models require input parameters similar to those used for analytical models, but their spatial distribution must be known to make the use of a numerical model warranted. Several well-documented and widely accepted numerical model codes are available for modeling the fate and transport of CAHs and fuel hydrocarbons dissolved in groundwater under the influences of advection, dispersion, sorption, and biodegradation. Specific numerical fate and transport models are described in Section D-4.

Numerical models require a reasonably good understanding of the three-dimensional distribution of both aquifer hydraulic properties and the contaminants. Implementation of a numerical model is much more complex than implementation of an analytical model, and generally requires an experienced hydrogeologist who is familiar with the model code. Most numerical groundwater-flow and transport model codes fall into one of the following four model types:

- finite difference;
- finite element;
- random walk; and
- method of characteristics (MOC).

These differing methods have been developed to address the multitude of problems presented by the number of physical and chemical processes that can affect groundwater flow and dissolved contaminant transport. Excellent descriptions of these methods may be found in the texts by Anderson and Woessner (1992) and Spitz and Moreno (1996).

Figure D.1.1 shows a decision process that can be used to determine if an analytical or a numerical model is most appropriate to simulate site conditions. The specific modeling objectives of the project, the available data, and the conceptual model should be the primary factors governing model selection. In addition, the user should avoid making the problem more complex than necessary. Spitz and Moreno (1996) note that:

> *Solutions to groundwater problems do not necessarily require the most sophisticated model. In each case the most appropriate model is the one that addresses the investigated problem with as little effort as necessary to represent the real system. The model should be simple enough to facilitate model efforts but not too simple so as to exclude features dominant to the investigated groundwater problem.*

Success in solute fate and transport modeling depends upon the ability to properly conceptualize the processes governing contaminant transport, to select a model that simulates the most important processes at a site, and to achieve reasonable model predictions. Keep in mind that any numerical model code or analytical solution selected for a demonstration of remediation by natural attenuation should be properly validated through sufficient previous application at a variety of field sites.

There is one final caveat that should be considered before deciding what type of model to use, as well as at all times during the modeling process. This concern has been articulated quite well by Spitz and Moreno (1996), who state that:

> *Transport models for advection and dispersion are at a mature stage of development and are applied with success to two- and three-dimensional transport problems. Transport modeling of chemically reacting contaminants, however, achieves only fair success if adsorption is linear. Besides large demands on computing power, uncertainties in describing complex reactions and difficulties in obtaining reliable field data limit modeling success. Transport predictions are more sensitive to a lack of field data than flow prognoses. Although the final objective of a model analysis is predictive, transport predictions in an absolute sense are impossible to achieve, even with the best models.*

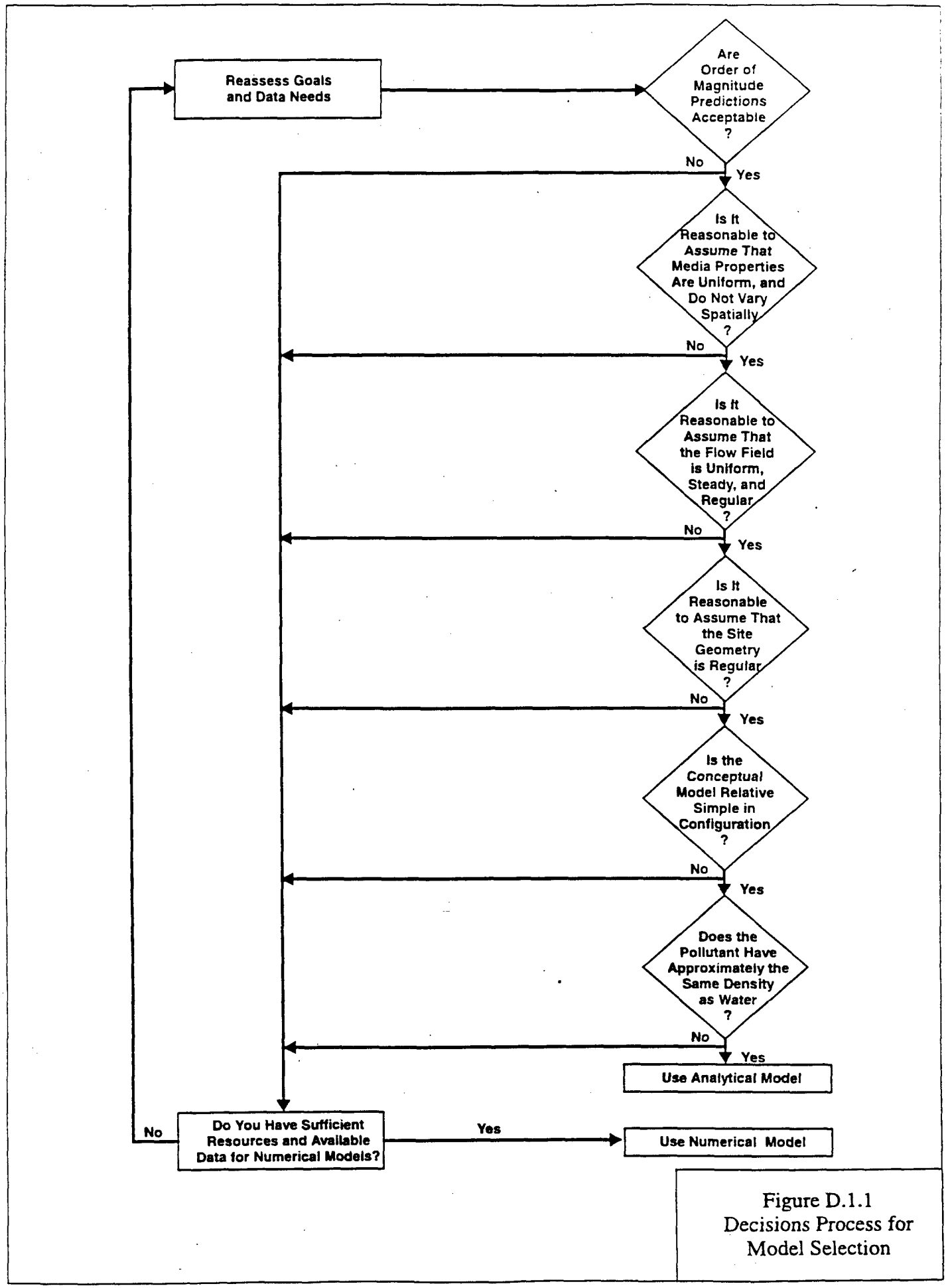

Figure D.1.1
Decisions Process for
Model Selection

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This is not to say that models are not useful or meaningful. Models are a powerful tool; however, as this passage implies, they do not provide definitive answers. With a good sense of the limitations imposed by the simplifying assumptions inherent in the models and the available data, the modeler and/or the model user should be able to apply the model and/or its results (as a tool) to reach reasonable conclusions and apply those conclusions appropriately. Failure to understand and work within the limitations of a particular model and data set will lead to erroneous conclusions that will hinder the application of remediation by natural attenuation.

The final decision to use an analytical or numerical solute transport model should be based on the complexity of the problem, the amount of available data, and the importance of the decisions that will be based upon the model. As an example, consider a site located 5 miles from the nearest potential receptor. The database for this site consists of five sampling points with one round of sampling data from each point. The aquifer system at the site consists of 50 feet of unconsolidated, well-sorted, medium-grained sand overlying a horizontal shale unit. The shallow water table is 5 feet below the surface. Such a site is an excellent candidate for an analytical model. Consider on the other hand, a site located approximately 1,000 feet from the nearest potential receptor. The database for this site consists of 40 data points for which there are 5 years of quarterly groundwater quality sample analyses. The aquifer at this site consists of 10 feet of poorly sorted, silty sand, underlain by 5 feet of well-sorted, medium-grained sand, underlain by 20 feet of silt. The quarterly groundwater quality data indicate that a dissolved contaminant plume is migrating downgradient from the source area. In this situation, a numerical model would be the most appropriate tool to predict the fate and transport of the dissolved contaminant plume.

D.1.3 IS A MODEL REALLY NECESSARY?

One of the first questions to ask before proceeding with implementation of a solute transport model is: "Is a model really necessary?" The answer to this question will depend on several factors, including the rate of plume migration and expansion and the locations of potential receptors. For example, if there are abundant historical data available for the site, and these data show that the dissolved contaminant plume has reached a steady-state configuration or is receding, then a solute transport model probably is not necessary to determine if potential receptors will be impacted. However, a model of this site would allow an investigator to estimate how long it will take for the plume to entirely degrade. If on the other hand, the plume is close to a potential receptor and there are no historical data available, then a solute transport model in conjunction with the appropriate data can be useful in predicting solute fate and transport, including clean up times and potential migration distance.

Two questions will invariably arise during a demonstration of remediation by natural attenuation. These questions are: 1) will potential receptors be impacted by the contaminant plume?, and 2) how long will the contaminant plume persist? If the proponent of natural attenuation is unable to provide plausible and defensible answers to these questions, it is unlikely that intrinsic remediation will be accepted by regulators. When properly used with an adequate database of appropriate data, solute transport models can help provide answers to these questions.

SECTION D-2

MODEL DEVELOPMENT AND IMPLEMENTATION

An overview of the steps that must be taken to successfully implement a groundwater flow and solute transport model is presented in this section. The majority of the material presented herein is applicable to both analytical and numerical solute transport models. A distinction is made when the material is relevant to one type of model. For further explanation and discussion of the theory and practice of modeling, the texts by Bear (1972 and 1979), Strack (1989), and Segol (1994) are recommended for the topic of analytical models, while the texts by Anderson and Woessner (1992) and Spitz and Moreno (1996) are recommended for the topic of numerical modeling.

D.2.1 DATA COLLECTION

Collection of data is a very important step in a model study, and the time needed to complete such a study is strongly dependent on the time needed to collect, analyze, and prepare model input data. Field data are necessary to produce model input, as well as to specify the problem to be addressed and to delineate the system to be simulated. Without adequate data, the quality and utility of the model results will be doubtful. Among the data required to complete a groundwater model (analytical or numerical), are the following:

- Hydraulic conductivity for all hydrogeologic units of concern;
- Initial hydraulic head distribution;
- Flow direction(s) and gradient(s);
- Effective porosity for all hydrogeologic units of concern;
- Coefficient(s) of hydrodynamic dispersion;
- Coefficient(s) of retardation;
- Initial solute concentrations;
- Contaminant source concentration configuration, and rate of source decay (or removal);
- Distribution and continuity of aquifer and aquitards (thickness, continuity, areal extent, interconnections, etc.);
- Groundwater recharge and discharge (precipitation infiltration, evapotranspiration,

pumpage from wells, discharges to surface water, etc.);

- Definition of physical and chemical boundary conditions; and
- Rates of chemical reactions, particularly biodegradation.

This is by no means an exhaustive list; some of the data are necessary for any model, some are useful only for certain types of model, and some data not listed above may be needed for specific model applications or codes. Also, some of the data listed above may need to be manipulated before use in a model. Ideally, collection and evaluation of data should be a dynamic process that takes place in conjunction with the formulation and calibration of the model. This would allow the investigator to determine what additional data could be collected to improve the model. Unfortunately, this is not always possible in practice.

Collection of field data for a model to evaluate natural attenuation is discussed in Appendix A, and premodeling calculations are discussed in Appendix C. As discussed in Appendix C, data that cannot be derived from field measurements can be taken from the literature, with appropriate caveats.

D.2.2 CONCEPTUAL MODEL

The first step specifically related to the actual process of modeling is development of the conceptual model. A conceptual model is simply an idealization of the groundwater flow and contaminant transport system based on the available geological, hydrological, climatological, contaminant, and geochemical data for the site. The purpose of the conceptual model is the integration of available data into a coherent representation of the system to be modeled. The conceptual model presents the current understanding of site conditions and the hydrogeologic system. After development, the conceptual model is used to aid in model selection and to develop the appropriate analytical or numerical solute transport model. When possible, the preliminary conceptual model should be developed before arriving in the field to collect additional data so that data collection points can be optimized. After collection of site-specific data during the iterative site-characterization phase of the natural attenuation demonstration, the preliminary conceptual model should be refined.

Successful conceptual model development involves:

- Definition of the problem to be solved;
- Designing the conceptual model;
- Determination of additional data requirements; and
- Integration of available data including:

- Local geologic and topographic maps
- Hydraulic data
- Site stratigraphy
- Contaminant concentration and distribution data (isopleth maps).

Most of the conceptual model development process will be completed when all of the maps, sections, and calculations discussed in section C-2 have been completed. The only requirement will then be to integrate these data into a coherent representation of the site and, if necessary, to determine what additional data needs to be collected to allow adequate representation of site conditions.

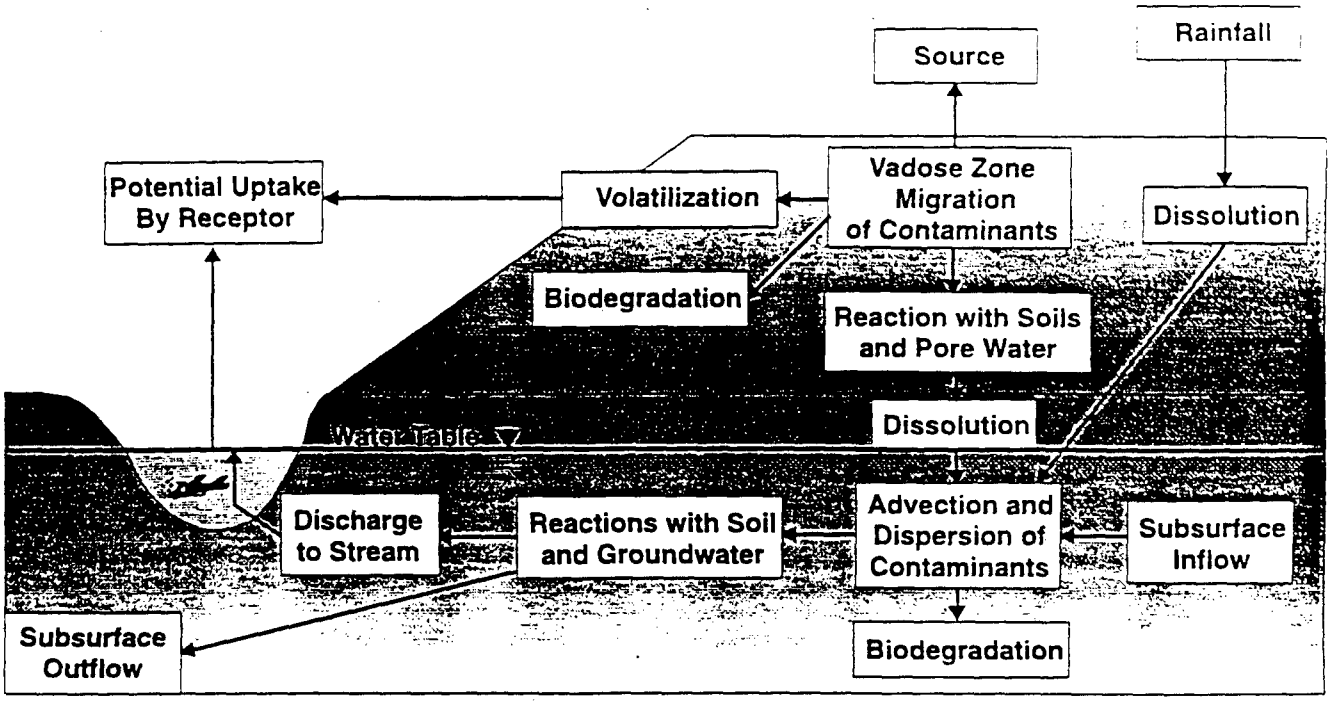
A conceptual model may be expressed in many ways, with different approaches suited for different groundwater systems and model objectives. In addition to a verbal description or a table listing model features, graphical methods are useful for describing a conceptual model. Suitable graphical methods include:

- a flow chart indicating interactions between elements of the problem;
- a hydrogeological cross-section labeled with key processes; and
- a three-dimensional diagram summarizing site conditions.

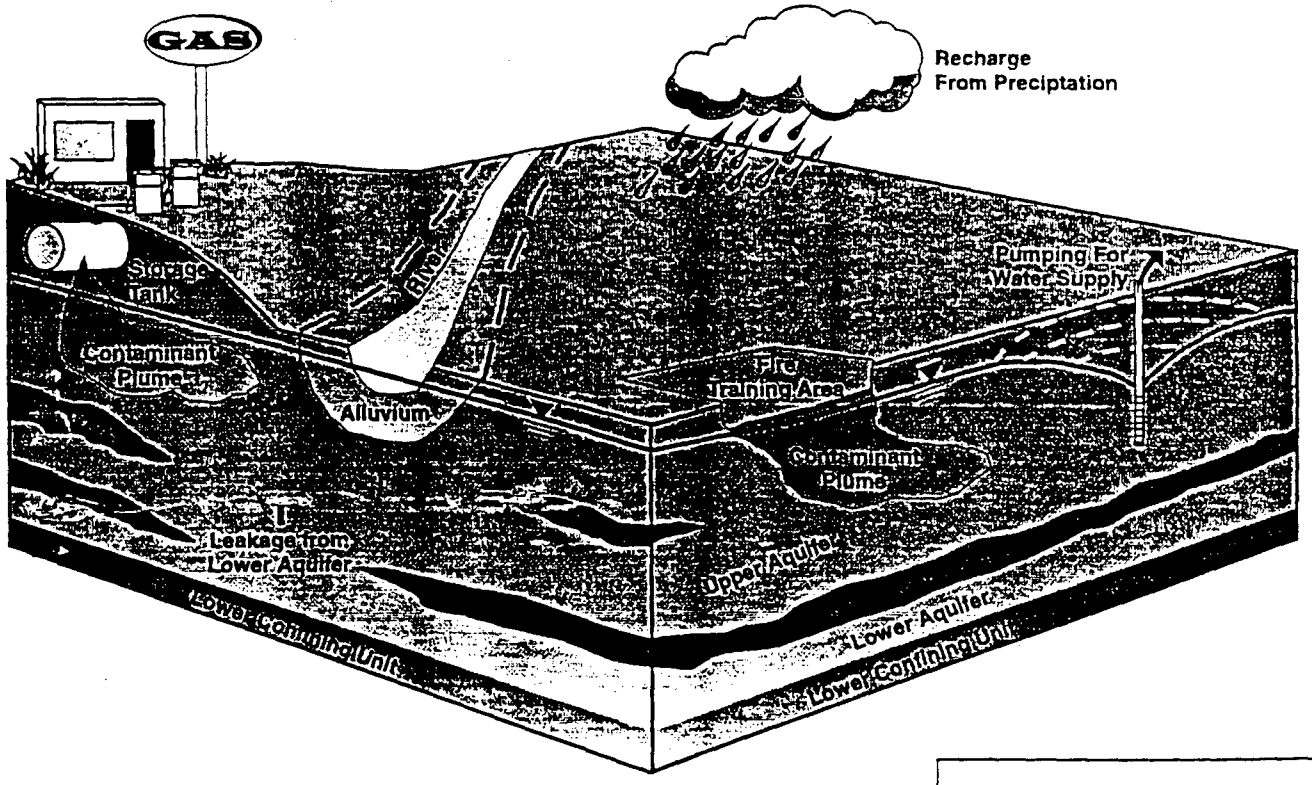
Figure D.2.1 shows two examples of graphical methods with which a conceptual model can be described. For verbal or graphical methods, the description of the conceptual model may be simple or complex, depending upon the type of model and the available data. Of course, any other method that suitably expresses the conceptual model would also be appropriate. The imagination of the modeler and the demands of the specific modeling task are the only limits on this process.

D.2.3 SELECTION OF ANALYTICAL SOLUTION OR NUMERICAL CODE

Selection of the analytical solution or model code is a step in which the modeler looks at the conceptual model and the available data and uses his/her professional judgment to select the most appropriate code. This process is not always a rational one; non-scientific considerations may weigh significantly on the ultimate decision. Some of the general considerations for deciding between analytical or numerical methods are presented in Section D.1.2, but there are other criteria to consider once one has collected data and formulated a conceptual model.



PROCESSES IN CROSS-SECTION



THREE-DIMENSIONAL SCHEMATIC

Figure D.2.1
Graphic Presentation
of Conceptual Models

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Spitz and Moreno (1996) outline three types of criteria that the modeler can use in selecting a model code or analytical solution. First, the user should consider the model objectives (i.e., what is the ultimate purpose of the modeling effort?). If only general or very approximate results are needed, the user might select an analytical method or a very simple numerical code. The more specific and detailed the results must be, the more likely it is that the selected method will require a sophisticated numerical model code. Second, the user should use technical criteria. In this case, the user determines if the chosen model(s) is capable of adequately representing the dominant flow and transport processes at the site. Finally, if a model meets the objectives and technical criteria, implementation criteria can be used to further narrow the choice. These criteria include considerations such as how well-documented and reviewed the model is, the degree to which the solutions have been verified and applied to similar sites, available technical support, computer hardware requirements, and if the model has a good track record of acceptability to reviewing or regulatory agencies.

These criteria can be summarized into three key questions:

- Can the model adequately simulate site conditions?
- Can the model satisfy the objectives of the study?
- Is the model verified and peer-reviewed, well documented, and reasonably well field-tested?

The most appropriate choice is often a compromise between the first two considerations, particularly because study objectives typically include time limits and financial constraints. This is one of the points where a modeler's experience and judgment may play an important role.

D.2.4 MODEL SETUP

The combined steps of model setup and model calibration make up over half of the total work in a modeling effort. Model setup includes selecting the model domain, discretizing the data in space and time, and assembling the discretized data in a form suitable for input to the numerical code or analytical solution. Choice of the domain and discretization will affect the resolution of the model and will also directly affect the cost of the modeling effort.

In general, analytical model setup can be accomplished much more quickly than for numerical models. Analytical modeling can be performed using commonly available spreadsheets, mathematical analysis programs such as MathCAD®, or codes written expressly for analytical modeling (e.g., BIOSCREEN, AT123D, SOLUTE, or PRINCE®). Because analytical solutions

are algebraic expressions, input into these models is very straightforward and usually consists of entering the parameter values in appropriate locations. Note that for computer codes, input and/or results may be entered or presented in a discretized manner because the code solves the equations at a given number of points. Because of the simplicity of analytical model input, most of the remaining discussion of model setup will be directed towards numerical modeling. Where appropriate, analytical model setup will also be discussed.

D.2.4.1 Model Domain

Selection of the model domain will not only determine what portion of the system of interest will be modeled, but can also affect the amount of computational effort required. Clearly, the model domain should cover the entire area within which the contaminant plume may travel and, if necessary, the domain should also include any receptors of concern. If necessary, velocity calculations or analytical models could be used to estimate potential travel distances. Domain boundaries will ideally coincide with natural groundwater boundaries such as rivers, lakes, groundwater divides, or aquifer boundaries. These boundaries should be distant from the area of concern (i.e., the part of the model in which transport will be modeled) to prevent boundary effects from affecting the solution. Where possible, the domain should be oriented so that the primary transport direction will be parallel to a model axis. This will reduce the potential effects of numerical dispersion. Finally, the domain should be an area for which adequate data is available, and the domain size should be selected to minimize the computational effort required to perform the simulation. Of course, compromise among these considerations will often be required and may result in less-than-ideal configurations in some respects.

For analytical models, choosing a domain size is often less important. Many models assume an infinite or semi-infinite aquifer, and will solve for the appropriate unknowns at specified points. However, for some software packages, the user does have to specify a domain in which the solutions are calculated at a fixed number of points. In this case, the user should again consider the potential travel distance ~~of~~the plume over the time period of interest and specify the domain accordingly. Location of the points where a solution is desired will depend on where solute concentration information is desired.

D.2.4.2 Discretization

In a numerical model, both time and space are divided into discretized elements for which solutions to the groundwater flow and solute transport equations are approximated. Spatial

discretization is accomplished by replacing the continuous hydrogeologic domain with a discretized domain consisting of an array of nodes and associated blocks or elements (a model grid). Temporal discretization involves defining time periods for which model calculations are made. In the case of a steady-state model, time is not discretized. However, because transport solutions nearly always involve a time element, groundwater flow models are typically the only part of a model that may be steady-state. Selection of the time steps and model grid spacing are important steps in model design because both of these factors will strongly influence the numerical results. Ideally, the modeler will be able to use small grid spacing and time steps so that the numerical approximation better represents the partial differential equation (Anderson and Woessner, 1992). Spitz and Moreno (1996) suggest that to produce the optimal discretization the modeler should try to:

- enhance the model solution stability and convergence;
- increase the model resolution;
- minimize numerical dispersion; and
- minimize computational requirements for memory, storage, and run-time.

How each of these goals is met will depend on the available data, the limitations of the model code, and the computer hardware available to the modeler. Compromise between these goals and the available resources (time, hardware, software, and personnel) will often dictate the resulting model discretization. Some general guidelines will be presented herein, but for more through discussions of these topics, modeling texts such as those by Anderson and Woessner (1992) or Spitz and Moreno (1996).

D.2.4.2.1 Model Grid Orientation and Spacing

Spatial discretization of a model domain is controlled by the grid orientation and spacing (cell size). Grid orientation is often controlled by large-scale hydrologic, geologic, or hydrogeologic features and will therefore not necessarily coincide with primary compass directions or property boundaries. The optimum orientation, as noted in the discussion of the model domain, will have the primary directions of flow and/or transport parallel to the grid axes. This may follow naturally when the grid is aligned parallel to natural features of the system. In the case of finite-element models, orientation will be accommodated by the spacing of the nodes and the shape of the elements because there is more flexibility in the grid shape and orientation. Where the system is known to be anisotropic, the primary directions of the hydraulic conductivity tensor will control the grid orientation.

Numerous factors must be considered when selecting the size of grid cells to be used. There is a trade-off between grid spacing, grid alignment, model accuracy, and being able to model the entire area potentially affected by the contaminant plume. As in differential calculus, the smaller the grid spacing, the more accurate the numerical model will be, and the numerical solution will approach the exact solution as the grid spacing approaches zero. Additionally, more grid nodes increases the demands placed on the computer and longer calculation times will result. Because large numerical errors may arise if the solute being modeled comes in contact with a model boundary, the model grid should be designed so that it is large enough that the solute plume will not intersect a model boundary. Otherwise, the solution routine used in the code should be able to handle such occurrences without producing an unstable solution.

Cell size can also affect the model by introducing numerical dispersion that is dependent on the relationship between the grid spacing and the contaminant velocity. Several considerations for grid spacing that will minimize numerical dispersion are discussed by Spitz and Moreno (1996), and a few of these are discussed here. For example, the cell size divided by the dispersivity (known as the Peclet number) should be no larger than 2, but this criterion is often relaxed where lower predictive accuracy is acceptable or where other constraints prevent optimization of this factor. In addition, to minimize problems with convergence of the numerical solution, the cell aspect ratios (i.e., the ratio of the x-dimension to the y-dimension of the cells) should be between 1:10 and 10:1. Finally, another rule-of-thumb is that the smoothness of the discretization (i.e., the difference in size of adjacent cells) should be such that the dimensions of cells are neither less than half nor twice as great as those of the adjacent cells. This will also minimize convergence problems.

D.2.4.2.2 Time Discretization

In numerical models, two types of time intervals that are used for arriving at solutions: time steps and stress periods. Time steps are required for transient calculations, and are the discrete time periods in which calculations are made. Their function is roughly analogous to that of the model grid, in that they allow the model to represent a continuous time domain by producing solutions for multiple discrete points. In general, the shorter the time step, the more closely the model will approximate the analytical solution. Time steps that are too small will require excessive computation time and memory, while time steps that are too large may introduce numerical dispersion or cause instability. In order to minimize numerical dispersion and maximize numerical stability, the modeler should strive for a Courant number (the product of the advective velocity and the time step, divided by the smallest cell dimension) that is less than 1. Essentially,

this implies that transport of a particle across a cell should take place over more than one time step.

Stress periods are intervals in which boundary conditions and stresses are constant and between which the boundary conditions and stresses change. Stress periods do not affect the model calculations, so they only need to represent actual time periods within which all boundary conditions and stresses are constant. However, stress periods can affect the selection of time steps. To avoid numerical dispersion, improve model stability, and allow more rapid solution convergence, time steps during changes in boundary conditions or stresses (i.e., at the beginning of stress periods) should be shorter.

D.2.4.3 Initial Conditions

Initial conditions are used to describe conditions such as the distribution of heads and concentrations at the instant a numerical simulation begins. Initial conditions must be specified for transient groundwater flow and solute transport problems. It is not necessary to define initial conditions for steady-state models, but doing so can save computational time. Initial conditions for a transient run are best derived from the results of a steady-state flow simulation or a transient transport simulation (imposed on either a transient of steady-state flow simulation) (Anderson and Woessner, 1992; Spitz and Moreno, 1996). Doing so will provide a mass-balanced starting point that will also be consistent with the model hydrologic inputs and parameters. For transport modeling, Spitz and Moreno (1996) warn that:

> *Specification of an observed concentration distribution (e.g., and interpreted plume based on observed concentrations) as initial conditions for a transient transport simulation often leads to erroneous predictions because a field program rarely measures the highest concentrations and differing interpolations would lead to widely varying predictions. Therefore it is better to use estimated source terms as a starting point for the transport model, even if the source is not well defined. These sources can be used to calibrate the transport model, and to predict the starting conditions for subsequent model runs.*

The following sections briefly describe the mathematical representation of initial conditions. Again, for more thorough descriptions and discussions, the texts by Anderson and Woessner (1992) and Spitz and Moreno (1996) are recommended.

D.2.4.3.1 Groundwater Flow

For groundwater flow models, initial conditions are used to specify the values of the variable under consideration (usually hydraulic head) at the instant the model simulation begins (i.e., at t = 0) and generally have the form:

$$h(x,y,z,0) = f(x,y,z) \qquad \text{eq. D.2.1}$$

Where f(x,y,z) is a function that describes the variation in hydraulic head, h, in the x, y, and z directions at time t = 0.

D.2.4.3.2 Solute Transport

Initial conditions for solute transport models are used to specify the solute concentration, C, in the system at the instant the model simulation begins (i.e., at t = 0) and have the form:

$$C(x,y,z,0) = f(x,y,z) \qquad \text{eq. D.2.2}$$

Where f(x,y,z) is a function that describes the variation in contaminant concentration in the x, y, and z directions at time t=0. Initial conditions for solute transport generally have the form:

$$C(x,y,z,0) = 0 \qquad \text{eq. D.2.3}$$

or

$$C(x,y,z,0) = C_i \qquad \text{eq. D.2.4}$$

Where: C = contaminant concentration
C_i = initial contaminant concentration
x = distance downgradient of the source
y = distance transverse to the source in the horizontal direction
z = distance transverse to the source in the vertical direction

Equation D.2.3 is used as the initial condition for systems devoid of contamination prior to the introduction of the contaminant or prior to the model simulation. Equation D.2.4 is used as the initial condition for systems that have dissolved contamination prior to the introduction of additional contamination or prior to the model simulation. As noted before, this distribution is best derived from a simulation (where possible). For analytical transport modeling, equation D.2.3 is the only initial condition that can be used. Analytical models are not truly transient, but they are able to provide solute concentrations at a given location and time.

D.2.4.4 Boundary Conditions

In defining the model area, the modeler must separate the area of interest from the surrounding system. Boundary conditions describe the interaction between the system being modeled and its surroundings or, for transport models, the loading of contaminant mass into the system. Proper design of model boundary conditions is therefore of great importance in numerical model implementation. Boundary conditions are used to include the effects of the system outside the area being modeled with the system being modeled, while at the same time allowing the isolation of the desired model domain from the larger system. In effect, the boundaries of the model tell the area immediately inside the boundaries what to expect from the outside world. The solution of any differential equation requires specification of the conditions at the periphery of the system. Model boundaries are thus mathematical statements that specify the dependent variable (head or contaminant concentration) or the flux (derivative of the head or contaminant concentration with respect to time) at the model grid boundaries.

Three types of boundary conditions generally are utilized to describe groundwater flow and solute transport. Boundary conditions are referred to as the first type (Dirichlet), the second type (Neumann), and the third type (Cauchy). Table D.2.1 summarizes boundary conditions for groundwater flow and solute transport.

Table D.2.1
Common Designations for Several Important Boundary Conditions
(Modified From Franke *et al.*, 1987)

Boundary Condition	Boundary Type	Formal Name	General Mathematical Description	
			Groundwater Flow	Contaminant Transport
Specified-Head or Specified-Concentration	Type One	Dirichlet	$H = f(x,y,z,t)$	$C = f(x,y,z,t)$
Specified-Flux	Type Two	Neumann	$\frac{\partial H}{\partial n} = f(x,y,z,t)$	$\frac{\partial C}{\partial n} = f(x,y,z,t)$
Head-Dependent or Concentration-Dependent Flux	Type Three (mixed-boundary condition)	Cauchy	$\frac{\partial H}{\partial n} + cH = f(x,y,z,t)$	$\frac{\partial C}{\partial n} + cC = f(x,y,z,t)$

In flow models, boundary conditions are ideally used to specify actual hydrogeologic boundaries to the system, such as streams, lakes, confining units, groundwater divides, or any geologic feature that may bound a system. Also, the boundaries may also be defined as areas

where properties (e.g., flux) are known and can be defined. Figure D.2.2 illustrates different types of boundary conditions for flow models. When using a numerical flow model, hydrologic boundaries such as constant-head features (e.g., lakes, etc.) or constant-flux features should, when possible, coincide with the perimeter of the model. In areas that lack obvious hydrologic boundaries, constant-head or constant-flux boundaries can be specified at the numerical model perimeter as long as the perimeter is far enough removed from the contaminant plume that transport calculations will not be affected.

In transport models, boundary conditions are used to specify contaminant sources such as NAPL bodies, dissolved mass entering through recharge, injection wells, surface water bodies, and leaking structures. Figure D.2.3 illustrates transport boundary conditions. Definition and quantification of such sources and representation of them in the model is an important part of the modeling process. Leaky structures, injection wells, and dissolved mass in recharge are often represented as specified-flux boundaries using the associated concentrations. Sources such as NAPL bodies may be represented as specified-concentration boundaries (limited by solubility constraints or observed maximum concentrations) or as specified-flux boundaries (for which the chemical dissolution rate must be known or estimated). However, in most cases, only the effects of the source are measured, not the source characteristics. The source must therefore be represented as a "black box" that produces appropriate concentrations or fluxes at selected points in the model. The source may be misrepresented under such a scenario, but there is often little choice in the matter.

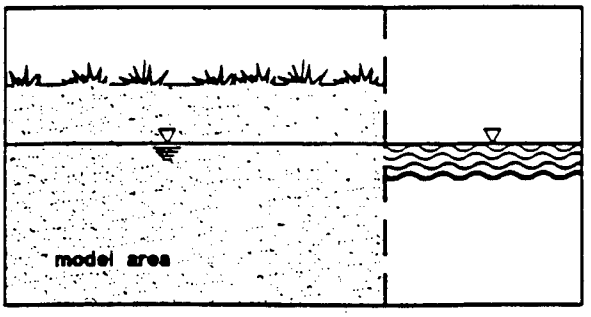
For coupled numerical flow and transport models, it is generally a good idea to make the modeled area large enough so that boundaries of the flow model can be placed far enough away from the plume that they will have minimal impact on the transport solution. This may not be possible in all cases, such as where the plume is near a surface water body. In some cases, it may be necessary to calibrate the model using different boundary conditions until a good match to observed conditions is achieved. In this case, sensitivity analyses should be performed to analyze the effects of various combinations of boundary conditions.

For analytical transport problems, one of the three types of transport boundary conditions will always be applied as a contaminant source. The solutions used in the analytical models are typically calculated using the assumption that the remaining boundaries are an infinite distance away from the source so that they do not affect the calculation of solute concentrations.

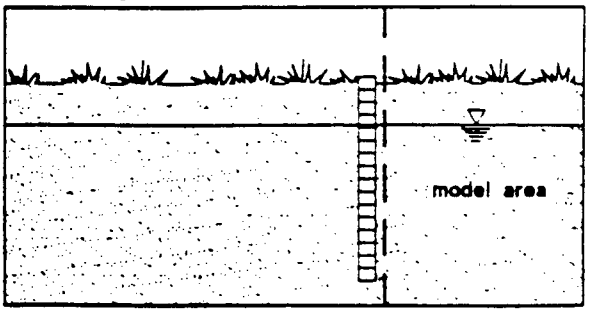
The following sections provide mathematical descriptions of boundary conditions used in flow and solute transport modeling. For more rigorous discussions and explanations of model

SPECIFIED HEAD OR FIRST TYPE OR DIRICHLET'S CONDITION

Surface water body interacting freely with aquifer

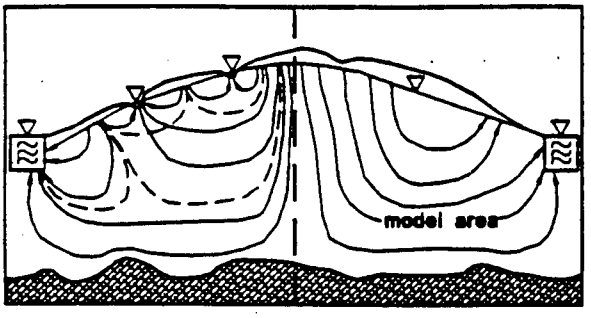


Measured groundwater head

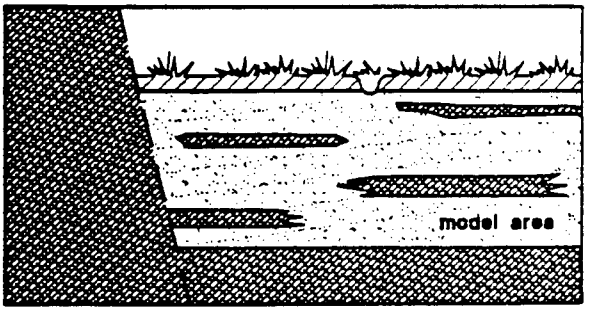


SPECIFIED FLUX OR SECOND TYPE OR NEUMANN'S CONDITION

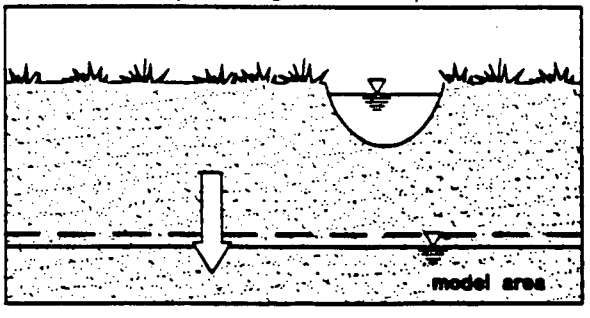
Groundwater divide or streamlines imposing no-flux conditions



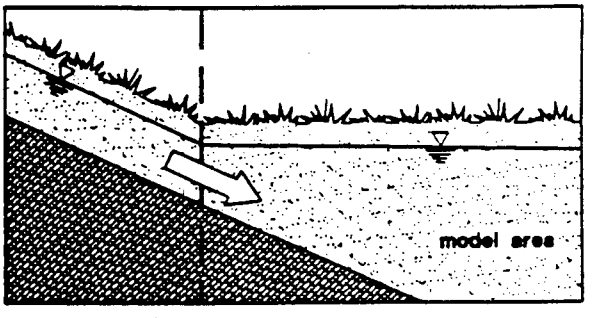
Fault imposing no-flux or fixed flux conditions



Free surface - positioning unknown a priori

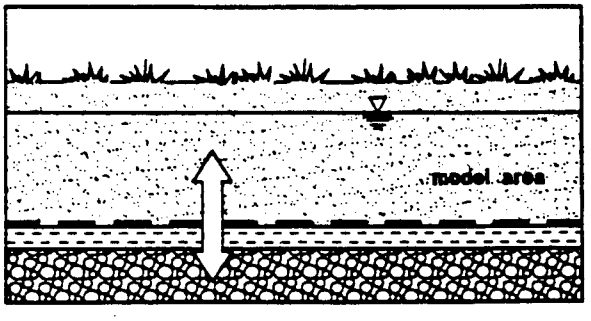


Subsurface inflow or outflow

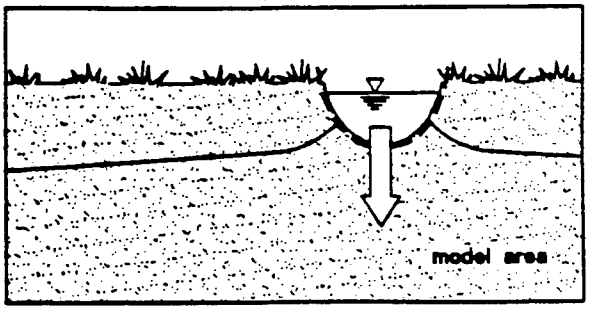


HEAD-DEPENDENT FLUX OR THIRD TYPE OR CAUCHY'S CONDITION

Aquitard separating adjacent groundwater systems



Surface water with semipermeable bed



— — — Model boundary

Source: Spitz and Moreno, 1996

Figure D.2.2
Examples of
Flow Model Boundary
Conditions

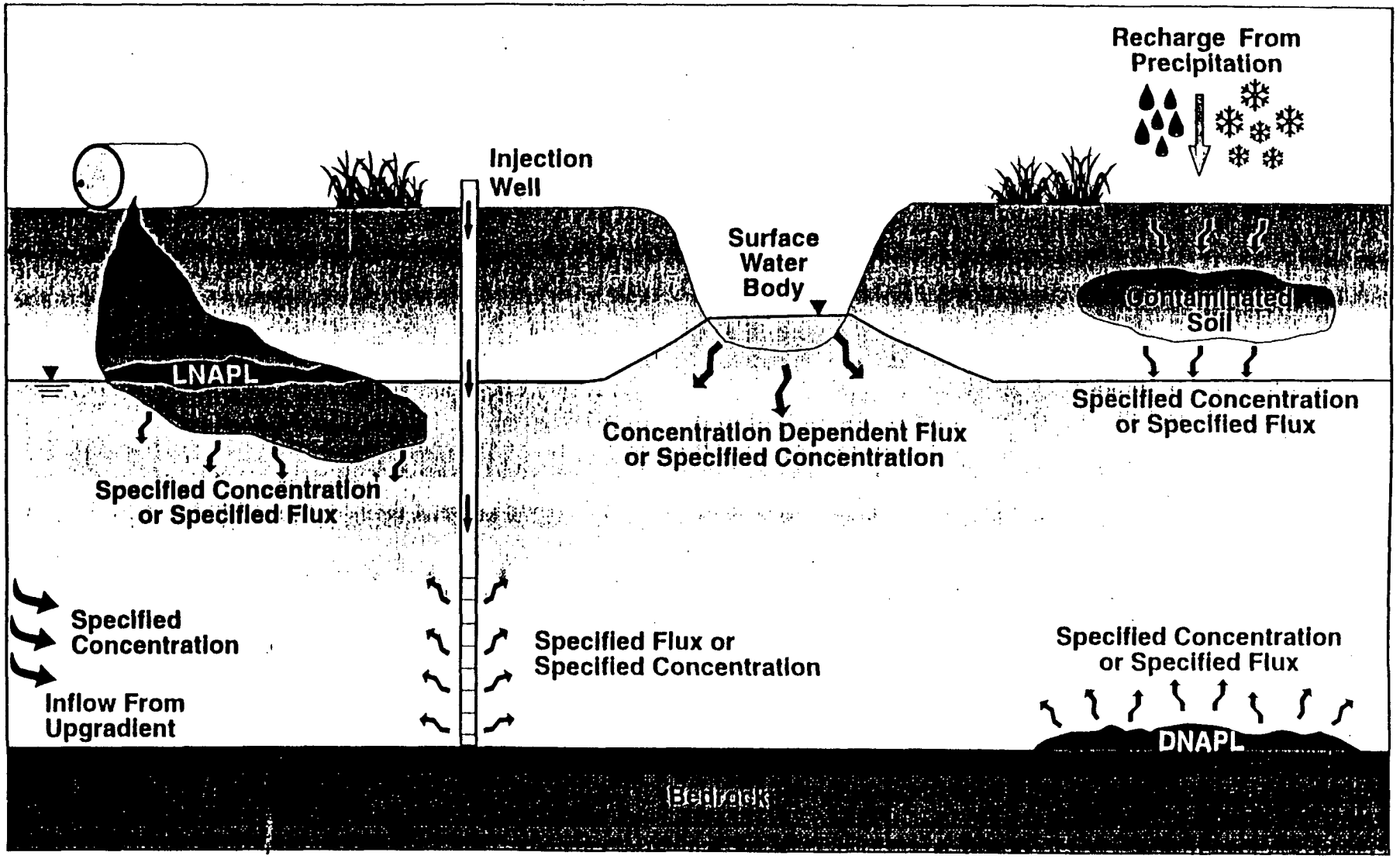


Figure D.2.3
Examples of Transport
Boundary Conditions

boundary conditions, refer to Bear (1972 and 1979), Strack (1989), and Segol (1994) are for the topic of analytical models, and Anderson and Woessner (1992) and Spitz and Moreno (1996) for numerical models.

D.2.4.4.1 First-Type Boundary Condition (Dirichlet, Specified-Head or -Concentration)

This type of boundary condition is referred to as the first-type boundary condition or the Dirichlet boundary condition. With this type of boundary condition, values of head (groundwater flow) or concentration (solute transport) are specified along the boundary. Type one boundary conditions are used to describe the boundary if the hydraulic head or solute concentration at the boundary is independent of flow conditions in the model domain. The constant-head or constant-concentration boundary is a special type of specified-head boundary wherein the head or solute concentration is fixed at the boundary.

D.2.4.4.1.1 Groundwater Flow (Specified-Head Boundary)

Specified-head boundaries (Dirichlet condition) are boundaries for which the hydraulic head is specified as a function of location and time. Specified-head boundaries are expressed mathematically as:

$$H = f(x,y,z,t) \qquad \text{eq. D.2.5}$$

Where: H = total hydraulic head
x = distance downgradient of the source
y = distance transverse to the source in the horizontal direction
z = distance transverse to the source in the vertical direction
t = time

Hydraulic head in surface water bodies is commonly a function of location and time. The type one boundary condition may be used to model the interaction between surface water bodies and groundwater, assuming the surface water body freely interacts with the aquifer. As an example, consider an aquifer that is bounded by a large stream whose stage is independent of groundwater seepage. Moving upstream or downstream along the boundary, the hydraulic head changes in relation to the slope of the stream channel, and decreases downstream. If the surface elevation of the stream is fairly constant in time, the head can be specified as a function of position alone, $H = f(x,y,z)$ at all points along the streambed. If the stream stage varies with time, the head is specified as a function of position and time, and $H = f(x,y,z,t)$ at all points along the streambed. In both examples, heads along the stream are determined by circumstances external to the

groundwater flow system and maintain these specified values throughout the problem solution, regardless of the stresses to which the groundwater system is subjected (Franke *et al.*, 1987).

Another way the specified head boundary condition is used is for those cases where a model boundary, for whatever reason, does not coincide with a physical boundary. For example, one or more of the nearest physical hydrogeologic boundaries for the modeled system may be far away from the area of interest, and incorporating them would make the model domain larger than feasible. In this case, the modeler may then specify heads at one or more of the model boundaries on the basis of measured or projected head data. When doing this, the modeler should take care to ensure that these boundaries are far enough away from the area of interest that the do not affect the model calculations in that area.

A constant-head boundary is a special type of specified-head boundary that occurs where a part of the boundary of the aquifer system coincides with a surface that has a total hydraulic head that is constant in both time and space. An example of a constant-head boundary would be a large lake where water levels do not fluctuate significantly through time. The hydraulic head is fixed (constant) for all points of this boundary, i.e.,

$$H = constant \qquad \text{eq. D.2 6}$$

Both specified-head and constant-head boundaries have an important "physical" characteristic in models of groundwater systems because in order to maintain the prescribed head, they provide an inexhaustible source of water. No matter how much water is removed from the system, the specified-head boundaries will continue to supply the amount of water necessary to maintain the head specified at the boundary, even if that amount is not reasonable in the real system (Franke *et al.*, 1987). Careful consideration should be given to this fact when a specified-head boundary is selected. It is generally considered acceptable to use this type of boundary as long as the boundary is located far enough from a pumping well that it will be unaffected or only minimally affected by pumping.

D.2.4.4.1.2 Solute Transport (Specified-Concentration)

Specified-concentration boundaries (Dirichlet condition) are boundaries for which the contaminant concentration is specified as a function of location and time. Specified-concentration boundaries are expressed mathematically as:

$$C = C_o(x,y,z,t) \qquad \text{eq. D.2.7}$$

Where: C = contaminant concentration
C_o = initial contaminant concentration
x = x coordinate of boundary
y = y coordinate of boundary
z = z coordinate of boundary
t = time

A constant-concentration boundary is a special type of specified-concentration boundary that occurs where a part of the boundary surface of the aquifer system coincides with a surface that has a contaminant concentration that is constant in both time and space. At the upgradient end of the system, the first-type boundary condition states that at x = 0, and for all time, t, the concentration is C_o (i.e., a continuous source of constant concentration). This is described mathematically as:

$$C(0,t) = C_o \qquad \text{eq. D.2.8}$$

This boundary condition is used to calculate concentrations in a system where there is a continuous source of dissolved contamination at the upgradient flow boundary. An example would be a light nonaqueous-phase liquid (LNAPL) spill that receives fresh product at a rate that is balanced by LNAPL mass loss through weathering. The maximum contaminant concentration in groundwater beneath the LNAPL plume is dictated by the partitioning relationships described in Section C.3.2.2. In reality, such a system is rare. Once a source of LNAPL contamination has been identified it is generally removed and the LNAPL is subjected to weathering though the processes of volatilization, dissolution, and biodegradation. Because of this, most contaminant source areas should be modeled as decaying sources; however, use of constant-concentration boundaries to simulate sources for periods without appropriate source or solute data is often used as part of the "black box" approach discussed in Section D.2.4.4.

D.2.4.4.2 Second-Type Boundary Condition (Neumann, Specified-Flux)

This type of boundary condition is referred to as the second-type boundary condition or the Neumann boundary condition. This boundary condition specifies the flux of groundwater or contaminant mass across the boundary, and is equated to the normal derivative of head or concentration with respect to the direction perpendicular to the flow boundary.

D.2.4.4.2.1 Groundwater Flow (Specified-Flux)

Specified-flux boundaries are boundaries for which the flux of water across the boundary can be specified as a function of position and time. Flux, q, is defined as the volume of water crossing

a unit cross-sectional area per unit time and, following Darcy's Law, is given by the hydraulic conductivity times the first derivative of head with respect to the direction perpendicular to the flow boundary. The units of flux are $L^3/L^2/T$. If the direction perpendicular to the boundary corresponds with an axis of hydraulic conductivity, then the flux is given by (Franke *et al.*, 1987):

$$q = -K\frac{\partial H}{\partial n} \qquad \text{eq. D.2.9}$$

Where: q = volumetric flux
K = hydraulic conductivity
H = total hydraulic head
n = distance perpendicular to the boundary

In the most general case, the flux across the boundary is specified as a function of position and time, i.e.:

$$q = f(x,y,z,t) \qquad \text{eq. D.2.10}$$

or, if K is constant:

$$\frac{\partial H}{\partial n} = f(x,y,z,t) \qquad \text{eq. D.2.11}$$

In some cases, the flux might be constant with time, but specified as a function of position, i.e.:

$$q = f(x,y,z) \qquad \text{eq. D.2.12}$$

or, if K is constant:

$$\frac{\partial H}{\partial n} = f(x,y,z) \qquad \text{eq. D.2.13}$$

In the simplest case, the flux across the boundary is specified in space and in time, i.e.:

$$q = constant \qquad \text{eq. D.2.14}$$

or, if K is constant:

$$\frac{\partial H}{\partial n} = constant \qquad \text{eq. D.2.15}$$

An example where the flux across the boundary is often assumed to be specified in space and in time is areal recharge to a water-table aquifer by infiltration.

No-flow boundaries (impervious boundaries) are a special type of specified-flux boundary where the flux is constant in space and time and is zero, i.e.:

$$q = constant = 0 \qquad \text{eq. D.2.16}$$

or, if K is a constant:

$$\frac{\partial H}{\partial n} = constant = 0 \qquad \text{eq. D.2.17}$$

Examples of no-flow boundaries include groundwater divides and impermeable hydrostratigraphic units.

It is important to note that in all three of the cases listed above, the flux across the boundary is specified prior to the modeling simulation, is not affected by stresses to the groundwater system, and therefore is not allowed to deviate from the value specified prior to modeling. For systems where the flux varies as a function of hydraulic head along the boundary, the third-type boundary condition should be used.

D.2.4.4.2.2 Solute Transport (Specified Concentration Gradient)

The second-type boundary condition specifies the concentration gradient across a section of the boundary surface and is described mathematically by the first derivative of concentration with respect to the direction perpendicular to the flow boundary.

In the most general case the concentration gradient is a function of location and time:

$$\frac{dC}{dn} = f(x,y,z,t) \qquad \text{eq. D.2.18}$$

Where: C = solute concentration
n = distance perpendicular to the boundary
x = distance downgradient of the source
y = distance transverse to ~~the source in the horizontal~~ direction
z = distance transverse to the source in the vertical direction
t = time

In some cases, the flux might be constant with time, but specified as a function of position:

$$\frac{dC}{dn} = f(x,y,z) \qquad \text{eq. D.2.19}$$

In the simplest case, the flux across the boundary is specified in space and in time:

$$\frac{dC}{dn} = constant \qquad \text{eq. D.2.20}$$

In some cases there may be no concentration gradient across the boundary. This is a special type of specified-concentration-gradient boundary where the concentration gradient is constant in space and time and is zero:

$$\frac{dC}{dn} = constant = 0 \qquad \text{eq. D.2.21}$$

D.2.4.4.3 Third-Type Boundary Condition (Cauchy, Variable-Flux)

The third-type boundary condition specifies the flux of groundwater (volumetric flow rate) or contaminant along the boundary as a function of hydraulic head or contaminant concentration, and is equated to the normal derivative of head or concentration with respect to the direction normal to the flow boundary and the hydraulic head or contaminant concentration. This type of boundary condition is referred to as the third-type boundary condition or the Cauchy boundary condition.

D.2.4.4.3.1 Groundwater Flow (Head-Dependent Flux Boundary)

This type of boundary condition is used to describe situations where the flux across a part of the boundary surface changes in response to changes in hydraulic head within the aquifer system adjacent to the boundary. In these situations the flux is a specified function of that head, and varies during the model simulation as the head varies (Franke *et al.*, 1987). Head-dependent flux boundaries (Cauchy or mixed-boundary conditions) occur where the flux across the boundary is calculated from a given boundary head value. This type of flow boundary is sometimes referred to as a mixed-boundary condition because it is a combination of a specified-head boundary and a specified-flow boundary. The general mathematical description of the variable-flux boundary is given by (Franke *et al.*, 1987):

$$q = -K\frac{\partial H}{\partial n} + cH \qquad \text{eq. D.2.22}$$

Where: q = volumetric flux
K = hydraulic conductivity
c = constant
H = total hydraulic head
n = distance perpendicular to the boundary

Head-dependent flow boundaries are used to model leakage across semipermeable boundaries. An example is the upper surface of an aquifer overlain by a semiconfining unit that is in turn overlain by a surface water body. Aquifers in contact with lakes typically exhibit this type of boundary condition because clay and silt tends to accumulate at the bottom of lakes. The flux across the semiconfining bed in this case is expressed mathematically as (Bear, 1979):

$$q = -K' \frac{(H_0 - H)}{B'} \qquad \text{eq. D.2.23}$$

Where: q = volumetric flux
H = head in the aquifer
H_0 = head in external zone (separated from the aquifer by semipermeable layer)
K' = hydraulic conductivity of semipermeable layer
B' = thickness of semipermeable layer

This relationship could also be used when the modeled area is a confined aquifers, but the overlying confining unit is leaky and the leakance across the unit is controlled by the head of the overlying aquifer.

D.2.4.4.3.2 Solute Transport (Concentration-Dependent Concentration Gradient)

This type of boundary condition is used where the concentration gradient across the boundary is dependent on the difference between a specified concentration on one side of the boundary and the solute concentration on the opposite side of the boundary (Wexler, 1992). For a one-dimensional system, this type of boundary condition is described mathematically as (Wexler, 1992; Bear, 1979):

$$v_x C - D_x \frac{\partial C}{\partial x} = v_x C_o, \qquad x = 0 \qquad \text{eq. D.2.24}$$

This boundary condition best describes solute concentrations at the upgradient boundary of a homogeneous flow system where a well-mixed solute enters the system by advection across the boundary and is transported downgradient from the boundary by advection and dispersion (Wexler, 1992).

D.2.5 MODEL CALIBRATION

To ensure that a groundwater flow and solute transport model is capable of accurately predicting the future extent and concentration of a contaminant plume, it must be calibrated to

observed hydraulic and contaminant data. Calibration involves adjustment of key model input such as hydraulic conductivity, dispersivity, soil sorption coefficient, recharge, effective porosity, boundary conditions, and biodegradation rate until an adequate match between observed and simulated hydraulics and contaminant distribution is achieved. Parameters should be varied within measured ranges, historical ranges, or ranges presented in the relevant literature, except possibly for those outside the area for which data is available. The range of values over which the data are varied will also depend on the uncertainty of the data. In general, the parameters that have the most impact on the results of contaminant fate and transport modeling are hydraulic conductivity, head distribution (gradient), boundary conditions, source strengths, and biodegradation rates. As part of the calibration process, the modeler will also perform an error analysis in an attempt to quantify how well the model approximates the natural system and to identify any sources of excess differences between measured and modeled values. An error analysis in its most basic form is simply the comparison of measured and simulated values.

Calibration is necessary to account for the uncertain data and for any unknown, unrepresented, or unmeasured conditions or processes. It is possible to allow a computer code to perform the calibration (i.e., to solve what is known as the inverse problem), but this requires not only specification of the known data, but the also the statistical uncertainty associated with the data. Often the data or other resources do not allow such a procedure, so most modelers resort to the trial-and-error method of calibration. In this method the modeler uses his/her experience and judgment in conjunction with the available data to reach a solution that meets whatever criteria are specified for calibration. This implies that a certain amount of experience is needed for modeling in this manner (as well as for automated calibration). However, even with limited experience, a modeler may be able to calibrate a model in a reasonable and efficient manner with good guidance, either from a peer or from the texts that have been repeatedly referenced throughout this appendix. Even for the experienced modeler, these texts can provide useful, objective, and structured procedures for calibrating a model and evaluating that calibration.

Numerical solute transport model calibration differs from analytical solute transport model calibration. Calibration of a numerical solute transport model is a two-step process; first the groundwater flow system is calibrated, and then the solute transport system is calibrated. Calibration of the numerical flow model demonstrates that the model is capable of matching hydraulic conditions observed at the site; calibration of a contaminant transport model superimposed upon the calibrated flow model helps to confirm that contaminant loading and transport conditions are being appropriately simulated. Groundwater flow is calibrated by altering transmissivity in a trial-and-error fashion until simulated heads approximate observed field values

within a prescribed accuracy. After calibration of the flow model, the numerical solute transport model should be calibrated by altering transport parameters (and hydraulic parameters, if results indicate the need to do so) in a trial-and-error fashion until the simulated contaminant plume approximates observed field values.

Because analytical models do not calculate head as a function of time (gradients and hydraulic head considerations are addressed by entering either a groundwater velocity or a gradient, a flow direction, and one reference head into the model), only solute transport can be calibrated. The analytical solute transport model is calibrated by altering hydraulic parameters and transport parameters in a trial-and-error fashion until the simulated contaminant plume approximates observed field values at specific locations or times.

D.2.5.1 Groundwater Flow Calibration

Calibrating the model to groundwater flow involves comparing measured water levels against simulated water levels over the same period of time. If the flow simulation is steady-state, then the simulated water levels could be compared with only one set of data or a set of mean water levels over a selected period (Anderson and Woessner, 1992). Hydraulic conductivity is an important aquifer characteristic that determines the ability of the water-bearing strata to transmit groundwater. Transmissivity is the product of the hydraulic conductivity and the thickness of the aquifer. In conjunction with boundary conditions, hydraulic conductivity or transmissivity values will govern the calculated head solution. An accurate estimate of hydraulic conductivity is also important to help quantify advective groundwater flow velocities and solute transport velocities. Other parameters that may be adjusted during flow model calibration include recharge, evapotranspiration, and hydraulic boundary conditions. However, most uncertainty will lie in the magnitude and variation in hydraulic conductivity or transmissivity and therefore variation of the values of those parameters will likely be relied on the most in order to calibrate a groundwater flow model.

The root mean squared (RMS) error is one method commonly used to express the average difference between simulated and measured heads (i.e., it is an error analysis tool). RMS error is the average of the squared differences between measured and simulated heads, and can be expressed as:

$$\mathrm{RMS} = \left[\frac{1}{n} \sum_{i=1}^{n} \left(h_m - h_s \right)_i^2 \right]^{0.5} \qquad \text{eq. D.2.25}$$

Where: n = the number of points where heads are being compared

h_m = measured head value

h_s = simulated head value.

The RMS error between observed and calibrated values should be such that the calculated calibration error is less than 10 percent of the average head drop over the model domain. If sufficient data are available, it may be possible to produce a model with a calibration error of less than 5 percent. Calibration error may be described by:

$$CE = \frac{RMS}{\Delta H_T} \bullet 100$$

Where: CE = Calibration error (as a percentage)

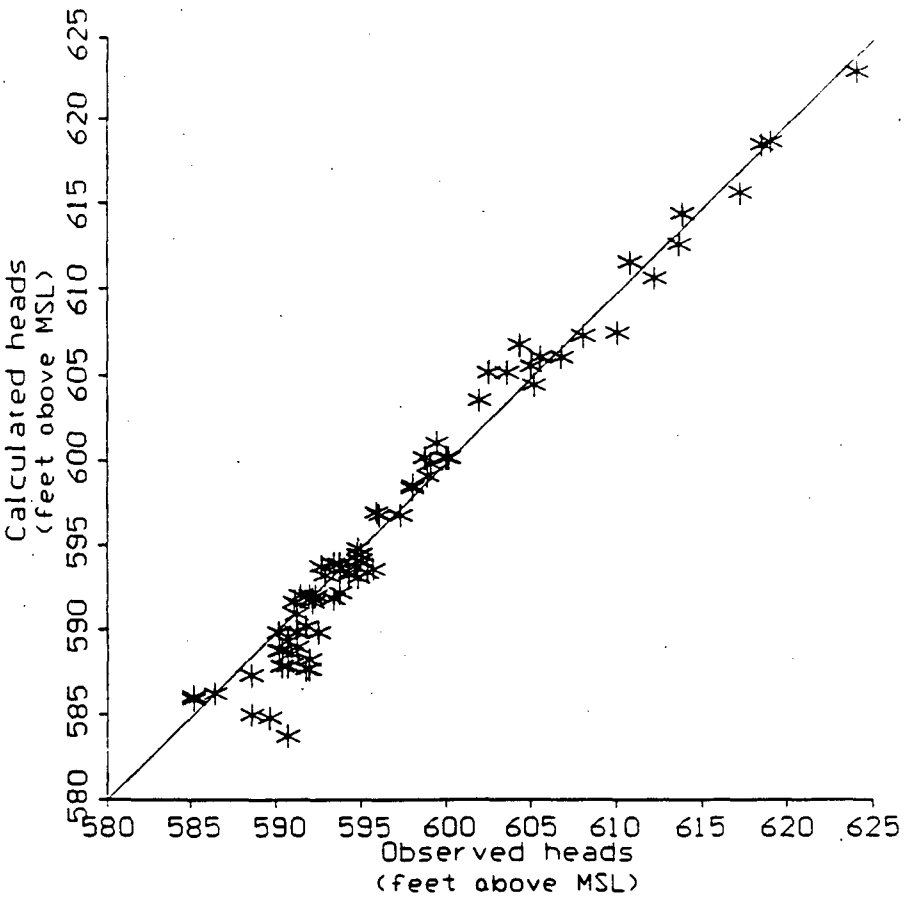
RMS = Root mean square error [L]

ΔH_T = Total head change over model domain [L]

Another qualitative method of checking the calibrated model head distribution and performing an error analysis involves a comparison of calculated heads and observed heads. When calculated heads are plotted versus observed heads, the points should scatter randomly about a straight line. Such a plot also can be used to check if there are any variations in the modeled head distribution that indicate a need to reevaluate parameters in a specific portion of the model domain (e.g., heads are consistently low in the vicinity of a boundary). Figure D.2.4 is an example of such a plot.

D.2.5.2 Calibrating the Model to Contaminant Distribution

Calibrating a model to contaminant fate and transport involves comparing the observed changes in plume extent and concentration to the predicted changes in extent and concentration over the same period of time. This requires historical contaminant data that may not be available



Mean error: -0.716 Mean abs. err: 1.32 RMS error: 1.815

Figure D.2.4

Example
Plot of Calibrated Heads
vs. Observed Heads

when the model is first developed. Because of this, there will be uncertainty in the model predictions and the model should be reevaluated as more groundwater analytical data become available.

Model input parameters affecting the distribution and concentration of the simulated contaminant plume should be modified so that model predictions match dissolved contaminant concentrations. To do this, model runs are made using the calibrated hydraulic parameters with available contaminant plume data. If the contaminant distribution is known at two different times, the plume may be calibrated over time, keeping in mind the uncertainty associated with the source term. Plume calibration is achieved by varying the source terms, decay coefficients, the coefficient of retardation, the effective porosity, and dispersivity until the contaminant plume is calibrated reasonably well to the existing plume in terms of migration distance, configuration, contaminant concentrations, and contaminant concentration changes in the plume area. As noted in Section D.2.4.4, the source terms are typically a significant source of uncertainty in the input and variation of the source terms is often a significant part the calibration process.

The calibration processes for analytical models and numerical models follow the same general steps as those outlined here. However, analytical models will only incorporate the transport portion of the calibration, with the flow component represented by a groundwater or contaminant velocity. Of course, calibration of an analytical model is less involved due to the simpler nature of the analytical models.

D.2.6 SENSITIVITY ANALYSIS

Any groundwater model is influenced by uncertainty owing to the inability to define the exact spatial and temporal distribution of aquifer and chemical parameter values at the field site. A sensitivity analysis is performed by varying model input parameters over reasonable ranges to establish the effect of uncertainty on the model. Sensitivity analyses should be performed on all models to evaluate the reasonableness of model predictions and identify any additional field data that may need to be collected.

The iterative model calibration process involves modifying several input parameters until a reasonable match of the hydraulic regime and contaminant fate and transport observations is reached. Thus, numerous variations of model input could produce the same results. To determine those model input parameters that have the greatest impact on modeling results, sensitivity analyses should be performed. Sensitivity analysis involves systematically varying model input parameters to determine the impact of different parameter values on the model

output. All solute transport models are sensitive to hydraulic conductivity (which has a great effect on transport velocity), dispersivity, retardation coefficients, and biodegradation rates. At a minimum, the sensitivity analyses must involve varying these model input parameters over the range of plausible values used during calibration.

The results of sensitivity analyses can be shown graphically, in table format, or simply written in the text. For simple numerical models or analytical models, a paragraph or two describing the changes made and how the results differed from the calibrated model may suffice. More complex models will require many different runs for the sensitivity analysis, and tables or pictures are more useful for presenting the greater amount of information that is generated. As an example, one could display modeled contaminant concentrations versus distance along the centerline of the plume for different runs in which the same parameter is varied. This manner of displaying data is useful for plumes that are elongate and fairly symmetric because the figures allow easy visualization of the changes in contaminant concentration caused by varying model input parameters. The results of the sensitivity analysis will tell the modeler which parameters have the greatest influence on the site model. This will allow the modeler to determine what input values to use so that the prediction scenarios are conservative.

In conjunction with (or as part of) the sensitivity analysis, the modeler may also provide an uncertainty analysis. This is done to determine the sensitivity of the model results to uncertainty in site-specific parameters. For example, a range of values for a specific parameter may be measured at a site, and the calibrated model may use an intermediate value. To check the sensitivity of the model to the uncertainty in this parameter, model runs would be made using the upper and lower values of the measured range of that parameter. By comparing the results of these model runs to the calibrated model results, the effects of uncertainty associated with that parameter and the effect of the uncertainty on model predictions can then be assessed. In effect, the uncertainty analysis is a focused sensitivity analysis in which the parameters are varied within a range indicated by a statistical evaluation of site data. Where limited data are available, such an analysis may not be feasible.

D.2.7 PREDICTION

After the solute transport model has been calibrated and the sensitivity analyses have been performed and interpreted, the model can be used to predict the fate and transport of contaminants. To do this, the model should be run with the input parameters determined to be most accurate based on model calibration and sensitivity analyses. Assumptions made in this step

should be made clear so that the entity that will ultimately use the results will understand this part of the model. As an example, assumptions about the contaminant source and how it may change over time should be made clear. As needed, multiple scenarios can be simulated to evaluate actions such as source removal or source reduction, or to evaluate a range of possible conditions. While the model predictions will yield specific values such as contaminant concentrations at specific times and locations, the modeler should make it clear that the reliability of the values is heavily dependent upon the model assumptions and the uncertainty of the available data. The modeler's interpretation of the uncertainty in the predictions and how best to use them should be included with the prediction results.

D.2.8 MODEL DOCUMENTATION AND REPORTING

Model documentation is a very important component of the modeling effort. If the reader cannot determine how the model was set up and implemented, the model is of little use. At a minimum, model documentation must include a discussion of how and why the model code was selected, a listing of all simplifying assumptions, boundary and initial conditions used, how model input parameters were determined (whether measured, estimated, or taken from literature), the process used to interpolate the data spatially, how the model was calibrated, and what types of sensitivity/uncertainty analyses were performed. Model set-up and results should be presented graphically unless the model is simple or an analytical model with a limited number of solution points. Figure D.2.5 gives an example table of contents from a report that was used to successfully implement intrinsic remediation at a site contaminated with fuel hydrocarbons and chlorinated solvents. Appendices E and F present examples of such reports.

D.2.9 POST-MODEL MONITORING, VERIFICATION, AND ADJUSTMENT

An important component of the intrinsic remediation demonstration is development of a long-term monitoring (LTM) plan that will allow the contaminant plume to be tracked through time. Long-term monitoring of the contaminant plume will allow the model to be verified (or validated). Verification is the process of demonstrating that the model is an adequate representation of the natural system, by using it to successfully predict data other than those used for the calibration. Ideally, a model will be verified before predictions are made, but in practice the constraints of data, time, and money will often rule out this step. However, a calibrated but unverified model can be used to make predictions as long as a careful sensitivity analysis is performed and evaluated.

Figure D.2.5

Example Table of Contents

There are several ways to verify a model. Typical ways a model may be verified include (Spitz and Moreno, 1996):

- using a model calibrated to steady-state conditions or a subset of the transient data to successfully predict transient data or a separate transient data set;
- using the model to successfully predict data not used in the calibration process (e.g. concentrations of solutes not considered during calibration);
- comparing model predictions with the results of other models of the similar situation (possibly using a different code or solution technique); and
- checking that data collected after model calibration and implementation supports the predictions made by the model.

If verification data do not agree with what the model predicted, then the model should be recalibrated using the new data. The last method is used frequently due to data constraints on using other methods, and the fact that it generally requires the least amount of additional work. It is the most practical and persuasive method, but requires that modeling and fieldwork be conducted together over some period of time. Fortunately, this method ties in neatly with the LTM component of a natural attenuation demonstration.

To demonstrate attainment with site-specific remediation goals and to verify the predictions made by the solute transport model developed for the site, the LTM plan consists of identifying the locations of two separate groundwater monitoring networks and developing a groundwater sampling and analysis strategy. The strategy described in this section is designed to monitor plume migration over time and to verify that intrinsic remediation is occurring at rates sufficient to protect potential receptors. In the event that data collected under the LTM program indicate that naturally occurring processes are insufficient to protect human health and the environment, contingency controls to augment remediation by natural attenuation can be implemented.

D.2.9.1 Monitoring Networks

Two separate sets of wells should be installed at the site as part of the intrinsic remediation with LTM remedial alternative. The first set should consist of at least four LTM wells located in, upgradient, and downgradient of the observed contaminant plume to verify the results of the solute transport model and to ensure that natural attenuation is occurring at rates sufficient to minimize plume expansion. This network of wells can consist of existing or newly installed wells screened within the shallow aquifer to provide short-term confirmation and verification of the quantitative groundwater modeling results. The second set of groundwater monitoring wells,

point-of-compliance (POC) wells, should be located downgradient from the plume along a line perpendicular to the groundwater flow direction. The purpose of the POC wells is to verify that no contaminant exceeding state, federal, or risk-based groundwater standards migrate beyond the area under institutional control. This network should consist of at least three groundwater monitoring wells. The LTM wells should be sampled for analysis of the parameters listed in Table 2.1. The POC wells should be sampled for those parameters required for regulatory compliance.

D.2.9.1.1 Long-Term Monitoring Wells

In at least four locations, groundwater wells within, upgradient, and downgradient of the observed contaminant plume should be used to monitor the effectiveness of intrinsic remediation in reducing total contaminant mass and minimizing contaminant migration at the site. At least one of these wells should be placed in the anaerobic zone, one should be placed in the aerobic zone, and another well is typically placed downgradient from the aerobic zone. An upgradient well provides background data. This network will supplement the POC wells to provide early confirmation of model predictions and to allow additional response time if necessary.

D.2.9.1.2 Point-of-Compliance Wells

Three POC monitoring wells should be installed downgradient from the leading edge of the contaminant plume. The purpose of the POC wells is to verify that no contaminated groundwater exceeding state, federal, or risk-based standards migrates beyond the area under institutional control. Although these wells should be placed beyond the point where model results suggest that the contaminant plume will migrate (at concentrations exceeding chemical-specific groundwater standards), these POC wells are the technical mechanisms used to demonstrate protection of human health and the environment and compliance with site-specific numerical remediation goals. As with the LTM wells, the POC wells must be screened in the same hydrogeologic unit(s) as the contaminant plume.

SECTION D-3

ANALYTICAL SOLUTE TRANSPORT MODELS

Analytical models provide exact, closed-form solutions to the governing advection-dispersion equations presented in Section D-1. The use of analytical models requires the user to make several simplifying assumptions about the solute transport system. For this reason, analytical models are most valuable for relatively simple hydrogeologic systems that are relatively homogeneous and isotropic and have uniform geometry (straight boundaries and constant thickness, width, and length). Heterogeneous and anisotropic hydrogeologic systems can be modeled using analytical models only if the system is simplified and average hydraulic characteristics are used. As an example, consider a hydrogeologic system composed of several layers with differing thicknesses and hydraulic conductivities. This system could be simulated using an analytical model by averaging the hydraulic conductivity over the entire thickness being modeled by dividing the sum of the products of each layer's thickness and hydraulic conductivity by the total aquifer thickness (Walton, 1991).

Table D.3.1 lists the analytical solutions presented in this section. Models based on these solutions are capable of simulating advection, dispersion, sorption, and biodegradation (or any first-order decay process). The assumptions required for each modeling scenario are listed in the relevant section. One-, two-, and three-dimensional analytical solutions to the advection-dispersion equation that are capable of simulating systems that have a continuing source of contamination or a source that is decaying over time are presented in this section (with the exception of a two-dimensional solution for a decaying source). Models that simulate a continuous source of contamination are good for determining the worst-case distribution of the dissolved contaminant plume. This is unrealistic, however, if for no other reason, because source concentrations decrease over time via natural weathering processes. As discussed in Appendix C, natural weathering processes can be slow, so it often will be necessary to implement an engineered solution for source removal. The models used to simulate a decaying source are especially applicable where an engineered solution is implemented for source removal. An important model input parameter for such models is the source decay rate. Appendix C discusses methods that can be used to quantify source-removal rates.

Table D.3.1

Analytical Models Commonly used to Simulate Solute Transport

Processes Simulated	Description	Authors	Section
One-Dimensional Models			
Advection, dispersion, linear sorption, and biodegradation - Constant Source Term	Solute transport in a semi-infinite system with a continuous source of contamination. Biodegradation is simulated using a first-order decay rate constant. Solute concentration is given as a function of time and distance	Bear, 1972; van Genuchten and Alves, 1982; and Wexler, 1992	D.3.2.1
Advection, dispersion, linear sorption, and biodegradation - Decaying Source Term	Solute transport in a semi-infinite system with a decaying source of contamination. Biodegradation is simulated using a first-order decay rate constant. Solute concentration is given as a function of time and distance	van Genuchten and Alves, 1982	D.3.2.2
Two-Dimensional Models			
Advection, dispersion, linear sorption, and biodegradation - Constant Source Term	Solute transport in a semi-infinite system with a continuous source of contamination. Biodegradation is simulated using a first-order decay rate constant. Solute concentration is given as a function of time and distance	Wilson and Miller, 1978	D.3.3.1
Three-Dimensional Models			
Advection, dispersion, linear sorption, and biodegradation - Constant Source Term	Solute transport in a semi-infinite system with a continuous source of contamination. Biodegradation is simulated using a first-order decay rate constant. Solute concentration is given as a function of distance from the source and time	Domenico, 1987	D.3.4.1
Advection, dispersion, linear sorption, and biodegradation - Decaying Source Term	Solute transport in a semi-infinite system with a decaying source of contamination. Biodegradation is simulated using a first-order decay rate constant. Solute concentration is given as a function of distance from the source and time	Domenico, 1987 modified for decaying source concentration	D.3.4.2

D.3.1 INITIAL AND BOUNDARY CONDITIONS FOR ANALYTICAL SOLUTE TRANSPORT MODELS

D.3.1.1 Upgradient (Inflow) Boundary Conditions

The first-type and third-type boundary conditions discussed in Section D-1 are used to describe solute concentrations at the upgradient (inflow) boundary of an analytical model. The third-type boundary condition is more accurate than the first-type boundary condition. This is because the first-type boundary condition assumes that the concentration gradient across the upgradient boundary is zero the instant flow begins (Wexler, 1992). This tends to overestimate the mass of solute in the system for early time (Wexler, 1992). Table D.3.2 lists typical boundary conditions used to describe the upgradient boundary of a solute transport system for analytical models.

Table D.3.2

Overview of Upgradient Boundary Conditions used to Simulate the Addition of Contaminants to a Hydrogeologic System

Type of Source Being Simulated	Type of Boundary	One-Dimensional Form
Constant Concentration	Type One	$C(0,t) = C_o$
Pulse-Type Loading with Constant Concentration	Type One	$C(0,t) = C_o,\ 0<t\le t_o$ $C(0,t) = 0,\ t>t_o$
Decaying Source, Exponential Decay with Source Concentration approaching 0	Type One	$C(0,t) = C_o e^{-\lambda t}$
Exponential Decay with Source Concentration approaching C_a	Type One	$C(0,t) = C_a + C_b e^{-\lambda t}$
Constant Flux with Constant Input Concentration	Type Three	$v_x C - D_x \left.\frac{\partial C}{\partial x}\right\|_{x=0} = v_x C_o$
Pulse-Type Loading with Constant Input Fluxes	Type Three	$v_x C - D_x \left.\frac{\partial C}{\partial x}\right\|_{x=0} = v_x C_o,\ 0<t\le t_o$ $v_x C - D_x \left.\frac{\partial C}{\partial x}\right\|_{x=0} = 0,\ t>t_o$

t_o = time at which concentration changes during pulse loading.
Source: Domenico and Schwartz (1990).

D.3.1.2 Downgradient (Outflow) Boundary Conditions

Solute transport systems can be simulated as systems of finite length, semi-infinite length, and infinite length. For systems where the outflow boundary is sufficiently far from the source of contamination that the downgradient boundary will not influence solute concentrations within the area of interest, the system can be treated as semi-infinite (Wexler, 1992). Semi-infinite systems are modeled using a first-type or second-type boundary condition at the downgradient boundary.

D.3.1.3 Lateral and Vertical Boundary Conditions

Lateral and vertical boundary conditions apply to two- and three-dimensional models only. One-dimensional models require only inflow and outflow boundaries. In two- and three-dimensional systems, impermeable or no-flux (no-flow) boundaries may be present at the base, top, or sides of the aquifer (Wexler, 1992). Because there is no flux across the boundary, and molecular diffusion across the boundary is assumed negligible, the general third-type boundary condition simplifies to a second-type boundary condition, and the boundary conditions are expressed as (Wexler, 1992):

$$\frac{dC}{dy} = 0, \quad y = 0 \text{ and } y = W \qquad \text{eq. D.3.1}$$

and

$$\frac{dC}{dz} = 0, \quad z = 0 \text{ and } z = H \qquad \text{eq D.3.2}$$

Where: C = contaminant concentration
y = distance in the y direction
W = width of the aquifer
H = height of the aquifer

In many cases, the lateral and vertical boundaries of the system may be far enough away from the area of interest that the system can be treated as being infinite along the y- and z- axes. If this is the case, then the boundary conditions are specified as (Wexler, 1992):

$$C=0, \frac{dC}{dy} = 0, \qquad y = \pm\infty \qquad \text{eq. D.3.3}$$

and

$$C=0, \frac{dC}{dz} = 0, \qquad z = \pm\infty \qquad \text{eq. D.3.4}$$

D.3.2 ONE-DIMENSIONAL ANALYTICAL MODELS

Models presented in this section include a solution for a semi-infinite system with a constant contaminant source of constant concentration and first-order decay of the solute (modified from Bear, 1972, by van Genuchten and Alves, 1982, and by Wexler, 1992,) and a solution for a semi-infinite system with a point source of diminishing concentration and first-order decay of solute (van Genuchten and Alves, 1982).

Equation D.1.1 is the one-dimensional partial differential equation describing transient solute transport with advection, dispersion, sorption, and first-order biodegradation in the saturated zone. For large values of time when the system has reached steady-state equilibrium, solute transport with advection, dispersion, sorption, and biodegradation is described by equation D.1.2. The biodegradation of BTEX compounds can commonly be approximated as a first-order process.

D.3.2.1 Semi-infinite System with Constant Source

One analytical solution for equation D.1.1 under the initial and boundary conditions listed below is given by (From Wexler, 1992, equation 60, p 18, modified from Bear, 1972, p. 630 and van Genuchten and Alves, 1982, p. 60):

$$C(x,t) = \frac{C_o}{2}\left\{\exp\left[\frac{x}{2\frac{D_x}{R}}\left(\frac{v_x}{R} - \sqrt{\left(\frac{v_x}{R}\right)^2 + 4\lambda\frac{D_x}{R}}\right)\right] \bullet erfc\left[\frac{x - t\sqrt{\left(\frac{v_x}{R}\right)^2 + 4\lambda\frac{D_x}{R}}}{2\sqrt{\frac{D_x}{R}t}}\right]\right.$$

$$\left. + \exp\left[\frac{x}{2\frac{D_x}{R}}\left(\frac{v_x}{R} + \sqrt{\left(\frac{v_x}{R}\right)^2 + 4\lambda\frac{D_x}{R}}\right)\right] \bullet erfc\left[\frac{x + t\sqrt{\left(\frac{v_x}{R}\right)^2 + 4\lambda\frac{D_x}{R}}}{2\sqrt{\frac{D_x}{R}t}}\right]\right\} \qquad \text{eq. D.3.5}$$

Where $C(x,t)$ = contaminant concentration at a distance, x, downgradient from source at time t
C_o = initial contaminant concentration at source
x = distance downgradient of upgradient boundary
t = time
D_x = longitudinal hydrodynamic dispersion coefficient
v_x = unretarded linear groundwater flow velocity
R = coefficient of retardation
λ = first-order decay rate constant for dissolved contaminant
erfc = complimentary error function (Table D.3.3)

Boundary Conditions:

$$C = C_o, \quad x = 0$$

$$C, \frac{\partial C}{\partial x} = 0, \quad x = \infty$$

Initial Condition:

$$C = 0, \quad 0 < x < \infty \quad \text{at } t = 0$$

Assumptions:

- Fluid is of constant density and viscosity
- Biodegradation of solute is approximated by first-order decay
- Flow is in the x-direction only, and velocity is constant
- The longitudinal hydrodynamic dispersion, D_x, is constant
- Sorption is approximated by the linear sorption model

Table D.3.3

Table of Error Functions

x	erf (x)	erfc(x)		x	erf(x)	erfc(x)
0	0	1		1.1	0.880205	0.119795
0.05	0.056372	0.943628		1.2	0.910314	0.089686
0.1	0.112463	0.887537		1.3	0.934008	0.065992
0.15	0.167996	0.832004		1.4	0.952285	0.047715
0.2	0.222703	0.777297		1.5	0.966105	0.033895
0.25	0.276326	0.723674		1.6	0.976348	0.023652
0.3	0.328627	0.671373		1.7	0.983790	0.016210
0.35	0.379382	0.620618		1.8	0.989091	0.010909
0.4	0.428392	0.571608		1.9	0.992790	0.007210
0.45	0.475482	0.524518		2.0	0.995322	0.004678
0.5	0.520500	0.479500		2.1	0.997021	0.002979
0.55	0.563323	0.436677		2.2	0.998137	0.001863
0.6	0.603856	0.396144		2.3	0.998857	0.001143
0.65	0.642029	0.357971		2.4	0.999311	0.000689
0.7	0.677801	0.322199		2.5	0.999593	0.000407
0.75	0.711156	0.288844		2.6	0.999764	0.000236
0.8	0.742101	0.257899		2.7	0.999866	0.000134
0.85	0.770668	0.229332		2.8	0.999925	0.000075
0.9	0.796908	0.203092		2.9	0.999959	0.000041
0.95	0.820891	0.179109		3.0	0.999978	0.000022
1	0.842701	0.157299				

erfc(x)=1-erf(x)

erfc(-x)=1+erf(x)

erf(-x)=-erf(x)

$$erf(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-u^2} du$$

For steady-state conditions, solute transport is described by equation D.1.2 and the solution reduces to (Wexler, 1992, equation 62, p. 20):

$$C(x) = C_o \exp\left[\frac{x}{2\frac{D_x}{R}}\left(\frac{v_x}{R} - \sqrt{\left(\frac{v_x}{R}\right)^2 + 4\lambda\frac{D_x}{R}}\right)\right] \qquad \text{eq. D.3.6}$$

Example D.3.1:

Given the hydraulic and contaminant transport parameters below plot the change in concentration through time at a location 30 m downgradient of the source using equation D.3.5. At what time does the concentration at this point reach steady-state equilibrium?

Solution:

Hydrogeologic Data

Hydraulic conductivity	$K = (3.15)\frac{m}{day}$	
Hydraulic gradient	$I = 0.02\frac{m}{m}$	
Effective porosity	$n_e = 0.25$	
Total porosity	$n = 0.35$	
Longitudinal dispersivity	$\alpha_x = 30 m$	
Initial Contaminant Concentration	$C_o = 12\frac{mg}{liter}$	

Retardation Coefficient Calculation

Contaminant Decay Rate	$\lambda = 0.01\frac{1}{day}$	
Soil sorption coefficient	$K_{oc} = 79\frac{mL}{gm}$	
Particle mass density (for quartz)	$\rho_s = 2.65\frac{gm}{cm^3}$	
Bulk density	$\rho_b = \rho_s(1-n)$	$\rho_b = 1.722\frac{gm}{cm^3}$
Organic carbon content	$f_{oc} = 0.8\%$	
Retardation coefficient	$R = 1 + \frac{\rho_b \cdot K_{oc} \cdot f_{oc}}{n_e}$	$R = 5.354$

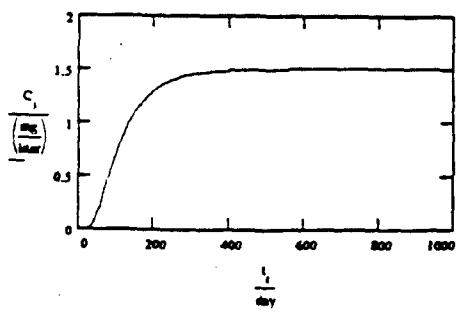
Groundwater Hydraulics Calculations

Groundwater velocity (pore-water) $v_x = \frac{K \cdot I}{n_e}$ $v_x = 0.252\frac{m}{day}$ Retarded Contaminant velocity $v_c = \frac{v_x}{R}$ $v_c = 0.047\frac{m}{day}$

Longitudinal dispersion coefficient $D_x = \alpha_x \cdot v_x$ $D_x = 7.56\frac{m^2}{day}$

Change in Concentration with Time Calculation $i = 1..1000$ $\Delta t = 1 day$ $t_i = \Delta t \cdot i$ $x = 30 m$

$$C_i = \frac{C_o}{2}\cdot\left[\exp\left[\frac{x}{2\frac{D_x}{R}}\left[\frac{v_x}{R} - \sqrt{\left(\frac{v_x}{R}\right)^2 + 4\lambda\frac{D_x}{R}}\right]\right]\left[1 - \operatorname{erf}\left[\frac{x - t_i\sqrt{\left(\frac{v_x}{R}\right)^2 + 4\lambda\frac{D_x}{R}}}{2\sqrt{\frac{D_x}{R}t_i}}\right]\right] + \exp\left[\frac{x}{2\frac{D_x}{R}}\left[\frac{v_x}{R} + \sqrt{\left(\frac{v_x}{R}\right)^2 + 4\lambda\frac{D_x}{R}}\right]\right]\left[1 - \operatorname{erf}\left[\frac{x + t_i\sqrt{\left(\frac{v_x}{R}\right)^2 + 4\lambda\frac{D_x}{R}}}{2\sqrt{\frac{D_x}{R}t_i}}\right]\right]\right]$$



$C_1 = 0\frac{mg}{liter}$ $C_{400} = 1.494\frac{mg}{liter}$

$C_{100} = 0.714\frac{mg}{liter}$ $C_{500} = 1.504\frac{mg}{liter}$

$C_{200} = 1.303\frac{mg}{liter}$ $C_{1000} = 1.508\frac{mg}{liter}$

$C_{300} = 1.455\frac{mg}{liter}$

Plume reaches steady-state equilibrium after approximately 400 days

D.3.2.2 Semi-infinite System with Decaying Source

The analytical relationships presented in the preceding section are useful for simulating solute transport at sites with a constant source of contamination. In reality, contaminant source concentrations generally decrease over time via weathering of mobile and residual LNAPL. Temporal variations in source concentrations are simulated using the third-type boundary condition. van Genuchten and Alves (1982) give a solution to equation D.1.1 for a decaying contaminant source and a solute subject to first-order decay. For cases where the decay rate for the dissolved contaminant, λ, is not equal to the decay rate for the source, γ:

$$C(x,t) = C_o A(x,t) + C_s E(x,t) \qquad \text{eq. D.3.7}$$

Where:

$$A(x,t) = \exp(-\lambda t)\left\{1 - \frac{1}{2}erfc\left[\frac{Rx - v_x t}{2\sqrt{D_x R t}}\right] - \left[\frac{v_x^2 t}{\pi D_x R}\right]\exp\left[-\frac{(Rx - v_x t)^2}{4D_x R t}\right]\right. \qquad \text{eq. D.3.8}$$
$$\left. + \frac{1}{2}\left[1 + \frac{v_x x}{D_x} + \frac{v_x^2 t}{D_x R}\right]\exp\left[\frac{v_x x}{D_x}\right]erfc\left[\frac{Rx + v_x t}{2\sqrt{D_x R t}}\right]\right\}$$

and

$$E(x,t) = \exp(-\gamma t)\left\{\left(\frac{v_x}{v_x + v_x\sqrt{1 + \frac{4D_x R}{v_x^2}(\lambda - \gamma)}}\right)\exp\left[\frac{\left(v_x - v_x\sqrt{1 + \frac{4D_x R}{v_x^2}(\lambda - \gamma)}\right)x}{2D_x}\right]erfc\left[\frac{Rx - tv_x\sqrt{1 + \frac{4D_x R}{v_x^2}(\lambda - \gamma)}}{2\sqrt{D_x R t}}\right]\right. \qquad \text{eq. D.3.9}$$
$$+\left(\frac{v_x}{v_x - v_x\sqrt{1 + \frac{4D_x R}{v_x^2}(\lambda - \gamma)}}\right)\exp\left[\frac{\left(v_x + v_x\sqrt{1 + \frac{4D_x R}{v_x^2}(\lambda - \gamma)}\right)x}{2D_x}\right]erfc\left[\frac{Rx + tv_x\sqrt{1 + \frac{4D_x R}{v_x^2}(\lambda - \gamma)}}{2\sqrt{D_x R t}}\right]$$
$$\left. + \frac{v_x^2}{2D_x R(\lambda - \gamma)}\exp\left[\frac{v_x x}{D_x} - (\lambda - \gamma)t\right]erfc\left[\frac{Rx + v_x t}{2\sqrt{D_x R t}}\right]\right\}$$

Where $C(x,t)$ = contaminant concentration at a distance, x, downgradient from the source at time t

C_o = initial dissolved contaminant concentration at boundary

C_s = concentration of injected contaminant (source term)

x = distance downgradient of upgradient boundary

t = time

D_x = longitudinal hydrodynamic dispersion coefficient

v_x = unretarded linear groundwater flow velocity

R = coefficient of retardation

λ = first-order decay rate constant for dissolved contaminant

γ = first-order decay rate constant for source term

Assumptions:

- Homogeneous, isotropic aquifer
- Fluid is of constant density and viscosity
- Biodegradation is approximately first-order
- Flow is in the x-direction only, and velocity is constant, uniform flow field
- The longitudinal hydrodynamic dispersion, D_x, is constant
- There is no advection or dispersion into or out of the aquifer
- Sorption is approximated by the linear sorption model.
- The source fully penetrates the aquifer

Boundary Conditions:

$$\left(-D_x \frac{\partial C}{\partial x} + v_x C\right)\Big|_{x=0} = v_x C_s \exp(-\alpha t)$$

$$\frac{\partial C}{\partial x}(\infty, t) = 0$$

Initial Condition:

$$C(x,0) = C_o$$

Because the source is decaying, the solute transport system will never reach truly steady-state conditions, and therefore, no steady-state solution is available.

Example D.3.2:

Consider a system where a fresh spill of mobile LNAPL consisting of fresh JP-4 jet fuel is floating on the water table in a medium- to coarse-grained sandy aquifer. Immediately after the spill, a mobile LNAPL recovery system was installed to remediate this continuing source of groundwater contamination, and a bioventing system was installed to remove fuel residuals from the unsaturated zone. It is estimated that it will take 8 years to reduce BTEX concentrations in the residual and mobile LNAPL to levels that will no longer cause dissolved groundwater contamination above regulatory guidelines. Based on the results of calculations completed using a conservative tracer, the first-order biodegradation rate constant is 0.026 per day. The hydraulic conductivity is 0.084 cm/sec and the hydraulic gradient is 0.046 m/m. The total organic carbon (TOC) content of the aquifer is 0.001 percent. The dispersivity is estimated to be 15 m. Will the plume reach the regulatory POC well located 450 m downgradient from the source along the property boundary in concentrations above regulatory guidelines? The applicable groundwater

standard for benzene is 5 µg/L. How long will it take for the dissolved plume to disappear at points located 10 and 100 m downgradient from the source? What will the contaminant distributions be at t = 1 year and t = 5 years.

Solution:

The first step is to determine the groundwater seepage velocity. From Appendix C, Table C.3.2, the effective porosity for medium- to coarse-grained sands ranges from 15 to 35 percent. Using the median effective porosity of 25 percent, the groundwater seepage velocity is (from equation C.3.6):

$$v_x = -\frac{0.0084\frac{cm}{sec} \bullet 0.046\frac{m}{m}}{0.25} = 1.34\frac{m}{day}$$

Because the organic carbon content of the aquifer is less than 0.1 percent, sorption is not expected to play an important role in slowing the contaminant plume, so the coefficient of retardation is assumed to be 1.0.

Next determine the first-order rate constant for the contaminant source, γ. Dissolved total BTEX concentrations in groundwater immediately beneath the mobile LNAPL plume were 35 mg/L before implementation of remedial actions. After 8 years, the dissolved total BTEX concentration in groundwater immediately beneath the mobile LNAPL plume will be 0.001 mg/L. Using the first-order relationship presented in equation C.3.31 (Appendix C) and substituting γ for λ, and solving for γ yields:

$$\gamma = -\frac{\ln\frac{C}{C_o}}{t} = -\frac{\ln\frac{0.001 mg/L}{35 mg/L}}{8 years} = 1.31/year = 0.0036/day$$

The use of a spreadsheet program or one of the mathematical software programs, such as Mathcad® simplifies solution of analytical models. The following pages illustrate the use of Mathcad® to solve this problem.

Contaminant Concentration at Point of Compliance Well

Hydraulic conductivity	$K = 0.0084 \frac{cm}{sec}$	Solute Decay Rate	$\lambda = 0.032 \frac{1}{day}$
Hydraulic gradient	$I = 0.046 \frac{ft}{ft}$	Source Decay Rate	$\gamma = 0.0036 \frac{1}{day}$
Effective porosity	$n_e = 0.25$	Groundwater velocity (seepage)	$v_x = \frac{K I}{n_e}$ $v_x = 1.335 \frac{m}{day}$
Longitudinal dispersivity	$\alpha_x = 15 m$	Retardation coefficient	$R = 1$
Concentration of Injected Contaminant	$C_s = 35 \frac{mg}{liter}$	Coefficient of Hydrodynamic Dispersion (Longitudinal)	$D_x = \alpha_x v_x$ $D_x = 20.031 \frac{m^2}{day}$
Initial Dissolved Contaminant Concentration	$C_o = 0 \frac{mg}{liter}$		

$i := 1..1500$ $\Delta t = 1 day$ $t_i = \Delta t \cdot i$ $x = 450 m$ $ug = \frac{mg}{1000}$

For Retarded Flow with Biodegradation and a Decaying Source (van Genuchten and Alves, 1982)

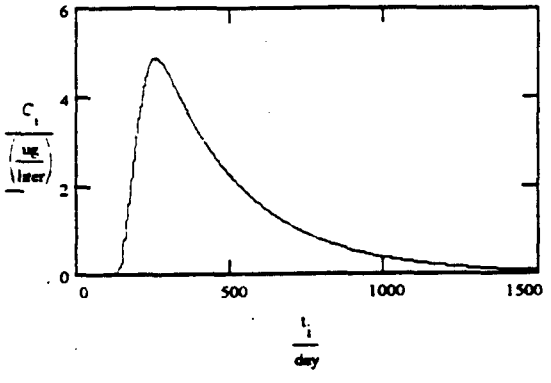
$$C_i = C_o \exp(-\lambda t_i) \left[1 - \frac{1}{2} \left(1 - \operatorname{erf} \frac{R x - v_x t_i}{2\sqrt{D_x R t_i}} \right) - \left(\frac{v_x^2 t_i}{\pi D_x R} \right)^{0.5} \exp\left[-\frac{(R x - v_x t_i)^2}{4 D_x R t_i} \right] - \frac{1}{2} \left(1 + \frac{v_x x}{D_x} + \frac{v_x^2 t_i}{D_x R} \right) \exp\left(\frac{v_x x}{D_x} \right) \left(1 - \operatorname{erf} \frac{R x + v_x t_i}{2\sqrt{D_x R t_i}} \right) \right]$$

$$+ C_s \exp(-\gamma t_i) \left[\left[\frac{v_x}{v_x + v_x \sqrt{1 - \frac{4 D_x R}{v_x^2}(\lambda - \gamma)}} \right] \exp\left[\frac{\left[v_x - v_x \sqrt{1 + \frac{4 D_x R}{v_x^2}(\lambda - \gamma)} \right] x}{2 D_x} \right] \left[1 - \operatorname{erf} \frac{R x - t_i \left[v_x \sqrt{1 + \frac{4 D_x R}{v_x^2}(\lambda - \gamma)} \right]}{2\sqrt{D_x R t_i}} \right] \right]$$

$$+ \left[\frac{v_x}{v_x - v_x \sqrt{1 - \frac{4 D_x R}{v_x^2}(\lambda - \gamma)}} \right] \exp\left[\frac{\left[v_x + v_x \sqrt{1 + \frac{4 D_x R}{v_x^2}(\lambda - \gamma)} \right] x}{2 D_x} \right] \left[1 - \operatorname{erf} \frac{R x + t_i v_x \sqrt{1 + \frac{4 D_x R}{v_x^2}(\lambda - \gamma)}}{2\sqrt{D_x R t_i}} \right]$$

$$+ \left[\frac{v_x^2}{2 D_x R (\lambda - \gamma)} \exp\frac{v_x x}{D_x} - \left[(\lambda - \gamma) t_i \right] \right] \left(1 - \operatorname{erf} \left(\frac{R x + v_x t_i}{2\sqrt{D_x R t_i}} \right) \right) \Bigg]$$

Total BTEX concentration versus time at the point of compliance well



Based on the model of van Genuchten and Alves (1982), the concentration of benzene at the POC well will not exceed the MCL

Contaminant Concentration versus Time at a Well Located 10 meters Downgradient of the Source Area

$K = 0.0084\frac{cm}{sec}$ $I = 0.046\frac{ft}{ft}$ $n_e = 0.25$ $v_x = \frac{K \cdot I}{n_e}$ $v_x = 1.335\frac{m}{day}$ $\alpha_x = 15\,m$ $D_x = \alpha_x \cdot v_x$ $D_x = 20.031\frac{m^2}{day}$

$\lambda = 0.032\frac{1}{day}$ $\gamma = 0.0036\frac{1}{day}$ $C_s = 35\frac{mg}{liter}$ $C_o = 0\frac{mg}{liter}$ $R = 1$

$i = 1..1700$ $\Delta t = 1\,day$ $t_i = \Delta t \cdot i$ $x = 10\,m$ $ug = \frac{mg}{1000}$

For Retarded Flow with Biodegradation and a Decaying Source (van Genuchten and Alves, 1982)

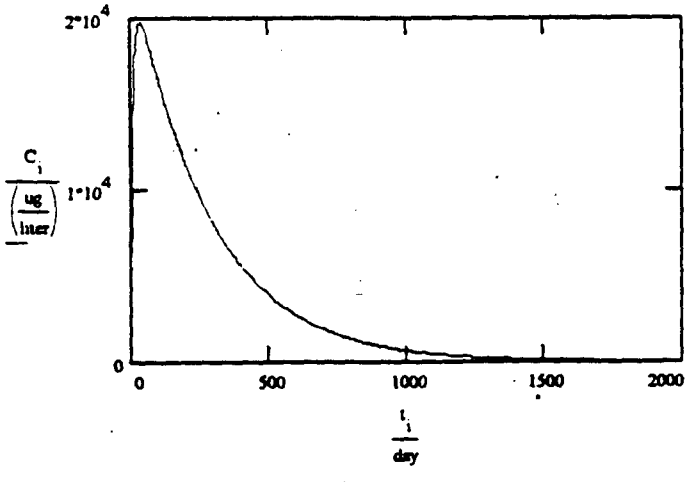
$$C_i = C_o \cdot \exp\left(-\lambda \cdot t_i\right)\left[1 - \frac{1}{2}\left(1 - \operatorname{erf}\left(\frac{R \cdot x - v_x \cdot t_i}{2\sqrt{D_x \cdot R \cdot t_i}}\right)\right) - \left(\frac{v_x^2 \cdot t_i}{\pi \cdot D_x \cdot R}\right)^{0.5} \cdot \exp\left[\frac{-\left(R \cdot x - v_x \cdot t_i\right)^2}{4 \cdot D_x \cdot R \cdot t_i}\right] + \frac{1}{2}\left(1 + \frac{v_x \cdot x}{D_x} + \frac{v_x^2 \cdot t_i}{D_x \cdot R}\right) \cdot \exp\left(\frac{v_x \cdot x}{D_x}\right)\left(1 - \operatorname{erf}\left(\frac{R \cdot x + v_x \cdot t_i}{2\sqrt{D_x \cdot R \cdot t_i}}\right)\right)\right]$$

$$+ C_s \cdot \exp\left(-\gamma \cdot t_i\right)\left[\left[\frac{v_x}{v_x + v_x\sqrt{1 + \frac{4 \cdot D_x \cdot R}{v_x^2}(\lambda - \gamma)}}\right] \cdot \exp\left[\frac{\left[v_x - v_x\sqrt{1 + \frac{4 \cdot D_x \cdot R}{v_x^2}(\lambda - \gamma)}\right] \cdot x}{2 \cdot D_x}\right]\left[1 - \operatorname{erf}\left[\frac{R \cdot x - t_i\left[v_x\sqrt{1 + \frac{4 \cdot D_x \cdot R}{v_x^2}(\lambda - \gamma)}\right]}{2\sqrt{D_x \cdot R \cdot t_i}}\right]\right]\right.$$

$$+ \left[\frac{v_x}{v_x - v_x\sqrt{1 + \frac{4 \cdot D_x \cdot R}{v_x^2}(\lambda - \gamma)}}\right] \cdot \exp\left[\frac{\left[v_x + v_x\sqrt{1 + \frac{4 \cdot D_x \cdot R}{v_x^2}(\lambda - \gamma)}\right] \cdot x}{2 \cdot D_x}\right]\left[1 - \operatorname{erf}\left[\frac{R \cdot x + t_i \cdot v_x\sqrt{1 + \frac{4 \cdot D_x \cdot R}{v_x^2}(\lambda - \gamma)}}{2\sqrt{D_x \cdot R \cdot t_i}}\right]\right]$$

$$\left. + \left[\frac{v_x^2}{2 \cdot D_x \cdot R \cdot (\lambda - \gamma)}\right] \cdot \exp\left[\frac{v_x \cdot x}{D_x} - \left[(\lambda - \gamma) \cdot t_i\right]\right]\left(1 - \operatorname{erf}\left(\frac{R \cdot x + v_x \cdot t_i}{2\sqrt{D_x \cdot R \cdot t_i}}\right)\right)\right]$$

Concentration versus time at a point 10 m downgradient of the source



BTEX will not be detected in the well located 10 m from the mobile LNAPL source after approximately 1650 days (4.5 years)

Contaminant Concentration versus Time at a Well Located 100 meters Downgradient of the Source Area

$K = 0.0084 \frac{cm}{sec}$ $I = 0.046 \frac{ft}{ft}$ $n_e = 0.25$ $v_x = \frac{K I}{n_e}$ $v_x = 1.335 \frac{m}{day}$ $\alpha_x = 15\,m$ $D_x = \alpha_x v_x$ $D_x = 20.031 \frac{m^2}{day}$

$\lambda = 0.032 \frac{1}{day}$ $\gamma = 0.0036 \frac{1}{day}$ $C_s = 35 \frac{mg}{liter}$ $C_o = 0 \frac{mg}{liter}$ $R = 1$

$i = 1 .. 1700$ $\Delta t = 1\,day$ $t_i = \Delta t \cdot i$ $x = 100\,m$ $ug = \frac{mg}{1000}$

For Retarded Flow with Biodegradation and a Decaying Source (van Genuchten and Alves, 1982)

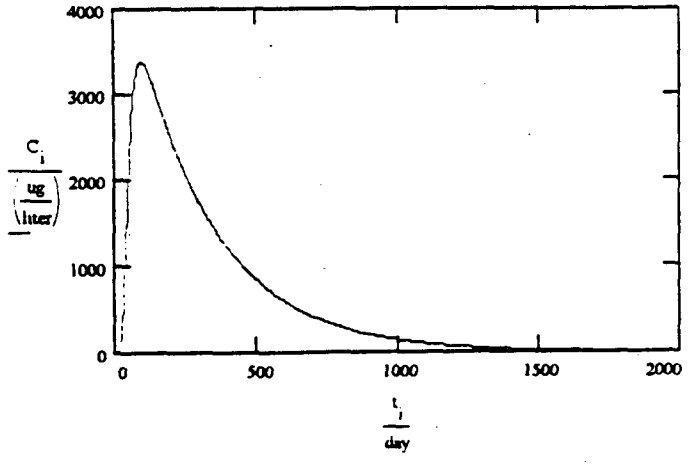
$$C_i = C_o \exp(-\lambda t_i) \left[1 - \frac{1}{2} \left(1 - \operatorname{erf} \frac{R x - v_x t_i}{2\sqrt{D_x R t_i}} \right) - \left(\frac{v_x^2 t_i}{\pi D_x R} \right)^{\frac{1}{2}} \exp\left[-\frac{(R x - v_x t_i)^2}{4 D_x R t_i} \right] + \frac{1}{2} \left(1 + \frac{v_x x}{D_x} + \frac{v_x^2 t_i}{D_x R} \right) \exp\left(\frac{v_x x}{D_x} \right) \left(1 - \operatorname{erf} \frac{R x - v_x t_i}{2\sqrt{D_x R t_i}} \right) \right]$$

$$+ C_s \exp(-\gamma t_i) \left[\left[\frac{v_x}{v_x + v_x \sqrt{1 - \frac{4 D_x R}{v_x^2} (\lambda - \gamma)}} \right] \exp\left[\frac{\left[v_x - v_x \sqrt{1 + \frac{4 D_x R}{v_x^2} (\lambda - \gamma)} \right] x}{2 D_x} \right] \left(1 - \operatorname{erf} \frac{R x - t_i v_x \sqrt{1 - \frac{4 D_x R}{v_x^2} (\lambda - \gamma)}}{2\sqrt{D_x R t_i}} \right) \right.$$

$$+ \left[\frac{v_x}{v_x - v_x \sqrt{1 + \frac{4 D_x R}{v_x^2} (\lambda - \gamma)}} \right] \exp\left[\frac{\left[v_x + v_x \sqrt{1 + \frac{4 D_x R}{v_x^2} (\lambda - \gamma)} \right] x}{2 D_x} \right] \left(1 - \operatorname{erf} \frac{R x + t_i v_x \sqrt{1 - \frac{4 D_x R}{v_x^2} (\lambda - \gamma)}}{2\sqrt{D_x R t_i}} \right)$$

$$\left. + \left[\frac{v_x^2}{2 D_x R (\lambda - \gamma)} \right] \exp\left[\frac{v_x x}{D_x} - [(\lambda - \gamma) t_i] \right] \left(1 - \operatorname{erf} \left(\frac{R x + v_x t_i}{2\sqrt{D_x R t_i}} \right) \right) \right]$$

Concentration versus time at a point 100 m downgradient of the source



BTEX will not be detected in the well located 100 m downgradient from the mobile LNAPL source after approximately 1650 days (4.5 years)

Contaminant Distribution after One Year

Hydraulic conductivtiy	$K = 0.0084 \frac{cm}{sec}$	Solute Decay Rate	$\lambda = 0.032 \frac{1}{day}$
Hydraulic gradient	$I = 0.046 \frac{ft}{ft}$	Source Decay Rate	$\gamma = 0.0036 \frac{1}{day}$
Effective porosity	$n_e = 0.25$	Initial Concentration of Injected Contaminant	$C_s = 35 \frac{mg}{liter}$
Longitudinal dispersivity	$\alpha_x = 15 m$	Initial Dissolved Contaminant Concentration	$C_o = 0 \frac{mg}{liter}$
Groundwater velocity (pore-water)	$v_x = \frac{K \cdot I}{n_e}$ $v_x = 1.335 \frac{m}{day}$	Retardation coefficient	$R = 1$
Longitudinal dispersion coefficient	$D_x = \alpha_x \cdot v_x$ $D_x = 20.031 \frac{m^2}{day}$		

$j = 0 .. 400$ $t = 365 day$ $\Delta x = 1 m$ $x_j = \Delta x \cdot j$ $ug = \frac{mg}{1000}$

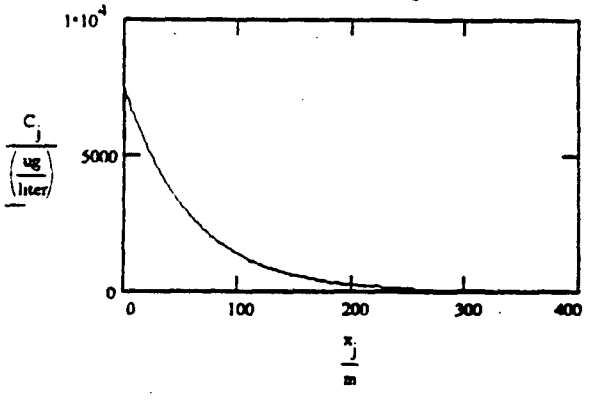
$$C_j = C_o \cdot \exp(-\lambda \cdot t) \cdot \left[1 - \frac{1}{2} \cdot \left(1 - \operatorname{erf}\left(\frac{R \cdot x_j - v_x \cdot t}{2 \cdot \sqrt{D_x \cdot R \cdot t}} \right) \right) - \left(\frac{v_x^2 \cdot t}{\pi \cdot D_x \cdot R} \right) \cdot \exp\left[- \frac{(R \cdot x_j - v_x \cdot t)^2}{4 \cdot D_x \cdot R \cdot t} \right] + \frac{1}{2} \cdot \left(1 + \frac{v_x \cdot x_j}{D_x} + \frac{v_x^2 \cdot t}{D_x \cdot R} \right) \cdot \exp\left(\frac{v_x \cdot x_j}{D_x} \right) \cdot \left(1 - \operatorname{erf}\left(\frac{R \cdot x_j + v_x \cdot t}{2 \cdot \sqrt{D_x \cdot R \cdot t}} \right) \right) \right]$$

$$+ C_s \cdot \exp(-\gamma \cdot t) \cdot \left[\left[\frac{v_x}{v_x - v_x \cdot \sqrt{1 + \frac{4 \cdot D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}} \right] \cdot \exp\left[\frac{\left[v_x - v_x \cdot \sqrt{1 + \frac{4 \cdot D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)} \right] \cdot x_j}{2 \cdot D_x} \right] \cdot \left[1 - \operatorname{erf}\left[\frac{R \cdot x_j - t \cdot v_x \cdot \sqrt{1 + \frac{4 \cdot D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}}{2 \cdot \sqrt{D_x \cdot R \cdot t}} \right] \right] \right] \ldots$$

$$\ldots + \left[\left[\frac{v_x}{v_x - v_x \cdot \sqrt{1 + \frac{4 \cdot D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}} \right] \cdot \exp\left[\frac{\left[v_x + v_x \cdot \sqrt{1 + \frac{4 \cdot D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)} \right] \cdot x_j}{2 \cdot D_x} \right] \cdot \left[1 - \operatorname{erf}\left[\frac{R \cdot x_j + t \cdot v_x \cdot \sqrt{1 + \frac{4 \cdot D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}}{2 \cdot \sqrt{D_x \cdot R \cdot t}} \right] \right] \right] \ldots$$

$$\ldots + \left[\left[\frac{v_x^2}{2 \cdot D_x \cdot R \cdot (\lambda - \gamma)} \right] \cdot \exp\left[\frac{v_x \cdot x_j}{D_x} - (\lambda - \gamma) \cdot t \right] \cdot \left(1 - \operatorname{erf}\left(\frac{R \cdot x_j + v_x \cdot t}{2 \cdot \sqrt{D_x \cdot R \cdot t}} \right) \right) \right] \Bigg]$$

Contaminant distribution along plume centerline at t = 1 year



Contaminant Distribution after Five Years

Hydraulic conductivity	$K = 0.0084 \frac{cm}{sec}$	Solute Decay Rate	$\lambda = 0.032 \frac{1}{day}$
Hydraulic gradient	$I = 0.046 \frac{ft}{ft}$	Source Decay Rate	$\gamma = 0.0036 \frac{1}{day}$
Effective porosity	$n_e = 0.25$	Initial Concentration of Injected Contaminant	$C_s = 35 \frac{mg}{liter}$
Longitudinal dispersivity	$\alpha_x = 15 m$	Initial Dissolved Contaminant Concentration	$C_o = 0 \frac{mg}{liter}$
Groundwater velocity (pore-water)	$v_x = \frac{KI}{n_e}$ $v_x = 1.335 \frac{m}{day}$	Retardation coefficient	$R = 1$
Longitudinal dispersion coefficient	$D_x = \alpha_x \cdot v_x$ $D_x = 20.031 \frac{m^2}{day}$		

$j = 0..400$ $t = 1825 day$ $\Delta x = 1 m$ $x_j = \Delta x \cdot j$ $ug = \frac{mg}{1000}$

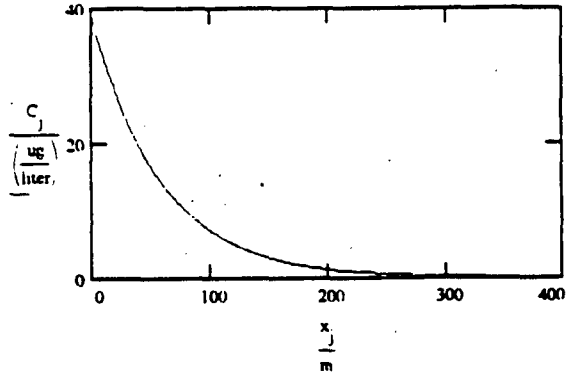
$$C_j = C_o \cdot \exp(-\lambda \cdot t) \cdot \left[1 - \frac{1}{2} \cdot \left(1 - \operatorname{erf}\left(\frac{R \cdot x_j - v_x \cdot t}{2\sqrt{D_x \cdot R \cdot t}} \right) \right) - \left(\frac{v_x^2 \cdot t}{\pi \cdot D_x \cdot R} \right) \cdot \exp\left[- \frac{(R \cdot x_j - v_x \cdot t)^2}{4 D_x \cdot R \cdot t} \right] + \frac{1}{2} \left(1 + \frac{v_x \cdot x_j}{D_x} + \frac{v_x^2 \cdot t}{D_x \cdot R} \right) \cdot \exp\left(\frac{v_x \cdot x_j}{D_x} \right) \cdot \left(1 - \operatorname{erf}\left(\frac{R \cdot x_j + v_x \cdot t}{2\sqrt{D_x \cdot R \cdot t}} \right) \right) \right]$$

$$+ C_s \cdot \exp(-\gamma \cdot t) \cdot \left[\left[\frac{v_x}{v_x - v_x \sqrt{1 + \frac{4 D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}} \right] \cdot \exp\left[\frac{\left[v_x - v_x \sqrt{1 + \frac{4 D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)} \right] \cdot x_j}{2 D_x} \right] \cdot \left[1 - \operatorname{erf}\left[\frac{R \cdot x_j - t \cdot \left[v_x \sqrt{1 + \frac{4 D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)} \right]}{2\sqrt{D_x \cdot R \cdot t}} \right] \right] \right.$$

$$+ \left[\frac{v_x}{v_x - v_x \sqrt{1 + \frac{4 D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}} \right] \cdot \exp\left[\frac{\left[v_x + v_x \sqrt{1 + \frac{4 D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)} \right] \cdot x_j}{2 D_x} \right] \cdot \left[1 - \operatorname{erf}\left[\frac{R \cdot x_j + t \cdot v_x \sqrt{1 + \frac{4 D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}}{2\sqrt{D_x \cdot R \cdot t}} \right] \right]$$

$$\left. + \left[\frac{v_x^2}{2 D_x \cdot R \cdot (\lambda - \gamma)} \right] \cdot \exp\left[\frac{v_x \cdot x_j}{D_x} - (\lambda - \gamma) \cdot t \right] \cdot \left(1 - \operatorname{erf}\left(\frac{R \cdot x_j + v_x \cdot t}{2\sqrt{D_x \cdot R \cdot t}} \right) \right) \right]$$

Contaminant distribution along plume centerline at t = 5 years



D.3.3 TWO-DIMENSIONAL ANALYTICAL MODELS

The model presented in this section is for a semi-infinite system with a constant source of constant concentration and first-order decay of solute (Wilson and Miller, 1978).

Equation D.1.3 is the two-dimensional partial differential equation describing transient solute transport with advection, dispersion, sorption, and first-order biodegradation in the saturated zone. For large values of time when the system has reached steady-state equilibrium, solute transport with advection, dispersion, sorption, and biodegradation is described by equation D.1.4 The biodegradation of BTEX compounds can commonly be approximated using first-order kinetics.

D.3.3.1 Continuous Source

Wilson and Miller (1978) give the following solution to equation D.1.3 (Bedient *et al.*, 1994, p. 136, eq. 6.27)

$$C(x,y,t) = \frac{f_m \exp\left(\frac{v_x x}{2D_x}\right)}{4\pi n_e \sqrt{D_x D_y}} W\left(u, \frac{r}{B}\right) \qquad \text{eq. D.3.10}$$

Where: f_m = continuous rate of contaminant injection per vertical unit aquifer [M/LT]

$$\gamma = 1 + 2\frac{B\lambda}{v_x}$$

$W\left(u, \frac{r}{B}\right)$ = Hantush Well Function

$$u = \frac{r^2}{4\gamma D_x t}$$

$$r = \sqrt{\left(x^2 + \frac{D_x y^2}{D_y}\right)\gamma}$$

$$B = 2\frac{D_x}{v_x}$$

Wilson and Miller (1978) give an approximate solution to the Hantush well function. This relationship is:

$$W\left(u,\frac{r}{B}\right) \approx \sqrt{\frac{\pi B}{2r}\exp\left(-\frac{r}{B}\right)erfc\left(-\frac{\frac{r}{B}-2u}{2\sqrt{u}}\right)} \qquad \text{eq. D.3.11}$$

This approximation is reasonably accurate (within 10 percent) for r/B>1, and more accurate (within 1 percent) for r/B>10 (Wilson and Miller, 1978).

D.3.4 THREE-DIMENSIONAL ANALYTICAL MODELS

Models presented in this section include a semi-infinite system with constant source of constant concentration and first-order decay of solute (Domenico, 1987) and a semi-infinite system with a decaying source and first-order decay of solute.

Equation D.1.5 is the three-dimensional partial differential equation describing transient solute transport with advection, dispersion, sorption, and first-order biodegradation in the saturated zone. For large values of time (when the system has reached steady state equilibrium), solute transport with advection, dispersion, sorption, and biodegradation is described by equation D.1.6. The biodegradation of BTEX compounds can commonly be approximated using first-order kinetics.

D.3.4.1 Continuous Source

Domenico (1987) developed an analytical solution for a finite (patch) source that incorporates one-dimensional groundwater velocity, longitudinal and transverse dispersion, and first-order decay. For transient conditions (equation D.1.5), the Domenico (1987) solution is given as:

$$C(x,y,z,t) = \frac{C_o}{8} \bullet \exp\left\{\frac{x}{2\alpha_x}\left(1-\sqrt{1+\frac{4\lambda R\alpha_x}{v_x}}\right)\right\} \bullet erfc\left[\frac{x - t\frac{v_x}{R}\sqrt{1+\frac{4\lambda R\alpha_x}{v_x}}}{2\sqrt{\alpha_x \frac{v_x}{R} t}}\right] \qquad \text{eq. D.3.12}$$

$$\bullet \left\{erf\left[\frac{y+\frac{Y}{2}}{2\sqrt{\alpha_y x}}\right] - erf\left[\frac{y-\frac{Y}{2}}{2\sqrt{\alpha_y x}}\right]\right\} \bullet \left\{erf\left[\frac{z+\frac{Z}{2}}{2\sqrt{\alpha_z x}}\right] - erf\left[\frac{z-\frac{Z}{2}}{2\sqrt{\alpha_z x}}\right]\right\}$$

Where $C(x,y,z,t)$ = contaminant concentration as a function of x,y,z, and t
C_o = initial dissolved contaminant concentration at boundary
x = distance downgradient of upgradient boundary
y = distance lateral to flow direction

z = vertical distance perpendicular to flow direction
Y = source dimension in y direction
Z = source dimension in z direction
t = time
D_x = longitudinal hydrodynamic dispersion
D_y = transverse hydrodynamic dispersion
D_z = vertical hydrodynamic dispersion
v_x = unretarded linear groundwater flow velocity
R = coefficient of retardation
λ = first-order decay rate constant for dissolved contaminant

For steady-state conditions this expression becomes (Domenico, 1987):

$$C(x,y,z,t) = \frac{C_o}{4} \bullet \exp\left\{\frac{x}{2\alpha_x}\left(1-\sqrt{1+\frac{4\lambda R\alpha_x}{v_x}}\right)\right\} \bullet \left\{erf\left[\frac{y+\frac{Y}{2}}{2\sqrt{\alpha_y x}}\right] - erf\left[\frac{y-\frac{Y}{2}}{2\sqrt{\alpha_y x}}\right]\right\} \bullet \left\{erf\left[\frac{z+\frac{Z}{2}}{2\sqrt{\alpha_z x}}\right] - erf\left[\frac{z-\frac{Z}{2}}{2\sqrt{\alpha_z x}}\right]\right\} \quad \text{eq. D.3.13}$$

Assumptions:

- Fluid is of constant density and viscosity
- Solute may be subject to first-order decay via biodegradation
- Flow is in the x-direction only, and velocity is constant
- The longitudinal dispersion, D_x, is constant
- Sorption is approximated by the linear sorption model.

D.3.4.2 Decaying Source

The change in concentration of a contaminant through time due to first-order decay is given by:

$$C(t) = C_o e^{-\gamma t} \quad \text{eq. D.3.14}$$

Where: $C(t)$ = Source concentration as a function of time
C_o = Initial source concentration
γ = First-order source decay rate constant

This relationship can be used to simulate a contaminant source that is undergoing remediation, either by engineered solutions or natural-weathering. Substituting the relationship for changing source concentration as a function of time C(t) for the constant initial concentration C_o in equation D.1.8 gives:

$$C(x,y,z,t) = \frac{C_o e^{-\gamma t}}{8} \bullet \exp\left\{\frac{x}{2\alpha_x}\left(1-\sqrt{1+\frac{4\lambda R\alpha_x}{v_x}}\right)\right\} \bullet erfc\left[\frac{x - t\frac{v_x}{R}\sqrt{1+\frac{4\lambda R\alpha_x}{v_x}}}{2\sqrt{\alpha_x \frac{v_x}{R} t}}\right] \qquad \text{eq. D.3.15}$$

$$\bullet \left\{erf\left[\frac{y+\frac{Y}{2}}{2\sqrt{\alpha_y x}}\right] - erf\left[\frac{y-\frac{Y}{2}}{2\sqrt{\alpha_y x}}\right]\right\} \bullet \left\{erf\left[\frac{z+\frac{Z}{2}}{2\sqrt{\alpha_z x}}\right] - erf\left[\frac{z-\frac{Z}{2}}{2\sqrt{\alpha_z x}}\right]\right\}$$

Where $C(x,y,z,t)$ = contaminant concentration as a function of x, y, z, and t
C_o = initial dissolved contaminant concentration at boundary
x = distance downgradient of upgradient boundary
y = distance lateral to flow direction
z = vertical distance perpendicular to flow direction
Y = source dimension in y direction
Z = source dimension in z direction
t = time
D_x = longitudinal hydrodynamic dispersion
D_y = transverse hydrodynamic dispersion
D_z = vertical hydrodynamic dispersion
v_x = unretarded linear groundwater flow velocity
R = coefficient of retardation
γ = first-order decay rate constant for contaminant source
λ = first-order decay rate constant for dissolved contaminant

Assumptions:

- Fluid is of constant density and viscosity
- Solute may be subject to first-order decay via biodegradation
- Source may be subject to first-order decay via weathering or engineered remediation
- Flow is in the x-direction only, and velocity is constant
- The longitudinal dispersion, D_x, is constant
- Sorption is approximated by the linear sorption model.

D.3.5 COMPUTER APPLICATIONS FOR ANALYTICAL MODELING

Depending upon the needs, resources, and skills of the modeler, analytical modeling can be performed using commonly available spreadsheets, mathematical analysis applications such as MathCAD®, or codes written expressly for analytical modeling. Use of spreadsheets requires the most effort on behalf of the modeler, owing to the need to set up the sheet, enter the appropriate

equations, and format the output. Mathematical analysis applications also require the user to enter the equations, but entering the equations and formatting the input and output can be much simpler and more intuitive than in a spreadsheet. However, once set up, both methods provide the modeler with a template that can be used repeatedly. For specific analytical modeling codes, the methods of input vary, as do the methods of displaying output. In general, though, these codes require the least amount of effort on behalf of the user.

A wide range of analytical solute transport modeling software is available. A partial list of codes is presented in Table D.3.4. Some of the codes are proprietary, and some are public domain. Proprietary codes often have graphical interfaces for processing input and output, resulting in a greater cost. Depending on the needs of the user, these extra costs may well be worth the time and labor for preparing and input and output that may be saved by using such a program. Other codes may be available; this is by no means an exhaustive list.

Table D.3.4

Listing of Analytical Solute Transport Models

Model Code Name	Capabilities	Distributor
AGU-10	Analytical flow, advective solute transport, advective-dispersive transport, and advective-dispersive transport with decay of source and solute. Based on American Geophysical Union's Water Resources Monograph 10 (Javandel *et al.*, 1984)	IGWMC; documentation includes AGU Monograph 10
AT123D	Based on analytical solution for transient one-, two-, or three-dimensional transport in a homogeneous isotropic aquifer with uniform regional flow. Allows for retardation, dispersion, and first-order decay, with differing source configurations and boundary conditions. Has a shell for pre- and post-processing. Authored by G.T. Yeh of Oak Ridge National Laboratories.	IGWMC
ONE-D	A package of five analytical solutions of the one-dimensional advective-dispersive transport equation with adsorption, dispersion, and first-order-decay options; also includes a zero-order production term. Written by M.T. van Genuchten and W.J. Alves of the US Department of Agriculture's Salinity Laboratory.	IGWMC
PLUME, PLUME2D	Analytical models for calculating point concentrations of solutes. Includes advection, dispersion, retardation, and first-order decay. Source terms can be varied over time (in discrete intervals). Written by P.K.M. van der Heijde of the IGWMC.	IGWMC

Table D.3.4 (concluded)

Listing of Analytical Solute Transport Models

Model Code Name	Capabilities	Distributor
PRINCE	A proprietary package of ten analytical solute transport and flow models, widely referred to as the Princeton Analytical Models. Seven solute transport models allow calculation of concentrations and breakthrough curves for one-, two-, and three-dimensional problem domains. Advection, dispersion, retardation, and first-order decay all can be simulated, along with a wide range of source terms (including multiple sources in two and three dimensions). A self-contained package with graphical user interface for pre- and post-processing.	Waterloo Hydrogeologic Software or IGWMC
SOLUTE	A menu-driven set of five different programs that provide the user with nine different types of analytical solute transport models. The nine models include one-, two-, and three-dimensional solutions with differing boundary conditions and options for retardation and first-order decay. Displays output graphically; output can also be used with other utilities for post-processing. Authored by M.S. Beljin and P.K.M. van der Heijde of IGWMC.	IGWMC
USGS-SOL	Analytical solutions describing advective-dispersive transport, as well as first-order decay and retardation. Includes one-, two-, and three-dimensional models with a limited number of boundary conditions. No pre-processor is provided, and the user must set up their own input files. Output can be sent to a file for use in other post-processors. Originally prepared by E.J. Wexler of the USGS.	IGWMC
WALTON35	A set of 35 analytical and numerical models for a variety of groundwater flow and solute transport problems. Input is interactive, and results can be saved to a file. Prepared by W.C. Walton in conjunction with the IGWMC.	IGWMC

SECTION D-4

NUMERICAL MODELS

D.4.1 OVERVIEW OF NUMERICAL MODELS

Numerical models provide inexact (relative to analytical methods) and, in some cases, nonunique solutions to the governing advection-dispersion equations presented in Section D-1. As with analytical models, the use of numerical models requires the user to make some simplifying assumptions about the solute transport system. However, fewer simplifying assumptions must be made, so numerical models can simulate more complex systems. Numerical model codes can be used to simulate complex hydrogeologic systems or contaminant transport affected by multiple reactions for which rates or properties may vary spatially. Heterogeneous and anisotropic hydrologic systems can be modeled using numerical models, as can transient flow systems (i.e., systems in which stresses, parameters, or boundary conditions affecting or controlling groundwater flow change over time). Another advantage of numerical models is that most codes are more flexible in allowing simulation of contaminant sources that vary over time, allowing more straightforward simulation of scenarios including source reduction through weathering or through engineered solutions. Section D-2 of this Appendix includes a more detailed discussion of specific topics relevant to numerical flow and transport modeling.

Success in groundwater solute fate and transport modeling using numerical methods depends upon the ability to properly conceptualize the processes governing contaminant transport, to select a model that simulates the most important processes at a site, and to understand the limitations of the solution methods and to and present model predictions that are reasonable within those limitations. When using a numerical transport model (and an associated flow model, if applicable), remember that implementation of a numerical model is much more complex than implementation of an analytical model, and generally requires at a minimum the supervision of an experienced hydrogeologist who is familiar with the model code. Also keep in mind the caveats regarding numerical flow and transport modeling that were presented in Section D.1.2. Keep in

Table D.4.1

Listing of Numerical Groundwater Flow and Solute Transport Models

Model Code Name	Capabilities	Distributor
AQUA	Two-dimensional, transient groundwater flow and transport. Aquifer may be heterogeneous and anisotropic, Can simulate advection, dispersion, linear sorption, and decay. A proprietary code with interactive/graphical interface.	Scientific Software Group
ASM	Aquifer Simulation Model for two-dimensional modeling of groundwater flow and solute transport. Uses random-walk method for solute transport, and can simulate advection, dispersion, linear sorption, and decay. Aquifer can be heterogeneous and anisotropic. Menu-driven, graphical interface. A proprietary program prepared by W. Kinzelbach (University of Heidelberg) and R. Rausch (University of Stuttgart).	IGWMC
BIO1D®	A one-dimensional model for simulation of biodegradation and sorption of hydrocarbons. Transport of substrates and electron acceptors is considered, assuming a uniform flow field. Several reaction options are available for biodegradation and sorption. Has a pre-processor and display graphics. A proprietary code developed at GeoTrans, Inc.	GeoTrans, Inc.; IGWMC
Bioplume II	A two-dimensional model for simulating transport of a single dissolved hydrocarbon species under the influence of oxygen-limited biodegradation, first-order decay, linear sorption, advection, and dispersion. Aquifer may be heterogeneous and anisotropic. Based on the USGS two-dimensional MOC model (including a finite-difference flow model) by Konikow and Bredehoeft (1978). Oxygen limited biodegradation is a reactive transport process. A public-domain code with a menu-driven preprocessor and limited post-processing abilities. Developed by Rifai *et al.* (1989) at Rice University.	IGWMC

Table D.4.1 (continued)

Listing of Numerical Groundwater Flow and Solute Transport Models

Model Code Name	Capabilities	Distributor
Bioplume III	Successor to Bioplume II. Two-dimensional model for reactive transport of multiple hydrocarbons under the influence of advection, dispersion, sorption, first-order decay, and reactant-limited biodegradation. Development commissioned by AFCEE. Anticipated release in late 1996. Will have interactive, graphical pre- and post-processing capabilities.	AFCEE (currently under development)
BioTrans®	A proprietary two-dimensional finite element transport code requiring flow velocity data from another code (e.g., MODFLOW). Models transport of multiple species under the influence of advection, dispersion, sorption, first-order decay, and oxygen-limited biodegradation. Allows internal computation of source terms due to dissolution of NAPL. Graphical, interactive user interface with pre- and post-processing capabilities. Prepared by Environmental Systems and Technologies, Inc.	Environmental Systems and Technologies, Inc.
FEMSEEP	A set of programs for solving steady-state and transient groundwater flow and solute transport problems in simplified two- and three-dimensional systems. Transport under the influence of advection, dispersion, linear sorption, and first-order decay may be simulated using finite element methods. A proprietary program with graphical and menu-driven user interfaces and pre- and post-processing capabilities. Prepared by D. Meiri of FEMSEEP Software, Inc.	FEMSEEP Software, Inc.; IGWMC

Table D.4.1 (continued)

Listing of Numerical Groundwater Flow and Solute Transport Models

Model Code Name	Capabilities	Distributor
FEMWATER, FEMWASTE	Finite-element flow (FEMWATER) and transport (FEMWASTE) models. FEMWATER can simulate variably saturated conditions in two and three dimensions. FEMWASTE can simulate transport in one, two, and three dimensions. The system may be heterogeneous and anisotropic, and the code can account for advection, dispersion, first-order decay, and 3 types of sorption. Public domain codes developed by researchers at Oak Ridge, National Laboratories. Some proprietary versions of FEMWATER are available; they are based on the Department of Defense's Groundwater Modeling System (GMS) modeling and data management package.	Oak Ridge National Laboratories, NTIS, distributors of proprietary GMS programs.
FLONET®, FLOTRANS®	Two-dimensional steady-state groundwater flow (FLONET) and transient solute transport (FLOTRANS) models for cross-sectional problems. FLOTRANS is an extension of FLONET that can simulate transport under the influence of advection, dispersion, linear sorption, and first-order decay. A proprietary program with an interactive graphical user interface and extensive pre- and post-processing capabilities. Developed by Waterloo Hydrogeologic Software, Inc.	IGWMC; Waterloo Hydrogeologic Software, Inc.
FTWORK	A block-centered finite-difference model for one, two, and three-dimensional flow and transport. The transport model includes advection, dispersion, first-order decay, and two types of sorption (linear and non-linear equilibrium). A public domain code that may be acquired with a proprietary (IGWMC) textual and menu-driven preprocessor and post-processor. Originally developed by Faust *et al.* (1990) at GeoTrans, Inc.	IGWMC; GeoTrans, Inc.

Table D.4.1 (continued)

Listing of Numerical Groundwater Flow and Solute Transport Models

Model Code Name	Capabilities	Distributor
HST3D	Program for simulating groundwater flow and associated heat and solute transport in three dimensions. Solute transport is for a single solute with advection, dispersion, linear sorption, and first-order decay. A public-domain code with no pre- and post-processors. Prepared by K.L. Kipp of the USGS.	IGWMC
MOC, USGS2D-MOC	A two-dimensional model for simulation of groundwater flow and non-conservative solute transport. Derived from the original model developed by Konikow and Bredehoeft (1978). The latest version (March 1995) simulates transport under the influence of advection, dispersion, first-order decay, reversible equilibrium-controlled sorption, and reversible equilibrium-controlled ion exchange. The flow model is a finite-difference model, while transport is simulated using MOC methods. A public-domain code with an interactive preprocessor.	IGWMC
MODFLOW	A block-centered finite-difference code for steady-state and transient simulation of groundwater flow in two and three dimensions. Consists of a main program and a large number of subroutines (modules) that are used to simulate a wide variety of boundaries and stresses on the hydrogeologic system. Originally coded by McDonald and Harbaugh (1988) of the USGS. Possibly the most widely used flow model in the US and Canada, MODFLOW can be used to generate flow fields that may be coupled with a wide variety of transport models (e.g., MT3D, BioTrans®, or RAND3D). The popularity of MODFLOW is also evidenced by the great number of proprietary pre- and post-processing programs that are available. MODFLOW is a public-domain code, although it is typically acquired in conjunction with a pre-/post-processing package.	USGS; IGWMC; in addition, many companies have developed pre- and post-processing programs with a wide variety of capabilities and features.

Table D.4.1 (continued)

Listing of Numerical Groundwater Flow and Solute Transport Models

Model Code Name	Capabilities	Distributor
MODFLOWP	An extension of MODFLOW that includes a package that uses nonlinear regression techniques to estimate model parameters under constraints given by the modeler. Model input includes statistics for analyzing the parameter estimates and the model to quantify the reliability of the resulting model, to suggest changes in model construction, and to compare results of models constructed in different ways. Prepared by M.C. Hill of the USGS. Requires a user with advanced skills.	USGS; IGWMC
MT3D	A three-dimensional transport model for simulation of advection, dispersion, linear or non-linear sorption, and first-order decay of a single species. Uses a modular structure similar to that of MODFLOW. Intended for use with any block-centered finite-difference flow model, such as MODFLOW, on the assumption that concentration changes will not affect the flow field. MT3D uses one of three methods (all based on MOC) for solution of the transport equation. Prepared by C. Zheng (for S.S. Papadopulos & Associates, Inc.), MT3D is available in public-domain and proprietary versions. Proprietary versions are typically the most advanced in terms of pre- and post-processing capabilities.	S.S. Papadopulos & Associates, Inc.; IGWMC; many versions available from many companies with pre- and post-processing programs with a wide variety of capabilities and features. Often coupled with MODFLOW in such codes. Public domain version may be acquired from USEPA.
RANDOM WALK	A code for simulation of two-dimensional groundwater flow and solute transport. Flow is simulated using either analytical solutions or a version of the PLASM finite-difference model (Prickett and Lonnquist, 1971). Transport is simulated using particle-tracking methods coupled with the random-walk technique for dispersion. The model also handles first-order decay, linear sorption, and zero-order production. A public domain code originally produced at the Illinois State Water Survey (Prickett *et al.*, 1981). The IGWMC version includes pre- and post-processing utilities.	IGWMC

Table D.4.1 (continued)

Listing of Numerical Groundwater Flow and Solute Transport Models

Model Code Name	Capabilities	Distributor
RAND3D	A three-dimensional version of the random walk algorithm developed by Prickett *et al.* (1981). RAND3D is designed to be coupled with MODFLOW input files for calculation of velocity vector files that are used to run the code. May be used for transient simulation of advection, dispersion, linear sorption, and zero-order, first-order, or variable-order-decay. Code has some pre- and post-processing capabilities. A proprietary code prepared by D. Koch of Engineering Technologies Associates and T.A. Prickett.	IGWMC
SUTRA	A code for simulating two-dimensional fluid movement and transport of energy or dissolved substances. May be used for saturated systems or variably saturated systems in profile view. Can simulate advection, dispersion, sorption, and first-order decay. A public-domain code originally prepared by C.I. Voss of the USGS. IGWMC version has a graphical post-processor.	IGWMC; USGS
SWICHA	A three-dimensional finite-element code for simulating steady-state and transient flow and transport in confined (fully saturated) aquifers. Transport includes advection, dispersion, sorption, and first-order decay. A public domain code with no pre- or post-processing capabilities. Authored by B. Lester of GeoTrans, Inc.	IGWMC
SWIFT, SWIFT/486	A fully three-dimensional finite-difference model for simulating flow and transport of fluid, heat, and solutes in porous and fractured media. Includes linear and nonlinear sorption, dispersion, diffusion, and decay, as well as dissolution, leaching, and dual porosity. An advanced code developed at Sandia National Laboratories (Reeves and Cranwell, 1981); now in the custody of GeoTrans, Inc. Public domain and proprietary versions of the code are available through IGWMC.	IGWMC

Table D.4.1 (concluded)

Listing of Numerical Groundwater Flow and Solute Transport Models

Model Code Name	Capabilities	Distributor
SWMS_2D	A two-dimensional model for simulating water and solute movement in variably saturated media. Includes dispersion, linear sorption, zero-order production, and first-order decay. A public domain code prepared by researchers at the US Salinity Lab. No pre- or post-processing utilities.	IGWMC
TARGET	A code for simulating two- and three-dimensional flow and transport under a wide variety of conditions. Can simulate advection, dispersion, diffusion, sorption, and first-order decay. A proprietary code prepared by workers at Dames & Moore, Inc. Has been used for a wide variety of applications.	Dames & Moore, Inc.

APPENDIX E

NATURAL ATTENUATION OF CHLORINATED ALIPHATIC HYDROCARBONS AT PLATTSBURGH AIR FORCE BASE, NEW YORK

NATURAL ATTENUATION OF CHLORINATED ALIPHATIC HYDROCARBONS AT PLATTSBURGH AIR FORCE BASE, NEW YORK

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INTRODUCTION

Activities at a former fire training area (Site FT-002) at Plattsburgh Air Force Base (AFB) in New York resulted in contamination of shallow soils and groundwater with a mixture of chlorinated solvents and fuel hydrocarbons. Groundwater contaminants include trichloroethene (TCE), *cis*-1,2-dichloroethene (*cis*-1,2-DCE), vinyl chloride, and benzene, toluene, ethylbenzene, and xylenes (BTEX). Table 1 contains contaminant data for selected wells at the site.

Table 1
Analytical Data, Plattsburgh Air Force Base

Point	Date	Distance From Source (feet)	TMB (µg/L)	BTEX (ug/L)	TCE (µg/L)	Total DCE* (µg/L)	Vinyl Chloride (µg/L)	Methane (µg/L)	Ethene (µg/L)	Chloride (mg/L)	Dissolved Oxygen (mg/L)	Nitrate (mg/L)	Iron (II) (mg/L)	Sulfate (mg/L)	Hydrogen (nanomolar)	TOC (mg/L)
A	Aug-95	0	1,757	16,790	25,280	51,412	0	1,420	<0.001	63	0.1	0.2	4.0	5.5	6.70	80
	May-96		828	6,598	580	12,626	0	1,600	<0.001	82	0.5	0.0	45.6	1.0	2.00	94
B	Aug-95	970	491	3,060	2	14,968	897	305	35.00	48	0.5	0.2	15.3	0.0	1.66	30
	May-96		463	4,198	1	9,376	1,520	339	13.00	43	0.1	0.0	16.0	0.0	1.40	31
C	Aug-95	1,240	488	3,543	3	10,035	1,430	1,010	182.00	46	0.4	0.2	13.8	0.0	NA	21
	May-96		509	3,898	1	10,326	1,050	714	170.00	57	0.2	0.0	19.3	0.0	11.13	24
D	Aug-95	2,050	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	May-96		9	89	0	1,423	524	617	4.00	14	0.2	0.1	2.5	1.5	NA	14
E	Aug-95	2,560	0	40	24	2,218	8	3,530	<0.001	20	0.9	0.3	0.7	0.5	NA	8
	May-96		0	40	17	1,051	12	1,800	<0.001	18	0.1	0.0	0.0	1.0	0.81	8
F	Aug-95	3,103	0	2	1	226	5	115	<0.001	3	0.4	10.4	0.0	14.7	0.22	NA
	May-96		0	2	0	177	4	44	<0.001	3	0.2	9.5	0.1	14.4	0.25	NA

* Greater than 99 percent of DCE is *cis*-1,2-DCE
NA = Not analyzed
Point A=MW-02-108, B=MW-02-310, C=84DD, D=84DF, E=34PLTW12, F=35PLTW13

Contaminant plumes formed by chlorinated aliphatic hydrocarbons (CAHs) dissolved in groundwater can exhibit three types of behavior based on the amount and type of primary substrate present in the aquifer. Type 1 behavior occurs where anthropogenic carbon such as BTEX or landfill leachate is being utilized as the primary substrate for microbial degradation. Such plumes typically are anaerobic, and the reductive dechlorination of highly chlorinated CAHs introduced into such a system can be quite rapid. Type 2 behavior occurs in areas that are characterized by high natural organic carbon concentrations and anaerobic conditions. Under these conditions, microorganisms utilize the natural organic carbon as a primary substrate and, if redox conditions are favorable, highly chlorinated CAHs introduced into this type of system will be reductively dechlorinated. Type 3 behavior occurs in areas characterized by low natural organic carbon concentrations, low anthropogenic carbon concentrations, and aerobic or weakly reducing conditions. Biodegradation of CAHs via reductive dechlorination will not occur under these conditions. However, biodegradation of the less chlorinated compounds, such as vinyl chloride can occur via oxidation.

Plattsburgh AFB is located in northeastern New York State, approximately 26 miles south of the Canadian border and 167 miles north of Albany, New York. Site FT-002 is located in the northwest corner of the base and is approximately 700 feet wide and 800 feet long. The site is located on a land surface that slopes gently eastward toward the confluence of the Saranac and the Salmon Rivers, which is located approximately 2 miles east of the

site. Site FT-002 was used to train base and municipal fire-fighting personnel from the mid- to late-1950s until the site was permanently closed to fire training activities in May 1989. Figure 1 is a map of the site.

Four distinct stratigraphic units underlie the site: sand, clay, till, and carbonate bedrock. Figure 2 shows three of the four stratigraphic units at the site. The sand unit consists of well-sorted, fine- to medium-grained sand with a trace of silt and generally extends from ground surface as much as 90 feet below ground surface (bgs) in the vicinity of the site. A 7-foot-thick clay unit has been identified on the eastern side of the site. The thickness of the clay on the western side of the site has not been determined. A 30- to 40-foot-thick clay till unit is also present from 80 to 105 feet bgs in the vicinity of the site. Bedrock is located approximately 105 feet bgs.

GROUNDWATER HYDRAULICS

The depth to groundwater in the sand aquifer ranges from 45 feet bgs on the west side of the site to zero on the east side of the runway, where groundwater discharges to a swamp (Figure 2). Groundwater flow at the site is to the southeast. The average gradient is approximately 0.010 foot per foot (ft/ft). Hydraulic conductivity of the upper sand aquifer was measured using constant drawdown tests and rising head tests. Hydraulic conductivity values for the unconfined sand aquifer underlying the site range from 0.059 to 90.7 feet per day (ft/day). The average hydraulic conductivity for the site is 11.6 ft/day. Freeze and Cherry (1979) give a range of effective porosity for sand of 0.25 to 0.50. Effective porosity was assumed to be 0.30. Using the horizontal gradient of 0.010 ft/ft, the average hydraulic conductivity value of 11.6 ft/day, and an effective porosity of 0.30 yields an average advective groundwater velocity for the unconfined sand aquifer of 0.39 ft/day, or approximately 142 ft/year. Because of low background total organic carbon concentrations at the site, retardation is not considered to be an important transport parameter.

GROUNDWATER AND LNAPL CHEMISTRY

Contaminants

Figure 1 shows the approximate distribution of light non-aqueous phase liquid (LNAPL) at the site. This LNAPL is a mixture of jet fuel and waste solvents that partitions BTEX and TCE to groundwater. Analysis of this LNAPL shows that the predominant chlorinated solvents are PCE and TCE; dichloroethene (DCE) and vinyl chloride are not present in measurable concentrations. For the most part, groundwater beneath and downgradient from the LNAPL is contaminated with dissolved fuel-related compounds and solvents consistent with those identified in the LNAPL. The most notable exceptions are the presence of *cis*-1,2-DCE and vinyl chloride, which, because of their absence in the LNAPL, probably were formed by reductive dechlorination of TCE.

The dissolved BTEX plume currently extends approximately 2,000 feet downgradient from the site, and has a maximum width of about 500 feet. Total dissolved BTEX concentrations as high as 17 milligrams per liter (mg/L) have been observed in the source area. Figure 3 shows the extent of BTEX dissolved in groundwater. As indicated on this map, dissolved BTEX contamination is migrating to the southeast in the direction of groundwater flow. Five years of historical data for the site shows that the dissolved BTEX plume is at steady-state equilibrium and is no longer expanding.

Detectable concentrations of dissolved TCE, DCE, and vinyl chloride currently extend approximately 4,000 feet downgradient from FT-002. Concentrations of TCE, DCE, and vinyl chloride as high as 25 mg/L, 51 mg/L and 1.5 mg/L, respectively, have been observed at the site. As stated previously, no DCE was detected in the LNAPL plume at the site and greater than 99 percent of the DCE found in groundwater is the *cis*-1,2-DCE isomer. Figure 3 shows the extents of CAH compounds dissolved in groundwater at the site. As indicated on this map, contamination is migrating to the southeast in the direction of groundwater flow. Five years of historical data for the site shows that the dissolved CAH plume is at steady-state equilibrium and is no longer expanding.

Indicators of Biodegradation

Figure 4 shows the distribution of electron acceptors used in microbially mediated oxidation-reduction reactions. Electron acceptors displayed in this figure include dissolved oxygen, nitrate, and sulfate. There is a strong correlation between areas with elevated BTEX concentrations and areas with depleted dissolved oxygen, nitrate, and sulfate. The absence of these compounds in contaminated groundwater suggests that aerobic respiration, denitrification, and sulfate reduction are working to biodegrade fuel hydrocarbons at the site.

Background dissolved oxygen, nitrate, and sulfate concentrations are on the order of 10 mg/L, 10 mg/L, and 25 mg/L, respectively.

Figure 5 shows the distribution of metabolic byproducts produced by microbially mediated oxidation-reduction reactions that biodegrade fuel hydrocarbons. Metabolic byproducts displayed in this figure include iron (II) and methane. There is a strong correlation between areas with elevated BTEX concentrations and areas with elevated iron (II) and methane. The presence of these compounds in concentrations above background in contaminated groundwater suggests that iron (III) reduction and methanogenesis are working to biodegrade fuel hydrocarbons at the site. Background iron (II) and methane concentrations are <0.05 mg/L and <0.001 mg/L, respectively. The pE of groundwater is shown in Figure 5. Areas of low pE correspond to areas with contamination. This is an indication that biologically mediated oxidation-reduction reactions are occurring in the area with groundwater contamination.

The distribution of chloride in groundwater is shown in Figure 3. This figure also compares measured concentrations of total BTEX and CAHs in the groundwater with chloride. There is a strong correlation between areas with contamination and areas with elevated chloride concentrations relative to measured background concentrations. The presence of elevated concentrations of chloride in contaminated groundwater suggests that TCE, DCE, and vinyl chloride are being biodegraded. Background chloride concentrations at the site are approximately 2 mg/L. The distribution of ethene in groundwater is shown in Figure 3. This figure also compares measured concentrations of total BTEX and CAHs in the groundwater with ethene. There is a strong correlation between areas with contamination and areas with elevated ethene concentrations relative to measured background concentrations. The presence of elevated concentrations of ethene in contaminated groundwater suggests that TCE, DCE, and vinyl chloride are being biodegraded. Background ethene concentrations at the site are <0.001 mg/L.

Dissolved hydrogen concentrations can be used to determine the dominant terminal electron-accepting process in an aquifer. Table 2 presents the range of hydrogen concentrations for a given terminal electron-accepting process. Much research has been done on the topic of using hydrogen measurements to delineate terminal electron-accepting processes (Lovley and Goodwin, 1988; Lovley *et al.*, 1994; and Chapelle *et al.*, 1995). Table 1 presents hydrogen data for the site.

Table 2

Range of Hydrogen Concentrations for a Given Terminal Electron-Accepting Process

Terminal Electron Accepting Process	Hydrogen Concentration (nanomoles per liter, nM)
Denitrification	< 0.1
Iron (III) Reduction	0.2 to 0.8
Sulfate Reduction	1 to 4
Methanogenesis	> 5

BIODEGRADATION RATE CONSTANT CALCULATIONS

Apparent biodegradation rate constants were calculated using the method presented in Wiedemeier *et al.*, (1995 and 1996) for trimethylbenzene. A modified version of this method that takes into account the production of chloride during biodegradation also was used to calculate approximate biodegradation rates. Table 3 presents the results of these rate constant calculations.

PRIMARY SUBSTRATE DEMAND FOR REDUCTIVE DECHLORINATION

In order for reductive dechlorination to occur, a carbon source that can be used as a primary substrate must be present in the aquifer. This carbon substrate can be in the form of anthropogenic carbon (e.g., fuel hydrocarbons) or native organic material.

Table 3

Approximate First-Order Biodegradation Rate Constants

Compound	Correction Method	A - B 0 - 970 ft (1/year)	B - C 970 - 1,240 ft (1/year)	C - E 1,240 - 2,560 ft (1/year)
TCE	Chloride	1.27	0.23	-0.30
	TMB	1.20	0.52	N/A
	Average	1.24	0.38	-0.30
DCE	Chloride	0.06	0.60	0.07
	TMB	0.00	0.90	N/A
	Average	0.03	0.75	0.07
VC	Chloride	0.00	0.14	0.47
	TMB	0.00	0.43	N/A
	Average	0.00	0.29	0.47
BTEX	Chloride	0.13	0.30	0.39
	TMB	0.06	0.60	N/A
	Average	0.10	0.45	0.39

Reductive Dechlorination Supported by Fuel Hydrocarbons (Type 1 Behavior)

Fuel hydrocarbons are known to support reductive dechlorination in aquifer material (Sewell and Gibson, 1991). The equation below describes the oxidation of BTEX compounds (approximated as CH) to carbon dioxide during reduction of carbon to chlorine bonds (represented as C-Cl) to carbon to hydrogen bonds (represented as (C-H).

$$CH + 2H_2O + 2.5C\text{-}Cl \rightarrow CO_2 + 2.5H^+ + 2.5Cl^- + 2.5C\text{-}H \qquad \text{eq. (1)}$$

Based on equation (1), each 1.0 milligram (mg) of BTEX that is oxidized via reductive dechlorination requires the consumption of 6.8 mg of organic chloride and the liberation of 6.8 mg of biogenic chloride. Trichloroethene loses two C-Cl bonds while being reduced to vinyl chloride. Based on equation (1), ½ x 2.5 = 1.25 moles of TCE would have to be reduced to vinyl chloride to oxidize one mole of BTEX to carbon dioxide. Therefore, 1.0 mg of BTEX oxidized would consume 12.6 mg of TCE. If DCE were reduced to vinyl chloride, each 1.0 mg of BTEX oxidized would consume 18.6 mg of DCE. To be more conservative, these calculations should be completed assuming that TCE and DCE are reduced to ethene. However, because the amount of ethene produced is trivial compared to the amount of TCE and DCE destroyed, we have omitted this step here.

Reductive Dechlorination Supported by Natural Organic Carbon (Type 2 Behavior)

Wershaw *et al.*, (1994) analyzed dissolved organic material in groundwater underneath a dry well that had received TCE discharged from the overflow pipe of a degreasing unit. The dissolved organic material in groundwater exposed to the TCE was 50.57 percent carbon, 4.43 percent hydrogen, and 41.73 percent oxygen. The elemental composition of this material was used to calculate an empirical formula for the dissolved organic matter, and to estimate the number of moles of C-Cl bonds required to reduce one mole of dissolved organic carbon in this material.

$$C_{1.0}H_{1.051}O_{0.619} + 1.38H_2O + 1.91C\text{-}Cl \rightarrow CO_2 + 1.91Cl^- + 1.91C\text{-}H + 1.91H^+ \qquad \text{eq. (2)}$$

Based on equation (2), each 1.0 milligram (mg) of dissolved organic carbon that is oxidized via reductive dechlorination requires the consumption of 5.65 mg of organic chloride and the liberation of 5.65 mg of biogenic chloride. Using equation (2), ½ x 1.91 = 0.955 moles of TCE would have to be reduced to vinyl chloride to oxidize one mole of organic carbon to carbon dioxide. Therefore, 1.0 mg of organic carbon oxidized would consume 10.5 mg of TCE. If DCE were reduced to vinyl chloride, each 1.0 mg of organic carbon oxidized would consume 15.4 mg of DCE.

Table 4 compares the electron donor demand required to dechlorinate the alkenes remaining in the plume with the supply of potential electron donors. Table 3 reveals that removal of TCE and *cis*-1,2-DCE slows or ceases between points C and E. This correlates with the exhaustion of BTEX in the plume. Over this interval, the supply

of BTEX is a small fraction of the theoretical demand required for dechlorination. There are adequate supplies of native organic matter, suggesting that native organic matter may not be of sufficient nutritional quality to support reductive dechlorination in this aquifer.

Table 4

Comparison of the Estimated Electron Donor Demand to Support
Reductive Dechlorination to the Supply of BTEX and Native Organic Carbon

Point	Chloride (mg/L)	Organic Chloride (mg/L)	BTEX Available (mg/L)	BTEX Demand (mg/L)	Total Organic Carbon Supply (mg/L)	Organic Carbon Demand (mg/L)
A	63	58.1	16.8	8.5	80.4	10.3
B	43	7.72	4.2	1.13	31.1	1.37
C	57	8.26	3.9	1.21	24.3	1.46
D	13.6	1.34	0.09	0.20	13.8	0.24
E	18.4	0.78	0.04	0.114	8.2	0.14

DISCUSSION AND CONCLUSIONS

Available geochemical data indicate that the geochemistry of groundwater in the source area and about 1,500 feet downgradient is significantly different than the groundwater found between 1,500 and 4,000 feet downgradient from the source. Near the source the plume exhibits Type 1 behavior. At about 1,500 feet downgradient from the source, the plume reverts to Type 3 behavior. Figure 6 shows the zones of differing behavior at the site.

Type 1 Behavior

In the area extending to approximately 1,500 feet downgradient from the former fire training pit (source area), the dissolved contaminant plume consists of commingled BTEX and TCE and is characterized by anaerobic conditions that are strongly reducing (i.e., Type 1 behavior). Dissolved oxygen concentrations are on the order of 0.1 mg/L (background = 10 mg/L), nitrate concentrations are on the order of 0.1 mg/L (background = 10 mg/L), iron (II) concentrations are on the order of 15 mg/L (background = <0.05 mg/L), sulfate concentrations are < 0.05 mg/L (background = 25 mg/L), and methane concentrations are on the order of 3.5 mg/L (background = <0.001 mg/L). Hydrogen concentrations in the source area range from 1.4 to 11 nanomolar (nM). As shown by Table 2, these hydrogen concentrations are indicative of sulfate reduction and methanogenesis, even though there is no sulfate available and relatively little methane is produced. Thus, reductive dechlorination may be competitively excluding these processes. In this area BTEX is being used as a primary substrate and TCE is being reductively dechlorinated to *cis-1,2*-DCE and vinyl chloride. This is supported by the fact that no detectable DCE or vinyl chloride was found in the LNAPL present at the site and is strong evidence that the DCE and vinyl chloride found at the site are produced by the biogenic reductive dechlorination of TCE. Furthermore, the dominant isomer of DCE found at the site is *cis*-1,2-DCE, the isomer preferentially produced during reductive dechlorination. Average calculated first-order biodegradation rate constants in this zone are as high as 1.24/year, 0.75/year, and 0.29/year for TCE, *cis-1,2*-DCE, and vinyl chloride, respectively. Figure 6 shows the approximate extent of this type of behavior. Because reductive dechlorination of vinyl chloride is slower than direct oxidation, vinyl chloride and ethene are accumulating in this area (Figure 7).

Type 3 Behavior

Between 1,500 and 2,000 feet downgradient from the source area, the majority of the BTEX has been biodegraded and the system begins to exhibit Type 3 behavior. Dissolved oxygen concentrations are on the order of 0.5 mg/L (background = 10 mg/L). Nitrate concentrations start increasing downgradient of where Type 3 behavior begins and are near background levels of 10 mg/L at the downgradient extent of the CAH plume. Iron (II) concentrations have significantly decreased and are on the order of 1 mg/L (background = <0.05 mg/L). Sulfate concentrations start increasing to 15 mg/L at the downgradient extent of the CAH plume. Methane concentrations are the highest in this area but could have migrated from upgradient locations. The hydrogen concentrations at points E and F are 0.8 nM and 0.25 nM, respectively, suggesting that the dominant terminal

electron-accepting process in this area is iron (III) reduction. These conditions are not optimal for reductive dechlorination and it is likely that vinyl chloride is being oxidized via iron (III) reduction or aerobic respiration. Average calculated rate constants in this zone are -0.3/year, 0.07/year, and 0.47/year for TCE, *cis-1,2*-DCE, and vinyl chloride, respectively. The biodegradation rates of TCE and DCE slow because reductive dechlorination stops when the plume runs out of primary substrate (i.e., BTEX). The rate of vinyl chloride biodegradation in this area increases, likely because vinyl chloride is being oxidized. Because biodegradation of vinyl chloride is faster under Type 3 geochemical conditions than the biodegradation of other CAH compounds, the accumulation of vinyl chloride ceases and the accumulated vinyl chloride rapidly degrades. Ethene concentrations also begin to decrease because ethene is no longer being produced from the reductive dechlorination of vinyl chloride (Figure 7).

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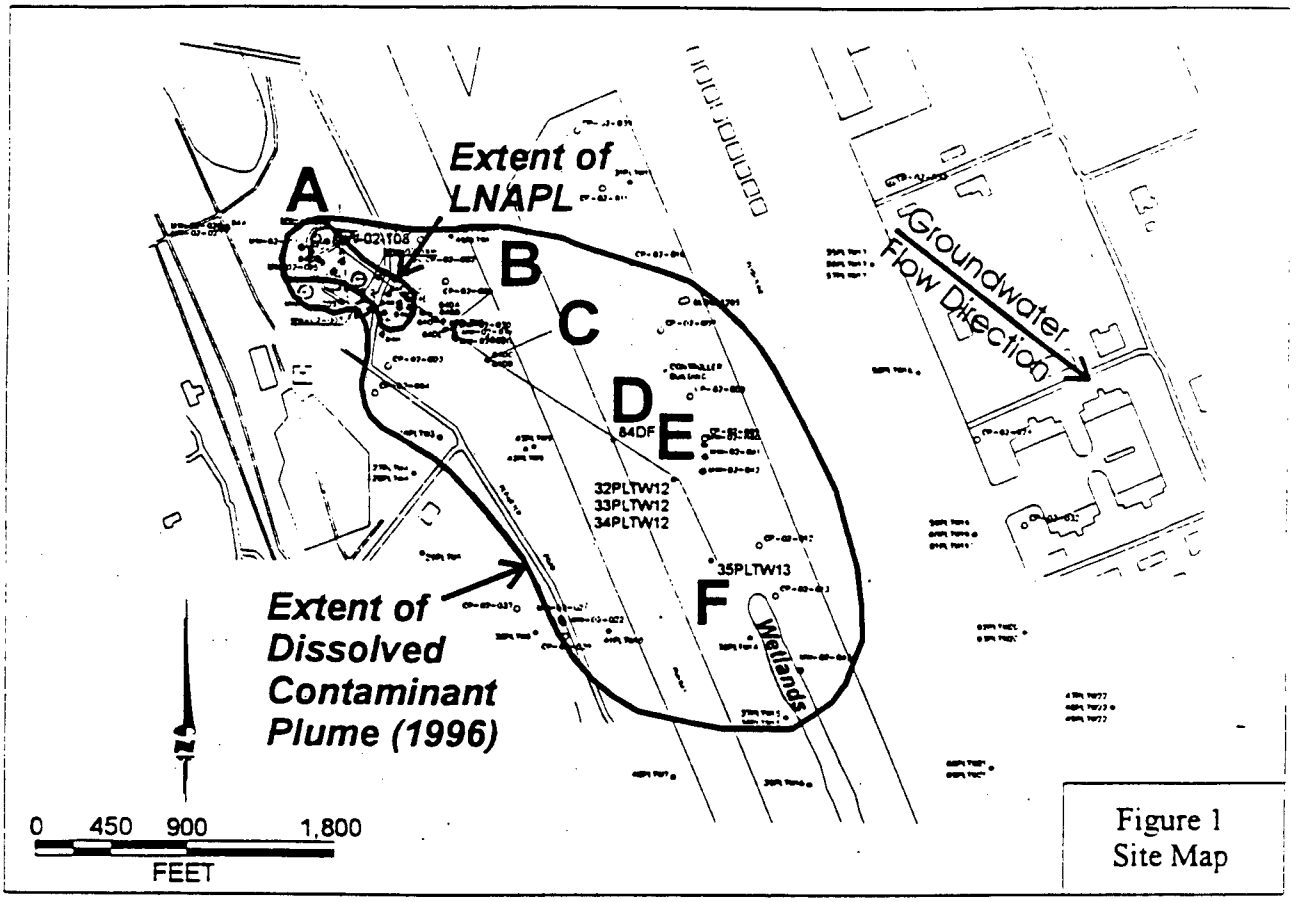

Figure 1
Site Map

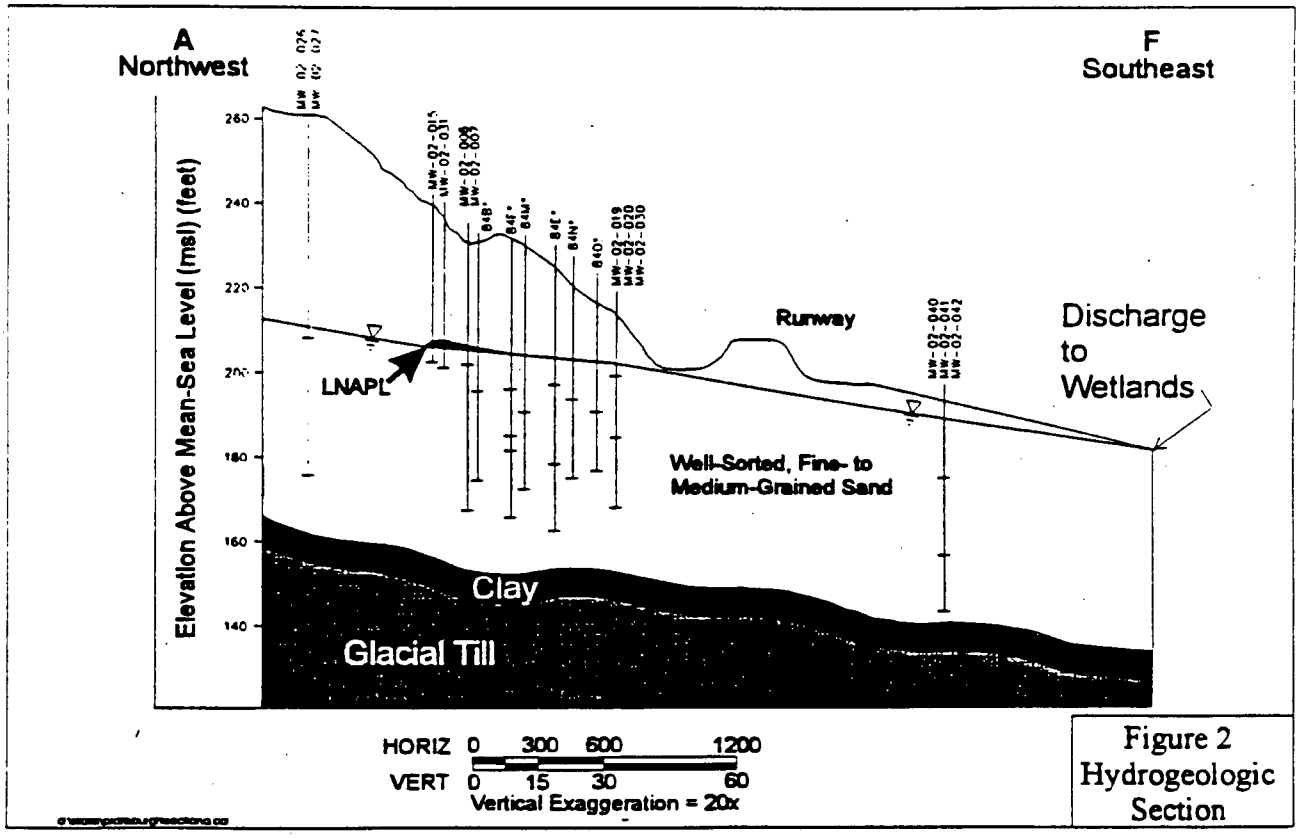

Figure 2
Hydrogeologic Section

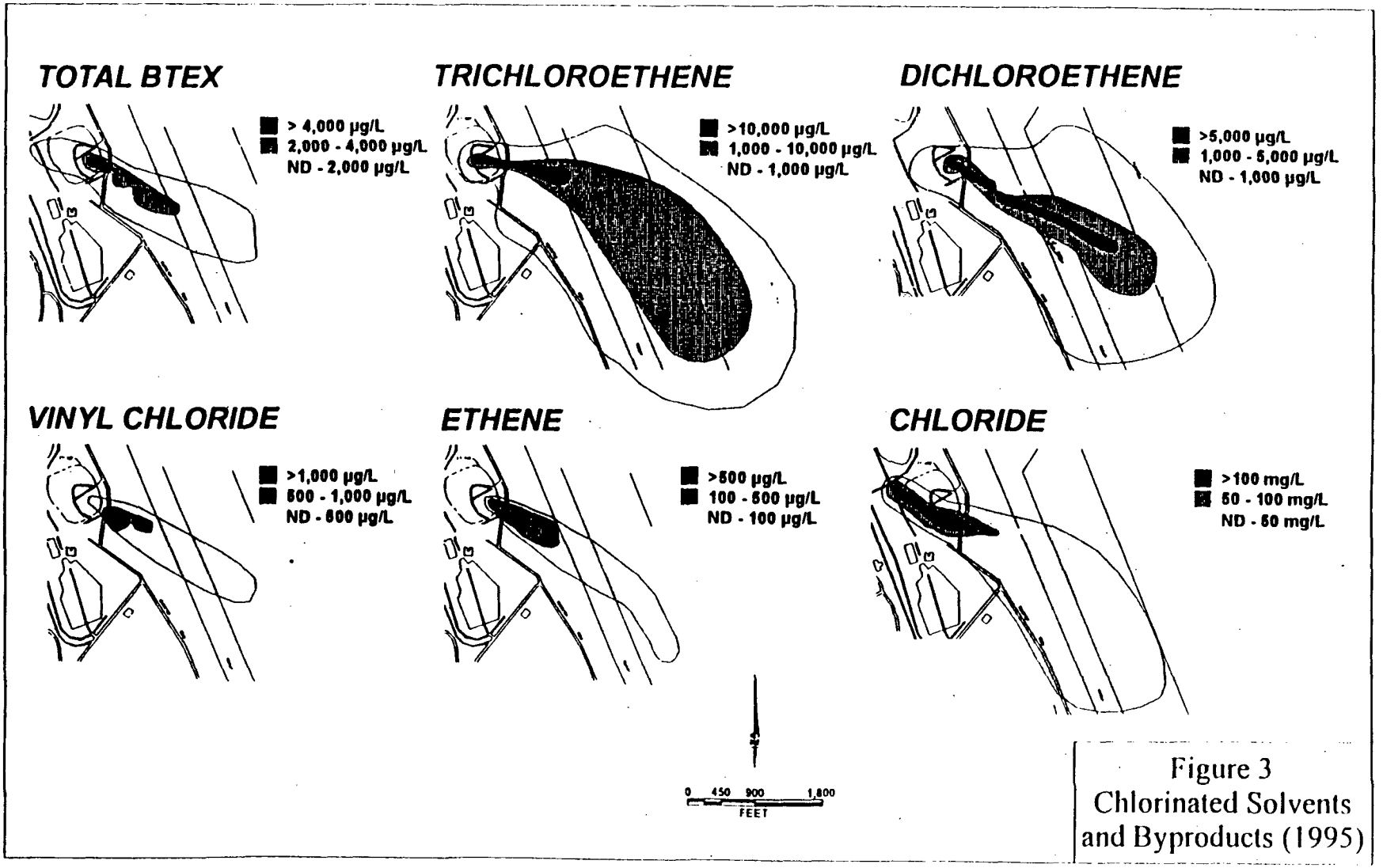

Figure 3
Chlorinated Solvents
and Byproducts (1995)

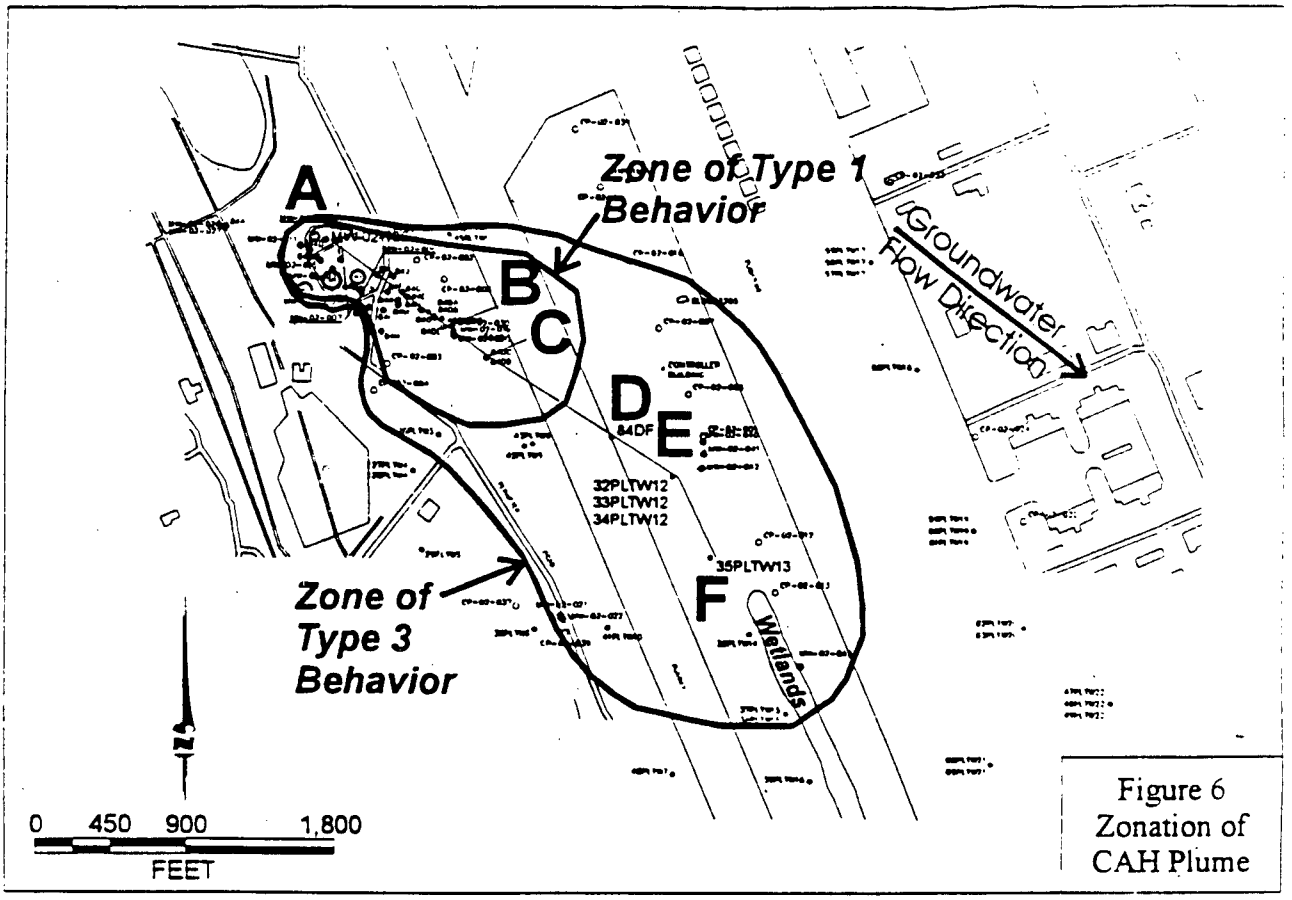

Figure 6
Zonation of CAH Plume

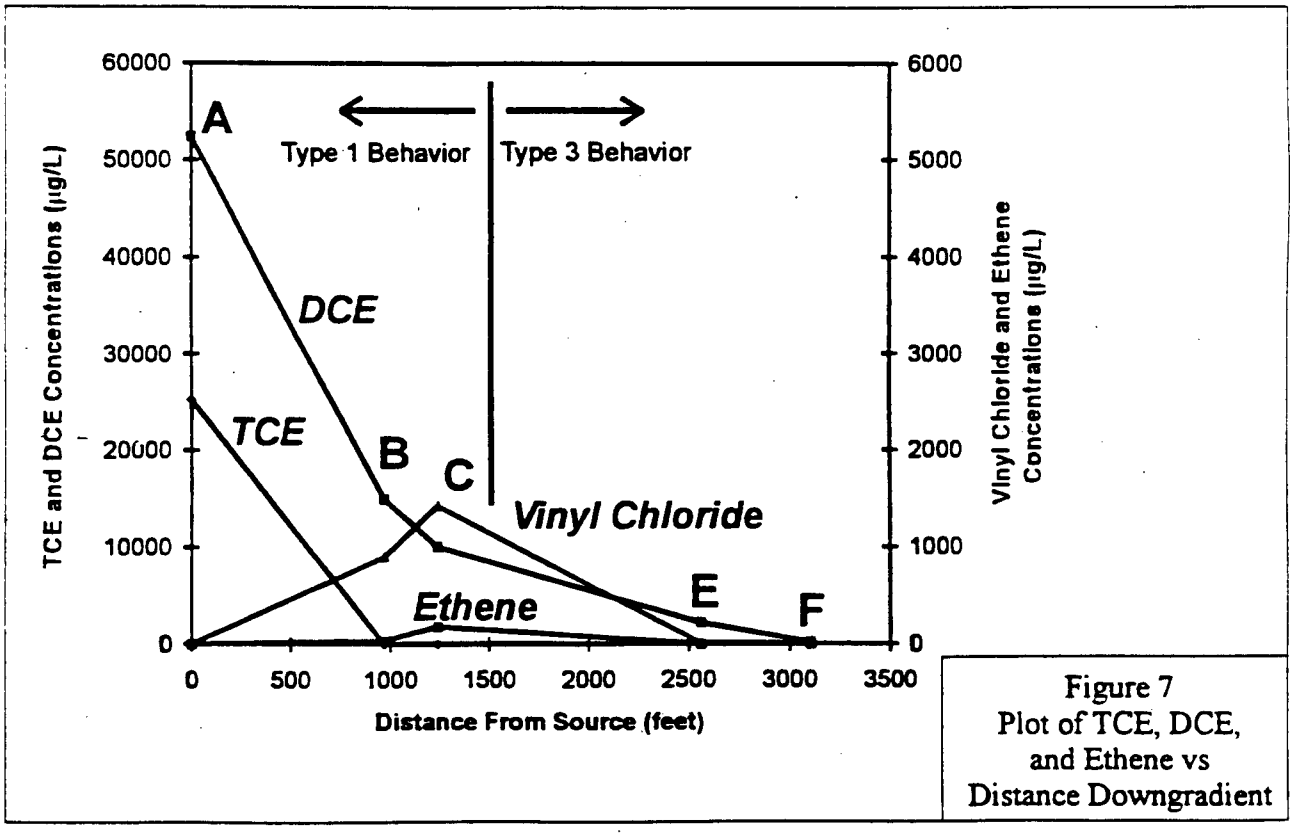

Figure 7
Plot of TCE, DCE, and Ethene vs Distance Downgradient

Wiedemeier, 1995 (b)

Patterns of Intrinsic Bioremediation at Two U.S. Air Force Bases

Todd H. Wiedemeier, Matthew A. Swanson, John T. Wilson, Donald H. Kampbell, Ross N. Miller, and Jerry E. Hansen

ABSTRACT

Intrinsic bioremediation of benzene, toluene, ethylbenzene, and xylenes (BTEX) occurs when indigenous microorganisms work to reduce the total mass of contamination in the subsurface without the addition of nutrients. A conservative tracer, such as trimethylbenzene, found commingled with the contaminant plume can be used to distinguish between attenuation caused by dispersion, dilution from recharge, volatilization, and sorption and attenuation caused by biodegradation. Patterns of intrinsic bioremediation can vary markedly from site to site depending on governing physical, biological, and chemical processes. Intrinsic bioremediation causes measurable changes in groundwater chemistry. Specifically, concentrations of contaminants, dissolved oxygen, nitrate, ferrous iron, sulfate, and methane in groundwater change both temporally and spatially as biodegradation proceeds Operations at Hill Air Force Base (AFB) and Patrick AFB resulted in fuel-hydrocarbon contamination of soil and groundwater. In both cases, trimethylbenzene data confirm that dissolved BTEX is biodegrading. Geochemical evidence from the Hill AFB site suggests that aerobic respiration, denitrification, iron reduction, sulfate reduction, and methanogenesis all are contributing to intrinsic bioremediation of dissolved BTEX. Sulfate reduction is the dominant biodegradation mechanism at this site. Geochemical evidence from Patrick AFB suggests that aerobic respiration, iron reduction, and methanogenesis are contributing to intrinsic bioremediation of dissolved BTEX. Methanogenesis is the dominant biodegradation mechanism at this site.

INTRODUCTION

Microorganisms obtain energy for cell production and maintenance by facilitating the transfer of electrons from electron donors to electron acceptors. This results in the oxidation of the electron donor and the reduction of the

electron acceptor. Common electron donors at fuel hydrocarbon-contaminated sites are natural organic carbon and fuel-related organic compounds, including BTEX. Electron acceptors are elements or compounds that occur in relatively oxidized form. Common electron acceptors found in groundwater include dissolved oxygen, nitrate, ferric iron (present as ferric trihydroxide), sulfate, and carbon dioxide. Microorganisms generally utilize electron acceptors in a preferred order while metabolizing fuel hydrocarbons (Bouwer 1992). Depending on the types of electron acceptors and nutrients present, pH conditions, and alkalinity, biodegradation can occur via aerobic respiration, denitrification, ferric iron reduction, sulfate reduction, or methanogenesis. Dissolved oxygen is utilized as the first and primary electron acceptor. After the dissolved oxygen is consumed, anaerobic microorganisms typically use electron acceptors in the following order of preference: nitrate, ferric iron, sulfate, and finally carbon dioxide. Environmental conditions and microbial competition will ultimately determine which processes will dominate at a given site. Vroblesky and Chapelle (1994) show that the dominant terminal electron accepting process can vary both temporally and spatially in an aquifer contaminated with fuel hydrocarbons.

Three lines of evidence can be used to document the occurrence of natural attenuation and intrinsic bioremediation (National Research Council 1993): (1) documented loss of contaminants at the field scale, (2) geochemical evidence, and (3) microcosm studies. The first line of evidence, documented loss of contaminants at the field scale, requires historical data. The second line of evidence, groundwater geochemistry, can be used to determine the relative importance of each of the mechanisms of natural attenuation and the mechanisms of intrinsic bioremediation that are operating at a site. The third line of evidence, the microcosm study, can be used to estimate rates of biodegradation. Other methods for determining biodegradation rates rely on chemical evidence and include use of a conservative tracer (Wiedemeier et al. 1995), or interpretation of a steady-state contaminant plume configuration (Buscheck and Alcantar 1995).

The simplified stoichiometry of benzene biodegradation involving common electron acceptors is shown in Table 1. The stoichiometry presented in Table 1 assumes that no cellular mass production occurs and therefore could be conservative by a factor of up to three. The stoichiometry of toluene, ethylbenzene, and xylene biodegradation is similar to that for benzene. These reactions cause measurable changes in groundwater chemistry. Evidence of these changes can be used to support the occurrence of intrinsic bioremediation and to determine which mechanisms of intrinsic bioremediation are most important at a given site.

PATTERNS OF INTRINSIC BIOREMEDIATION AT HILL AIR FORCE BASE, UTAH

Previous investigations at the petroleum, oil, and lubricants (POL) facility at Hill AFB, Utah, determined that JP-4 jet fuel had been released into the soil

TABLE 1. Stoichiometry of common biodegradation reactions.

Benzene Biodegradation Reactions	Mass Ratio of Electron Acceptor to Benzene	Mass Ratio of Metabolic By-Product to Benzene	Average Mass Ratio of Electron Acceptor to Total BTEX [a]	Average Mass Ratio of Metabolic By-Product to Total BTEX[a]	Mass of BTEX Degraded per Unit Mass of Electron Acceptor Utilized (mg)[a]	Mass of BTEX Degraded per Unit Mass of Metabolic By-Product Produced (mg)[a]
$7.5O_2 + C_6H_6 \Rightarrow 6CO_{2,g} + 3H_2O$ Benzene oxidation /aerobic respiration	3.1:1	—	3.14:1	—	0.32	—
$6NO_3^- + 6H^+ + C_6H_6 \Rightarrow 6CO_{2,g} + 6H_2O + 3N_{2,g}$ Benzene oxidation / denitrification	4.8:1	—	4.9:1	—	0.21	—
$60H^+ + 30Fe(OH)_3 + C_6H_6 \Rightarrow 6CO_2 + 30Fe^{2+} + 78H_2O$ Benzene oxidation / iron reduction	41.1:1	21.5:1	—	21.8:1	—	0.05
$7.5H^+ + 3.75SO_4^{2-} + C_6H_6 \Rightarrow 6CO_{2,g} + 3.75H_2S^o + 3H_2O$ Benzene oxidation / sulfate reduction	4.6:1	—	4.7:1	—	0.21	—
$4.5H_2O + C_6H_6 \Rightarrow 2.25CO_{2,g} + 3.75CH_4$ Benzene oxidation / methanogenesis	—	0.77:1	—	0.78:1	—	1.28

(a) Simple average of all BTEX compounds based on individual compound stoichiometry. This stoichiometry assumes no cellular mass is produced.

and shallow groundwater. The chronology of the JP-4 spill or spills is not known. The facility began operating in the early 1950s. Site characterization methods used to evaluate intrinsic bioremediation included Geoprobe® sampling of groundwater, cone penetrometer testing (CPT), soil borehole drilling, soil sample collection and analysis, monitoring well installation, sampling and analysis of groundwater from monitoring wells, and aquifer testing.

Site Geology and Hydrogeology

Hill AFB is located on a bench of the Wasatch Mountains on the edge of the Great Salt Lake Basin. Surface topography at the site slopes to the southwest. Shallow sediments consist of light reddish-brown to dark gray, cohesive clayey silts to silty clays. This unit is 1.2 to 4.6 m thick and is underlain by poorly to moderately sorted, yellowish-brown to reddish-brown, silty fine-grained sands that coarsen downward into a 0.9- to 6.7-m-thick sequence of moderately sorted, medium- to coarse-grained sands. Underlying the sands is a sequence of competent, thinly interbedded clay to silty clay and fine- to very fine-grained, clayey sand and silt of unknown thickness. This sequence of interbedded clay and fine-grained sand and silt acts as an effective barrier to the downward migration of water and contaminants, as indicated by geochemical data. Upward hydraulic gradients in the area also prevent downward migration of the contaminant plume.

The water table aquifer is present in the medium- to coarse-grained sands described above. The water table is present between 1.5 and 6.1 m below ground surface (bgs), and groundwater flow is to the southwest with an average horizontal gradient of 0.048 m/m. Available data suggest that there is almost no seasonal variation in groundwater flow direction or gradient at the site. Based on slug tests and pumping tests, the average hydraulic conductivity for the shallow medium- to coarse-grained sands of the shallow saturated zone is 0.0084 cm/s. With a gradient of 0.046 m/m, a hydraulic conductivity of 0.0084 cm/s, and an assumed effective porosity of 0.25, the average advective groundwater velocity is 1.34 m/day, or approximately 488 m/year. Because of the low total organic carbon (TOC) concentration and clay mineral content observed in the shallow saturated zone at this site, retardation of the BTEX compounds due to sorption is not expected to be a significant process affecting solute transport.

Figures 1a through 1f show the POL facility and the immediately adjacent area. These figures include data collected from 12 monitoring wells in the source area north of 6th Street in December 1993/January 1994. These wells cover a very small area relative to the extent of the dissolved plume, and these data represent the only data available for this area.

Nature and Extent of Contamination

Figure 1a shows the approximate extent of mobile light nonaqueous-phase liquid (LNAPL) at the site, the main source of BTEX dissolved in groundwater.

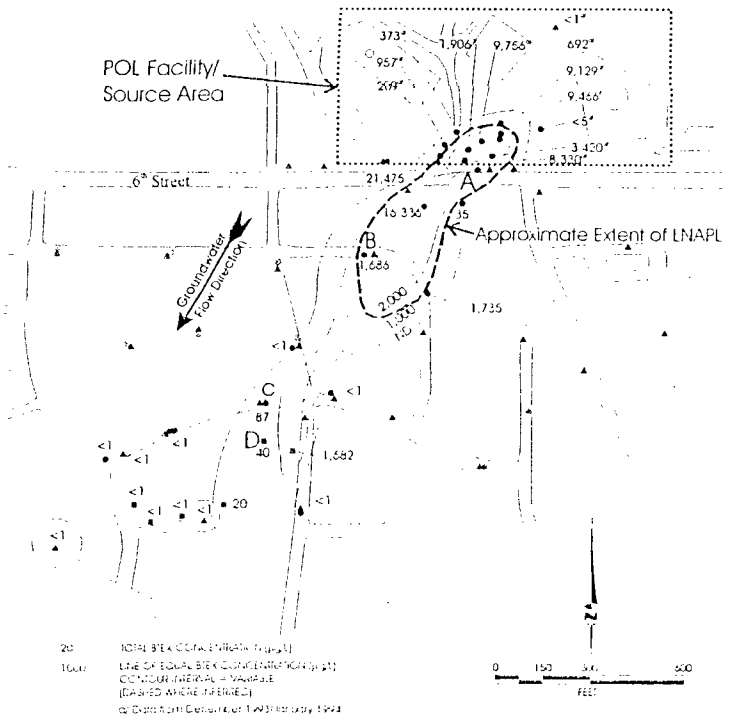

FIGURE 1a. Distribution of total BTEX in groundwater and approximate extent of LNAPL at Hill AFB, Utah (where 1 ft = 0.3 m).

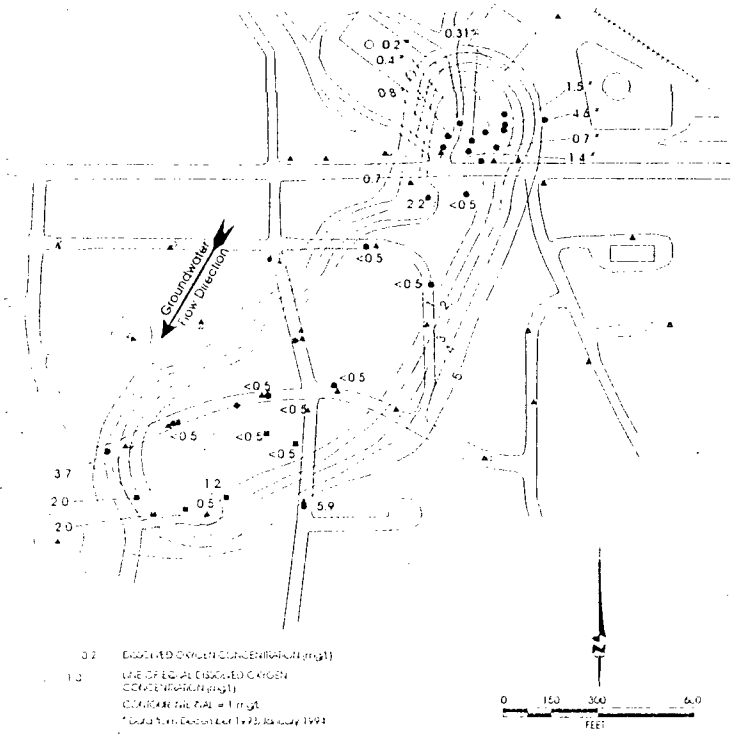

FIGURE 1b. Distribution of dissolved oxygen in groundwater at Hill AFB, Utah (where 1 ft = 0.3 m).

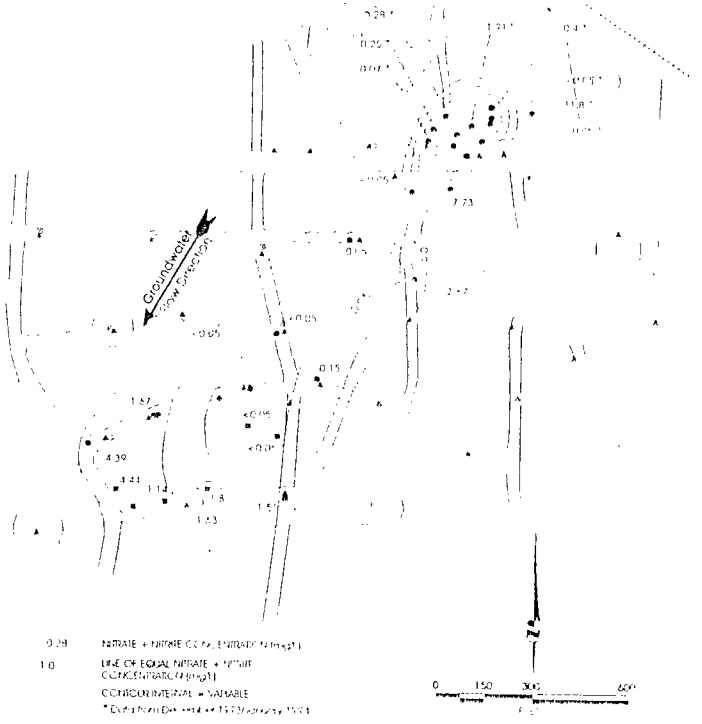

FIGURE 1c. Distribution of nitrate + nitrite in groundwater at Hill AFB, Utah (where 1 ft = 0.3 m).

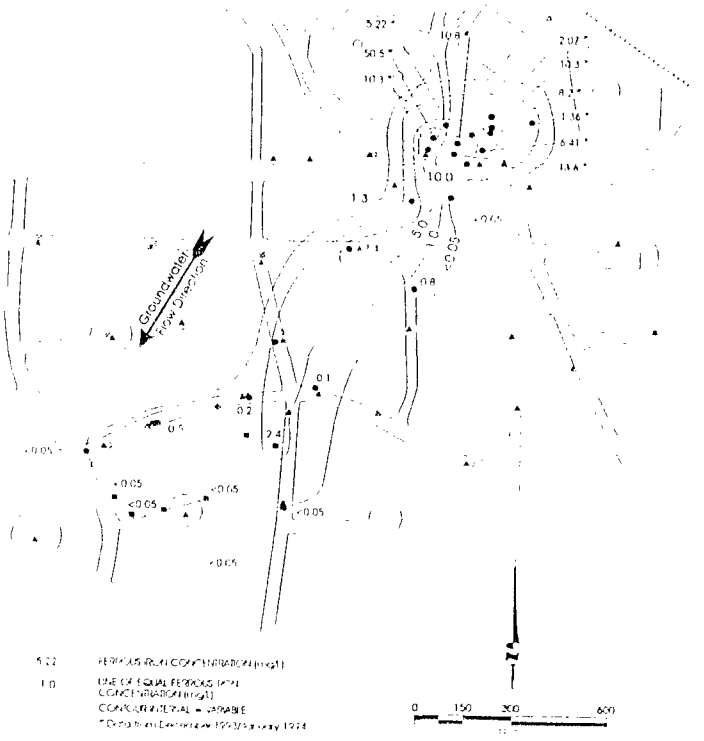

FIGURE 1d. Distribution of ferrous iron in groundwater at Hill AFB, Utah (where 1 ft = 0.3 m).

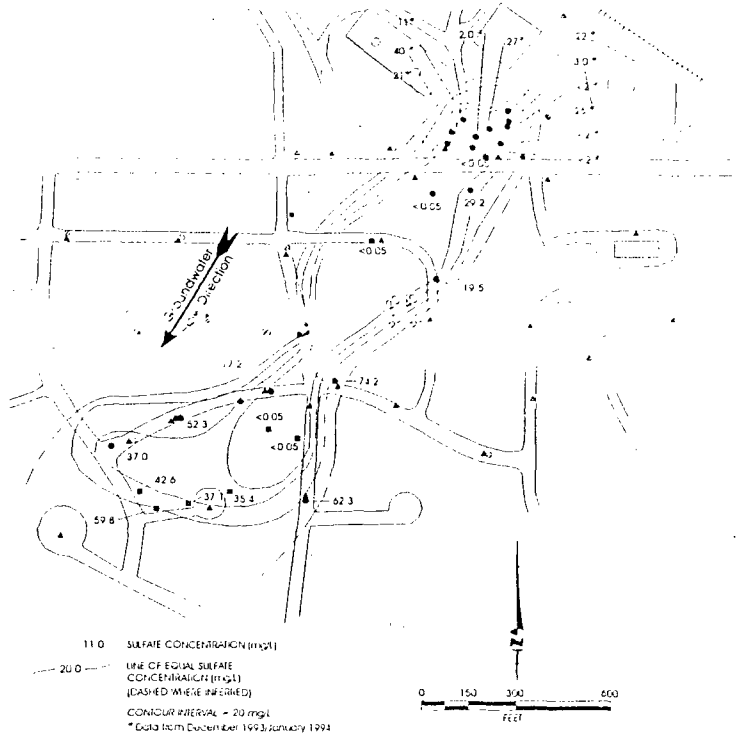

FIGURE 1e. Distribution of sulfate in groundwater at Hill AFB, Utah (where 1 ft = 0.3 m).

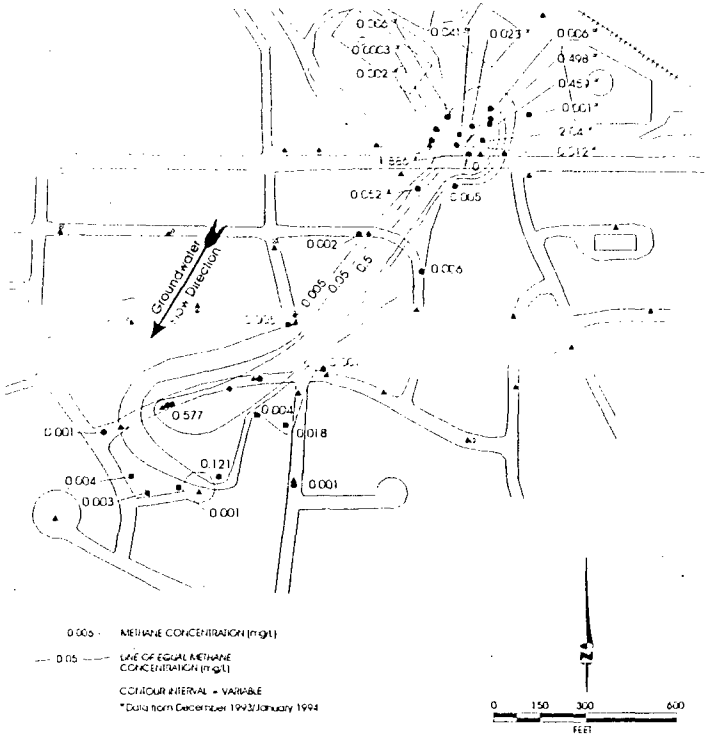

FIGURE 1f. Distribution of methane in groundwater at Hill AFB, Utah (where 1 ft = 0.3 m).

The LNAPL plume is composed of weathered JP-4 released from the POL facility. Measured residual total BTEX concentrations in soil decrease rapidly outside the area of mobile LNAPL contamination. The highest dissolved BTEX concentration observed in groundwater during this study was 21,475 µg/L. Figure 1a is also an isopleth map that shows the distribution of total BTEX dissolved in groundwater in July 1994. Dissolved BTEX contamination is migrating to the southwest, in the direction of groundwater flow.

Documented Loss of Contaminants at the Field Scale

Dissolved BTEX data collected in 1992, 1993, and 1994 indicate that the dissolved BTEX plume has reached steady-state conditions, and although fluctuations in contaminant concentrations were observed during this period, the plume is not expanding or migrating further downgradient. Based on the calculated advective velocity of the groundwater, the contaminant plume should have migrated approximately 442 m downgradient between August 1993 and July 1994. Available geochemical data suggest that the stabilization of the BTEX plume such a short distance downgradient of the source is primarily the result of intrinsic bioremediation, as discussed in the following sections.

To determine what portion of observed decreases in contaminant concentrations can be attributed to biodegradation, measured BTEX concentrations must be corrected for the effects of dispersion, dilution from recharge, volatilization, and sorption. A convenient way of doing this is to use a compound present in the dissolved hydrocarbon plume that has sorptive and volatilization properties similar to those of BTEX and that is recalcitrant under anaerobic conditions. One tracer compound that is useful in some, but not all, groundwater environments is trimethylbenzene (TMB). The three isomers of this compound (1,2,3-TMB, 1,2,4-TMB, and 1,3,5-TMB) have Henry's law constants and soil sorption coefficients that are similar to the BTEX compounds. Also, the TMB isomers are generally present in sufficient quantities in fuel mixtures to be readily detectable when dissolved in groundwater and are fairly recalcitrant in the anaerobic portion of the plume. The degree of recalcitrance of TMB is site-specific and the use of this compound as a tracer must be evaluated on a case-by-case basis.

The corrected concentration of a compound is the concentration of the compound that would be expected at one point (B) located downgradient of another point (A) after correcting for the effects of dispersion, dilution from recharge, volatilization, and sorption between points A and B. One method of calculating the corrected concentration is given by (Wiedemeier et al. 1994):

$$C_{B,corr} = C_B\left(\frac{TMB_A}{TMB_B}\right) \quad (1)$$

Where $C_{B,corr}$ = corrected concentration of compound of interest at Point B
C_B = measured concentration of compound of interest at Point B

TMB_A = measured concentration of trimethylbenzene at Point A
TMB_B = measured concentration of trimethylbenzene at Point B

TMB is slightly more hydrophobic than the BTEX compounds and is not entirely recalcitrant under anaerobic conditions. However, if any TMB mass is lost to the processes of biodegradation or preferential sorption, the relationship shown above is more conservative (i.e., a lower mass lost due to biodegradation will be calculated).

At Hill AFB, four points along the groundwater flow path were chosen for comparison of corrected and observed BTEX concentrations to assess the effects of dispersion, dilution from recharge, volatilization, and sorption (Figure 1a). Table 2 shows corrected BTEX concentrations and the percent of BTEX lost due to biodegradation between these points. The calculations presented in this table confirm that biodegradation of the BTEX compounds is occurring at this site. The specific mechanisms of intrinsic bioremediation operating at Hill AFB are discussed below.

Mechanisms of Intrinsic Bioremediation at Hill AFB

The information presented in the preceding section shows that intrinsic bioremediation of dissolved BTEX is occurring at the POL site. Geochemical data can now be used to determine which mechanisms of intrinsic bioremediation are operating at the site and the relative importance of each mechanism.

General Groundwater Geochemistry. General ambient groundwater geochemistry at the site is conducive to intrinsic bioremediation. Total alkalinity at the site is fairly high, and ranges from 349 to 959 mg/L. This amount of alkalinity is sufficient to buffer potential changes in pH caused by biologically mediated BTEX oxidation reactions. Groundwater pH at the POL facility ranges from 6.3 to 8.3 standard units. This range of pH is optimal for BTEX-degrading microbes. The average temperature of groundwater is 18°C. The reduction/oxidation (redox) potential ranges from 274 to –190 millivolts (mV). Areas at the site with low redox potentials coincide with areas of BTEX contamination; low dissolved oxygen, nitrate, and sulfate concentrations; and elevated ferrous iron and methane concentrations. This suggests that dissolved BTEX at the site is subjected to a variety of biodegradation processes including aerobic respiration, denitrification, iron reduction, sulfate reduction, and methanogenesis.

Aerobic Respiration. Figure 1b shows the distribution of dissolved oxygen in groundwater in July 1994. Comparison of Figures 1a and 1b shows that areas with elevated total BTEX concentrations have depleted dissolved oxygen concentrations. A similar trend was observed in August 1993. This is an indication that aerobic biodegradation of BTEX is occurring at the site. With a background dissolved oxygen concentration of approximately 6 mg/L, the shallow groundwater at this site has the capacity to assimilate 1,900 µg/L of total BTEX, based on the stoichiometry presented in Table 1.

TABLE 2. BTEX lost due to biodegradation, Hill AFB, July 1994.

	Location (meters Downgradient of Source)									
Compound	Point A (0) Measured Concentration (µg/L)	Point B (137) Measured Concentration (µg/L)	Point B Corrected Concentration[a] (µg/L)	Percent Lost to Biodegradation[b] Between A and B	Point C (305) Measured Concentration (µg/L)	Point C Corrected Concentration (µg/L)	Percent Lost to Biodegradation Between B and C	Point D (335) Measured Concentration (µg/L)	Point D Corrected Concentration (µg/L)	Percent Lost to Biodegradation Between C and D
benzene	5,600	458	2,693	57	7	8	100	1	1	92
toluene	5,870	10	59	99	10	11	0	1	1	95
ethylbenzene	955	454	2,667	0	23	25	100	4	4	97
p-xylene	1,620	272	1,597	2	26	28	99	12	13	90
m-xylene	5,130	442	2,599	54	18	20	100	19	21	0
o-xylene	2,300	51	300	89	3	3	100	6	7	0
Total BTEX	21,475	1,686	9,915	58	87	95	99	40	47	85
trimethylbenzene	2,123	361	2,123	0	330	361	0	295	330	0

(a) See text for calculation of corrected concentration.
(b) Percent lost to biodegradation = $((Measured_A - Corrected_B)/(Measured_A - Measured_B))*100$.

Denitrification. Figure 1c shows the distribution of nitrate + nitrite (as N) in groundwater in July 1994. Comparison of Figures 1a and 1c shows that areas with elevated total BTEX concentrations have depleted nitrate + nitrite concentrations. Comparison of Figures 1b and 1c shows that areas with depleted dissolved oxygen concentrations have depleted nitrate + nitrite concentrations. Similar trends were observed in August 1993. These relationships provide strong evidence that anaerobic biodegradation of the BTEX compounds is occurring at the site through the microbially mediated process of denitrification. Background nitrate + nitrite (as N) concentrations are about 8.0 mg/L, which is equivalent to 29 mg/L of NO_3^-. This nitrate (as NO_3^-) concentration was calculated by assuming that all nitrate + nitrite (as N) is present as nitrate. This assumption is valid because nitrite is metastable in the groundwater environment and nitrite is seldom present in concentrations large enough to influence the ionic balance to a noticeable degree (Hem 1985). This is especially true in uncontaminated (background) areas where denitrification is not occurring. Ionic nitrate and nitrite data collected in January 1994 confirm this. With a background nitrate (as NO_3^-) concentration of approximately 29 mg/L, the shallow groundwater at this site has the capacity to assimilate 6,000 µg/L of total BTEX during denitrification, based on the stoichiometry presented in Table 1.

Iron Reduction. Figure 1d shows the distribution of ferrous iron in groundwater in July 1994. Comparison of Figures 1a and 1d shows that areas with elevated total BTEX concentrations have elevated ferrous iron concentrations. A similar trend was observed in August 1993. This is an indication that ferric iron is being reduced to ferrous iron during biodegradation of BTEX compounds. Background ferrous iron concentrations are less than 0.05 mg/L. The highest measured ferrous iron concentration was 50.5 mg/L. This suggests that the shallow groundwater at this site has the capacity to assimilate 2,300 µg/L of total BTEX during iron reduction, based on the stoichiometry presented in Table 1. This calculation is based on observed ferrous iron concentrations, and not on the amount of ferric hydroxide available in the aquifer. Therefore, potential iron assimilative capacity could be much higher.

Sulfate Reduction. There was no clear relationship between BTEX and sulfate concentrations in August 1993. Figure 1e shows the distribution of sulfate in groundwater in July 1994. Comparison of Figures 1a and 1e shows that by July 1994, areas with elevated total BTEX concentrations had depleted sulfate concentrations. This is an indication that anaerobic biodegradation of the BTEX compounds is occurring at the site through the microbially mediated process of sulfate reduction. With a background sulfate concentration of about 100 mg/L, the shallow groundwater at this site has the capacity to assimilate 21,000 µg/L of total BTEX during sulfate reduction, based on the stoichiometry presented in Table 1.

Methanogenesis. Available geochemical evidence suggests that methanogenesis, like sulfate reduction, may have become a more important BTEX-degradation mechanism between August 1993 and July 1994. There was no clear relationship between BTEX and methane concentrations in August 1993. Figure 1f shows the distribution of methane in groundwater in July 1994. Comparison of Figures 1a and 1f shows that areas with elevated total BTEX concentrations have elevated methane concentrations. This is an indication that anaerobic biodegradation of the BTEX compounds is occurring at the site through the microbially mediated process of methanogenesis with carbon dioxide serving as the electron acceptor. This is consistent with other electron acceptor data collected at the site, with the area having elevated methane concentrations being confined to areas with depleted dissolved oxygen, nitrate, and sulfate concentrations and elevated ferrous iron concentrations. The highest measured methane concentration within the BTEX plume was 2.04 mg/L, and background concentrations are less than 0.001 mg/L. This suggests that the shallow groundwater at this site has expressed the capacity to assimilate 2,600 µg/L of total BTEX during methanogenesis, based on the stoichiometry presented in Table 1. These calculations are based on observed methane concentrations and not on the amount of carbon dioxide available in the aquifer. Therefore, methanogenic assimilative capacity could be much higher.

Total Expressed Assimilative Capacity

The data presented in the preceding sections suggest that mineralization of BTEX compounds is occurring through the microbially mediated processes of aerobic respiration, denitrification, iron reduction, sulfate reduction, and methanogenesis. On the basis of site geochemical data and the stoichiometry presented in Table 1, the expressed BTEX assimilative capacity of groundwater at the POL facility is at least 33,800 µg/L (Table 3). The measured concentrations of ferrous iron and methane may not be the maximum expressed or achievable. The highest dissolved BTEX concentration observed at the site was 21,475 µg/L. On the basis of the calculations presented in the preceding sections and observations made at this site over the period from August 1993 through July 1994, groundwater in the vicinity of the POL facility has sufficient assimilative capacity to degrade dissolved BTEX that partitions from the LNAPL plume into the groundwater before the plume migrates 500 m downgradient from the source area. The difference between observed assimilative capacity and the highest BTEX concentration probably results from the biodegradation of other petroleum-related compounds, such as naphthalene, dissolved in the groundwater.

PATTERNS OF INTRINSIC BIOREMEDIATION AT PATRICK AIR FORCE BASE, FLORIDA

An estimated 700 gal (2,659 L) of unleaded gasoline was released into the soil and shallow groundwater at the Base Exchange (BX) Service Station (Site ST-29), Patrick AFB, Florida, in 1986. Several investigative techniques,

TABLE 3. Expressed assimilative capacity of site groundwater.

Process	Expressed BTEX Assimilative Capacity (μg/L)	
	Hill AFB	Patrick AFB
Aerobic Respiration	1,900	1,200
Denitrification	6,000	—
Ferric Hydroxide Reduction	2,300	90
Sulfate Reduction	21,000	—
Methanogenesis	2,600	17,400
Expressed Assimilative Capacity	33,800	18,690
Highest Observed Total BTEX Concentration	21,475	7,304

including soil and groundwater sampling and aquifer testing, were utilized at this site. Cone penetrometer testing and hollow-stem auger drilling were used to collect stratigraphic information and soil samples. Groundwater samples were collected at monitoring points installed in CPT holes and at monitoring wells. Slug tests were conducted in monitoring wells.

Site Geology and Hydrogeology

Patrick AFB lies on a narrow barrier island that parallels the eastern Florida coastline and is bounded on the east by the Atlantic Ocean (230 m east of the site) and on the west by the Banana River (730 m west of the site). The ground surface at Site ST-29 slopes gently westward toward the Banana River.

Shallow subsurface deposits at Site ST-29 consist of fine- to coarse-grained marine sand that is poorly to moderately sorted and contains up to 40% shell fragments. These sand deposits extend to a depth of approximately 7.6 m and contain interspersed organic matter. The Caloosahatchee Marl formation underlies the sands at this site and acts as an aquitard. The water table is present at depths of 1.22 to 1.52 m bgs and is unconfined. Groundwater elevation data indicate that flow is to the west, toward the Banana River and away from a divergent groundwater divide located along the eastern edge of the site. Water level measurements indicate that the local horizontal hydraulic gradient is approximately 0.002 m/m. Vertical hydraulic gradients measured in monitoring point nests range from 0.000 m/m to 0.003 m/m (downward).

Results of slug testing indicate that the average hydraulic conductivity of the shallow saturated zone is approximately 0.026 cm/s. With a gradient of 0.002 m/m, a hydraulic conductivity of 0.026 cm/s, and assuming an effective porosity of 0.35, the average advective groundwater velocity is 0.13 m/day or approximately 48 m/year. On the basis of measured TOC concentrations in uncontaminated areas at the site, a median retardation factor of 2.6 was

calculated for benzene. This gives an estimated retarded solute transport velocity of 18.3 m/year.

Nature and Extent of Contamination

Figures 2a through 2d show the distribution of soil contamination, dissolved BTEX, electron acceptors, and metabolic by-products at Patrick AFB, Florida. Mobile LNAPL has not been detected in monitoring wells or monitoring points at Site ST-29. Residual BTEX contamination resulting from vertical and lateral migration of hydrocarbons is found over the area indicated in Figure 2a. The highest observed concentration of residual total BTEX in soil is 1,236 mg/kg. Benzene was detected in this sample at 6.99 mg/kg.

Figure 2a also shows the distribution of total BTEX dissolved in groundwater. Dissolved BTEX contamination is migrating to the west in the direction of groundwater flow. Dissolved BTEX contamination at Patrick AFB is limited to the shallow saturated zone. The maximum dissolved BTEX concentration observed at the site in March 1994 was 7,304 μg/L. It is likely that dissolved BTEX concentrations were much higher shortly after the spill occurred in 1986 [potentially as high as 120 mg/L, based on equilibrium partitioning considerations (American Petroleum Institute 1985)].

Documented Loss of Contaminants at the Field Scale

Three points along the groundwater flow path were chosen to correct observed BTEX concentrations for the effects of dispersion, dilution from recharge, sorption, and volatilization (Figure 2a). Point A was chosen to coincide with the highest observed dissolved BTEX concentration. Points B and C are located 38 m and 98 m, respectively, downgradient of point A.

Table 4 shows TMB-corrected BTEX concentrations and the percent of each BTEX compound lost via biodegradation between Points A and B and B and C. The results of these calculations indicate that TMB is not entirely recalcitrant under the conditions found at this site (benzene concentrations were higher at Point B than at Point A). However, any biodegradation of TMB results in underestimation of the percentage of BTEX biodegraded, so the calculations presented in Table 4 are conservative, and confirm that biodegradation is occurring. The mechanisms of intrinsic bioremediation likely operating at this site are discussed below.

Mechanisms of Intrinsic Bioremediation at Patrick AFB

The information presented in the preceding section shows that intrinsic bioremediation of dissolved BTEX is occurring at Site ST-29. Geochemical data can now be used to determine which mechanisms of intrinsic bioremediation are operating at the site and the relative importance of each mechanism.

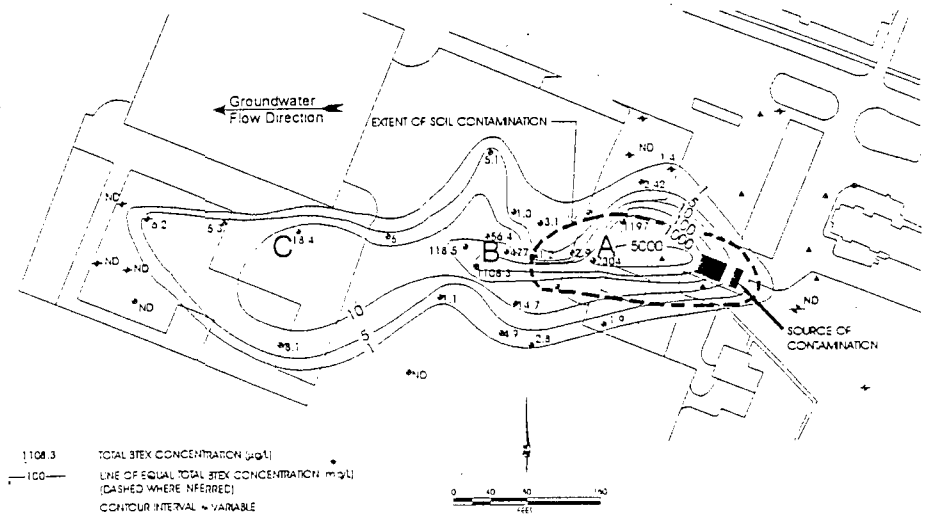

FIGURE 2a. Distribution of total BTEX in groundwater at Patrick AFB, Florida (where 1 ft = 0.3 m).

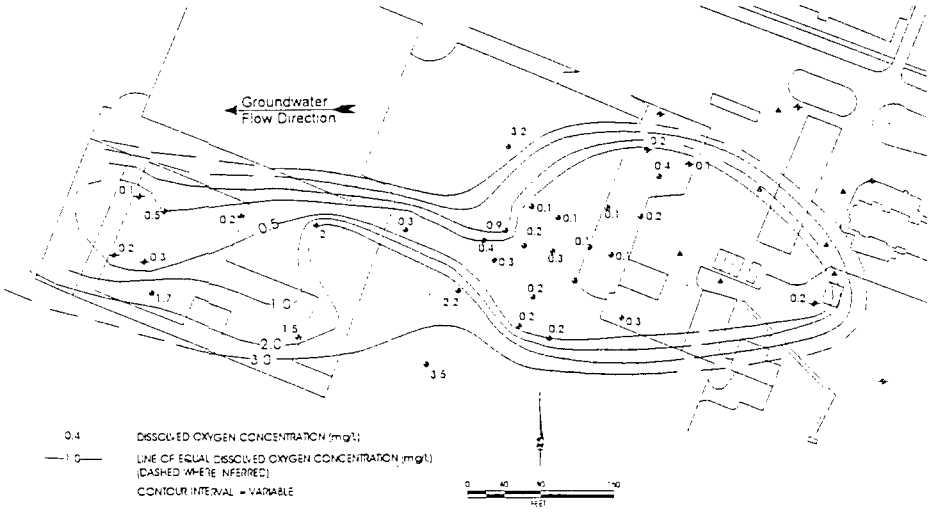

FIGURE 2b. Distribution of dissolved oxygen in groundwater at Patrick AFB, Florida (where 1 ft = 0.3 m).

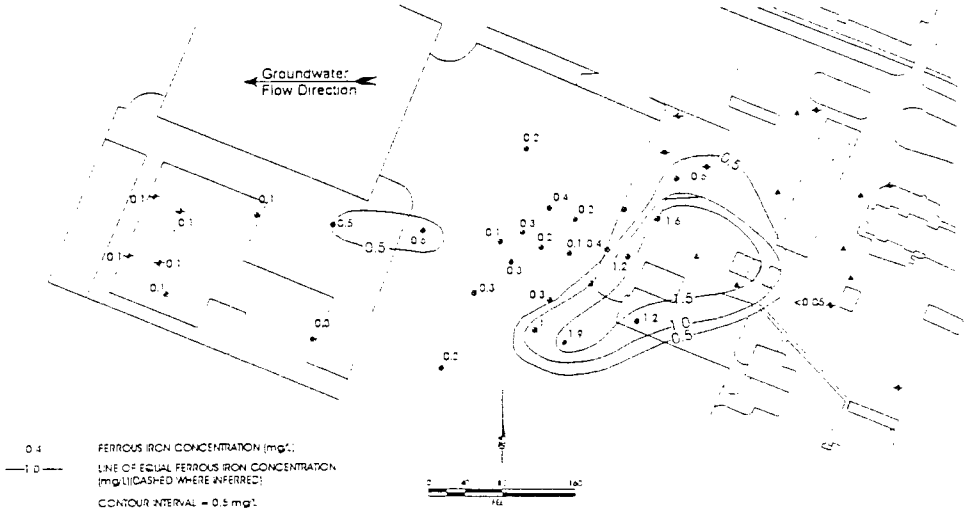

FIGURE 2c. Distribution of ferrous iron in groundwater at Patrick AFB, Florida (where 1 ft = 0.3 m).

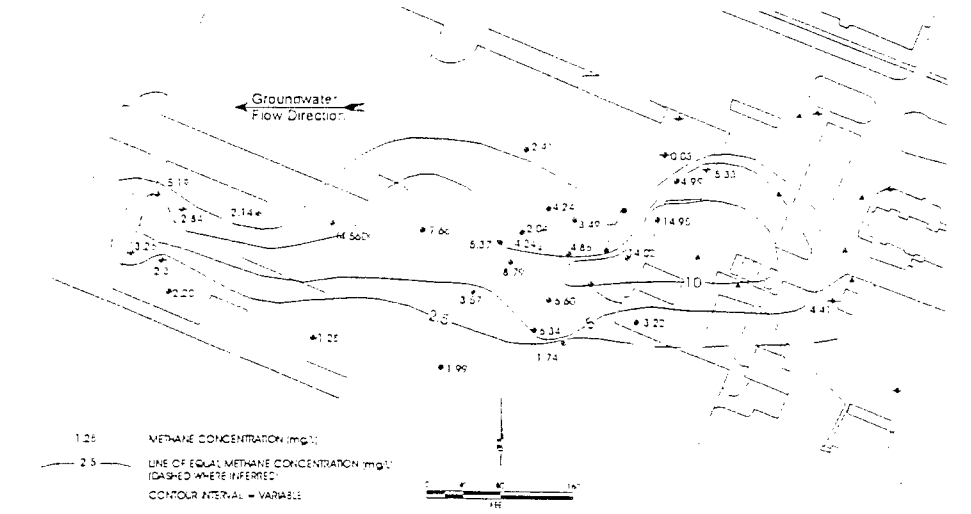

FIGURE 2d. Distribution of methane in groundwater at Patrick AFB, Florida (where 1 ft = 0.3 m).

TABLE 4. BTEX lost due to biodegradation, Patrick AFB, March 1994.

	Location (meters downgradient of highest BTEX concentration)						
Compound	Point A (0) Measured Concentration (µg/L)	Point B (38) Measured Concentration (µg/L)	Point B Corrected Concentration[a] (µg/L)	Percent Lost to Biodegradation[b] Between A and B	Point C (98) Measured Concentration (µg/L)	Point C Corrected Concentration (µg/L)	Percent Lost to Biodegradation Between B and C
benzene	724	960	25,714	0	1	9	99
toluene	737	17	455	39	2	19	0
ethylbenzene	823	12	321	62	2	19	0
p-xylene	1,220	39	1,045	15	4	37	6
m-xylene	2,410	37	991	60	7	65	0
o-xylene	1,390	44	1,179	16	4	37	18
trimethylbenzene	750	28	750	0	3	28	0

(a) See text for calculation of corrected concentration.
(b) Percent lost to biodegradation = $((Measured_A - Corrected_B)/(Measured_A - Measured_B))*100$.

General Groundwater Geochemistry. The ambient groundwater geochemistry at the site is conducive to intrinsic bioremediation. Total alkalinity at the site varies from 148 mg/L to 520 mg/L and is sufficient to buffer potential changes in pH caused by biologically mediated BTEX oxidation reactions. Groundwater pH at Site ST-29 ranges from 6.7 to 7.6 standard units, well within the optimal range of 6 to 8 for BTEX-degrading microbes. Temperatures in the shallow saturated zone range from 24.7 to 27.8°C. These are relatively high temperatures for shallow groundwater, suggesting that bacterial growth rates could be high. The redox potential at Site ST-29 ranges from 54 mV to –295 mV. Areas of the site with low redox potential coincide with areas of high BTEX contamination, low dissolved oxygen concentrations, slightly elevated ferrous iron concentrations, and significantly elevated methane concentrations. These characteristics suggest that dissolved BTEX at the site is subjected to a variety of biodegradation processes including aerobic respiration, iron reduction, and methanogenesis.

Background nitrate concentrations are extremely low at this site, ranging from less than 0.05 mg/L to 0.29 mg/L. Nitrate reduction cannot be a significant BTEX removal mechanism because sufficient quantities of nitrate are not available for metabolism. Although sulfate concentrations are fairly high at this site (up to 86 mg/L), no relationship between sulfate and BTEX is apparent.

Aerobic Respiration. Figure 2b shows the distribution of dissolved oxygen in groundwater at Site ST-29. Comparison of Figures 2a and 2b shows that areas with elevated total BTEX concentrations coincide with areas having depleted dissolved oxygen concentrations. This is an indication that aerobic biodegradation of the BTEX compounds is occurring at the site. With a background dissolved oxygen concentration of approximately 3.7 mg/L, the shallow groundwater at this site has the capacity to assimilate 1,200 μg/L of total BTEX, based on the stoichiometry presented in Table 1.

Iron Reduction. Figure 2c shows the distribution of ferrous iron in groundwater at Site ST-29. Comparison of Figures 2a and 2c shows that areas with elevated total BTEX concentrations have slightly elevated ferrous iron concentrations. This suggests that ferric iron is being reduced to ferrous iron during biodegradation of BTEX compounds. Background ferrous iron concentrations are about 0.1 mg/L. The highest measured ferrous iron concentration within the BTEX plume was 1.9 mg/L, suggesting that the shallow groundwater at this site has expressed the capacity to assimilate at least 90 μg/L of total BTEX during iron reduction, based on the stoichiometry presented in Table 1. This calculation is based on observed ferrous iron concentrations and not on the amount of ferric hydroxide available in the aquifer. Therefore, iron assimilative capacity could be much higher.

Methanogenesis. Figure 2d shows the distribution of methane in groundwater. Comparison of Figures 2a and 2d shows that areas with elevated total

BTEX concentrations correlate with elevated methane concentrations. This is an indication that anaerobic biodegradation of the BTEX compounds is occurring at the site. This is consistent with other electron acceptor and redox potential data for this site. The highest measured methane concentration was 14.6 mg/L. Background concentrations of methane are about 1 mg/L. This suggests that the shallow groundwater at this site has expressed the capacity to assimilate at least 17,400 μg/L of total BTEX during methanogenesis, based on the stoichiometry presented in Table 1. These calculations are based on observed methane concentrations and not on the amount of carbon dioxide available in the aquifer. Therefore, methanogenic assimilative capacity could be much higher.

Total Expressed Assimilative Capacity. The data presented in the preceding sections suggest that mineralization of BTEX compounds is occurring through the microbially mediated processes of aerobic respiration, iron reduction, and methanogenesis. On the basis of site geochemical data and the stoichiometry presented in Table 1, the expressed BTEX assimilative capacity of groundwater at Site ST-29 is at least 18,690 μg/L (Table 3). The measured concentrations of ferrous iron and methane may not be the maximum achievable. The highest dissolved BTEX concentration observed at the site was 7,304 μg/L. On the basis of the calculations presented in the preceding sections, and on site observations, groundwater at Site ST-29 has sufficient assimilative capacity to degrade dissolved BTEX that partitions from the residual phase in soil into the groundwater before the plume migrates 400 m downgradient from the source area.

CONCLUSIONS

The prevailing mechanisms of natural attenuation and intrinsic bioremediation site depend on the governing physical and chemical characteristics of the shallow subsurface. Two lines of evidence were used to document the occurrence of intrinsic bioremediation in this paper: documented loss of contaminants at the field scale, and geochemical evidence. Field and geochemical data indicate that intrinsic bioremediation is occurring at both Hill AFB and Patrick AFB. Available geochemical data suggest that patterns of intrinsic bioremediation are different at each of these Air Force bases. However, anaerobic processes account for the greatest mass of BTEX destroyed at both sites. This pattern is typical of most of the sites studied by the authors to date using the technical protocol developed by the Air Force Center for Environmental Excellence (Wiedemeier et al. 1994).

Historical data and geochemical evidence show that intrinsic bioremediation of dissolved BTEX is occurring at the POL facility at Hill AFB. Geochemical evidence suggests that aerobic respiration, denitrification, ferric iron reduction, sulfate reduction, and methanogenesis are the primary processes

contributing to microbial degradation of BTEX at Hill AFB. The distribution of electron acceptors and metabolic byproducts relative to total BTEX concentrations changed noticeably between August 1993 and July 1994. In August 1993, there was good a correlation between areas with depleted dissolved oxygen, depleted nitrate, elevated ferrous iron, and elevated BTEX concentrations. No correlations between sulfate, methane, and BTEX concentrations were apparent at this time. By July 1994, however, areas with depleted sulfate and elevated methane concentrations exhibited an excellent correlation with areas containing elevated BTEX concentrations. This suggests that sulfate reduction and methanogenesis are becoming more important microbial degradation mechanisms as the plume matures. As indicated by expressed assimilative capacity, sulfate reduction is now the dominant mechanism of BTEX biodegradation at this site (Table 3). Vroblesky and Chapelle (1994) show that the dominant terminal electron accepting processes in an aquifer with fuel hydrocarbon contamination can vary both temporally and spatially due to consumption, recharge, and migration of electron acceptors.

Geochemical data show that intrinsic bioremediation of dissolved BTEX is occurring at Site ST-29 at Patrick AFB. These data suggest that aerobic respiration and methanogenesis are the primary processes contributing to microbial degradation of BTEX at Patrick AFB. Reduction of ferric iron also appears to play a limited role in microbial degradation of BTEX at this site. There is good correlation between areas with depleted dissolved oxygen, elevated ferrous iron, elevated methane, and elevated BTEX concentrations at the site. No correlation between nitrate, sulfate, and BTEX concentrations was apparent in March 1994. In contrast to the site at Hill AFB, it appears that aerobic respiration at the periphery of the plume and methanogenesis in the anaerobic core of the plume are the primary microbiologically mediated BTEX oxidation processes operating at Patrick AFB. As indicated by expressed assimilative capacity, methanogenesis is the dominant mechanism of BTEX biodegradation at this site (Table 3).

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American Petroleum Institute. 1985. *Laboratory Study on Solubilities of Petroleum Hydrocarbons in Groundwater.* API Publication Number 4395.

Bouwer, E.J. 1992. "Bioremediation of Subsurface Contaminants." In R. Mitchell (Ed.), *Environmental Microbiology.* Wiley-Liss, New York, NY.

Buscheck, T.E. and C.M. Alcantar. 1995. "Regression Techniques and Analytical Solutions to Demonstrate Intrinsic Bioremediation." In R.E. Hinchee, I.T. Wilson, and D.C. Downey (Eds.), *Intrinsic Bioremediation,* pp. 109-116. Battelle Press.

Hem, J.D. 1985. *Study and Interpretation of the Chemical Characteristics of Natural Water.* United States Geological Survey Water Supply Paper Number 2254, 263 p.

National Research Council. 1993. *In Situ Bioremediation, When does it Work?* National Academy Press. Washington, DC.

Vroblesky, D.A., and F.H. Chapelle. 1994. "Temporal and spatial changes of terminal electron-accepting processes in a petroleum hydrocarbon-contaminated aquifer and the significance for contaminant biodegradation." *Water Resources Research, 30*(5)1561-1570.

Wiedemeier, T.H., D.C. Downey, J.T. Wilson, D.H. Kampbell, R.N. Miller, and J.E. Hansen. 1994. Technical Protocol for Implementing the Intrinsic Remediation with Long-Term Monitoring Option for Natural Attenuation of Fuel Contamination Dissolved in Groundwater (Draft). Air Force Center for Environmental Excellence, Brooks Air Force Base, TX.

Wiedemeier, T.H., M.A. Swanson, R.T. Herrington, J.T. Wilson, D.H. Kampbell, R.N. Miller, and J.E. Hansen. 1995. Comparison of Two Methods for Determining Biodegradation Rate Constants at the Field Scale. In Preparation.

State of New Mexico
NVIRONMENT DEPARTMEI
Harold Runnels Building
1190 St. Francis Drive, P.O. Box 26110
Santa Fe, New Mexico 87502
(505) 827-2850

MARK
SECRE

GARY E. JOHNSON
GOVERNOR

EDGAR T. THORN
DEPUTY SECRETA

February 16, 1995

John A. Miller
Environmental Remediation Manager
Dowell Schlumberger Incorporated
P.O. Box 4378
Houston, Texas 77210-4378

RE: APPROVAL FOR SOIL VAPOR EXTRACTION SYSTEM EXPANSION AND ADDITIONAL INVESTIGATION WORK PLANS AT THE DOWELL SCHLUMBERGER FACILITY, ARTESIA, NEW MEXICO.

Dear Mr. Miller:

The Remediation Section of the Ground Water Protection and Remediation Bureau of the New Mexico Environment Department (NMED) has completed its reviews of the work plans for performing additional investigation and for expansion of the soil vapor extraction system (SVES), dated November 28, 1994 and January 11, 1995, respectively. NMED grants approval for both work plans pursuant to New Mexico Water Quality Control Commission (WQCC) regulation 1-203.

As discussed with Dowell Schlumberger (DS), the proposed SVES expansion, which addresses remediation of off-site contamination, is considered an interim corrective action at this point, since the investigation to define the furthest off-site extent of ground water contamination emanating from the facility is on going.

NMED also understands that difficulties in securing access to private land down-gradient from the facility, for the purpose of installing monitor wells, has forced DS to locate these off-site wells on publicly-owned right-of-way property. Although this provides limited flexibility in placement of wells, DS has communicated to NMED that it will locate the wells as close to the down-gradient vector emanating from the northeast corner of the facility as possible. Doing so will minimize the number of down-gradient wells necessary to characterize the off-site expression of the contaminant plume. Please be advised that it is the intent of NMED to require that DS ultimately pursue the down-gradient contamination to fully define the extent of concentrations above WQCC standards.

Please notify NMED at least five working days prior to any planned field activities so that we may be present to observe and obtain split samples. Should you have any questions regarding this letter, please contact Mr. Jeff Walker of my staff at (505) 841-9466. Your continued voluntary cooperation in this matter is greatly appreciated.

Sincerely,

Dennis McQuillan

Dennis McQuillan, Program Manager
Remediation Section
Ground Water Protection and Remediation Bureau

DM/JW

cc: Garrison McCaslin, NMED District IV Manager
Tony Moreland, USTB
File-District I
Ronald M. Eddy
Sherman & Howard L.L.C.
First Interstate Tower North
633 17th St., Suite 3000
Denver, CO 80202
Marcy Leavitt, Chief, GWPRB

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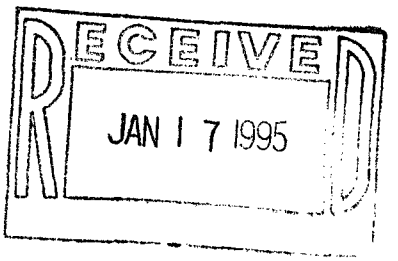
January 13, 1995



Tony Moreland, Project Manager
New Mexico Environment Department
Underground Storage Tank Bureau, Reimbursement Program
P.O. Box 26110
Santa Fe, New Mexico 87502

RE: Claim: Phase 4, Tasks 1 and 2 (1993)

Dear Tony:

This letter, and its attachments, comprise a claim submittal for Phase 4 work conducted at the Dowell Schlumberger Incorporated (Dowell) facility in Artesia, New Mexico between June 21, 1993 and November 20, 1993.

The Phase 4 workplan was approved by the New Mexico Environment Department (NMED) in letters dated September 10, 1993 and February 2, 1994. Phase 4 work included the following tasks:

Task 1: "Finalize plans and specs and submit reclamation proposal", and

Task 2: "Distribute plans, bid assistance, select and award contract".

This claim submittal includes two copies of the following documents:

- a completed claim form,
- cost detail forms,
- invoices in the standard format,
- receipts for expenses and subcontractors,
- copies of Dowell's canceled checks (including the front and back) for invoices #14295, #14587, and #14657 (check #017979, #071849, and #081799 respectively), and
- a signed and notarized affirmation form (two originals are provided).

OTHER LOCATIONS

1949 SUGARLAND DRIVE, SUITE 134
SHERIDAN, WYOMING 82801
(307) 672-0761
FAX (307) 674-4265

701 ANTLER DRIVE, SUITE 233
CASPER, WY 82601
(307) 473-2707
FAX (307) 237-0828

In accordance with the NMED Corrective Action Fund Reimbursement Program Claim Form Instructions, a W-9 form is not provided since Dowell has previously received a payment from the state.

Dowell received a determination of their compliance status from the NMED on October 7, 1994. Based on this late date, Western Water Consultants, Inc. (WWC) requests "late reimbursement" on behalf of Dowell for Phase 4 work qualifying under the reimbursement program.

Your consideration of this claim is greatly appreciated. If you have any questions or need additional documentation, please feel free to call me at 307/742-0031.

Sincerely,

Lisa Jarvis

Lisa Jarvis, Geologist

LJ/jb
Enclosures
cc: John Miller, Dowell
Jeff Walker, NMED/Ground-water Bureau (w/out attachments)
File: 90-125L-A & E

Schlumberger Dowell

Jeff Walker

Jeff –

Apologize for sending to wrong address. Here's another copy.

John

1/6/95

John Miller

Schlumberger Dowell

Jeff Walker

Jeff –

Apologize for sending to wrong address. Here's another copy.

John

1/6/95

John Miller

Schlumberger

Oilfield Services Shared Resources

John A. Miller
Remediation Manager

November 28, 1994

Mr. Jeff Walker
Groundwater Protection and Remediation Bureau
New Mexico Environment Department
Harold Runnels Building
1190 St. Francis Drive
Santa Fe, NM 97502

Re: Work Plan for Additional Investigation, Dowell Schlumberger Incorporated
Artesia, New Mexico Facility

Dear Mr. Walker:

Enclosed is a copy of the work plan for additional investigation at our facility in Artesia, New Mexico. The work plan includes drilling two down-gradient groundwater monitoring wells and three grouped wells completed at different intervals in the upper part of the alluvium. We would like to install the new wells in time to sample them in late January 1995, concurrent with regular quarterly monitoring of existing wells.

If you have any questions, please contact me at 713-275-8498.

Sincerely,

John A. Miller

JAM:lb

Enclosure

cc: Tony Moreland NMED - UST Bureau (with enclosure)
WWC, Laramie

P.O. Box 2727, Houston, Texas 77252-2727
300 Schlumberger Drive, Sugar Land, Texas 77478
(713) 275-8498 (713) 275-8526 (fax)

Schlumberger Oilfield Services

Oilfield Services Shared Resources

John A. Miller
Remediation Manager

November 28, 1994

Mr. Jeff Walker
Groundwater Protection and Remediation Bureau
New Mexico Environment Department
Harold Runnels Building
1190 St. Francis Drive
Santa Fe, NM 97502

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Sincerely,

John A. Miller

JAM:lb

Enclosure

cc: Tony Moreland NMED - UST Bureau (with enclosure)
WWC, Laramie

P.O. Box 2727, Houston, Texas 77252-2727
300 Schlumberger Drive, Sugar Land, Texas 77478
(713) 275-8498 (713) 275-8526 (fax)

Schlumberger Oilfield Services

Oilfield Services Shared Resources

FAX

DATE: 2/3/95 No. PAGES: 4

TO: BAIRD SWANSON / JEFF WALKER FAX NO. 505-884-9254

FROM John A. Miller
Remediation Manger

FAX NO.: 713/275-8526
Phone No: 713/275-8498

Message: ARTESIA

EXPANDED DRAWING SHOWING LOCATION OF MW-18. IF LABORATORY RESULTS FROM MW-18 SHOW A PROBLEM, WE CAN COME BACK AND GO FURTHER OUT.

300 Schlumberger Drive
Sugar Land, TX 77478

P. O. Box 2727
Houston, TX 77252-2727

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FACSIMILE COMMUNICATION:

Job Number 90-125L.3

COMPANY: Dowell Schlumberger Incorporated

ATTENTION: John Miller

FACSIMILE NO: (713) 275-8526

This page and the following 2 *pages, totaling* 3 *pages, are*

FROM: Robin Daly

DATE: 2/2/95

If there are any problems with this transaction, please
Telephone: (307) 742-0031
Fax: (307) 721-2913

OTHER LOCATIONS

1849 SUGARLAND DRIVE, SUITE 134
SHERIDAN, WYOMING 82801
(307) 672-0761
FAX (307) 674-4265

701 ANTLER DRIVE, SUITE 233
CASPER, WY 82601
(307) 473-2707
FAX (307) 237-0828

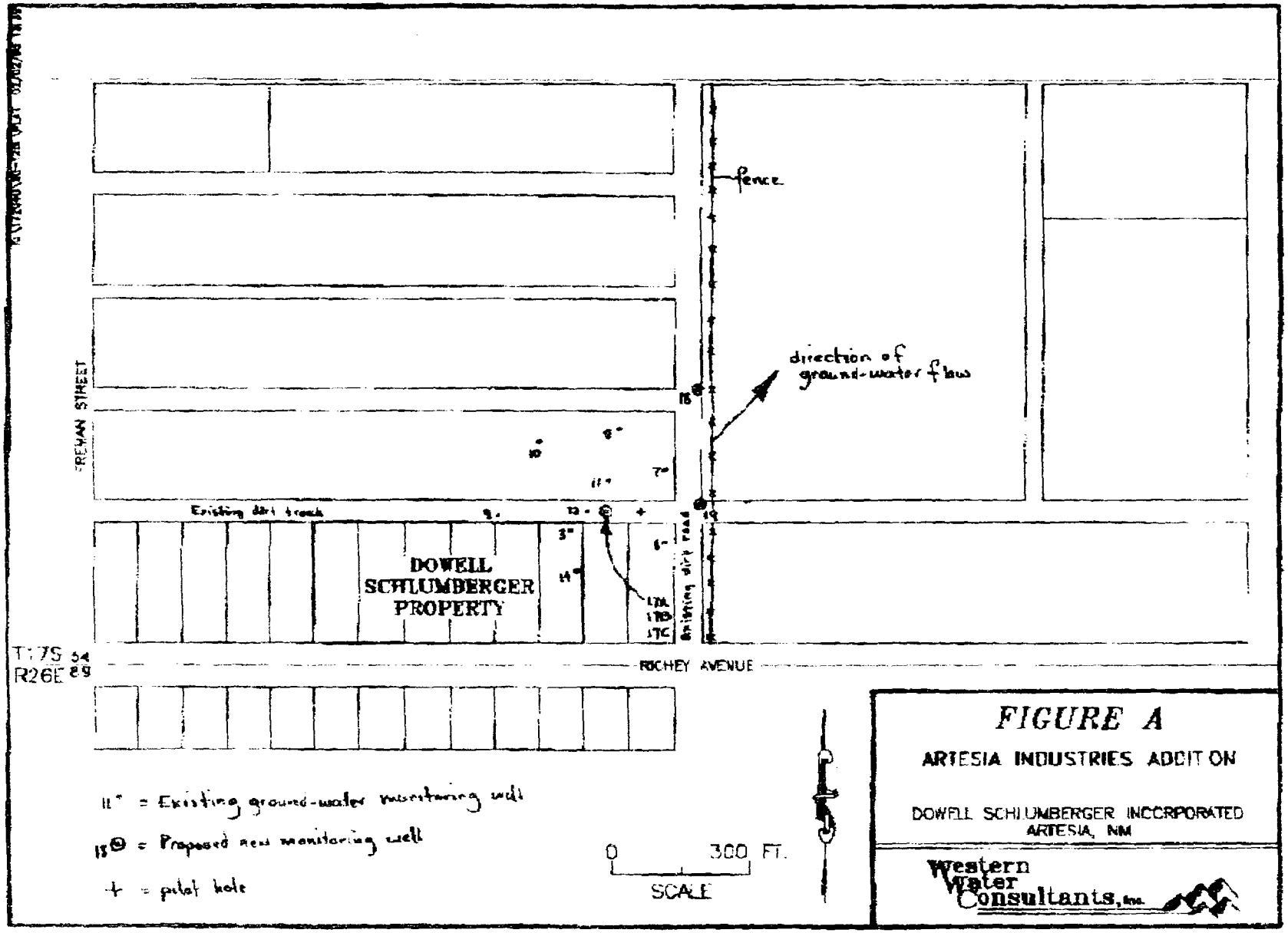
MEMO

TO: John Miller
FROM: Robin Daley
RE: Location of proposed downgradient ground-water monitoring wells in Artesia, NM.
DATE: 2/2/95

Here is the information requested on the proposed locations for the two downgradient ground-water monitoring wells northeast of the Dowell facility in Artesia, New Mexico. I have included a digitized map of the county plat for the Artesia Industries Addition where the facility is located (Figure A). The plat map we received from Eddy County is not suitable for faxing.

The final locations of the downgradient wells will be determined in the field. We plan to have a surveyor locate the platted and dedicated county rights-of-way so that we will be sure to position the wells on the county land. Other factors which will influence well locations are direction of ground-water flow (probable plume migration) and location of physical features such as fences, roads, and utilities. Our objective will be to locate the wells downgradient of the northeast corner of the Dowell facility while keeping them in the county right-of-way and making adjustments for existing roads and fences. The locations marked on Figure A represent my best estimate of the well locations, given the above constraints.

If you have trouble reading the faxed map, let me know.


fence
direction of ground-water flow
FREHAN STREET
Existing dirt track
DOWELL SCHLUMBERGER PROPERTY
existing dirt road
T. 17S
R26E
ROCHEY AVENUE
11" = Existing ground-water monitoring well
15 = Proposed new monitoring well
+ = pilot hole
0 300 FT.
SCALE
FIGURE A
ARTESIA INDUSTRIES ADDITON
DOWELL SCHLUMBERGER INCORPORATED
ARTESIA, NM
Western Water Consultants, Inc.

9:1 Refutation of Dowell-Schlumberger's Denial of the occurrence of DNAPL @ Artesia, NM

- Movement of DNAPLs and DNAPL behavior is only loosely coupled, if at all, to the behavior of water. ... forces that control the rate, flow direction and ultimate fate of DNAPL are different ... (than) those that control the distribution of dissolved-phase plumes

- ... Conventional drilling technologies have a high potential for promoting vertical movement of DNAPL (MW-3, MW-12 placed near source-wastewater-treatment reservoir)

- Movement and distribution of DNAPL is difficult to determine even at sites with relatively homogeneous soil and a known, uniform DNAPL source. Artesia's geology/stratigraphic column is complex (silts and clays interbedded w/ gypsum, fine sands and limestone gravels.

PHASE 5: FILE INFORMATION

Company Name:	Western Water Consultants, Inc.
Address:	611 Skyline Road, Laramie, Wyoming 82070
Telephone Number:	307/742-0031
Contact:	Lisa Jarvis
Client's Name:	Dowell Schlumberger Incorporated (Dowell)
Address:	300 Schlumberger Drive, Sugarland, Texas 77478
Telephone Number:	713/275-8498
Contact:	John Miller
Vendor's Federal Tax ID#:	38-2397173
Name of Site:	Dowell Schlumberger Incorporated, Artesia, New Mexico
Phase #:	Phase 5 Work Conducted During the Following Quarters: May 1, 1994 - July 31, 1994, and August 1, 1994 - October 31, 1994.
Task #:	1 - Soil Vapor Extraction System Operation and Maintenance 2 - Quarterly Ground-water Monitoring and Reporting

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December 14, 1994

Tony Moreland, Project Manager
New Mexico Environment Department
Underground Storage Tank Bureau, Reimbursement Program
P.O. Box 26110
Santa Fe, New Mexico 87502

RE: Phase 5 Work Plan and Cost Detail Forms

Dowell Schlumberger Incorporated
500 East Richey Avenue
Artesia, New Mexico 88210

Dear Tony:

This letter is in response to recent telephone conversations in which we discussed deficiencies in Dowell Schlumberger Incorporated's (Dowell) submittals to the New Mexico Environment Department (NMED) under the Underground Storage Tank Reimbursement Program.

This letter, and its attachments, should complete the preclaim submittal for work proposed and conducted under Phase 5 at Dowell's Artesia, New Mexico site.

Submittal Format

To assist NMED's review process, preclaim information is submitted on the old (pre-October 1994) cost detail forms. A 12/1/94 telephone conversation with Rita Gonzalez (NMED) indicated this approach would be acceptable.

Phase 5 Workplan and Cost Detail Forms

According to NMED's records, a work plan and associated cost detail forms for Phase 5 work was submitted June 28, 1993. This preclaim covered work conducted during the following two quarters:

OTHER LOCATIONS

1949 SUGARLAND DRIVE, SUITE 134
SHERIDAN, WYOMING 82801
(307) 672-0761
FAX (307) 674-4265

701 ANTLER DRIVE, SUITE 233
CASPER, WY 82601
(307) 473-2707
FAX (307) 237-0828

- November 1, 1993 - January 31, 1994, and

- February 1, 1994 - April 30, 1994.

According to your record review, a work plan and cost detail forms were never submitted for the subsequent two quarters:

- May 1, 1994 - July 31, 1994, and

- August 1, 1994 - October 31, 1994.

To complete Dowell's Phase 5 submittal, the following documents have been prepared and are attached for your review and approval:

- a work plan for "Operation and Maintenance of Two Soil Vapor Extraction Systems", and

- cost detail forms for Phase 5 work, including:

  Task 1: "Soil Vapor Extraction System Operation and Maintenance", and

  Task 2: "Quarterly Ground-water Monitoring and Reporting".

Again, thank you for your help. If you have any questions or need additional documentation, please call me at 307/742-0031.

Sincerely,

Lisa Jarvis

Lisa Jarvis, Geologist

LJ:sb
Enclosures
cc: John Miller, Dowell Schlumberger Incorporated
Jeff Walker, NMED/Ground-water Division
File: 90-125L-E

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611 SKYLINE ROAD, P.O. BOX 4128 • LARAMIE, WYOMING 82071 • (307) 742-0031 • FAX (307) 721-2913

PHASE 5: WORK PLAN FOR OPERATION AND MAINTENANCE OF TWO SOIL VAPOR EXTRACTION SYSTEMS

Dowell Schlumberger Incorporated (Dowell)
500 East Richey Avenue
Artesia, New Mexico 88210

December 14, 1994

This work plan describes work conducted during the following two quarters:

- May 1, 1994 - July 31, 1994, and
- August 1, 1994 - October 31, 1994.

Task	Description
1	Soil Vapor Extraction System Operation and Maintenance:
	- Conduct quarterly site visits to check and record operations.
	- Check air emissions.
	- Repair or replace parts (e.g., air filters, carbon canisters, and blower oil).
	- Document site visit.
2	Quarterly Ground-water Monitoring and Reporting:
	- Conduct quarterly ground-water monitoring activities.
	- Prepare quarterly status reports and submit to the New Mexico Environment Department/Underground Storage Tank Bureau (assume two submittals under this work plan).

OTHER LOCATIONS

1949 SUGARLAND DRIVE, SUITE 134
SHERIDAN, WYOMING 82801
(307) 672-0761
FAX (307) 674-4265

701 ANTLER DRIVE, SUITE 233
CASPER, WY 82601
(307) 473-2707
FAX (307) 237-0828

NEW MEXICO CORRECTIVE ACTION FUND PROGAM
COST DETAIL FORM

Claim # _____ X check if this is a continuation sheet.
Facility # 563001
Owner # 563

CIRCLE ONE ONLY: MSA PHASE 1 PHASE 2 PHASE 3 PHASE 4 (PHASE 5)

CIRCLE ONE ONLY: (PRE-CLAIM) CLAIM PRIOR CLAIM

TASK 1 (brief narrative description):

Soil Vapor Extraction System Operation and Maintenance

PROFESSIONAL SERVICES

Labor Category	Rate	Unit	Total
Project Manager (Sr. Prof. 3)	$59.00/hr.	10	$ 590.00
Project Engineer (Sr. Prof. 3)	59.00/hr.	20	1,180.00
Project Hydrogeologist (Jr. Prof. 2)	43.50/hr.	20	870.00
Field Technician (Super Tech.)	38.25/hr	30	1,147.50
Drafting (CADD Operator)	31.00/hr.	10	310.00
Secretary (Clerical)	23.75/hr.	10	237.50
Subtotal			$ 4,335.00

EXPENSES

Description	Rate	Unit	Total
Mileage	0.25/Mile	800	$ 200.00
Per Diem	65/day	2	130.00
PPE	25/day	2	50.00
PID	30/day	2	60.00
GC	60/spl	10	600.00
CADD Station	15/hr.	10	150.00
Parts	L.S.	750	750.00
Subtotal			$ 1,940.00

SUBCONTRACTOR

Description	Rate	Unit	Total
None			
Subtotal			

Monthly
GRAND TOTAL $ 6,275.00/Sampling Event
$12,550.00/2 Sampling Events

NEW MEXICO CORRECTIVE ACTION FUND PROGAM
COST DETAIL FORM

Claim # _____ _x_ check if this is a continuation sheet.
Facility # 563001
Owner # 563

CIRCLE ONE ONLY: MSA PHASE 1 PHASE 2 PHASE 3 PHASE 4 (PHASE 5)

CIRCLE ONE ONLY: (PRE-CLAIM) CLAIM PRIOR CLAIM

TASK 2 (brief narrative description):

Quarterly Ground-Water Monitoring and Reporting

PROFESSIONAL SERVICES

Labor Category	Rate	Unit	Total
Project Manager (Sr. Prof. 3)	$59.00/hr.	20	$1,180.00
Project Hydrogeologist (Jr. Prof. 2)	43.50/hr.	50	2,175.00
Drafting (CADD Operator)	31.00/hr.	20	620.00
Secretary (Clerical)	23.75/hr.	10	237.50
Clerk	20.00/hr.	10	200.00
Subtotal			$4,412.00

EXPENSES

Description	Rate	Unit	Total
Mileage	0.25/Mile	800	$ 200.00
Per Diem	65/dy.	4	260.00
Bailers	6/ea.	20	120.00
PID	30/dy.	4	120.00
Water Level Probe	25/dy.	4	100.00
Shipping	200.00	L.S.	200.00
Copies	100.00	L.S.	100.00
Telephone	50.00	L.S.	50.00
Subtotal			$1,150.00

SUBCONTRACTOR

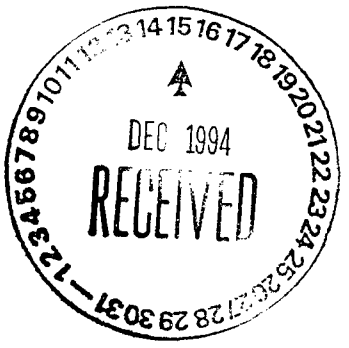
Description	Rate	Unit	Total
Laboratory - EPA Method 8240, GW	$175.00/ Sample	20	$3,500.00
Subtotal			

Quarterly GRAND TOTAL	$9,062.00/Sampling Event

Grand Total (Tasks 1 and 2): $30,674.00
(2 Sampling Events)

$18,124.00/2 Sampling Events

PHASE 5 (1994-1995): FILE INFORMATION



Company Name:	Western Water Consultants, Inc.
Address:	611 Skyline Road, Laramie, Wyoming 82070
Telephone Number:	307/742-0031
Contact:	Lisa Jarvis
Client's Name:	Dowell Schlumberger Incorporated (Dowell)
Address:	300 Schlumberger Drive, Sugarland, Texas 77478
Telephone Number:	713/275-8498
Contact:	John Miller
Vendor's Federal Tax ID#:	38-2397173
Name of Site:	Dowell Schlumberger Incorporated, Artesia, New Mexico
Phase #:	Phase 5 (1994-1995)
Task #:	1 - Soil Vapor Extraction System Operation and Maintenance 2 - Quarterly Ground-water Monitoring and Reporting

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December 9, 1994

Tony Moreland, Project Manager
New Mexico Environment Department
Underground Storage Tank Bureau, Reimbursement Program
P.O. Box 26110
Santa Fe, New Mexico 87502

RE: Phase 5 (1994-1995) Work Plan and Cost Detail Forms

Dowell Schlumberger Incorporated
500 East Richey Avenue
Artesia, New Mexico 88210

Dear Tony:

The following documents are submitted for your review and approval:

- a proposed work plan for "Operation and Maintenance of Two Soil Vapor Extraction Systems", and

- Cost Detail Forms (CDFs) for proposed Phase 5 (1994-1995) work, Tasks 1 and 2.

Work described in the work plan under Phase 5, Tasks 1 and 2, will be conducted during the following four quarters:

November 1, 1994	}	
December 1994	}	first quarter
January 31, 1995	}	
February 1, 1995	}	
March 1995	}	second quarter
April 30, 1995	}	
May 1, 1995	}	
June 1995	}	third quarter
July 31, 1995	}	

OTHER LOCATIONS

1949 SUGARLAND DRIVE, SUITE 134
SHERIDAN, WYOMING 82801
(307) 672-0761
FAX (307) 674-4265

701 ANTLER DRIVE, SUITE 233
CASPER, WY 82601
(307) 473-2707
FAX (307) 237-0828

August 1, 1995 }
September 1995 } fourth quarter
October 31, 1995 }

Projected costs on the CDFs reflect proposed increases in Western Water Consultants, Inc.'s billing rates for 1995. Actual costs may be less than those projected and will be addressed in subsequent claims for Phase 5 (1994-1995) work.

If you have any questions, please call me at 307/742-0031.

Sincerely,

Lisa Jarvis

Lisa Jarvis
Geologist

LJ:sb
Enclosures
cc: John Miller, Dowell Schlumberger Incorporated
Jeff Walker, NMED/Ground-water Division
File: 90-125L-E

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611 SKYLINE ROAD, P.O. BOX 4128 • LARAMIE, WYOMING 82071 • (307) 742-0031 • FAX (307) 721-2913

PHASE 5 (1994-1995)

WORK PLAN FOR OPERATION AND MAINTENANCE OF TWO SOIL VAPOR EXTRACTION SYSTEMS

Dowell Schlumberger Incorporated (Dowell)
500 East Richey Avenue
Artesia, New Mexico 88210

December 9, 1994

Task	Description
1	Soil Vapor Extraction System Operation and Maintenance:
	- Conduct quarterly site visits to check and record operations.
	- Check air emissions.
	- Repair or replace parts (e.g., air filters, carbon canisters, and blower oil).
	- Document site visit.
2	Quarterly Ground-water Monitoring and Reporting:
	- Conduct quarterly ground-water monitoring activities.
	- Prepare quarterly status reports and submit to the New Mexico Underground Storage Tank Bureau (assume four submittals under this work plan).

OTHER LOCATIONS

1949 SUGARLAND DRIVE, SUITE 134
SHERIDAN, WYOMING 82801
(307) 672-0761
FAX (307) 674-4265

701 ANTLER DRIVE, SUITE 233
CASPER, WY 82601
(307) 473-2707
FAX (307) 237-0828

NEW MEXICO CORRECTIVE A[illegible] FUND COST DETAIL FORM--SUMMARY SHEET

Site Name Dowell Schlumberger Incorporated (Dowell) Site Address 500 East Richey Avenue, Artesia, New Mexico 88210

Circle only one: *Workplan* *Claim*

Circle only one:
Minimum Site Assessment
Phase 1--Hydrogeo Investigation
Phase 2--Free Product/ Saturated Soil Recovery
Phase 3--Reclamation Proposal
Phase 4--Reclamation Implementation
Phase 5--Operations and Maintenance

TASK # 1 : (brief description) Soil Vapor Extraction System Operation and Maintenance

NMED Use Only: Project Manager | Auditor

SUMMARY SHEET	TOTAL
PROFESSIONAL SERVICES	$19,280.00
TAXABLE EXPENSES	
TAXABLE SUBCONTRACTORS	
TAXABLE SUBTOTAL	
NMGRT RATE _____ X TAXABLE SUBTOTAL =	
TOTAL	$19,280.00
NONTAXABLE EXPENSES	$ 7,280.00
NONTAXABLE SUBCONTRACTORS	$ 4,200.00
NONTAXABLE SUBTOTAL	$11,480.00
GRAND TOTAL OF CLAIM	$30,760.00

NEW MEXICO CORRECTIVE ACTIO 'D COST DETAIL FORM--PROFESSIONAL SERVICES

Site Name Dowell Schlumberger Incorporated (Dowell) **Site Address** 500 East Richey Avenue Artesia, New Mexico 88210

Circle only one: *Workplan* *Claim*

Circle only one:
Minimum Site Assessment
Phase 1--Hydrogeo Investigation
Phase 2--Free Product/ Saturated Soil Recovery
Phase 3--Reclamation Proposal
Phase 4--Reclamation Implementation
Phase 5--Operations and Maintenance

TASK # 1 : (brief description) Soil Vapor Extraction System Operation and Maintenance

NMED Use Only

PROFESSIONAL SERVICES	Invoice #	Rate	Unit	# of Units	Total	Project Manager	Auditor
Project Manager	N/A	$65.00	Hour	10	$ 650.00		
Project Engineer	N/A	65.00	Hour	20	$1,300.00		
Project Scientist	N/A	48.00	Hour	20	$ 960.00		
Field Technician II	N/A	43.00	Hour	30	$1,290.00		
Draftsperson I	N/A	35.00	Hour	10	$ 350.00		
Secretary	N/A	27.00	Hour	10	$ 270.00		
				Subtotal	$4,820.00/ Sampling Event		
Subtotal					$19,280.00/ 4 Sampling Events		

10/13/94.R

NEW MEXICO CORRECTIVE ON FUND COST DETAIL FORM--EXPENSES

Site Name Dowell Schlumberger Incorporated (Dowell) **Site Address** 500 East Richey Avenue, Artesia, New Mexico 88210

Circle only one: *Workplan* *Claim*

Circle only one:
Minimum Site Assessment
Phase 1--Hydrogeo Investigation
Phase 2--Free Product/ Saturated Soil Recovery
Phase 3--Reclamation Proposal
Phase 4--Reclamation Implementation
Phase 5--Operations and Maintenance

TASK # 1 : (brief description) Soil Vapor Extraction System Operation and Maintenance

NMED Use Only: Project Manager | Auditor

EXPENSES	Invoice #	Rate	Unit	# of Units	Total
Nontaxable					
Mileage	N/A	$ 0.25	Mile	800	$ 200.00
Per Diem	N/A	75.00	Day	2	$ 130.00
Personal Protection Equip.	N/A	30.00	Day	2	$ 60.00
PID	N/A	40.00	Day	2	$ 80.00
GC	N/A	60.00	Sample	10	$ 600.00
System Parts	N/A	At cost	----	---	$ 750.00
				Subtotal	$1,820.00/ Sampling Event
Nontaxable subtotal		(	4 sampling events)		$7,280.00
Taxable					
Taxable subtotal					----

NEW MEXICO CORRECTIVE ACTION) COST DETAIL FORM--SUBCONTRACTOR CHARGES

Site Name Dowell Schlumberger Incorporated (Dowell) Site Address 500 East Richey Avenue, Artesia, New Mexico 88210

Circle only one: *Workplan* *Claim*

Circle only one:
Minimum Site Assessment
Phase 1--Hydrogeo Investigation
Phase 2--Free Product/ Saturated Soil Recovery
Phase 3--Reclamation Proposal
Phase 4--Reclamation Implementation
Phase 5--Operations and Maintenance

TASK # 1 : (brief description) Soil Vapor Extraction System Operation and Maintenance

NMED Use Only: Project Manager | Auditor

SUBCONTRACTORS	Invoice #	Rate	Unit	# of Units	Total
Nontaxable					
Cardinal Laboratories	N/A	$150	Sample	7	$1,050.00
				Subtotal	$1,050.00/ Sampling Event
Nontaxable subtotal			(4 Sampling Events)		$4,200.00
Taxable					
Taxable subtotal					----

10/13/94/KF

NEW MEXICO CORRECTIVE A[ction] FUND COST DETAIL FORM--SUMMARY SHEET

Site Name Dowell Schlumberger Incorporated (Dowell) Site Address 500 East Richey Avenue, Artesia, New Mexico 88210

Circle only one: *Workplan* *Claim*

Circle only one:
Minimum Site Assessment
Phase 1--Hydrogeo Investigation
Phase 2--Free Product/ Saturated Soil Recovery
Phase 3--Reclamation Proposal
Phase 4--Reclamation Implementation
Phase 5--Operations and Maintenance

TASK # 2 : (brief description) Quarterly Ground-water Monitoring and Reporting

SUMMARY SHEET	TOTAL
PROFESSIONAL SERVICES	$19,560.00
TAXABLE EXPENSES	
TAXABLE SUBCONTRACTORS	
TAXABLE SUBTOTAL	$19,560.00
NMGRT RATE _____ X TAXABLE SUBTOTAL =	
TOTAL	$19,560.00
NONTAXABLE EXPENSES	$ 4,120.00
NONTAXABLE SUBCONTRACTORS	$16,000.00
NONTAXABLE SUBTOTAL	$20,120.00
GRAND TOTAL OF CLAIM	$39,680.00

NMED Use Only

Project Manager	Auditor

NEW MEXICO CORRECTIVE ACTIO 'D COST DETAIL FORM--PROFESSIONAL SERVICES

Site Name Dowell Schlumberger Incorporated (Dowell) Site Address 500 East Richey Avenue Artesia, New Mexico 88210

Circle only one: *Workplan* *Claim*

Circle only one:
Minimum Site Assessment
Phase 1--Hydrogeo Investigation
Phase 2--Free Product/ Saturated Soil Recovery
Phase 3--Reclamation Proposal
Phase 4--Reclamation Implementation
Phase 5--Operations and Maintenance

TASK # 2 : (brief description) Quarterly Ground-water Monitoring and Reporting

PROFESSIONAL SERVICES	Invoice #	Rate	Unit	# of Units	Total
Project Manager	N/A	$65.00	Hour	20	$1,300.00
Project Scientist	N/A	$48.00	Hour	50	$2,400.00
Draftsperson I	N/A	$35.00	Hour	20	$ 700.00
Secretary	N/A	$27.00	Hour	10	$ 270.00
Clerk	N/A	$22.00	Hour	10	$ 220.00
					$4,890.00/ Sampling Event
Subtotal					$19,560.00/ 4 Sampling Events)

NMED Use Only

Project Manager	Auditor

NEW MEXICO CORRECTIVE ON FUND COST DETAIL FORM--EXPENSES

Site Name Dowell Schlumberger Incorporated (Dowell) **Site Address** 500 East Richey Avenue, Artesia, New Mexico

Circle only one: *Workplan* *Claim*

Circle only one:
Minimum Site Assessment
Phase 1--Hydrogeo Investigation
Phase 2--Free Product/ Saturated Soil Recovery
Phase 3--Reclamation Proposal
Phase 4--Reclamation Implementation
Phase 5--Operations and Maintenance

TASK # 2 : (brief description) Quarterly Ground-water Monitoring and Reporting

NMED Use Only

EXPENSES	Invoice #	Rate	Unit	# of Units	Total	Project Manager	Auditor
Nontaxable							
Mileage	N/A	$ 0.25	Mile	800	$ 200.00		
Per Diem	N/A	$65.00	Day	2	$ 130.00		
Personal Protection Equip.	N/A	$30.00	Day	2	$ 60.00		
Disposable Bailers	N/A	$ 8.00	Bailer	20	$ 160.00		
PID	N/A	$40.00	Day	2	$ 80.00		
Fluid Level Detector	N/A	$25.00	Day	2	$ 50.00		
Copies	N/A	$ 0.05	Page	2000	$ 100.00		
Telephone Charges	N/A	At Cost	----	----	$ 50.00		
Shipping	N/A	At Cost	----	----	$ 200.00		
				Subtotal	$1,030.00/ Sampling Event		
Nontaxable subtotal		(4	Sampling	Events)	$4,120.00		
Taxable							
Taxable subtotal					----		

10/13/04/K7

NEW MEXICO CORRECTIVE ACTION) COST DETAIL FORM--SUBCONTRACTOR CHARGES

Site Name: Dowell Schlumberger Incorporated (Dowell)

Site Address: 500 East Richey Avenue, Artesia, New Mexico 88210

Circle only one: *Workplan* *Claim*

Circle only one:
Minimum Site Assessment
Phase 1--Hydrogeo Investigation
Phase 2--Free Product/ Saturated Soil Recovery
Phase 3--Reclamation Proposal
Phase 4--Reclamation Implementation
Phase 5--Operations and Maintenance

TASK # 2 : (brief description) Quarterly Ground-water Monitoring and Reporting

NMED Use Only: Project Manager | Auditor

SUBCONTRACTORS	Invoice #	Rate	Unit	# of Units	Total
Nontaxable					
Hydrologic Laboratories	N/A	$200.00	Sample	20	$4,000.00
				Subtotal	$4,000.00 / Sampling Event
Nontaxable subtotal		(4	Sampling	Events)	$16,000.00
Taxable					
Taxable subtotal					----

PHASE 3: FILE INFORMATION

Company Name: Western Water Consultants, Inc.
Address: 611 Skyline Road, Laramie, Wyoming 82070
Telephone Number: 307/742-0031
Contact: Lisa Jarvis

Client's Name: Dowell Schlumberger Incorporated (Dowell)
Address: 300 Schlumberger Drive, Sugarland, Texas 77478
Telephone Number: 713/275-8498
Contact: John Miller
Vendor's Federal Tax ID Number: 38-2397173

Name of Site: Dowell Schlumberger Incorporated, Artesia, New Mexico

Phase #: Phase 3

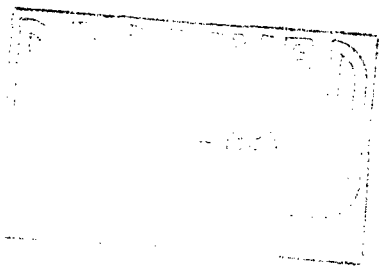
Task #: Tasks 1, 2, and 3

Work Plan Approval Letter Date:

- Phase 3, Task 1: No work plan approval letter exists
- Phase 3, Task 2: 7/29/93
- Phase 3, Task 3: 7/29/93

Billing Period:

- Phase 3, Task 1: 9/22/92 - 2/20/93
- Phase 3, Task 2: 2/21-93 - 6/20/93
- Phase 3, Task 3: 6/21/93 - 7/21/93



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611 SKYLINE ROAD, P.O. BOX 4128 • LARAMIE, WYOMING 82071 • (307) 742-0031 • FAX (307) 721-2913

December 6, 1994

Tony Moreland, Project Manager
New Mexico Environment Department
Underground Storage Tank Bureau, Reimbursement Program
P.O. Box 26110
Santa Fe, New Mexico 87502

RE: Phase 3 Preclaim and Claim Submittals for Reimbursement

Dear Tony:

This letter is in response to our 9/8/94 telephone conversation in which we discussed deficiencies in Dowell Schlumberger Incorporated's (Dowell) submittals to the New Mexico Environment Department under the Underground Storage Tank Reimbursement Program.

This letter, and its attachments, should complete both preclaim and claim submittals for all work proposed and conducted under Phase 3 at Dowell's Artesia, New Mexico site.

With this submittal, Western Water Consultants, Inc. (WWC) requests "late reimbursement" on behalf of Dowell for all Phase 3 work qualifying under the reimbursement program. Dowell received a determination of their compliance status on October 7, 1994.

Submittal Format

To assist NMED's review process, additional documentation for Phase 3 work is submitted on the old forms (pre-October 1994). A 12/1/94 telephone conversation with Rita Gonzalez, New Mexico Environment Department, indicated this approach would be acceptable for past preclaims and claims.

Phase 3 Preclaims

According to WWC's records, three preclaims were submitted under Phase 3:

- Preclaim #1 for Phase 3 work conducted between 9/22/92 and 2/20/93.
  Task 1: Develop Cleanup Plan
  - SVE Design
  - Prepare Plans and Specifications

OTHER LOCATIONS

1949 SUGARLAND DRIVE, SUITE 134
SHERIDAN, WYOMING 82801
(307) 672-0761
FAX (307) 674-4265

701 ANTLER DRIVE, SUITE 233
CASPER, WY 82601
(307) 473-2707
FAX (307) 237-0828

- Preclaim #2 for Phase 3 work conducted between 2/21/93 and 6/20/93.
  Task 2: Ground-water Monitoring and Reporting

- Preclaim #3 for Phase 3 work conducted between 6/20/93 and 7/20/93.
  Task 3: Resample MW-3
  Redevelop All Monitoring Wells
  Reporting

Per our 9/8/94 conversation, there are three deficiencies associated with the Phase 3 preclaims: 1) a work plan was never submitted for Preclaim #2, 2) the cost detail form for Preclaim #2 needed to be modified to reflect per diem and mileage rates approved by the New Mexico Environment Department/Underground Storage Tank Bureau's contractor fee schedule, and 3) the cost detail form for Preclaim #3 also needed to be modified to reflect approved per diem and mileage rates.

These deficiencies have been addressed and the following documents are attached:

- A work plan for Preclaim #2 (dated 12/6/94),

- A modified Cost Detail Form for Preclaim #2, and

- A modified Cost Detail Form for Preclaim #3.

Additionally, you indicated you did not have a copy of the work plan for Preclaim #3. A copy is attached for your files.

These documents should complete Dowell's preclaim submittals for Phase 3.

Phase 3 Claims

Claims for work completed under Preclaims #1, #2 and #3 have already been submitted by Dowell.

According to our 9/8/94 conversation, work proposed under Preclaims #2 and #3 was approved in a June 29, 1993 letter from yourself. Claims for Phase 3 work conducted between 2/21/93 and 6/20/93, and 6/20/93 and 7/20/93 were submitted January 19, 1994 by Dowell.

Thank you for your patience and help - if you have any questions or need additional documentation, please feel free to call me at 307/742-0031.

Sincerely,

Lisa Jarvis

Lisa Jarvis, Geologist

LJ/jb
Enclosure
cc: John Miller, Dowell
Jeff Walker, NMED/Ground-water Bureau ✓
File: 90-125L-E

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MODIFIED WORK PLAN FOR GROUND-WATER MONITORING AND REPORTING ACTIVITIES

Artesia, New Mexico
December 6, 1994 (Submittal for March 1993)

1.0 INTRODUCTION

The following Work Plan describes additional ground-water monitoring and reporting activities to be conducted at the Dowell Facility in Artesia, New Mexico on March 16, 1993.

2.0 ACTIVITIES

Activities included under this work plan are as follows:

1. Measure static water levels in each of 15 wells.

2. Evacuate 3 well volumes; collect ground-water samples from each well.

3. Document sampling activities and analytical results. Submit results to NMED/UST Program.

OTHER LOCATIONS

1949 SUGARLAND DRIVE, SUITE 134
SHERIDAN, WYOMING 82801
(307) 672-0761
FAX (307) 674-4265

701 ANTLER DRIVE, SUITE 233
CASPER, WY 82601
(307) 473-2707
FAX (307) 237-0828

NEW MEXICO CORRECTIVE ACTION FUND PROGAM
COST DETAIL FORM

Claim # _____ ___ check if this is a continuation sheet
Facility # 563001
Owner # 563

CIRCLE ONE ONLY: MSA PHASE 1 PHASE 2 (PHASE 3) PHASE 4 PHASE 5

CIRCLE ONE ONLY: (PRE-CLAIM) CLAIM PRIOR CLAIM

TASK 2 (brief narrative description):

Ground-water monitoring and reporting
2/21/93 - 6/20/93

(Modified Preclaim 12/6/94)

PROFESSIONAL SERVICES

Labor Category	Rate	Unit	Total
Staff Hydrogeologist (Jr. Prof. 2)	$43.50/hr.	40 hr.	$ 1,740.00
Project Manager (Sr. Prof. 3)	59.00/hr.	10 hr.	590.00
Drafting (CADD Operator)	31.00/hr.	10 hr.	310.00
Secretary (Clerical)	23.75/hr.	10 hr.	237.50
			$2,877.50
Subtotal			

EXPENSES

Description	Rate	Unit	Total
Mileage	$0.25/mile	400	$ 100.00
Per Diem	$65/day	1	65.00
Equipment	230.00	L.S.	230.00
Copies	0.10	200	20.00
Telephone	50.00	L.S.	50.00
Shipping	200.00	L.S.	200.00
			$ 665.00
Subtotal			

SUBCONTRACTOR

Description	Rate	Unit	Total
Laboratory - EPA Method 8240 GW Samples	$175.00 Sample	20 Samples	$3,500.00
Subtotal			$3,500.00

GRAND TOTAL	$7,042.50

NEW MEXICO CORRECTIVE ACTION FUND PROGAM
COST DETAIL FORM

Claim # _____ ___ check if this is a continuation sheet.
Facility # 563001
Owner #563

CIRCLE ONE ONLY: MSA PHASE 1 PHASE 2 PHASE 3 PHASE 4 PHASE 5

CIRCLE ONE ONLY: PRE-CLAIM CLAIM PRIOR CLAIM

TASK 3 (brief narrative description):

Resample MW-3
Redevelop all monitoring wells (Modified Preclaim 12/6/94)
Reporting
6/21/93 - 7/20/93

PROFESSIONAL SERVICES

Labor Category	Rate	Unit	Total
Scientist (Jr. Prof. 2)	$43.50/hr.	30	$ 1,305.00
Project Manager (Sr. Prof. 3)	59.00/hr.	10	590.00
Staff Hydrogeologist (Jr. Pro. 2)	43.50/hr.	10	435.00
Drafting (Cadd Operator)	31.00/hr.	5	155.00
Secretary (Clerical)	23.75/hr.	5	118.75
			$2,603.75
Subtotal			

EXPENSES

Description	Rate	Unit	Total
Mileage	$0.25/mile	400	$ 100.00
Bailers	$ 6.00/ea.	20	$ 120.00
Per Diem - Meals, room	$65.00/day	1	65.00
PID	$30.00/day	1 Day	30.00
Personal Protective Equip,	$25.00/day	1 Day	25.00
Shipping	$100.00	LS	100.00
Telephone	$ 50.00	LS	50.00
Copies	$ 50.00	LS	50.00
Subtotal			$540.00

SUBCONTRACTOR

Description	Rate	Unit	Total
Laboratory - EPA Method 8240	$175/ Sample	2	$350.00
Subtotal			

GRAND TOTAL	$3,493.75

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WESTERN WATER CONSULTANTS, INC.

Engineering • Hydrology • Hydrogeology • Waste Management • Construction Administration

611 SKYLINE ROAD, P.O. BOX 4128 • LARAMIE, WYOMING 82071 • (307) 742-0031 • FAX (307) 721-2913

WORK PLAN FOR RESAMPLING

MW-3 AND REDEVELOPING MONITORING WELLS

Artesia, New Mexico
June 23, 1993

1.0 INTRODUCTION

The following is a Work Plan for additional ground-water monitoring activities to be conducted at the Dowell Schlumberger Incorporated Facility in Artesia, New Mexico. Western Water Consultants, Inc. of Laramie, Wyoming has tentatively scheduled the work to occur on June 30, 1993.

2.0 ACTIVITIES

The activities are as follows:

1. Develop/purge all ground-water monitoring wells which occur at the site of 10 well volumes. All purge water will be containerized in 55 gallon drums, labelled as to the contents and stored until disposal can be arranged.

2. Monitoring well MW-3 will be sampled following development and analyzed for organic compounds in accordance with EPA Method 8240.

3.0 DOCUMENTATION

Following completion of the work, results will be documented and tabulated.

OTHER LOCATIONS

1949 SUGARLAND DRIVE, SUITE 134
SHERIDAN, WYOMING 82801
(307) 672-0761

701 ANTLER DRIVE, SUITE 233
CASPER, WY 82601
(307) 473-2707

STATE OF NEW MEXICO
ENVIRONMENT DEPARTMENT

December 12, 1994

RECEIVED
DEC 15 1994
USTB - ALBQ.

Mr. John A. Miller
Dowell Schlumberger Inc.
P. O. Box 4378
Houston, TX 77210-4378

RE: WORKPLAN DISAPPROVAL FOR ADDITIONAL INVESTIGATIONS AT THE DOWELL SCHLUMBERGER FACILITY IN ARTESIA, NEW MEXICO

Dear Mr. Miller:

The New Mexico Environment Department (NMED) Underground Storage Tank Bureau has reviewed and disapproved for reimbursement purposes, the workplan dated November 28, 1994 for the above-referenced activity from your consultant, Western Water Consultants, Inc. (WWCI).

This workplan is disapproved because the current remediation system is efficiently cleaning up the petroleum hydrocarbon contamination and associated ground water monitoring wells are sufficient for monitoring the progress of cleanup. The proposed activities are required by the Departments' Ground Water Protection and Remediation Bureau and should be completed pursuant to their regulatory authority.

If you have any questions, you may contact me at (505) 827-0158.

Sincerely,

Anthony Moreland
Geologist
Underground Storage Tank Bureau

cc: Lisa L. Jarvis, P.G., Western Water Consultants, Inc., P. O. Box 4128, Laramie, WY 82071
Kathleen A. Garland, Manager, Reimbursement Program
Baird Swanson, Geologist, NMED District I Office
NMED District IV Office, Roswell

Bruce King
Governor

Judith M. Espinosa
Secretary

Ron Curry
Deputy Secretary

Harold Runnels Building
1190 St. Francis Drive
P.O. Box 26110
Santa Fe, NM 87502
(505) 827-2850
FAX (505) 827-2836

(Dennis

The Dow Chemical Company
Midland, Michigan 48674

2030 DOW CENTER
October 12, 1994

VIA FEDERAL EXPRESS

RECEIVED
OCT 13 1994
GROUND WATER BUREAU

Ms. Marcy Leavitt
Chief
Ground Water Protection and Remediation Bureau
Harold Runnels Building
1190 St. Francis Drive
Santa Fe, NM 87502

DOWELL SCHLUMBERGER FACILITY IN ARTESIA, NEW MEXICO

Dear Ms. Leavitt:

On September 16, 1994, Mr. John Miller received a letter from you requesting that additional assessment work be performed outside the boundaries of the Dowell Schlumberger (DSI) facility in Artesia, New Mexico in an attempt to define a plume of contamination which you allege is emanating from the DSI facility.

We are of the opinion that we have been able to define the degree of contamination emanating from the DSI facility and that we have been successfully remediating such contamination through the use of our soil vapor extraction system. On October 4, 1994, we were able to meet with Mr. Jeff Walker and Mr. Baird Swanson in regard to this matter; they helped clarify for us the desires of the NMED in regard to this request.

Though we do not agree that such additional work is necessary, we are proceeding to meet the needs of the NMED in regard to this matter. We will, however, need additional time in which to respond to NMED in regard to this request. Our attempts to draft a detailed plan which will meet the needs of the NMED in this regard have been slowed by the requirements of the task along with the fact that our principal geologist on this project has been serving on jury duty for the past two weeks.

We hereby request an extension of 30 days for the submittal of the requested document to NMED. Your consideration of this matter will be most appreciated.

Please give me a call if you have any questions in regard to this request.

Sincerely yours,

Brent W. Schindler

Brent W. Schindler
Attorney
517-636-5410
517-638-9564 (fax)

lbr/BWS.478

Baird, 10/25/94
I called & granted them the extension. D. McQ.

Schlumberger

Oilfield Services Shared Resources

John A. Miller
Remediation Manager

via Fedex

September 23, 1994

Mr. Jeff Walker
Ground Water Protection and Remediation Bureau
New Mexico Environment Department
NMED District I
4131 Montgomery Blvd. NE
Albuquerque, NM 87109

Re: Dowell Schlumberger Facility
Artesia, NM

Dear Mr. Walker:

Enclosed are a copy of the plans for installation of the Soil Vapor Extraction System and the Soil Vapor Extraction System Quarterly Report dated August 1994.

Per our conversations yesterday and today, we plan to meet with you and Baird Swanson on October 4 at 1:30 p.m. As I stated, our consultant has initiated the water supply well survey and is evaluating air sparging options and adjustments to our SVE system.

We will provide preliminary concepts in our October 4 meeting. We would like to develop our concepts and discuss them in detail with our environmental consulting firm's project manager and principal design engineer in an on-site meeting at the Artesia facility the week of October 24.

If I can be of further assistance, please call me at 713-275-9848.

Sincerely,

John A. Miller

JAM:ph

Enclosure

cc: Baird Swanson, NMED District 1
Tony Moreland, USTB
Susan Fields, WWC
Brent Schindler
Carey Brannan

P.O. Box 2727, Houston, Texas 77252-2727
300 Schlumberger Drive, Sugar Land, Texas 77478
(713) 275-8498 (713) 275-8526 (fax)

FILE COPY

STATE OF NEW MEXICO
ENVIRONMENT DEPARTMENT

September 8, 1994

CERTIFIED MAIL
RETURN RECEIPT REQUESTED

John A. Miller
Environmental Remediation Manager
Dowell Schlumberger Incorporated
P.O. Box 4378
Houston, Texas 77210-4378

RE: NOTIFICATION OF REGULATED DISCHARGE, DOWELL SCHLUMBERGER INCORPORATED FACILITY, ARTESIA, NEW MEXICO.

Dear Mr. Miller:

The Remediation Section of the Ground Water Protection and Remediation Bureau (GWPRB) of the New Mexico Environment Department (NMED) has completed its review of ground water monitoring data supplied to us through your office as part of the ongoing UST Bureau site investigation and remediation. The GWPRB understands that a UST removal action and soil and ground water investigations have led to a soil vapor extraction system (SVES) recently being installed at the Dowell Schlumberger (DS) facility to address the remediation of petroleum hydrocarbon contaminants (BTEX) associated with the former USTs. While the SVES will address BTEX contamination in the on-site soils and ground water, the GWPRB is very concerned about the off-site, down-gradient monitor wells which continue to show chlorinated solvents at concentrations significantly above New Mexico Water Quality Control Commission (WQCC) regulation standards. This letter shall serve as Notification of Discharge applicable under WQCC regulation 1-203.

Harold Runnels Building
1190 St. Francis Drive
P.O. Box 26110
Santa Fe, NM 87502
(505) 827-2850
FAX (505) 827-2836

Recent ground water monitoring data indicates that, while the SVES appears to be having a positive affect on remediation of on-site BTEX contamination, it is not affecting chlorinated solvent contamination in ground water down-gradient and off-site of the facility. WQCC regulation 1-203.A.6 requires that DS submit to GWPRB a preliminary Corrective Action Plan. An approvable plan will include, at a minimum, a proposal to investigate, monitor and remediate the chlorinated solvent plume emanating from the DS facility.

DS must submit a corrective action plan to GWPRB within 45 days of receipt of this letter which addresses the following:

1) A plan to: a) define the horizontal and vertical extent and magnitude of chlorinated solvent ground water contamination, b) quarterly monitor contamination identified by the investigation and c) design and implement ground water remediation both on and off-site.

2) Water supply well inventory down-gradient from the site within a 2-mile radius.

3) Proposed schedule of implementation of above items.

Monitoring and reporting on a quarterly basis may be combined with on-going UST submittals to avoid duplication of effort in the future.

Please notify NMED at least five working days prior to any planned field activities so that we may be present to observe and obtain split samples. Should you have any questions regarding this letter, please contact Mr. Jeff Walker of my staff at (505) 841-9466. Your continued voluntary cooperation in this matter is greatly appreciated.

Sincerely,

Dale M. Doremus for Marcy Leavitt

Marcy Leavitt, Chief
Ground Water Protection and Remediation Bureau

ML/JW/jw

cc: Garrison McCaslin, NMED District IV Manager
Dennis McQuillan, Remediation Section Manager
Coby Muckelroy, HRMB
Tony Moreland, USTB
Ronald M. Eddy

Sherman & Howard L.L.C.

ATTORNEYS & COUNSELORS AT LAW
FIRST INTERSTATE TOWER NORTH
633 SEVENTEENTH STREET, SUITE 3000
DENVER, COLORADO 80202
TELEPHONE: 303 297-2900
FAX: 303 298-0940
OFFICES IN: COLORADO SPRINGS
RENO • LAS VEGAS

RONALD M. EDDY
DIRECT DIAL NO. (303) 299-8338

August 4, 1994

Ms. Mary Leavitt
Chief, Groundwater Protection Remediation Branch
New Mexico Environment Department
1190 St. Francis Dr.
P.O. Box 26110
Santa Fe, NM 87502-6110

Re: Dowell Facility, Artesia, New Mexico/H. Donald Kiddy

Dear Ms. Leavitt:

This letter is in regard to the Dowell Schlumberger facility located in Artesia, New Mexico. I represent H. Donald Kiddy, who owns property immediately adjacent to the Dowell facility. Contamination from the Dowell facility has impacted the groundwater beneath Mr. Kiddy's property.

It is my understanding that your office will be working with Dowell to evaluate and, as appropriate, remediate the contamination arising from the Dowell facility. Mr. Kiddy is pleased that your office is taking this important role and looks forward to a successful cleanup program to be implemented by Dowell.

In order to monitor investigative and remedial activities, I would appreciate receiving a copy of all the correspondence between Dowell Schlumberger and the New Mexico Environment Department as well as any documents, reports, or other materials which are submitted by or on behalf of Dowell as part of those activities. (For example, it is my understanding that the Department will contact Dowell within the next week or so to request additional information regarding the contamination and Dowell's proposed investigation/remediation strategy and an associated timeline. I would appreciate receiving a copy of that letter as well as any previous and future correspondence.)

Please send the materials to me at the above address. Thank you for your attention to this matter. Please contact me if you have an questions regarding Mr. Kiddy's property.

Very truly yours,

/s/ RONALD M. EDDY

Ronald M. Eddy

RME:lw
cc: Mr. Baird Swanson
Mr. Jeff Walker
Mr. H. Donald Kiddy

CLIENT Dowell Schlumberger, Inc.

PROJECT 037-14-AN

LOCATION Artesia, NM

WELL NO. MW-1

WELL LOG

ELEVATION
Ground
Casing 3358.00'
Water Level 15.32'

CASING 0.020" Millslot 2" PVC Screen TD (30') to 10', flush joint 2" blank to su
COMPLETION 8/16 sand TD to 9', bentonite to
CEMENT Portland Cement 7' to surface

DEPTH	SYMBOL	SAMPLE LOG	COMPLETION: 12" Manhole Cover / HOLE SIZE	DEPTH
		Gravels: Well Rounded in clay matrix, HNU reading 0 ppm	4 3/4"	
		Clay: White, Buff, Soft, Damp, Caliche Rock inclusions	Cement	
5		Split Spoon 5'-7' HNU reading 0ppm		5
			bentonite	
10		Clay: White, Buff, Some Brown, Moist Split Spoon 10'-12' HNU reading 0ppm		10
15		Split Spoon 15'-17' HNU reading 25ppm Clay: Brown, Some Orange, Abundant Sand		15
20			8/16 Sand	20
		Clay: Light Brown, Abundant Sand, VFG, Trace Caliche	0.020" Millslot 2" PVC Screen	
25				25
30		Total Depth 30'	End Cap	30

▼ WATER LEVEL
PUMP SETTING
CEMENT
BENTONITE SEAL
GRAVEL PACK
PERFORATIONS

REED & ASSOCIATES, INC.
Hydrologists and Environmental Consultants
AUSTIN • CORPUS CHRISTI • MIDLAND

CLIENT Dowell Schlumberger Inc.

PROJECT 037-14-AN

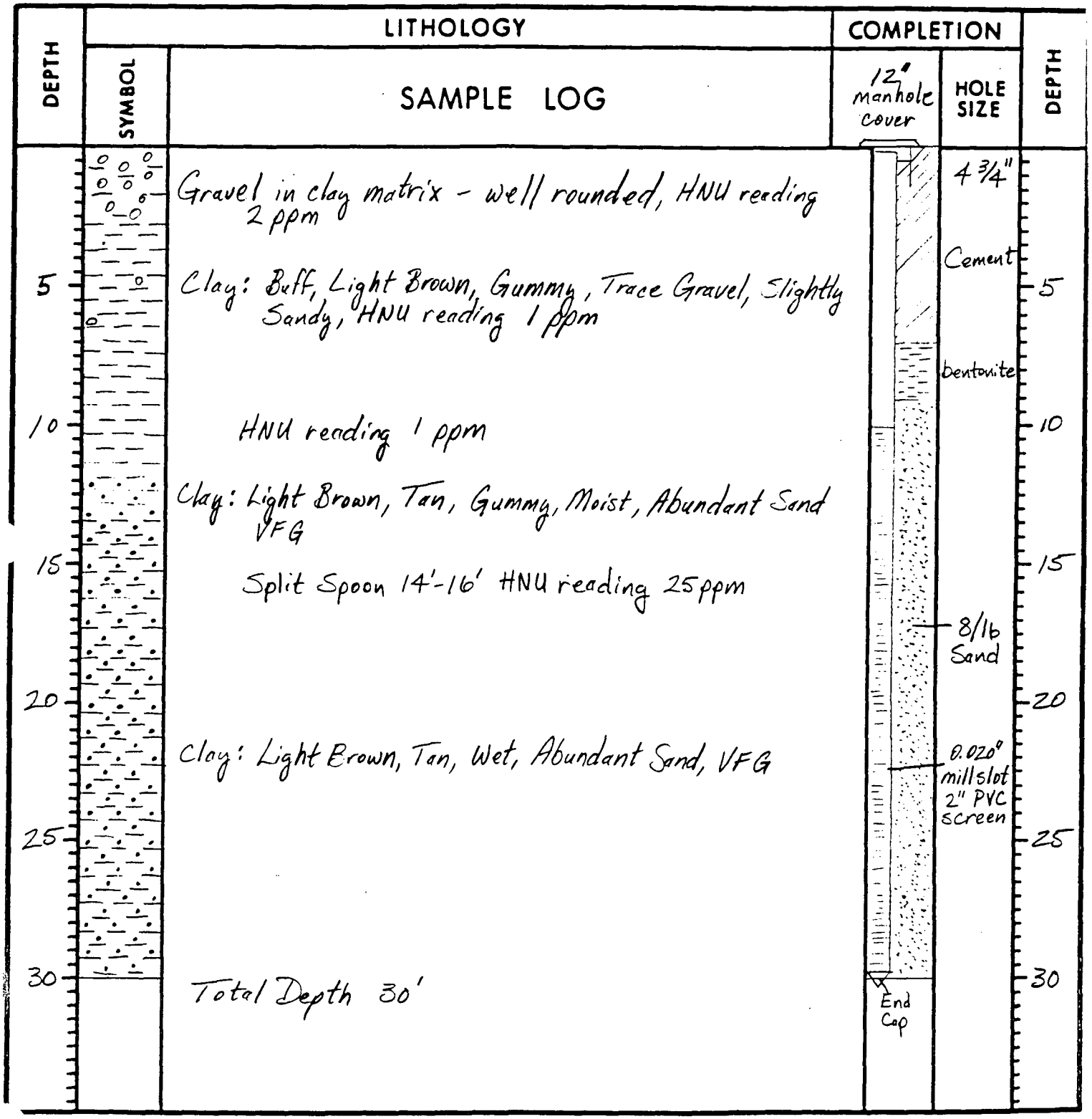
LOCATION Artesia, NM

WELL NO. MW-2

WELL LOG

ELEVATION
Grou
Casing 3356.97'
Water Level 14.71'

CASING 0.020" millslot flushjoint 2" PVC Scre
TD(30') to 10', flushjoint 2" blank to surface,
COMPLETION 8/16 Sand TD to 9', bentonite to
CEMENT Portland cement 7' to surface



▼ WATER LEVEL
-o- PUMP SETTING
CEMENT
BENTONITE SEAL
GRAVEL PACK
PERFORATIONS

REED & ASSOCIATES, INC.
Hydrologists and Environmental Consultants
AUSTIN • CORPUS CHRISTI • MIDLAND

CLIENT Dowell Schlumberg Inc.

PROJECT 037-14-AN

LOCATION Artesia, NM

WELL NO. MW-3

WELL LOG

ELEVATION
Grou
Casing 3355.78'
Water Level 14.53'
CASING 0.020" millslot flushjoint 2"PVC s
TD(30) to 10', 2" flushjoint blank to surfa
COMPLETION 8/16 sand TD to 7'; bentonite t
CEMENT Portland cement 5' to surface

DEPTH	SYMBOL	SAMPLE LOG	COMPLETION: 12" Manhole cover / HOLE SIZE	DEPTH
		Clay: Buff, White, Crumbly, Some caliche and gravel, HNU reading 20 ppm	4 3/4"	
		Split Spoon 2'-4' HNU 0 ppm		
5		Clay: Buff, Tan, Gummy, Gypsum inclusions	bentonite	5
10		Clay: Tan, Buff, Gummy, Some Silty, Trace black to gray staining, HNU reading 25 ppm		10
15		Clay: Buff, White, Gummy, 80% Stained Black to Gray, Hydrocarbon Odor	8/16 Sand	15
		Split Spoon 15'-17', HNU reading 140 ppm		
20		Clay: Buff, Grey, Gummy, Moist, 90% Stained Gray to Black from hydrocarbons, Hydrocarbon Odor	0.020" millslot 2" PVC Screen	20
25		Clay: As Above		25
30		Total Depth 30'	End Cap	30

▼ WATER LEVEL
PUMP SETTING
CEMENT
BENTONITE SEAL
GRAVEL PACK
PERFORATIONS

REED & ASSOCIATES, INC.
Hydrologists and Environmental Consultants
AUSTIN • CORPUS CHRISTI • MIDLAND

CLIENT Dowell Schlumberger Inc.

PROJECT 037-14-AN

LOCATION Artesia, NM

WELL NO. MW-4

WELL LOG

ELEVATION
Ground
Casing 3360.62'
Water Level 18.08' (Aboveground completion)
CASING 0.020" millslot flush joint 4" PVC Scre
TD(50) to 10'; 4" flush joint blank to 3' AGL
COMPLETION 8/16 Sand TD to 9', bentonite to
CEMENT Portland Cement 7' to surface

DEPTH	SYMBOL	LITHOLOGY — SAMPLE LOG	COMPLETION (7" Steel Casing)	HOLE SIZE	DEPTH
		Gravel: Variable colors, well rounded		7 7/8"	
		Clay: White, Buff, Soft, Damp, Trace Gravel		Cement	
				bentonite	
10		Clay: White, Buff, Tan, Gummy, Moist, HNU reading 0ppm			10
		Split Spoon 15'-17', HNU reading 60ppm			
20		Clay: Light Brown to Brown, Trace Orange, Abundant Sand - Tan, VFG		8/16 Sand	20
		Clay: Light Brown, Tan, Wet, Abundant Sand, VFG			
30		Clay: As Above, trace odor		0.020" millslot 4" PVC screen	30
40		Sand: Tan, VFG, Wet, well sorted and rounded, some Clay - gummy			40
		Sand: Tan, Buff, VFG, loose, well sorted and rounded, wet, no odor			
50		Total Depth 50'	End Cap		50

▽ WATER LEVEL
-o- PUMP SETTING
▨ CEMENT
▩ BENTONITE SEAL
▩ GRAVEL PACK
▤ PERFORATIONS

REED & ASSOCIATES, INC.
Hydrologists and Environmental Consultants
AUSTIN • CORPUS CHRISTI • MIDLAND

CLIENT Dowell Schlumberger Inc.

PROJECT 037-14-AN

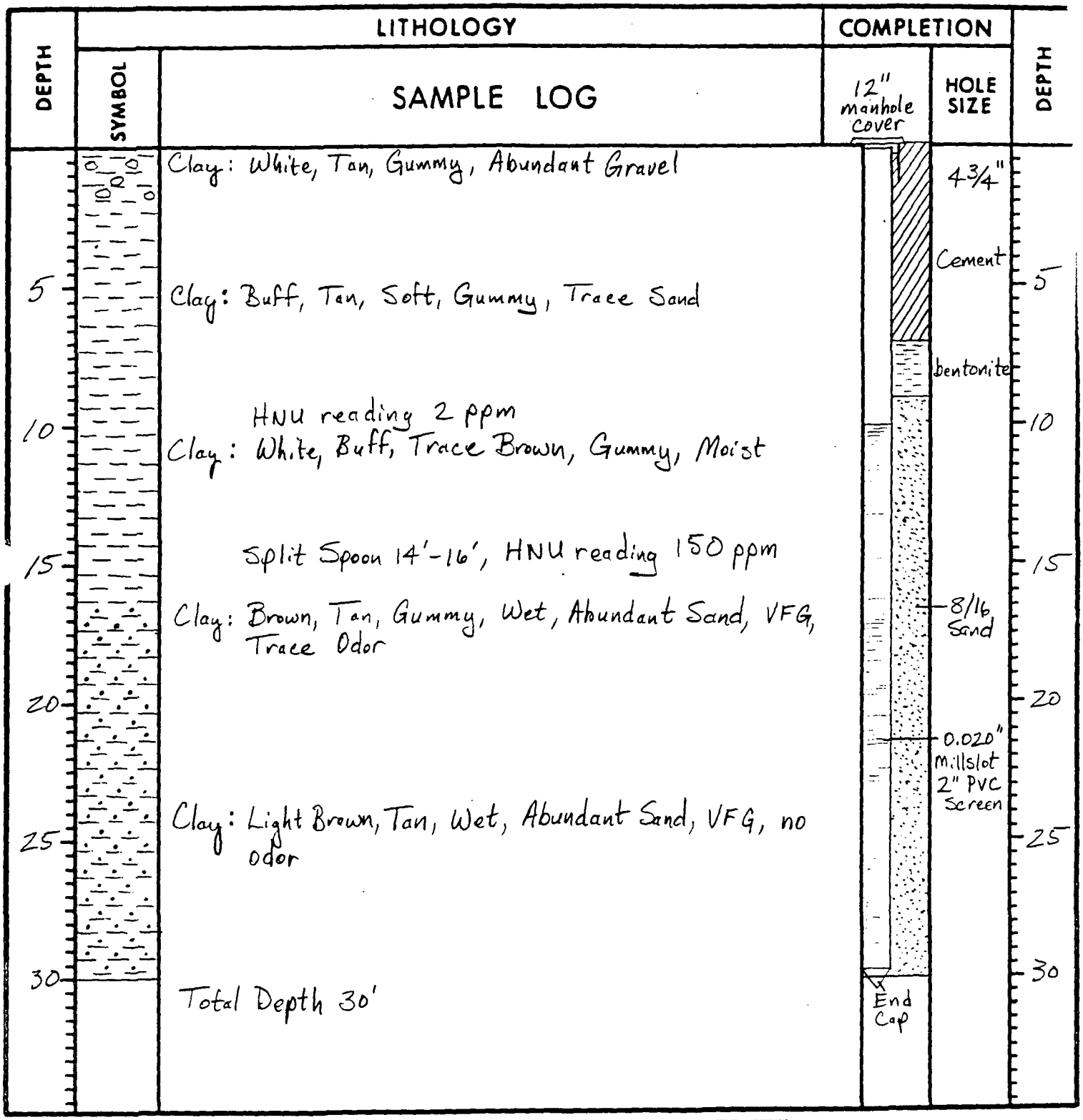
LOCATION Artesia, NM

WELL NO. MW-5

WELL LOG

ELEVATION
Ground
Casing 3357.27'
Water Level 15.04'

CASING 0.020" millslot flushjoint 2"PVC Scr. TD(30') to 10', flushjoint 2" blank to surface.
COMPLETION 8/16 Sand TD to 9', bentonite to ;
CEMENT Portland Cement 7' to surface



▼ WATER LEVEL
-o- PUMP SETTING
▨ CEMENT
▤ BENTONITE SEAL
▦ GRAVEL PACK
☰ PERFORATIONS

REED & ASSOCIATES, INC.
Hydrologists and Environmental Consultants
AUSTIN • CORPUS CHRISTI • MIDLAND

CLIENT Dowell Schlumberger Inc.

PROJECT 037-14-AN

LOCATION Artesia, NM

WELL NO. MW-6 (offsite)

WELL LOG

ELEVATION
Ground
Casing 3358.25'
Water Level 17.58

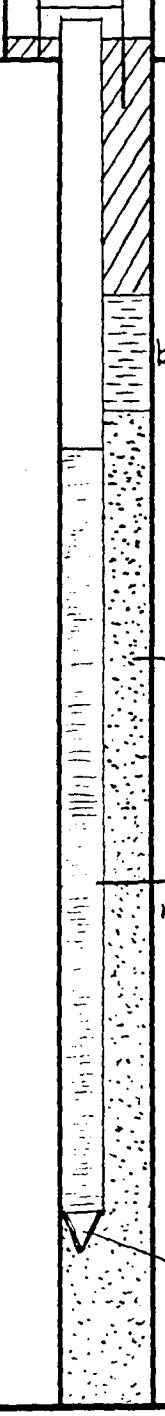
CASING 0.020" millslot flushjoint 2" PVC Screen 30' to 10', flushjoint 2" blank to surface

COMPLETION 8/16 sand 35' to 9', bentonite to 6

CEMENT Portland Cement 6' to surface

DEPTH	SYMBOL	SAMPLE LOG
0		Clay: White, Tan, Buff, Gummy, Trace Gravel
5		Clay: Buff, Tan, Soft, Gummy, Trace Silt
10		Clay: Brown, Tan, Gummy, Trace Silt, no odor
15		Clay: Tan, Light Brown, Gummy, Wet, Abundant Silt, no odor
20		Clay: Light Brown, Tan, Gummy, Wet, Abundant Sand, VFG, no odor
25		Clay: As Above, no odor
30		
35		Total Depth 35'

COMPLETION



HOLE SIZE: 4 3/4"

DEPTH: 0, 5, 10, 15, 20, 25, 30, 35

▼ WATER LEVEL
-o- PUMP SETTING
▨ CEMENT
▨ BENTONITE SEAL
▨ GRAVEL PACK
▨ PERFORATIONS

REED & ASSOCIATES, INC.
Hydrologists and Environmental Consultants
AUSTIN • CORPUS CHRISTI • MIDLAND

CLIENT Dowell Schlumberg, Inc.

PROJECT 037-14-AN

LOCATION Artesia, NM

WELL NO. MW-7 (off site)

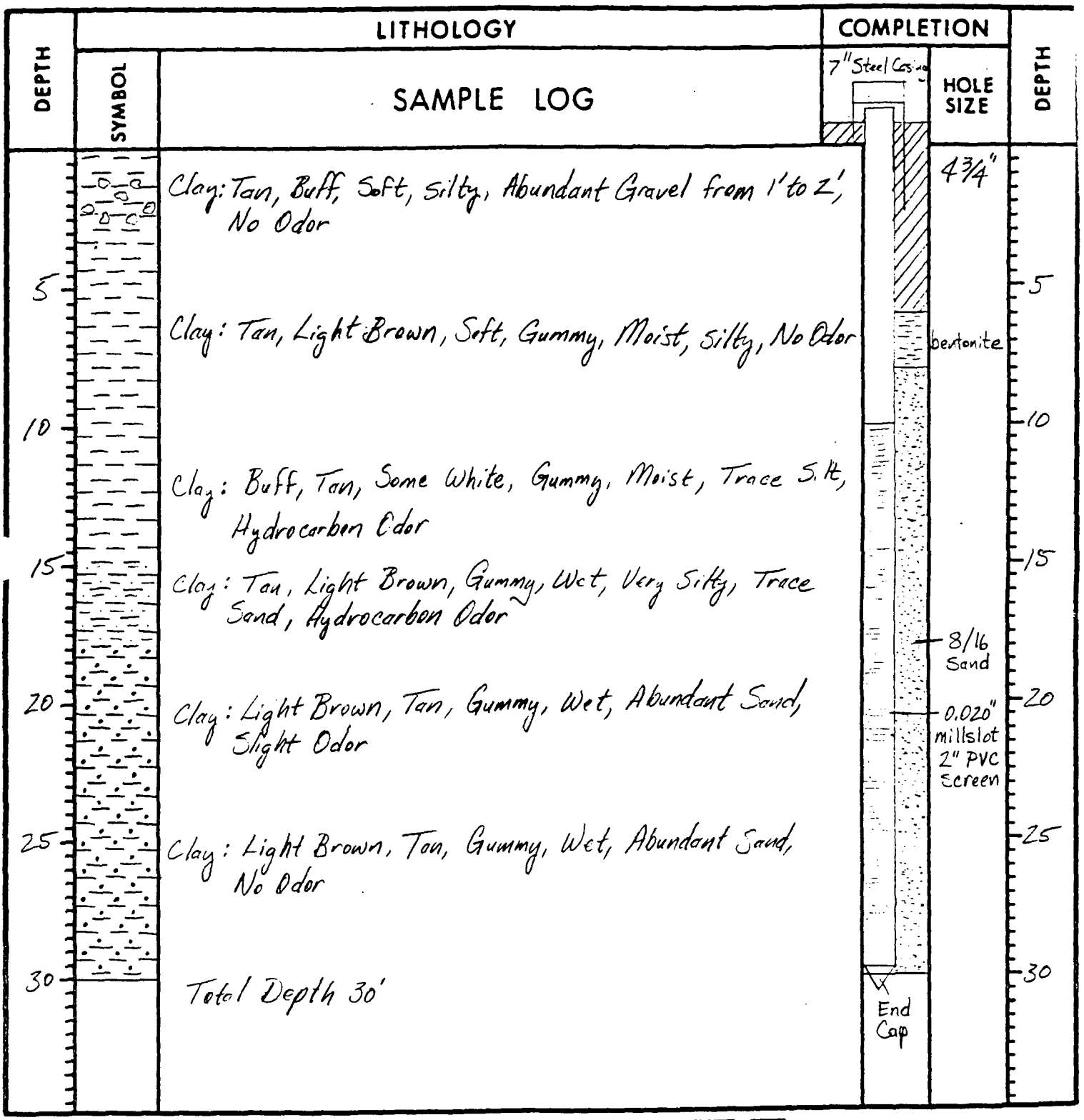
WELL LOG

ELEVATION
Grou "
Casing 3355.27'
Water Level 17.02

CASING 0.020" millslot flushjoint 2" PVC Scree. (30')TD to 10', flushjoint 2" blank to Surface

COMPLETION 8/16 Sand to 8', bentonite to 6'

CEMENT Portland Cement 6' to surface



▼ WATER LEVEL
-o- PUMP SETTING
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GRAVEL PACK
PERFORATIONS

REED & ASSOCIATES, INC.
Hydrologists and Environmental Consultants
AUSTIN • CORPUS CHRISTI • MIDLAND

LI T Dowell Schlumberger Inc.

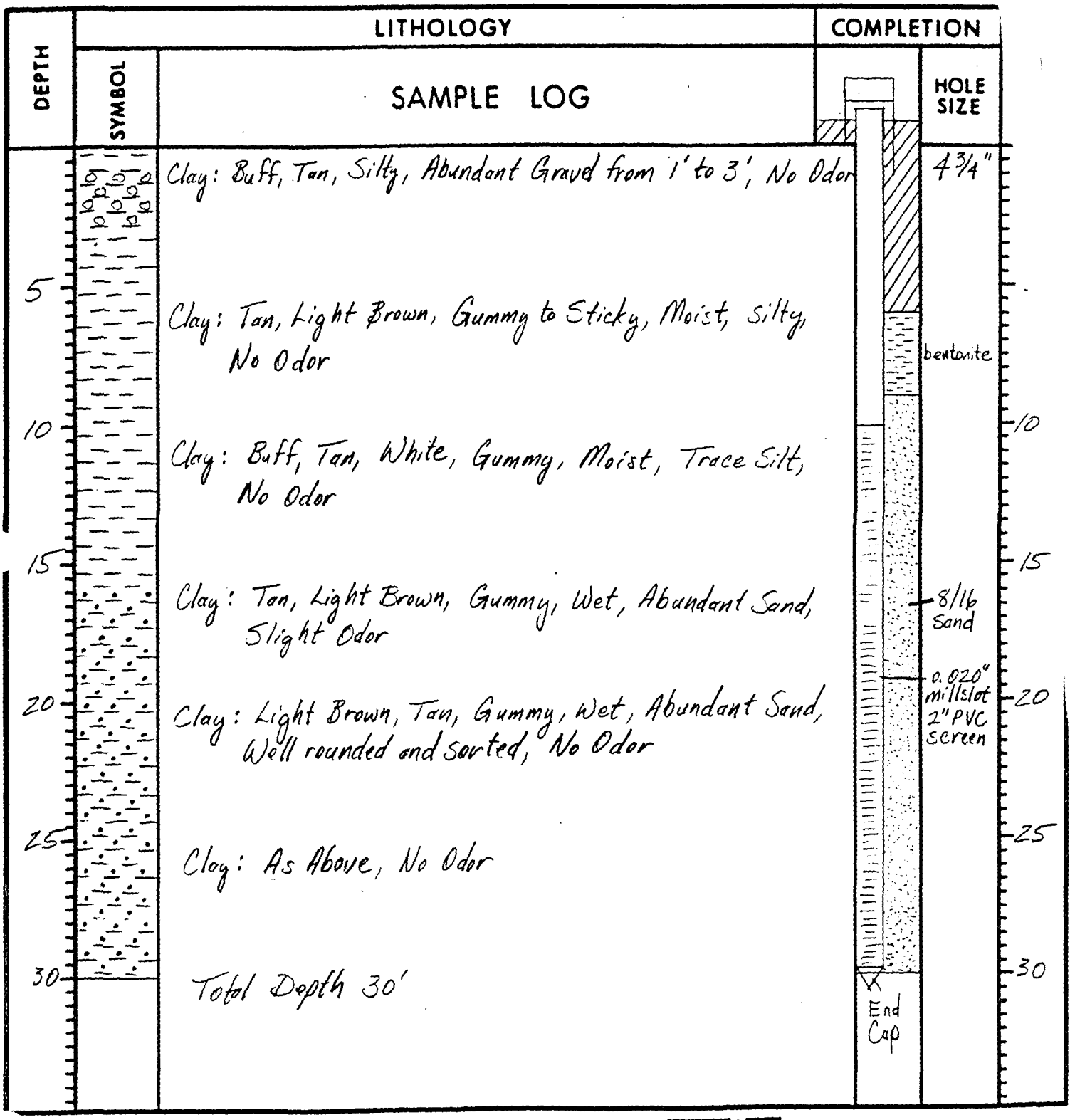
PROJECT 037-HAN

LOCATION Artesia, NM

WELL NO. MW-8

WELL LOG

ELEVATION
Gro el
Casing 3358.87
Water Level 18.14
CASING 0.020" millslot flushjoint 2
TD(30') to 10', flushjoint 2" PVC blank t
COMPLETION 8/16 Sand to 9', bentonite t
CEMENT Portland cement 6' to surfa



WATER LEVEL
PUMP SETTING
CEMENT
BENTONITE SEAL
GRAVEL PACK
PERFORATIONS

REED & ASSOCIATES, INC.
Hydrologists and Environmental Consultants
AUSTIN • CORPUS CHRISTI • MIDLAND

Schlumberger Dowell

Dowell Schlumberger Incorporated
P.O. Box 4378
Houston, Texas 77210-4378
(713) 275-8400

December 3, 1993

Baird Swanson
Groundwater Protection and Remediation Division
New Mexico Environment Department
District 1 Office
4131 Montgomery Blvd., N.E.
Alburquergue, NM 87109

RE: Dowell Schlumberger Incorporated Facility
Artesia, New Mexico

Dear Mr. Swanson:

Enclosed per your request are copies of well logs for Monitor Wells 1 thru 8. If I can be of further assistance, please call me at (713) 275-8498.

Sincerely,

John A Miller

John A. Miller
Environmental Remediation Manager

Schlumberger Dowell

Dowell Schlumberger Incorporated
P.O. Box 4378
Houston, Texas 77210-4378
(713) 275-8400

November 23, 1993

Baird Swanson
Groundwater Protection and Remediation Division
New Mexico Environmental Department
District 1 Office
4131 Montgomery Blvd, N.E.
Albuquerque, NM 87109

RE: Dowell Schlumberger Incorporated Facility
Artesia, New Mexico

Dear Mr. Swanson:

Enclosed for your review are copies of the following documents:

a. Site Investigation Report prepared by Western Water Consultants Inc., dated April 5, 1991.

b. Additional Assessment and Remediation Feasibility Testing Report prepared by Western Water Consultants Inc., dated November 20, 1991.

c. Results of March 1993 Groundwater Monitoring Event, Dowell Schlumberger Incorporated letter dated 2 June 1993.

I have also enclosed a brief chronology that identifies earlier investigative and UST removal work which was provided to the New Mexico Environmental Improvement Division. These reports detail source removal actions; a phased investigation of soil and groundwater to include a soil vapor survey followed by borings and monitor wells for soil and groundwater samples; and a pump test and soil vapor extraction pilot test to evaluate remedial options.

On November 18, 1993, we met on-site with Anthony Moreland, NMED UST Bureau to discuss his letter of October 26, 1993 which approved our Soil Vapor Extraction (SVE) system. Our environmental consultant, Western Water Consultants has analyzed the site ground-water data in accordance with the EPA report on DNAPL Site Evaluation, Cohen and Mercer, February 1993, EPA/ 600/R-93/022. This analysis used the procedures listed under paragraph 9.10.2 Indirect Detection of DNAPL Presence, paragraph 9.10.2.1 Effective Solubility, and Table 7-4 Indications of DNAPL presence based on examination of subsurface samples and data (based on Newell and Ross, 1992; Cherry and Feenstra, 1991; and Cohen etal 1992). Table 1 shows the maximum concentrations of

chlorinated hydrocarbons detected at the Dowell Schlumberger facility, the maximum concentration detected a percentage of pure phase solubility, and 1% of the pure phase solubility in water. The EPA's current rule of thumb for relating ground-water concentrations of chlorinated hydrocarbons to the presence of a DNAPL is the presence of concentrations greater than 1% to 10% of the individual pure phase solubility. As table 1 clearly shows, only a single chlorinated hydrocarbon compound reaches .3% of pure phase solubility and all others are 1 to 4 orders of magnitude smaller than this percentage. This indicates the presence of a DNAPL is highly unlikely.

Our soil vapor extraction pilot test indicates a radius of influence of eleven feet. As conservative measure, we are spacing the extraction wells based on a radius of influence of 7.5 feet. SVE has had great success in removing volatile organic compounds from soils in other sites. Concurrent groundwater sampling has shown striking reductions in concentrations of compounds detected in groundwater. As we explained to Mr. Moreland, potential SVE installation bidders performed a site visit on November 18, bids are due on December 3 and, dependent on equipment availability, we plan to conduct field work in December/January. To evaluate the SVE system's effectiveness, we plan to sample the groundwater monitor wells prior to system start-up and then quarterly for one year. After the second quarter of operation, a progress report will be subnmitted. If additional measures, such as air sparging, are recommended, they will be evaluated at that time. Because the system will start-up in the winter, we expect the mass of contaminant removed and air flow to increase in the summer months. A full one-year system evaluation showing seasonal variations is desired and will be provided in another report.

Please call me at (713) 275-8498 if you wish to arrange an on site meeting to discuss the enclosed reports and our remediation plans.

Sincerely,

John A. Miller
Environmental Remediation Manager

cc: Mr. Anthony Moreland, NMED UST Bureau
Susan Fields, WWC

ARTESIA NEW MEXICO INVESTIGATION CHRONOLOGY

DATE	ACTION	RESULTS
JUN 1989	Reed & Associates (RAI) performed a Soil Vapor Survey followed by Boreholes for Soil Samples and GW Samples.	Results to Suzanne Fouty Sept. 29, 1989
JUL/AUG 1989	RAI removed 11 USTs	
AUG 1989	RAI Installed 5 Monitor Wells (MW) on Dowell property	Result to S. Fouty Sept. 14, 1989
OCT/NOV 1989	RAI Installed 3MWs N and E of Dowell	Results to S. Fouty April 4, 1990
JAN 1991	Western Water Consultants (WWC) installed 4MWs and 4 borings	Report dated April 5, 1991
SEP 1991	WWC installed 3MWs and MW16. Performed 24-hour. pump test on MW-16 and a SVE pilot test (ROI 11 feet).	Report dated November 20, 1991.

TABLE 1. MAXIMUM CONCENTRATIONS OF CHLORINATED HYDROCARBONS AT THE DOWELL SCHLUMBERGER INCORPORATED FACILITY, ARTESIA, NEW MEXICO

COMPOUND	MAXIMUM CONCENTRATION (historic) *(mg/l)*	WELL	MAX.CONC. as a % of PURE PHASE SOLUBILITY *(%)*	PURE PHASE SOLUBILITY IN WATER *(mg/l)*	1% OF PURE PHASE SOLUBILITY *(mg/l)*	REFERENCE
1,1-DCA	0.14	MW-3, MW-12, MW-14	0.003	5060 at 25C	51	Howard (1990)
1,2-DCA	0.004	MW-3	0.00005	8690 at 25C	87	Cohen and Mercer (1993)
1,1-DCE	0.47	MW-11	0.019	2500 at 25C	25	Howard (1989)
1,1,1-TCA	0.26	MW-3	0.017	1495 at 25C	15	Howard (1990)
1,1,2-TCA	0.002	MW-3	0.00005	4420 at 20C	44	Howard (1990)
TCE	0.26	MW-12	0.024	1100 at 25C	11	Howard (1990)
PCE	0.46	MW-14	0.307	150.3 at 25C	1.5	Howard (1990)

REFERENCES

Howard, P.H., 1989, Handbook of Organic Fate and Exposure Data for Organic Chemicals, Volume I, Large Production and Priority Pollutants; Lewis Publishers.

Howard, P.H., 1990, Handbook of Organic Fate and Exposure Data for Organic Chemicals, Volume II, Solvents; Lewis Publishers.

Cohen, R.M. and Mercer, J.W., 1993, DNAPL Site Evaluation; U.S. EPA, EPA/600/R-93/022.

Schlumberger Dowell

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(713) 275-8400

VIA FEDEX

2 June 1993

Mr. Anthony Moreland
Underground Storage Tank Bureau
New Mexico Environment Department
1190 St. Francis Drive
Sante Fe, NM 87503

RE: Results of the March 1993 Groundwater Monitoring Event
Dowell Schlumberger Incorporated Facility, Artesia, New Mexico

Dear Mr. Moreland:

As you are aware, Western Water Consultants, Inc. (WWC) conducted groundwater monitoring at the Dowell Schlumberger Incorporated facility in Artesia, New Mexico on March 16 and 17, 1993. Split samples were collected by you at monitoring wells MW-1 through MW-5, and MW-12.

Water levels were measured at all wells prior to bailing and are presented in Table 1. The potentiometric surface map generated from the March 1993 data is shown in Figure 1.

The analytical results from the March 1993 samples are presented in Table 2, along with results from the January, September and November 1991 samples for comparison. Laboratory analytical reports for the March samples are appended to this letter.

If you have questions or comments, please call me at (713) 275-8498/8492.

Sincerely,

John A. Miller
Environmental Coordinator

JAM/dd

Enclosures

cc: WWC, Laramie

TABLE 1. GROUND-WATER MEASUREMENTS AND ELEVATIONS, DOWELL SCHLUMBERGER FACILITY, ARTESIA, NEW MEXICO.

WELL #	DATE	DEPTH TO GROUND WATER (ft)	MEASURING POINT ELEVATION* (ft)	GROUND-WATER ELEVATION* (ft)
MW-1	1-23-91	17.41	100.56	83.15
	9-13-91	16.04		84.52
	11-22-91	14.50		86.06
	3-16-93	13.72		86.84
MW-2	1-23-91	16.95	99.56	82.61
	9-13-91	15.01		84.55
	11-22-91	13.76		85.80
	3-16-93	13.16		86.40
MW-3	1-23-91	17.28	98.33	81.05
	9-13-91	14.66		83.67
	11-22-91	13.63		84.70
	3-16-93	12.89		85.44
MW-4	1-23-91	20.17	103.18	83.01
	9-13-91	18.54		84.64
	11-22-91	17.15		86.03
	3-16-93	16.49		86.69
MW-5	1-23-91	17.20	99.87	82.67
	9-13-91	15.52		84.35
	11-22-91	14.19		85.68
	3-16-93	13.47		86.40
MW-6	1-23-91	19.59	100.84	81.25
	9-13-91	17.43		83.41
	11-21-91	16.30		84.54
	3-16-93	15.57		85.27
MW-7	1-23-91	19.01	100.23	81.22
	9-13-91	17.43		82.80
	11-21-91	16.00		84.23
	3-16-93	14.91		85.32
MW-8	1-23-91	20.16	101.47	81.31
	9-13-91	18.80		82.67
	11-21-91	17.29		84.18
	3-16-93	16.03		85.44
MW-9	1-26-91	20.08	102.18	82.10
	9-13-91	18.93		83.25
	11-21-91	17.35		84.83
	3-16-93	16.19		85.99
MW-10	1-26-91	19.68	101.34	81.66
	9-13-91	18.56		82.78
	11-21-91	16.96		84.38
	3-16-93	15.64		85.70

TABLE 1. GROUND-WATER MEASUREMENTS AND ELEVATIONS, DOWELL SCHLUMBERGER FACILITY, ARTESIA, NEW MEXICO (continued).

WELL #	DATE	DEPTH TO GROUND WATER (ft)	MEASURING POINT ELEVATION* (ft)	GROUND-WATER ELEVATION* (ft)
MW-11	1-26-91	19.27	100.60	81.33
	9-13-91	17.81		82.79
	11-21-91	16.35		84.25
	3-16-93	15.20		85.40
MW-12	1-26-91	19.24	100.69	81.45
	9-13-91	17.59		83.10
	11-21-91	16.21		84.48
	3-16-93	15.22		85.47
MW-13	9-13-91	15.10	99.25	84.15
	11-21-91	13.95		85.30
	3-16-93	13.22		86.03
MW-14	9-13-91	14.60	98.74	84.14
	11-21-91	13.61		85.13
	3-16-93	13.00		85.74
MW-15	9-13-91	16.30	100.05	83.75
	11-21-91	15.01		85.04
	3-16-93	13.95		86.10
MW-16	9-13-91	18.83	103.37	84.54
	11-21-91	17.39		85.98
	3-16-93	NM		NM

NOTES:
* = measured from a temporary benchmark of arbitrary elevation = 100.00 feet. Benchmark is located on the concrete right up against the east shop wall, at the northeast corner of the shop.
NM = not measured