# Investigation of Biogeochemical Degradation Pathway of Chlorinated Aliphatic Hydrocarbons



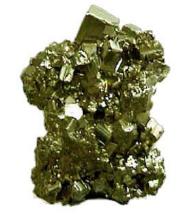
## **Background/Objectives**

Historic chemical manufacturing operations at a facility located in South America have resulted in the release of chlorinated aliphatic hydrocarbons (CAHs) into soil and groundwater. Several laboratory and field investigative procedures were utilized to investigate the degradation of these CAHs via natural biotic and abiotic processes. These studies sought to identify the mechanism of degradation (if present) as well as the feasibility of utilizing these intrinsic degradation processes as part of an overall groundwater remedial approach. Specifically, the presence of reactive iron minerals and their correlation to observed degradation of CAHs was of primary interest.



#### **Biogeochemical Remediation**

- The ability of iron minerals to degrade chlorinated aliphatic hydrocarbons (CAHs) is a well-known process.
- Iron minerals known to degrade CAHs include iron sulfides (e.g., mackinawite, pyrite), iron oxides (e.g., magnetite, green rust) and others.

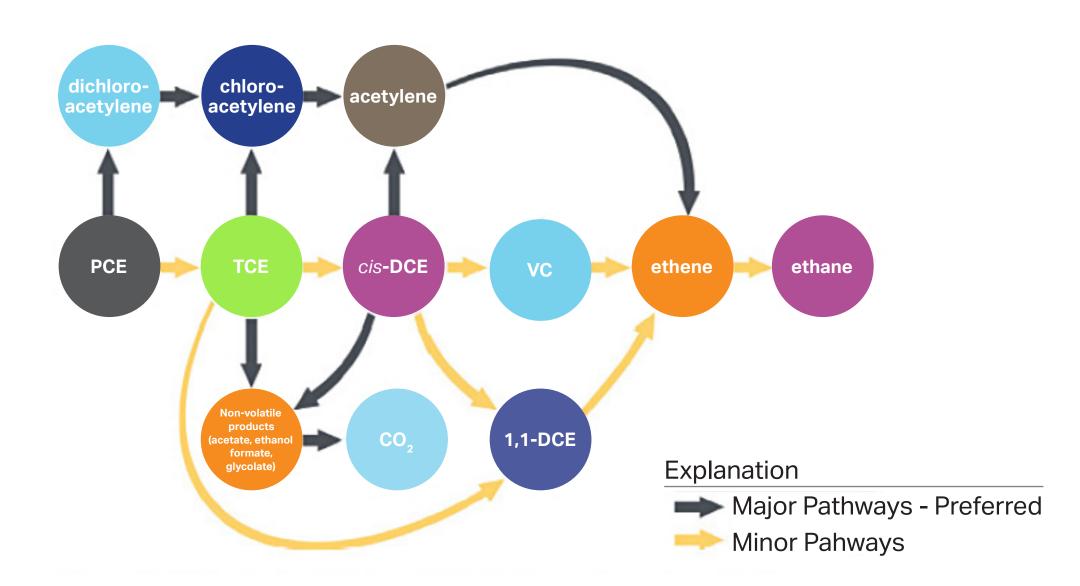




Pyrite FeS<sub>2</sub>

Magnetite  $Fe_{3}O_{4}$ 

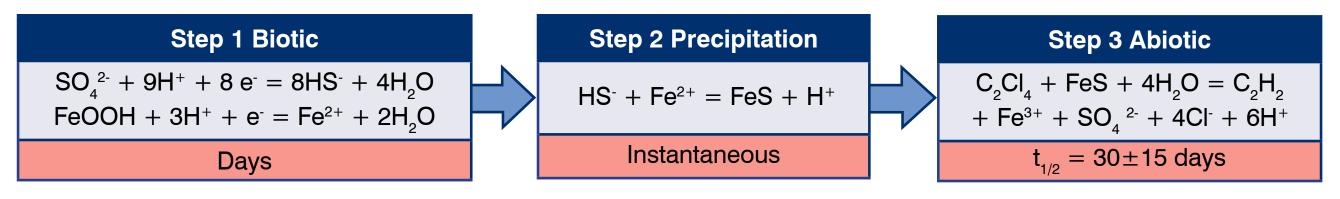
 The mechanism of degradation is poorly understood but is likely similar to the mechanism of zero valent iron (ZVI).



Chlorinated Ethene Abiotic Transformation Pathways (Courtesy of Battelle)

 Reactive minerals can be formed under certain biogeochemical conditions. Groundwater environments that contain elevated iron, sulfur and labile organic carbon can form these reactive minerals via biotic mechanisms. In this situation,

reactive minerals are formed by sequential biotic and abiotic reactions. This process is termed In Situ Biogeochemical Transformation (ISBGT).



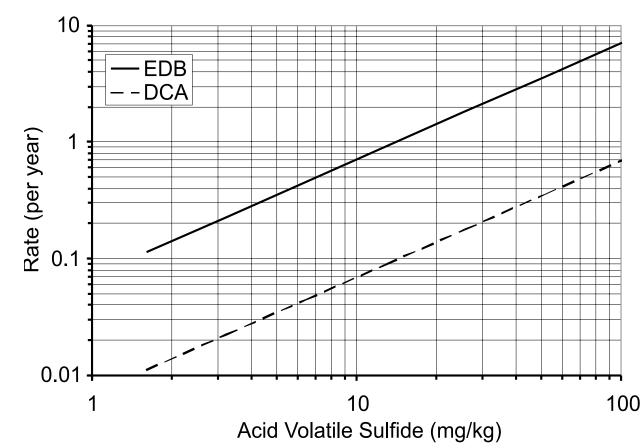
Reaction Chemistry during ISBGT Processes (Courtesy of Battelle)

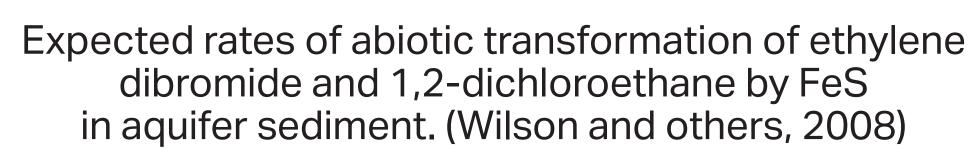
 Reactive minerals can be artificially created in situ by addition of one or more of the three amendments required to biogenically create them.

Sulfate	Iron	Organic Carbon
	Solid Am	nendments
Calcium Sulfate	Hematite	Mulch
	Magnetite	Cotton Gin
	Liquid Ar	nendments
Magnesium Sulfate	Iron Sulfate Iron Chloride	Lactate
Sodium		Vegetable C
Sulfate		Lecithin
Iron Sulfate		

Typical Amendments Used in Engineered ISBGT Systems (Courtesy of Battelle)

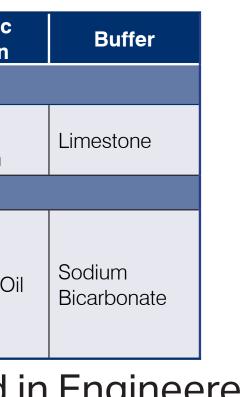
 Reactive minerals can be effective for degradation of fuel additives such as 1,2-dibromoethane and 1.2-dichloroethane.





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 Multidisciplinary approach performed to investigate occurrence and activity of reactive minerals

Groundwater Geochemistry	Soil Analysis	Microbial Analysis
Dissolved Oxygen pH Oxidative Reductive Potential Dissolved/ Total Iron	Bioavailable Iron Mineral Surface Area & Grain Size Scanning Electron Microscopy of Mineral Surfaces	Iron-Reducing Bacteria Sulfate-Reducing Bacteria Total Bacteria
Sulfate Sulfide Methane Total Organic Carbon	Acid Volatile Sulfides Chromium Reducible Sulfides X-ray Diffraction Magnetic Susceptibility	

Multidisciplinary Approach to Evaluating ISBGT at a Site (Courtesy of Battelle)

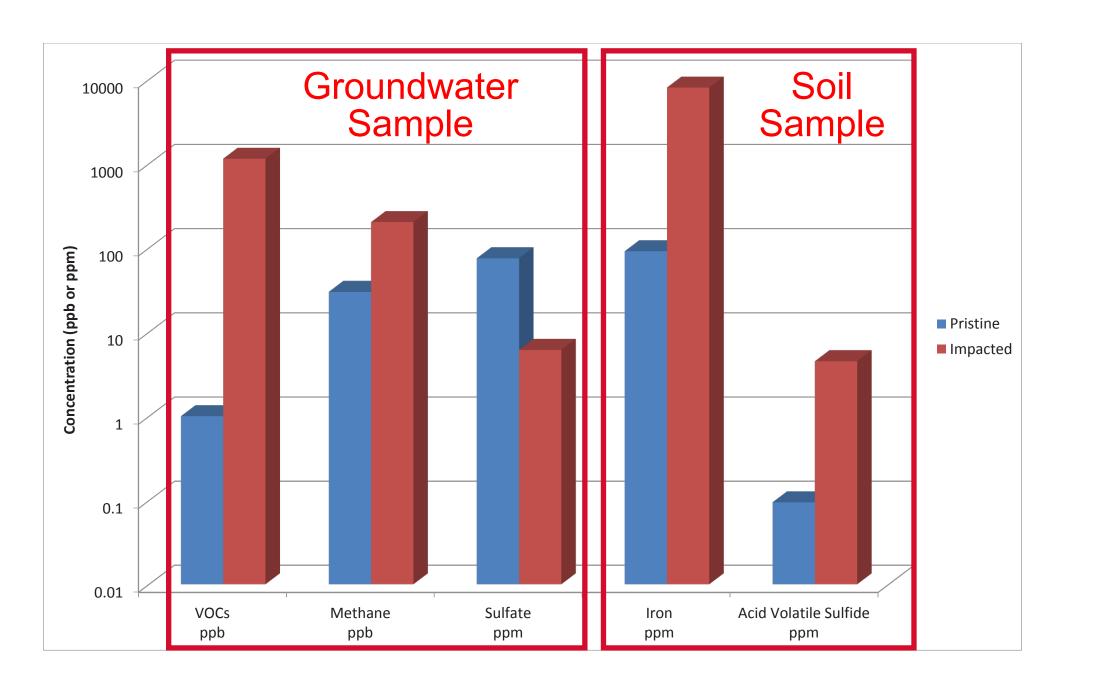
• Existing geochemical data suggest the presence of anaerobic microbial terminal electron accepting processes, such as iron and sulfate reduction and methanogenesis. Areas containing elevated CAH concentrations in groundwater contained high ferrous iron, increased methane and decreased sulfate concentrations.

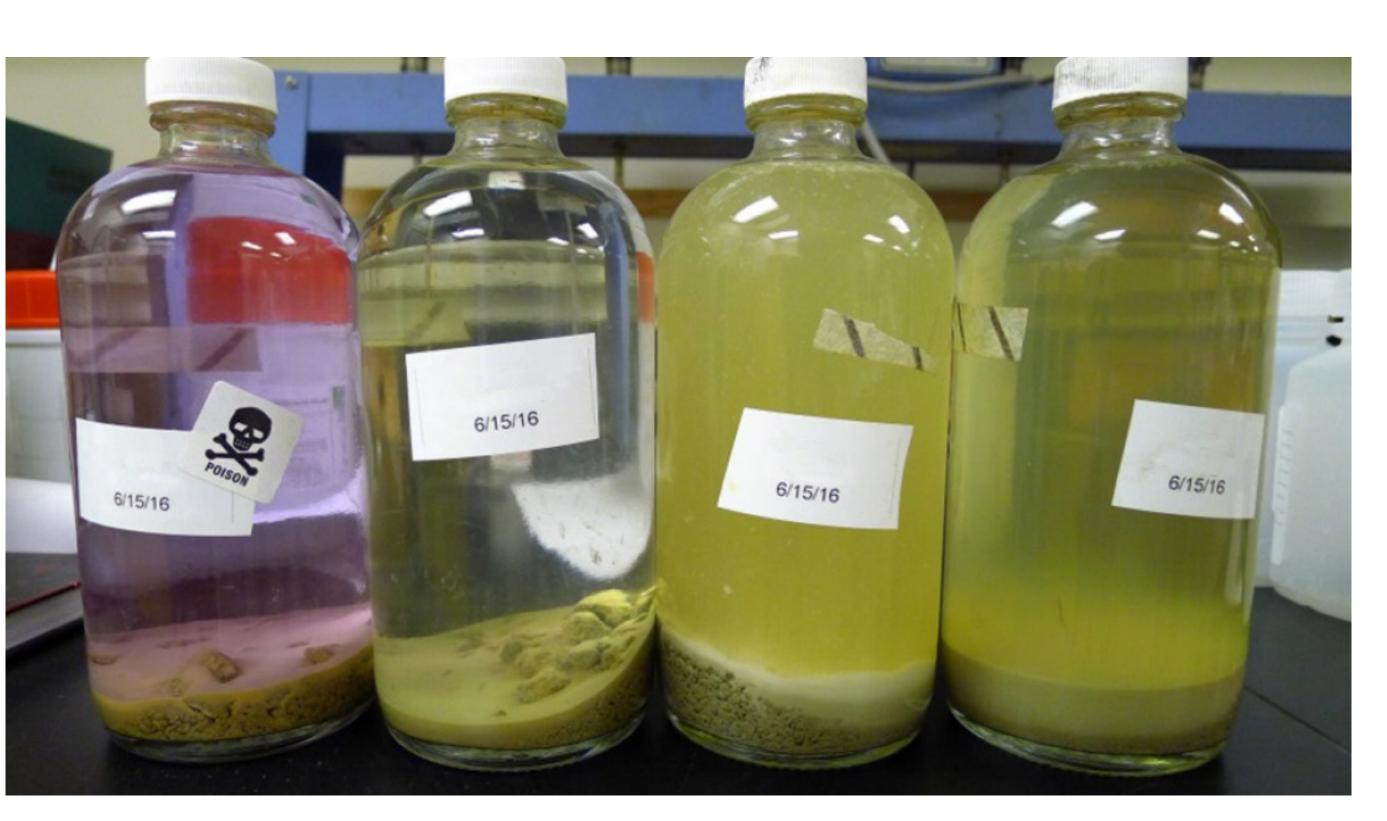
### **Microcosm Study**

- Laboratory microcosm study performed using site soil and groundwater to investigate intrinsic abiotic/biotic degradation and the potential for in situ bioremediation via the addition of emulsified vegetable oil.
- Abiotic control treatments of the microcosm study observed decreases in parent compounds, no increases in daughter products and increases in ethene. This may indicate that the elevated iron sulfides and/or magnetic iron minerals observed in the field studies are actively reducing CAHs.
- Biotic microcosms stimulated with emulsified vegetable oil yielded no significant accumulation of dechlorination byproducts despite their observation in site monitoring wells.
- Lack of biotic degradation mechanisms may be attributed to the excessively high chloroform concentrations, which can inhibit microbial dechlorination.

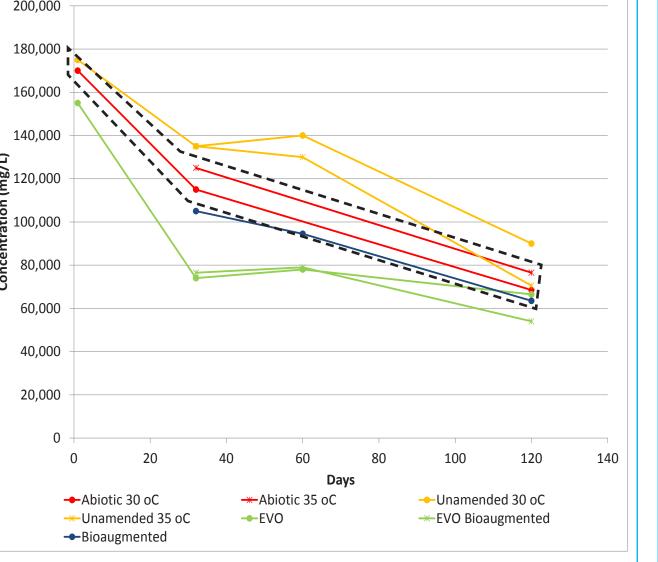
### **Field Study**

- Sulfide analysis demonstrated that biogenic iron sulfide soil concentrations were an orderof-magnitude higher in samples collected from impacted areas than pristine areas. This observation shows that reactive minerals are present and being formed via intrinsic processes.
- Magnetic susceptibility analysis observed detectable levels of magnetic minerals; these values were similar between the pristine and impacted samples (~1x10<sup>-7</sup> m<sup>3</sup>/kg).

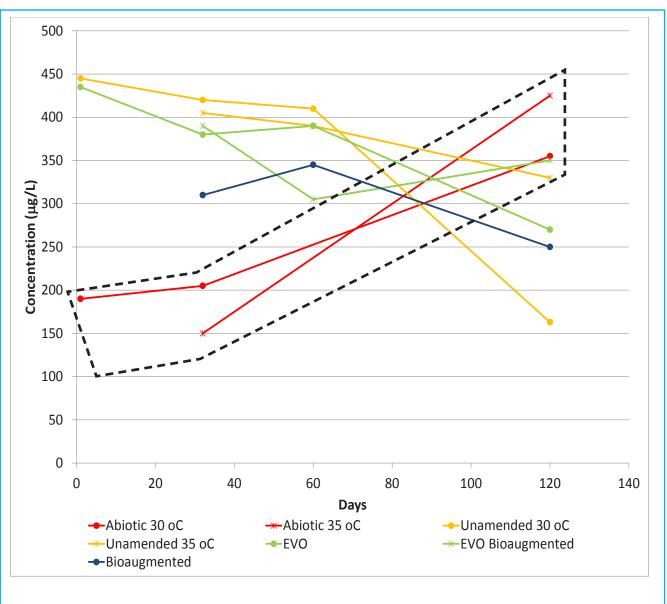




1,1,2-Trichloroethane

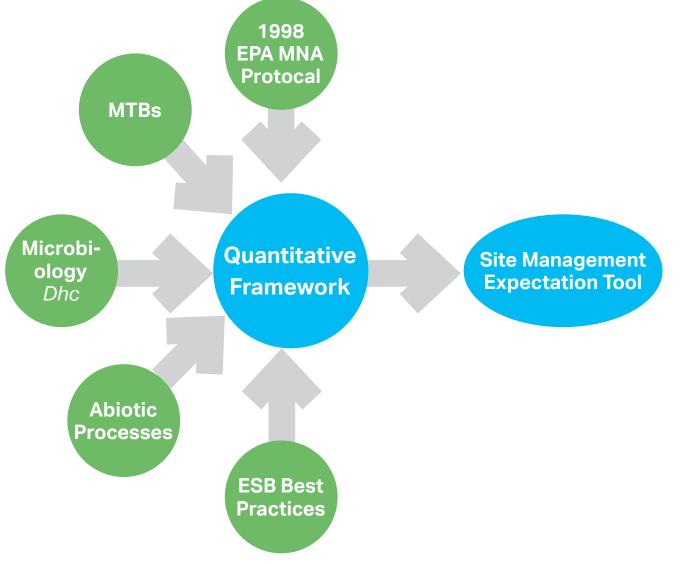


Ethene



microcosm data.





- ethenes of approximately 5 years.
- abiotic degradation pathways.

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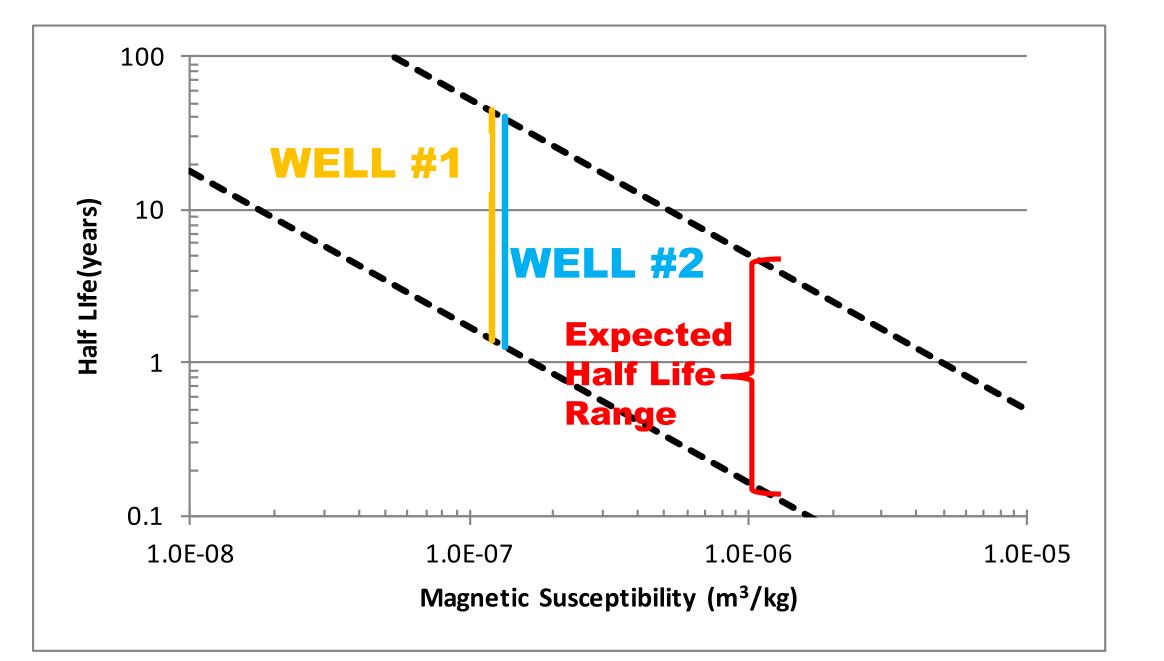


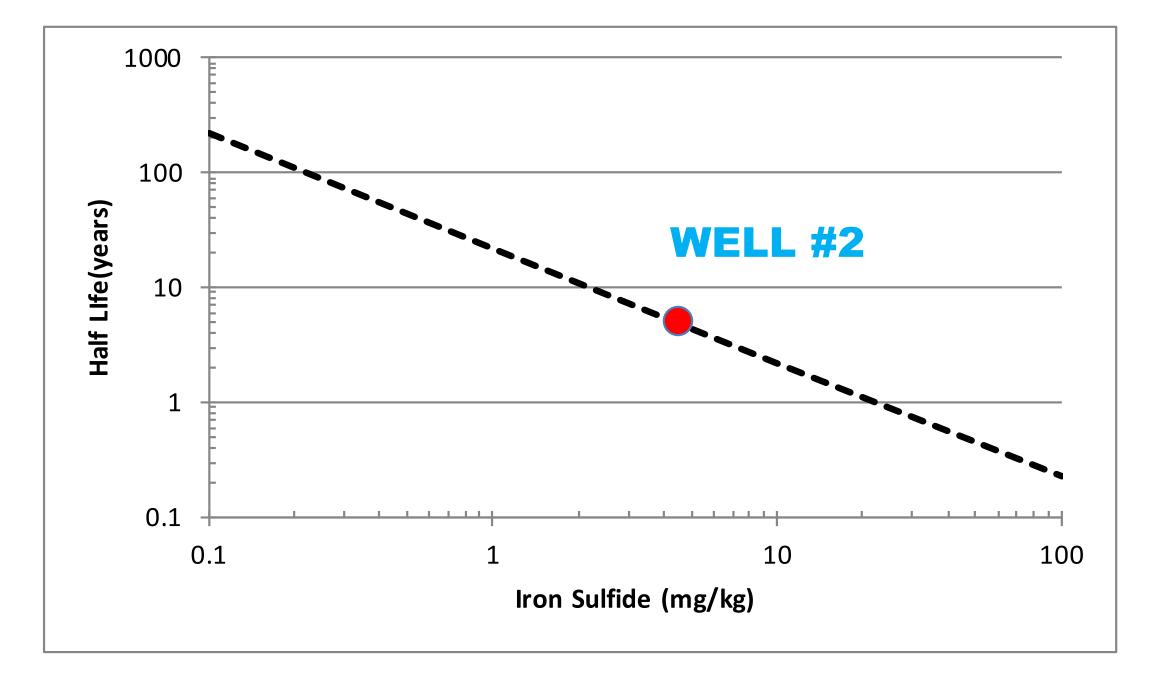
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## **Data Interpretation**

• The Biological Pathway Identification Tool (BioPIC) was utilized to interpret the results of the field and

> **BioPIC: Pathway Identification Criteria** A Decision Guide to Achieve Efficient Remediation of Chlorinated Ethenes





 Magnetic susceptibility analysis suggest half-lives of chlorinated ethenes ranging from 1 to 44 years.

• Iron sulfide analysis suggest a half-life of chlorinated

• Based on site-specific concentrations of CAHs, these intrinsic degradation rates are insufficient to address source areas within a reasonable time period (e.g., less than 30 years). However, these rates may possibly be effective for lower concentration areas throughout the plume. Future remedial alternatives, currently being evaluated, may include addition of carbon substrate and sulfate to yield both biotic and

#### References

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