Specific UV Absorbance of Aldrich Humic Acid: Changes during Transport in Aquifer Sediment

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This study examined the transport behavior of Aldrich humic acid (AHA) in low natural organic carbon content sediment contaminated with tetrachloroethene (PCE), for comparison to a nonionic surfactant mixture previously examined in the same system. Tracking of individual molecular weight (MW) fractions of AHA was attempted by UV absorbance, followed by conversion to mass of carbon using specific ultraviolet absorbance (SUVA) (UV absorbance per mass of carbon) measurements. The analysis required determination of variations of SUVA with MW, which showed a maximum at 10,000 Daltons. Furthermore, SUVAs of AHA MW fractions greater than about 10,000 Daltons increased following AHA interaction with sediment in batch experiments, and this was associated with AHA-driven leaching of cations from the sediment. AHA transport was examined in a series of three columns representing the up-gradient, residual-zone, and down-gradient portions of a DNAPL contaminated site. SUVAs of larger MW AHA fractions cycled through decreased, increased, and eventual return to influent values during the early, intermediate, and final stages of breakthrough, respectively. These variations were attributable to a combination of preferential adsorption of low MW fractions of the AHA during early breakthrough and AHA-driven leaching of sediment cations during intermediate breakthrough, with eventual exhaustion of sediment cation complexation during the final stage of breakthrough. The complex variations in SUVA precluded accurate conversion of measured UV absorbance to carbon mass. However, the effect of AHA loss to sediment on the solubilizing capacity of the AHA solution was indicated by the breakthrough behavior of AHA-solubilized PCE, which showed that AHA loss from the aqueous phase during transport in this system did not decrease the solubilizing capacity of the AHA mixture.

Introduction

Recent interest in soil humic acids as potential solubilizing agents for cleanup of dense nonaqueous phase liquids (DNAPL) has been driven by the need to develop agents that retain high solubilizing capacities during transport through subsurface media. Humic acids are polydisperse mixtures of heterogeneous weak polyelectrolytes dominated by carboxylic and phenolic acidic functionality and displaying varying degrees of aromaticity (1–3). Humic acids are not presently among the leading candidate agents for DNAPL solubilization since their solubilizing capacities for nonpolar contaminants are generally lower than those of other candidate solubilizing agents, such as properly chosen surfactant mixtures, and since their transport behavior at high concentrations is poorly known (4–8). Among the leading candidate agents for DNAPL solubilization (e.g. anionic surfactants, alcohols, etc.) are nonionic surfactants, which are mixtures of similar amphiphilic molecules that may display differing sorption characteristics and contaminant solubilization properties. However, variations in sorption behaviors among oligomers within nonionic surfactant mixtures have been shown to cause fractionation of these mixtures during transport in porous media (9–14). Fractionation by sorption loss may decrease the solubilizing capacity of the aqueous surfactant mixture (14, 15) as well as increase the extent of contaminant partitioning to the porous media (16, 17), phenomena that are each detrimental to remediation efforts. Fractionation of humic acids during transport in groundwater is also a concern. Preferential adsorption of larger MW components of humic acids mixtures has been observed on iron oxides (18–23), aluminum oxides (23, 24), and clays (25). AHA components are preferentially adsorbed to activated carbon (26, 27), indicating a strong potential for fractionation during transport in subsurface media. The effect of fractionation on the DNAPL removal efficiencies by candidate solubilizing mixtures needs to be compared in order to compare their performance in a given system.

In this study, batch and column experiments were performed to examine fractionation of Aldrich humic acid (AHA) during transport in DNAPL-contaminated aquifer sediment and to examine the associated effects of the capacity of the mixture to solubilize tetrachloroethene (PCE) DNAPL. Comparison is made to results obtained for a nonionic surfactant mixture previously examined in the same system (14, 17). In the course of these studies it was found that the specific ultraviolet absorbance (SUVA) of AHA varied among the molecular weight (MW) fractions of AHA and also varied in response to AHA interaction with the sediment. Variation of SUVA with MW has been previously examined for aquatic (20, 23–24, 28, 29) and terrestrial (27, 30–32) humic acids, and changes in SUVA of aquatic humic acids have been reported in response to interaction with model materials such as iron and aluminum oxides (20, 23). However, few studies have examined variation of SUVA among MW fractions of terrestrial humic acids, and fewer have examined changes in SUVA resulting from humic acid interaction with aquifer sediment.

Methods

Reagents: Although the humic acid examined in this study, AHA, is not necessarily representative of all terrestrial humic acids (33), it is readily available and could potentially serve in aquifer remediation. AHA (Aldrich Chemical, Milwaukee, WI) was purified according to International Humic Substances Society (IHSS) protocol (34). Briefly, AHA was suspended in pure water (Milli-Q, Millipore Corporation) and adjusted to pH 10 using 0.1M KOH. The solution was stirred overnight under N2 atmosphere and then centrifuged at 2500g for 45 min (GS-6 Centrifuge, Beckman Instruments, Fullerton, CA). The supernatant was then acidified with 6 M HCl to ~pH 1 and centrifuged again (as described above). Following centrifugation, the supernatant was discarded, and the precipitant was resuspended in 0.1 M HCl/0.3 M HF and centrifuged (as described above). Resuspension and centrifugation were repeated three times. The precipitant was
freeze-dried (Trezzene 4.5, Labconco, Kansas City, MO) and stored at 4 °C.

Reagents other than humic acid were used as received from the manufacturer. Tetrachloroethene (PCE) (Aldrich, reagent grade, 99+%) was used to represent DNAPL in the column experiments. PCE was stained by adding Oil-Red-O (Sigma Inc.) to a concentration of about 0.01% to allow visual recognition of DNAPL residual. The addition of Oil-Red-O has been shown to not affect PCE dissolution (35).

Artificial groundwater (AGW) was used in all experiments and prepared according to Scholl et al. (20). The AGW was comprised of 1.4E-4 M MgSO4 and 1.4E-4 M KNO3, 1.4E-4 M MgSO4 and prepared according to Scholl et al. (20). Individual sample analyses were not replicated. The addition of Oil-Red-O was performed on AGW solution (100 mg L−1) to a final concentration of 0.01% to allow detection of DNAPL residual. The addition of Oil-Red-O comprises a minor portion of the ultraviolet absorbance and carbon content of bulk AHA. Injection of AHA was repeated four times to yield quartile samples of each MW fraction collected from the HPSEC effluent. The four UV absorbance measurements corresponding to each MW fraction were averaged to determine the combined errors of the UV absorbance and HPSEC measurements (εSUVA) for that MW fraction.

The total organic carbon content (TOC) of the AHA MW fractions was determined using a total organic carbon analyzer (TOC-5000A, Shimadzu Corp.) with a high sensitivity catalyst. The sample analyzed for each MW fraction was composited from the four quadruplicates collected from the HPSEC effluent. The error of the TOC analyses (εTOC) was determined by averaging the triplicate TOC measurements for each fraction.

SUVA was determined for each MW fraction from the quotient of the corresponding UV absorbance and TOC measurements. UV absorbance response was determined to be linear over the TOC range examined in this study, this result being due to dilution and distribution of the AHA signal across the elution period during HPSEC analyses. The error in SUVA relative to the mean SUVA (εSUVA) was determined for each MW fraction as follows

\[
\epsilon_{SUVA} = \sqrt{\left(\frac{\epsilon_{SUVA}}{M_{SUVA}}\right)^2 + \left(\frac{\epsilon_{TOC}}{M_{TOC}}\right)^2}
\]

where \(\epsilon_{SUVA} / M_{SUVA}\) and \(\epsilon_{TOC} / M_{TOC}\) are the errors relative to the mean values of the quadruplicate absorbance and triplicate TOC measurements, respectively. Weight-averaged MW (\(M_w\)) was determined from the HPSEC chromatograms and measured SUVAs using the protocol described by Kilduff et al. (27), except that the relationship between SUVA and MW was measured directly in our study, obviating the iterative determination of this relationship described in their study. The UV absorbances of AGW and PCE were shown to be negligible in HPSEC analyses by comparison of results for AHA-free AGW and AHA with PCE. TOC values of HPSEC effluent fractions from injection of AHA-free AGW were less than 10% of, and were subtracted from, the TOC values from the corresponding MW fractions of AHA.

**ICP-AES and GC Analyses.** Inductively coupled plasma atomic emission spectrometry (ICP-AES) was performed on blank (not equilibrated with sediment) and sediment pre-equilibrated AHA solutions in order to determine potential differences in the concentrations of major cations in the two solutions (Perkin-Elmer Plasma 400 ICP Emission Spectrometer). An argon-plasma flame was utilized for the analyses with an argon flow rate 15 L min−1. Analyses were conducted for Ca2+ (λ = 393.366 nm), K+ (λ = 766.490 nm), Cu2+ (λ = 324.754 nm), Na+ (λ = 589.392 nm), Fe3+ (λ = 236.204 nm), Al3+ (λ = 396.152 nm), Mn2+ (λ = 257.610 nm), Mg2+ (λ = 279.553 nm), and Zn2+ (λ = 213.823 nm). Samples were centrifuged to settle suspended solids, and the supernatant was directly analyzed at a solution sampling flow rate.
of 1.0 mL min\(^{-1}\). The sampling tubing was rinsed with Milli-Q (approximately 1 mL) between each sample until a baseline detector response was achieved. PCE concentrations were determined by gas chromatography (GC), as described in John et al. (17).

**Batch Experiments.** Equilibrium adsorption of sediment preequilibrated AHA to sediment was examined using the protocols described in John et al. (17), with AHA concentrations ranging from 0.05 to 5.0 g L\(^{-1}\), and a 72 h equilibration period as determined appropriate in preliminary batch tests at 5.0 g L\(^{-1}\) AHA concentration sampled over 5 days. No precipitation of purified AHA was observed under the experimental conditions, other than where noted below.

PCE solubilization by sediment preequilibrated AHA and sorption of sediment preequilibrated AHA to PCE DNAPL were examined using the protocols described in John et al. (17) except for use of a 5:1 volume ratio of aqueous solution to nonaqueous PCE. The AHA concentrations examined were the same as that used in the AHA adsorption experiments.

Sorption of AHA to PCE DNAPL, and PCE and AHA to sediment, was determined in batch experiments by difference in concentrations before and after equilibration with PCE DNAPL and sediment, respectively. All samples were replicated and averaged to yield estimates of standard error. The equilibrium distribution constant for PCE between AHA and water, \(K_{\text{d,sw}}\), was determined from the PCE concentration relative to the AHA concentration (as carbon) in the AHA concentration sampled over 5 days. This high AHA concentration was about a factor of 15 greater than the aqueous HA concentration required to fully saturate AHA adsorption to the sandy aquifer sediment (based on HPSEC chromatograms) and therefore resulted in negligible AHA loss from the aqueous phase. The concentrated sediment preequilibrated AHA solution was then diluted to the desired concentrations using sediment preequilibrated AGW (14 mL AGW: 25 g sediment, 15 g L\(^{-1}\) NaBr) and full AHA breakthrough, \(C_0\), being the concentration of the influent solution. Retardation of solubilized PCE was determined by integration of the area above the total PCE breakthrough curve over the period between average tracer breakthrough (100 mg L\(^{-1}\) NaBr) and full AHA breakthrough.

**Columns Experiments.** Fractionation during transport was studied using three-columns in series, to represent the up-gradient, residual, and down-gradient zones of a DNAPL-contaminated site. PCE DNAPL was emplaced in the residual-zone column at a residual content of about 22% of the pore volume, which was determined gravimetrically to be \(\sim 21.5\) mL and \(\sim 16.4\) mL in the residual-free and residual-zone columns, respectively. The columns, packing procedure, conditioning protocol, and PCE emplacement procedure are described in Bao et al. (14). Sediment preequilibrated AHA solution (5 g L\(^{-1}\), \(\mathrm{pH} = 6.8\)) was introduced continuously in down-flow mode to the up-gradient (uppermost) column of these columns, following flushing of the system (5 min) with carbon dioxide. Ten percent of the solution flow was split prior to the residual-zone and down-gradient columns to allow collection of samples for AHA and PCE analysis. The experiments were conducted under high (0.343 mL min\(^{-1}\)) or low flow rate (0.115 mL min\(^{-1}\)) conditions. Samples for AHA analyses were collected in 2 mL amber glass autosampler vials (12 × 32 mm, with red PTFE/white silicon and polypropylene closure) and 0.15 mL glass inserts for samples from the up-gradient and residual-zone columns. Samples for PCE analyses were collected directly from the column effluent tubing using a 5 \(\mu\)L-glass syringe for direct injection into the gas chromatograph (described above). After each injection, the syringe was rinsed with water and methanol. Tracer (100 mg L\(^{-1}\) KBr) breakthrough experiments were conducted using an online conductivity meter.

In the column experiments, pore volumes were not a useful measure of time when comparing results between the three columns, which had differing aqueous pore volumes, differing velocities, and which were in series. To allow comparison of breakthrough between the columns, measured sampling times were modified by adding to the experimental sampling time the residence times (aqueous pore volume divided by flow rate) of water in all subsequent columns to yield “equalized time”. The effluent of each of the three columns at a given equalized time represented the same parcel of water exiting each of the three columns. Comparison between experiments was facilitated by normalization of equalized time to the total residence time of water in the three-column system, to yield system pore volumes.

Initial batch experiments showed that equilibrium with sediment altered the SUVAs of larger MW fractions of AHA (described below). Hence, AHA solution was preequilibrated with sediment (sediment preequilibrated AHA) prior to introduction to the sediment in column studies. To avoid loss of AHA to sediment during the preequilibration step, a concentrated (15 g L\(^{-1}\)) AHA solution (14 mL) was equilibrated with sediment (25 g) while rotating end over end for 48 h, as determined appropriate by preliminary experiments at 15 g L\(^{-1}\) sampled over 5 days. This high AHA concentration was about a factor of 15 greater than the aqueous HA concentration required to fully saturate AHA adsorption to the sandy aquifer sediment (based on HPSEC chromatograms) and therefore resulted in negligible AHA loss from the aqueous phase. The concentrated sediment preequilibrated AHA solution was then diluted to the desired concentrations using sediment preequilibrated AGW (14 mL AGW: 25 g sediment, rotated end over end for 48 h). This was done in order to preserve the chemistry of the free aqueous and humic phases, as was indicated successful by the constancy of the HPSEC chromatograms among the diluted samples. The specific conductance of the HPSEC mobile phase was a factor of 75 greater than that of the sediment preequilibrated AHA solution, thereby mitigating artifacts arising from changes in AHA solution chemistry due to interaction with sediment.

The mass of solubilized PCE that exited each column was quantified by integrating the area below the total PCE breakthrough curve for PCE concentrations greater than normal water solubility. Mass of AHA and surfactant sorbed in each column was determined by integration of the area above the breakthrough curve to \(C_0\) or \(C_0\) over the period between average tracer breakthrough (100 mg L\(^{-1}\) NaBr) and full AHA breakthrough, \(C_0\), being the concentration of the influent solution. Retardation of solubilized PCE was determined by integration of the area above the total PCE (dissolved and solubilized) breakthrough curve over the period between average tracer breakthrough and complete solubilized PCE breakthrough. Retarded PCE mass included the effects of AHA or surfactant sorption and kinetic limitations on PCE dissolution-solubilization. The gravimetrically determined aqueous porosity in the residual-zone column (16.4 mL) matched the porosity determined from tracer breakthrough, indicating that the majority of aqueous pore space was advective.

**Results**

**SUVA versus MW.** The HPSEC chromatogram of blank AHA (not preequilibrated with sediment) (Figure 1) showed two distinct peaks: a larger broad peak centered on 5000 daltons and a smaller sharp peak at the high MW cutoff for the column (~100K), the latter representing molecules too large to enter the internal pore space of the column packing material. SUVAs determined for MW fractions separated by UF showed decreasing SUVA with increasing MW (Figure 2), in agreement with SUVA versus MW relationships reported for other terrestrial HA fractionated by UF (27). SUVAs of MW fractions collected from HPSEC effluent showed a maximum in the
soil-derived humic acids, ref 30 MW observed for low MW fractions (< 10 000 Daltons) from at least some sources. and the correspondingly low MW fractions of terrestrial humic possible structural similarities between aquatic humic acids (all MWs with increasing MW (> 10 000 Daltons) of this result contrasts against others showing decreasing SUVA for six soil humic acids separated by Sephadex gel. However, Agreement between M_w from HPSEC and the nominal UF filter cutoffs for this filter system corroborates results of Chin and Gschwend (41). It is well documented that UF tends to overestimate MW relative to HPSEC, and increasingly so for higher MW (27, 29, 37), due to the fact that high MW UF filters are calibrated to globular proteins. Overestimation has also been attributed to clogging of the UF membranes with HA during separation by UF (37). The agreement between UF and HPSEC reported here may derive from the careful avoidance of clogging of the UF membrane with high MW HA, by use of low AHA concentrations and small AHA volumes in these filters (as described above).

The M_w of the blank AHA was indicated by HPSEC measurements to be about 13 200 (Daltons), in reasonable agreement with other M_w values for AHA determined by HPSEC calibrated with proteins (~15 000 Daltons) (42), and by field flow fractionation (~14 500 Daltons) (43). The M_w values determined using HPSEC may be either overestimated (due to charge exclusion with respect to the solid phase) or underestimated (due to possible hydrophobic interaction with size exclusion gels) (37, 44). Corrections for these effects were not attempted in this investigation; however, charge exclusion effects were minimized by the high ionic strength of the mobile phase. Furthermore, the goal was to examine fractionation of AHA by comparing the breakthrough behaviors of the various MW fractions. Hence, potential inaccuracy in absolute MW did not significantly affect the analyses.

**SUVAs of Sediment Preequilibrated AHA.** Chromatograms shifted toward higher MW after initial equilibration with sediment (Figure 1), herein referred to as sediment preequilibrated AHA. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses showed increases in concentrations of Ca^{2+}, Al^{3+}, and Fe^{3+} in AHA solution (100 mg L^{-1} as organic matter) by factors of about 10, 6, and 5, respectively, following preequilibration of AHA solution with sediment (data not shown). Additionally, order of magnitude increases in the inorganic carbon concentration (from 2 to 20 mg L^{-1}) in AHA solution (100 mg L^{-1} as organic matter) after equilibration with sediment, along with AHA-induced increases in solution pH only in the presence of sediment (inset Figure 1), indicate that dissolution of sediment CaCO_3 was driven by AHA. The chromatogram shift likely resulted from changes in solution chemistry associated with AHA-driven leaching of cations from the sediment. Similarly, increased SUVAs of aquatic natural organic matter following reaction with goethite was attributed to “red shifts” in light absorbance spectra, or excessive light scattering, due to dissolution of goethite by the natural organic matter (23). Addition of moderate amounts of salts of two cations (0.00005–0.005 M CaCl_2 and Al_2(SO_4)_3) resulted in chromatogram shifts toward higher MW similar to those observed after preequilibration with sediment and proportional to the concentration ratios of cation to AHA (data not shown). Addition of FeCl_3 was also investigated but was prevented by precipitation of AHA at low concentrations of FeCl_3.

SUVAs were examined in order to determine whether chromatogram shifts toward higher MW during interaction...
with sediment indicated changes in extensive properties of the AHA (increased mass in the high MW fractions via aggregation) or changes in intensive properties of the AHA (increased SUVA of the high MW fractions). SUVAs of AHA were increased in the MW range \( > 10,000 \) Daltons following preequilibration with sediment (Figure 2). The corresponding \( M_w \) was 13,600, a value close to that of the blank solution (13,200), indicating that the observed chromatogram shift to higher MW was largely attributable to increases in SUVAs, as opposed to changes in carbon mass in this MW range. Previous investigators examining terrestrial humic acid adsorption to activated carbon have reasonably concluded that \( \text{Ca}^{2+} \) complexation caused aggregation of other soil-derived HA in the aqueous phase, since HPSEC chromatograms indicated greater \( M_w \) in the presence, relative to the absence, of \( \text{Ca}^{2+} \) (39). However, the authors assumed that SUVAs remained constant during interaction with the activated carbon. Based on the results presented in this paper, it is possible that the apparent shifts in \( M_w \) in the presence of cations were due in part to increased SUVAs, rather than being solely due to aggregation of HA molecules.

**Accuracy of SUVAs.** Accuracy of the SUVAs was examined for sediment preequilibrated AHA ranging in concentration from 0.05 to 5 g L\(^{-1}\) (as organic matter). The known concentration of bulk AHA (from dilution of a standard concentration of AHA) was compared to the concentration determined by conversion of UV absorbances via SUVAs followed by summation of carbon mass for all MW fractions. The known AHA concentration was converted to carbon mass by the factor 0.68 (68% carbon, as determined by TOC measurements). Very good agreement between the known and analytically determined AHA concentrations were observed (Figure 3 top), indicating that the experimentally determined relationship between SUVA and MW was accurate. However, significant discrepancies at the lowest AHA concentrations resulted from slight shifts in the chromatograms toward lower MW with decreased AHA concentration (Figure 3, bottom). The measured bulk AHA concentration, as % of the known C value, was 80%, 87%, and 90% for the 34 mg L\(^{-1}\), 68 mg L\(^{-1}\), and 170 mg L\(^{-1}\) solutions, respectively. Note that higher concentrations showed lesser errors and that the log scale (Figure 3, top) accentuates the errors at low concentrations. SUVAs were determined from concentrated AHA solution to allow sufficient carbon for TOC analyses following HPSEC fractionation.

**SUVAs in Column Experiments.** During breakthrough in the triple column experiments, normalized concentrations of the \( > 5000 \) Dalton fractions of sediment preequilibrated AHA achieved values above unity based on carbon concentrations calculated using the SUVA of sediment preequilibrated AHA (Figures 4 and 5). The rise above unity was temporary, producing a “hump” in the breakthrough curves for larger MW fractions (Figures 4 and 5). Corresponding to the hump in the breakthrough curves, the HPSEC chromatograms shifted to higher MW (data not shown). At later times full breakthrough was achieved, that is, the chromatograms returned to equivalence with those of the sediment preequilibrated influent solution (\( C/C_0 \) was near unity), indicating that the process that produced the “hump” was eventually exhausted. During early breakthrough (prior to the hump), the SUVAs of all MW fractions of AHA exiting the up-gradient column decreased relative to those of the influent solution (sediment preequilibrated AHA) (Figure 6), as determined by analysis of effluent samples using the techniques described above. The decrease in SUVAs during initial breakthrough was not due to chromatogram shifts.

**FIGURE 3.** Expected (from dilution) versus analytically determined (measured) bulk AHA concentrations (as C) (top). Shifts in HPSEC chromatograms toward lower MW with decreased AHA concentration (bottom).

**FIGURE 4.** Breakthrough of four MW fractions of AHA in the series of three sediment columns at the low flow rate (0.0628 cm/min). Concentrations were converted using SUVAs of the influent solution (sediment preequilibrated AHA). The dashed horizontal line indicates the influent concentration. Equalized time is described in the text. Selected MW fractions are shown for clarity.
with sample concentration, since the early breakthrough sample had an AHA concentration of \( \sim 2 \text{ g L}^{-1} \) (as organic matter), which would shift insignificantly relative to the 5 g L\(^{-1}\) concentration used to determine the SUVAs. Furthermore, the observed decrease in SUVAs would require a chromatogram shift in the opposite direction to that observed for low AHA concentrations (Figure 3). During intermediate breakthrough (hump breakthrough), the SUVAs in all MW fractions increased relative to the influent solution (Figure 6), with the largest increases being associated with the \( >5000 \text{ Dalton} \) fractions. Upon full breakthrough, the SUVAs matched those of the influent solution (Figure 6). Notably, the “hump” in the breakthrough curves increased with flow rate (Figures 4 and 5), whereas the associated SUVAs were relatively independent of flow rate (Figure 6). This is likely due to greater AHA adsorption and dampening of the apparent height of the “hump” at the lower flow rate.

**Batch Experiments.** Since SUVAs depended in a complex fashion on the extent of AHA breakthrough in the sediment columns (and presumably also the extent of equilibration in batch experiments), it was not possible to accurately monitor sorption and potential fractionation of AHA (as C) in the batch and column experiments using SUVAs. It was observed, however, that HPSEC chromatograms of AHA were negligibly affected by equilibration with PCE DNAPL in the batch experiments, indicating negligible sorption of AHA to PCE DNAPL and negligible effect of solubilized PCE on the SUVAs of AHA MW fractions. The equilibrium solubilization constant for PCE by AHA (\( K_{\text{dom}} \)) was found to be 230 mL g\(^{-1}\), a value nearly a factor of 2 higher than the value of \( K_{\text{dom}} \) for nonpurified AHA (125 mL g\(^{-1}\)) \(^7\). The equilibrium constant, \( K_{\text{d,PCE}} \), for the distribution of PCE between the stationary phase and bulk solution increased negligibly relative to the value observed in the absence of AHA (0.0353 mLg\(^{-1}\)), indicating that adsorption of AHA to sediment negligibly affected PCE partitioning to that phase.

**Column Experiments.** At both flow rates, the concentration of dissolved PCE in the effluent solution of the residual-zone column prior to AHA breakthrough matched that expected from equilibrium dissolution of PCE in water (190 mg L\(^{-1}\)) (Figure 7). This result indicates that dissolution of residual PCE into AGW was not kinetically limited under the conditions of the column experiments. Shown for reference is the breakthrough of bulk AHA determined by totaling the

![Image 5](https://example.com/image5.png)

**FIGURE 5.** Breakthrough of four MW fractions of AHA in the series of three sediment columns at the high flow rate (0.187 cm/min). Concentrations were converted using SUVAs of the influent solution (sediment preequilibrated AHA). The dashed horizontal line indicates the influent concentration. Equalized time is described in the text. Selected MW fractions are shown for clarity.

![Image 6](https://example.com/image6.png)

**FIGURE 6.** SUVA versus MW for various stages of breakthrough in the up-gradient sediment column and the low flow rate (top) and high flow rate (bottom).

![Image 7](https://example.com/image7.png)

**FIGURE 7.** Breakthrough of solubilized PCE (open symbols) and bulk AHA (closed symbols) in the three-column series at the low flow rate. Mean breakthrough time of the conservative tracer is shown by the vertical line. Influent concentration of the solubilizing agent is shown by the dashed horizontal line at \( C/C_{\text{in}} = 1 \). Equilibrium concentration of solubilized PCE is shown by dashed horizontal line above \( C/C_{\text{solv}} \) PCE above 2.0. Equalized time and System Pore Volume are described in the text.

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concentrations (as C) of all AHA MW fractions after conversion of measured UV absorbance using SUVAs of sediment preequilibrated AHA. The bulk AHA concentrations therefore do not account for variations in SUVA that occurred during breakthrough, and so detailed comparison of AHA and PCE breakthrough would be inappropriate.

AHA-solubilized PCE breakthrough shows that dispersion plus AHA losses to the stationary phase in the up-gradient and residual-zone columns delayed the breakthrough of solubilized PCE relative to the mean tracer breakthrough (shown by the vertical line, Figure 7). At the low flow rate, the breakthrough concentration of AHA-solubilized PCE from the residual-zone column (Figure 7) reached the equilibrium value (shown by the dashed horizontal line) rapidly relative to what was observed previously in this system for a nonionic surfactant mixture (14). Given that a correction for variations in SUVA would retard rather than speed AHA breakthrough relative to what is shown in Figure 7 (SUVA were inflated during the "hump"), it is clear that breakthrough of solubilized PCE did not lag significantly behind the breakthrough of AHA, indicating that the loss of AHA from solution did not significantly alter the solubilizing capacity of the mixture.

AHA-solubilized PCE breakthrough in the residual-zone column was less retarded at the high flow rate relative to the low flow rate (Table 1). AHA-solubilized PCE mass in the down-gradient column (beyond what occurred in the residual-zone column) was also less retarded with increasing flow rate. These decreases were likely due to increased kinetic limitations on AHA adsorption to sediment with increasing flow rate.

### Discussion

#### Variations in SUVAs

The column experiments revealed cyclic alterations in the SUVAs of MW fractions of AHA that were not observed during static preequilibration with sediment. The decrease in SUVAs during early breakthrough in the column experiments may have been related to adsorption loss of AHA to sediment. Preferential loss of low MW components during early breakthrough was indicated by increased $M_w$ to 17 700 (low flow rate) and 13 600 (high flow rate), values significantly greater than those observed for the blank (13 200) and sediment preequilibrated (13 600) AHA solutions. It has been previously shown that lower MW components have much greater diffusivities and so reach sediment surfaces faster relative to larger MW components (19, 42). Decreased SUVAs of bulk humic acid solution have observed to occur in response to preferential adsorption of high MW components to metal oxides (23). However, it is not clear what mechanism would be responsible for the decreases in SUVAs of individual MW fractions observed in our study.

Increased SUVAs above the influent values during the "hump" portion of breakthrough could potentially result from displacement of the adsorbed lower MW components by larger MW components (22), resulting in enrichment of these lower MW components in the aqueous phase. However, as shown in Figure 8, at no time did the carbon mass of any MW fraction exceed that of the influent solution, indicating that no significant enrichment in the aqueous phase occurred for any MW fractions of AHA. It should be noted that the lines connecting the data in Figure 8 serve only to associate the data points, which are discrete representations of the carbon mass in each MW fraction. The corresponding values of $M_w$ were between 13 500 and 13 700 during the "hump" and "full" stages of breakthrough at both flow rates, excepting a value of 14 500 for "hump" breakthrough at the low flow rate. The similarity of these $M_w$ values to one another and to those of blank and sediment preequilibrated AHA further indicate that increased SUVAs during intermediate "hump" breakthrough did not result from displacement-driven enrichment of low MW fractions in the aqueous phase. Instead, increased SUVAs during intermediate breakthrough likely represents effects of AHA-driven leaching of sediment cations, as was observed in the batch experiments. The eventual return to influent SUVAs during full breakthrough indicates exhaustion of cation leaching from sediment. This return was not observed in batch experiments due to lack of replacement of the aqueous phase in those closed systems. Unfortunately, pH, conductance, and major cation concentrations were not monitored in column effluent samples due to inadequate sample volumes (14).
to their small volume, hence, further studies will be required to fully understand the mechanisms governing the observed changes in SUVA. The results indicate that decreased SUVAs during early breakthrough were associated with preferential adsorption of low MW components, whereas increased SUVAs during intermediate breakthrough were associated with AHA-driven leaching of sediment cations.

**AHA Transport Effects on PCE Solubilization.** Despite the inability to quantitatively correct for variations in SUVAs, the results indicate that transport behaviors in this DNAPL-contaminated sediment contrast strongly for AHA and nonionic surfactants. AHA adsorption to sediment did not affect partitioning of PCE to the stationary phase, whereas surface aggregation of the low MW (hydrophobic) nonionic surfactant oligomers on the sediment caused the formation of a hydrophobic surface phase on the sediment that increased $K_{D, PCE}$ by a factor of about 4 (17). With respect to sorption to DNAPL, AHA showed no measurable sorption to PCE, whereas the low MW nonionic surfactant oligomers partitioned to PCE DNAPL to extents that significantly decreased the solubilizing capacity of the nonionic surfactant mixture (14). It was observed that increased flow rate decreased the retardation of AHA-solubilized PCE exiting the residual-zone column, whereas it had been previously observed that increased flow rate increased the retardation of surfactant-solubilized PCE exiting this column, due to kinetic limitations of PCE dissolution-solubilization exceeding kinetic limitations on surfactant loss to DNAPL (14). Solubilization capacities of AHA and the nonionic surfactant mixtures for PCE also contrast strongly with the equilibrium constant for PCE distribution between water and the solubilizing agent being about a factor of 3 lower for AHA ($K_{d, W} = 230 \text{ mL g}^{-1}$) relative to the nonionic surfactant ($K_{d, mass} = 700 \text{ mL g}^{-1}$) (17).

Normalizing the mass of PCE exiting each column by the mass of agent (as C) introduced to the system (Table 1), allowed comparison of PCE removal efficiencies by AHA and the nonionic surfactant mixture previously examined in this system. After passage of 1.5 system pore volumes of solubilizing agent, the overall mass of PCE removed per mass of agent introduced to the system was similar for AHA and the nonionic surfactant at both flow rates. The similar performances by the two agents resulted mainly from loss of nonionic surfactant to PCE DNAPL, which compromised the solubilizing capacity of the surfactant mixture for PCE (14). At 2.5 system pore volumes, when the bulk of surfactant loss to sediment and DNAPL had largely ceased, the efficiency of the surfactant was about a factor of 2 greater than the efficiency of AHA due to the greater solubilizing capacity of the surfactant. Despite a factor of 3 greater PCE solubilizing capacity of the nonionic surfactant mixture relative to AHA, the DNAPL removal efficiencies of the two agents were similar during breakthrough, due to greater sorption fractionation of the surfactant during transport in this system.

The results indicate that humic acids can be as effective as some nonionic surfactant mixtures during the transient stages of a surfactant flush (during equilibration of the solubilizing agent with the sediment and DNAPL phases). However, the mass concentration of the solubilizing agents examined here (0.2–0.5% for the surfactant and AHA, respectively), were at least 1 order of magnitude lower than values typically used during a surfactant flush. The experiments described therefore emphasized the transient period of the flush relative to what would be observed at higher agent concentrations.

Concomitant lengthening of the flush period. It remains to be determined whether this context is realistic, and whether humic acids would show advantages over anionic surfactants in such a context.

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**Literature Cited**


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