Sorption of Naphthalene onto Natural and Surfactant-Amended Soils

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Abstract: Surfactant amendment has been proposed as a means to stabilize or mobilize groundwater contamination by modifying the soil's natural sorption characteristics in situ. The importance of the native soil's characteristics with regard to contaminant sorption and the effect of surfactant amendment were evaluated using three varied soil samples and naphthalene as a model contaminant. As expected, soils with high cationic exchange capacity and organic matter content tend to have the greatest ability to sorb naphthalene and the surfactant cetylpyridinium chloride. Micelle formation was noted in the presence of weakly sorbing natural soil, though not in the more reactive soil samples. Surfactant amendment significantly increased naphthalene sorption capacity for sterilized, nonreactive sand, increasing the partitioning coefficient, K_d, by 50%, and decreasing sorption among soils with high natural sorption capacity, partitioning naphthalene back into the aqueous phase.

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Introduction

Prior studies have demonstrated that surfactants can modify the sorptive capacity of soils (Crocker et al. 1995; Deitsch and Smith 1995; Edwards et al. 1991; Moon et al. 2003; Sheng et al. 1998). Because of their ability to affect the sorption and desorption of hydrophobic organic compounds, surfactants have potential for use in soil and groundwater treatment and protection. Surfactants are amphiphiles, possessing a hydrophobic hydrocarbon chain and a hydrophilic end, which may be positively charged, negatively charged, or neutral. As a result of this structure, a surfactant molecule may dissolve in water as a monomer, adsorb at an interface, or be incorporated with other surfactant molecules as part of a micelle (Edwards et al. 1991). At surfactant concentrations less than the critical micelle concentration (CMC), surfactant molecules exist predominantly in monomeric form, with some fraction being adsorbed at system interfaces. At surfactant concentrations greater than the CMC, additional surfactant is incorporated into the bulk solution through micelle formation (Martin et al. 1969).

Because of the amphiphilic nature of surfactants, they have potential for use in two remedial strategies: either to increase sorption onto soil surfaces, thereby creating an in situ permeable reactive barrier (Moon et al. 2003), or to increase contaminant mobility in soil washing or soil flushing by promoting the desorption of sorbed hydrophobic organic contaminants (McDermott et al. 1989; Moon et al. 2003; Nash and Traver 1986; Rajput et al. 1989). Sorption is enhanced by coating the surfaces of subsurface soils with strongly sorbing cationic surfactants, which can enhance the partitioning of hydrophobic contaminants out of the groundwater (Wagner et al. 1994). Mobilization strategies rely on anionic or nonionic surfactants, which are less likely to sorb to soil surfaces, thereby promoting the desorption of hydrophobic contaminants (Moon et al. 2003). The challenge in applying surfactants in soil and groundwater remediation is to understand the interaction between surfactants, soil, and contaminants, and to optimize conditions to promote the desired effect. To date there have been no definitive studies comparing the effect of different soil characteristics on surfactant applications in these remedial systems.

The goal of this study is to evaluate the effect of surfactants on the sorption of organic contaminants onto soil surfaces. The study was carried out by modifying three soils with the addition of cetylpyridinium chloride (CPC) to determine its impact on soil sorption capacity using the common hydrophobic organic contaminant, naphthalene. Three soil samples, which vary in cationic exchange capacity (CEC) and organic matter content, typically quantified by the fraction of organic carbon (f_{oc}), were used to study the interactions among CPC, soils, and naphthalene, and to better understand the conditions necessary for surfactant applications. Naphthalene sorption was compared between the three soil samples both before and after amendment with the surfactant CPC. While amendment with CPC was expected to increase naphthalene sorption, the effect of surfactant amendment was more complex, depending on soil characteristics, such as CEC and organic matter content, and naphthalene solution concentrations. Results of the study are expected to be useful in creating site conditions necessary for successful surfactant applications.

Methods and Materials

Chemical Reagents

Naphthalene (Fisher Scientific, Waltham, Massachusetts, 99.5%) was selected as the model groundwater contaminant because it is a commonly used representative of polycyclic aromatic hydrocarbons (PAHs), a class of contaminants that has critical bioavailability issues at numerous contaminated sites (Rittmann et al. 1994; Dzombak and Luthy 1984). Selection of a remedial strategy for

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Table 1. Soil Characteristic Parameters (Data Courtesy of Agri Analysis, Inc., Leola, Pennsylvania)

Soil	CEC (meq/100 g)	Organic matter (%)	Soil pH
A	0.3	0.4	5.5
B	8.6	1.7	4.0
C	2.9	0.1	7.2

PAH contamination often depends on the sorption/desorption characteristics of the soil-groundwater system.

Cetylpyridinium chloride ($C_{21}H_{38}ClN$) (Aldrich, St. Louis, Missouri) is a cationic surfactant with CMCs determined experimentally to be in the range of $3.6–8.3 \times 10^{-4}$ M (123.8–300.0 mg/L) (Kibbey and Hayes 1993; Mandal and Nair 1991; Monticone et al. 1994), with its micellar surface surrounded by positive charges. In solution, the apparent CMC decreases with increasing hydrocarbon concentration in solution (Monticone et al. 1994). The surfactant CPC is biodegradable by aquatic or soil-based microorganisms (Swisher 1970) and has, therefore, been used for separating anionic pollutants from the soil matrix by micelle surface binding (Baek and Yang 2004; Guo et al. 1997) via electrostatic attraction force.

Soil Samples

Three soil samples were selected to represent a range of conditions impacting naphthalene sorption and CPC amendment. Laboratory analyses were conducted by Agri Analysis, Inc. (Leola, Pennsylvania) to determine soil sample parameters: CEC, organic matter content, and soil pH (Table 1). The three soil samples include sand with a low CEC and organic content (Soil A), natural aquifer material with a high CEC and organic content (Soil B), and a standard embankment material with a moderate CEC but low organic content (Soil C).

Soil A, which was chosen to provide a relatively unreactive baseline, is the Mystic White II coarse sand ($d_{10} = 0.8$ mm) from the U.S. Silica Company (Berkeley Springs, West Virginia). It was prepared following the procedures from Murphy et al. (1997). First, trace contaminants were removed by washing with 0.25 M NaOH solution for 12 h, followed by 0.25 M HNO_3 for 12 h. Then, after thorough rinsing with deionized water to return the pH to approximately 7, the sand was autoclaved. Soil B is a natural aquifer material taken from drill cuttings at the Russell Road Landfill on the Marine Corps base in Quantico, Virginia. Cuttings were taken from the Quantico Formation (also known as the Quantico Slate), a layer of poorly metamorphosed slate composed of dark-gray to black, thinly foliated slate and chlorite-actinolite green schist. Soil C is of the type used by Maryland State Highway Administration for highway embankment construction and is classified as SC (sand with clay) by the United Soil Classification System. Because of the presence of clay, Soil C consists of particles that are much finer than Soils A and B (36% fine particles).

Amended-Soil Preparation Method

CPC sorption capacity was determined for all three soils by adding CPC in distilled water solutions of 1.7, 3.4, 10.2, 17, 23.8, 34, 102, and 170 mg/L in duplicate to 40 mL amber vials containing 1 g of soil and filled with solution to capacity. The pH value of the solutions was adjusted to 9, 2 mL were removed and analyzed to determine the initial CPC concentration, and the samples were rotated end-over-end for 48 h. A mixing time of 48 h was assumed adequate to reach equilibrium based on similar studies (Burris and Antworth 1992) and preliminary experiments. Subsequently, the samples were centrifuged at 1,500 revolutions per minute (rpm) for 10 min, filtered through a 0.2 μm polytetrafluoroethylene filter (Pall Acrodisc), and the final CPC concentration determined by ultraviolet-visible (UV-Vis) spectrophotometry. Sorption capacity was determined as the difference between the initial and equilibrium CPC concentrations.

CPC modified soils were prepared in a large batch sorption experiment by adding 18 g of each soil type to 1 L narrow mouth bottles, followed by 1 L of 1×10^{-4} M (34 mg/L) CPC-deionized water solution, adjusted to a pH of 9. This concentration was chosen because it showed the best results in the CPC sorption isotherms and is below the CMC of 123.8–300.0 mg/L (Kibbey and Hayes 1993; Mandal and Nair 1991; Monticone et al. 1994). Small aliquots of the solution were taken and analyzed spectrophotometrically to determine the initial CPC concentration. Bottles were mixed on a horizontal shaker table for 48 h, after which time, samples were filtered as described above and analyzed with the spectrophotometer to determine the final CPC concentration, and calculate the amount of CPC sorbed. Amended soils were then drained, oven dried at 110°C for 2 days, and cooled to room temperature before proceeding with naphthalene sorption studies.

Naphthalene Sorption onto Soils Experiments

Prior to performing the sorption isotherm experiments, the equilibration time for naphthalene sorption was determined experimentally. Soil C was used to determine equilibration time based on its low organic matter content and theoretical low sorption rate. Samples nominally containing 1.0 g of Soil C and 40 mL of 6.38 mg/L naphthalene solution in 40 mL amber vials with no headspace were mixed end-over-end for intervals of 8, 20, 32, 54, 78, 100, and 124 h in duplicate. At each interval, duplicate samples were removed and centrifuged at 1,500 rpm. A 1 mL sample of supernatant was taken from each vial for naphthalene analysis by gas chromatography (GC). GC analysis was performed by liquid-liquid extraction and splitless injection on a Hewlett-Packard (HP) (Wilmington, Delaware) GC model 6890 equipped with a flame ionization detector (FID), following the method outlined by Seagren and Moore (2003). Experimental results suggest that naphthalene sorption reached equilibrium after 100 h. Therefore, samples were rotated end-over-end for 124 h in all naphthalene sorption experiments to ensure equilibrium was reached. Sorption isotherms were determined for each soil type by adding naphthalene solutions of 0.5, 1, 2, 3, 4, 5, 7.5, 10, 15, and 20 mg/L in duplicate to 40 mL amber vials containing 1 g of soils and no headspace. The initial naphthalene concentration was determined by removing 2 mL and analyzing via spectrofluorophotometry. After 124 h, the samples were centrifuged and filtered as described above, and the final naphthalene concentration determined by spectrofluorophotometry. Naphthalene sorption per mass of soil was obtained by the concentration difference method, and sorption isotherms were prepared for both the unmodified soils and those amended with CPC.

Analytical Methods

All CPC measurements were made by ultraviolet-visible spectrophotometry using a Shimadzu UV160U spectrophotometer (Tokyo, Japan) at wavelength 258 nm (Fox and Whitesell 2003; Chakraborty et al. 2005) with 2 mL of supernatant. CPC detection limit using spectrophotometry was found to be 2.0 mg/L. Naphthalene concentrations for sorption isotherms were analyzed by spectrofluorophotometry using the method described by Song and Seagren (2008). Specifically, measurements were made using a Shimadzu RF-5301PC spectrofluorophotometer with an excitation wavelength of 273 nm and an emission wavelength of 336 nm. The detection limit for naphthalene using the spectrofluorophotometric method was experimentally determined to be 0.0165 mg/L (Demirkan et al. 2011).

Results and Discussion

CPC Amendment of Soil

CPC sorption on the three soils followed two patterns, with Soil A displaying a linear isotherm and Soils B and C absorbing all CPC from solution. CPC sorption for Soil A showed a weakly sloped linear isotherm ($K_d = 0.020$ L/g, $R^2 = 0.78$) for low (<50 mg/L) initial CPC concentrations, whereas samples with high initial CPC concentrations (102 mg/L and 170 mg/L) produced a significant increase in aqueous CPC. Because this behavior was only detected for a poorly adsorbing soil at high concentrations, near the CMC (123.8–300.0 mg/L) (Kibbey and Hayes 1993; Monticone et al. 1994; Sata 1957), it is attributed to the formation of micelles, which can cause UV spectrophotometer detection problems (Dominguez et al. 1997; Suzuki 1970). Because of this, Soil A samples with initial CPC concentrations above 34.0 mg/L were not considered for the remainder of this study. For the measurable CPC concentration range, the highest calculated sorbed CPC concentration on Soil A was 0.6 mg CPC/g soil.

Soils B and C have significantly higher CPC sorption capacity because of their high CEC values and/or high organic matter contents. In the Soil B and C sorption tests, CPC equilibrium concentrations were reduced to below detection limit (2 mg/L), with no detectable pattern relative to initial CPC concentrations, including those samples with initial concentrations greater than 100 mg/L. It follows that CPC sorption on these soils was limited by the amount of CPC in solution (1.7–170 mg/L), which remained well below the soil's theoretical sorption capacity of 731 and 247 mg/L CPC for Soils B and C, respectively, assuming 100% coverage of cation exchange sites. For the maximum CPC concentration tested (170 mg/L), the mean sorbed CPC concentrations were 6.71 and 6.41 mg CPC/g for Soils B and C, respectively.

Naphthalene Sorption onto Unmodified Soils

Naphthalene sorption isotherms for unmodified soil demonstrate a difference in sorption capacity related to soil properties. The results also provide an important baseline for comparison with the naphthalene sorption capacity of the surfactant-amended material.

Soil A, the sterilized coarse sand, exhibited relatively low naphthalene sorption because of its low CEC and organic matter (Table 1). Within the test range of 0.5–20 mg/L, this soil showed no detectable sorption between 0.5 and 7.0 mg/L; however, naphthalene was removed from solution by sorption at concentrations greater than 11 mg/L (Fig. 1). The experimental isotherm is approximately linear ($R^2 = 0.42$), with a K_d value of 0.0034 L/g (Table 2), similar to other naphthalene sorption studies with sterile sand (Warith et al. 1999). Soil B, the natural aquifer material, showed the greatest capacity for naphthalene sorption, resulting in a linear isotherm ($R^2 = 0.91$), with K_d of 0.18 L/g (Table 2, Fig. 1). This is likely caused by Soil B's high organic matter content, with additional sorption potentially related to the high CEC, which is consistent with the observation of organic compounds partitioning into an organic phase consisting of polymeric natural organic materials associated with a mineral phase (Chiou et al. 1983). Soil C, a typical highway fill material (sand with clay), has an intermediate capacity for naphthalene sorption, with a linear partition coefficient similar to Soil B ($K_d = 0.13$ L/g, $R^2 = 0.89$; Table 2, Fig. 1).

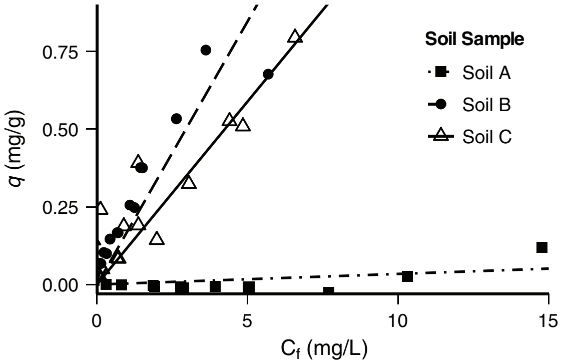

Fig. 1. Naphthalene sorption isotherms for unmodified Soils A, B, and C, with the sorbed concentration at equilibrium, q, plotted as a function of the final equilibrium aqueous concentration, C_f; each data point represents results from a single vial; lines are best-fit linear regressions through the data

Table 2. Linear Partition Coefficient (K_d) for Naphthalene Sorption onto Natural and Surfactant Modified Soil

Soil	Natural (L/g)	Surfactant-modified (L/g)	Change (%)
A	0.0034	0.0051	50.3
B	0.18	0.053	(−70.6)
C	0.13	0.041	(−68.5)

The unmodified naphthalene sorption results are consistent with the hypothesis that soils with high organic matter content (Soil B) and/or cationic exchange capacity (Soils B and C) produce the greatest naphthalene sorption capacity. As reviewed by Ball et al. (1997), surface adsorption to mineral surfaces may be as important as partitioning into a natural organic phase in some situations, such as when very little organic matter is present (e.g., Ball and Roberts 1991), and when an especially strong adsorbing phase, such as kerogen or shale, is present (e.g., Weber et al. 1992). Consistently, even though Soil C has the lowest organic matter content, it is substantially finer grained than the other two soils tested, providing more surface area per gram of material, which may also contribute to its sorption capacity, in addition to that of an intermediate CEC. Accordingly, the observed naphthalene sorption capacities of Soils B and C are much higher than that of Soil A.

Naphthalene Sorption onto Soils Amended by CPC

Analysis of CPC-modified Soil A supports the hypothesis that the addition of cationic surfactants increases soil sorption capabilities. While native Soil A produced undetectable sorption until naphthalene concentrations were rather high (>7.5 mg/L), surfactant-modified Soil A produced detectable sorption across all concentrations (Fig. 2). The K_d value for CPC-modified Soil A is 0.0051 L/g ($R^2 = 0.69$), an increase of approximately 50% when compared to unmodified Soil A (0.0034 L/g, Table 2). This corresponds to an increase in sorbed fraction from 7.8 to 11.3% by mass, which is a significant increase though it still remains much less than the sorption capacity of Soils B and C. The increase of sorption capacity of CPC-amended Soil A is consistent with the results found by Steinberg et al. (1999), who observed enhanced sorption of benzene (at moisture contents greater than ~1–1.5%) on surfactant-treated soils, resulting from the formation of a hydrophobic region or layer on the surface of the soil.

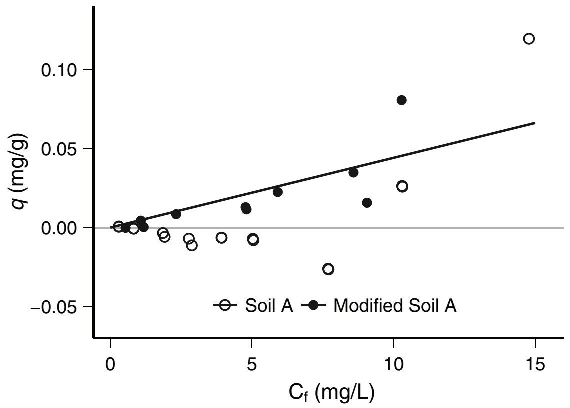

Fig. 2. Naphthalene sorption isotherms for surfactant-modified and natural Soil A, with the sorbed concentration at equilibrium, q, plotted as a function of the final equilibrium aqueous concentration, C_f; each data point represents results from a single vial; lines are best-fit linear regressions through the data

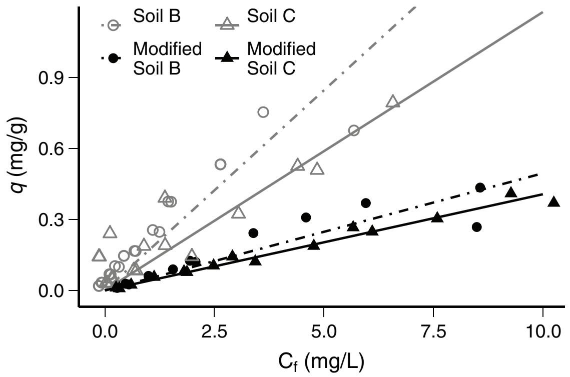

Fig. 3. Naphthalene sorption isotherms for surfactant-modified and natural Soils B and C, with the sorbed concentration at equilibrium, q, plotted as a function of the final equilibrium aqueous concentration, C_f; each data point represents the results from a single vial; lines are best-fit linear regressions through the data

In comparison, addition of surfactant to Soils B and C, which have a naturally high capacity for naphthalene sorption, decreased the soils' naphthalene sorption capacity (Fig. 3). The reduction of K_d in these soils by 29–32% reduced the fraction of sorbed naphthalene from 76.5–81.8 to 50.6–57.0%. The physical and chemical processes driving this decrease are complex (Luthy et al. 1997) and would require a more mechanistic study. However, based on these batch sorption results and laboratory observations, it appears that CPC desorbed from the soil surface, enhancing the solubility of naphthalene. This explanation was supported by noticeable foaming in syringes used to measure the supernatant. As there was no surfactant in solution initially, this foaming could only be explained by surfactant desorption. This is not surprising, as the sorption of organic cations to soil has been proven to be reversible (Brown and Burris 1996). Surfactant desorption was further confirmed by testing two supernatant samples of each soil type for the presence of CPC after equilibration using the methods described previously. Supernatant samples from Soils A, B, and C contained an average of 7.1, 15.8, and 13.7 mg/L CPC, respectively, which corresponds to desorption of 78.9, 49.5, and 42.1% from the original soil-bound CPC. These values confirm that CPC desorbed from the soil surface in significant amounts. The greatest fraction of CPC desorption occurred with the relatively unreactive Soil A. Nevertheless, for CPC-amended Soil A, there was still an increase in the sorption of naphthalene, as discussed above, because the original sorption capacity was so low that any remaining sorbed CPC increased the amount of naphthalene sorption. In comparison, for already reactive Soils B and C with naturally sorbed fractions of 81.8 and 76.5%, respectively, the desorbed aqueous CPC allowed for higher naphthalene partitioning into the solution, equilibrating so that nearly equal parts naphthalene were sorbed and in solution. Similar results were found by Crocker et al. (1995), who showed rapid desorption of naphthalene on hexadecyltrimethylammonium (HDTMA)-modified soils when changes were made to the aqueous solution.

Conclusions

This study was designed to evaluate the use of surfactants as they apply to sorption and desorption of hydrocarbon contaminants on soil surfaces. Batch sorption experiments with three soils confirmed that soils with high CEC and organic matter content have a greater capacity for both naphthalene and surfactant sorption, and therefore higher partition coefficients, K_d. Importantly, in the presence of relatively unreactive soils, i.e., low CEC and organic matter content, micelle formation occurs at the CMC, while in the presence of highly sorptive soils, CPC is sorbed onto soil surface because of the higher sorption capacity, and micelles do not form at initial concentrations close to the CMC.

The effect of surfactant amendment on soil's ability to sorb hydrophobic organic compounds showed a more complex relationship. For soils with low natural sorption capacity (low CEC, low organic matter content), cationic surfactants tend to increase sorption significantly. In the case of sterilized coarse sand in this experiment, the partition coefficient increased by 50% from 0.0034 to 0.0051 L/g because of the addition of a CPC layer. This increase remains an order of magnitude below the other natural soils used in this study, which may still limit its effectiveness as a permeable reactive barrier. For soils with high sorption capacity, such as the natural aquifer cuttings and embankment fill material tested in this study, surfactant instead tends to desorb from the surfactant-modified soil surface, resulting in sufficiently high aqueous concentrations to cause a decrease in the naphthalene sorption capacity.

Surfactants have great potential for modifying soil characteristics in remediation applications requiring enhanced sorption, such as in situ permeable reactive barriers, or applications requiring desorption, such as soil washing or soil flushing. But engineers must be cognizant of the native soil and surfactant interaction properties prior to designing a remedial approach using cationic surfactants. This study evaluates a small sample of potential soil-surfactant-hydrocarbon combinations and attempts to describe the findings based on presumed mechanisms to generalize the results. However, additional research is needed to thoroughly examine the full range of soils, surfactants, and hydrocarbon compounds; to identify the characteristics that interact to control sorption; and to evaluate the long-term stability of compounds bound to a surfactant layer.

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