

# Abiotic Degradation of PCE and TCE by Magnetite and Clay Minerals

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**Background/Objectives.** Tetrachloroethylene (PCE) and trichloroethylene (TCE) have been heavily used as commercial and industrial solvents for decades. PCE and TCE are toxic and are among the most frequently detected groundwater contaminants. Natural attenuation of PCE and TCE through biological degradation has been extensively studied and is widely accepted to contribute to PCE and TCE degradation. It is still unclear, however, whether abiotic degradation of PCE and TCE by reduced iron (Fe) minerals, natural organic matter, and reduced sulfur species contributes to natural attenuation.

**Approach/Activities.** We measured the reduction of PCE and TCE by magnetite, clay minerals, and field soil samples in batch reactors over a range of environmental conditions. We measured TCE and PCE loss, as well as accumulation of products, including dichloroethenes, acetylene, ethene, and ethane. In addition, we characterized the soil samples using wet chemical extractions, X-ray diffraction, and  $^{57}\text{Fe}$  Mössbauer spectroscopy.

**Results/Lessons Learned.** We present evidence that suggests magnetite and clay minerals are *alone* unlikely to reduce PCE and TCE fast enough to significantly contribute to the natural attenuation of PCE and TCE in anoxic plumes. Under reducing conditions where high concentrations of ferrous iron may be present, however, active precipitation of metastable, intermediate phases in the presence of magnetite or clay minerals form and may contribute to abiotic natural attenuation of PCE and TCE. More specifically, we found in the absence of added Fe(II), neither stoichiometric magnetite nor Fe(II)-bearing clay minerals reduced PCE and TCE over a three month period. When Fe(II) is added to magnetite suspensions, PCE and TCE are reduced under Fe(II) and pH conditions that appear to be controlled by the solubility of ferrous hydroxide,  $\text{Fe}(\text{OH})_2(\text{s})$ . Reduction rates are slow with only 1 to 30% carbon products (primarily acetylene) accumulating over several months. We conducted a similar set of experiments with  $\text{Fe}(\text{OH})_2(\text{s})$  alone and found that, compared to in the presence of magnetite,  $\text{Fe}(\text{OH})_2(\text{s})$  reduces PCE and TCE only at Fe(II) concentrations that are too high ( $\geq 13$  mM, 726 mg/L) to be representative of natural aquifer conditions. Similarly, Fe(II)-reacted clay minerals only reduced PCE and TCE at very high Fe(II) concentrations ( $\geq 19.9$  mM, 1111 mg/L) and pH conditions supersaturated with respect to  $\text{Fe}(\text{OH})_2(\text{s})$ . In contrast to magnetite, a mixed-valent Fe(II)-Fe(III) phase formed as a result of electron transfer from aqueous Fe(II) to clay mineral Fe(III) and  $\text{Fe}(\text{OH})_2(\text{s})$  was only observed and reactive towards PCE and TCE in the absence of clay mineral and in the presence of Fe-free clay mineral. Our results suggest that magnetite and clay minerals present in aquifer sediments alone are unlikely to reduce PCE and TCE sufficiently fast to contribute to natural attenuation of PCE and TCE. The lack of compelling evidence for PCE and TCE reduction by magnetite raises important questions regarding the current application of using magnetic susceptibility as a potential indicator for abiotic natural attenuation. Dynamic conditions and high Fe(II) concentrations that favor active precipitation of minerals, such as  $\text{Fe}(\text{OH})_2(\text{s})$  in the presence of magnetite or clay minerals, however, may lead to PCE and TCE reduction that could help attenuate PCE and TCE.