

Abiotic Dechlorination of Trichloroethene by Naturally Occurring Ferrous Minerals under Aerobic and Anaerobic Condition

Charles E. Schaefer (schaeferce@cdmsmith.com; CDM Smith, Edison, NJ); Paul Ho (CDM Smith, Bellevue, WA), Erin Berns and Charles Werth (University of Texas, Austin, TX)

Background/Objectives. Persistence of chlorinated solvents such as tetrachloroethene (PCE) and trichloroethene (TCE) in low permeability clayey and silty materials is an ongoing challenge at many sites. Contaminants in these low permeability zones often remain following implementation of in situ remedial approaches such as bioaugmentation or chemical oxidation, and can serve as a long-term source impacting groundwater. Several recent studies have shown that ferrous minerals naturally present in low permeability matrices can facilitate the slow dechlorination of PCE and TCE. However, insight into the clay mineral properties that control these reactions, and understanding the role which dissolved oxygen may play in the kinetics of these reactions, remains poorly understood.

Approach. Abiotic dechlorination of TCE was measured and assessed in natural clayey materials (gamma-irradiated) using a series of bench-scale batch systems. Experiments were performed under aerobic and anaerobic conditions, and both reduced gas and volatile fatty acids transformation products were evaluated over a 3-month duration. Generation of hydroxyl radicals was also quantified, and mineral analyses (including ferrous iron content and magnetic susceptibility) were performed on all soils tested.

Results. In the absence of oxygen, TCE dechlorination proceeded via a reductive pathway generating acetylene and ethene. Reductive dechlorination rate constants up to $3.1 \times 10^{-5} \text{ d}^{-1}$ were measured, after scaling to in situ solid water ratios. In the presence of oxygen, TCE dechlorination proceeded via an oxidative pathway generating formic/glyoxylic and glycolic/acetic acids, and oxidative dechlorination rate constants (again scaled to in situ conditions) up to $7.4 \times 10^{-3} \text{ d}^{-1}$ were measured. These rates correspond to half-lives of 60 and 0.25 years for abiotic TCE dechlorination under anaerobic and aerobic conditions, respectively, indicating the potentially large impact of aerobic TCE oxidation in the field. For both reductive and oxidative TCE dechlorination pathways, measured first-order rate constants increased with increasing ferrous iron content, suggesting the role of iron oxidation. Hydroxyl radical formation was measured and increased with increasing oxygen and ferrous iron content. Rate constants associated with TCE oxidation products increased with increasing rates of hydroxyl radical generation, and are zero in the presence of a hydroxyl radical scavenger, suggesting that oxidative TCE dechlorination is a hydroxyl radical driven process.

These results suggest that abiotic dechlorination via ferrous minerals in clays can play an important role with respect to long-term contaminant natural attenuation. While the high dechlorination rates associated with oxidative aerobic dechlorination processes have significant potential for chlorinated ethene impacted sites, the extent to which these oxidative processes occur in situ requires further study.