Sorption Nonlinearity for Organic Contaminants with Diesel Soot: Method Development and Isotherm Interpretation

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An experimentally practical and precise flocculation-based method was developed, tested, and applied to determine phenanthrene and 1,2,4-trichlorobenzene sorption with NIST SRM 2975 diesel particulate matter. Following an initial equilibration period, polyaluminum chloride (PACl) solution was added to the sorption tubes in order to facilitate the formation of flocculated aggregates of soot particles. After separation of the solids through centrifugation, supernatant concentrations were determined as with conventional batch methods. The flocculation-based method was tested on three kinds of soot and then used to evaluate sorption kinetics and equilibrium with SRM 2975. Kinetic results showed that wetting of the soot required more than 20 days, but that 60 days was sufficient to achieve equilibration with both water and phenanthrene. Sixty-day isotherms for both phenanthrene and 1,2,4-trichlorobenzene were strongly nonlinear. At approximate 10^{-3} of solubility, carbon-normalized distribution coefficients (K_{oc}) were 10−20 times higher than those for absorption to sediment organic matter. Measurements at closer to solubility indicated much lower K_{oc}, suggesting a total sorption capacity at aqueous solubility that is of similar magnitude to that in sediment organic matter. Independent analysis of extractable hydrocarbons suggests that absorption into a native hydrocarbon phase was not a major component of sorption.

Introduction

Sorption of organic contaminants by soils, sediments, aquifer solids, and landfill solids has a major influence on the fate of chemical pollutants in the environment, including a direct impact on bioavailability, transport by fluids, and rates of transformation. Recent evidence has shown that such sorption can be strongly influenced by the presence of black carbon (BC) phases, such as the soot and char particles formed by the incomplete combustion of biomass or fossil fuels (*1−11*).

Black carbon in the environment results from either direct pyrolysis or incomplete combustion of carbon-based materials and can include both the chars that are formed by pyrolysis of unburned residual materials and the soots that

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are formed as condensation products from gas-phase emissions (*4, 12, 13*). One important form of environmental black carbon is the particulate matter emitted in diesel engine exhausts, hereafter referred to as diesel soot. Diesel engines have been in existence since the late 1800s and have found widespread application for heavy-duty engines since World War II. In fact, all heavy-duty trucks built since 1997 have been equipped with diesel engines because of their better fuel efficiency relative to gasoline engines (*14*). On the other hand, diesel engines are known to emit more particulate matter per mile driven and are now well-known to be the primary source of vehicular particulate emissions to the environment (*14*).

Despite the ubiquity of diesel particulate matter in the environment and its recognized impact on contaminant fate, little is known about the physical and chemical properties of different kinds of soot and other BC materials, particularly in regard to their interactions with hydrophobic organic chemicals (HOCs). Aqueous sorption isotherm data for HOCs with pure soot materials are not yet widely available in the scientific literature, and previously applied experimental sorption methods (*6, 15, 16*) are not appropriate for kinetic tests or practical for study using large numbers of replicates at multiple concentrations.

A key challenge to developing both practical and precise sorption methods with soot and soot-like materials is that conventional techniques of centrifugation do not remove many of the very fine soot particles from aqueous suspension. This problem has been previously observed, for example, by several investigators who have studied the NIST diesel particulates (*6, 15, 16*). In particular, the combination of small particle size and low solid density prevent effective settling by centrifugation. In our own preliminary investigations, this was evidenced by high turbidity of centrifuge supernatants (0.75 NTU) and an accumulation of soot particles at the air−water interface. Aggregation could alleviate these difficulties but does not occur in the absence of chemical modifications, presumably because soot particle stability is maintained by surface charge.

Prior investigators have overcome these difficulties by using methods that avoid soot−water separation. For example, Bucheli and Gustafsson (*6*) developed an air-bridge technique for measuring sorption of added polycyclic aromatic hydrocarbons (PAHs) with diesel soot SRM 1650. This technique eliminates the need to separate soot from water by establishing equal aqueous phase activity in a separate soot-free vessel. Very long experimental times (e.g. 123 days for phenanthrene) are required, however, to achieve the necessary 3-way equilibrium in the water/air/solid system. Such long times are experimentally inconvenient and prevent an independent assessment of equilibration kinetics. The same authors also developed and applied a cosolvent-based HPLC column technique to measure soot−water distribution coefficients K_{sc} (*6*). Such column experiments, however, are not well suited for determining details of a nonlinear sorption isotherm. This is because the column breakthrough results occur over a wide range of concentrations that are affected not only by equilibrium sorption but also by processes of mass transfer and hydrodynamic dispersion that are difficult to properly characterize and isolate. A second difficulty with this method is that the required high concentration of methanol cosolvent is expected to remove native hydrocarbons from the diesel soot (*6*). In fact, Bucheli and Gustafsson were sufficiently concerned with this effect that they pretreated SRM 1650 material with 100% methanol in order to obtain reproducible results

on extracted sample (6). Such native PAHs are important components of the sorbent, however, and are likely to affect sorption characteristics by occupying sorption sites and/or by comprising a separate organic phase that can serve as an effective absorption medium for hydrophobic sorbates (8). For these reasons, the behavior of cosolvent-modified soot is not likely to reflect that of the original soot material.

Jonker and Koelmans (15, 16) have developed and applied a three-phase equilibration method that avoids soot−water separation by using a third phase (a solid strip of polyoxy-methylene) to measure aqueous activity. With this method, data interpretation requires separation and extraction of the solid strips as well as independent study of mass transfer limitations and equilibrium properties of this third phase. Although the investigators were able to successfully apply the method to measure PAH and polychlorinated biphenyl (PCB) sorption and desorption with five different soots, it is a fairly laborious approach that is impractical for kinetic studies.

Another possible approach is to chemically modify the soot surfaces and to thereby facilitate their flocculation into larger aggregates. Flocculation-based techniques for desta-bilizing colloids and achieving solid−water separation have been well established in water treatment (17) and, more recently, have been applied to sorption and desorption experiments with dissolved humic acid (18) and industrial lagoon sediments (19). In the work described here, we have modified the flocculation-based approach by using a pre-hydrolyzed form of aluminum salt (polyaluminum chloride or PACl) as the source for the aluminum hydrolysis products that facilitate charge neutralization. We developed this method independently from (and concurrently to) Hong et al.'s recent development and application of a high-dose aluminum-sulfate-based flocculation method to measure PAHs desorption from lampblack (8). Compared to the method of Hong et al., our technique requires the addition of a much smaller amount of a less acidic flocculant, thus avoiding the production of large quantities of new hydroxide solids and large changes in pH.

In this paper, we present the development of the PACl-based flocculation approach to batch sorption studies, its evaluation by several different control studies, and its application to evaluate some kinetic and equilibrium aspects of HOC sorption by NIST SRM 2975 diesel soot in aqueous solution. We have used the method to obtain sorption isotherms for phenanthrene and 1,2,4-trichlorobenzene (TCB) with SRM 2975 over a wide range of aqueous concentrations. The results revealed highly nonlinear sorption that we considered in terms of both dual-mode and single-mode isotherm formulations.

Isotherm Modeling

For modeling nonlinear adsorption to BC materials, the Freundlich isotherm equation is a practical and historically popular approach. For our purposes, we applied the following form of the Freundlich equation, which has been modified for use in terms of relative aqueous concentration (C_e/S_w) (4, 20):

$$q_{ad,e} = K_f^* (C_e/S_w)^n \tag{1}$$

Here, $q_{ad,e}$ is the adsorbed concentration at equilibrium (e.g., in units of $\mu g/g$), n is an empirical exponent (typically of a value less than 1), and K_f^* ($\mu g/g$) is the modified Freundlich coefficient. The Freundlich equation has previously been used to describe adsorption of several PAHs and PCBs with diesel soot SRM 1650 and sediments containing soots (5, 6, 21).

Although eq 1 is useful as an empirical fitting tool, its parameters have only qualitative mechanistic relevance. Polanyi adsorption potential theory is an alternative approach for modeling adsorption that also allows empirical fitting of data but provides more explicit consideration of the relation between the adsorbed volume of a sorbate and the sorbate's adsorption potential, thereby offering a possibly more effective means of comparing results among sorbates (4, 22−25). One mathematical formulation for a Polanyi-based adsorption isotherm that has been commonly used is the Dubinin-Astakhov (DA) equation (26):

$$q'_{ad,e} = q'_{ad,max} \exp\left[-c\left[\frac{RT\ln(S_w/C_e)}{N}\right]^d\right] = q'_{ad,max} \exp\left[-c\left(\frac{\epsilon_{sw}}{N}\right)^d\right] \tag{2}$$

Here $q'_{ad,e}$ is the adsorbed volume of sorbate (μL sorbate/g sorbent), $q'_{ad,max}$ is the maximum adsorption capacity (μL sorbate/g sorbent), and $\epsilon_{sw} = RT\ln(S_w/C_e)$ is the adsorption potential (Joule/mol). For weakly polar sorbates adsorbing on black carbon surfaces, the normalizing factor N can be usefully equated to V_s (mL/mol) and the quantity $RT\ln(S_w/C_e)/V_s$ is the adsorption potential density (3, 7, 23). This leaves $q'_{ad,max}$, c, and d as fitting parameters for the isotherm. The DA equation was also used successfully by Kleineidam et al. for sorption isotherms obtained for several black carbon materials (3).

The aforementioned isotherm modeling approach may not be sufficient if data are also being influenced by a strong linear absorption component (4). In this context, BC materials such as diesel soots and lampblack are known to contain various amounts of PAHs and other hydrocarbons that are normal components of sooting flames and can be incorpo-rated into the soot structure at the time of formation (8, 27−32). Such authigenic (native) hydrocarbons can occur in soot materials either as adsorbed species or as part of an organic phase (solid or liquid) that may be either physically entrapped within the solid matrix (16) or condensed external to the graphitic matrix (8). To the extent that any such organic phases are accessible to solution and liquidlike in their behavior, they may serve as media for linear absorption of HOCs.

To model absorption in combination with a nonlinear adsorption, numerous investigators have applied a "dual domain" sorption formulation as more fully reviewed in Allen-King et al. (4). The dual domain model has the following form:

$$q_e = q_{ad,e} + q_{op,e} = q_{ad,e} + f_{op} K_{op} C_e \tag{3}$$

Here, $q_{ad,e}$ is the adsorbed concentration, f_{op} is the mass fraction of the organic phase relative to the total sorbent mass, and K_{op} is a partition coefficient for absorption into an organic phase (op).

Recently, a model of this form has been applied to explain the important role of an "oily phase" in accounting for PAH sorption within lampblack materials with different PAH contents (8). In many cases, $q_{ad,e}$ can be dominant at low aqueous concentrations of adsorbate and $q_{op,e}$ dominant at high concentrations of adsorbate (i.e. at concentrations sufficiently high as to effectively saturate the adsorption domain). On the other hand, if the amount of the absorbing domain is negligibly low, the total sorption (q_e) will be dominated by adsorption ($q_{ad,e}$) at all concentrations.

In this work, we have used independent estimates of solvent extractable organic phase and PAH content to assess whether the amounts of extractable hydrocarbons in diesel soot particulate matter SRM 2975 are sufficient to act as significant absorption domains. We also considered the

possibility that a nonextractable phase of unknown amount of partitioning carbon could be acting as an absorbing domain.

Experimental Section

Sorbates and Flocculant. ^{14}C-Labeled phenanthrene and 1,2,4-trichlorobenzene (TCB) and nonlabeled TCB were obtained from Sigma-Aldrich (Saint Louis, MO). Certified standard solutions of nonlabeled phenanthrene in methanol (5 μg/μL) were obtained from Ultra Scientific (North Kingstwon, RI). For batch sorption experiments with soots, single-solute spiking solutions were prepared by adding mixtures of ^{14}C-labeled and nonlabeled chemicals to the HPLC-grade methanol. Specific activities of ^{14}C-labeled phenanthrene and TCB were 8.2 mCi/mmol and 3.3 mCi/mmol, respectively. Table 1S in the Supporting Information shows physicochemical properties of the studied solutes.

Although our ^{14}C-labeled chemicals had a reported purity of >99% from the supplier, transformation during storage is possible, and previous studies have shown the potential for significant errors in sorption experiments as a result of contaminated ^{14}C-labeled chemicals (33−35). Therefore, the radio-chemical purity of ^{14}C-labeled stock solutions was confirmed for all three chemicals immediately prior to use. The method and results of these purity checks can be found in the Supporting Information. Briefly, all solutes were confirmed to be more than 97% pure when used.

For flocculation, a polyaluminum chloride (PACl) solution with specific gravity of 1.23 was obtained from Delta Chemical Corporation (Baltimore, MD). This material has a concentration of 10.5 wt % as Al_2O_3 (or 34200 mg/L as Al) and a minimum basicity of 70%. Basicity is defined as the degree to which the hydrogen ions produced by hydrolysis are preneutralized (17). Flocculant solutions with Al concentrations varying from 86 mg/L to 3360 mg/L were made by diluting this concentrated PACl solution with Milli-Q water (Millipore, Billerica, MA).

Black Carbon Materials. The National Institute of Standards and Technology (NIST) has developed and characterized two diesel particulate standard referent materials (SRMs): SRM 1650a, Diesel Particulate Matter, and SRM 2975, Diesel Particulate Matter (Industrial Forklift). Although SRM 1650a had been the primary sorbent studied by prior investigators (6, 16), this material was out of stock at the time of this study; therefore, we chose to use SRM 2975 as a model diesel material. This material was used as received from NIST. Fresh hexane soot and oxidized hexane soot samples were used to study the flocculation mechanism. These materials were provided by Dr. D. Smith (University of Denver) and were formed using conditions reported in Chughtai et al. (36, 37). A natural wood char material (NC2) was used for comparative flocculated vs nonflocculated sorption experiments. This material was obtained from the grinding of burned wood pieces collected from the New Jersey Pine Barrens in April of 2002, sieved to pass a 400 mesh size (37 μm) screen, homogenized, and split for subsequent use in the manner described by Nguyen et al. for related char materials (38).

The black carbon materials were characterized with regard to total carbon content, combustion-resistant carbon content as determined by the method developed by Gustaffson et al. (39), surface O/C ratios (as determined by XPS), bulk elemental composition (C,H,O), and BET surface area. In addition, diesel soot, hexane soot, and oxidized hexane soot used in flocculation studies were evaluated for electrophorentic mobility as a test of surface charge. Methods and results for the various characterization efforts can be found in the Supporting Information and in ref 38.

Preliminary Tests for Flocculation Efficacy, Optimal Flocculant Dose, and Flocculation Mechanism. We conducted a standard jar test to study flocculation mechanism and to find an optimal dose for PACl to use toward the solid−liquid separation in subsequent sorption studies. For the preliminary studies, we evaluated the flocculation of diesel soot SRM 2975, hexane soot, and oxidized hexane soot. For the diesel soot SRM 2975, three solid/water ratios (0.0092 mg/mL, 0.0266 mg/mL, and 0.0343 mg/L) were selected as appropriate to roughly simulate the solid/water ratios used in subsequent sorption experiments. Two solid/water ratios (0.0087 and 0.0265 mg/mL) were chosen for fresh hexane soot. A solid/water ratio of 0.0087 mg/mL was used for oxidized hexane soot.

For each soot, an appropriate mass was added to a 250 mL dry beaker, and the beaker was then filled with 200 mL of synthetic groundwater containing 5 mM $CaCl_2$ and 0.02% NaN_3 (by weight). To facilitate wetting, entrainment, and dispersion of the soot particles, beakers were then placed in an ultrasonic bath for two minutes, during which time they were also manually stirred with a stainless steel spatula. For each soot and solid/water ratio studied, a jar test was conducted using six doses of PACl. After spiking with between 2 and 70 μL of PACl solution, the six beakers of each jar test set were stirred at 100 rpm for one minute and then at 20 rpm for 5 h. After overnight settling (around 14 h), 50 mL of the solution was withdrawn from each beaker and transferred to a glass centrifuge tube (Pyrex #8422). Centrifugation was conducted at 3500 rpm for 1 h, after which the turbidity was measured (Hach model 2100A turbidimeter, Loveland, CO). Optimal PACl dose was defined as the dose that provided minimal turbidity in the final sample (0.1 NTU or lower in all cases).

Batch Sorption Methodology. To develop a batch sorption methodology for use with soot particles, we modified the flocculation-based method of Laor and Rebhun (18) for use with soot as sorbent and PACl as flocculant. To maintain uptake from solution at between 20% and 85%, we used solid/water ratios of 1.2 mg soot /125 mL and 6.2 mg soot/63 mL for isotherm experiments with phenanthrene and 1,2,4-TCB, respectively. Amber glass bottles with Teflon-lined screw caps (Qorpak # 2118 and 2119) were used for all sorption experiments. All glassware was cleaned of any organic residues by combustion at 550 °C for 5 h. Water containing 5 mM $CaCl_2$ (to maintain a constant ionic strength and facilitate coagulation) and 0.02% NaN_3 (to prevent bacterial growth) (7, 10, 40) was used for all sorption experiments. Hereafter, this solution will be referred to as synthetic groundwater. After the addition of between 1.1 and 1.3 mg of soot and 100 mL of synthetic groundwater to each vessel, the bottles were capped and shaken by hand to suspend the soot particles. Bottles were then filled almost to the rim with synthetic groundwater, using care so that no liquid or solids overflowed. Subsequently, the bottles were rotated end-over-end at a speed of 12 revolutions per minute for 1 day to prewet the soot particles. As described subsequently, some samples were prewetted for longer periods as part of control studies. After the prewetting period, the test solute was spiked into the sorption bottles using a microsyringe that was modified by adding a 20-μL capillary glass pipet external to the syringe needle. This pipet served as a prophylactic shield against the direct adherence of floating soot to the syringe needle. This raises the water level negligibly, because of the small volume of the shield ($\sim$280 μL). Following the spiking and prior to final sealing of the bottle, the glass capillary shield was dropped inside the bottle. Thus, any soot particles that may have adhered to the glass surface were retained in the bottle to equilibrate with sorbate and water. After all bottles were spiked, they were capped tightly with Teflon-lined plastic screw caps and then rotated continuously at a

TABLE 1. Values of K_{oc} at Low C_e for Phenanthrene with Soot Samples

solids	measured log K_{oc} [a] (time of equilibration; C_e/S_w)	method	reference
SRM 2975	5.92 (59 days; 1.0×10^{-3})	flocculation-based batch	this work
SRM 2975	5.98 (123 days; 1.0×10^{-3})	air bridge	this work
SRM 2975	5.29 (59 days; 7.0×10^{-3})	flocculation-based batch	this work
SRM 1650	5.25 (134 days; 1.0×10^{-2})	air-bridge	(6)
SRM 1650	6.30	cosolvent-HPLC column	(6)
SRM 1650	5.30 (28 days; 1.5×10^{-2})	three-phase equilibrium and solid-phase extraction	(16)
traffic soot	5.73 (28 days; 1.5×10^{-2})	three-phase equilibrium and solid-phase extraction	(16)
oil soot	4.57 (28 days; 1.5×10^{-2})	three-phase equilibrium and solid-phase extraction	(16)
wood soot	4.61 (28 days; 1.5×10^{-2})	three-phase equilibrium and solid-phase extraction	(16)
coal soot	4.34 (28 days; 1.5×10^{-2})	three-phase equilibrium and solid-phase extraction	(16)

[a] $K_{oc} = K_d/f_{oc}$. Unit of K_{oc} is mL water/g organic carbon.

speed of 12 revolutions per minute. Sorption experiments were conducted for various equilibration times. For experiments that were longer than one week, the samples were rotated continuously for the first week, once a day for 15 min during weeks two and three, once every 2 days during weeks four and five, and once a week after the fifth week. On the last day before sampling, the samples were rotated continuously to ensure a homogeneous soot/water suspension.

At the end of the sorption equilibration, soot−water separation was achieved by means of flocculation with PACl in 50 mL Pyrex centrifuge tubes for both sorbates. On the day of sampling, the aqueous suspension from the sorption bottles was transferred into two 50-mL centrifuge tubes sealed with Teflon-lined septa (Kimble #73818-24) and plastic screw caps (Supelco #2-3283). Then, the predetermined optimal dose of flocculant solution was spiked into each tube, as appropriate for the solid−water ratio of the samples. After spiking, all tubes were shaken by hand 10 times, then by a horizontal mechanical shaker with 1-D translation along the length of the tubes at a speed of 100 SPM (strokes per minute) for one minute, followed by 40 SPM for 4 h. Flocs were observed to form in all tubes after 4 h. All tubes were then removed from the shaker and left to settle under stagnant conditions for 2 h, followed by centrifugation at 3500 rpm for 1 h.

Centrifugation was not conducted immediately after horizontal shaking because unsettled flocs tended to loosely adhere to the tube wall during centrifugation and could subsequently be broken and remixed with water. Even after centrifugation, a small number of fine flocs remained on the water surface, perhaps because of air entrapment within the flocs. Inadvertent dispersal and sampling of these floating flocs were avoided by carefully withdrawing and disposing the top water layer with a glass pipet. A second glass pipet was then used to withdraw 1 mL of soot-free water from the middle of the tubes. This water was subjected to scintillation counting (Model LS3801, Beckman Instrument, Fullerton, CA) for 10 min to determine aqueous solute concentrations. Sorbed concentrations were then determined by difference as in prior work (33). An account of solute losses was made using results obtained from blank (solid-free) samples that were subjected to all sorption conditions and transfer operations. Such losses were accounted by assuming partition to headspace that was proportional to aqueous concentration. The mass accounted in this way was always low (only 6.8% ± 1.9% for 88 days equilibration time)−see the Supporting Information for details.

For every long-term experiment (59 days and longer), we included a set of solute-free soot suspension bottles that were prepared identically as the sorption bottles. This set of solute-free bottles was used to pretest the optimal flocculant doses that had been predetermined from jar tests. In all cases, turbidity measurements on the test bottles proved that the predetermined optimal doses achieved excellent soot/liquid separation.

Control Studies for the Flocculation-Based Batch Sorption Methodology. The reliability of the flocculation-based batch sorption methodology was tested using four types of control studies, as more fully described in the Supporting Information. The four types of study and principal results are briefly described below.

(i) An air-bridge equilibration study was used to test completeness of solid−liquid separation. For this test, batch-bottle supernatant was brought to equilibrium with soot-free water under a common gas phase, using replicate gastight systems into which perchloroethylene (PCE) had been added. (PCE was selected as a volatile sorbate that could more rapidly achieve equilibrium in the air-bridge system, as more fully described in the Supporting Information.) Excellent agreement of the aqueous-phase PCE concentrations confirmed that there was no effect of unseparated soot colloids.

(ii) To test for possible effects of PACl on solute loss (such as sorption to aluminum hydroxide precipitates), equal amounts of sorbate were added to sorbent-free batch bottles that contained varying amounts of PACl and also to PACl-free controls. The results of these studies (Supporting Information, Table 2S) confirmed that there was no sorbate loss owing to PACl alone.

(iii) To specifically test for possible effects of PACl on BC sorption, comparative sorption studies were conducted with and without flocculant addition, using a natural wood char that had similar surface area and O/C ratio as the SRM 2975 soot, but for which solid/liquid separation did not *require* the flocculant addition. Results of these studies (Supporting Information) confirmed that there was no measurable effect of PACl addition on isotherm results.

(iv) Finally, results from the flocculation-based batch sorption methodology were directly tested against results obtained using an air bridge technique that was adapted from the method of Bucheli and Gustaffson (6). These tests were conducted under assumed equilibrium conditions (see the Supporting Information) and at a single selected concentration ($C_e = 0.02$ μg/mL). No statistical difference in results was observed between the two methods−see Table 1 of Results.

Sorption Kinetics and the Effects of Prewetting Time. Two separate experiments with diesel soot SRM 2975 and phenanthrene were performed to determine the effect of prewetting and equilibration time on sorption. For the first set of kinetic experiments, we conducted a sorption rate study with soot suspensions that had been preequilibrated with synthetic groundwater for only 1 day before solute spiking. The equilibration times with solute were 3, 7, 13, 19, 32, 59, and 88 days, with 4 or 5 sample replicates evaluated at each time tested.
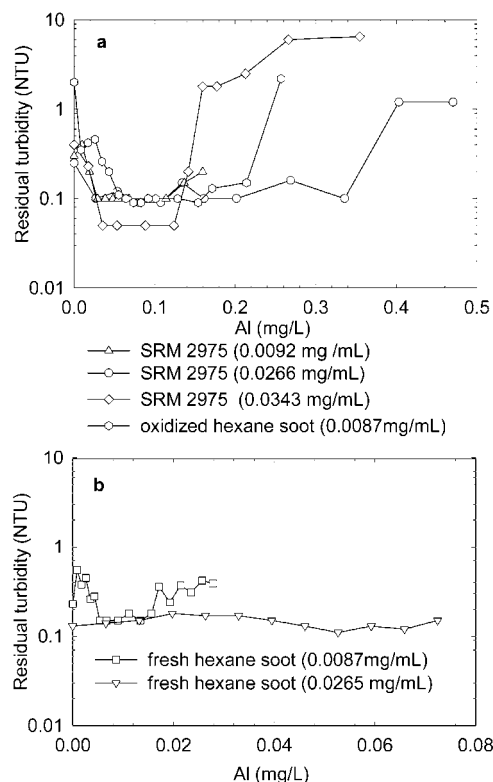
FIGURE 1. Jar test data for the PACl-assisted flocculation of (a) diesel soot SRM 2975 and hexane oxidized soot and (b) fresh hexane soot. Numbers in parentheses are the soot concentrations in synthetic groundwater.

Because the results of these studies suggested the possibility that slow water uptake was affecting phenanthrene sorption (see subsequent results), we specifically tested the effect of prewetting time on 7-day phenanthrene sorption results. Seven days is a somewhat arbitrary selection, chosen to represent a nonequilibrium time in order to evaluate the effects of prewetting time on phenanthrene sorption kinetics. Seven days were chosen over longer equilibration periods because of a concern that longer times might allow equilibration with water to simultaneously occur, thereby negating our ability to see the anticipated effect of prewetting time on phenanthrene uptake kinetics. For this test, replicate samples of soot suspensions in synthetic groundwater were prewetted for periods of 1, 20, 60, and 136 days before spiking with phenanthrene. After 7 days of equilibration with phenanthrene, aqueous samples were taken for the analysis and comparison of sorption results. Initial aqueous concentration C_o was on the order of 0.02 μg/mL for all kinetic study samples.

Sorption Isotherm Evaluation. For single-solute isotherm studies with TCB and phenanthrene over a range of aqueous concentrations (initial aqueous concentration C_o between $0.007S_w$ and $0.8S_w$ for phenanthrene and $0.0006S_w$ and $0.8S_w$ for TCB), a prewetting time of 1 day and an equilibration time of 59 days were used. To avoid the occurrence of photolytic oxidation of phenanthrene (41), all samples were kept in the dark throughout their equilibration. Temperature was maintained constant in an environmentally controlled room at 22 ± 1 °C. The method used for data analysis can be found in the Supporting Information.

Results

Preliminary Tests for Flocculation Efficacy, Optimal Flocculant Dose, and Flocculation Mechanism. Figure 1a shows the turbidity of supernatant fluid (on a logarithmic scale) as a function of PACl dose for diesel soot and hexane oxidized
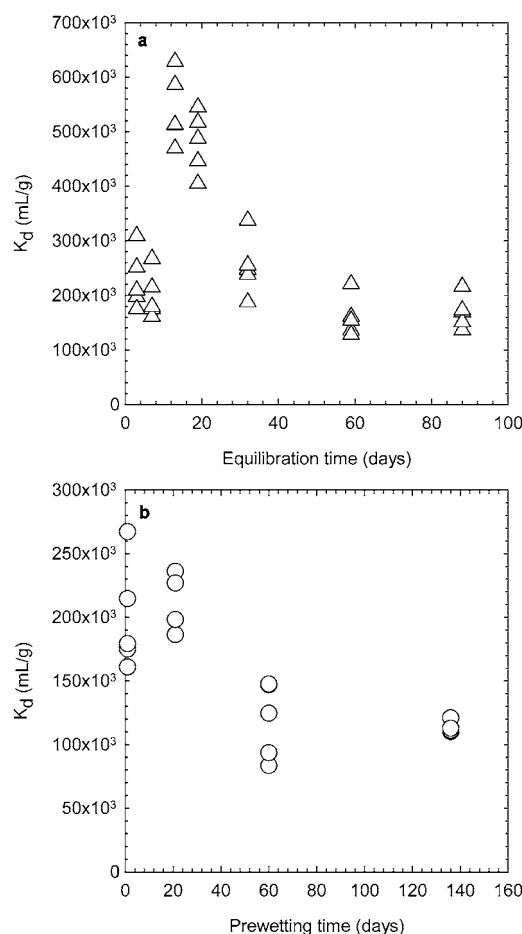

FIGURE 2. (a) Sorption distribution coefficients (K_d) vs time for phenanthrene uptake by SRM 2975. Prewetting time was 1 day for all samples. (b) Effect of prewetting on sorption of phenanthrene with SRM 2975. Equilibration time with sorbate was 7 days for all experiments.

soot. For both materials at the selected solid/water ratios of 0.0092 mg/mL, 0.0266 mg/mL, and 0.0343 mg/mL, the optimal dose was between 0.05 mg/L to 0.12 mg/L (as Al), with order-of-magnitude higher turbidities observed at lower or higher doses. As shown in Figure 1b, the optimal dose for fresh hexane soot was much lower than that for oxidized hexane soot (0.006 mg/L vs 0.06 mg/L). In our experiments, pH was between 6.7 and 6.9 with no PACl added and was somewhat lower (6.1) for samples spiked at the highest dose of PACl. On the basis of the results shown in Figure 1a, we selected 0.07 mg/L (as Al) for an optimum dose at the solid/water for phenanthrene sorption experiments (0.009 mg/mL).

For sorption experiments with TCB, the solid/water ratio was roughly 0.1 mg/mL, which is somewhat different from that studied above. For this case, we estimated the optimal PACl dose by assuming that the optimal dose is proportional to the solid/liquid ratio. Because the measured dose for solid/water ratio of 0.0343 is 0.1 mg/L, the required dose at the solid/water ratio of 0.1 was determined to be 0.27 mg/L. In all cases, the volume of PACl solution added to a 50 mL centrifuge tube was in the range of 2–4 μL.

Sorption Kinetics and the Effects of Prewetting Time. For the kinetic experiments, where soot suspension had been preequilibrated with water for only 1 day before solute spiking, K_d values increased over the course of equilibration time between 3 days and 13 days but then decreased at longer times up until 59 days (Figure 2a). For a prewetting time of 88 days, statistical student t-tests showed that the average
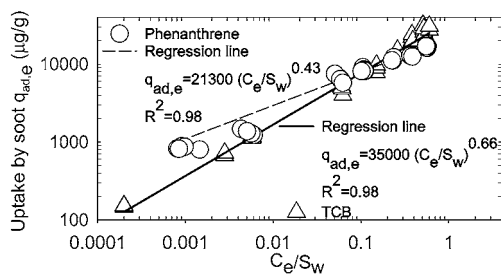
FIGURE 3. Sorption isotherms for phenanthrene and TCB with SRM 2975. Equations shown are for the solubility-normalized Freundlich isotherm equation with K_f^* in units of μg/g.
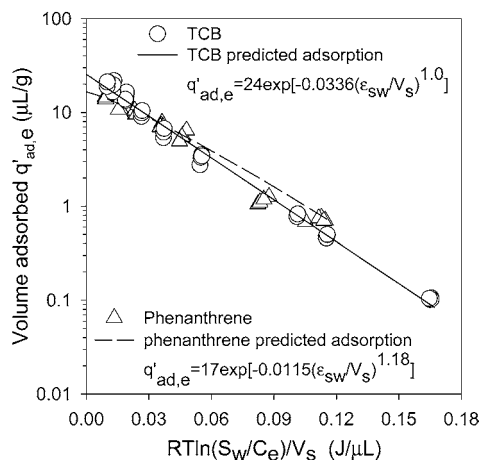

FIGURE 4. Polanyi-based adsorption isotherms for phenanthrene and TCB with SRM 2975. V_s is the molar volume of solute. $RT \ln(S_w/C_e)/V_s$ is the adsorption potential density. See Isotherm Modeling for details. Further details of the isotherm fits are provided in Table 4S (case 3 with $f_{op}K_{op} = 0$).

K_d was not significantly different from that observed at 59 days (2 sided t-test; $\alpha = 0.05$). Final aqueous concentrations (C_e/S_w) for these kinetic experiments varied between 0.003 and 0.007.

The experiment to test the effect of prewetting time on 7-day phenanthrene sorption showed decreasing K_d with increasing prewetting time, up until 60 days of prewetting (Figure 2b). Statistical student t-tests showed that the average K_d for the prewetting time of 60 and 136 days was not significantly different (2 sided t-test; $\alpha = 0.05$). Final relative aqueous concentrations (C_e/S_w) for these experiments ranged from 0.005 to 0.007.

Sorption Isotherm Evaluation. Final relative concentrations (C_e/S_w) for the full isotherm experiments ranged from 0.001 to 0.6 for phenanthrene and from 0.0002 to 0.6 for TCB. The data were modeled using both a normalized Freundlich isotherm (eq 1) and a dual domain model using a Polanyi-based approach for modeling adsorption (eq 3 with $q_{ad,e}$ modeled using eq 2 and alternative assumed values for $f_{op}K_{op}$, as described subsequently under Discussion). Model fits for the Freundlich approach and for 100% Polanyi-based adsorption (dual domain model with $f_{op}K_{op} = 0$) are shown in Figures 3 and 4, respectively. The Freundlich model fits shown in Figure 3 clearly illustrate the highly nonlinear nature of the isotherms, with Freundlich exponent values far less than 1.0 ($n = 0.43$ and 0.66 for phenanthrene and TCB, respectively). For both types of modeling, aqueous solubility of solid phenanthrene was used, as consistent with Manes' approach for applying Polanyi theory (23). Tables 3S and 4S in the Supporting Information show parameter confidence levels and some goodness-of-fit criteria (mean-weighted square error) for the two models as well as fitting results for other dual domain modeling assumptions as further de-

scribed under Discussion. In general, the goodness-of-fit measures were roughly the same for all of the approaches at that assumed very low partition contribution.

Discussion

Tests for Flocculation Efficacy, Optimal Dose, and Mechanism. According to the aluminum coagulation diagram of Amirtharajah and Mills (42), the combination of sweep floc and charge neutralization occurs at Al concentrations from 0.11 mg/L to 1.07 mg/L. In our experiments, the optimal dose for soot suspension (0.05 mg/L to 0.27 mg/L) is only slightly above the solubility limit for Al and is primarily in the range of charge neutralization. If ion adsorption and charge neutralization is, in fact, the primary mechanism of flocculation, we would expect an overdose effect at higher PACl concentrations, because of the development of net positive charge on particles. Such an overdosing effect is apparent in our results (Figure 1a,b) and is taken as an indication that charge neutralization was the predominant flocculation mechanism in our system.

Charge neutralization as the dominant mechanism is also suggested by the comparison of results with the fresh hexane soot (Figure 1b) to those obtained with the oxidized hexane soot and SRM 2975 (Figure 1a). Compared to fresh hexane soot, oxidized hexane soot has higher surface O/C ratios (0.21 vs 0.10) and is believed to contain more negatively charged oxygen functionalities. Studies of electrophorentic mobility confirmed the existence of negative charge at neutral pH and also confirmed that the net surface charges of these particles increased in the same order as the required flocculant dose—that is, charge and dose both increased from hexane soot to diesel soot to oxidized hexane soot (see the Supporting Information). These results are consistent with our expectation that positively charged polymerized aluminum species function by neutralizing negative charge on the soot surface.

In their study of PAH desorption from lampblack-impacted soils, Hong et al. (8) also used a flocculation-based sorption method but with much higher doses of a different flocculant (aluminum sulfate, or alum). The alum addition in those experiments (1.5 mL of 0.1 M aluminum sulfate added to 1 L of water) was sufficient to form a substantial volume of aluminum hydroxide precipitates, especially after the pH was adjusted back to neutral with 1 N NaOH. By contrast, the use of small volumes of concentrated and prehydrolyzed PACl achieves flocculation primarily by charge neutralization and avoids the complications of sample dilution, pH adjustment, and substantial solids production.

Sorption Kinetics and the Effects of Prewetting Time. Phenanthrene sorption results obtained using samples prewetted for 1 day (Figure 2a) showed that the phenanthrene K_d was stable after 59 days, with statistically identical results obtained on samples analyzed 59 days and 88 days after the addition of phenanthrene (2-sided t-test; $\alpha = 0.05$). Of special interest in Figure 2a, however, is the fact that K_d reached a maximum value after 13 days and declined thereafter. We hypothesized that the strong phenanthrene sorption at these earlier times was because the 1-day prewetting time was insufficient for the soot to fully equilibrate with water, thereby leaving more adsorption sites available for phenanthrene. Prewetting experiments were therefore designed to specifically evaluate the effect of prewetting time on results, using a constant 7-day phenanthrene equilibration time. These results, shown in Figure 2b, provide additional support for our hypothesis. In particular, the results confirm that 7-day phenanthrene sorption is stronger in samples that have not yet fully equilibrated with water, and they also show that samples prewetted for 60 days behave similarly to those prewetted for a longer time (136 days). For samples subjected to 60 or more days of wetting, presumably all of the

hydrophilic (water wettable) sites are fully occupied by water and the 7-day K_d for phenanthrene is no longer a function of wetting time (Figure 2b). The results shown in Figure 2b are a clear indication that water equilibration requires between 20 and 60 days to achieve and that prewetting times of 20 days or lower will have important impacts on phenanthrene sorption kinetics. Thus, a proper evaluation of phenanthrene sorption kinetics under fully prewetted conditions would require multiple phenanthrene equilibration periods on samples for which phenanthrene addition was postponed until after 60 days of prewetting. Such tests were beyond the scope of the current work, however, which did not have kinetics as a focus. Instead, we take the results of Figure 2a as justification for our conclusion that 1 day of prewetting and 59 days of phenanthrene equilibration are sufficient for water and phenanthrene equilibrium to be obtained. In this regard, we are assuming that the equilibrium condition is unaffected by whether phenanthrene or water adsorption occurs first.

Sorption Isotherm Evaluation. (i) It is instructive to make a **comparison of results with prior findings** by considering the data in the context of simple distribution coefficients normalized to carbon content (K_{oc}), as commonly used for other types of organic matter. Table 1 shows the values of log K_{oc} measured for SRM 2975, together with prior results obtained by others at similar aqueous concentrations and using soot formed from different fuels. Only the methanol-treated samples (cosolvent column results) show a substantially different K_{oc} from that observed in this study. For the cosolvent system, a much higher value was observed, suggesting that the methanol prewash may have removed competing organic chemicals from soot adsorption sites. Additional discussions of these results can be found in the Supporting Information.

A log K_{oc} value of 4.36 for phenanthrene with sediment organic matter was originally reported by Karickhoff et al. (*43*), and values between 4.38 and 4.53 have been recently reported for other river sediments (*44*). The work presented here suggests a log K_{oc} value for SRM 2975 at low aqueous concentration (log $K_{oc} = 5.92$ at $C_e/S_w = 0.001$) that is roughly 1.3 orders of magnitude higher than the sediment-based estimates. On the other hand, when phenanthrene concentration is high ($C_e/S_w = 0.56$), sorption to soot is about the same as sorption to sediment organic matter (log $K_{oc} = 4.45$ for soot). The K_{oc} values for TCB range between 4.38 (at $C_e/S_w = 0.0002$) and 3.24 (at $C_e/S_w = 0.60$), which can be compared to a value of roughly 3.4 for sediment organic matter. This latter estimate is based on log K_{ow} of 4.02 (*45*) and the log K_{oc}-log K_{ow} correlation proposed by Xia for benzene, chlorinated benzene, substituted benzenes, and PCBs with aquatic sediments (*4, 46*). Thus, the log K_{oc} values for soot at high C_e/S_w could possibly reflect absorption with an organic phase, for example as implied by eq 3 for a case where q_{ad} is no longer an important contribution at high C_e/S_w. In the following section, we explore whether solvent extractable compounds could be providing such a phase, as was previously concluded by others studying lampblack material (*8*).

(ii) We explore **the potential for absorption to an extractable organic phase** by using an independent estimate of the maximum possible amount of absorption to solvent extractable organic chemical components (case 1) or to native PAHs (case 2).

For case 1, we use independent NIST measures of the amount of extractable organic chemicals present in the soot ($f_{op} = 0.027$ g extractable mass/g soot) (*28*) as our estimate of the mass fraction of the organic phase. For purposes of comparison with prior work by Hong et al. (*8*), we also include a case 2, in which only the identified and quantified PAHs are considered when estimating the amount of organic phase

that contributes to absorption (i.e. $f_{op}K_{op} = f_{PAHs}K_{PAHs}$). Here, f_{PAHs} is the fraction of natively bound PAHs in soot material. For our material, the summed concentration of 40 identified PAHs is $f_{PAHs} = 120 \times 10^{-6}$ g PAHs/g soot. (See the Supporting Information for details.)

For both case 1 and case 2, we estimate the partition coefficient to the organic phase (K_{op}) at its maximum possible value by assuming an ideal organic phase with the activity coefficient equal to one (i.e. $\gamma_{op} = 1$ mol op/mol solute). Following the approach for estimating partition coefficient to natural organic matter (K_{oc}) reported by Schwarzenbach et al. (*41, 47*) and Allen-King et al. (*4*), the maximum partition coefficient can be estimated as follows:

$$K_{op} = \frac{1}{\gamma_{op} \times (\overline{V_{op}} \times \rho_{op}) \times S} \tag{4}$$

Here, S is the subcooled liquid solubility of a solid solute or the aqueous solubility of a liquid solute (mol solute/mL water), and $\overline{V_{op}} \times \rho_{op}$ is the product of molar volume and density which corresponds to the average molecular weight of the organic phase in units of (g op)/(mol op). For both case 1 and case 2, we assume that the organic phase is similar to that in coal tar, with an average molecular weight on the order of 210 g/mol, as previously assumed by others (*8, 48*). For case 1, combining eqs 3 and 4 gives estimates of the absorption contribution to the distribution coefficient ($f_{op}K_{op}$) as 670 and 3700 mL/g for TCB and phenanthrene, respectively. These values are roughly two and five times lower than the lowest K_d values (1400 mL/g for TCB and 20 000 mL/g for phenanthrene), as measured at high values of C_e/S_w (approximately 0.6). For case 2, the distribution coefficients are 3 and 16 mL/g for TCB and phenanthrene, respectively. These values are 3−4 orders of magnitude lower than the lowest measured K_d values. We note that the summed concentration of 40 identified PAHs is equal to only 0.4% of the fraction of total extractable mass and that the results for the first case clearly represent a much higher estimate for possible absorption contribution than the approach previously taken by Hong et al. (*8*). Regardless of the approach taken, however, we conclude that absorption to solvent-extractable phases comprises only a small fraction of phenanthrene sorption to diesel soot SRM 2975. Our higher estimate suggests that such absorption may contribute up to a maximum of 50% of the observed TCB sorption at high C_e/S_w.

The above results are consistent with suggestions made by Hong et al. on the basis of desorption data for six lampblack samples (*8*). These authors suggested that surface adsorption was likely the governing mechanism for all lampblacks that had relatively low concentrations of identified PAHs (from 700 to 12 846 mg/kg lampblack). In contrast, coal-tar-type absorption was found to be a dominant mechanism only for lampblack samples containing high PAHs concentrations (from 23 962 to 41 905 mg/kg lampblack). For the SRM 2975 studied here, the summed concentration of identified PAHs is roughly seven times smaller than that for the lowest lampblack value evaluated by Hong et al.

Unlike prior sorption results for sediments dominated by partition (*7, 49*), the sorption nonlinearity observed for soot in this work persisted at even the highest concentrations studied. Nonetheless, it is possible that absorption played a more prominent role than our case 1 and case 2 estimates would suggest. In particular, it is possible that there is an unknown amount of absorbing phase, above that quantified through solvent extraction. For this case, subsequently referred to as case 3, we modeled our data with a form of the

dual domain model in which the fraction of absorbing organic carbon is also used as a variable (eq 5).

$$q_e = q_{ad,e} + K_{oc}f_{oc}C_e =$$
$$(q_{ad,\max}' \times \rho) \exp\left[-c\left(\frac{\epsilon_{sw}}{N}\right)^d\right] + K_{oc}\,f_{oc}C_e \quad (5)$$

The model was fit to data by varying the fraction of absorbing carbon between zero (only adsorption) and the total measured carbon content, $f_{oc} = 0.817$. We assumed $\log K_{oc}$ to be the maximum expected value for sediment organic matter (4.53 for phenanthrene and 3.4 for TCB). With $K_{oc}\,f_{oc}$ prespecified (in trial-and-error mode), the three fitting parameters for automated optimization were still $q'_{ad,\max}$, c, and d. As shown in the Supporting Information, the fitting results (Table 4S, Figures 1S and 2S) revealed that for both solutes, $f_{oc} = 0$ (no absorption) gave the best fit with the lowest standard deviation and mean weighted square errors. The quality of fit, however, was essentially equivalent to those obtained at very low values of f_{op} (e.g., case 1 and case 2, see Figures 1Sa–c and 2Sa–c). On the other hand, the quality of fit was substantially worse if f_{oc} was assumed to be more than 20% of the total measured carbon (see Figures 1Sd–f and 2Sd–f).

(iii) The above results (i.e., that absorption may be relatively unimportant for SRM 2975) suggest that our sorption isotherm data can be well described by means of **Polanyi modeling of the overall nonlinear isotherm** (case 3 with $f_{oc} = 0$). Results of such modeling are shown in Figure 4 for phenanthrene and TCB in terms of Polanyi coordinates and in Figures 1Sa and 2Sa (Supporting Information) in terms of conventional relative concentration units.

Figure 4 shows plots of volume adsorbed per mass of diesel soot against adsorption potential density. Compared to TCB, more phenanthrene was sorbed to the diesel soot at low relative concentrations (i.e., at higher values of adsorption potential density). This is perhaps explained by the greater van der Waals interaction between the planar phenanthrene aromatic rings and the planar sheets of the soot matrix (*16*, *50*, *51*). In contrast, the maximum adsorption capacity (in either volumetric or mass units, $q'_{ad,\max}$ or $q_{ad,\max}$) is higher for TCB (24 μL/g or 35 mg/g) than for phenanthrene (17 μL/g or 19 mg/g)—see Table 4S for details. This may reflect better access of TCB to the smaller micropores because of its smaller size (160 Å³ for TCB vs 213 Å³ for phenanthrene). (Estimated values of molar and molecular volume for both compounds are provided in Table 1S.) Another explanation could be less efficient packing of solid crystallite phenanthrene compared to liquefied TCB in soot pores at 22 °C. Less efficient packing for adsorption has been implied by prior work on activated carbon (*23*, *52*, *53*) and has also been suggested for describing the sorption of PAHs and chlorinated benzenes by sediment that contains high surface area carbonaceous materials (HSACM) (*7*).

The values of maximum adsorption capacity ($q'_{ad,\max}$) described above are consistent with those of other adsorbates on activated carbons, provided that one properly normalizes for the vastly different specific surface areas of the two types of materials. More specifically, a $q_{ad,\max}$ value on the order of 0.25 mg/g per 1 m²/g of surface area has been estimated for activated carbon, as based on reported adsorption data and assuming an adsorbate density of roughly 1 g/mL (*49*, *53*). On this basis, the maximum adsorption capacity for diesel soot SRM 2975 (with surface area of 127 m²/g) would be estimated at approximately 32 mg/g. The maximum observed adsorption capacity for this material (as extrapolated from measured sorption data) is 35 mg/g for TCB and 19 mg/g for phenanthrene. These values are reasonably close to our a priori estimate and thus provide additional support for our

conclusion that adsorption is the dominant sorption mechanism in this material, even at high C_e/S_w.

Overall, our results confirm that sorption with soot is substantially higher than sorption with sediment organic matter at low concentrations and that sorption is strongly nonlinear in a manner expected for adsorption processes. The extractable organic content of SRM 2975 is sufficiently low that the isotherm sorption data over the full concentration range for SRM 2975 can be well modeled using a single adsorption isotherm. Moreover, the quality of model fit was poor if more than 20% of measured carbon was assumed to act as a linear absorption medium. In this context, we suggest that the agreement of K_{oc} values obtained at high C_e/S_w with those obtained for sediment organic matter may simply reflect that the extent to which the HOC volumetrically "fills" the sorbent at conditions near S_w is approximately the same for the soot as for sediment organic matter, when both are normalized for the amount of carbon present (i.e., when reported as K_{oc}). In any case, the highly nonlinear nature of the overall isotherm and the especially strong adsorption at low values of C_e/S_w will have important implications for understanding contaminant fate and remediation in sediments and soils that contain soot carbon.

Supporting Information Available

Additional information on the purity check of ¹⁴C-labeled chemicals, the characterization of the black carbon materials, details of control studies, details of methods used for analyzing batch sorption, additional discussion of the comparison of soot K_{oc} values from this work with those of prior investigators, and the following additional results: (1) Physiochemical Properties of Studied Solutes (Table 1S), (2) Sorbate Recovery in Blank (Solid-free) Samples with and without PACl (Table 2S), (3) Fitted Parameters of Observed Sorption Data by Freundlich Isotherms (Table 3S), and (4) Fitted Parameters of Observed Sorption Data by Dual Domain Model (Table 4S, Figures 1S and 2S). This material is available free of charge via the Internet at http://pubs.acs.org.

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