# Bioremediation of Hydrocarbons in Landfarms

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# Outline of Testimony

- Composition of crude oil and condensate
- Biodegradability of hydrocarbons
- What is bioremediation and what makes it work?
- What happens in a typical landfarm?
- Bioavailability and the bioremediation endpoint
- The bioremediation endpoint as an environmentally acceptable endpoint
  - Toxicity reduction
  - TPH reduction

# Outline of Testimony

- Recommended practice for permitted landfarms treating petroleum hydrocarbons
- OCD requirements inconsistent with recommended practice
- Bioremediation in the presence of chlorides
- Simplified recommended practice for small, registered landfarms
- Benefits of simplified rules for small landfarms
- Protective closure standards for landfarms

# What's in crude oil and condensate and what do we want to get rid of?

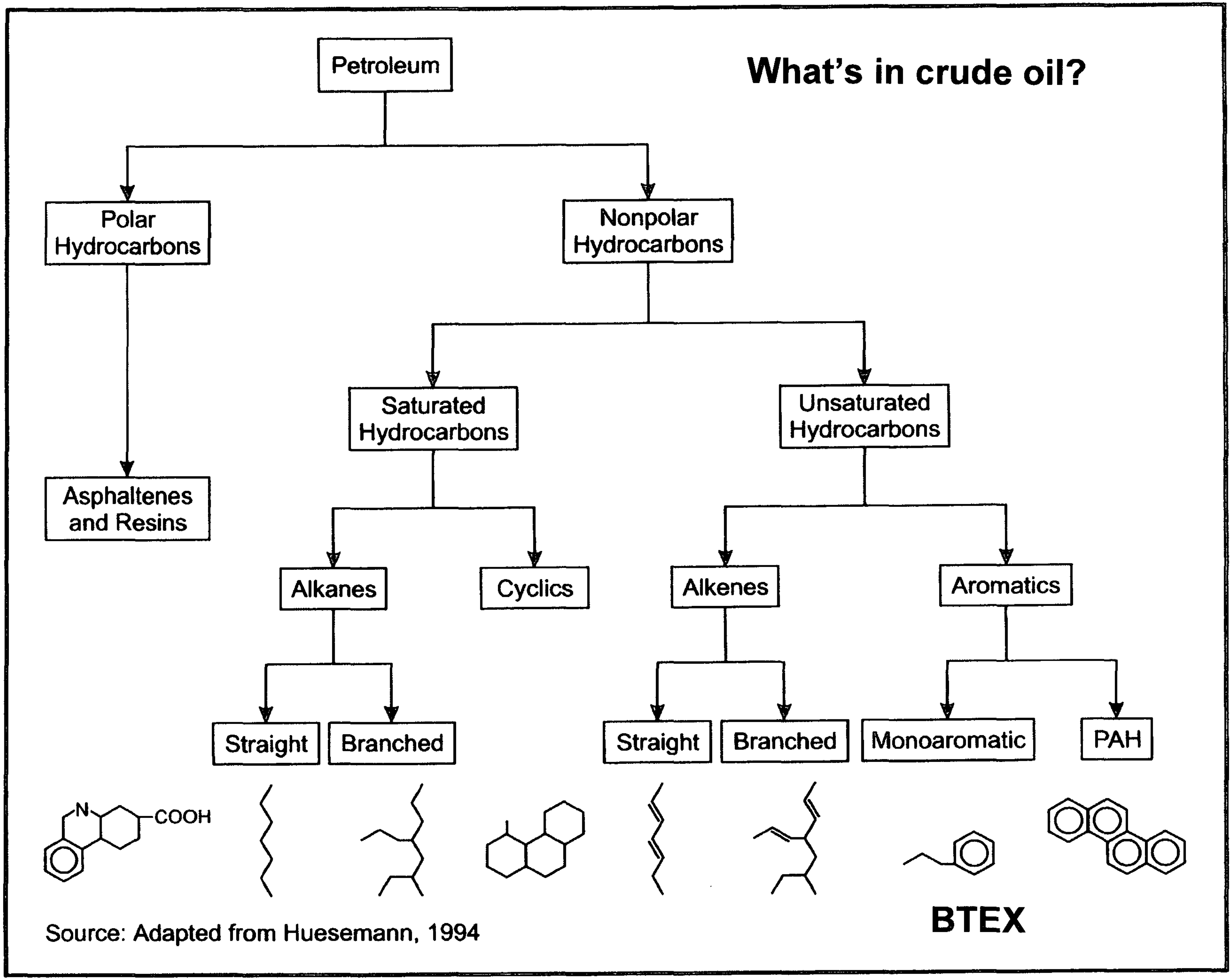
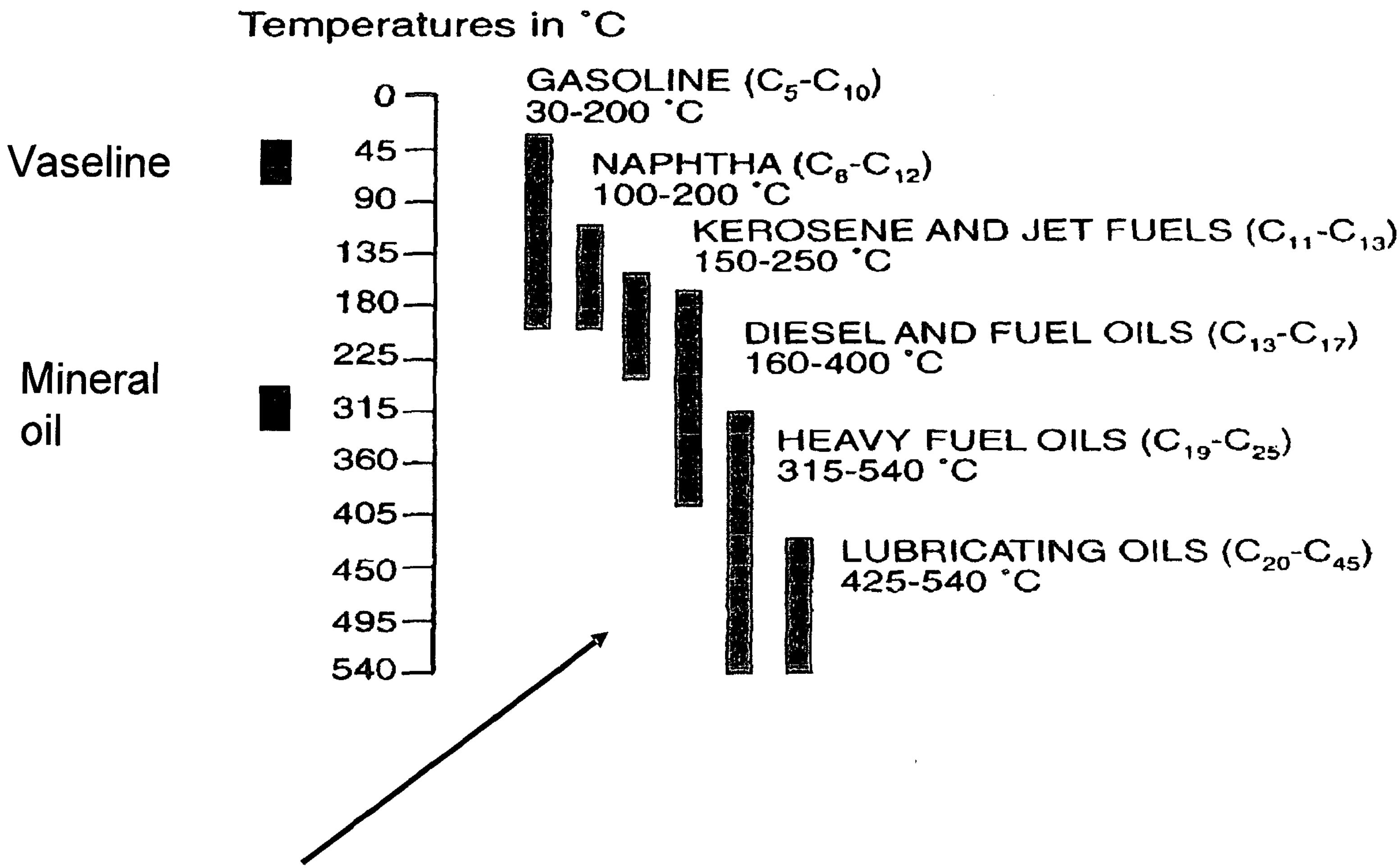
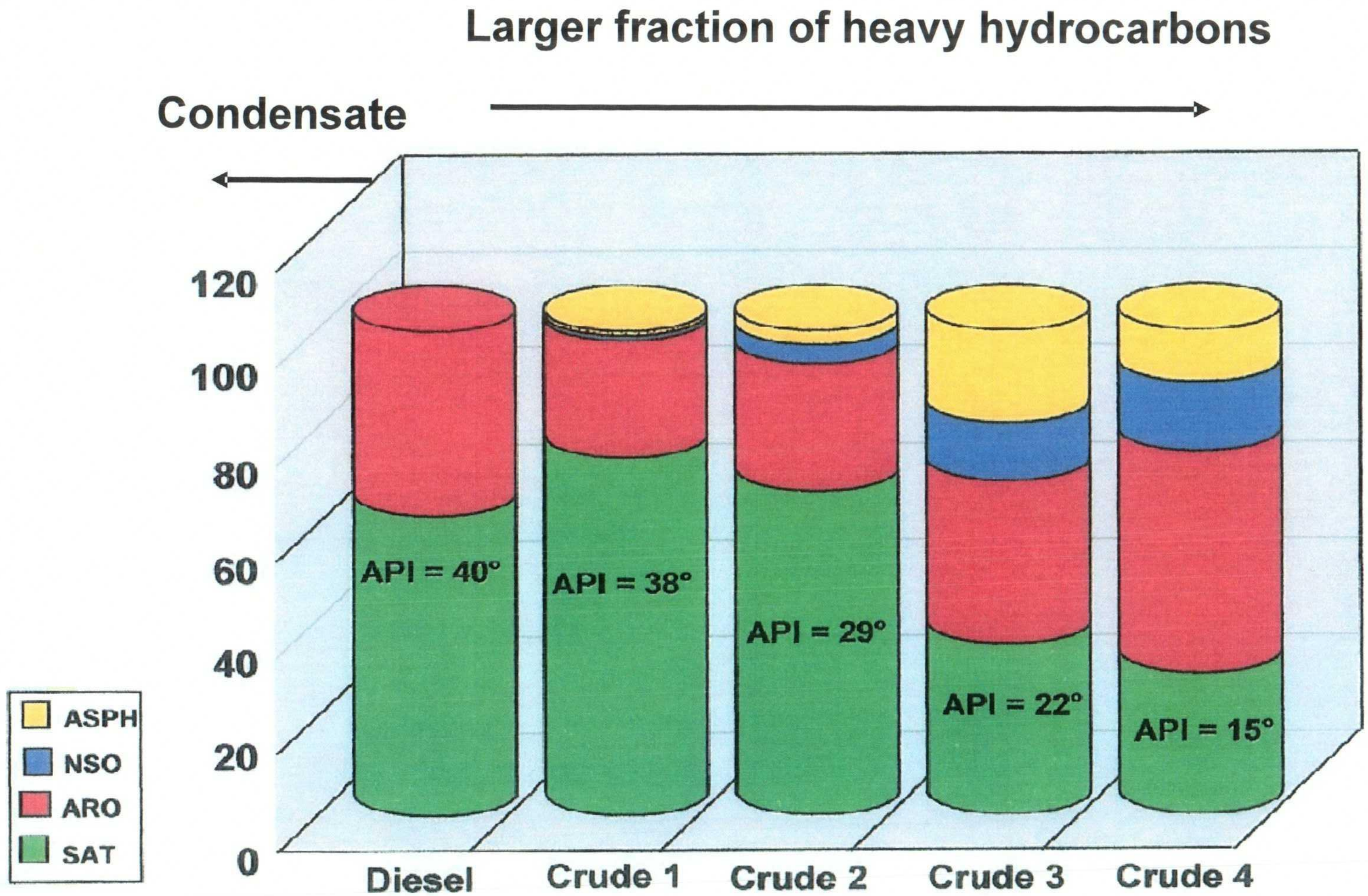



Illustration of the types of organic compounds in petroleum



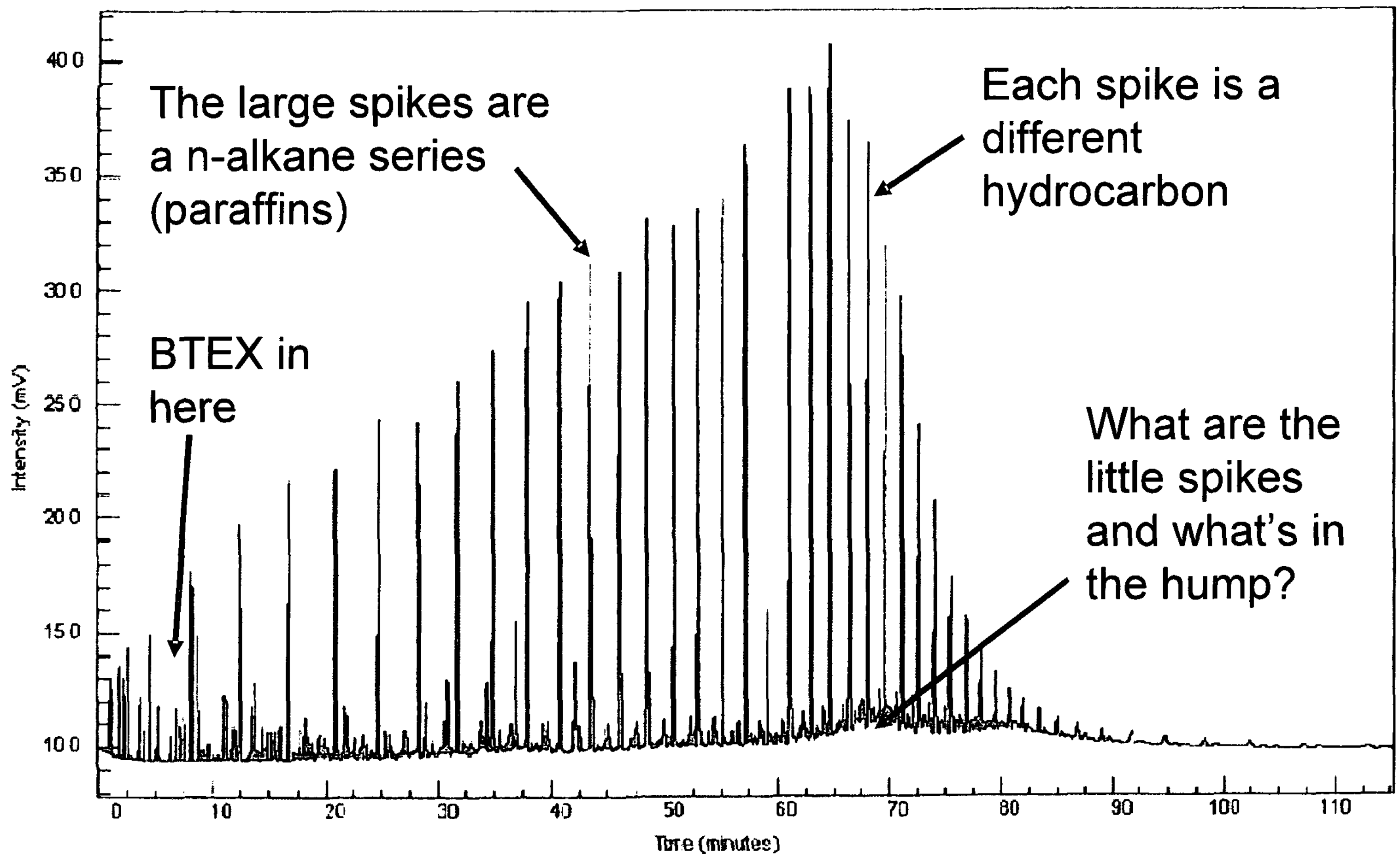

**Boiling point and carbon number ranges for six common crude oils**



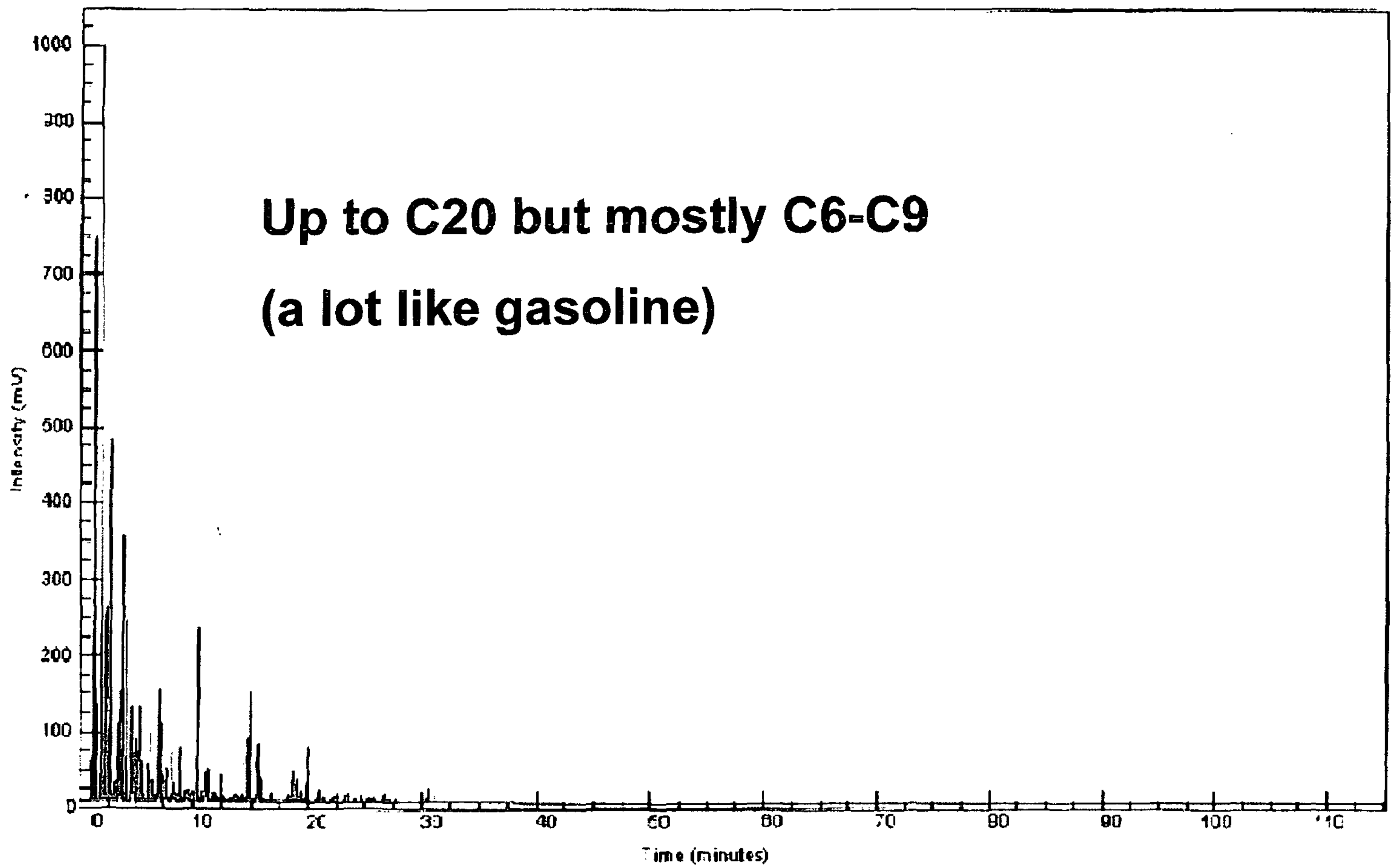

ASPH = asphaltenes; NSO = polar hydrocarbons; ARO = aromatics; SAT = saturates

# GC Analysis of a Crude Oil

**Increasing carbon number ⟶ up to ~C45**



# GC Analysis of a Condensate

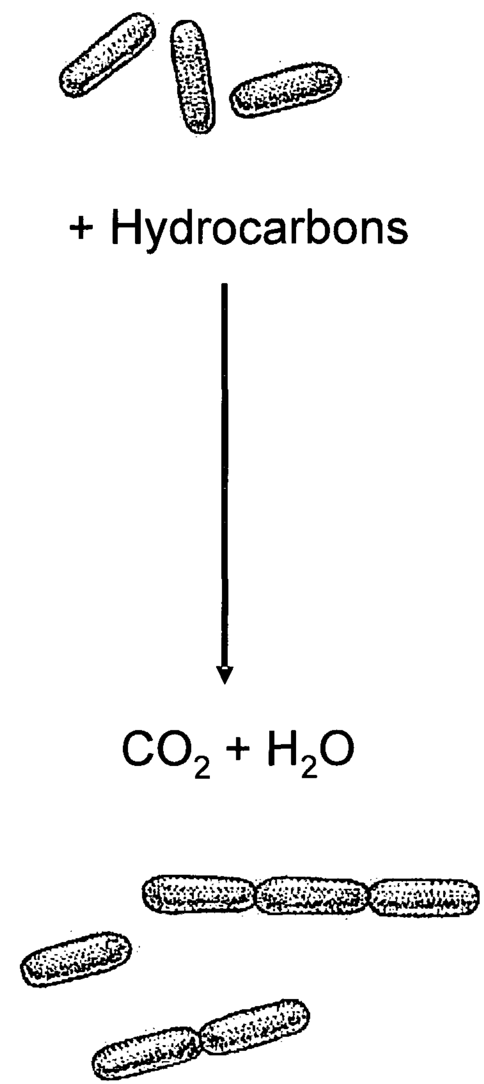


Crude oil is composed of a large number of different hydrocarbons but they can be grouped into classes with similar properties.  We will see that how they behave in the environment depends a lot on class and carbon number.

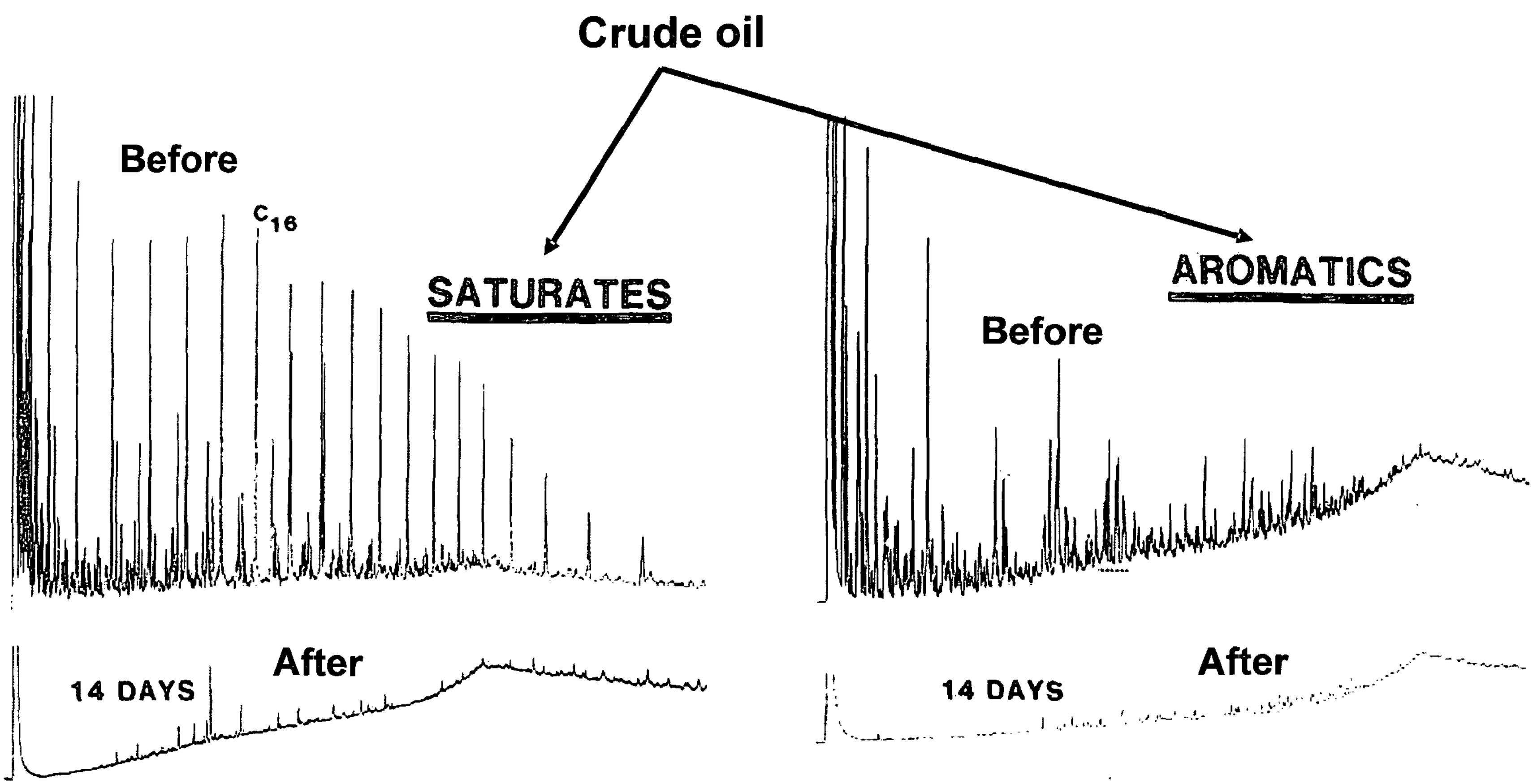
Now let's talk about the bioremediation process – How does it work?

# Biodegradation of Hydrocarbons

- Hydrocarbons have been present in nature for millions of years
- Microorganisms which use hydrocarbons for food are widely distributed in nature in:
  - Soil
  - Sea water
  - Surface water and groundwater

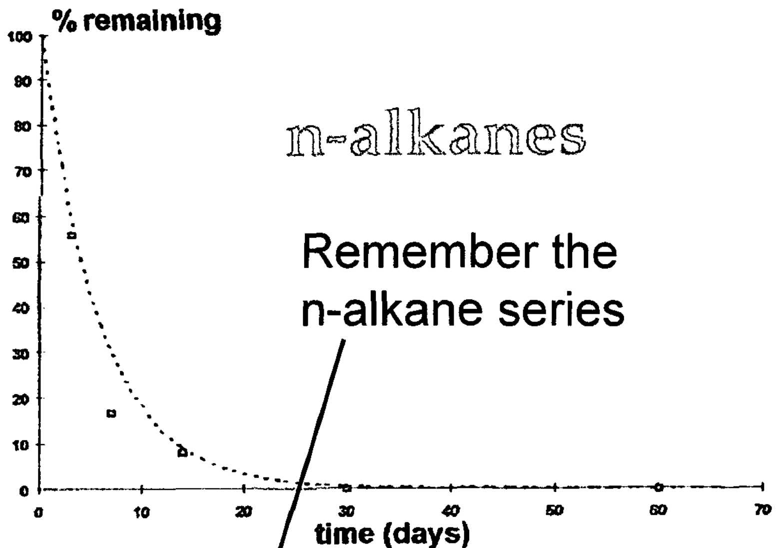


# Most hydrocarbons are biodegradable

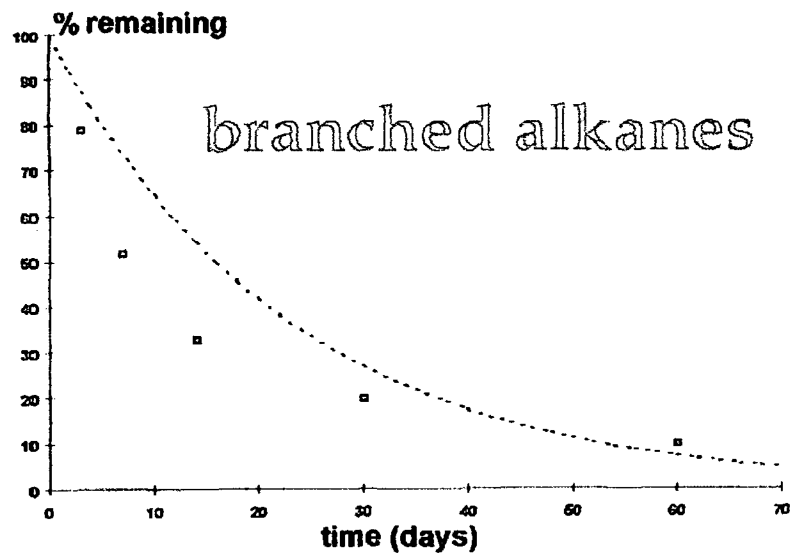


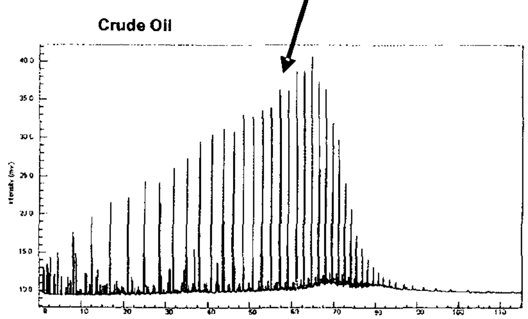

In raw sea water with nutrient supplement

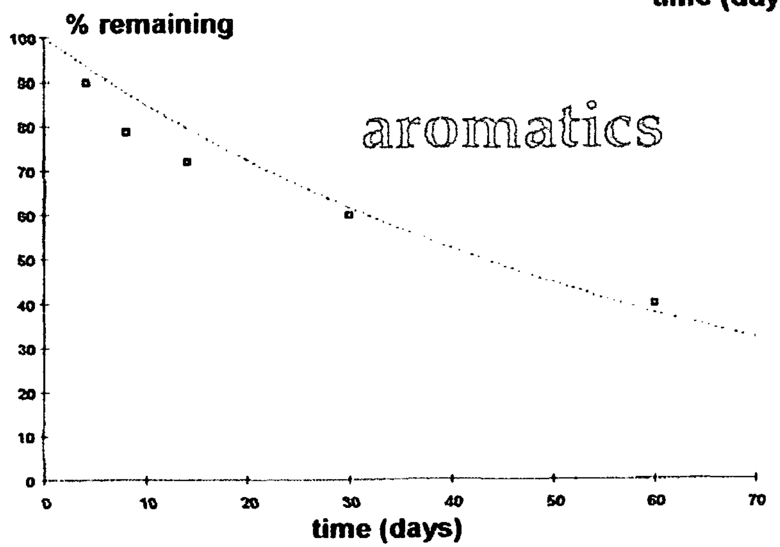
# Different classes of hydrocarbons biodegrade at different rates




Remember the n-alkane series



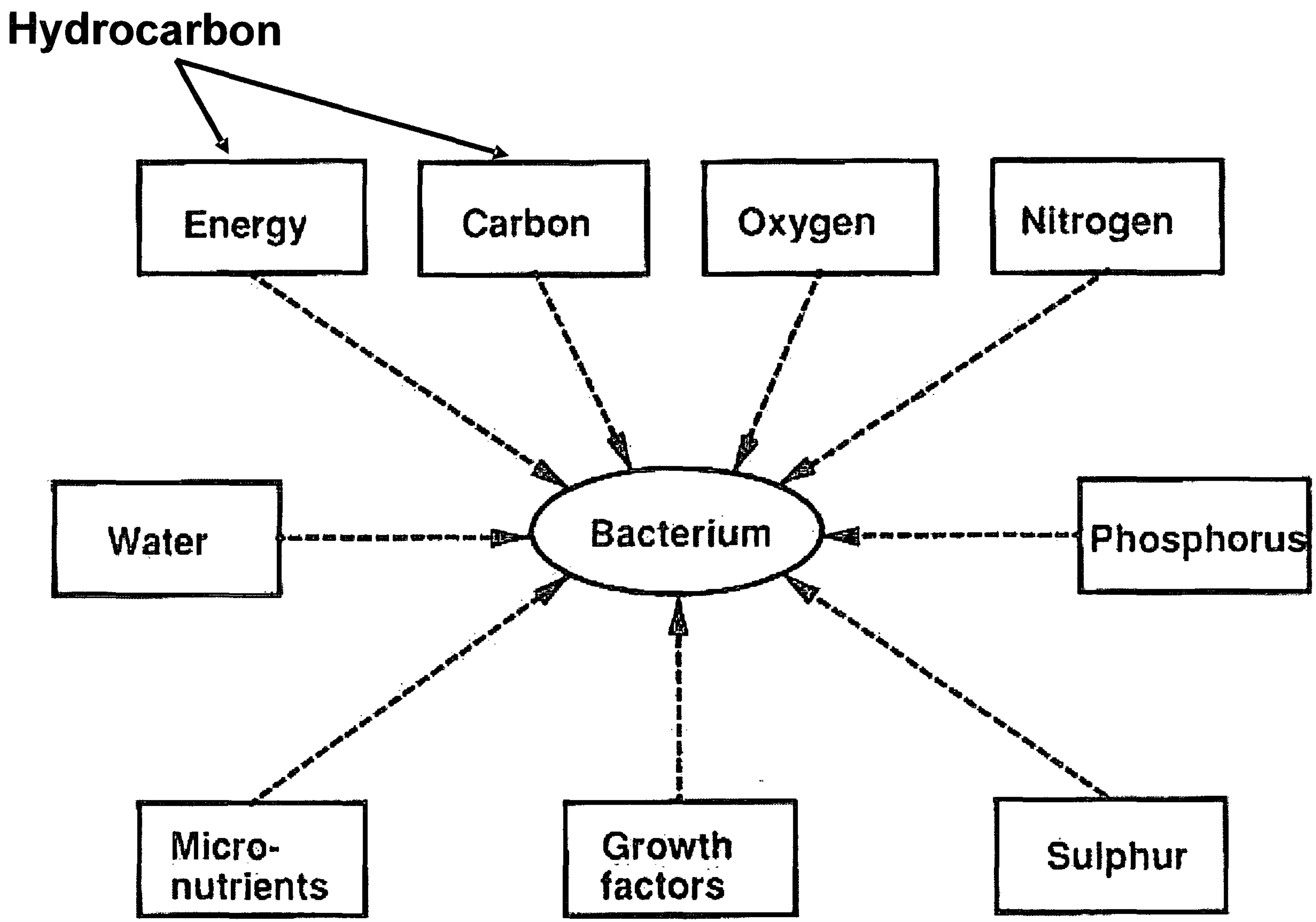



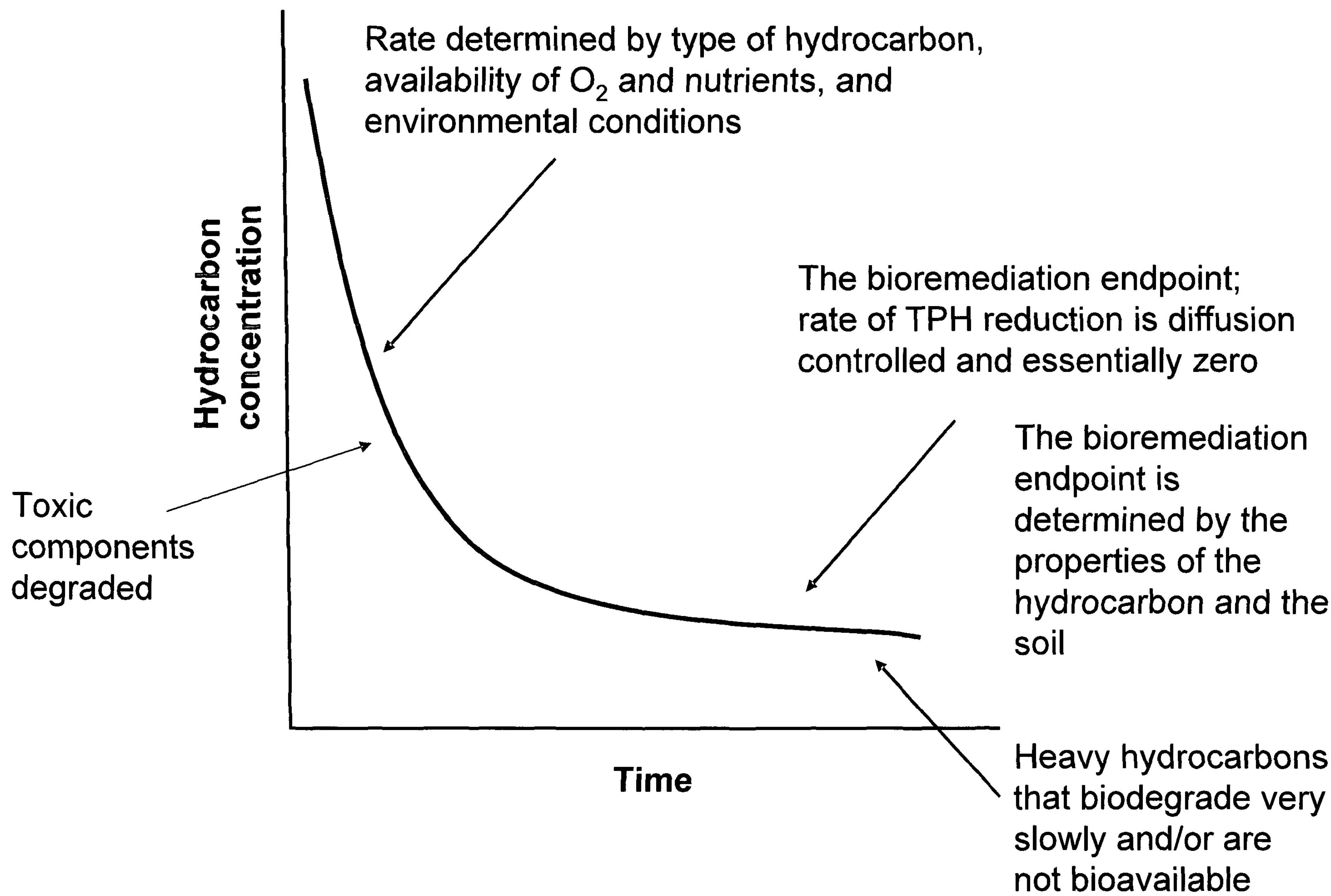
# Hydrocarbons in soil

- If many hydrocarbons are biodegradable and hydrocarbon degraders are everywhere, why doesn't an oil spill just go away by itself?
  - Microbes need more that hydrocarbon in their diet – must have source of nitrogen and phosphorus
  - Microbes must have oxygen
  - Environmental conditions must be right
    - temperature
    - pH
    - Moisture
  - Microbes and hydrocarbons need to get together
- When we do bioremediation we are just making sure that all this happens – looks like gardening doesn't it! (We'll talk about specifics later)

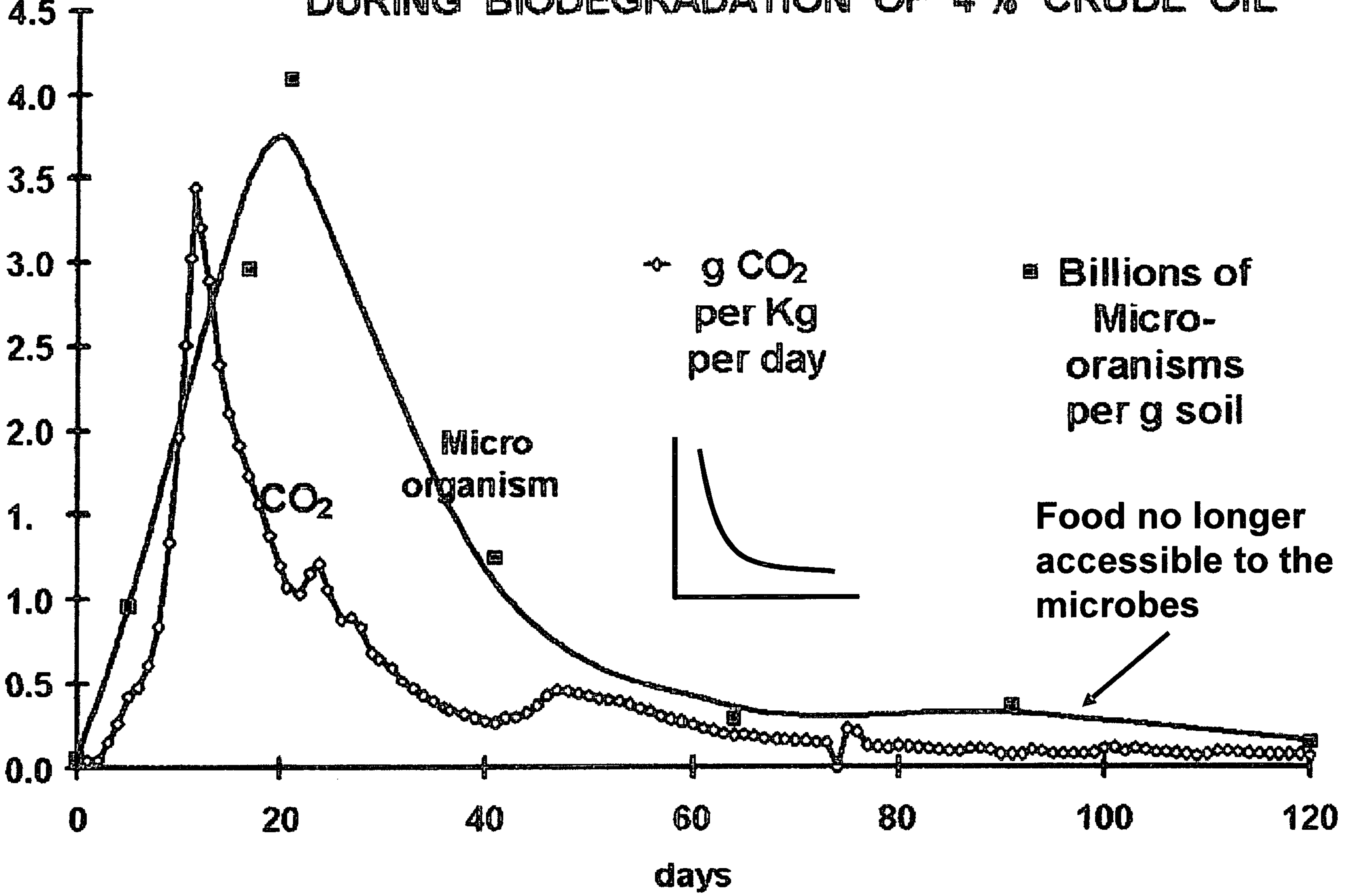
# What it takes to grow a microbe



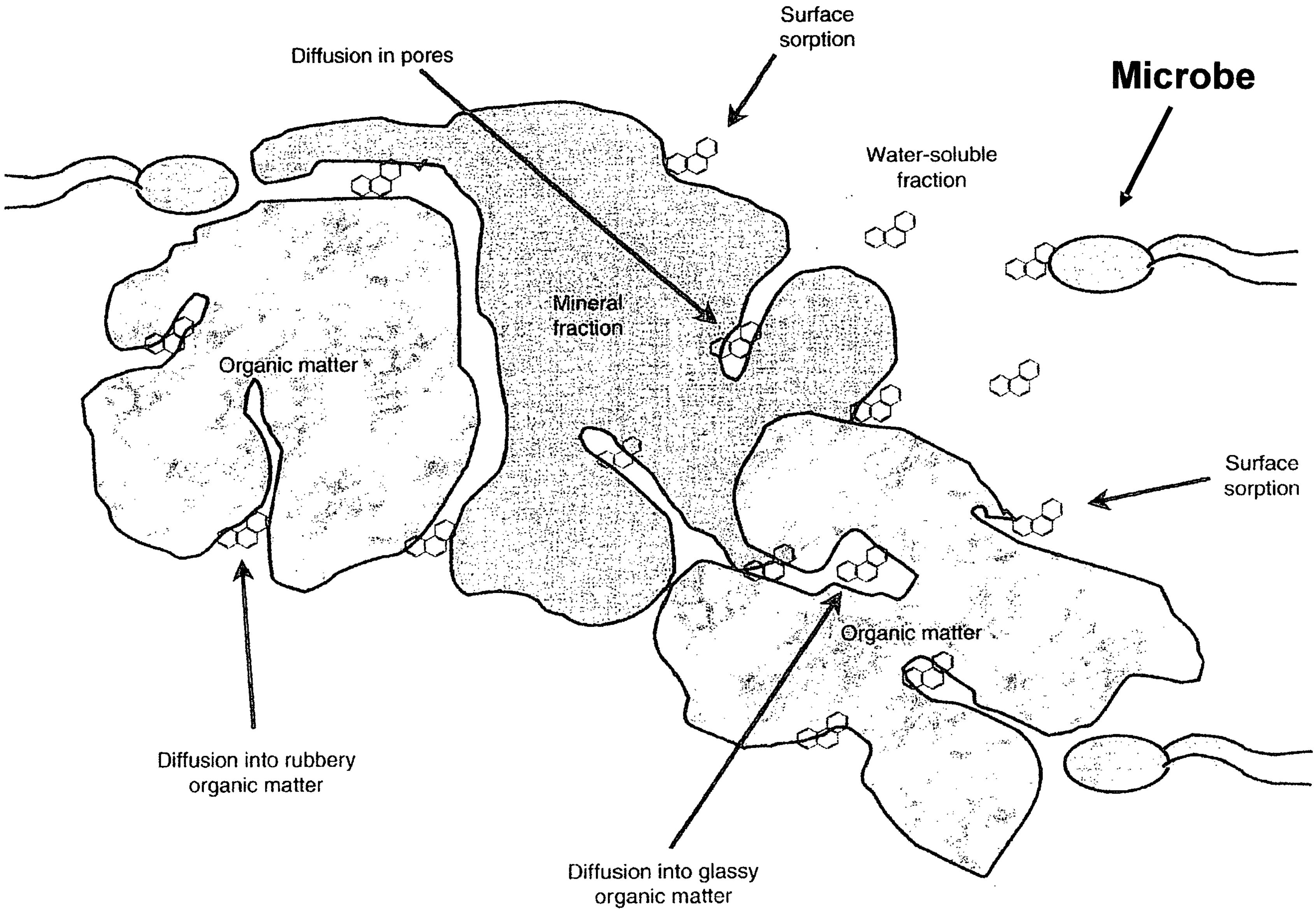
# Bioremediation of Hydrocarbons in a Landfarm



## $CO_2$ RESPIRATION RATE AND PLATE COUNT NUMBERS DURING BIODEGRADATION OF 4 % CRUDE OIL



# Hydrocarbons (especially heavy hydrocarbons) can become immobilized in soil



# A quick review

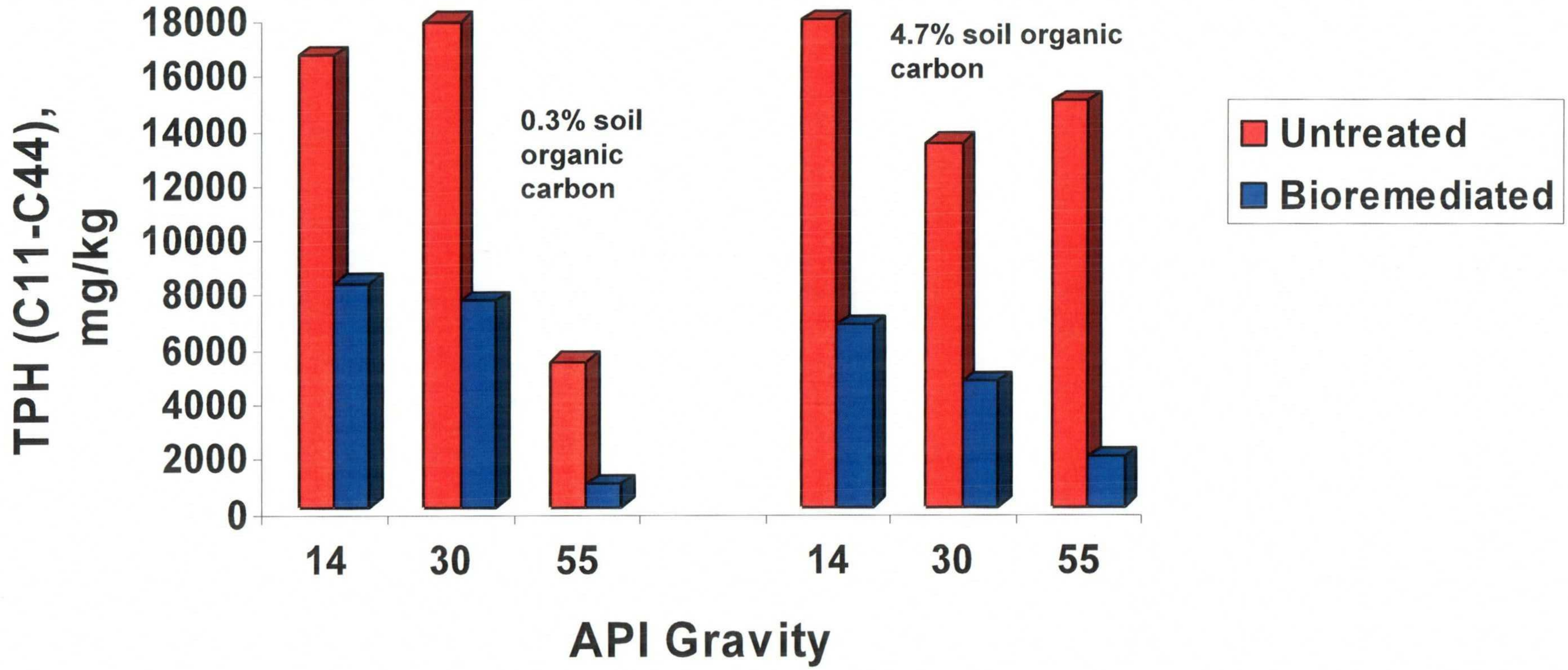
- Many microbes can use hydrocarbons as food and these microbes are widely distributed in nature
- Many types of hydrocarbons can be bioremediated
- Bioremediation is just gardening (That’s why they call it (landfarming”)
- When bioremediation reaches is natural endpoint there are still hydrocarbons in the soil but, as we will see, toxic hydrocarbons have been eliminated

# Is a bioremediation endpoint an environmentally acceptable endpoint?

# Salinitro et al., Environmental Science and Technology, 31, 1769-1776 (1997)

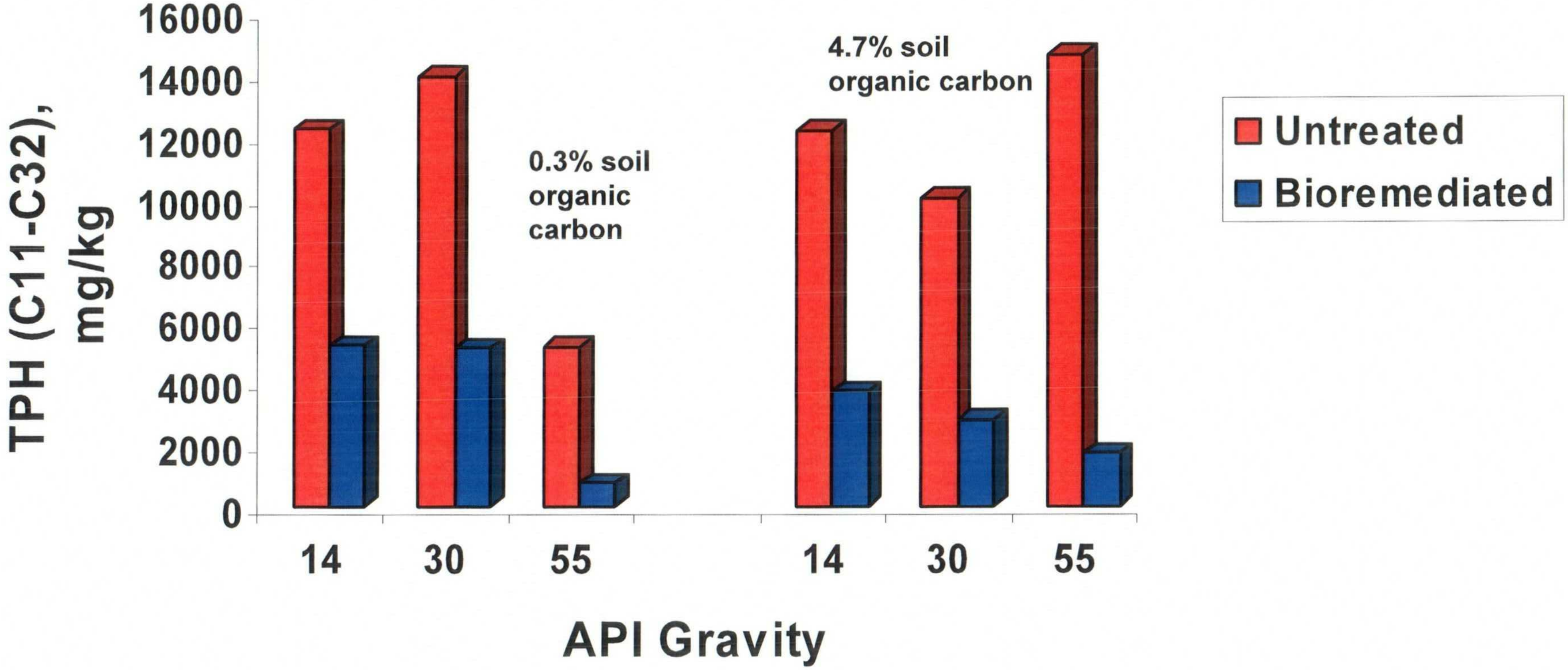
- Published in the most rigorously reviewed environmental journal in the world
- Identified in an EPA publication as being of the highest scientific quality
- Authors investigated the effects of API gravity and soil organic matter on the bioremediation endpoint
  - TPH endpoints
  - Toxicity
    - Earthworm
    - Microtox
    - Seed germination
  - Hydrocarbon leaching potential

# Bioremediation Endpoints; Effect of API Gravity and Soil Organic Matter



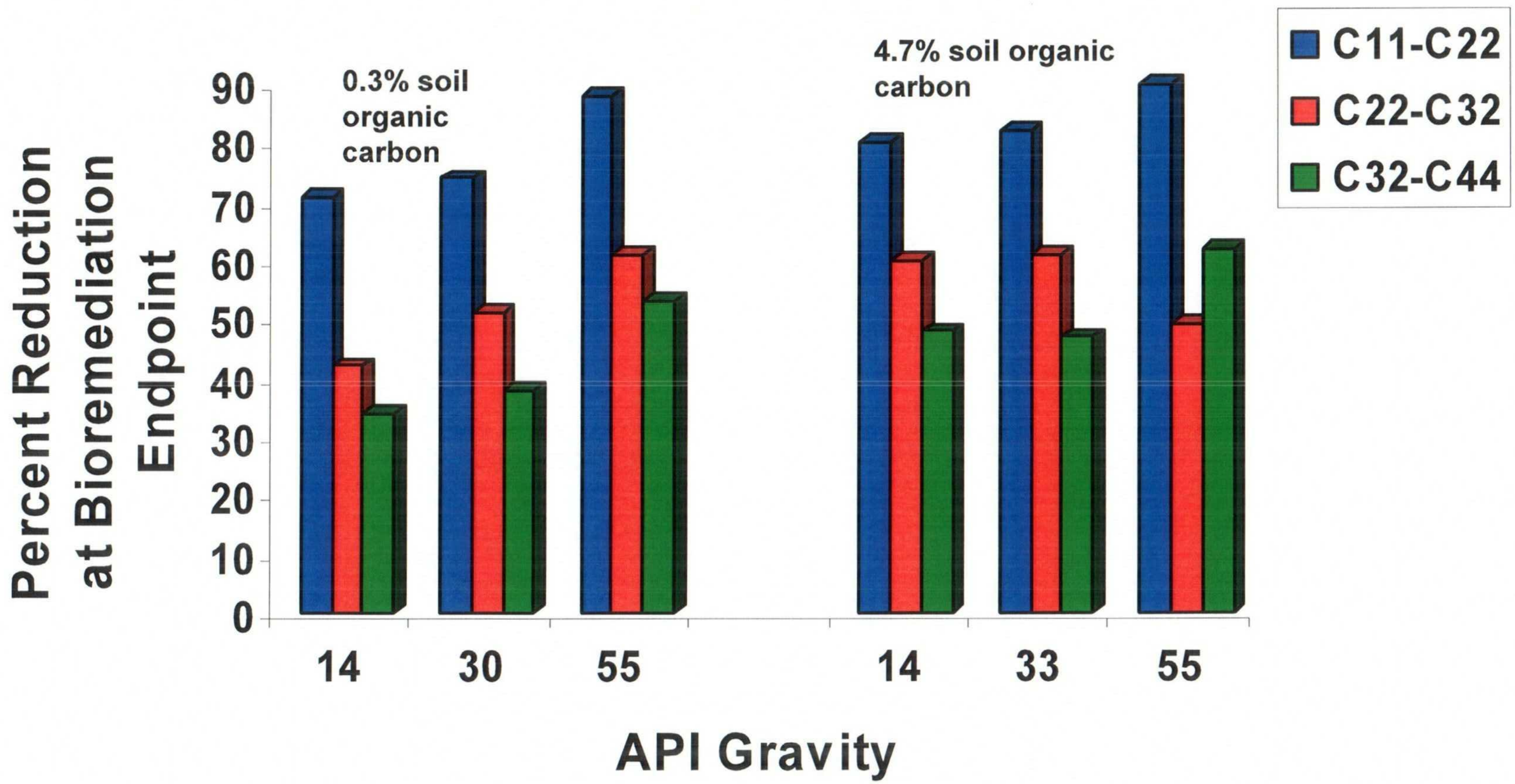

Salinitro et al., Environmental Science and Technology, **31**, 1769-1776 (1997)

## Bioremediation Endpoints; Effect of API Gravity and Soil Organic Matter




Salinitro et al., Environmental Science and Technology, **31**, 1769-1776 (1997)

# Bioremediation of Carbon Fractions: Effect of API Gravity and Soil Organic Matter



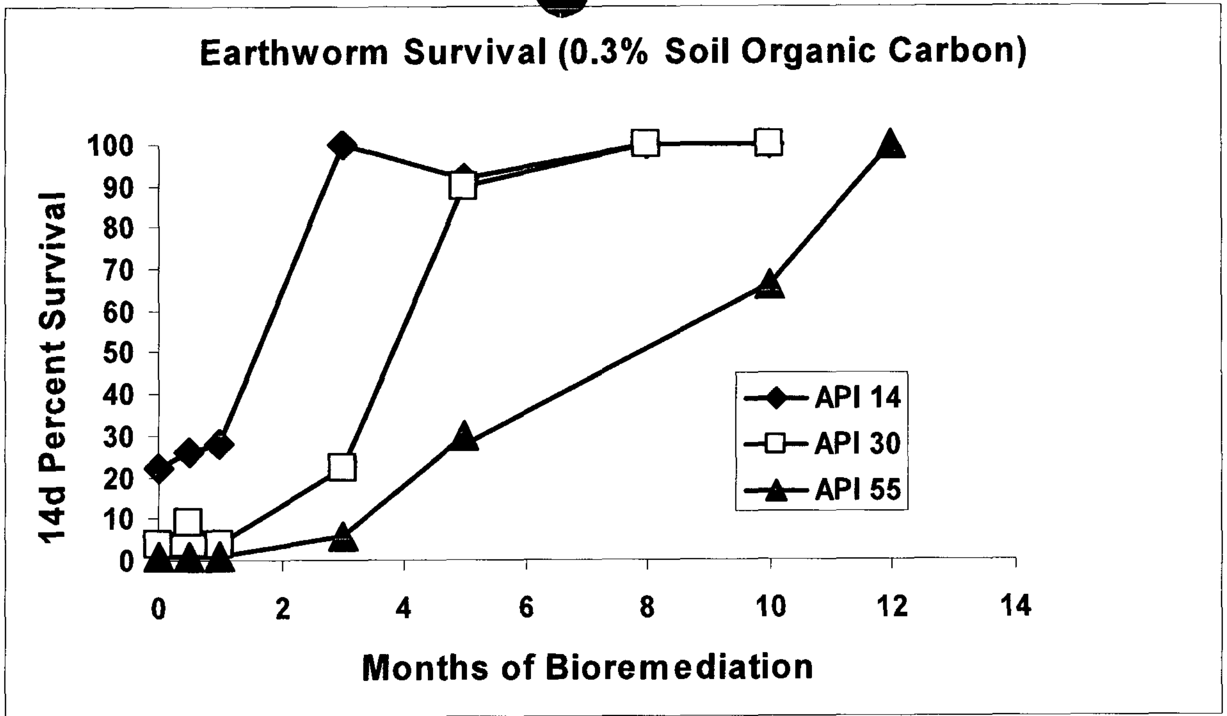

Salinitro et al., Environmental Science and Technology, **31**, 1769-1776 (1997)

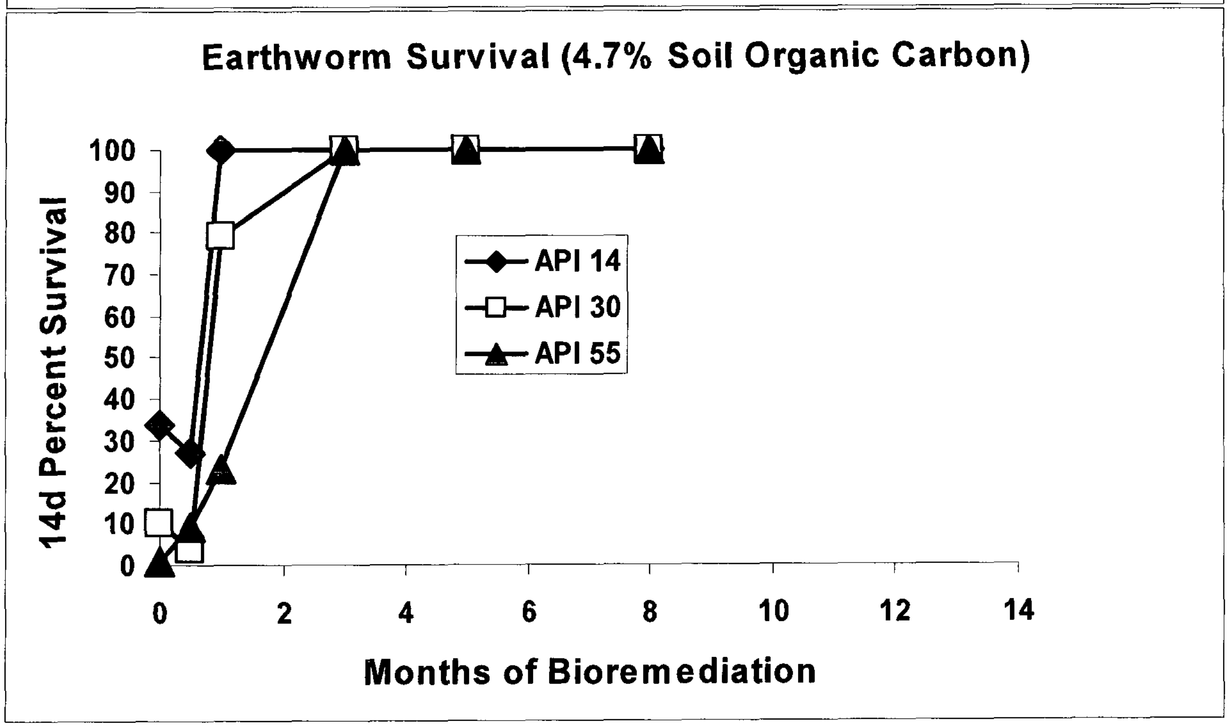
# BTEX Bioremediation Endpoints: Effect of API Gravity and % Soil Organic Carbon

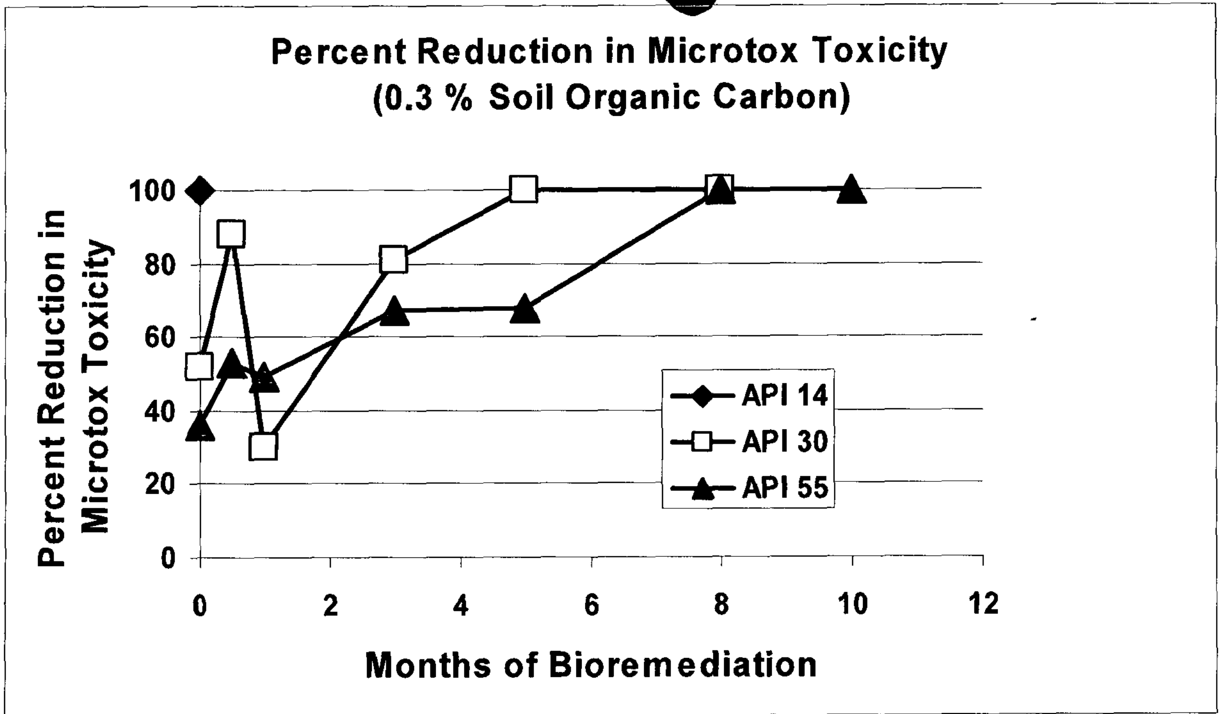
| % Soil Organic Carbon | API Gravity | Benzene Untreated (mg/kg) | Benzene Bioremediated (mg/kg) | TEX Untreated (mg/kg) | TEX Bioremediated (mg/kg) |
|---|---|---|---|---|---|
| 0.3 | 14 | <0.02 | <0.02 | 1.6 | <0.02 |
| | 30 | 3.2 | <0.02 | 256 | <0.02 |
| | 55 | 63.7 | <0.02 | 1027 | <0.02 |
| 4.7 | 14 | 1.8 | <0.02 | 43.4 | <0.02 |
| | 30 | 10.0 | <0.02 | 35.0 | <0.02 |
| | 55 | 53.0 | <0.02 | 1624 | <0.02 |

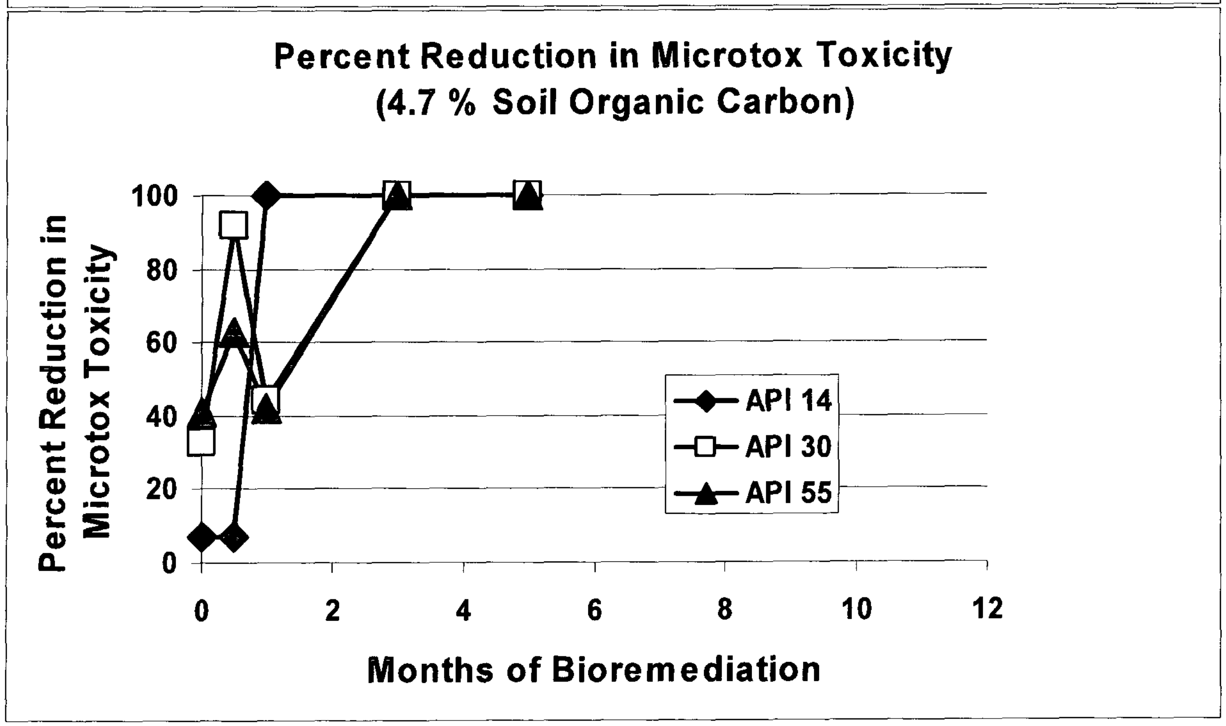
Salinitro et al., Environmental Science and Technology, **31**, 1769-1776 (1997)

Salinitro et al., Environmental Science and Technology, **31**, 1769-1776 (1997)



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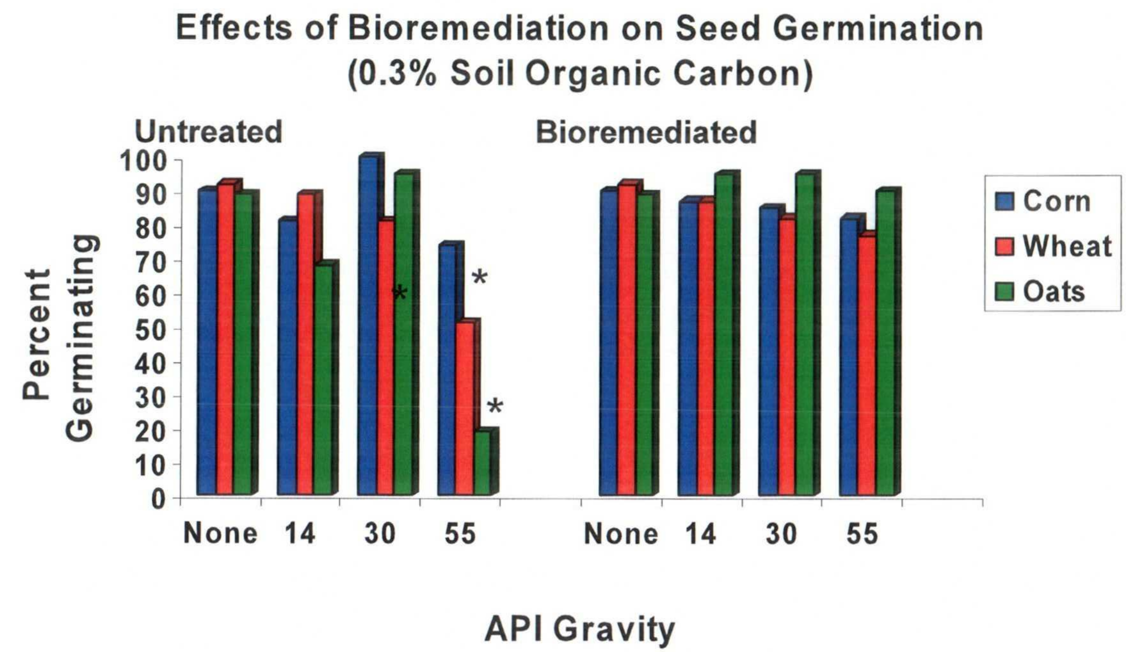
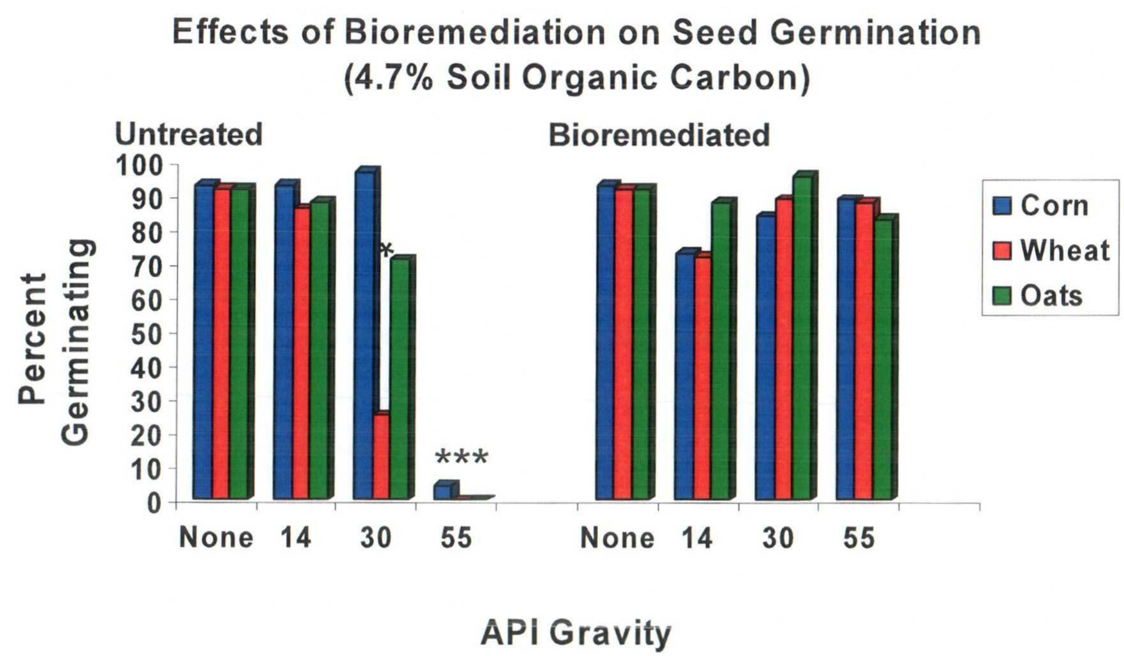



*Statistically different from control

# Protocol for Leaching Potential Studies

- Batch soil extraction
  - 20 g bioremediated soil extracted with 200 mL aliquots of 0.01 M $CaSO_4$ – 2% sodium azide (inhibits further biodegradation) for 24-48 hrs
  - Modification of California Wet Extraction Test Procedure
  - Extracts analyzed for TPH, BTEX, O&G, and metals
- Column leaching studies
  - 500 g soil untreated or biotreated soil packed in 2" X 6" column
  - Columns operated in upflow to simulate a water leaching flow rate of 1 ft/d. Column leachates analyzed for TPH, O&G, BTEX, and metals

Salinitro et al., Environmental Science and Technology, **31**, 1769-1776 (1997)

# Batch Extraction Hydrocarbon (O&G) Levels After Bioremediation

**O&G (mg/L) after extraction**

| % Organic Carbon | API Gravity | 1* | 2 | 3 | 5 |
|---|---|---|---|---|---|
| 4.7 | 14 | 15 | 11 | 7 | <5 |
| | 30 | 30 | 17 | 12 | 9 |
| | 55 | 12 | <5 | <5 | <5 |
| 0.3 | 14 | 16 | 11 | 9 | 6 |
| | 30 | 31 | 16 | 14 | 8 |
| | 55 | <5 | <5 | <5 | <5 |

*number of extractions

TPH concentrations all < 5 mg/L

BTEX concentrations all < 5 µg/L

No heavy metals detected

Salinitro et al., Environmental Science and Technology, **31**, 1769-1776 (1997)

# Soil Column BTEX Levels in Leachate (μg/L) Before and After Bioremediation

| | | B | B | TEX | TEX |
|---|---|---|---|---|---|
| **% Organic Carbon** | **API Gravity** | **Untreated** | **Bioremediated** | **Untreated** | **Bioremediated** |
| 4.7 | 14 | <2 | <2 | 17 | 2 |
| | 30 | 630 | <2 | 5260 | 8 |
| | 55 | 4900 | <2 | 18270 | 6 |
| 0.3 | 14 | 160 | <2 | 700 | <2 |
| | 30 | 1660 | <2 | 5980 | 48 |
| | 55 | 7690 | <2 | 16980 | 5 |

No heavy metals detected

Salinitro et al., Environmental Science and Technology, **31**, 1769-1776 (1997)

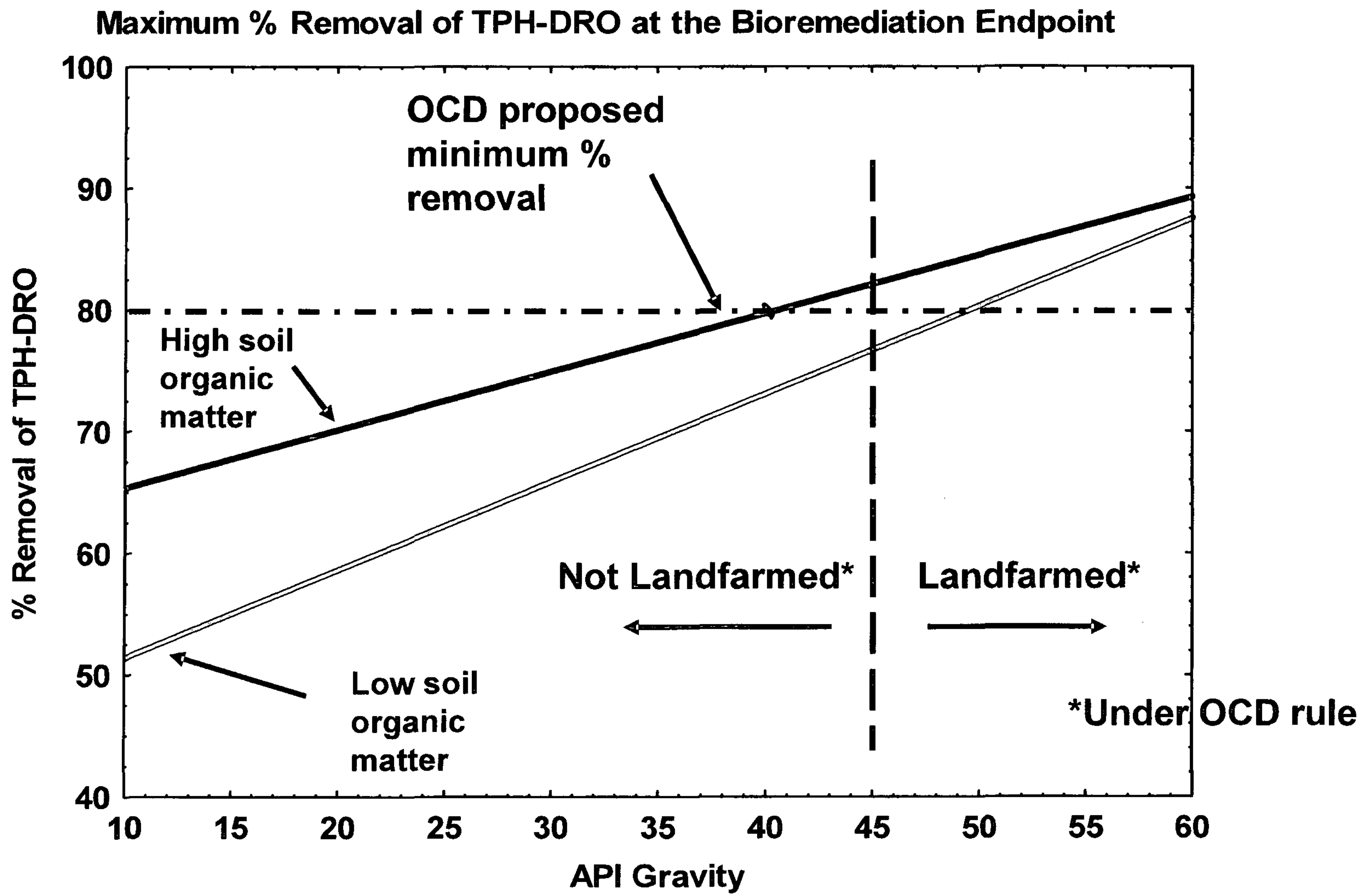
# The Removal of Hydrocarbon Toxicity in Soil by Bioremediation Has Been Widely Reported

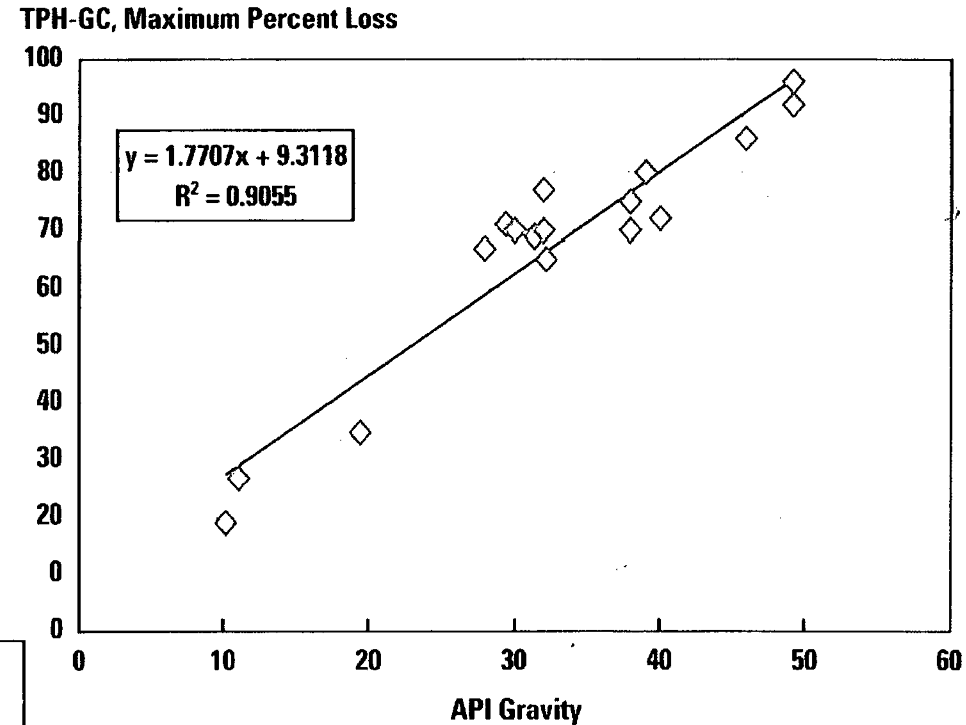
| **Reference** | **Hydrocarbon Type** | **Toxicity Metric** |
|---|---|---|
| Hanna and Weaver, Plant and Soil Science, **240**, 127-132 (2002) | Crude oil | Earthworm survival |
| Visser and Danielson, CAPP Publ. 1995-0004, CAPP (1995) | Crude oil | Earthworm survival<br>Seed germination<br>Plant root elongation |
| Chaineau et al., Water, Air, and Soil Pollution, **144**, 419-440 (2003) | Crude oil | Earthworm survival<br>Seed germination<br>Microtox |
| Tang et al., Environmental Science and Technology, **32**, 3586-3590 (1998) | PAHs | Earthworm survival |
| Hund and Trannspurger, Chemosphere, **29**, 371-390 (1994) | PAHs | Earthworm survival<br>Plant survival<br>Nematode survival |
| Salanitro et al., Environmental Science and Technology, **31**, 1769-1776 (1997) | Light, medium, and heavy crude oils | Earthworm survival<br>Seed germination<br>Plant growth<br>Microtox |

| **Reference** | **Hydrocarbon Type** | **Toxicity Metric** |
|---|---|---|
| Haeseler et al., Environmental Science and Technology, **24**, 4379-4384 (1999) | PAHs | Microtox<br>Genotoxicity |
| Bundy et al., Soil Biology and Biochemistry, **36**, 1149-1159 (2004) | Paraffin<br>Motor oil | Microtox |
| Saterbak et al., Environmental Toxicology and Chemistry, **19**, 2643-2652 (2000) | Crude oil | Earthworm survival<br>Seed germination |
| Wang and Bartha, Biology and Biochemistry, **22**, 501-505 (1990) | Jet fuel<br>Diesel<br>Heating oil | Microtox<br>Seed germination<br>Plant growth |
| Van Gestel et al., Environmental Toxicology and Chemistry, **20**, 1438-1449 (2001) | Crude oil<br>Refined product mixture | Microtox<br>Earthworm survival<br>Plant growth<br>Algae survival<br>*Daphnia magna* survival |
| Molina-Barahona et al., Environmental Toxicology, **20**, 100-109 (2005) | Diesel | Plant growth<br>*Daphnia magna* survival |

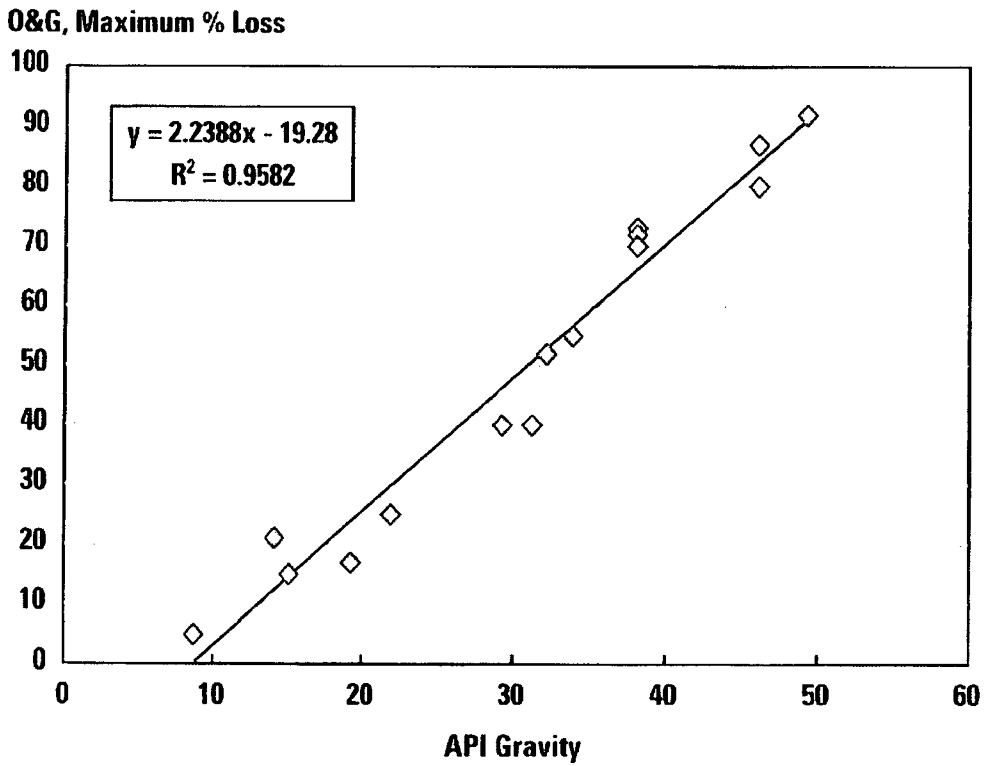
| Reference | Hydrocarbon Type | Toxicity Metric |
|---|---|---|
| Siddiqui and Adams, Environmental Toxicology, **17**, 49-62 (2002) | Diesel | Seed germination |
| Marwood et al., Environmental Toxicology and Water Quality, **13**, 117-126 (1998) | Diesel | Seed germination<br>Seedling emergence<br>Root elongation |
| Renoux et al., Microbial Processes in Bioremediation, **3**, 259-264 (1995) | Crude oil | Earthworm survival<br>Seed germination<br>Plant growth |
| Baek et al., Journal of Environmental Science and Health, **39**, 2465-2472 (2004) | Crude oil | Plant growth |

# What the Salinitro study says about the bioremediation endpoint



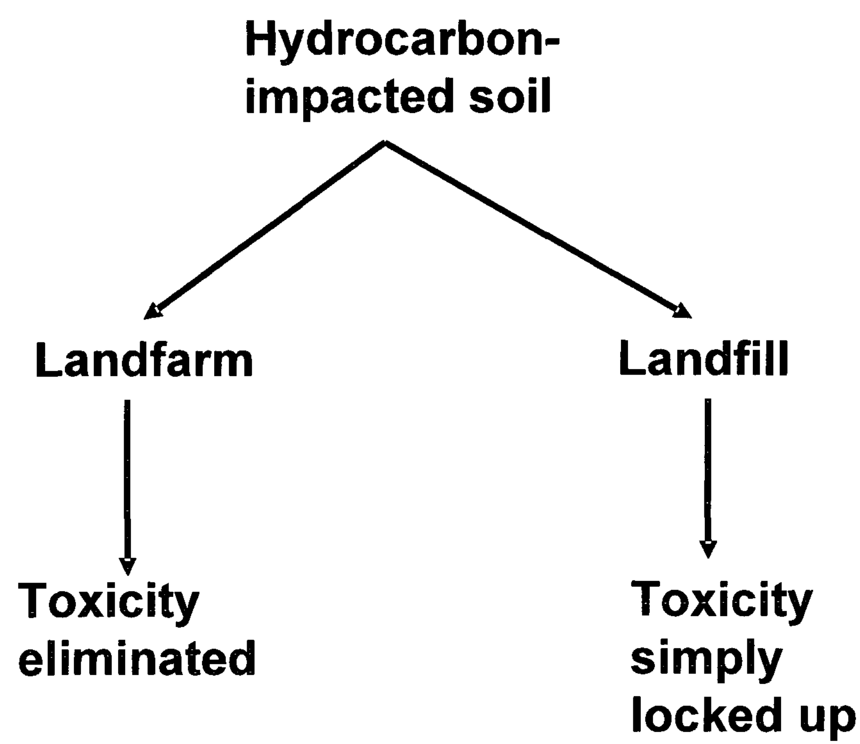



**Source: "A Summary of the DOE/PERF Bioremediation Workshop" (2003)**



# Another quick review

- Science supports the fact that the bioremediation endpoint is environmentally acceptable
- Bioremediation of hydrocarbon in soil eliminates toxicity as measured by a variety of metrics

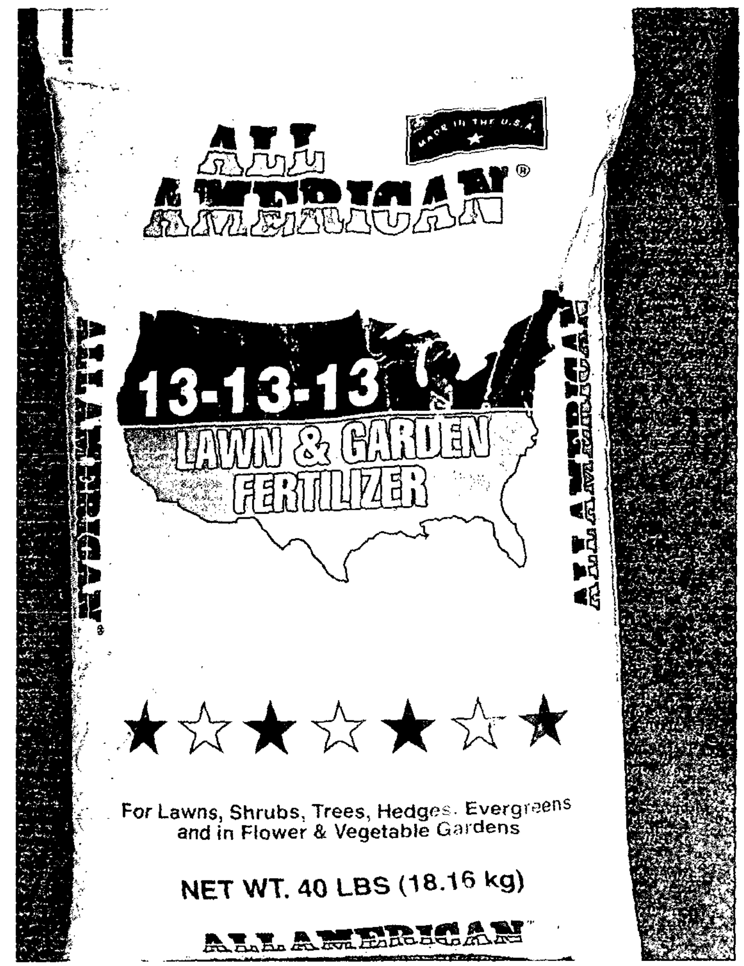



**Which option is ultimately more protective?**

# Now let's look at the details of landfarming recommended practice

This is going to sound like an agricultural college textbook

Remember it's just good gardening



# Recommended Practice for Permitted Landfarms

- Exempt waste amenable to landfarming:
  - Crude oil impacted soil
  - Condensate impacted soil
  - Drill cuttings
  - Tank bottoms

Tier 1

Tier 2

# Recommended Practice for Permitted Landfarms

- Hydrocarbon loading
  - Biodegradation **rates** in a landfarm strongly correlate with the hydrocarbon interfacial area/mass ratio (i.e., the amount of hydrocarbon surface compared to the total hydrocarbon mass)
  - Microbes munch on hydrocarbon at a water-hydrocarbon interface
    - Biodegradation **rates** decrease with increasing hydrocarbon loading
    - Biodegradation **rates** decrease with decreasing API gravity
      - Increasing viscosity decreases mixing efficiency
  - It's a matter of efficiency of operations – rates vs. endpoints

# Recommended Practice for Permitted Landfarms

- Organic matter
  - Blending organic matter into landfarm lift soil, while not required for successful landfarming, can have several benefits including:
    - Improved moisture retention
    - Improved soil structure and better aeration
    - Establishing a fertility base to improve re-vegetation upon closure

# Recommended Practice for Permitted Landfarms

- pH
  - Optimum pH is 6-8
  - Monitored monthly and adjusted if necessary
  - Acidifying amendments (to lower pH) include:
    - Aluminum sulfate [$Al_2(SO_4)_3$]
    - Ferrous sulfate ($FeSO_4$)
    - Sulfur
  - Neutralizing acidity (to raise pH):
    - Lime [$CaO/Ca(OH)_2$]

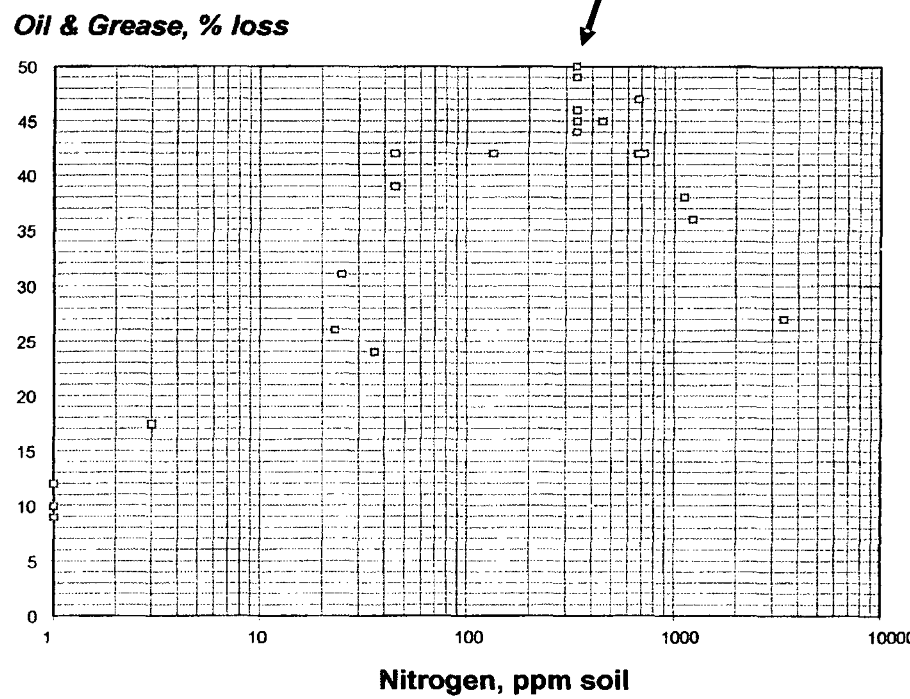
# Recommended Practice for Permitted Landfarms

- Tilling
  - The benefits of frequent tilling of the landfarm lift include:
    - Maintaining a soil structure in the lift conducive to good oxygen transfer from the atmosphere
    - Vertical mixing of the lift ensures that the entire soil depth in the lift spends some time in the upper most active zone of biodegradation
    - More uniform distribution of nutrients in the soil profile
  - The landfarm lift should be tilled at least twice monthly with a tillage depth equal to the depth of the lift.

# Recommended Practice for Permitted Landfarms

- Nutrients
  - The most effective nutrients for landfarms are inorganic sources N and P, i.e. common agricultural fertilizers
    - Optimum N concentrations: 50-200 mg/kg (ppm)
    - Optimum P concentrations: 25-50 mg/kg (ppm)
    - Monitor monthly with field kits

N conc. above 500 ppm are inhibitory to microbes



# Recommended Practice for Permitted Landfarms

- Moisture
  - Optimum soil moistures for biodegradation are typically 60-80% of field capacity
    - This gives plenty of moisture for microbes but allows large macropores to exist in the soil for oxygen transfer
    - Saturation results in anaerobic conditions
    - Monitor at least weekly

# Recommended Practice for Permitted Landfarms

- Hydrocarbon analysis for operational monitoring of each lift
  - There are alternatives to lab-based hydrocarbon analysis for <u>operational</u> monitoring
    - EPA SITE Program certified field kits available
    - Produce results comparable to 8015M and recommended as reliable field test kits
    - Lower cost than 8015M
    - Real-time answers

# Recommended Practice for Permitted Landfarms

- Hydrocarbon analysis for lift closure
  - Tier 1
    - Bioremediation endpoint
  - Tier 2
    - Bioremediation endpoint
    - Additional site specific risk-based screening levels as appropriate

# Recommended Practice for Permitted Landfarms

- Hydrocarbon analysis for lift closure
  - Documenting the bioremediation endpoint
    - Should be attempted when two conditions are met:
      - the landfarm has been operated following recommended practice for a minimum treatment time
      - field measurements of TPH levels indicate that the lift is at or near the end of the treatment cycle

# Recommended Practice for Permitted Landfarms

| Hydrocarbon source | Recommended metric for bioremediation endpoint | Minimum treatment months |
|---|---|---|
| Crude oil, tank bottoms, drill cuttings | TPH-DRO | 12 |
| Gas condensate | TPH-GRO | 6 |
| Mixed waste with both types of hydrocarbons | TPH-DRO and TPH-GRO | 12 |

# Recommended Practice for Permitted Landfarms

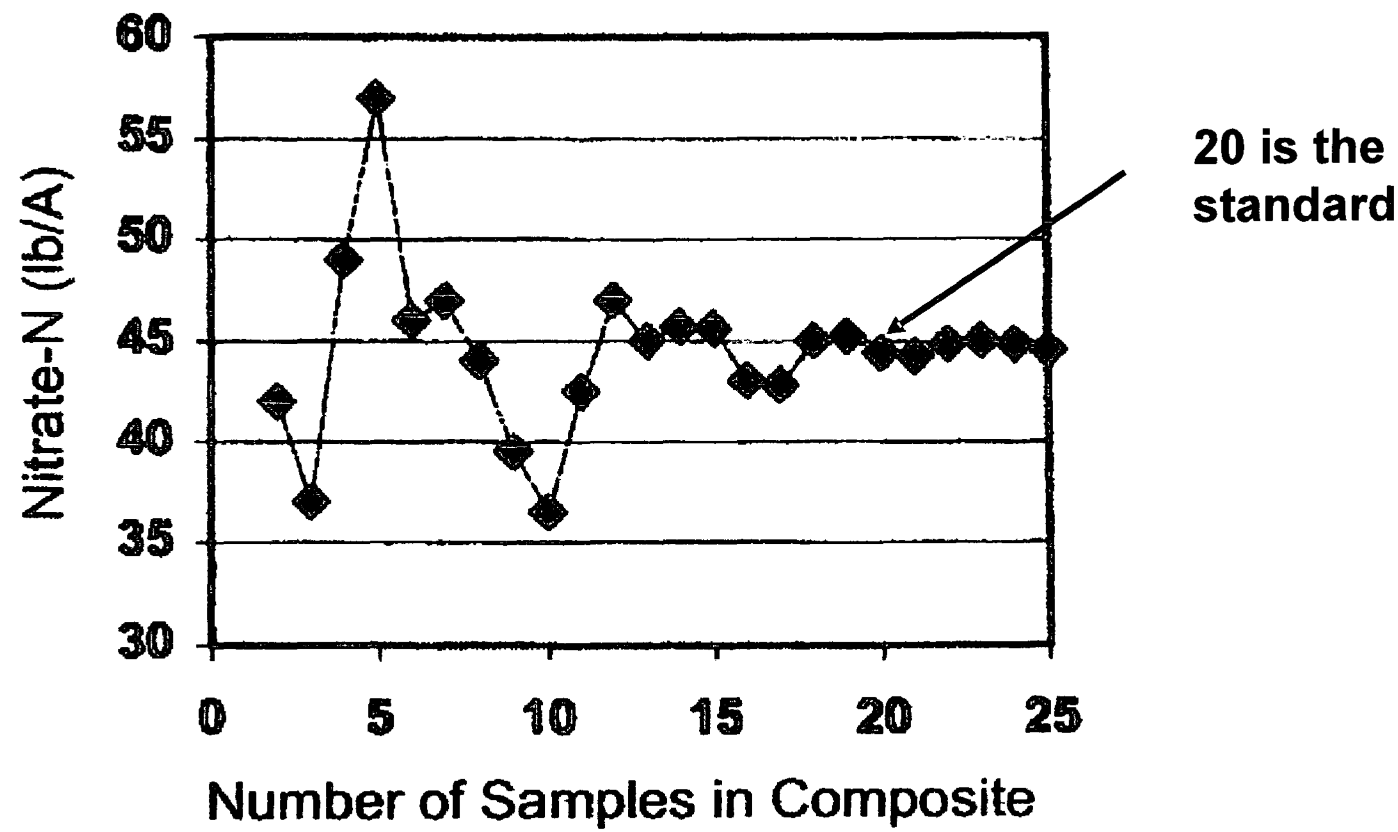
- Hydrocarbon analysis for lift closure
  - A treatment month is defined as a 30-day increment in which the maximum 4-inch bare soil temperature is above 50 °F
  - The bioremediation endpoint can be documented by two successive TPH-DRO or TPH-GRO measurements at least one treatment month apart that are statistically the same.

# Recommended Practice for Permitted Landfarms

- Composite Sampling
  - A soil sample representative of the average concentration of nutrients or hydrocarbon requires composite sampling
  - Each area of the landfarm lift with distinguishing characteristics should be sampled separately
    - Areas with different wastes applied (hydrocarbon type, loadings, chloride concentrations, etc.)
    - Areas with distinctly different soil textures
    - Areas with distinctly different drainage patterns

# Recommended Practice for Permitted Landfarms

How many discrete samples per composite?



# Recommended Practice for Permitted Landfarms

- Temperature
  - The landfarm operator has little control of temperature in the landfarm
  - Biodegradation rates decrease with decreasing soil temperature (thus the need to define a “treatment month”)
  - In cold periods the operator should expect slower rates of hydrocarbon removal and slower rates of nutrient utilization
    - Less need for monitoring
    - Less need for tilling

# Recommended Practice for Permitted Landfarms

- Adding the next lift
  - Each new lift should be tilled to incorporate the top two inches of the lift below
  - This will provide an inoculum of microbes already adapted to the hydrocarbon and environmental conditions.

# A quick review

- What do we need to promote effective bioremediation of hydrocarbon-impacted soils?
  - Nutrients (N,P)
  - Moisture
  - Good aeration (tilling and organic matter)
  - The right pH
  - Warm temperatures
- These are the same requirements of a healthy garden. If it's good for your tomatoes it's good for bioremediation too.

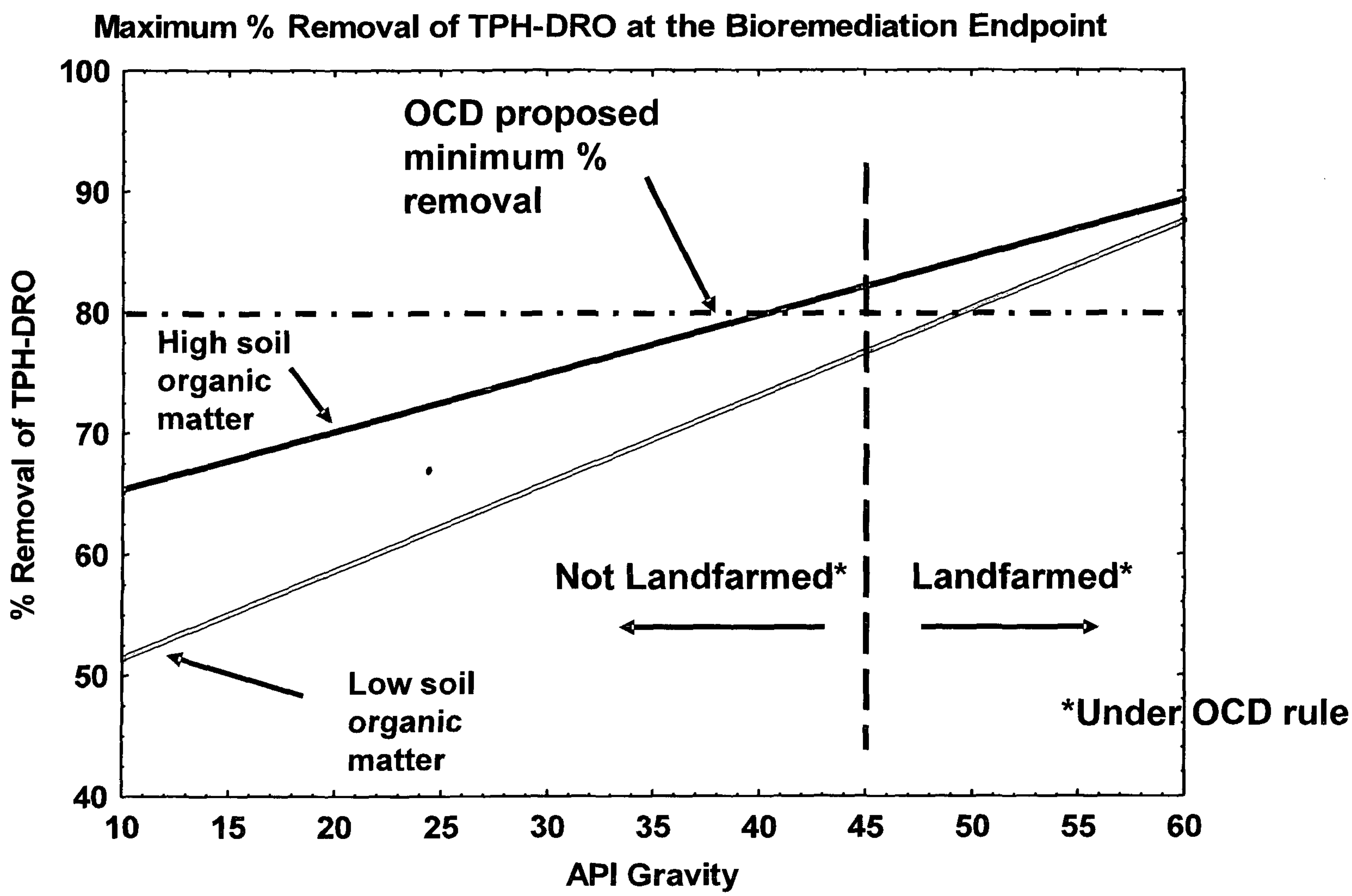
# Some problems with the OCD rule

- I would like to turn my attention now to requirements in the OCD rule that are inconsistent with recommended practice:
  - Unnecessary restraints on the use of the bioremediation endpoint approach in permitted landfarms
  - Unnecessary restrictions on hydrocarbon loading
  - Unnecessary requirements for characterization of the soil under the landfarm
  - Limiting the use of the bioremediation endpoint approach to permitted landfarms only
  - Unnecessarily limiting the size of registered landfarms
  - Restrictions on chlorides which are inconsistent with the science of hydrocarbon biodegradation in soil

# OCD requirements inconsistent with recommend practice for landfarms

- G(7)(a)(iii) –requirement for minimum TPH reduction of 80% when using the bioremediation endpoint approach
  – Not supported by science as required to be protective of public health, groundwater, and the environment
  – This requirement will effectively prevent the use of the bioremediation approach
  – Is the issue weathered asphaltic material?
    - Establish a maximum visible solid phase hydrocarbon (3%) 1% and size
  – Is it too open ended?
    - Establish a maximum residual TPH at the endpoint (1% total extractable petroleum hydrocarbons)

# Remember what the Salinitro study says about the bioremediation endpoint



# OCD requirements inconsistent with recommend practice for landfarms

- G(7)(c)(iii) –requirement for maximum hydrocarbon loading of 5%
  - Not supported by science - hydrocarbons are effectively bioremediated at higher loadings
  - It's a matter of efficiency (rates of biodegradation)
  - Biodegradation rates decrease with increasing hydrocarbon loading and decreasing API gravity
  - Hydrocarbon loading will be self regulating
    - Operator will balance rates against endpoint

# OCD requirements inconsistent with recommend practice for landfarms

- G(9)(c)(i) –Requirements for long list of analyses of native soil before addition of first lift – unnecessarily burdensome and not relevant to the bioremediation process in the lift soil
  - Soil porosity
  - Soil bulk density
  - Soil pH
  - Moisture content
  - Field capacity
  - Organic matter content
  - Soil temperature
  - Soil nutrients (C:N:P)
  - Oxygen content
  - SAR
  - EC
  - Soil structure
  - Soil composition

Not relevant

Vague

**Who will use this information and for what?**

# OCD requirements inconsistent with recommend practice for landfarms

- Bioremediation endpoint approach not allowed for small, registered landfarms
  - No scientific justification for this restriction
  - Lift closure standards proposed in H(5)(a)(iii): total extractable hydrocarbons < 1000 mg/kg and TPH-GRO+TPH-DRO , 500 mg/kg
    - No small landfarm facility treating crude oil-impacted soil will be able to comply
    - Bioremediation should be the go-to technology of choice to eliminate the toxicity of hydrocarbon impacted soils for the benefit of public health, groundwater and the environment

# OCD requirements inconsistent with recommend practice for landfarms

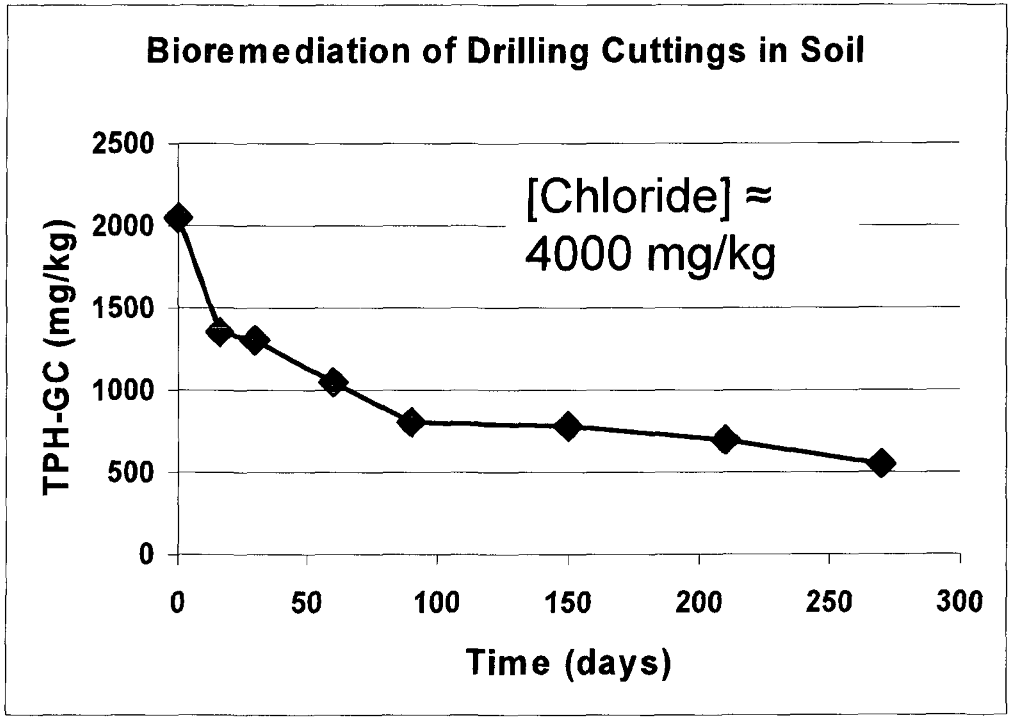
- A(1)e: Registered landfarms limited to 1400 $yd^3$
  - No scientific justification
  - Increasing the size to 2 acres (6400 $yd^3$)
    - allows the operator to make more efficient use of personnel, large equipment, water sources, and sources of organic matter
    - any measure that increases the efficiency of bioremediation will inherently increase protection of human health, groundwater and the environment

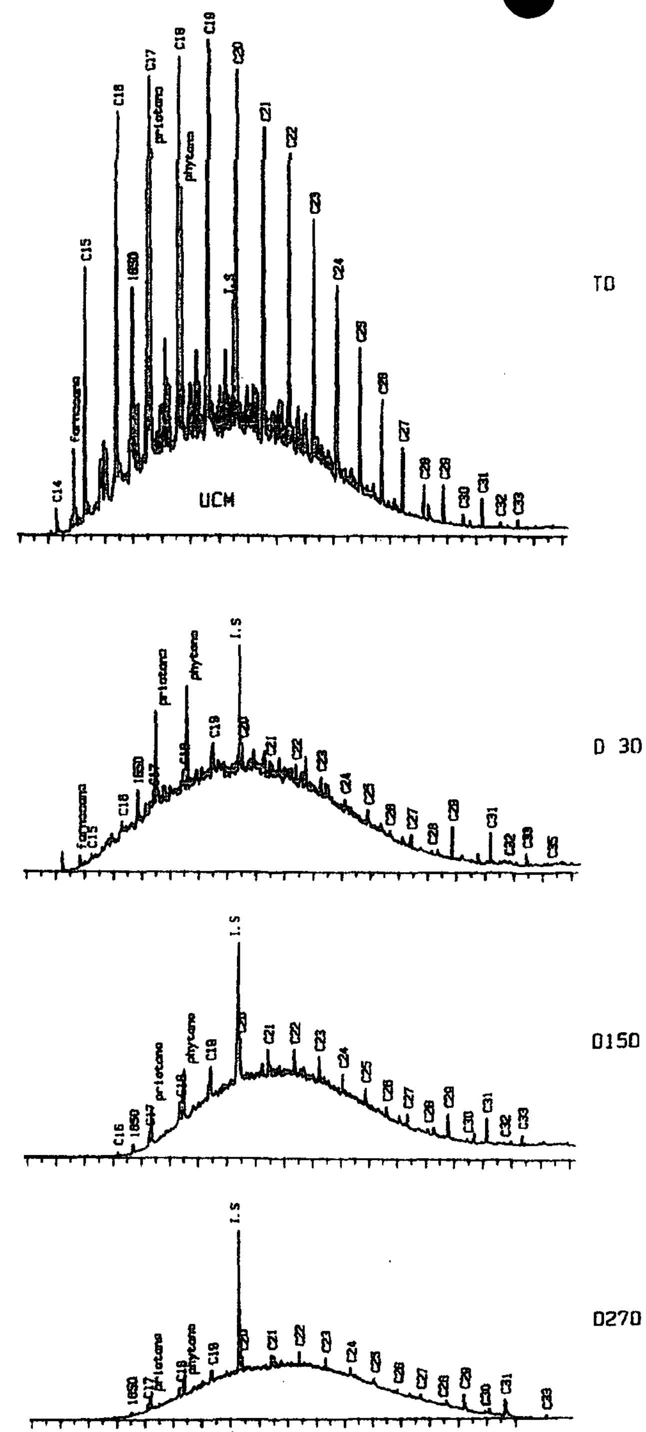
# G(1)(a), continued

- It is a common misconception that soils impacted with chlorides are sterile
- The peer-reviewed scientific literature shows that:
    - Bioremediation of hydrocarbons can occur at chloride concentrations in excess of 1000 mg/kg.
    - Over time hydrocarbon-degrading organisms in a landfarm can adapt and become more tolerant of chlorides.
    - Landfarms can be managed to minimize ~~attenuate~~ the effects of chlorides on the rate of bioremediation of hydrocarbons.

# OCD requirements inconsistent with recommend practice for landfarms

- G(1)(a): Restricts chloride concentration in wastes received by landfarms to 1000 mg/kg
  - With respect to bioremediation of hydrocarbons, the 1000 mg/kg chloride limitation on materials received by a landfarm is not supported by science.



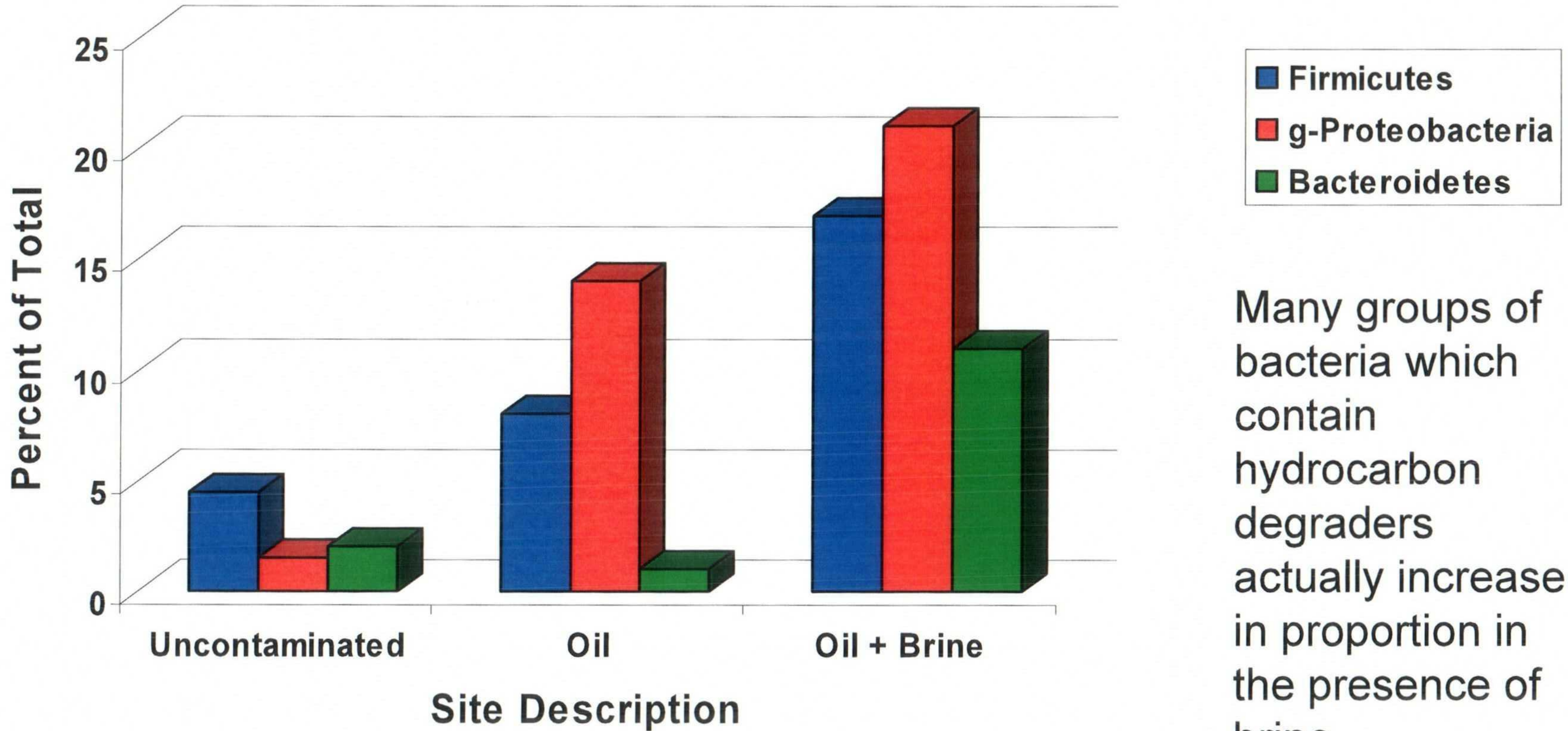




Chaineau et al., Environmental Science and Technology **29**, 1615-1621 (1994)

# Bioremediation of a Spill of Crude Oil and Brine

| Site | Treatment | Microbial Count (cells/g) | $[Cl^-]$ (mg/kg) | TPH Half-life (days) |
|---|---|---|---|---|
| 1 | Hay; fertilizer; one-time ripping | $3.1 \times 10^8$ | 2600 | 346 |
| 2 | One-time ripping; interception trench | $3.6 \times 10^8$ | 1600 | 277 |
| 3 | Hay; fertilizer; one-time ripping; interception trench | $3.6 \times 10^8$ | 3000 | 177 |
| Uncontaminated | | $6.8 \times 10^8$ | | |

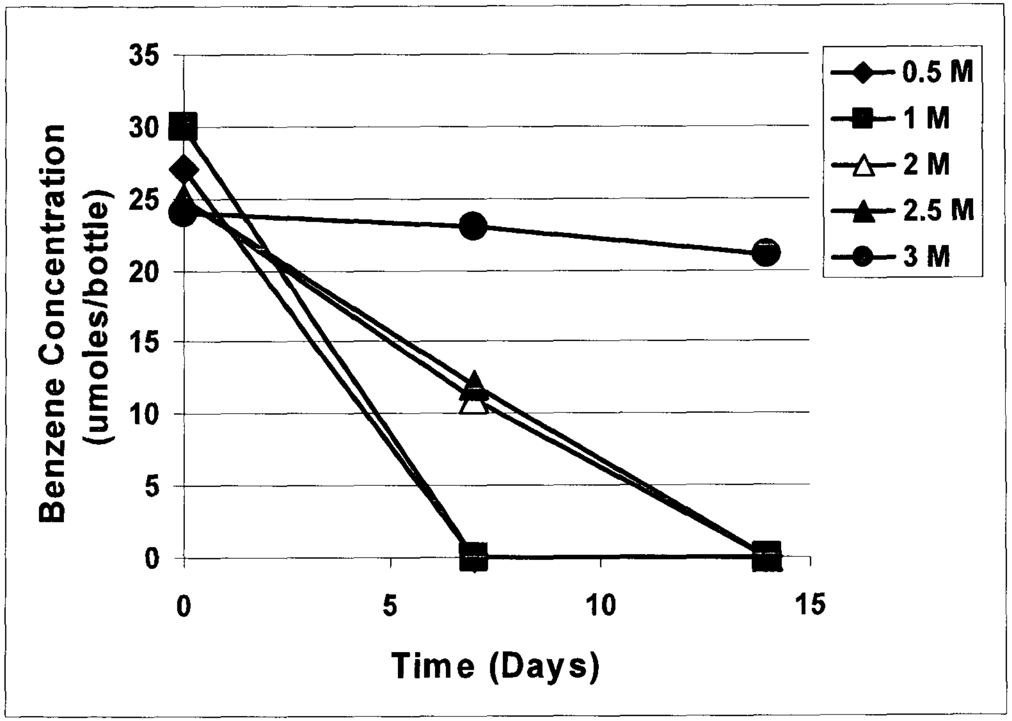
Sublette et al., Environmental Geosciences, **12**, 115-125 (2005)




Many groups of bacteria which contain hydrocarbon degraders actually increase in proportion in the presence of brine

Sublette et al., Oilfield Brine Remediation Symposium, Baton Rouge, LA (2005)

# Salt-tolerant Benzene Degrader Enriched from Oil-Brine Impacted Soil from Seminole County, OK




Nicholson and Fathepure, Applied and Environmental Microbiology, **70**, 1222-1225 (2004)

1 M NaCl translates into a chloride concentration in soil of about 5000 mg/kg

Basis: Loamy soil

Soil moisture of 19.5%

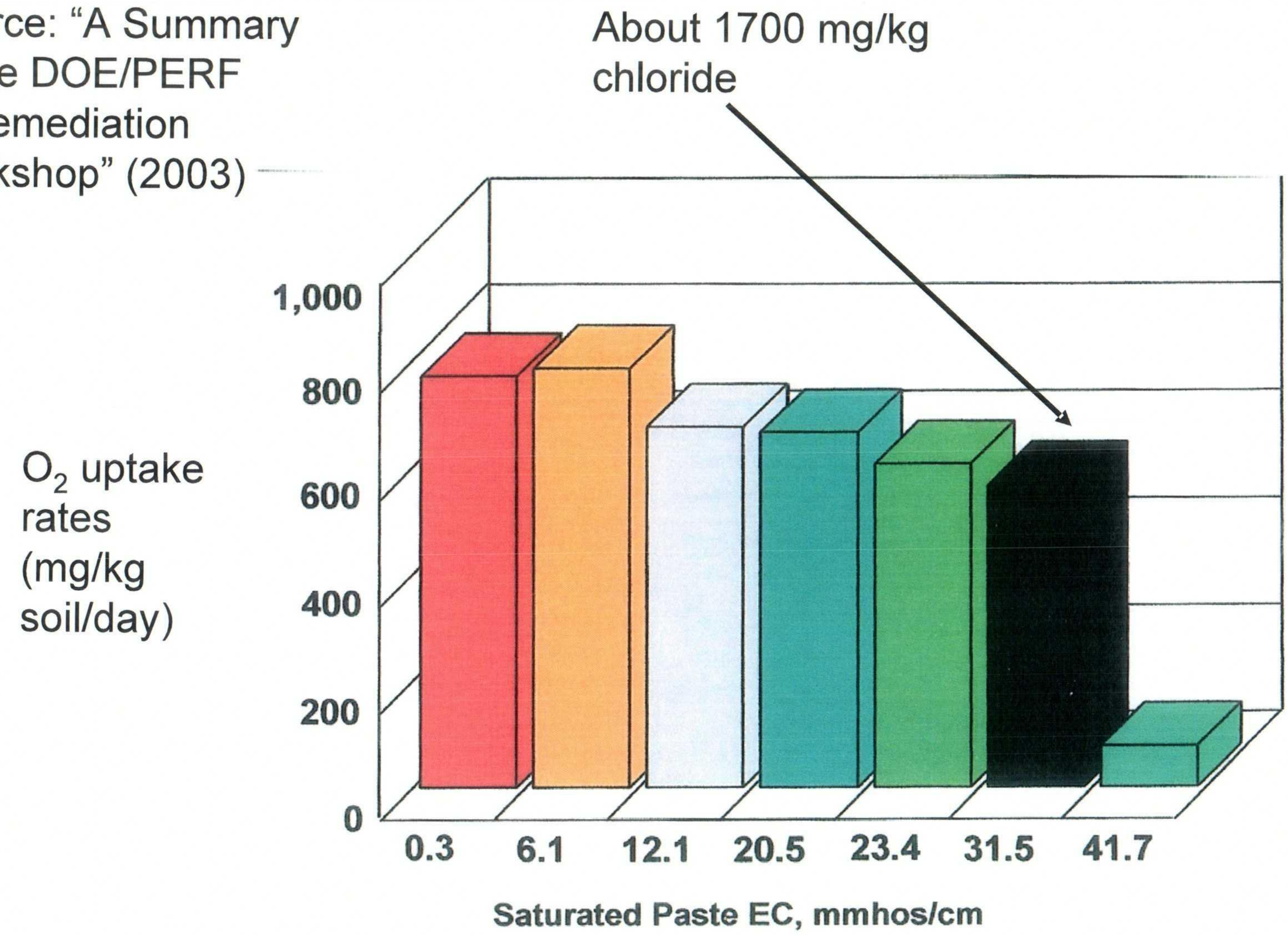
(75% of field capacity)*

8% unavailable water*

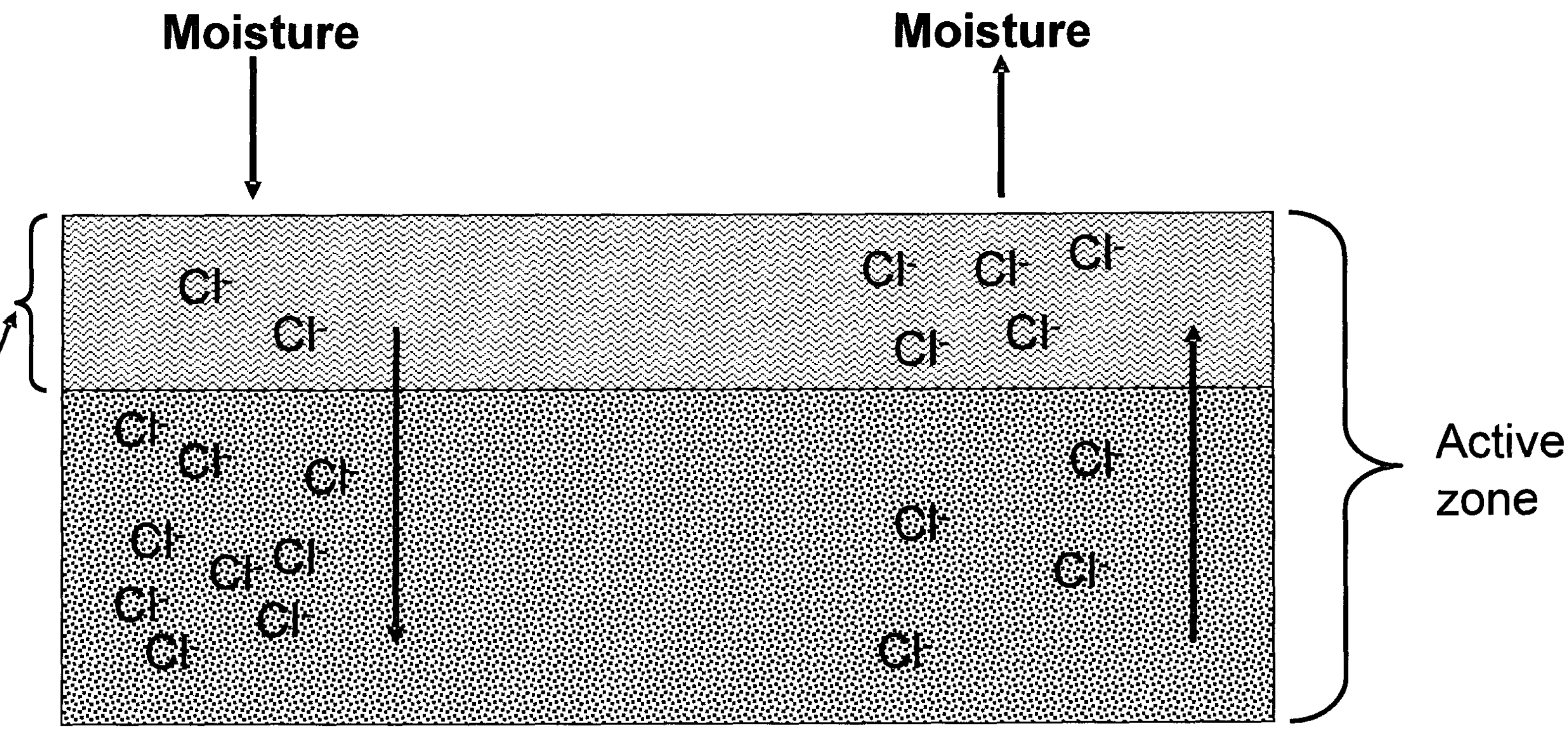
Enrichment culture dominated by several species of *Marinobacter*, same DNA sequences seen in bacteria from the Mediterranean Sea, oil refinery effluent, deep ocean vents, and offshore oil wells

*Brady and Weil, Nature and Properties of Soil, Prentice Hall Publishers (1999)

Source: "A Summary of the DOE/PERF Bioremediation Workshop" (2003)



# Management to Attenuate Effects of Salts in a Landfarm: Movement of Chlorides




Highest $O_2$ concentrations – highest rates of hydrocarbon degradation

**Tilling followed by addition of moisture creates a low concentration of chlorides in the most active zone of bioremediation.**

# A quick review

- There is no scientific basis for restricting the bioremediation endpoint approach option to just permitted landfarms
- Current TPH closure standards for registered landfarms cannot be met with crude oil
- Increasing the size of registered landfarms increases efficiency in terms of utilization of resources
- There is no reason not to allow some flexibility in hydrocarbon loadings
- Requirements for extensive characterization of the native soil under a landfarm is unnecessarily burdensome requiring the collection of data that no one will use

# A quick review

- Chlorides do not sterilize soils
- Bioremediation of hydrocarbons can occur at chloride concentrations > 1000 mg/kg
- Microbes in landfarms can become adapted to elevated chlorides over time
- Landfarms can be operated in such as way as to mitigate the effects of high chloride concentrations on hydrocarbon biodegradation
  - Look at an ag extension office publication on how to seed saline soil – the same concepts are recommended

Let's talk some more about small registered landfarms

Bioremediation should be **encouraged** in these small landfarms and regulations made as easy to understand and follow as possible. It will pay dividends by eliminating toxicity in landfarming versus storing hydrocarbon-impacted soils in landfills.

# Small Registered Landfarms

- < 2 acres
- < 3 years operation
- Inherently less risk to public health, groundwater and the environment
- Regulations should be simple and easy to understand
  - Will result in more utilization of bioremediation as a treatment option with less toxic hydrocarbons sent to the state's landfills

# Simplified recommended practice as developed by IPEC – It's just good gardening

- Loading
  - No hydrocarbon wet soil
- Fertilizer
  - Cheap agricultural fertilizer like 13-13-13
  - Small incremental additions
  - Warm months only
- Soil structure
  - Organic matter
- Tilling
- Moisture
  - Garden center type moisture meter
  - Soil ball test
- Warm weather
  - Don't start when it's cold
- Hydrocarbon monitoring
  - Sniff test

# Does it work?

***Response of field inspectors when asked to comment on the impact of the distribution of simple guidelines for landfarming***

"Small operators have been afraid to bring up anything about remediation because they felt they would open up a can of worms costing a lot of money. Now they are finally understanding the importance and are willing to clean up around their wellheads and take care of small spills. Using a visual aid such as the guidelines has made it so much easier to explain remediation to the operators plus they have it to refer to when needed."

*Charles Hennessee, District Manager, OCC District III*

"The program has been a great success getting these environmental teachings out to the operators. It has had a vital impact and has resulted in more compliance. I think the video was excellent. The guidelines are a great help especially to the smaller operators. We need this program to continue."

*Ron Smith, Field Supervisor, OCC District III*

"Operators seem to understand the importance of cleaning up the soil more since the IPEC materials have been out."

*Gayland Darity, Field Supervisor, OCC District III*

"They (the bioremediation guidelines) play a good role in helping to diffuse tense situations with landowners when you can pull out the guidelines and read off what needs to be done.  The landowners then realize you know what you're doing and have a plan."

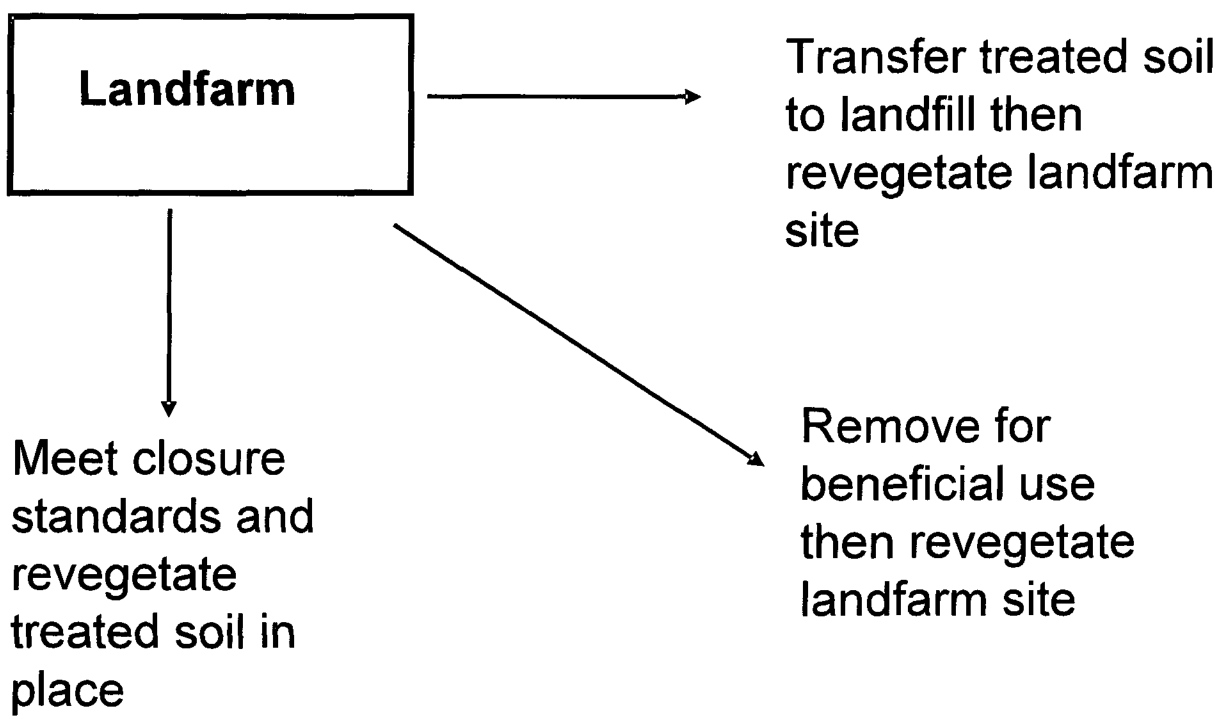
*Pat Brown, Field Inspector, OCC District I*

"A positive impact has been made in the Oklahoma Panhandle area because a lot of the operators have never been given any information of spill clean ups, except to dig and carry or cover. Operators now have a more positive outlook on how to treat spills. They now know if they follow the recommendations of IPEC and be pro-active about the spill, all enforcement actions of the OCC will be minimal."

*Richard Kersey, Field Inspector, OCC District II*

# Some observations and recommendations on closure of landfarms

Subsequent to protection of public health, groundwater, and the environment, the ultimate goal of closure of a landfarm is sustainable revegetation



# What are appropriate closure standards?

- Protect public health, groundwater and the environment
  - The bioremediation endpoint is protective of public health and groundwater for Tier 1; Bioremediation endpoint plus site-specific, risk-based screening levels are protective for Tier 2
  - The bioremediation endpoint is protective of the environment if the site can be revegetated after treatment
    - The only issue with respect to hydrocarbons is hydrophobicity in treated soil

# What do we know about hydrophobicity?

- Hydrophobicity is caused by the coating of soil particles with hydrophobic or “water repelling” organic matter
- Many soils are naturally hydrophobic (a major cause is fire)
- Li et al. (1997) showed that bioremediated soil with 2% extractable hydrocarbons failed to support healthy plant growth because the soil would not hold water (not because of any toxicity)

Li et al., Plant and Soil, **192**, 219-226 (1997)

# What do we know about hydrophobicity?

- Roy et al. (2003), in a study of a old weathered oil-impacted sites in Alberta, concluded that hydrocarbon-induced hydrophobicity is "relatively rare" and probably a product of a combinations of circumstances including
  - properties of the crude oil
  - dryness of the soil at the time of first contact with hydrocarbon
  - prolonged exposure to hot dry weather

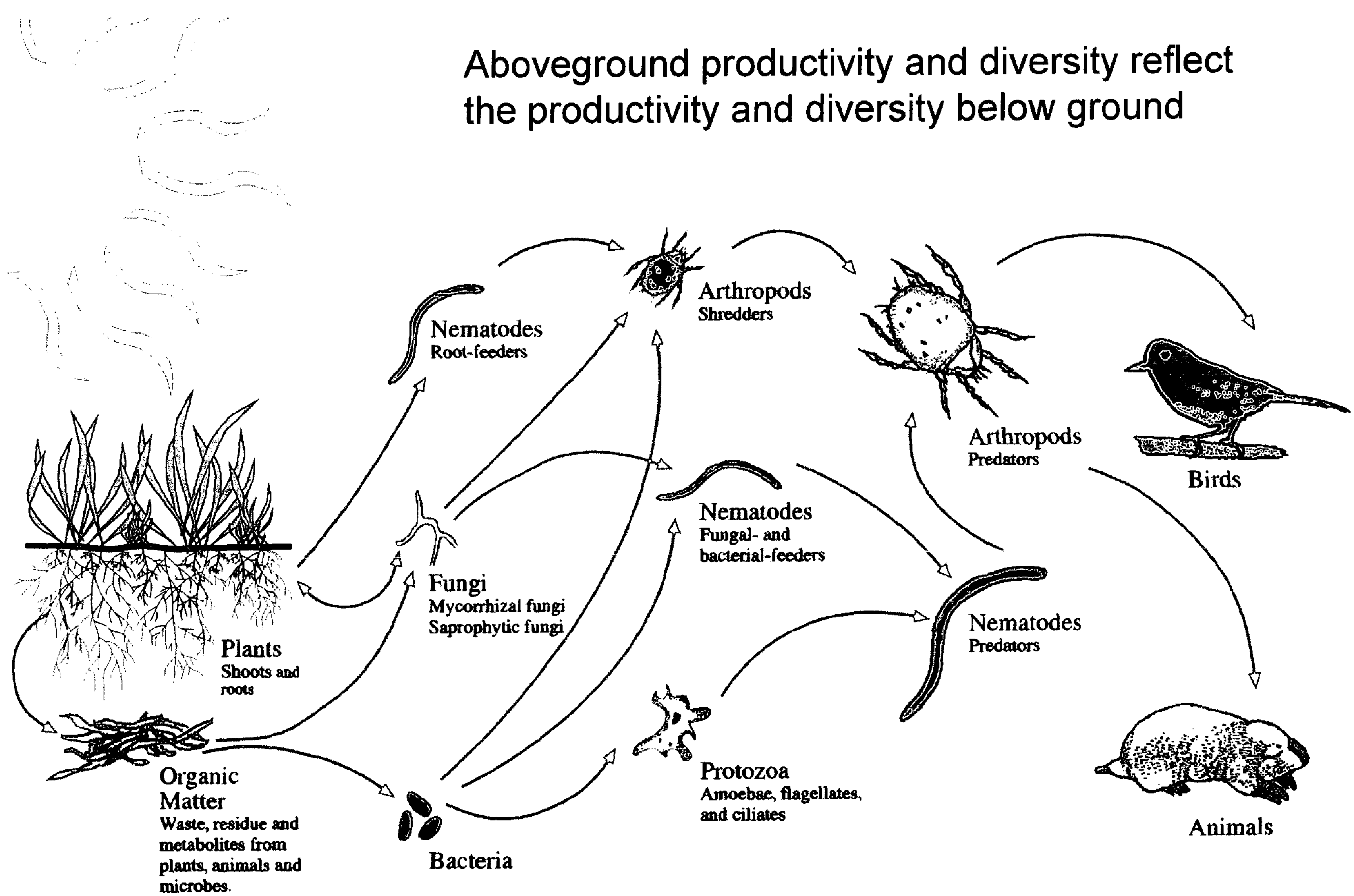
Roy et al., J. Environmental Quality, **32**, 583-590 (2003)

# What can we do about hydrophobicity?

- Hydrophobicity is counteracted by hydrophilic organic matter (hay or manure, for example)
  - Increases water holding capacity of the soil
  - Increases contact of water with hydrophobic soil particles making them more likely to wet
- So hydrophobicity in soil is treatable (and agricultural handbooks can tell you how)!
  - **If** it is problem

# Sustained vegetation is an indicator of soil health

Aboveground productivity and diversity reflect the productivity and diversity below ground



# Conclusions

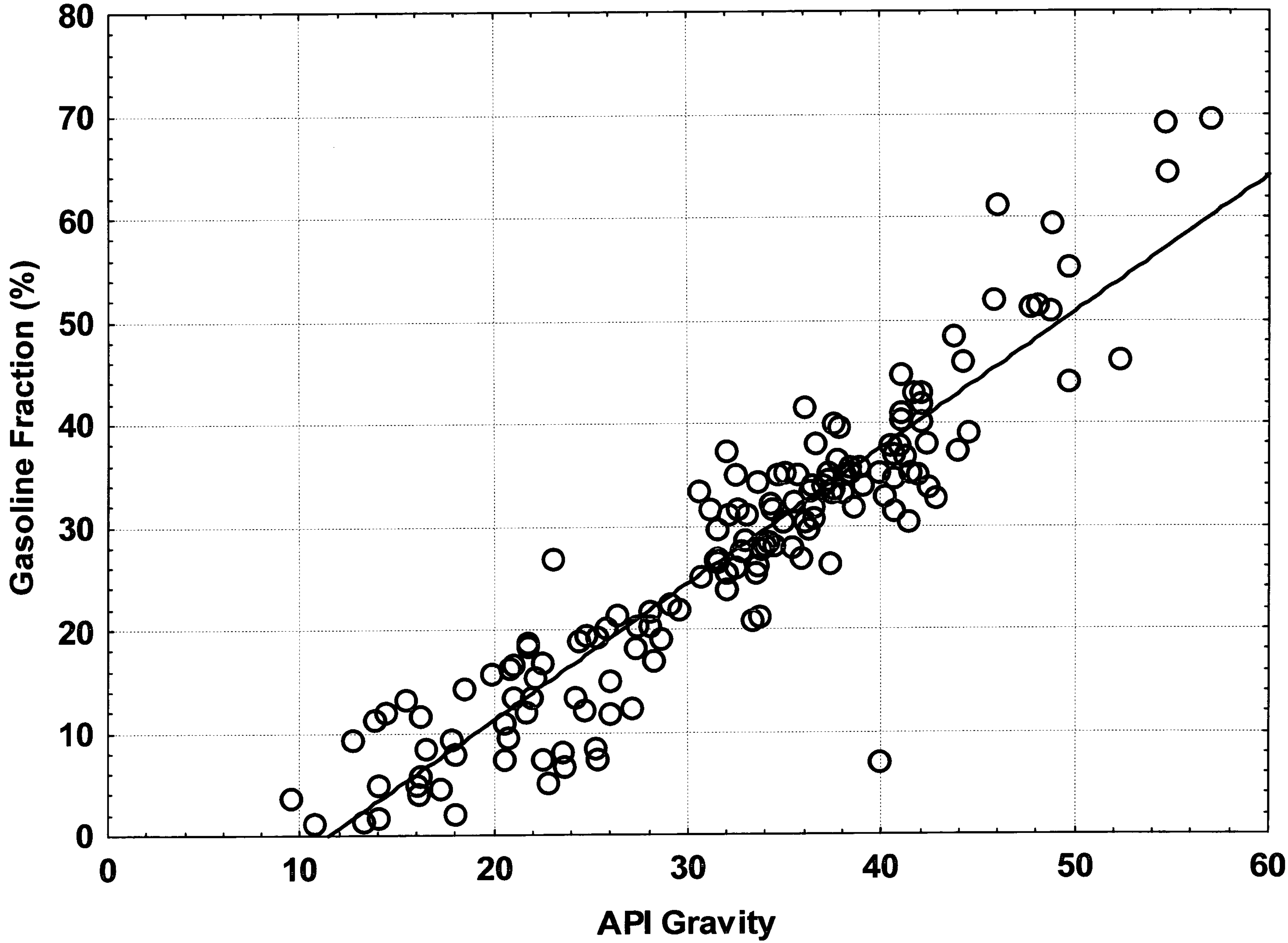
- Landfarming eliminates the threat of toxic, mobile hydrocarbons to public health, groundwater, and the environment
- Landfarming is a short-term (<3 years) and long-term solution to the threat of toxic, mobile hydrocarbons
- Landfarming eliminates toxic, mobile hydrocarbons through treatment not isolation
- Regulations that facilitate the use of landfarming will minimize the landfilling of hydrocarbon-impacted soil
- Landfarming is effective and easy to implement– it's just good gardening

# Estimating DRO Concentration in Bioremediated Soil with 1% TEPH

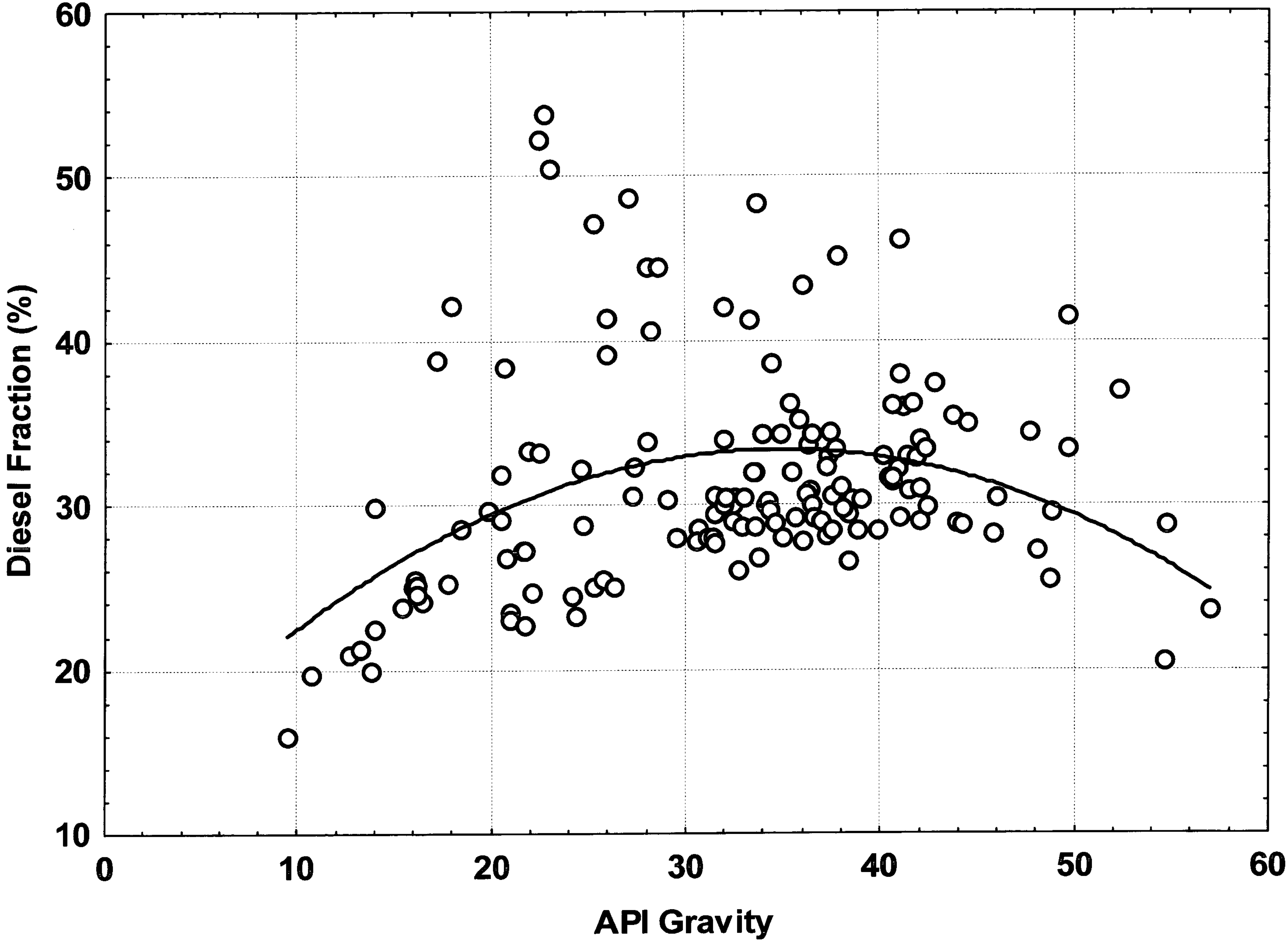
Ex A

# Basis

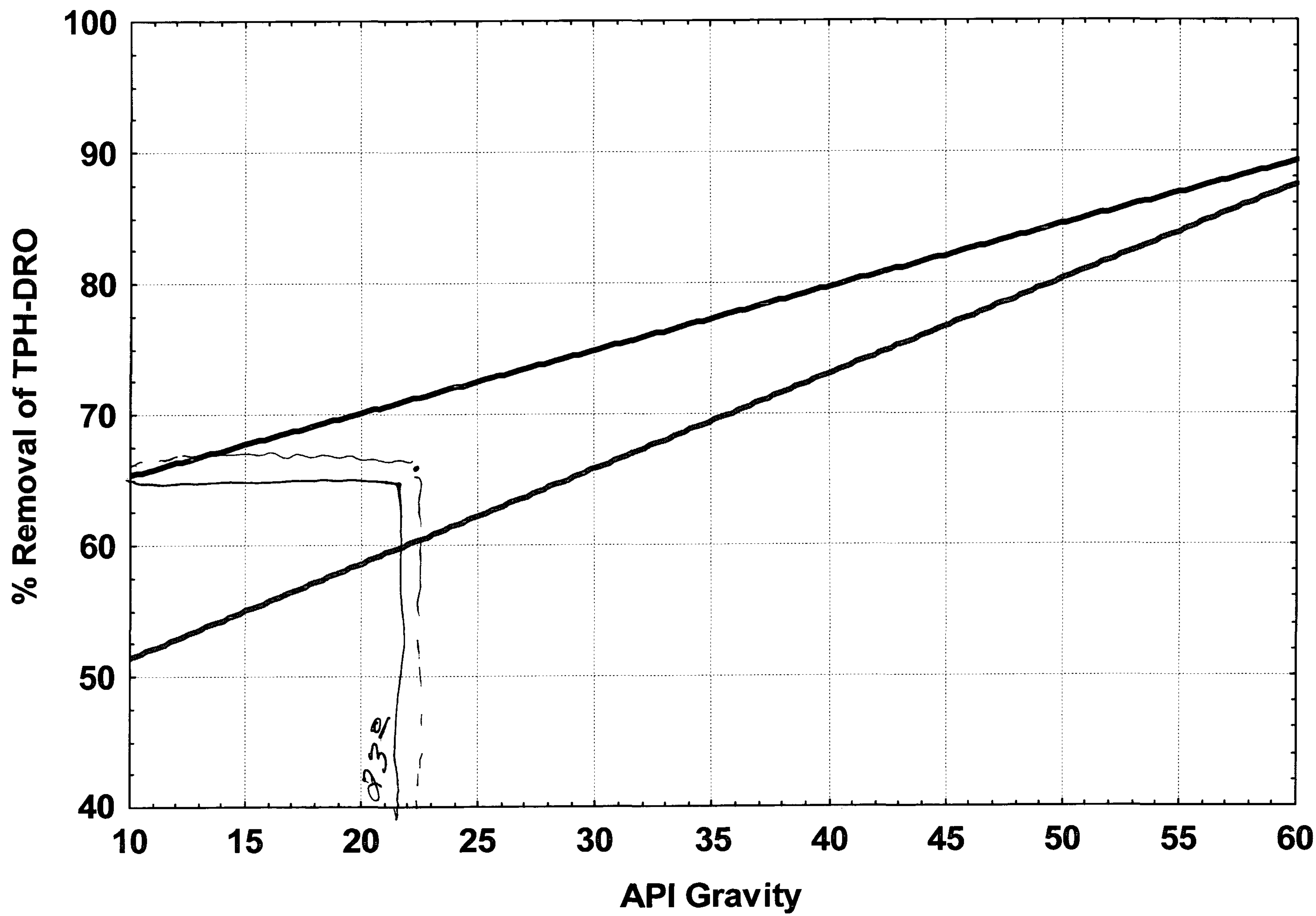
- Gasoline and diesel fractions of 150 crude oils worldwide
  - Linear fit of gasoline fractions data vs API gravity
  - Polynomial fit of diesel fraction data vs API gravity
- Assumptions in calculating DRO concentration in bioremediated soil with 1% TEPH:
  - All GRO removed at bioremediation endpoint
  - % Removal of DRO estimated using Salinitro data
  - Negligible removal of hydrocarbons above diesel range



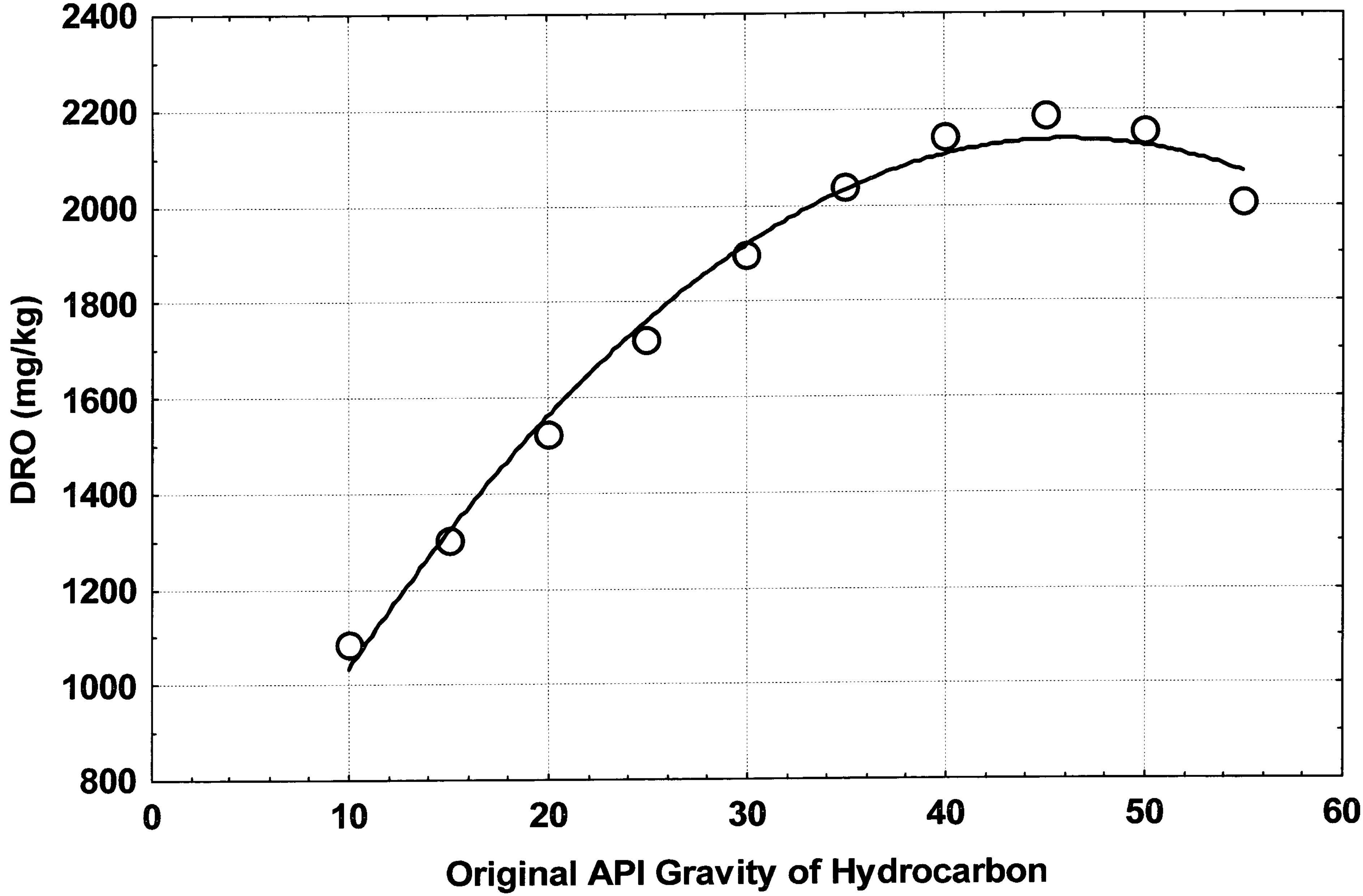
Gasoline Fraction (%)
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
API Gravity


Diesel Fraction (%)
60
50
40
30
20
10
0
10
20
30
40
50
60
API Gravity

## Maximum % Removal of TPH-DRO at the Bioremediation Endpoint



DRO Concentration at 1%Total Extractable Petroleum Hydrocarbons Bioremediated Soil



# Sampling for TPH in Landfarms: Establishing Statistical Validity

Ex 13

# Detecting the Bioremediation Endpoint

| Hypothesis | Decision | Decision |
|---|---|---|
| $H_o$: $\mu_1 - \mu_2 = 0$ | Accept $H_o$ | Reject $H_o$ |
| True | Correct decision | Type I error<br>Consequence: Failure to detect true endpoint; continue treatment and resample |
| False | Type II error<br>Consequence: Lift closed prematurely | Correct decision |

# Site Closure

| Hypothesis | Decision | Decision |
|---|---|---|
| $H_o$: $\mu < 1\%$ TEPH | Accept $H_o$ | Reject $H_o$ |
| True | Correct decision | Type I error<br>Consequence: Failure to close; continued treatment and sampling |
| False | Type II error<br>Consequence: Site closed with TPH > 1% TEPH | Correct decision |

# Statistical Analysis of Landfarm Samples

- Statistical analysis of a set of composite samples
  - More likely to be normally distributed than set of discrete samples
    - Increases validity of the analysis
  - Mean of a set of composite samples likely to have a smaller standard deviation than a set of discrete samples

# Student's t Test

- Well known and widely used statistical test
- Compares means of two sets of data - are the means the same or different?
  - Example: Comparing two sets of analyses of TPH in a landfarm to determine if the bioremediation endpoint has been achieved
- Compare the mean of a set of data to a fixed number - are they the same or different?
  - Example: Comparing a set of TPH analyses in a landfarm to determine if the desired endpoint (1% TEPH) has been achieved
- For both analyses we must chose the desired level of confidence - Do we want to make the right decision 9 times out of 10? 95 times out of 100? 99 times out of 100?
  - Higher confidence requires more sampling and increased cost for analysis

# Power of a t Test

- Power = 1 – $\beta$ where $\beta$ = probability of a Type II error
  - So we want high power (low $\beta$)
- Determining number of composite samples required to achieve acceptable power
  - Estimate the standard deviation
  - Fix $\alpha$ (probability of a Type I error)
  - Choose a maximum acceptable alternate mean if Type II error is made
  - Estimate number of samples
  - Calculate power (specific software usually required)
  - Repeat calculation until estimated number of samples results in desired power

# Some Results ($\alpha = 0.1$, one sided)

- Std dev = 5%
- Maximum acceptable mean = 1.1% TEPH
- Result: $N = 3$ gives $p = 0.91$
  - Probability of Type II error with mean > 1% is about 9%
  - This is the Industry Committee's recommendation