# The Importance of Abiotic Transformations in Natural Attenuation of Contaminated Groundwater

## Introduction and Purpose

Abiotic processes refer to contaminant degradation without the direct involvement of living organisms. A classic example is reduction of chlorinated organic contaminants using zero-valent iron ($Fe^o$). In contrast, biotic processes rely on microbes to achieve contaminant degradation. It is noteworthy that many abiotic transformations are facilitated indirectly by the activity of microbes, a process referred to as biologically-mediated abiotic degradation. Abiotic processes are applicable to a wide range of contaminants, including most chlorinated organic solvents, pesticides, munitions constituents, insensitive munitions, and nitrobenzenes. The focus of this fact sheet is on chlorinated ethenes. For sites where active remediation has been in place for many years, documenting the occurrence of abiotic processes may facilitate a transition to monitored natural attenuation (MNA), defined by EPA as "the reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remediation objectives within a timeframe that is reasonable compared to that offered by other more active methods."

## Technology Background

Abiotic degradation of groundwater contaminants occurs via a reaction with minerals in contact with the groundwater. Table 1 summarizes the minerals commonly associated with abiotic degradation of chlorinated ethenes and are likely involved in degradation of other compounds. The two minerals that have received the most attention are makinawite (FeS) and magnetite ($Fe_3O_4$). Both are naturally occurring, while FeS is also present in zero-valent iron permeable reactive barriers. He et al. (2015) concluded that a general trend exists with respect to mineral reactivity for degradation of chlorinated solvents that can be approximated as follows: (disordered-FeS) > (FeS) > ($Fe^o$) > ($FeS_2$)> (sorbed $Fe^{2+}$)> (green rust) = (magnetite) > (biotite) = (vermiculite).

Among the minerals listed in Table 1, magnetite has received a significant level of attention. This is in part because it is relatively easier to estimate its presence based on the magnetic susceptibility (MS) of a sample. Collecting core samples to determine the minerals present is often a costly endeavor. When sediment samples are not available, a downhole sonde can be used to estimate MS when the well liner is constructed of PVC. Nevertheless, the role of magnetite as a catalyst for abiotic processes has recently been challenged (Culpepper et al., 2018).

The accessibility of minerals for reaction with contaminants is an important consideration for predicting reactivity. A commonly applied method for predicting available Fe is extraction with a dilute hydrochloric acid (HCl) solution.  Stronger acid solutions can be used to assess the "bulk Fe" present. Measurement of acid volatile sulfides (AVS) has been used as a surrogate for the amount of sulfide present as iron monosulfides such as mackinawite, while chromium extractable sulfur (CrES) has been used to indicate the fraction of total sulfide correlating to elemental sulfur ($S^0$) and pyrite ($FeS_2$). Total sulfur bearing minerals are estimated by summing the AVS and CrES.

**Table 1. Minerals Associated with Abiotic Degradation of Chlorinated Ethenes\***

| Name | Structure |
|---|---|
| Mackinawite | $(Fe,Ni)_{1+x}S$ (where x = 0 to 0.11); most typically FeS (tetragonal) |
| Pyrite | $FeS_2$ |
| Magnetite | $Fe_3O_4$ |
| Goethite | $\alpha$-FeO(OH) |
| Hematite | $Fe_2O_3$ |
| Green Rust | $Fe^{2+}$ and $Fe^{3+}$ cations, $O_2^-$ and $OH^-$ anions, with loosely bound $[CO_3]^{2-}$ groups and $H_2O$ molecules between the layers |
| Biotite | $K(Mg,Fe)_3AlSi_3O_{10}(F,OH)_2$ |
| Vermiculite | $(Mg,Fe^{2+},Fe^{3+})_3[(Al,Si)_4O_{10}](OH)_2 \cdot 4H_2O$ |
| Zero Valent Zinc | Zn(0) |
| Troilite | FeS (hexagonal) |

\* Lee and Batchelor (2002); Liang et al.  (2009).

For tetrachloroethene (PCE) and trichloroethene (TCE), abiotic degradation occurs via reductive and/or oxidative pathways. Reduction includes ß-elimination (i.e., dihaloelimination), resulting in formation of chloroacetylene and acetylene. Unlike biotic processes, sequential formation of dichloroethenes (DCE) and vinyl chloride (VC) is a minor abiotic pathway. Abiotic oxidative pathways result in the formation of organic acids and carbon dioxide.

| Application of Abiotic Degradation | Collecting and Evaluating Evidence | Case Study |
|---|---|---|

## Application of Abiotic Degradation: Transitioning to MNA

At many hazardous waste sites, large groundwater plumes with dilute contaminants pose a major challenge. Active remediation is a costly endeavor at these sites and the range of clean-up options is limited by the dilute nature of the plumes. In some instances, field monitoring data suggest that the contaminants are undergoing degradation along the flow path. The absence of easily identifiable degradation products that are a signature of biotic degradation (e.g., accumulation of reductive dechlorination daughter products) make it difficult to demonstrate that degradation is occurring. In cases such as these, contaminant degradation may be occurring via abiotic pathways. Site managers need guidance on how to determine if abiotic processes explain contaminant degradation, and if so, at what rate. Documenting the contribution of abiotic processes may permit transition of the site to MNA.

Figure 1 provides an example decision flow chart to help determine when a site is ready to transition to MNA, starting with updates to the conceptual site model (CSM) to determine if remedial action objectives (RAOs) are being met. Sites with current or previous active remediation activities may be good candidates for considering a transition to abiotic MNA. Perhaps of greatest interest is pump and treat. A first step in considering if it is reasonable to stop pumping is to use historical groundwater monitoring data to extract a rate constant for degradation, and then calculate if that rate is sufficient to meet the criteria for MNA as a remedy or a risk management option. Evidence will also be needed to validate that abiotic degradation is occurring (see below).

Other forms of active remediation that create conditions conducive to subsequent transitioning to abiotic MNA as a polishing step include in situ chemical oxidation (ISCO), in situ bioremediation (ISB), and thermal remediation. ISCO via persulfate catalyzed with iron chloride and citric acid leads to high levels of dissolved sulfate and dissolved iron. This creates reducing conditions that favor the formation of reactive FeS, which is associated with abiotic transformation of contaminants (Table 1). ISB typically involves the addition of biodegradable substrates such as emulsified vegetable oil and lactic acid. This creates reducing conditions that favor the formation of reduced minerals, along with sulfate reduction. As microbial activity diminishes, abiotic processes may begin to dominate transformation of contaminants at lower concentrations. Thermal remediation typically increases the biodegradability of naturally occurring organic matter. As with ISB, this can lead to conditions that favor the formation of reactive minerals.
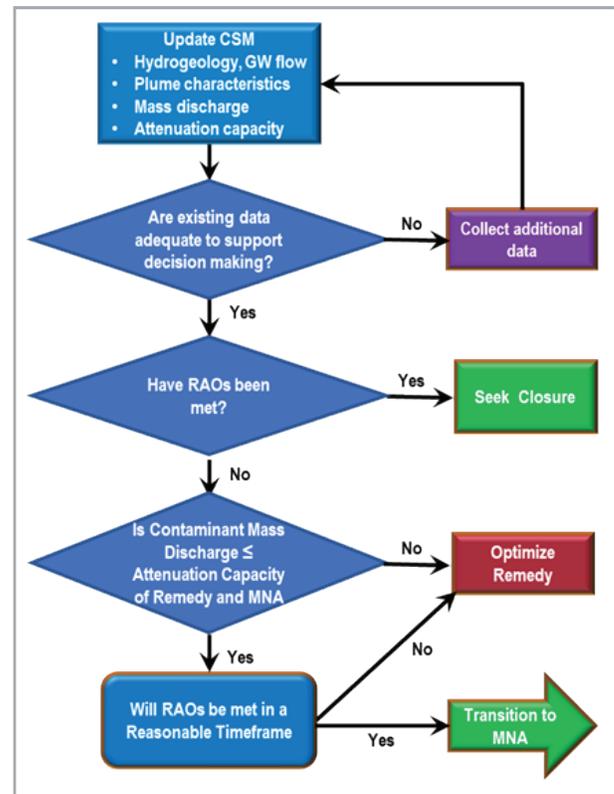


Figure 1: Decision Flowcart for Transitioning to MNA.

## Collecting and Evaluating Evidence in Support of Abiotic Processes

A phased approach is recommended for collecting and evaluating evidence to document the occurrence of abiotic degradation (Figure 2).

**Phase I (Moderate Cost):**

• Determine if monitoring well data indicates that there is mass loss along the axis of the plume.

• Measure dissolved gases in groundwater associated with abiotic degradation. Acetylene is at the top of this list because it is unique to abiotic degradation of PCE and TCE. However, the presence of ethene and ethane, in the absence of DCEs and VC, is also supportive, as is the presence of propane and butane.

- Assess geochemistry: A fact sheet titled "In Situ Biogeochemical Transformation Processes for Treating Contaminated Groundwater" prepared by NAVFAC (2014) provides a summary of groundwater geochemical parameters that may impact abiotic processes, including dissolved oxygen, pH, oxidation/reduction potential, total iron, sulfate, sulfide, methane, and total organic carbon. Ferrous iron (Fe[II]) and manganese (Mn[II]) are also important parameters that may impact these processes. For aquifer sediments, relevant geochemical parameters may include MS, AVS, and chromium reducible sulfur. It is also advisable to collect data on iron- and sulfate-reducing bacteria.

- Assess mineralogy: Information on the types of minerals present provides evidence in support of abiotic transformation. The most direct method to assess mineralogy is to analyze samples of aquifer material. However, the cost to obtain such samples may be prohibitive. A new tool developed with support from ESTCP ER19-5190 shows promise to overcome this limitation. These samplers consist of a slotted polyvinyl chloride (PVC) casing that houses a solid porous medium contained within a permeable mesh. The PVC casing is lowered into an existing well where ambient flow of groundwater leads to formation of mineral precipitates or transformation of minerals in the trap. The minerals formed are representative of the mineralogy in the aquifer.

**Phase I ($)**
- Assess plume stability based on mass loss and daughter products (acetylene, ethene, and ethane)
- Assess geochemistry: redox, $O_2$, $Fe^{2+}$, sulfides, sulfate
- Assess mineralogy (MS, XRD) for Fe bearing minerals
- Assess iron and sulfate-reducing microbes

**Phase II ($$)**
- Analyze contaminants using CSIA to gain insight into mechanisms and rate constants
- Check for acetylenotrophs, complex resistivity

**Phase III ($-$$)**
- $^{14}C$ assays can be used to determine rate constants based on product formation

**Figure 2: Phased Approach to Data Collection.**

**Phase II (Intermediate Cost):**

- Evaluate groundwater samples for enrichment in isotopes of carbon, chlorine, and hydrogen. Compound specific isotope analysis (CSIA) provides information on the occurrence of degradation for biotic and abiotic processes. For chlorinated ethenes, analysis of ratios of stable isotopes of carbon and chlorine ($\delta^{13}C$ and $\delta^{37}Cl$) afford an opportunity to document degradation based on enrichment, as well as providing rate constants when enrichment data are available along the axis of a plume or as a function of time in laboratory studies.

- Use biomarkers to check for the presence of acetylenotrophs (i.e., microbes that use acetylene as their source of carbon and energy). Acetylene rarely accumulates to levels that are easy to detect because it is subject to further reduction to ethene and ethane (which may also form biotically), or consumption by acetylenotrophs.

- Evaluate solid samples for complex resistivity (CR). CR is an emerging geophysical technique with strong sensitivity to iron minerals, particularly magnetite.

**Phase III (Moderate to Intermediate Cost):**

- The products of abiotic degradation are difficult to discern from background levels. Microcosm studies that employ $^{14}C$-labeled contaminants offer a definitive approach to determining that abiotic degradation is occurring, as well as the rate. The advantage of this approach is the ability to track all of the degradation products, from both reductive and oxidative processes. Rate constants are determined based on the rate of accumulation of $^{14}C$-labeled products. To help understand the role of magnetic materials in abiotic transformation of chlorinated ethenes, the Strategic Environmental Research and Development Program (SERDP) is sponsoring a project (ER20-1368) that is evaluating aquifer sediments from different sites using the $^{14}C$ assay.

**Software:** Several software tools are available to assess the potential for remediation, although the degradation components of most tools are focused mainly on biological processes. BioPic is currently the only tool that explicitly incorporates abiotic processes for chlorinated ethenes (Lebrón et al., 2015). The procedure involves estimating a first order degradation rate constant based on groundwater monitoring data. The field rate constant and MS (serving as a surrogate for magnetite) are compared to field and laboratory data that correlate the rate constants with MS. If the field rate constant and MS fall within a defined range, it allows the user to conclude that the mass MS can explain the apparent in situ rate of cis-1,2-dichloroethene (cDCE) degradation. BioPic also incorporates evaluation of CSIA data for abiotic degradation mediated by magnetite or FeS.

# CASE STUDY

## Case Study

## Abiotic Degradation of TCE and cDCE at the Twin Cities Army Ammunition Plant

**Project Objective:** A microcosm study was performed to determine if the decrease in TCE and cDCE in groundwater at the Twin Cities Army Ammunition Plant (TCAAP) near St. Paul, Minnesota can be explained by abiotic degradation.

**Site Background:** Groundwater at the TCAAP Building 102 site is contaminated with TCE and other solvents. Fe and Mn reducing conditions prevail. TCE and cDCE as high as 17 and 4.4 mg/L, respectively, have been observed (Figure 3). There is a substantial decrease in the concentrations along the axis of the plume, but the decrease is not accompanied by reductive dechlorination daughter products. The groundwater has a low level of dissolved iron, consistent with the presence of dissolved oxygen.
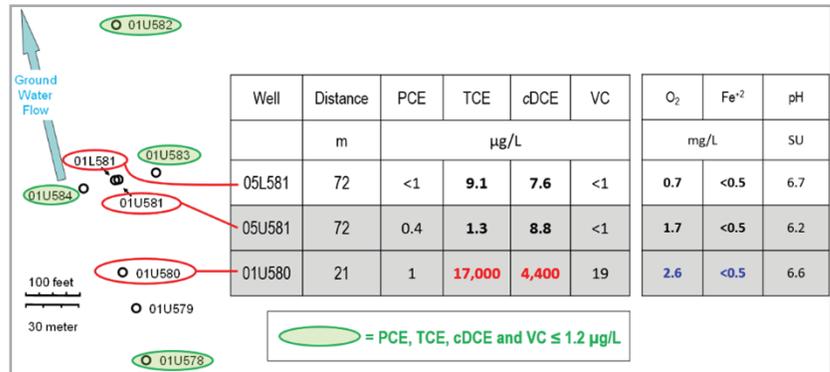


**Figure 3. Building 102 plume at TCAAP.**

| Well | Distance | PCE | TCE | cDCE | VC | $O_2$ | $Fe^{+2}$ | pH |
|---|---|---|---|---|---|---|---|---|
| | m | | | µg/L | | | mg/L | SU |
| 05L581 | 72 | <1 | 9.1 | 7.6 | <1 | 0.7 | <0.5 | 6.7 |
| 05U581 | 72 | 0.4 | 1.3 | 8.8 | <1 | 1.7 | <0.5 | 6.2 |
| 01U580 | 21 | 1 | 17,000 | 4,400 | 19 | 2.6 | <0.5 | 6.6 |

= PCE, TCE, cDCE and VC ≤ 1.2 µg/L

**Results:** Approximately 50 m downgradient from the highest concentrations of TCE and cDCE, the levels decline below 10 µg/L. Microcosms were prepared with soil and groundwater from the site; autoclaving was used to create abiotic conditions. The autoclaved microcosms were incubated for approximately 2.5 years. There was greater loss of mass for TCE and cDCE in the microcosms compared to container controls. The rates of removal for TCE were $0.95 \pm 0.31$ yr$^{-1}$ in the autoclaved microcosms and $0.51 \pm 0.13$ yr$^{-1}$ in the container controls. For cDCE, the rates of removal were $0.65 \pm 0.20$ yr$^{-1}$ in the autoclaved microcosms and $0.21 \pm 0.04$ yr$^{-1}$ in the container controls. CSIA results demonstrated enrichment in $\delta^{13}$C-TCE. MS measurements suggest the presence of reactive magnetic materials. Abiotic processes are presumed to be the driver behind attenuation of the TCE and cDCE.

## Disclaimer

## References

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