

**Summary of PNNL Component of Project #86729
Mechanisms of CCl₄ Retention and Slow Release in Model Porous Solids and
Sediments**

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Research Objective: Provide a better description of the processes by which non-polar compounds are retained by sediments and subsequently released. The objective will be reached through a combination of theory and experimentation with model porous materials and natural sediments. Focus is on the behavior of carbon tetrachloride in aquifer sediments.

Research Progress and Implications:

Migration resistant fractions (MRF) of carbon tetrachloride (CCl₄) and chloroform (CHCl₃) have been detected and quantified in Hanford Site aquifer sediments (Figure 1). The MRF is a portion of a polluted sediment's contaminant inventory that exhibits slow release. Slow release and degradation are key processes that contribute to organic contaminant transport and fate in a plume long after the major portion of the contaminant inventory of a source term has been depleted or removed. CCl₄ retention (31% of the total mass in sediment) and slow release was limited to a sample of Ringold formation mud (82% silt/clay content). In contrast, CHCl₃ exhibited 90% retention in Ringold formation mud and also exhibited 60% and 70% retention in sediment with low silt/clay content (8 to 14%). Ease of solvent extraction of residual CCl₄ and CHCl₃ from sediment indicates the compounds are not permanently sequestered. With the experimental environment the same for both CCl₄ and CHCl₃ differences in retention behavior has to reside in the structural and chemical differences in these molecules and the way they interact with the mineralogical and organic carbon components of sediment. The low organic carbon content of these sediments (0.02% to 0.09%) suggests that restriction within intraparticle micropores and/or intraparticle pore spaces of the sediment mineralogical fraction may be a contributing process to MRF accumulation and accumulation differences observed.

The presence of these fractions coupled with lower than expected concentrations of CCl₄ in the sediments suggest the occurrence of natural attenuation in Hanford's CCl₄ plume. The presence of CCl₄ in an MRF increases residence time, an important condition that allows natural attenuation processes to work (e.g., hydrolysis of CCl₄ to CHCl₃) to remove CCl₄ in Hanford groundwater. In addition, MRF appears to be a significant storage place for some CHCl₃ against rapid aquifer migration. Natural attenuation is a potential strategy to help achieve closure at Hanford's CCl₄ site after every effort has been made to remove source contamination using available technology.

This project reports the first measurements of CCl₄ and CHCl₃ partition coefficients in contaminated Hanford sediments with varying physical/chemical properties. CCl₄ and chloroform (CHCl₃) partition coefficients (K_d) calculated from desorption experiment-



Figure 1. Sediment from the Ringold Formation (364-366 ft depth below ground surface) at the DOE's Hanford Site is shown within the sample collector.

derived retardation factors ranged from 0.106 L/kg to 0.367 L/kg and 0.084 L/kg to 0.432 L/kg. These values were 3 to 8 times and 12 to 23 times larger, respectively, than would be estimated based on the low organic carbon content of the sediments (0.017 to 0.059%) and the normalized sorption coefficient (K_{oc}) of CCl_4 or $CHCl_3$. Estimates based on sediment surface area were also lower than observed. The CCl_4 values are an improvement over and can replace estimated or assumed values as they are more accurate and less conservative than those that have previously been used to model CCl_4 transport in Hanford groundwater, thus improving site assessment decision-making. The discovery of CCl_4 and $CHCl_3$ MRF suggests the need to develop a numerical descriptor for MRF for incorporating into future versions of transport models.

The work may also apply to conditions at DOE's Savannah River and Idaho sites where volatile chlorinated hydrocarbon compounds (i.e., CCl_4 , trichloroethene and tetrachloroethene) contaminate low organic carbon aquifer sediments.

Time course experiments were conducted on the microscale where synthesized pillared clays and porous silicas were exposed to different mixtures of tribromofluoromethane (TBFM-a surrogate for CCl_4), CCl_4 and water. Samples from the different times of exposure were analyzed by small angle x-ray scattering (SAXS) at the Advanced Photon Source at Argonne National Laboratory. For experiments with TBFM, SAXS analysis

included the use of X-rays that were above and below the K-absorption edge of Br, thus allowing discrimination among the types of pores being filled. Clear evidence of filling of pores in a zeolite-structured silica sample (i.e., large pores connected to small pores like beads on a necklace) was observed by TBFM. Similar evidence of pore filling was observed for an aluminum-pillared clay. Evidence for filling of intraparticle pore space was observed for both silica and pillared clays, and confirmed by control experiments with glass beads. Results from these experiments lend support to the hypothesis that the micro/macro pore spaces in the silt/clay fractions of Hanford sediments are the site of MRF accumulation

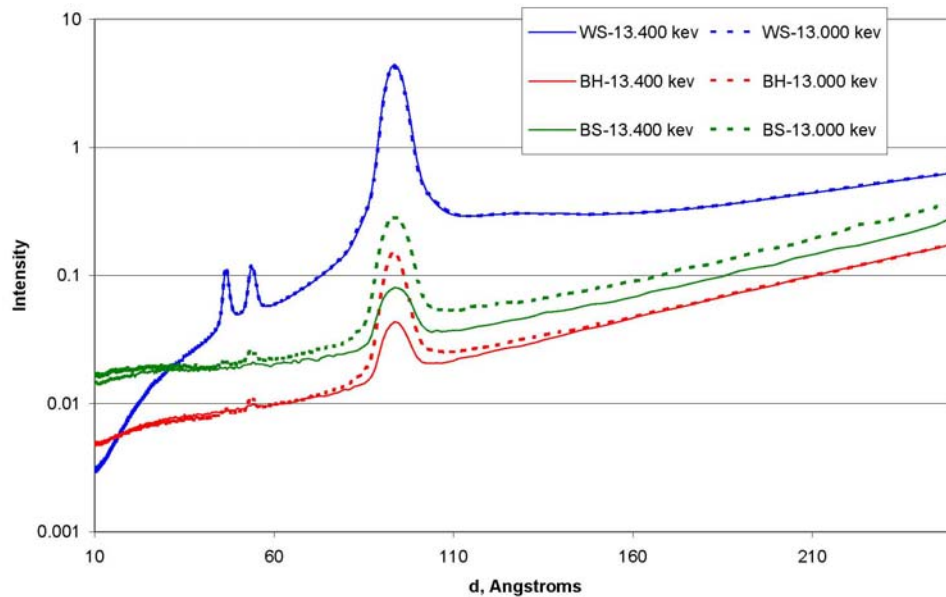


Figure 2. Anomalous small-angle x-ray scattering plots for a zeolitic-structured silica sample reacted with water (WS) or two levels of TBFM (BH, BS). Peaks correspond to pores, and the difference between dashed and solid lines indicates pore filling by TBFM.

Planned Activities:

Future activities will focus on:

- Determination of release rates for CCl_4 and CHCl_3 from MRF in sediments with a broad range of physical/chemical properties to support numerical descriptor of MRF development. MRF will be produced by way of artificial aging of sediments using circulating supercritical carbon dioxide containing CCl_4 and/or CHCl_3 .
- Extension of pore filling experimentation to competitive effects between water and TBFM/ CHCl_3 including studies with selected Hanford sediment or sediment fractions.
- Linkage of behavior observed at the different scales will be accomplished through the coupling of model results (i.e., Lattice Boltzmann simulations and continuum-based modeling) obtained at the different scales. Collectively, these results will lead to an improved conceptual model of CCl_4 subsurface transport that includes the effects of MRF.

Information Access:

No web page has been developed for this project. Additional information can be obtained by contacting the lead project PI, Robert Riley, at robert.riley@pnl.gov.