

# Abiotic Degradation of Chlorinated Ethenes by Iron Minerals: Over Two Decades Now

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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. Of these reactions, reduction by reduced Fe minerals has been discussed as a particularly promising pathway for natural attenuation of chlorinated solvents. In particular, magnetite, a common mixed-valent Fe mineral, has been suggested to be responsible for PCE and TCE attenuation at some field sites despite slow rates of PCE and TCE reduction by magnetite observed in laboratory experiments.

Here we present new findings on the reduction of PCE and TCE by magnetite, clay minerals, and soil samples from a TCE plume and compare our results with published field data. We will also use our findings to revisit the major lessons learned from over two decades of research in this area.

**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.** Our results indicate that magnetite reacts only slowly with TCE ( $t_{1/2} = 7.6$  years) and is not reactive with PCE over 150 days over a broad range of conditions. Faster PCE and TCE reduction, however, occurs when aqueous Fe(II) is added to magnetite suspensions under conditions that appear to be controlled by the solubility of ferrous hydroxide,  $\text{Fe}(\text{OH})_2(\text{s})$ . More specifically, we found that PCE and TCE reduction occurred in the presence of magnetite when Fe(II) and pH values were such that  $\text{Fe}(\text{OH})_2(\text{s})$  was expected to precipitate. In addition, we found that  $\text{Fe}(\text{OH})_2(\text{s})$  reduces PCE and TCE at high Fe(II) concentrations as well. Our results indicate that magnetite reduction of PCE and TCE is slow and unlikely to contribute significantly to natural attenuation of PCE and TCE. Similarly, chemically reduced Fe-rich and Fe-poor clay minerals did not reduce PCE or TCE under identical conditions as applied in the magnetite experiments. Interestingly, addition of Fe(II) at concentrations and pH values favoring  $\text{Fe}(\text{OH})_2(\text{s})$  formation did not result in increasing PCE or TCE reduction as observed for magnetite. Solid phase characterization indicates that added Fe(II) was partially oxidized to Fe(III) by electron transfer to clay mineral Fe(III), resulting in secondary precipitates different from  $\text{Fe}(\text{OH})_2(\text{s})$ . Our results suggest that Fe-bearing clay minerals will not contribute to natural attenuation of PCE and TCE and might even inhibit the formation of other, more reactive transient Fe(II) species.