



Intercalation of trichloroethene by sediment-associated clay minerals

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HIGHLIGHTS

- ▶ We examined intercalation of TCE by clay minerals associated with aquifer sediments.
- ▶ Results show greater d-spacing for samples treated with aqueous TCE solution.
- ▶ These results indicate that TCE was intercalated by the clay minerals.

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ABSTRACT

The objective of this research was to examine the potential for intercalation of trichloroethene (TCE) by clay minerals associated with aquifer sediments. Sediment samples were collected from a field site in Tucson, AZ. Two widely used Montmorillonite specimen clays were employed as controls. X-ray diffraction, conducted with a controlled-environment chamber, was used to characterize smectite interlayer d-spacing for three treatments (bulk air-dry sample, sample mixed with synthetic groundwater, sample mixed with TCE-saturated synthetic groundwater). The results show that the d-spacing measured for the samples treated with TCE-saturated synthetic groundwater are larger (~26%) than those of the untreated samples for all field samples as well as the specimen clays. These results indicate that TCE was intercalated by the clay minerals, which may have contributed to the extensive elution tailing observed in prior miscible-displacement experiments conducted with this sediment.

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1. Introduction

Pump-and-treat systems are widely used to remediate hazardous waste sites wherein groundwater is contaminated by compounds such as trichloroethene (TCE). It is well known that removal of contaminant mass by pump and treat becomes less effective over time, with a persistent mass discharge causing greatly extended operational periods. One mechanism potentially responsible for this persistent mass discharge is “back diffusion”, wherein dissolved contaminant stored in lower-permeability layers diffuses into the higher-permeability zones that are more readily flushed via pump and treat. Because the lower-permeability layers typically contain high fractions of clay minerals, a question of great interest is whether contaminant–clay interactions may

influence the back-diffusion process. For example, intercalation of TCE into the interlayer spaces of clay minerals could potentially exacerbate diffusive mass-transfer limitations.

The potential for TCE intercalation was discussed recently by Aggarwal et al. (2006), who examined the impact of interlayer cation on the relative magnitude of sorption of TCE by homoionic saponite (a smectite clay). Results from their analysis show that the interlayer space is 3, 3, and 6 Å for Cs-saturated, K-saturated, and Ca-saturated saponite, respectively. They noted that TCE, a planar molecule, is approximately 3–3.5 Å thick, sufficiently small to fit within the interlayer space. Modeling by Farrell et al. (2002) indicated that TCE sorption was energetically most favorable in pores that are minimally large enough to accommodate a TCE molecule. Spaces of this size range are present in the interlayer spaces of clay minerals. Using molecular dynamics simulations, Teppen et al. (1998) showed that it was possible for TCE molecules to exist in the interlayer spaces of pyrophyllite clay.

Amarasinghe et al. (2009) observed that the d-spacing increased from 9.83 Å to 12.18 Å when liquid TCE was mixed with

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Na-Montmorillonite (SWy-2). Intercalation into interlayer spaces of smectites has been documented for several other organic compounds. Boyd et al. (2001) reported the intercalation of substituted nitrobenzenes in smectite clays SAz-1 and SWy-2. In a study on the thermodynamics of nitroaromatic compound adsorption from water by homoionic K^+ and Ca^{2+} smectite SWy-2 (Ca-SWy-2 and K-SWy-2), Li et al. (2004) suggested that nitroaromatic compounds are sorbed strongly by K-smectites because they form inner- and/or outer-sphere complexes with K^+ cations located in clay interlayer spaces. Sheng et al. (2001, 2002) reported intercalation of several pesticides by a number of smectite clays.

The objective of this research was to examine the potential for intercalation of TCE by clay minerals associated with aquifer sediments. Sediment samples were collected from a field site in Tucson, AZ. Two widely used Montmorillonite specimen clays were used as controls. X-ray diffraction (XRD), conducted with a controlled-environment chamber, was used to characterize smectite interlayer d-spacing for three treatments (bulk air-dry sample, sample mixed with synthetic groundwater, sample mixed with TCE-saturated synthetic groundwater).

2. Materials and methods

2.1. Materials

An electrolyte solution composed of $Ca(NO_3)_2$, $CaCl_2$, $MgSO_4$, $NaHCO_3$, and $NaCl$ was used for all experiments. This solution, referred to as the synthetic groundwater solution, was developed to represent the chemical composition of the groundwater at the field site. The concentrations used for the $Ca(NO_3)_2$, $CaCl_2$, $MgSO_4$, $NaHCO_3$, and $NaCl$ were 9 mg/L, 85 mg/L, 124 mg/L, 171 mg/L, and 20 mg/L, respectively. Trichloroethene (ACS reagent grade, $\geq 99.5\%$ purity) was obtained from Sigma–Aldrich Chemical Company. The reference clay controls were obtained from the Clay Minerals Society (Chantilly, Virginia), and comprised Na-Montmorillonite (SWy-2) from Wyoming and Ca-Montmorillonite (STx-1b) from Texas.

Sediments used in this study were collected from two sites within the Tucson International Airport Area Superfund complex, located in Tucson, Arizona. Sediment samples were collected from locations at Air Force Plant 44 (AFP44) and the Three Hangars Complex at the Tucson International Airport. Sediments were collected from a depth interval of 44–46 m BGS (Below Ground Surface), designated the “finer zone”, as well as a depth interval of 46–48 m BGS, designated the “coarser zone”, for a core collected from well M-72 borehole at AFP44. A sample was also collected from boring B-119 in the depth interval 41.9–43 m BGS at AFP44. Another field sample was collected from the depth interval 28.9–30 m BGS from boring CRA-26 at the Three Hangars Complex.

For the 44–46 m BGS M-72 sample, the average sand, silt, and clay fractions were 89.5% ($\pm 0.6\%$), 4.1% ($\pm 0.6\%$), and 6.4% ($\pm 1.0\%$), respectively. For the 46–48 m BGS M-72 sample, the average sand, silt, and clay fractions were 97.1%, 1.2%, and 1.7%, respectively. The average percent total carbon and organic carbon equaled 0.06% ($\pm 0.01\%$) and 0.03% ($\pm 0.009\%$), respectively, for these samples. For the borehole B-119 sample, the average sand, silt, and clay fractions were 52.5%, 26.5%, and 21.0%, respectively. For the borehole CRA-26 sample, the average sand, silt, and clay fractions were 0.1%, 36.4%, and 63.5%, respectively.

Subsamples of the sediments were analyzed by XRD to qualitatively identify clay mineral composition. Analysis of the material from borehole B-119 shows that the clay minerals present in the clay-sized fraction ($< 2 \mu m$) are kaolinite, muscovite/illite, smectite, and minor amounts of chlorite, and that the non-clay minerals present in the clay-sized fraction are quartz and feldspar. Analysis

of the clay size fraction from CRA-26 shows that the same clay minerals and non-clay minerals are present. Analysis of the sediment collected from borehole M-72 showed large amounts of smectite, with smaller amounts of mica and kaolinite.

Additionally, quantitative analysis of the clay and non-clay materials was performed for samples from boreholes B-119 and CRA-26. The sample from CRA-26 contained 17.6% quartz, 5.4% potassium feldspar (microcline), 3.5% plagioclase (oligoclase), 4.4% calcite, 4.8% kaolinite, 42.6% muscovite/illite, and 21.6% smectite (Montmorillonite). The sample from B-119 contained 42.3% quartz, 10.7% potassium feldspar (microcline), 12.8% plagioclase (oligoclase), 3.7% calcite, 1.3% kaolinite, 21.1% muscovite/illite, and 8.0% smectite (Montmorillonite).

2.2. Methods

For the XRD experiments, sediment and specimen-clay subsamples were subjected to two treatments: synthetic groundwater and TCE-saturated synthetic groundwater (~ 1100 mg/L TCE). In addition, an untreated (air-dry) subsample was analyzed with XRD to develop a baseline diffractogram for each sediment and specimen clay. Prior to treatment, the sediment samples were air dried and ground to a uniform fine consistency. The sediment samples (~ 1 – 5 g) were added to 20 mL glass gas-tight vials, after which ~ 15 mL of solution was added. The samples were incubated for 1 day prior to analysis with XRD. The bottles were shaken periodically to ensure adequate mixing of the solution and sediment.

Sediment samples were subjected to XRD analysis with a PANalytical X'Pert MPD Pro powder diffractometer. Measurements were made with copper $K\alpha$ radiation, a variable divergence slit, and a graphite post-diffraction monochromator. A gas-tight sample environment around the samples was provided by an Anton Paar TTK 450 sample stage operated at ambient temperature and saturated with TCE vapor during the relevant experiments. An approximately 150 mg moist sample was placed in the chamber. The samples were still moist, but to a lesser extent, at the end of the analysis.

Samples were scanned from 1 to $22^\circ 2\theta$ using a step size of 0.04° and a count time of 8 s. Occasional samples were scanned to a larger final diffraction angle to confirm the identity of minerals, especially non-clays. For all samples, the diffractograms showed quartz peaks at positions that were close to the expected position ($20.88^\circ 2\theta$), providing an internal check on diffraction angle. Jade[©] and High-Score[©] software were used to analyze the XRD data to determine specific locations ($^\circ 2\theta$) of peaks. The $^\circ 2\theta$ peak locations obtained during the XRD measurement were used to calculate the d-spacing using standard methods (e.g., Stanjek and Hausler, 2004).

3. Results and discussion

The results of the XRD measurements for Na-Montmorillonite (SWy-2) are presented in Fig. 1. The baseline scan for untreated Na-Montmorillonite, shown as the solid line in Fig. 1, shows a smectite peak at $8.35^\circ 2\theta$. This measurement was used to calculate a d-spacing of 10.6 Å. Chipera and Bish (2001) measured a d-spacing of 11.2 Å for SWy-2. Diffractograms of smectite clays exhibit variability due to relative humidity and other factors (Chipera and Bish, 2001). Considering this variability, the d-spacing of the smectite clay measured in the current experiment is within the range of literature values quoted by Chipera and Bish (2001). The XRD measurements for the treated SWy-2 samples are compared to this baseline scan to determine if a change in the d-spacing occurred as a result of treatment.

One of the TCE-saturated synthetic groundwater treatments shows a well-defined smectite peak at $4.85^\circ 2\theta$ with a d-spacing

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