

**Abiotic Transformation of Perchloroethylene in Homogeneous
Dithionite Solution and in Suspensions of Dithionite-Treated Clay
Minerals**

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Abstract. The reductive dechlorination of perchloroethylene (PCE) in homogeneous solutions of dithionite and at the surfaces of dithionite-citrate-bicarbonate (DCB) treated ferruginous smectite and Na-montmorillonite was studied. Transformation products of PCE identified in dosed dithionite-treated samples included TCE, DCE, 1,1,2-trichloroethane (TCA), 1,1-dichloroethane (DCA), chloroacetylene, acetylene, ethene, and ethane. The decomposition of dithionite to sulfate yielded both protons and electrons necessary for hydrodechlorination (hydrogenolysis) of PCE. Dithionite treatment of the Fe-poor Na-montmorillonite enhanced reductive dechlorination of PCE relative to dithionite treated Fe-rich ferruginous smectite, within the range of 11.5 to 137.8 mM dithionite. For the same dithionite concentration, the kinetics of the heterogeneous reactions of PCE was generally faster than that of the homogeneous reaction, and higher concentrations of TCE were measured in the heterogeneous reactions. Interestingly, increases in the mass of the clay minerals used, Fe²⁺ content in the clay mineral structure, or the dithionite concentration used, did not necessarily enhance the abiotic

transformation of PCE, as would otherwise be predicted. The most efficient reductive dechlorination of PCE was observed with 0.5% clay (m/v) treated with 34.5 mM dithionite buffered at pH 8.5. The solid-state transfer of electrons to surfaces and edges, rather than the redox capacity, limited the dechlorination of PCE by reduced ferruginous smectite and/or suspensions containing a higher clay mass. The greater reactivity of dithionite-reduced montmorillonite than similarly treated ferruginous smectite is attributed to: (1) the well documented layer collapse and aggregation of chemically reduced clays which increases with the clay's iron content, (2) the location of solid-phase Fe^{2+} in the reduced clay mineral and whether it is accessible or inaccessible for reaction with PCE at the mineral edges and surfaces where the reactions are thought to occur, and (3) the greater swellability of montmorillonite versus ferruginous smectite. The faster dechlorination rate of PCE observed with dithionite-reduced Fe-poor montmorillonite than similarly reduced iron-rich ferruginous smectite suggests that the use of dithionite barriers for *in-situ* treatment of chlorinated solvent plumes should not be limited to aquifers with Fe-rich sediments.