Development of a Surrogate Sediment To Study the Mechanisms Responsible for Adsorption/Desorption Hysteresis

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A surrogate sediment was developed to reduce some of the complexity in the structural aspects of the adsorbed organic carbon phase. Layers of an anionic surfactant were sorbed to colloidal anatase to produce an organic carbon phase that had hydrophobic regions and resisted desorption. The surrogate is verified as a model sediment by comparing the results of contaminant [2,2′,5,5′- tetrachlorobiphenyl (PCB) and naphthalene] adsorption and desorption batch experiments to the results of similar experiments performed on a well-studied natural sediment. The surrogate exhibited adsorption of contaminants via a hydrophobic interaction in the same magnitude as to a natural sediment for the two different hydrophobic organic contaminants in 0.1 or 0.15 M NaCl solution. The sorption of PCB to the surrogate at varied organic carbon contents was observed to follow a linear adsorption isotherm. Desorption experiments were conducted by successive dilutions. Both the surrogate and natural sediment were observed to exhibit similar desorption behavior. The solution concentration during desorption was lower than predicted by the adsorption isotherm and remained unchanged from 4 h to 168 days. The heterogeneous nature of sediments should be greatly reduced in the surrogate yet desorption still appears to be low.

Introduction

The adsorption—desorption characteristics of hydrophobic organic chemicals play an important role in their fate and transport. The fate of these chemicals is largely determined by their sorption, which is thought to occur as a result of partitioning into the soil or sediment. Many of these hydrophobic chemicals are observed to persist in the environment even though they are volatile or highly degradable. This persistence exacerbates the remediation or cleanup of these often regulated compounds. In transport modeling, sorption is often simplified by assuming a linear and reversible adsorption isotherm. This assumption has been questioned due to experimental and field results, which cannot be adequately modeled by this approach. Chemicals with various hydrophobicities, e.g., polychlorinated biphenyls, pesticides, polynuclear aromatic hydrocarbons, and halogenated aliphatic hydrocarbons, have been found to resist desorption ([1—6]). The sorbents in these studies include topsoil, aquifer materials, and sediments with different particle sizes, mineral compositions, surface areas, and organic matter contents. The desorption from this resistant fraction is often very slow, with an estimated half-life on the order of months to many years ([2—4, 7—14]). The size of this resistant fraction may increase with time as the chemical remains on the sediment ([2, 15—17]). The desorption of the resistant fraction has been observed to inversely depend on the applied concentration. The processes by which organic compounds become increasingly resistant to desorption in soil and sediments are poorly understood. Two interpretations are used commonly to account for the differences between simple local linear equilibrium and observed adsorption and desorption behavior of hydrophobic hydrocarbons: slow kinetics and irreversibility ([7—9, 11, 15, 18, 19]). In addition to these two interpretations, numerous other explanations have been advanced, including various experimental artifacts, adsorbate heterogeneity, nonlinear Freundlich or Langmuir behavior, to mention a few [see Brusseau and Rao ([15]) for an excellent review of these effects]. Many studies have been performed to characterize the adsorption and desorption interaction mechanisms. However, the complex nature of soils and sediments has led to difficulty in determining the mechanisms that govern the sorption and release of these hydrophobic compounds. The goal of the present research has been to develop a simplified surrogate adsorption—desorption system to simulate the actual soil and sediment interactions with hydrophobic hydrocarbons and to verify it by comparison of the sorption behavior of two contaminants with that of a well-studied natural sediment (Lula). To accomplish this, the characteristics of soils and sediments that contribute to their adsorption—desorption behavior must be identified.

Soil is comprised of aggregated colloids and particulate materials. Colloids in aquatic systems exist as a variety of inorganic and organic materials ([20]). In the colloidal phase, organic matter can occur as individual macromolecules (e.g., dissolved organic matter: humic and fulvic acid) or associated with mineral oxide sols ([21]). Dissolved humic acids may form pseudomicelles, which are similar to true surfactant micelles since they form a hydrophobic microenvironment ([22, 23]). However, this environment may be larger and looser than true micelles due to structural constraints of the humic acid ([24]). Rearrangement of the soil matrix, such as in humic acid aggregates, as well as formation and deformation of colloidal aggregates can occur due to changes in environmental conditions such as pH and ionic strength. Depending on the salt concentration, humic acids may form hydrophobic aggregates that phase separate (high salt concentration) or form localized hydrophobic microenvironments (at lesser salt concentrations). This behavior may not be true of all humic acids

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since molecular makeup, such as aromaticity and aliphatic content, may effect their microorganization (*24*). This would suggest that the particle-associated contaminants may be trapped inside the humic or soil aggregates.

Both organic matter and ionic surfactants can adsorb to charged surfaces in the environment. Both sorbed natural organic matter and man-made surfactants that contain organic carbon have been observed to remove hydrophobic organic contaminants from solution (*25–29*). There is considerable uncertainty about the structure and manner in which natural organic matter is adsorbed or attached to the inorganic portion of soil. There is less uncertainty about the mechanism of attachment of ionic surfactants to inorganic materials, and for this reason a surfactant-coated mineral has been used to study the mechanism of hydrocarbon adsorption and desorption. The plot of the adsorption isotherm for ionic surfactants to a charged surface can be described by three regions (*30–33*). At low concentrations (below the critical micelle concentration, cmc), ionic surfactants adsorb due to electrostatic forces between the charged surface and the oppositely charged surfactant ion (region 1) (*34*). For adsorption under high salt concentrations, region 1 is not present due to competition with small salt ions (*35*). At higher surfactant concentrations, hemicelles begin to form due to interactions between the hydrophobic tails of the surfactant molecules, which result in a rapid increase in the adsorption of surfactant (region 2). Hemicelles are surface aggregates of adsorbed surfactant ions that are formed at a bulk concentration considerably lower than the cmc (*36, 37*). The rapid increase in adsorption during this stage is due to both electrostatic forces between the surface and the surfactant ion with additional adsorption due to hydrophobic attraction between the tail groups of the surfactants forming hemicelles. After enough surfactant has adsorbed to the surface, it becomes neutralized, and surfactant molecules are no longer attracted to the it by electrostatic forces. At this point, the adsorption of surfactant levels off (region 3) since only hydrophobic interactions between the tail groups are present. At high initial surfactant concentrations (above the cmc), the surfactant probably exists as a bilayer or admicelle and the charge of the surface is now that of the surfactant (*38*).

The purpose of this study was to develop a surrogate sediment that has adsorption–desorption behavior similar to that of a natural sediment. The following sediment characteristics were used to design the surrogate sediment: (1) sediments are composed of organic and inorganic materials; (2) the organic matter can exist adsorbed to charged surfaces; and (3) hydrophobic organic contaminants have been observed to partition to soil relative to the amount of organic carbon they contain. The surrogate designed to meet these characteristics was an anionic surfactant sorbed to colloidal anatase, which is considered to be nonporous (*6*) and positively charged at a low pH (*39*). The anionic surfactant chosen was sodium dodecyl benzene sulfonate. The intention of the authors was not to use a structural model for a humic material but to use a surrogate that would mimic the characteristics of humic material responsible for its ability to adsorb and desorb hydrophobic organic contaminants. The anionic surfactant was sorbed at concentrations high enough to form hemicelles on the particles. This produced a particle surface with an adsorbed organic carbon phase possessing a hydrophobic interior. 2,2′,5,5′-Tetrachlorobiphenyl and naphthalene were used as the model contaminants. To establish the surrogate sediment, the adsorption and desorption behavior of the above-mentioned contaminants were compared with a natural sediment.

Experimental Section

Sorbents. The charged inorganic phase used to sorb the organic phase to prepare a surrogate sediment was TiO_2 obtained from Aldrich Chemical Co. (Milwaukee, WI), confirmed by X-ray diffraction to be 99.9% pure anatase. The BET surface area is 9.47 m^2/g determined by adsorption of nitrogen gas (Micromeritics, Inc.). The average particle diameter is 393 nm and has low polydispersivity measured by photon correlation spectroscopy at an angle of 60° on a Malvern System 4700 (Malvern Instruments Inc.). The microporosity of the particles is negligible, as determined by mercury porisimetry (Micromeritics, Inc.). Anatase was reported to have a zero point of charge of 6.3 pH with a maximum charge density of about 9.9 $\times$ 10 $^{-7}$ C/m^2 (*40*).

The source of the natural sediment used for comparison was located near the margin of a flood plain of a small river at the Johnson Ranch in Lula, OK. The sediment has a 0.27% organic carbon content. Further information and preparation methods for this soil have been described in the literature (*8, 41*).

Sorbates and Chemicals. Sodium dodecyl benzene sulfonate (SDBS, $C_{12}H_{25}C_6H_4SO_3^-$ Na^+), a commercial anionic surfactant, was used as a sorbed organic carbon source. SDBS (Rhodocal DS 10 formerly SiponateDS 10) was obtained in dry flake form from Alcolac, now Rhone-Poulenc. The SDBS was 96% active and used without further purification. SDBS solutions were prepared in concentrations ranging from 0.109 to 25.3 mM in 0.10 M sodium chloride (Fisher Scientific), in 0.01 M sodium acetate (Mallinckrodt), and with 0.01 M sodium azide (Kodak) as a bacterial inhibitor (adjusted to a pH of 2.5 with HCl). No difference in adsorption of surfactant or contaminants was observed with early experiments using formaldehyde compared to sodium azide. The cmc was measured by monitoring the air–water surface tension changes for different surfactant concentrations using a ring tensiometer (CSC Scientific DuNOUY Model).

The contaminants used were radiolabeled [^{14}C]-2,2′,5,5′-tetrachlorobiphenyl (PCB) and [^{14}C]naphthalene (Sigma Chemical Co.), which could be detected at low concentrations. Upon receipt, both the radiolabeled compounds were tested for identity and purity by comparing the GC retention time of cold compound isomers to that of ^{14}C-labeled compounds. The radiolabeled PCB had a specific activity of 12.2 mCi/mmol and was diluted in methanol to prepare a stock solution of 9.88 mCi/L (or 236.26 mg/L). PCB solution concentrations ranged from 1 to 13 μg/L prepared in 0.10 M sodium chloride (Fisher Scientific), in 0.01 M sodium acetate (Mallinckrodt), and with 0.01 M sodium azide (Kodak) as a bacterial inhibitor (adjusted to a pH of 2.5 with HCl) for surrogate sediment experiments. A 12 μg/L PCB solution was prepared in 0.15 M sodium chloride and 0.025 M sodium monobasic phosphate (adjusted to a pH 5.9) for Lula sediment experiments. The radiolabeled naphthalene had a specific activity of 6.8 mCi/mmol and was diluted in methanol to prepare a stock solution of 11.93 mCi/L (or 266.7 mg/L). A solution of 135 μg/L naphthalene was prepared in 0.10 M sodium chloride (Fisher Scientific), in 0.01 M sodium acetate (Mallinckrodt), and with 0.01M sodium azide (Kodak) as a bacterial inhibitor (adjusted to

a pH of 2.5 with HCl). Periodically the purity and concentration of PCB were checked by GC. Chemicals used in this research were reagent grade or better except where specified otherwise. All solutions were prepared with Millipore water (Millipore Milli-Q50).

Adsorption−Desorption Experiments. The adsorption−desorption experiments were performed in batch reactors that consisted of an amber glass vial (Fisher Scientific Catalog No. 03-339-21N) of approximately 45-mL total volume and capped with a Teflon septum (Pierce). Two large amber 8-oz. bottles (Porpak No. 7720B obtained from Fisher Scientific and made by All-Pak) were used for surfactant adsorption−desorption experiments. All vials and bottles were cleaned with a 2% detergent solution (Pierce RBS 35, IL), heated to 50 °C, and rinsed with deionized water. The vials were rinsed with acetone (EM Science), dried, rinsed in trichlorotrifluoroethane (Fisher Scientific), and oven baked at 200 °C for 6 h. Previously, all glassware was soaked in Micro (Baxter, NJ) for 15 min, rinsed with deionized water, rinsed with acetone, and dried at 200 °C for several hours in a constant temperature oven. However, adsorption of PCB to the vessel alone using the initial cleaning procedure resulted in an 80% loss of PCB to the apparatus. Altering the cleaning procedure and using new vessels reduced the loss to the vessel to between 5 and 11% for PCB and below 5% for naphthalene.

Surfactant adsorptions and desorptions were performed to develop an organic coated substrate for later use in contaminant adsorption and desorption experiments. Initially (for surfactant adsorption), 4 or 40 g of dry TiO₂ was added to the vessel, followed by the addition of 40 mL or 180 mL of 0.109−25.3 mM surfactant solution. The vials were placed in a shaker bath (Yamato, Model 1290, Japan), which was operated at low speed and room temperature. After the desired contact time, the solution and solid phase were separated by centrifugation at $300-1000g$ (international clinical centrifuge, W. H. Curtin Co.) for 15 min. A sample of the solution was analyzed for SDBS by UV absorbance at 261 nm (Varian spectrophotometer Model DMS 100). After initial adsorption, samples were either desorbed or another successive adsorption was performed by replacement of 85−90% (determined by weight) of the solution with electrolyte or fresh surfactant solution of the same initial concentration. All vials were shaken after replacement of solution. The successive adsorption experiments were later desorbed in the same manner as described previously. The adsorption and desorption times varied from 2 h to 7 days. From one to seven successive adsorptions were performed, and 5−15 desorptions were performed following the desired number of successive adsorption steps.

The solid phase concentration of SDBS, Γ (μmol/m²), was calculated from the difference in solution phase concentrations:

$$\Gamma = (C_I - C_a)\frac{V_W}{W_S SSA} \qquad (1)$$

where C_I is the initial surfactant concentration (μM), C_a is the surfactant concentration in the vial after adsorption (μM), V_W is the volume of solution (L), W_S is the mass of TiO₂ (g), and SSA is the specific surface area of TiO₂ (m²/g). Also, at various times the surfactant concentration on the solid was measured by the stripping surfactant off TiO₂ by raising the pH, lowering the ionic strength, and measuring the resulting solution on a Varian UV spectrophotometer (Model DMS 100).

Contaminant adsorption−desorption experiments were performed using the previously described batch reactors. Four grams (dry weight) of sorbent was placed in each vial followed by the addition of 40 mL of the desired concentration of contaminant. Varied sorbents were used either for verification of the surrogate as a model adsorbent or as controls. The sorbent was one of the following: Lula sediment, nonsurfactant-coated anatase, or a concentrated wet slurry of anatase with varied solid phase concentrations of surfactant. The varied solid phase surfactant concentrations were produced by the successive adsorption of surfactant followed by several desorption steps to remove excess surfactant from the solution and or solid phase. The removal of surfactant from the surface may produce a surface with a combination of monolayer, bilayers, or admicelles. The vials were placed on a horizontal shaker or tumbled end over end for desired contact times. No difference in sorption was observed with the different shaking methods. Quoted from Pignatello and Xing (*42*): "Film diffusion is potentially rate-limiting for the initial fast stage of sorption; but is not likely to be important in long-term phenomena we have been considering". The same should be true for the experiments in this study. The samples were again separated by centrifugation, and the solution phase concentration of contaminant was analyzed by liquid scintillation counting (Beckman LS 3801). After adsorption, desorption experiments were performed by successive replacement of electrolyte solution; for the TiO₂ surrogate sediments, 90−95% of the water was replaced, and for the Lula sediments, 75% of the water was replaced in each desorption step. The samples were again separated by centrifugation, and the solution phase concentration of contaminant was analyzed by liquid scintillation counting (Beckman LS 3801). The adsorption contact times varied from 15 min to 6.5 days while the desorption times varied from 15 min to 168 days. From 4 to 19 desorption steps were performed following each adsorption step. PCB adsorption−desorption experiments were performed on varied organic carbon (OC) contents in separate reactors and are listed in Table 1.

Solvent Extraction. The mass balance was determined by extracting the PCB off the solid with acetone at the end of adsorption−desorption experiments. A small amount of pore water (about 5% v/v) was left in the compacted solid after the solution was removed and before the addition of acetone. The amount of PCB recovered from the acetone extraction was confirmed to be 2,2′,5,5′-tetrachlorobiphenyl by GC/ECD (Hewlett Packard) analysis.

Results and Discussion

The adsorption−desorption behavior and cmc of the surfactant were studied to gain insight into the structure of the adsorbed layer and to create a surrogate that can adsorb and desorb hydrophobic contaminants in a similar manner as a natural sediment.

Critical Micelle Concentration (cmc). The surface tension of SDBS solution in 0.1 M NaCl at a pH of 2.5 was measured at varying surfactant concentrations. From the reduction in surface tension measurements with increasing concentration, a cmc of 75 mg/L (or 0.215 mM) was determined. The measured cmc is similar to the literature values of 34 mg/L (or 0.097 mM) for SDBS at 0.1 M ionic strength and pH 7.9 (*5*) and 250 mg/L (or 0.768 mM) at 0.01

Summary of PCB and Naphthalene Adsorption Experiments onto Surfactant-Coated Anatase and Lula Sediment

| experiment no.	organic carbon content (%)	adsorption time (days)	$C_{initial}$ (μg/mL)	C_{aq} (μg/mL)	$q_{adsorbed}$ (μg/g)	K_p (cm³/g)	log K_{oc}
			PCB on SDBS-Coated Anatase				
1	0.046	0.50	0.01057	0.00482	0.0534	11.08	4.38
2	0.089	0.50	0.01057	0.00352	0.0665	18.88	4.33
3	0.097	0.50	0.01059	0.00339	0.0673	19.84	4.31
4	0.488	0.50	0.01059	0.00104	0.0936	89.81	4.27
5	0.264	0.63	0.01057	0.00163	0.0853	52.19	4.30
6	0.570	0.0104	0.01165	0.0012	0.0996	83	4.16
7	0.575	0.073	0.01165	0.0015	0.0979	65.3	4.06
8	0.572	0.135	0.01165	0.00153	0.0979	64	4.05
9	0.568	0.177	0.01165	0.0014	0.102	72.9	4.11
10	0.575	1	0.01165	0.00081	0.1053	130.2	4.36
11	0.568	0.99	0.01165	0.00099	0.1017	102.4	4.26
12	0.540	6.5	0.01322	0.00112	0.1206	107.5	4.30
			PCB on Lula Sediment				
L1	0.270	1	0.01212	0.00173	0.0986	56.84	4.32
L2	0.270	1	0.01212	0.00161	0.0979	60.83	4.35
			Naphthalene on SDBS-Coated Anatase				
N	0.591	1	0.1348	0.0775	0.438	5.648	2.98
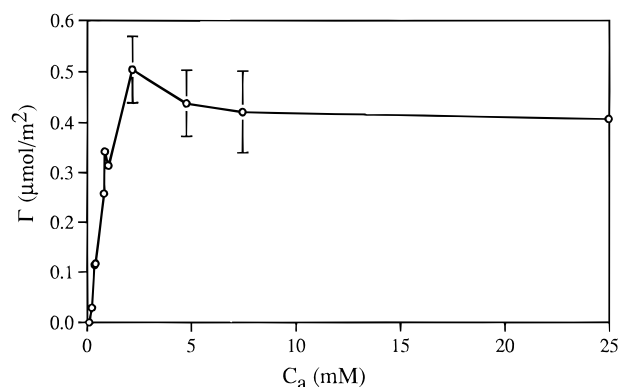
FIGURE 1. Adsorption of SDBS onto anatase at pH 2.5 and 0.1 M NaCl, where Ca is the equilibrium solute phase SDBS concentration and Γ is the solid phase SDBS concentration.
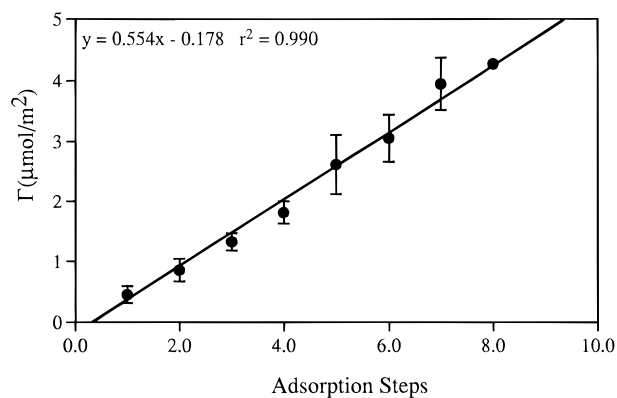

FIGURE 2. Cumulative adsorption of SDBS on to anatase versus successive adsorption steps. All experiments were performed in 0.1 M NaCl at a pH of 2.5 and various initial SDBS solution concentrations. For the first step, the average adsorption over a concentration range of 2.2−25 mM was 0.42 ± 0.14 μmol/m². For the second adsorption step, the initial concentration ranged from 2.2 to 7.5 mM. The other successive adsorption steps are averaged values for a concentration range of 4.5−7.5 mM. The standard deviation is indicated by the vertical bands through the points.

M NaCl (*43*). The cmc of SDBS in deionized water is reported as 414 mg/L (or 1.2 mM) (*44*). The reduction of the cmc values with increasing salt concentration is consistent with prevalent theory and observations (*45, 46*).

Adsorption of SDBS. The adsorption isotherm of SDBS in 0.1 M NaCl pH 2.5 solution to anatase is plotted in Figure 1. The adsorption appeared to reach equilibrium in 2 h and remained unchanged for 7 days. The adsorption of SDBS to anatase reached a plateau at about 700 mg/L (2.15 mM), and the maximum solid phase concentration of SDBS was between 0.407 and 0.504 μmol/m², which corresponds to 4.5×10^{-7} C/m² of anatase and is about equal to half the estimated charge on the solid (*40*). This is similar to the amount found by Siracusa and Somasundaran (*5*) for SDBS adsorption onto kaolinite: 0.816 μmol/m² or 8.1×10^{-7} C/m². As described in the Introduction, this is a typical shape for an adsorption isotherm of an anionic surfactant to a positively charged solid. This behavior is illustrated by the steep incline while the surfactant is attracted by both electrostatic and hydrophobic interactions followed by a leveling off as the charge on the solid is neutralized. The maxima at about $C_a = 2$ mM is similar to that observed by Somasundaran et al. (*47*), who propose that it is probably due to precipitation.

Figure 2 is a plot of the cumulative adsorption density of SDBS on anatase versus successive adsorption steps. All adsorptions experiments were performed in 0.1 M NaCl at a pH of 2.5 and various initial surfactant concentrations above 2.2 mM, which should result in maximum adsorption for a single-step adsorption such as in Figure 1. For the first step, the average adsorption over a concentration range of 2.2 to 25 mM was 0.45 ± 0.07 μmol/m². After the first adsorption, the remaining solution is removed, and an SDBS solution at the same initial concentration as the first adsorption step is added to the batch reactor. The additional adsorption of SDBS to the solid is determined by a change in the solution concentration. The second adsorption step resulted in continued adsorption (another 0.44 μmol/m²) at initial concentrations ranging from 2.2 to 7.5 mM. The same procedure was repeated, and the surfactant continued to adsorb to the surface at a similar incremental mass for six more successive adsorption steps. The data can be fitted by linear regression with a slope of 0.556 μmol/m² per step ($r^2 = 0.993$). It is surprising that anatase adsorbed a fixed additional increment of SDBS each time the mother liquor was poured off the solid and replaced
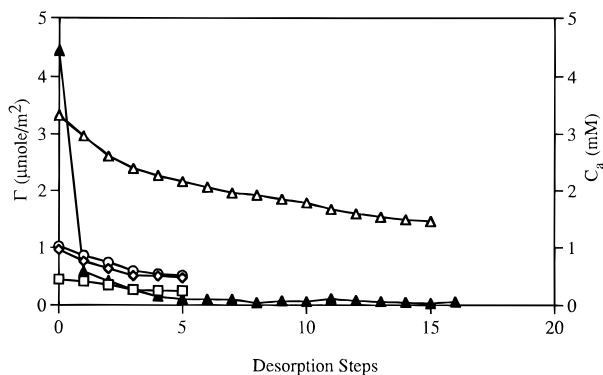
FIGURE 3. Plot of successive desorption of SDBS from anatase after 1 (□), 2 (◇, ○) and 7 (△) successive adsorption steps. The solid triangles (▲) represent the desorption solution concentrations (Ca) for SDBS adsorbed in seven successive adsorption steps versus desorption step. All successive desorption experiments were diluted with solutions containing 0.1 M NaCl at a pH of 2.5.

but not when the surfactant is left in contact with the solid for an extended period of time. Similarly, Siracusa and Somasundaran (*5*) mention that they found continued adsorption of SDBS to kaolinite when upon dilution the SDBS concentration was still above the cmc. This multiple layer adsorption of SDBS to anatase may also be a consequence of a process similar to multiple layer Langmuir-Blodgett type adsorption which has been demonstrated for similar materials (*48*–*50*). In Langmuir–Blodgett-type adsorption, a monolayer of an organic substance on the surface of a liquid can be transferred to a solid (such as a glass slide) by pulling the slide through the monolayer (under constant surface pressure), which then coats the surface. Repetitively dipping the slide produces more layers on the slide on each pass through the monolayer.

Desorption of SDBS. Figure 3 is a plot of the successive desorption of SDBS from anatase after one, two, and seven successive adsorption steps. The different amounts of sorbed surfactant represent varied organic carbon content to simulate sediment organic matter. Initially, the SDBS desorbed rapidly from the solid. After about half of the SDBS on the solid had desorbed, the rate slowed considerably and the solution concentration reduced to a low level. This low level release of surfactant from the solid may be due to the presence of a relatively insoluble phase since the Kraft temperature is 32 °C (*51*). The SDBS was removed from the solid by raising the pH and disaggregating the particles by lowering the ionic strength. Stripping the surfactant off the solid confirmed that 42–54 % of the total amount remains on the solid even after contaminant adsorption–desorption experiments. The loss of surfactant to the formation of a monolayer on the liquid surface would account for less than 1% of the surfactant on the solid recovered at the end of the experiments. The surfactant-coated particles gradually formed loose aggregates. At the end of SDBS adsorption–desorption experiments, the anatase particle aggregates were from 30 to 80 μm in diameter as estimated by settling velocity. Despite the loose aggregation of the colloidal particles, no change in the adsorption or desorption amount or kinetics was observed.

Adsorption of Contaminants. Several aspects of contaminant adsorption and desorption to the surrogate are described and compared to a natural sediment. The inclusion of the adsorption and desorption behavior is to verify the surrogate as a model sediment. Hydrophobic

contaminants are assumed to partition predominately to organic carbon in sediments. The proposed surrogate contains an organic carbon phase, and the adsorption of hydrophobic contaminants can be represented by the following expression for the organic carbon-based partition coefficient (K_{oc}) (*52*) for both the natural sediment and the surrogate:

$$K_{oc} = \frac{K_p}{f_{oc}} \qquad (2)$$

where f_{oc} is the weight fraction of organic carbon in sediments or in this case surfactant-coated anatase, and K_p is the equilibrium partition coefficient (cm³/g). The adsorption of PCB and naphthalene to surfactant-coated anatase and Lula sediment was determined to be linear and could be modeled with the following equilibrium expression for K_p:

$$K_p = \frac{q_{adsorbed}}{C_{aq}} \qquad (3)$$

where C_{aq} is the aqueous phase solute concentration after the adsorption experiment (μg/mL) and $q_{adsorbed}$ is the solid phase concentration of contaminant (μg/g). Similar to surfactant adsorption, the contaminant solid phase concentration ($q_{adsorbed}$) is determined by the amount that disappeared from the solution phase at the end of the adsorption experiment:

$$q_{adsorbed} = (C_{initial} - C_{aq})\frac{V_W}{W_S} \qquad (4)$$

where $C_{initial}$ is the initial concentration of solute (μg/mL), V_W is the volume of solution (mL), and W_S is the mass of solid (g). Mass balance analyses of selected experiments were determined by comparing the mass calculated at the completion of the test with mass recovered by solvent extraction. The mass balance was determined by comparing the percentage mass recovered from extraction to the total mass adsorbed on to the solid: This yields a more stringent mass balance criterion than recovery compared to the total mass initially added to the system (*5*). Still, the mass balance was better than 95%. The solid phase concentrations of PCB adsorbed to anatase without surfactant coating at initial concentrations of 0.01–0.012 μg/ml alone were 0.0073–0.011 μg/g.

Table 1 lists 12 PCB adsorption experiments where both the surfactant contents of the anatase and equilibrium time were varied. Two PCB adsorption experiments were performed on natural Lula sediment for comparison to the surrogate sediment (experiments L1 and L2). One naphthalene adsorption experiment was performed on the surrogate sediment to compare to previously reported adsorption experiments on Lula sediment (*8*). Contaminant adsorption experiments for both natural and surrogate sediments are included to verify that partitioning occurs by a similar process. The organic carbon content due to adsorbed SDBS varied by about a factor of 10 from 0.046% to 0.57%, and the contact time varied from 0.5 to 6.5 days. Figure 4 is a plot of the equilibrium partition coefficient (K_p, cm³/g) versus the organic carbon content (OC, %) for anatase (Table 1). Note that the partition coefficient (K_p) is linearly related to the organic carbon content with a slope of 183.21 cm³/g, which corresponds to an organic carbon-
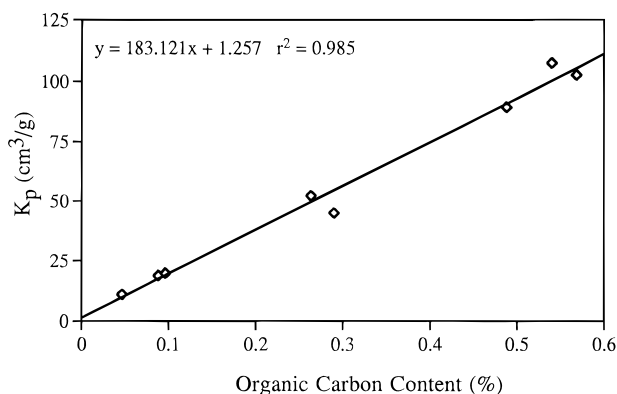
FIGURE 4. Plot of organic carbon (OC) content versus the partition coefficient (K_p, cm³/g) of PCB to surfactant-coated anatase (for adsorption times greater than or equal to 0.5 day). Experiments were performed in 0.1 M NaCl at a pH of 2.5 and are listed in Table 1.

based partition coefficient of $10^{4.26}$ cm³/g. The K_{oc} values for PCB adsorption to surfactant-coated anatase in Table 1 range from $10^{4.26}$ to $10^{4.38}$ cm³/g. The log K_{oc} values for PCB adsorbed to Lula sediment were $10^{4.32}$ and $10^{4.35}$ cm³/g, similar to the value obtained for partitioning to surfactant-coated anatase. The organic based partition coefficient (K_{oc}) values for PCB found in the literature range from $10^{3.87}$ to $10^{6.4}$ cm³/g for various humic acids, sediments, and soil samples (*53*). The similarity of the observed K_{oc} values to those reported and predicted by the K_{ow} in the literature suggests that the partitioning is probably hydrophobic in nature.

The affect of equilibrium time on the adsorption of PCB to surfactant-coated anatase was also studied (Table 1). For adsorption times below 0.5 day, the K_{oc} value was between $10^{4.05}$ and $10^{4.16}$. From 0.5 to 6.5 days, the observed partition coefficient ($\sim 10^{4.3}$) appeared to remain unchanged. The adsorption appears to have reached equilibrium within 0.5 day. The equilibration times for sorption of PCB to sediments and soils reported in the literature have ranged from 3 h to years (*54*).

Naphthalene adsorption—desorption (experiment N) was studied using the surfactant-coated anatase for comparison to Lula sediment. The sorbent had an organic carbon content of 0.59%, the initial concentration of naphthalene was 0.135 μg/mL, the adsorption time was 1 day, and the $q_{adsorbed}$ was 0.438 μg/g, which resulted in a K_p of 5.648 cm³/g and a K_{oc} of $10^{2.98}$ cm³/g. These values are similar to the K_{oc} found by Kan et al. (*8*) of $10^{2.92}$ cm³/g for sorption to Lula soil and are within the range of values found in the literature ($10^{2.66}-10^{3.17}$) for sorption to soils/sediments (*52, 55, 56*). All of these observations support the use of surfactant-coated anatase as a reasonable surrogate for natural sediments or soils.

Successive Desorption. The solution phase concentration of contaminant for each desorption step is comprised of the concentration which desorbs during that step plus the concentration remaining in the vial after decanting. Stepwise desorption from the solid phase can be calculated via the following expression (*8*):

$$\Delta q_{i,\text{desorbed}} = [C_i - C_{i-1}(1 - r)]\frac{V_W}{W_S} \quad (5)$$

where $\Delta q_{i,\text{desorbed}}$ is the change in the solid phase concentration (μg/g) during the ith desorption step, C_i and C_{i-1} are the solution phase contaminant concentrations (μg/

ml) between successive steps, and r is the fraction of supernatant liquid replaced at each dilution. The value of C_{i-1} for the first desorption step refers to the solution phase concentration at the end of the corresponding adsorption experiment, C_{aq}. The "r" in this study was between 0.90 and 0.95 and was determined by weight difference in each experiment. The cumulative fraction of solute, initially on the solid, which desorbed by the end of n desorption steps was calculated via the following equation:

$$\text{fraction}-\text{solute}-\text{desorbed (experimental)} = \frac{\sum_{i=1}^{i=n}\Delta q_{i,\text{desorbed}}}{q_{\text{adsorbed}}} \quad (6)$$

If it is assumed that desorption is ideal and linear and that K_p remains constant, then the fraction of solute desorbed after n desorption steps can be calculated by using the following formula (*8*):

$$\text{fraction}-\text{solute}-\text{desorbed (predicted)} = \left(\frac{r}{K_p\dfrac{W_S}{V_W} + (1 - r)}\right)\sum_{i=1}^{i=n}\left(\frac{K_p\dfrac{W_S}{V_W} + (1 - r)}{K_p\dfrac{W_S}{V_W} + 1}\right)^i \quad (7)$$

where all of the terms are as defined previously.

The results of ten desorption experiments are summarized in Table 2. The experiment numbers in Table 2 correspond to the adsorption experiments listed in Table 1. The cumulative total amount of solute to be desorbed was calculated (for all successive desorption steps) using eq 6 and listed in column 5. The predicted amount to be desorbed, calculated with eq 7, is listed in column 6. Finally, the percentage of the expected desorption is listed in column 7 and varies from 17% to 87%. If the desorption reactions were describable by the adsorption isotherm, then the percentage of expected desorption should be 100%. None of the experiments were observed to desorb the predicted amount determined from the adsorption isotherm. For the desorption of PCB from the proposed surrogate material, the fractional desorption appears to be related inversely to the amount of OC on the anatase. Both Carroll et al. (*11*) and Pignatello et al. (*57*) have observed a similar linear decrease in the amount of contaminant desorbed from natural sediments as the fraction OC increased, suggesting also that the surfactant-coated anatase is possibly a reasonable surrogate system for natural sediments. The concentration of PCB for a single dilution remained at 0.313 $\pm$ 0.016 μg/L for desorption times between 4 h and 168 days. This suggests that either desorption had reached equilibrium within 4 h or that the half-life was considerably longer than 168 days. Since the anatase was nonporous and the adsorbent was a discrete layer of surfactant, there is no reason to expect an exceptionally long desorption half-life. The predicted concentration after one dilution should have been 0.745 μg/L. A number of investigators have demonstrated that uptake and release can be characterized by slow diffusion processes (*58*) into either highly constricted pore networks or diffusion of solute through sediment organic matter. Pignatello and Xing (*42*), in a review article, discuss that the inverse relation of sediment

TABLE 2

Summary of PCB Desorption from Surfactant-Coated Anatase and Lula Sediment

exp. no.	organic carbon content (%)	q_{ads} (μg/g)	no. of desorption steps (n)	fraction-solute-desorbed (experimental) eq 7	fraction-solute-desorbed (predicted) eq 8	percentage of expected desorption (%)
			PCB on SDBS Coated Anatase			
1	0.046	0.053	12	0.609	1	61
2	0.089	0.066	19	0.639	1	64
3	0.097	0.067	19	0.493	1	49
4	0.488	0.093	15	0.214‡	0.820	26
5	0.264	0.085	15	0.160	0.938	17
10	0.575	0.105	5	0.084	0.270	31
12	0.54	0.121	8	0.173	0.497	35
			PCB on Lula Sediment			
L1	0.27	0.099	4	0.113	0.458	25
L2	0.27	0.098	6	0.156	0.596	26
			Naphthalene on SDBS Coated Anatase			
N	0.59	0.438	5	0.853	0.979	87

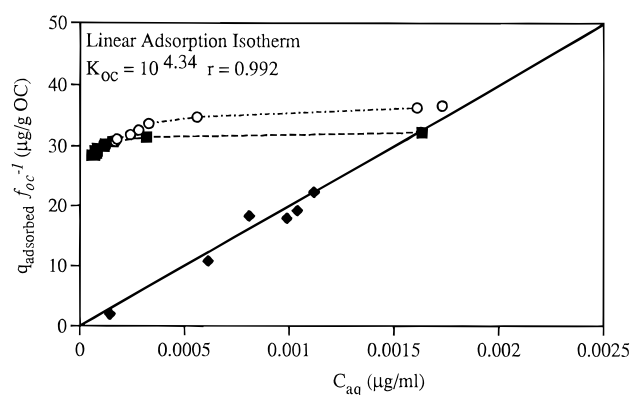[a] It is expected that in the first 5−7 steps half of the desorption was due to loss of surfactant coating.

FIGURE 5. Plot of the OC content normalized solid phase PCB concentration ($q_{adsorbed}/f_{oc}$ in μg/g OC) versus the solution phase concentration (C_{aq}) of PCB. The adsorption data for the surrogate experiments ($\blacklozenge$) from Table 2 were fitted with a linear regression (solid line). The dotted lines are a comparison of the desorption isotherms of both Lula (experiment L1, $\bigcirc$) and surrogate sediment (experiment 5, $\blacksquare$) using the data from Table 2. The solution conditions for the surrogate experiments were 0.1 M NaCl at a pH of 2.5 and for the Lula experiments were 0.15 M NaCl at a pH of 5.9.

OC to the mass transfer parameters supports both the organic matter diffusion model and the sorption-retarded pore diffusion model. Caroll et al. (*11*) described the slow desorption in their results of PCB from Hudson River sediments as being due to partitioning to two phases in the organic matter. They further described and modeled these two phases as rubbery and glassy polymers where diffusion through the rubbery stage is fast and slow through the glassy stage. The surrogate should reduce the heterogeneous nature of the organic phase, yet desorption does not reach expected solution concentrations and remains unchanged for 4 h to 168 days.

To better illustrate the amount desorbed per step and to directly compare the desorption from the surfactant-coated anatase to the Lula natural sediment, the adsorption (for surrogate experiments) and desorption isotherms (for experiment L2 and experiment 5) normalized to their OC contents are plotted in Figure 5. Both the surrogate and Lula sediment have similar OC contents, and their K_p values listed in Table 1 are 52.2 and 60.8 mL/g, which yield very similar normalized K_{oc} values (column 8 of Table 1). The solid line and solid diamonds in Figure 5 represents the

linear adsorption isotherm. The desorption patterns for both the natural (open circles) and surrogate sediment (solid squares) were similar and did not conform to the same path as the adsorption isotherm. Pignatello and Xing (*42*) discuss that the heterogeneous nature of soil and sediments has led to problems in studying long-term desorption particularly since the sorption or diffusion medium is never homogeneous. The heterogeneity is not only due to the structure of the organic components but also due to variations in pore size, particle size, and dispersivity. These variations should be greatly reduced by the system presented, yet desorption does not conform to the adsorption isotherm and is similar to a natural sediment.

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