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Summary of PNNL Component of Project #86729
Mechanisms of CCl$_4$ Retention and Slow Release in Model Porous Solids and Sediments

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Research Objective: A migration-resistant fraction (MRF) is a portion of polluted sediment's contaminant inventory that exhibits slow release. MRF's are formed as a result pollutant aging. Slow release is a key process that controls 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. Slow release rates are not well understood nor are they commonly accounted for in subsurface numerical transport models. In this project, we propose to study the accumulation and slow-release behavior of carbon tetrachloride (CCl$_4$) MRF as a function of time, contaminant concentration and different physicochemical properties of sediments. Experiments will be conducted at macro- and microscopic scales under saturated conditions. The results will be used to 1) develop a mechanistic description of slow release of CCl$_4$ in the subsurface environment and 2) lay the groundwork for improving the robustness of numerical models that predict organic contaminant transport and fate under natural conditions. The outcomes of this study are expected to improve the conceptual model of CCl$_4$ subsurface transport at different physical scales and have an impact on remediation and site closure decision-making at DOE sites, especially in situations involving the potential application of natural attenuation.

Research Progress and Implications: This report summarizes work after 1 1/2 years of a three-year project.

MRFs are formed when hydrophobic organic compounds slowly accumulate in the mineral pores and natural organic matter of soild and sediments over several years. This is referred to as the aging process. Previous efforts to understand and quantify the effects of aging have been hindered by an inability to accurately simulate the aging process on a short timescale. We have demonstrated that circulating supercritical CO$_2$ (SC-CO$_2$) can be used to rapidly prepare artificially aged materials for studying slow-release behavior of volatile organic compounds (e.g., carbon tetrachloride) for the macro-scale experiments proposed in this project.

We interfaced a FTIR spectrometer to a supercritical fluid loading apparatus using a high-pressure flow cell with a 1 mm pathlength. Infrared spectra of supercritical carbon dioxide and xenon were obtained at several temperature and pressure conditions. Xenon was evaluated because we anticipated that the strong absorbance of carbon dioxide would interfere with the measurement of certain compounds of interest. We next measured the infrared spectra of several selected halocarbons in supercritical xenon and carbon dioxide (Figure 1). The two sets of spectra are very similar, although the band intensities are slightly reduced in SC-CO$_2$, and some of the bands associated with C-X stretches are partially or fully masked by CO$_2$ absorbance in the SC-CO$_2$ spectra. Nonetheless, the unique spectral fingerprints of the compounds investigated demonstrate that multiple compounds (e.g., a contaminant and its degradation products) can be monitored simultaneously using FTIR spectroscopy. Moreover, the spectra indicate that the use of supercritical xenon as a solvent is unnecessary for monitoring the compounds in this study. This is advantageous because CO$_2$ is cheaper and more widely available than xenon.

Varying amounts of CCl$_4$, a volatile contaminant of concern at the Hanford site, were mixed with SC-CO$_2$ (200 atm, 35 °C), and the spectra of the resulting solutions were measured (Figure 2a). The apparent wavenumber shift in the spectra with increasing concentration was determined to be a non-linear artifact associated with the infrared detector. Single-wavelength calibration on the

shoulder of the primary absorbance band (793 cm^{-1}) produced excellent results over a broad concentration range (Figure 2b). Based on the variability of the SC-CO$_2$ baseline, we determined the detection limit to be approximately 2 mM. If desired, lower concentrations could be measured using a wavelength near the center of the absorbance band.

Infrared detection was used to monitor the artificial aging of two soils (Hanford and Iron River) with CCl$_4$. In each experiment, a SC-CO$_2$ solution containing CCl$_4$ was circulated for 4 hours through a soil column. Periodically, infrared spectra of the supercritical fluid were measured, and decreases in concentration were attributed to incorporation of the CCl$_4$ into the soil (Figure 3). Estimates of soil concentrations from the infrared spectra were approximately 2 to 4 times higher than the concentrations determined from off-line gas chromatograph (GC) analyses of soil extracts. We believe the discrepancies were caused by partial removal of CCl$_4$ from the soil during depressurization of the loading apparatus and sample instability (i.e., volatilization of the CCl$_4$) prior to the GC analysis. Despite potential changes in samples during depressurization, this research has demonstrated that FTIR spectroscopy is a powerful tool for monitoring the progress of artificial aging experiments. Future work may enable us to closely relate FTIR-based concentration estimates to final loaded concentrations.
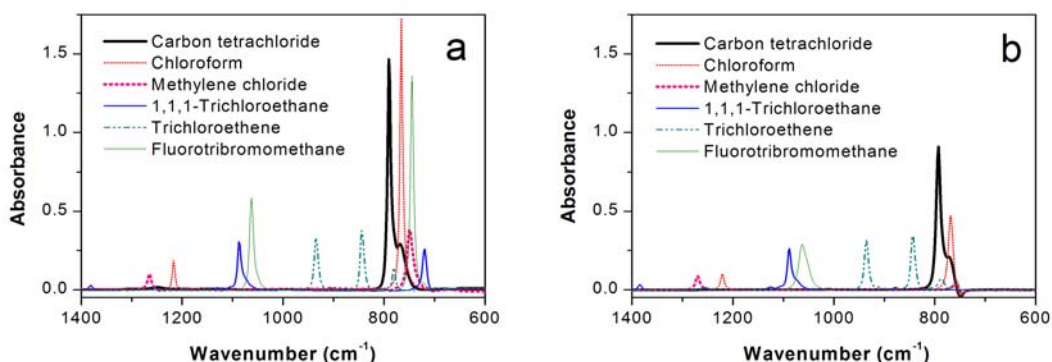

Figure 1. FTIR absorbance spectra of selected halocarbons in (a) supercritical Xe and (b) SC-CO$_2$. Temperature and pressure were held constant at 35 °C and 200 atm.
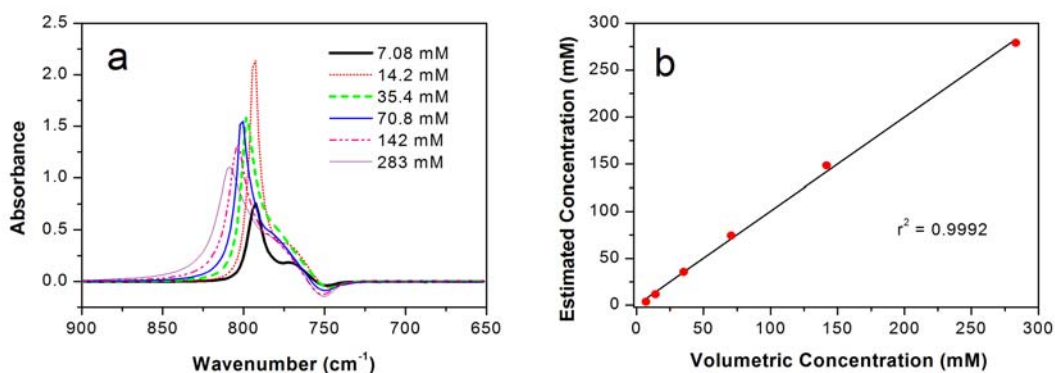

Figure 2. Quantitation of CCl$_4$ in SC-CO$_2$: (a) FTIR spectra of CCl$_4$ solutions (b) single-wavelength calibration results (814 cm^{-1}).
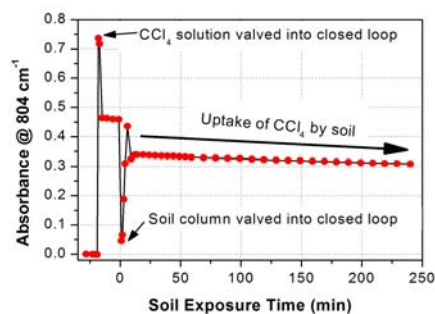
Figure 3. Loading of Iron River soil (4.5% Organic carbon) with carbon tetrachloride

Results of this study were reported at the 227th American Chemical Society Meeting, March 28 to April 1, 2004 and are currently being prepared for submission to the Journal of Applied Spectroscopy for publication.

Planned Activities:

In a joint study between this project and a project funded by Fluor Hanford, Inc., CCl_4 contaminated sediments collected from four different depths in the Hanford site's unconfined aquifer (anticipated collection in July 2004) will be subjected to laboratory column desorption/sorption experimentation. From these experiments, evidence for CCl_4 MRF will be obtained and quantified (magnitude and behavior) as a function of sediment physical/chemical properties. For the first time, CCl_4 partition coefficients and associated uncertainties will be obtained from naturally contaminated Hanford sediments. Such data will improve the predictability of modeling CCl_4 migration in Hanford aquifer sediments. An open literature publication acknowledging EMSP contribution to this study is anticipated early in FY 05.

In a separate study, results from the desorption/sorption experimentation with CCl_4 contaminated sediments will be used to demonstrate that CCl_4 behaves similarly in sediments that were subjected to aging using the supercritical fluid/FTIR technology (technology verification). Following successful verification, a number of sediments from different Hanford subsurface formations and selected other DOE sites (e.g., INEEL) whose physicochemical properties were characterized this past year, will be subjected to rapid aging with CCl_4 using the supercritical fluid/FTIR technology. The magnitude and behavior of MRF as a function of time, CCl_4 concentration, and different sediment properties will be determined as a first step in accounting for the effect of MRF in models that predict CCl_4 transport in aquifer sediments. Submission of an open literature publication in FY 05 is anticipated describing the results of this study.

A more mechanistic understanding of migration resistant fraction (MRF) magnitude and behavior will be assessed through study of CCl_4 pore filling and emptying at the meso/microscopic scale (i.e., subparticle level). In the latter part of FY04 we will complete the structural characterization of the model porous materials we have obtained or synthesized. Materials include a range of porous silicas having narrow pore size distributions centered at 3.5, 6.5, and 15 nm, activated carbons, and titanium-oxide pillared smectites having a range of pillaring densities. The techniques used include pore size distribution data based on BET measurements, X-ray diffraction, transmission electron microscopy, and X-ray scattering. The structural information will serve as input to guide the microscopic modeling associated with this effort and will provide the basis for a peer-reviewed publication to be submitted in the first half of FY05.

This work will be extended in FY05 to measuring directly how the MRF changes with pore structure. We plan to conduct X-ray scattering studies to measure filling and emptying of discrete pore sizes as a function of aging time. This work will be done using CBr_3F as an X-ray sensitive analog for CCl_4 We will supplement this work with other analyses of "quenched" samples by transmission electron microscopy and BET sorption to monitor the pore behavior. We expect this work to result in at least one peer-reviewed publication to be submitted by the end of FY05.

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. Macroscale data (e.g., CCl_4 diffusion coefficients and sediment MRF capacity) will have be generated under saturated conditions. Such data can be used to parameterize numerical models to account for the effects of MRF in simulating CCl_4 transport in the subsurface environment and influence DOE contaminant site remediation and closure decision-making.