

## Natural Attenuation Study

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## Natural Attenuation Study

- Study Plan approved
- Completed literature review on biodegradation of chemicals in soil
- Began soil sampling to compare current chemical concentrations in Area IV soils to historical concentrations





#### Overview of literature review findings:

- Petroleum hydrocarbons biodegrade readily
- Chlorinated chemicals are not as easily biodegraded
- Possibility to increase biodegradation rates of certain chemicals using in-situ biostimulation and/or bioaugmentation
  - <u>Biostimulation</u>: Adding nutrients, surfactants, etc. to enhance biodegradation by indigenous microorganisms
  - <u>Bioaugmentation</u>: Adding microorganisms with known chemicaldegrading capability

Overview of literature review findings:

- Planned additional field tests could provide useful information for more accurate estimation of biodegradation rates (e.g. soil temperature, oxygen availability, mercury speciation, etc.)
- Published studies were used to estimate natural attenuation times for Area IV soils, but the predicted rates varied
- Laboratory microcosm experiments are planned in the bioremediation study to
  - more accurately estimate natural attenuation rates for Area IV soils
  - test the efficacy of various biostimulation and/or bioagumentation strategies





Petroleum Hydrocarbons



(e.g. octane)

- Chains of carbon atoms form the molecular structure
- Carbon chains with fewer carbon atoms are more volatile, water soluble, and amenable to degradation converted to CO<sub>2</sub> and water
- Carbon chains with more carbon atoms are less volatile, water soluble, and are harder to biodegrade





- Petroleum Hydrocarbons (cont'd.)
  - Biodegradation times (rule of thumb):
    - C7 C9: 2 years
    - C10 C14: 5 years
    - C15 C36: 10 years
  - Biostimulation through adding chemicals, nutrients, or soil bulking material (e.g., straw, rice hulls) may speed up/shorten biodegradation times
  - Bioaugmentation through adding bacteria and/or fungi can speed up biodegradation times





Polyaromatic Hydrocarbons (PAHs)



(Anthracene)

- PAHs are ringed compounds (multiple fused benzene rings) typically found in crude petroleum and tars, but are also created during the burning of organic matter in nature
- The more benzene rings, the more difficult to biodegrade
- Like petroleum chemicals, the lighter/fewer ringed PAHs are more volatile and water soluble and more biodegradable





- PAHs Cont'd.
  - Biodegradation times (rule of thumb):
    - 2 rings: 1-10 years
    - 3 rings: 10-25 years
    - 4-6 rings: 50-200+ years
  - Biodegradation is complex because different soil microbes are typically required for degradation depending on PAH ring structure
  - Soil fungi may be more adept at biodegrading larger PAH molecules
  - Biostimulation/Bioagumentation is an important consideration





Polychlorinated Biphenyls (PCBs)



- Chlorinated 2-ring aromatic compounds that are very stable in the environment – present as a mixture
- Stability is related to the degree of chlorination (number of chlorine atoms comprising the PCB molecule)
- More chlorines means longer biodegradation time
- PCBs exhibit very low volatility and solubility
- PCBs have been shown to "weather" in soil, which slows biodegradation





- Polychlorinated Biphenyls (PCBs) Cont'd.
  - Reported rates of PCB biodegradation are extremely low, even under ideal conditions. PCBs need to be dechlorinated as part of their degradation
  - Bacterial dechlorination can only occur in an anaerobic environment
  - Once dechlorinated the remaining biphenyl can be degraded aerobically
  - Soil fungi have been shown effective at degrading PCBs and do not require combined anaerobic/aerobic processes
  - Biostimulation and bioagumentation using dechlorinating bacteria has some promise, but such bioaugmentation would only be effective under anaerobic conditions





Dioxins (Polychlorinated dibenzo-p-dioxins) and furans



- Chlorinated, multiple-ringed compounds created through burning of organic matter with chlorine – present as a mixture
- Like PCBs, dioxins are very stable in the environment
- Stability is related to the degree of chlorination
- Dioxins exhibit very low volatility and solubility
- Dioxins have been shown to "weather" in soil, causing slower biodegradation rates.





- Dioxins (Polychlorinated dibenzo-p-dioxins, furans) Cont'd.
  - Biological degradation of dioxins has similar considerations as for PCBs (anaerobic/aerobic bacteria)
  - Biodegradation by fungi has been demonstrated
  - Biostimulation/bioagumentation has some promise

Natural Attenuation Study: Comparison of current and historical chemical concentrations

- Collected soil samples at locations with historic data to evaluate chemical degradation at site
  - Petroleum results promising
  - PAH results are mixed
  - More sampling needed to provide statistical basis
  - Additional sampling planned







#### Natural Attenuation Chemical Field Sampling

Petroleum hydrocarbon results:

- Chemical concentrations decreased to below or near AOC level: 8 samples
- Chemical concentrations decreased significantly, but not to below or near AOC level: 3 samples
- Chemical concentrations increased: 2 samples
- Chemical concentrations increased and decreased, depending on equivalent carbon range: 2 samples

#### Natural Attenuation Contaminant Field Sampling

#### Chemical concentrations decreased to below or

near AOC (8 samples):



#### Natural Attenuation Contaminant Field Sampling

# Chemical concentrations decreased significantly, but not below AOC (3 samples):



#### Natural Attenuation Contaminant Field Sampling

Chemical concentrations increased (2 samples):



## Natural Attenuation Study: Preliminary Conclusions from Field Study

Preliminary observations in the comparison of recent soil data with historical data:

- Total Petroleum Hydrocarbons
  - 54% decrease in soil concentration over 5 to 10 years
  - Average biodegradation rate 0.29 mg/kg/day
- Polyaromatic hydrocarbons
  - PAH concentrations increased at more locations than they decreased
- PCB and dioxin data not yet analyzed
- More data needed for adequate statistical analysis
- In future will look for changes in chemical composition indicating biodegradation





## Natural Attenuation Conclusions so far...

- Literature review suggests that all chemicals in Area IV soils will eventually biodegrade, but some compounds will degrade very slowly.
- Measurement of chemical concentrations in soils will require more sampling to provide meaningful statistics.
- Laboratory microcosm experiments should provide a more site-specific and accurate prediction of biodegradation rates.
- Biostimulation and/or bioaugmentation may accelerate biodegradation

