Data Needs for Effective Application of MNA and In-Situ Bioremediation
Featuring Framework to Apply Novel Molecular and Other Screening Tools for MNA Evaluations

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In 1998 the USEPA released the *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water*. This was followed in 1999 by the OSWER Directive 9200.4-17P *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites*. The two documents provide the framework for application of MNA at USEPA enforcement actions. Although the science and logic in these two documents are still sound, the science has moved on and much more is known today about the mechanisms of biological and abiotic degradation of chlorinated organic solvents. In 2011, the Environmental Security Technology Certification Program (ESTCP) funded a project with the goal of integrating the new science into the structure of the original USEPA documents. The project created a decision logic that was incorporated into a new screening tool that can be used to determine if MNA might be appropriate for a site. The Biological Pathway Identification Criteria screening tool (BioPIC), also incorporates two major pathways for abiotic degradation of chlorinated ethylenes.

The screening tool is built around extracting and then evaluating rate constants for degradation of chlorinated ethylenes in ground water. A computer model of the transport and fate of the chlorinated ethylenes in ground water at the site is used to extract rate constants for degradation of PCE, TCE, DCE, and Vinyl Chloride from the long term monitoring data. Then the model is run forward in time to see if the concentrations of chlorinated ethylenes can be expected to exceed regulatory standards at any time in future at some point of compliance at the boundary of the facility. If they do not, MNA is a plausible remedy or portion of the remedy for groundwater contamination at the site. Then the screening tool can be used to systematically evaluate other information to determine if indicators or predictors of a particular mechanism can provide a second line of evidence for the rate constant. The mechanisms that are evaluated include anaerobic biological reductive dechlorination, aerobic biodegradation, abiotic degradation in magnetite and abiotic degradation on iron monosulfide.

Anaerobic biological reductive dechlorination is evaluated by comparing the abundance of the *Dehalococcoides mccartyi* 16S RNA marker (*Dhc*) to the bulk field scale rate constant. If the abundance and rate constant for the site being evaluated falls within the range of values from a set of benchmark sites, the abundance of *Dhc* provides a second line of evidence that biological reductive dechlorination is a plausible explanation for the bulk rate of attenuation at the site.

The same approach is used to evaluate abiotic degradation of chlorinated ethylenes on magnetite in aquifer sediment. The quantity of magnetite is estimated from the mass magnetic susceptibility of the sediment. The magnetic susceptibility of the aquifer sediment and the rate constant are compared to the magnetic susceptibility and rate constants from benchmark sites. If the magnetic susceptibility and rate constant are within the range of values for the benchmark sites, then the value for magnetic susceptibility provides a second line of evidence for abiotic degradation.

A different approach is taken to evaluate abiotic degradation on iron monosulfide (FeS). Geochemical data is used to calculate the accumulation of reactive FeS in the aquifer sediment, and the bulk rate constant for degradation in the plume is compared to the rate constant that would be expected for the amount of FeS that can be expected to accumulate in the aquifer.

At the present level of development BioPIC provides a qualitative line of evidence for aerobic biodegradation of DCE or Vinyl Chloride. If dissolved oxygen is present in the ground water, then DCE and Vinyl Chloride are presumed to degrade. Low concentrations of methane and Iron(II) are used to confirm that concentrations of dissolved oxygen in the well water actually represent the concentration of dissolved oxygen in the ground water.