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
  - Biostimulation: Adding nutrients, surfactants, etc. to enhance biodegradation by indigenous microorganisms
  - Bioaugmentation: Adding microorganisms with known chemical-degrading 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 bioaugmentation strategies
Natural Attenuation Literature Review

Petroleum Hydrocarbons

- 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 CO₂ and water
- Carbon chains with more carbon atoms are less volatile, water soluble, and are harder to biodegrade
Natural Attenuation Literature Review

- 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
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/Bioaugmentation is an important consideration
Natural Attenuation Literature Review

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 volatilility 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 bioaugmentation using dechlorinating bacteria has some promise, but such bioaugmentation would only be effective under anaerobic conditions.
Natural Attenuation Literature Review

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.
Natural Attenuation Literature Review

- 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/bioaugmentation 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
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):

![Bar chart showing concentration levels over different carbon ranges from C8-C11 to C30-C40. The AOC concentration level is marked at 5 mg/kg.]

- C8-C11: 11 mg/kg
- C12-C14: 11 mg/kg
- C14-C20: 8.8 mg/kg
- C21-C30: 52 mg/kg (AOC Concentration)
- C30-C40: 11 mg/kg
Natural Attenuation Contaminant Field Sampling

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

**Equivalent Carbon Ranges**

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<th>Range</th>
<th>Concentration (mg/kg)</th>
<th>Date</th>
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<tbody>
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<tr>
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<tr>
<td>C30-C40</td>
<td>120</td>
<td>11/21/2013</td>
</tr>
</tbody>
</table>
Natural Attenuation Contaminant Field Sampling

Chemical concentrations increased (2 samples):

![Graph showing chemical concentrations increased over time](chart.png)
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.