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Impact of Clay Minerals and DOM on the Competitive Sorption/Desorption of PAHs

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Two model compounds were used to investigate sorptive phenomena of a silty-sand soil under single and binary solute systems at different concentrations. In the sorption isotherms, the presence of phenanthrene (PHE) exhibited a statistically significant ($P < 0.05$) sorption competition over pyrene (PYR), regardless of the concentration. PYR influenced the PHE isotherms only when it was present at 15 mg/L. The concentration dependence in sorption competition was only evident for the more hydrophobic PYR. In the presence of PHE, the fraction of desorbed PYR was significantly increased with an increase in PYR concentration. PHE desorption enhancement was the most observable with the higher initial concentration (15 mg/L). However, the presence of PYR did not affect PHE desorption. This study found that, based on equivalent solid mass, soils containing only clay minerals sorbed 12.2% more PHE than soils with only soil organic matter (SOM) for 3 mg/L PHE. Clay minerals also impacted desorption as evidenced by a 65% decrease in desorbed PYR fraction compared with when the soil only contained SOM. The dissolved organic matter (DOM) amendment did not increase desorption. Instead, PHE desorption was significantly inhibited by the added DOM. For this study, co-sorption was found to be the mechanism for the inhibited desorption.

KEY WORDS: *co-solute, co-sorption, competition, phenanthrene (PHE), pyrene (PYR).*

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INTRODUCTION

POLYCYCLIC aromatic hydrocarbons (PAHs) have been identified as the primary contaminant in a variety of soils, sediments, and natural waters. For soil and sediment systems, sorption and desorption are important factors governing the environmental fate of PAHs. The extent of sorptive phenomena is dependent on the specific soil-contaminant combination as well as the physicochemical property of the environment. It is well known that sorption of hydrophobic contaminants to clay minerals dominates in dry soils, while partitioning to the soil organic matter (SOM) is often the main interaction for saturated soils (Chiou *et al.*, 1983; Karickhoff *et al.*, 1979; Murphy *et al.*, 1990). Furthermore, SOM is typically the principal PAH sorbent under hydrated conditions if present at a sufficient level, whereas both SOM and clay minerals can significantly affect sorption when the SOM content is low (i.e., <6% SOM) (Ball and Roberts, 1991; Chiou, 1989; Hassett and Banwart, 1989; Murphy *et al.*, 1990).

Because contaminants are released to the environment as multisolute mixtures rather than a single solute, the sorption characteristics of the individual compound can be modified by the presence of other co-solutes (Peng and Dural, 1998). Therefore, the different sorption characteristics of compounds in the absence and in the presence of other contaminants should also be assessed. In conducting these assessments, it should be noted that sorption phenomenon can be further confounded by the presence of other sorptive material such as dissolved organic matter (DOM). The extent to which SOM (Chiou *et al.*, 1998; Kile *et al.*, 1995) and DOM may sorb a specific compound is dependent on the fraction of aromatic or aliphatic moieties present (Chefetz *et al.*, 2000).

The impact of DOM on desorption of sorbed chemicals has not been widely studied (Barriuso *et al.*, 1992; Plaehn *et al.*, 1999). This is surprising because DOM is known to enhance the water solubility and subsequent desorption of several PAHs (Abdul *et al.*, 1990; Barriuso *et al.*, 1992; Chiou *et al.*, 1986; Lassen and Carlsen, 1997). However, DOM can also reduce the mobility of PAHs due to co-sorption or cumulative sorption (Abdul *et al.*, 1990; Totsche *et al.*, 1997). Thus, the extent of DOM-PAH interaction is not only specific with respect to the PAHs molecular structure (Johnson and Amy, 1995; Whitehouse, 1985), but also a function of the quantity (i.e., concentration) and quality (i.e., aromatic or aliphatic content) of the DOM (Benoit *et al.*, 1996; Chefetz *et al.*, 2000; Raber *et al.*, 1998; Whitehouse, 1985). Researchers have shown that both commercial humic and fulvic acids are not representative of the natural SOM (Graber and Borisover, 1998) or subsequent DOM (Raber *et al.*, 1998). In fact, the investigators emphasized that the sorptive phenomena that arose when commercial humic and fulvic acids were used often led to misrepresentative results.

The primary objective for this study was to evaluate the sorption and desorption of pyrene (PYR) and phenanthrene (PHE) in a natural soil. To achieve this objective, three key subtasks were investigated: (1) the occurrence of competitive sorption for a co-solute system, (2) contribution of clay minerals and SOM to PAH sorptive phenomena, and (3) the influence of DOM on the desorption of single and binary solutes.

Materials and Methods

Bulk and Subsoil Sources

Clean silty sand soil originating from Colombia, SA, was sampled at a depth of 0 to 60 cm and characterized. The soil characterization yielded a pH of 3.56 in 0.01 *M* $CaCl_2$ and 4.04 in water. The clay and silt contents were determined to be 180 g/kg clay and 200 g/kg silt, respectively, following ASTM method D2487. The total organic carbon (TOC) was determined to be 17.7 g/kg (Shimadzu TOC-5000 analyzer). The SOM was then estimated to be 3.54% based on its measured TOC (Ranney, 1969). A sodium acetate-sodium chloride saturation and magnesium nitrate extraction method resulted in a 4.24 meq/100 g cation exchange capacity (CEC). X-ray diffraction (Siemens D500 model) identified the primary clay components to be 20% vermiculite and 49% kaolinite. Smectite was not detected in the soil. After characterization, the soil was sieved to particle size of less than 2 mm and air-dried before initiating the experiments.

To investigate the contribution of SOM or clay minerals to the sorption and desorption of the model PAHs, two subsoils were prepared: one without SOM and the other without clay fractions (<2.0 μm diameter). The bulk soil was repeatedly treated with hot 30% hydrogen peroxide (H_2O_2) to remove the SOM (Kunz and Dixon, 1982). To verify an acceptable SOM removal was achieved, the TOC content of the treated subsoil was measured via a TOC analyzer. The TOC of SOM-removed subsoil was found to be 1.6 ± 0.3 g/kg (90% reduction). A similar SOM reduction was reported by Hyeong and Capuano (2000), whose removal efficiency was 85 to 96% by using the same methodology. A mass balance determined that less than 1% of the clay minerals was lost during the removal of SOM.

The bulk soil was treated as outlined by Gee and Bauder (1982) and Jackson (1985) to remove the clay fraction. It should be noted that although clay minerals can be present in other size fractions, the largest portion is in the clay-size fraction (i.e., <2 μm) (Christensen, 1992; Wattel-Koekkoek *et al.*, 2001). A standard hydrometer analysis (ASTM D2487-93) was used to quantify the extent of clay removal. Using this approach a 99% clay removal efficiency was achieved. During the clay removal, there was a 4% loss in silt fraction (~10 g/kg); however, this was not taken into consideration in this study. SOM losses were not detectable.

Chemical Sources

PYR was purchased in excess of 98% purity from Aldrich Chemical Company. PHE at 96% purity was obtained from Sigma Chemical Co. Each stock solution of 100 mg/L was prepared in HPLC-grade hexane (Fisher Scientific). Both background solution reagents, calcium chloride ($CaCl_2$) and sodium azide (NaN_3), were obtained from Fisher Scientific and dissolved in distilled water. $CaCl_2$ (0.5 m*M*) was used to poise the ionic strength and NaN_3 (200 mg/L) to prevent any microbial activity during the experiment.

Collection of Natural DOM

The DOM-rich solution was extracted from a natural sandy lean clay soil with an organic carbon content of 44.6 g/kg. A complete characterization of this soil has been reported elsewhere (Ramirez and Cutright, 2001). A 1:10 ratio (g soil to mL water) was agitated in a Labline environmental shaker at 125 rpm and 28 ± 2°C. After 2 days, the supernatant was collected via centrifugation at 1070 g for 20 min. A Shimadzu TOC Analyzer was used to detect the dissolved organic carbon (DOC) concentration in the supernatant. In this study, the DOM concentration was assumed to be equivalent (for comparisons between different DOM concentrations only) to the DOC concentration because no external carbon source was involved in the DOM collection. It is important to note that the actual DOM concentration is greater than the DOC concentration. This is due to other components such as hydrogen, oxygen, and nitrogen, which comprise approximately 35% of organic matter (Sparks, 1995).

Single Solute Sorption and Desorption Experiments

Triplicate samples were used for the individual sorption experiment, in which PYR or PHE in hexane was added to each reactor (heavy-duty 40 mL PYREX tube) to yield initial concentrations of 3, 5, 7, 10, and 15 mg/L. After the hexane was evaporated, 4 g of soil and 40 mL of the background solution were added to each reactor. Thus, if 100% sorption by soil was initially achieved, the spiked concentrations corresponded to 30, 50, 70, 100, and 150 mg/kg soil. The rationale for spiking high concentrations was to simulate natural soils subject to high PAH contamination. PYR or PHE concentration in industrially contaminated soils was found to be 150 to 230 mg/kg of the 1000 mg total PAH/kg soil (Cornelissen *et al.*, 1998).

The reactors were sealed, vortexed for 20 s, and then placed on a shaker bath operated at 24 ± 2°C and 125 rpm. After reaching the thermodynamic sorption equilibrium time that had been determined to be 24 h for PYR and 144 h for PHE in previous studies (Hwang, 2002; Hwang *et al.*, 2000; Ramirez and Cutright, 2001), the reactors were centrifuged with IEC Centra-4B centrifuge at 1070 g for 20 min. Thirty-five mL of supernatant were decanted and analyzed via a fluorescence spectrometry.

Desorption isotherm experiments were initiated immediately after the sorption isotherms were determined. The decanted amount (35 mL) was replaced with the fresh background solution. The reactors were returned to the shaker bath for the allocated desorption equilibrium time (144 h for both PYE and PHE) as determined by the desorption kinetic study (Hwang, 2002; Hwang *et al.*, 2000). The desorption process was repeated three times for each reactor. After centrifugation, the solution-phase PYR or PHE concentrations were analyzed by fluorescence spectrometry.

It is important to note that the sorption-desorption kinetics may differ significantly for the bulk and subsoils. For instance, bulk soils will have different surface areas than soils with the SOM or clay minerals removed, thereby impacting the extent of sorption-desorption. However, this phenomenon and its impact were not evaluated in this study at this time. The kinetics were conducted solely on bulk soil. Sorption-desorption comparisons were based on total amount sorbed/desorbed to/from the bulk and subsoils where the SOM or clay minerals were removed.

To evaluate the influence of the natural DOM on desorption of the sorbed PYR or PHE, a concurrent desorption study was conducted. In this desorption experiment, a DOM-rich solution (17.87 ± 0.72 mg/L as DOC) replaced the supernatants instead of refreshing them with the background solution. To poise the ionic strength and prevent the microbial activity during this experiment, $CaCl_2$ (0.5 m*M*) and NaN_3 (200 mg/L) were also added to the DOM-rich solution. As with the previous experiments, blank samples containing the target compounds and the background solution were monitored. The blank samples indicated that there were no measurable losses due to sorption to the reactor walls or compound volatilization.

Binary Solute Sorption and Desorption Experiments

For the binary solute system, PHE and PYR were applied simultaneously with the different concentration combinations. PYR sorption and desorption were evaluated as a function of concentrations (3, 5, 7, 10, and 15 mg/L) in the presence of 0, 3, and 15 mg/L PHE. Simultaneously, PHE-sorptive behavior was also investigated as function of concentrations (3, 5, 7, 10, and 15 mg/L) in the presence of 0, 3, and 15 mg/L PYR. Each treatment combination was conducted in duplicate. The experimental method was identical to that of the single solute system. The only difference was that a 144-h equilibrium time was used for both sorption and desorption to assure the steady-state conditions for both PAHs. A synchronous scan method via a fluorescence spectrometry was applied to simultaneously detect

PHE and PYR in the solution phase after each sorption-desorption step (Matuszewska and Czaja, 2000; Vo-Dinh, 1978).

Analytical Methods

A Perkin-Elmer LS-50B fluorescence spectrometer was used to detect the solution phase concentration of PYR or PHE. For the single solute system, the optimal excitation and emission wavelengths determined were λ_{ex} = 335 nm and λ_{em} = 378 nm for PYR detection and λ_{ex} = 253 nm and λ_{em} = 365 nm for PHE detection. In the synchronous scan method for the binary solute system, a constant wavelength interval, $\Delta\lambda$ = 112 nm (365 nm (λ_{em}) to 253 nm (λ_{ex})), was used for PHE detection, while $\Delta\lambda$ = 44 nm (379 nm to 335 nm) was used for PYR detection. Additional studies with DOM did not yield a fluorescence intensity in either the single or synchronous scans. Therefore, DOM would not interfere with solute quantification.

The compound sorbed to the soil was recovered via Soxhlet extraction with methylene chloride over 15 h. The extract was redissolved in hexane and analyzed by the fluorescence spectrometer. The mass balance between the compound in the solution- and in the soil-phase was within a ±5% error range. Each reactor was rinsed with solvent, and the resulting solution was analyzed to verify that the compound had not sorbed to the reactor walls. The solvent rinse did not yield detectable levels of PYR and PHE.

TOC in the solution phase was measured using a Shimadzu TOC-5000A Analyzer (Kyoto, Japan) with a 680°C combustion temperature. For quantifying the extent of SOM removal, TOC of the treated subsoil was measured with solid sample module (combustion at 900°C and acidification at 200°C). The analyzer was calibrated following manufacture’s guidelines.

The quality of the DOM was determined via solid-state ^{13}C-NMR. The spectra were obtained using a Varian Unityplus-200 (4.7T) Spectrometer equipped with a Doty Scientific supersonic VTMAS probe. All samples were packed into 7-mm silicon nitride rotors with Kel-F end caps. Spectra were acquired at a spinning speed of 5 kHz. All ^{13}C chemicals shifts were corrected by using hexamethylbenzene (δ_{Me} = 17.3 ppm) as an external reference. CP/MAS spectra were acquired with a 1 to 2 s relaxation delay, 1 ms contact time, 55 kHz spin lock field, and 60 kHz decoupling field.

RESULTS AND DISCUSSION

Sorption Isotherms

Figure 1 is a plot of PYR sorption isotherms in the single and binary solute systems. PHE data are presented in Figure 2. As mentioned earlier, sorption equilibrium was

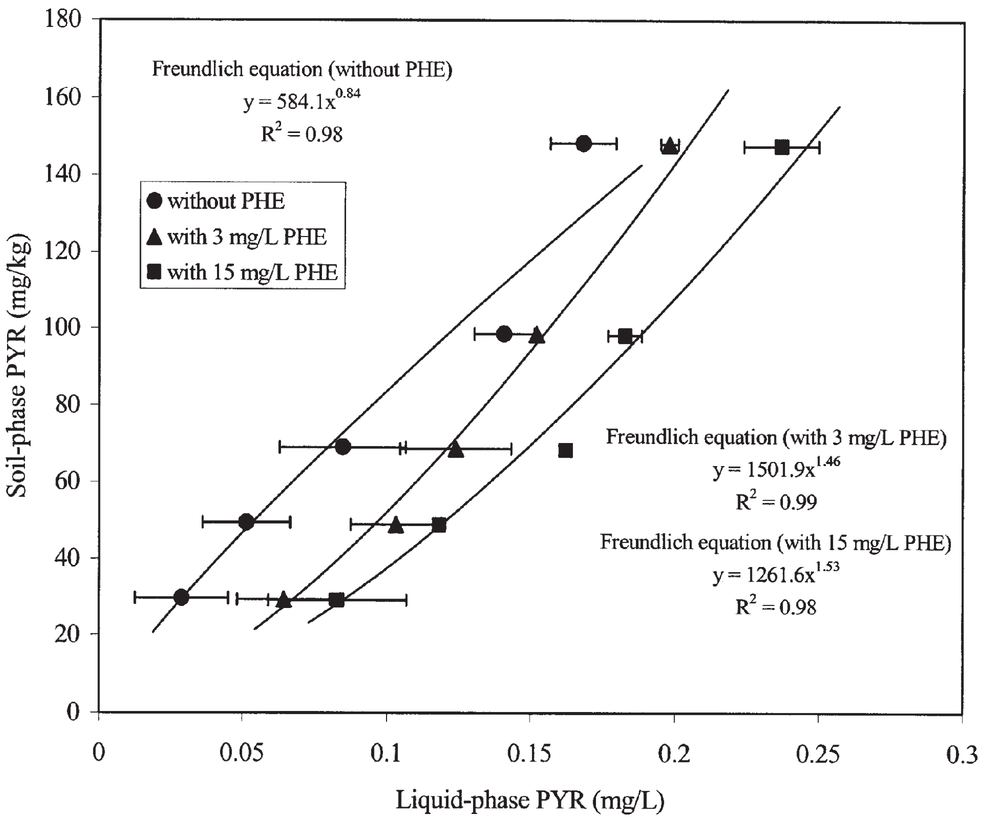


FIGURE 1

PYR sorption isotherms in the absence and in the presence of PHE. Data are means of triplicate samples for the single solute system and duplicate samples for the binary solute system. Error bars are standard deviations. Error bars on y-axis are hidden behind the data points (within range of 0.01 to 0.24 mg/kg).

attained by 24 and 144 h for PYR and PHE, respectively, in the single solute system. The difference in time required for sorption equilibrium for the single solute system was based on the physicochemical characteristic of the solute. For instance, the partitioning coefficient (log K_{ow}) was reported to be 4.57 for PHE and 5.18 for PYR (Karickhoff *et al.*, 1979). Furthermore, PHE had a greater solubility (1.29 mg/L) than PYR (0.135 mg/L) (Mackay and Shiu, 1977). Therefore, the shorter sorption equilibrium time for PYR was attributed to its greater hydrophobicity than that of PHE (Hassett *et al.*, 1981).

Sorption isotherms were fit by the Freundlich equation

$$q_e = K_f C_e^{1/n}$$

where q_e is the compound sorbed per mass of soil, C_e is the solution-phase concentration of compound, K_f is the Freundlich sorption coefficient, and $1/n$ is the

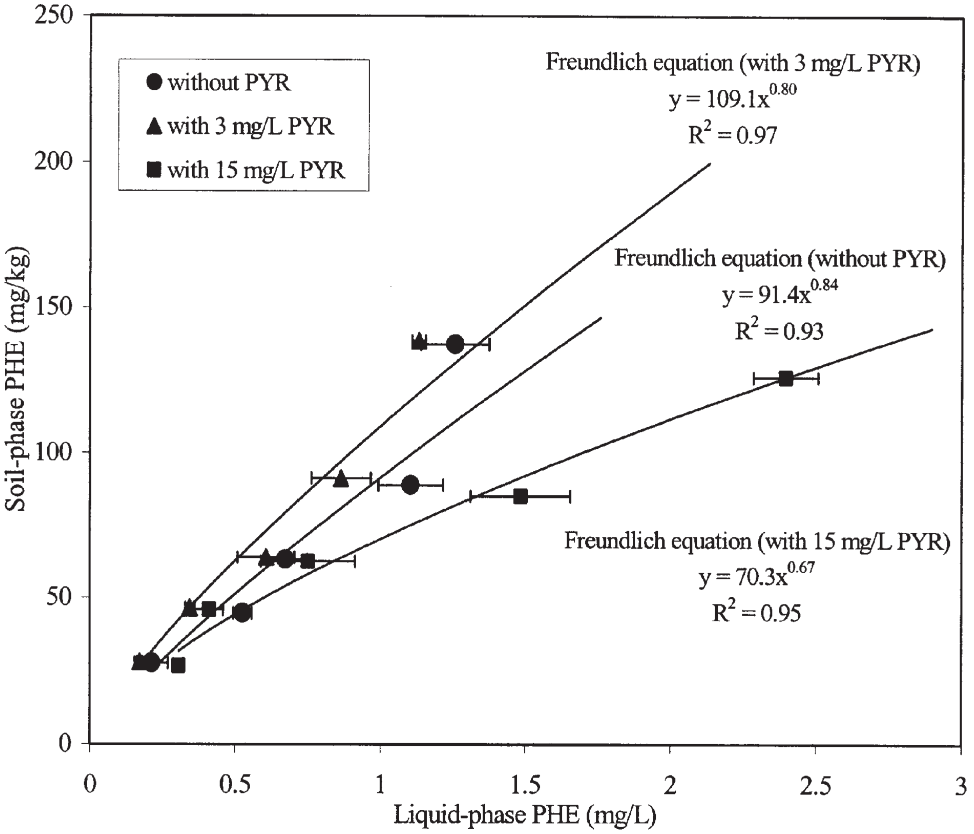


FIGURE 2

PHE sorption isotherms in the absence and in the presence of PYR. Data are means of triplicate samples for the single solute system and duplicate samples for the binary solute system. Error bars are standard deviations. Error bars on y-axis are hidden behind the data points (within range of 0.10 to 1.72 mg/kg).

Freundlich exponent. As shown, the K_f of PYR was increased from 584 to 1502 in the presence of 3 mg/L PHE as a co-solute, and to 1262 with 15 mg/L PHE. However, the two increased K_f values were not significantly different from each other ($P > 0.05$). At the same time, the presence of PHE made PYR isotherms more nonlinear ($1/n \neq 1$), regardless of PHE concentration (3 or 15 mg/L). The two $1/n$ values were not statistically different ($P < 0.05$). Because the isotherms have different slopes, it was difficult to interpret the full extent of PHE impact on PYR isotherms. However, it was evident that a lesser amount of PYR was sorbed when in the presence of PHE regardless of the PHE concentration used. The difference in the PYR isotherms in the presence of PHE was attributed to PYR being displaced from the more favorable sorption sites. The fact that this displacement occurred even at low PHE concentrations implies that PYR did not bind to the SOM solely as a result of the strong competitive effect of PHE.

Figure 2 reveals that the presence of 3 mg/L PYR increased the PHE K_f from 91 to 109 ($P > 0.05$). When PYR was added at 15 mg/L, it substantially decreased PHEs K_f to 70 ($P < 0.05$). The linearity of PHE sorption remained relatively constant from $1/n = 0.84$ to 0.80 with 3 mg/L PYR > 0.05), but decreased to 0.67 with 15 mg/L PYR ($P < 0.05$). From a statistical viewpoint, the presence of 3 mg/L PYR did not create any change in PHE isotherms. However, phenomenologically, PHE isotherms with 15 mg/L PYR indicated that a relatively high amount of PYR should be present to yield significant competitive sorption inhibition. This was not an expected result because PYR is more hydrophobic and therefore should easily displace less hydrophobic PHE for the given sorption sites when they co-exist (Xing *et al.*, 1996). However, this study indicated that 3 mg/L PYR was not sufficient enough to inhibit PHE sorption or to facilitate its displacement.

The concentration dependence of the competitive inhibition of a co-solute was investigated further. Figure 3a contains the PYR sorption results when different initial PHE concentrations (0, 3, 5, 7, 10, and 15 mg/L) were applied with either 3 or 15 mg/L PYR. In order to compare the results, the sorbed amounts in the binary systems were normalized to the single solute system by dividing the binary system data by the single solute values. As shown, the impact of co-solute (PHE) varied, with the highest initial PYR concentration (15 mg/L) exhibiting the least inhibition by PHE. However, with the 3 mg/L initial PYR concentration, competition was evident even with low PHE concentrations. Xing *et al.* (1996) found that a co-solute to solute molar ratio of 5 or 10 was required to give an appreciable competition. However, the current study shows that the substantial co-solute (PHE) to solute (PYR) sorption competition was mainly dependent on the initial solute concentration. As such, when the more hydrophobic PYR was present at a high enough concentration (i.e., 15 mg/L), it would preferentially sorb over the less hydrophobic PHE, regardless of the amount of co-solute added. Conversely, PHE's sorption competition could be attributed to the co-solute to solute molar ratio when PYR was present at a lower concentration (i.e., 3 mg/L).

PHE sorption demonstrated a different pattern when PYR was applied at the different concentrations (Figure 3b). Regardless of the initial PHE concentration, the competitive inhibition by the more hydrophobic PYR occurred when it was present at a higher concentration (i.e., 15 mg/L), regardless of whether the less hydrophobic PHE was present at 3 or 15 mg/L. Therefore, the results indicated that the competition based on the co-solute to solute molar ratio (Xing *et al.*, 1996) was not a universal rule, or in a linear relationship. Instead, it was found that the governing factor for the sorption competition in this study was the initial concentration of the more hydrophobic PYR when it was present with the hydrophilic PHE.

The contribution of SOM and clay minerals to contaminant sorption amount was investigated with the subsoils in the single-solute system to determine whether clay

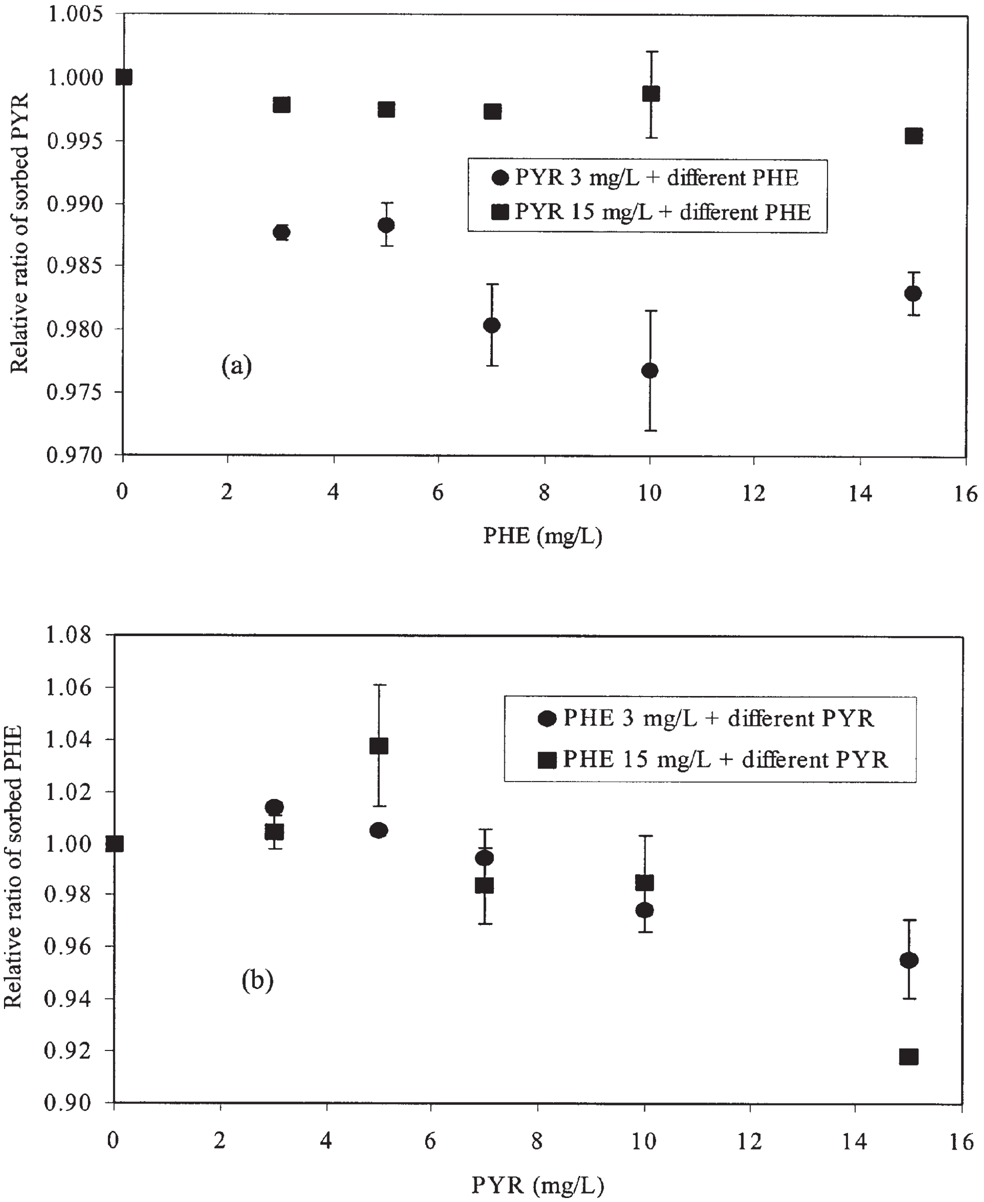


FIGURE 3

Relative sorption ratio of solute in the presence of different co-solute concentrations: (a) PYR with PHE and (b) PHE with PYR. The normalization was conducted by dividing each of duplicate sorbed amounts for the binary systems by the average sorbed solute when it was present alone.

minerals could play a role in PAHs sorption. As seen in Table 1, the amount of sorbed PYR and PHE was slightly reduced in both SOM and clay removed subsoils compared with that in the bulk soil. The decrease in sorbed amount was more

TABLE 1
Contribution of SOM and Clay Minerals to PAH Sorption and Desorption

		PYR (mg/kg)		PHE (mg/kg)	
Soil sample	[mg/L][a]	Sorption[b]	Desorption[c]	Sorption	Desorption
Bulk soil	3	29.35 (±0.02)[d]	2.59 (±0.05)	29.14 (±0.78)	7.54 (±2.39)
	15	49.14 (±0.09)	3.77 (±0.50)	140.35 (±0.85)	43.80 (±0.17)
Soil w/o SOM	3	28.96 (±0.05)	2.91 (±0.07)	27.26 (±0.05)	17.71 (±0.33)
	15	148.58 (±0.03)	4.49 (±0.07)	137.99 (±0.68)	68.20 (±1.20)
Soil w/o clay	3	28.70 (±0.12)	3.97 (±0.03)	23.70 (±0.15)	24.32 (±0.65)
	15	147.75 (±0.04)	12.76 (±0.06)	134.34 (±0.23)	75.34 (±2.12)

Note:
[a] initially added concentration.
[b] sorbed amount after 24-h sorption contact time.
[c] total amount desorbed after 3-time desorption (24-h desorption each time).
[d] standard deviation (n = 3 for bulk soil and n = 2 for others).

observable in clay-removed subsoil. When PYR was applied at 3 mg/L, the clay-removed subsoil only sorbed 0.88% (28.70 vs. 28.96 mg/kg) less PYR than the SOM-removed subsoil and thus was statistically insignificant. Furthermore, a 0.55% smaller but statistically insignificant ($P > 0.05$) PYR sorption was observed in the clay-removed subsoil than that in the SOM-removed subsoil when PYR was added at 15 mg/L (147.75 vs. 148.58 mg/kg). These phenomena were more appreciable for PHE sorption. The clay-removed subsoil sorbed less PHE than the SOM-removed subsoil. PHE sorption was increased by 13.1% (23.70 vs. 27.26 mg/kg) and 2.60% (134.34 vs. 137.99 mg/kg) when the initial PHE concentration was 3 and 15 mg/L, respectively ($P < 0.05$). For this study, the clay minerals had a greater impact on sorption when PAHs were applied at the lower concentration than at the higher concentration (i.e., 3 mg/L vs. 15 mg/L PAHs). This was especially true for PHE ($P < 0.05$).

Desorption Amount

Figure 4a is a plot of the total desorbed amount of PYR using a sequential three-step desorption process. As anticipated for the single solute system, PYR desorption was increased as the initial PYR concentration increased. (In this desorption section, the initial concentration means the compound concentration spiked at the initiation of sorption study.) For example, when 3 mg/L PYR was applied, only 0.32 mg/kg was released into the solution phase, whereas 5.03 mg/kg was desorbed with 15 mg/L of the initial PYR concentration. When PHE was applied in the binary solute system, the PYR desorption amount was substantially increased. For example, for 15:15 mg/L PYR:PHE there was a 53.2% increase in the amount of PYR desorbed. The initial PHE concentration (3 or 15 mg/L) did not yield substantial PYR desorption enhancement when PYR was present below 7 mg/L. However, 15 mg/L PHE produced a desorption enhancement for PYR concentrations greater than 10 mg/L. This phenomenon was the most noticeable when PHE was also present at a higher concentration.

As expected based on the hydrophobicity and solubility, PHE was less resistant to desorption than PYR (Figure 4b). The ease of desorption increased with the applied concentration. For example, 31.40 mg/kg of PHE was desorbed for 15 mg/L PHE compared with 9.57 mg/kg for 3 mg/L. In the binary solute system where PYR was added at either 3 or 15 mg/L, the desorbed PHE amount was statistically insignificant (i.e., desorption very close to the single solute system). Therefore, it is found that once PYR and PHE sorption attained thermodynamic equilibrium, the presence of PYR could not affect PHE desorption. This can be partially attributed to the weaker binding strength of PHE in comparison to PYR's. However, PYR's stronger binding should have also resulted in the displacement of PHE. The apparent inability for PYR to significantly impact PHE desorption at low concentrations may have been due to the displacement rate being slower than PHE's

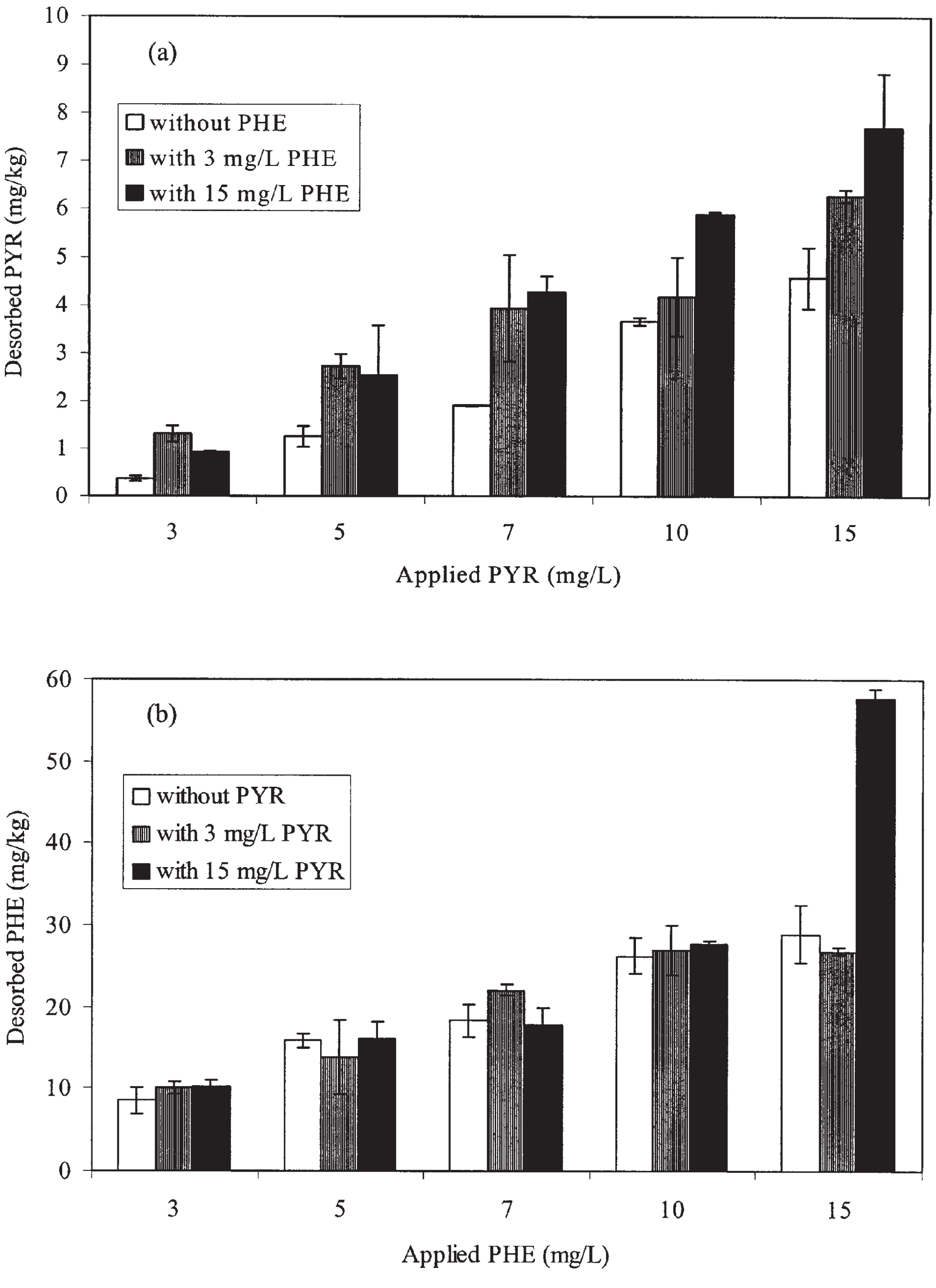


FIGURE 4

Total desorbed PYR (a) and PHE (b) through desorption. Error bars are standard deviations of triplicates in the binary solute system and of duplicates in the single solute system.

desorption rate. Because the displacement was not studied, its impact cannot be validated or invalidated at this time. An exception was found when PHE and PYR were both added at 15 mg/L. Two potential reasons for desorption enhancement when both PAHs were added at high concentrations can include limited sites in the soil matrix or the presence of multiple binding layers. Both scenarios result in an easier desorption (Froment and Bischoff, 1990).

Contribution of SOM and Clay Minerals

For the SOM-removed subsoil, the amount of the desorbed PYR was similar to that of the bulk soil (Table 1). However, when clay minerals were removed, a significant amount of PYR was desorbed. For instance, 3.97 and 12.76 mg/kg PYR was desorbed when it was added at 3 and 15 mg/L, respectively. These numbers indicate that when the SOM was the only sorbent in the clay-removed subsoil, the desorbed PYR amount was 1.5 (3 mg/L dosage)- to 3.4 (15 mg/L)-time greater, compared with the values for the bulk soil. The contribution of clay minerals to PHE desorption was more significant for the lower initial concentration. For example, the desorbed amount was increased by 3.2 (3 mg/L PHE) to 1.7 (15 mg/L) times for the clay-removed subsoil.

When only clay minerals were present as the sorbent, PYR desorption was decreased by 26.7 and 64.8% for the concentrations of 3 and 15 mg/L, respectively, compared with the desorption from the subsoil, which had SOM alone. A similar decrease was found for 3 mg/L PHE (27.2% reduction), but only a 9.5% reduction was observed when PHE was added at 15 mg/L. As found earlier in the subsoil sorption study, the clay contribution to PHE sorption was 2.6% greater than SOM when PHE was added at 15 mg/L, whereas the clay contribution was substantial (12.22%) for 3 mg/L PHE. Therefore, the desorption-resistant fraction was attributed to the PAH binding to the clay minerals. The fraction of compound bound onto the SOM surfaces was easily desorbed due to relatively weak binding forces (partitioning). As such, PAH desorption from the subsoil containing only SOM was easier than desorption from the bulk soil and subsoil containing clay minerals.

Influence of DOM on Desorption Amount

Table 2 shows the difference in the desorbed amount of PYR between two desorption experiments: one for the replacement of supernatants with the fresh background solution and the other with DOM-rich solution. In the single solute system, the influence of the DOM on the fraction of desorbed PYR was varied but not statistically significant ($P > 0.05$). This was attributed to the strong sorption affinity of PYR to the soil matrix as well as the relatively low DOM concentration used.

TABLE 2
PYR Desorption with and without PHE with Respect to the Solution Type used for Desorption

Initial PHE (mg/L)	Initial PYR (mg/L)									
	3		5		7		10		15	
	BG[a]	DOM[d]	BG	DOM	BG	DOM	BG	DOM	BG	DOM
0	0.32[b]	0.40	1.41	1.10	1.90	1.92	3.61	3.76	5.03	4.13
	(±0.08)[c]	(±0.01)	(±0.79)	(±0.12)	(±0.40)	(±0.45)	(±0.30)	(±0.09)	(±0.34)	(±1.26)
3	1.31	1.14	2.73	1.90	3.94	1.99	4.19	3.23	6.28	3.70
	(±0.17)	(±0.01)	(±0.26)	(±0.12)	(±1.12)	(±0.31)	(±0.82)	(±0.12)	(±0.13)	(±0.26)
5	0.92	0.99	—[c]	—	—	—	—	—	6.09	3.83
	(±0.14)	(±0.12)	—	—	—	—	—	—	(±0.19)	(±0.14)
7	1.53	1.01	—	—	—	—	—	—	6.50	3.54
	(±0.11)	(±0.06)	—	—	—	—	—	—	(±0.09)	(±0.10)
10	1.29	1.00	—	—	—	—	—	—	6.43	3.10
	(±0.36)	(±0.19)	—	—	—	—	—	—	(±0.18)	(±0.14)
15	0.93	2.28	2.55	1.01	4.28	3.76	5.90	3.37	7.71	3.72
	(±0.03)	(±0.67)	(±1.04)	(±0.11)	(±0.33)	(±0.03)	(±0.05)	(±0.13)	(±1.12)	(±0.22)

Note: [a] background solution.
[b] unit = mg PYR/kg soil.
[c] standard deviation (n = 3 in the single solute system and n = 2 in the binary system).
[d] DOM solution.
[e] combinations not studied.

In the binary solute system, the DOM addition decreased PYR desorption, except for the 3 mg/L PYR-15 mg/L PHE system. In comparison, PHE desorption was significantly inhibited with the addition of DOM solution (Table 3). The extent of inhibition was more evident with the high initial solute concentration over a wide range of co-solutes. For example, the DOM addition reduced PHE desorption amount by 16% (i.e., 31.4 mg/kg vs. 26.4 mg/kg for 15 mg/L PHE alone), whereas a 78% reduction was found for the 15 mg/L PHE-15 mg/L PYR combination (57.6 mg/kg vs. 12.4 mg/kg).

The decrease in the desorbed PAH amount can be explained by either cumulative sorption or co-sorption. Cumulative sorption results when the DOM interacts with the soil first, followed by PAH sorption to new sorption site (DOM) on the soil (Abdul *et al.*, 1990; Totsche *et al.*, 1997). For co-sorption, the DOM interacts with PAH and then the DOM-PAH associate is sorbed by the soil (Totsche *et al.*, 1997). A more significant inhibition in PHE desorption than PYR desorption can be attributed to the compound-dependent interaction with DOM. Johnson and Amy (1995) found that solubility enhancement by DOM were greater for more hydrophobic PAH (benz[*a*]anthracene vs. anthracene). Whitehouse (1985) also documented that the interaction of contaminant with the DOM was compound specific.

In order to elucidate the reasonable mechanism for the decreased desorption amount by the DOM addition, an experiment on the DOM profile was conducted. For this purpose, reactors without compound were monitored in the exactly same methods that used for the sorption and desorption experiments described earlier. As seen in Figure 5, for the reactors refreshed with the background solution, the DOM production was not appreciable but was maintained at ~1.5 mg/L after three-time successive decant and refill, regardless of the desorption starting point (i.e., after 24- or 144-h sorption). Meanwhile, the DOM concentration of the reactors refilled with the DOM-rich solution was not significantly changed throughout the desorption experiment (~14.7 to 17.1 mg/L). This relatively constant DOM concentration indicated that the added DOM did not sorb to the soil ($P > 0.05$). Therefore, cumulative sorption was not the governing mechanism responsible for inhibiting PAH desorption, but co-sorption was.

The DOM-associated PAHs might have different physicochemical characteristics from those of either DOM or PAHs alone. The increased hydrophobicity of the DOM-PAHs complex could result in greater sorption affinity (co-sorption) to the soil matrix than either DOM or PAHs. Further investigation on the co-sorption of DOM-PAHs associates was performed using half the concentration of the DOM solution used previously. For this purpose, the DOM-rich solution (17.87 ± 0.72 mg/L as DOC) was diluted with distilled water to a concentration of 9.55 ± 0.24 mg/L as DOC. Figure 6a and 6b show desorption tendency of PYR and PHE, respectively, depending on the type of the solution used in desorption step. The hypothesis underlying this experiment was that if a lower DOM concentration was used, desorption would be increased more than the case with the higher DOM solution due to a decrease in co-sorption tendency.

TABLE 3
PHE Desorption With and Without PYR with Respect to the Solution Type Used for Desorption

Initial PYR (mg/L)	Initial PHE (mg/L)									
	3		5		7		10		15	
	BG[a]	DOM[d]	BG	DOM	BG	DOM	BG	DOM	BG	DOM
0	9.57[b] (±0.22)[c]	7.36 (±0.55)	16.51 (±0.33)	15.23 (±0.67)	19.71 (±0.37)	16.96 (±0.94)	27.79 (±2.73)	24.77 (±3.61)	31.40 (±3.31)	26.42 (±1.63)
3	10.07 (±0.77)	4.56 (±0.11)	15.83 (±1.76)	6.66 (±0.27)	22.08 (±0.66)	6.82 (±0.16)	27.03 (±3.02)	8.87 (±0.20)	26.81 (±0.46)	12.39 (±0.32)
5	8.53 (±0.39)	4.68 (±0.02)	—[c] —	— —	— —	— —	— —	— —	25.29 (±1.79)	9.27 (±0.96)
7	8.89 (±0.66)	3.85 (±0.64)	— —	— —	— —	— —	— —	— —	36.05 (±3.92)	13.16 (±0.34)
10	8.94 (±0.84)	5.16 (±0.02)	— —	— —	— —	— —	— —	— —	39.49 (±1.93)	13.58 (±0.38)
15	10.32 (±0.70)	5.22 (±0.21)	16.11 (±2.11)	11.37 (±1.53)	17.88 (±2.08)	5.46 (±0.13)	27.71 (±0.30)	8.22 (±0.38)	57.64 (±1.27)	12.44 (±0.27)

Note:
[a] background solution.
[b] unit = mg PHE/kg soil.
[c] standard deviation (n = 3 in the single solute system and n = 2 in the binary system).
[d] DOM solution.
[e] combinations not studied.

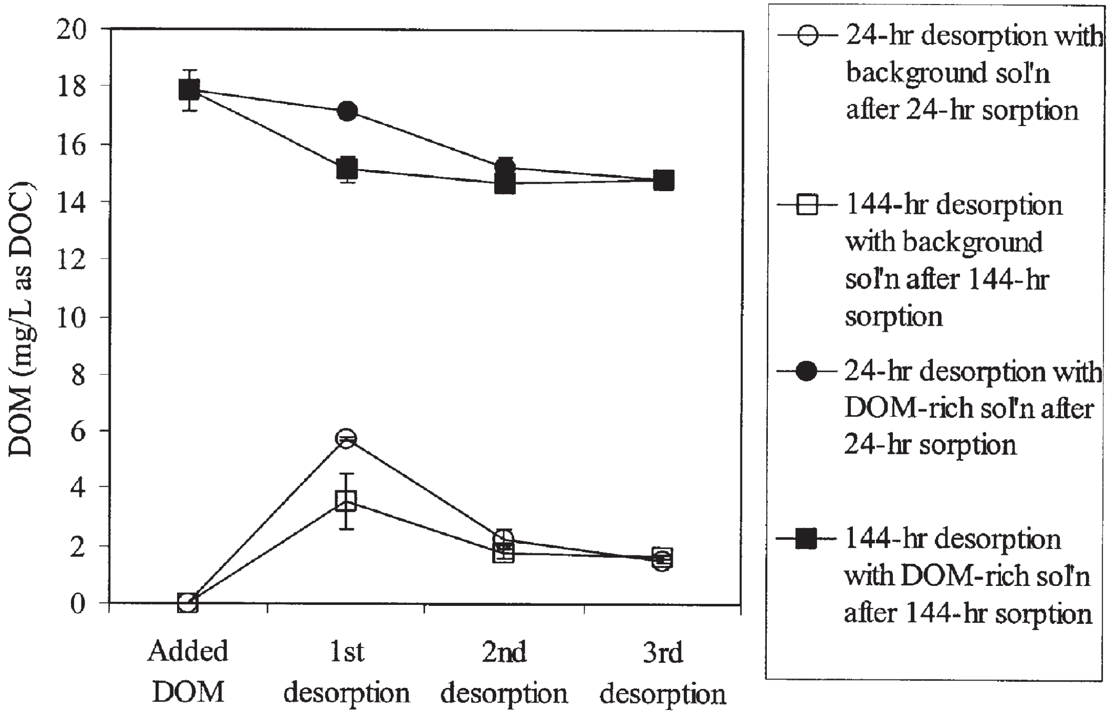
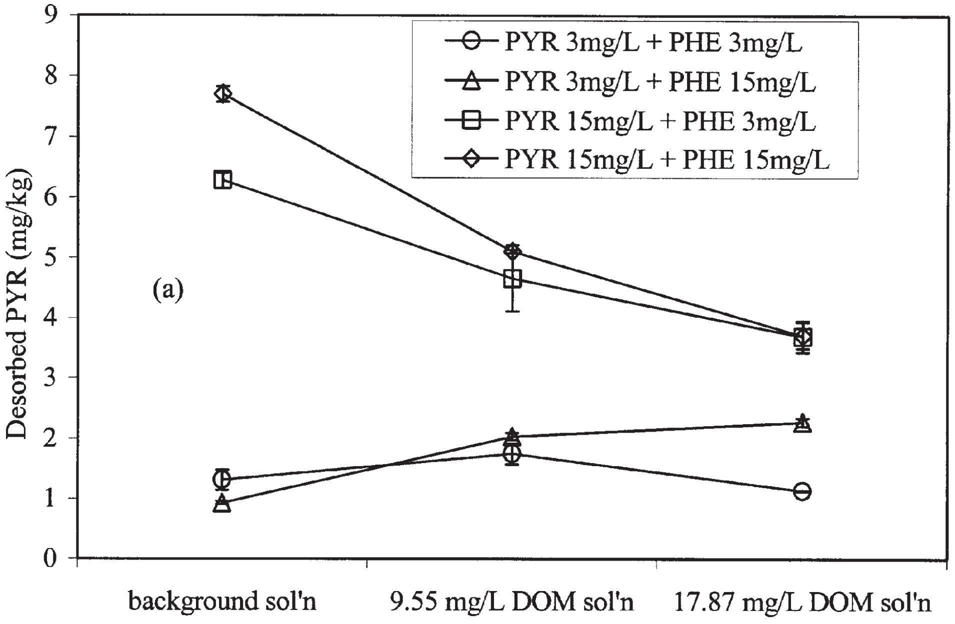


FIGURE 5

DOM profile in the experiment without PAHs. Data are means of duplicate samples with standard deviations.



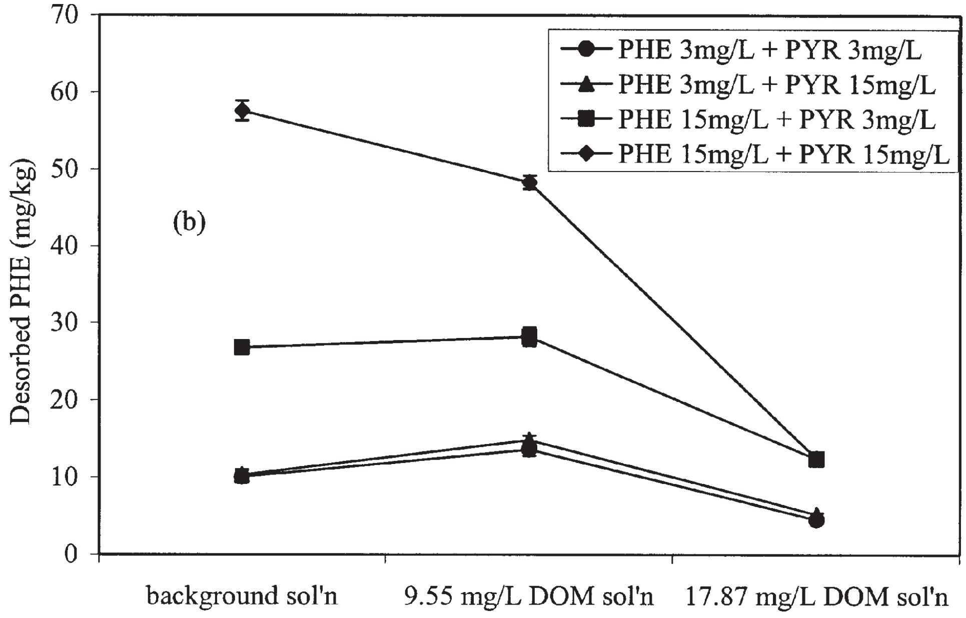


FIGURE 6

Compound desorption depending on the solution type used for desorption: (a) PYR desorption and (b) PHE desorption. Data are means of duplicate samples with standard deviations.

As shown in Figure 6, the hypothesis was confirmed as the desorbed amount of PYR with the 9.55 mg/L DOM solution was approximately the average of desorption by the background and 17.87 DOM solutions. For PHE desorption, the desorbed amount by the 9.55 mg/L DOM solution was close to the amount by the background solution. These results depict a smaller occurrence of co-sorption of the DOM-PAHs complex due to a lack of sufficient DOM concentration.

Along with the quantity, the DOM quality can also result in different interaction phenomena. Based on the ^{13}C-NMR analysis in this study (Figure 7), the spectrum of DOM from the SOM-rich soil had four major peaks at ~35, ~75, ~130, and ~170 ppm, whereas the DOM from the model soil had only two major peaks at ~35 and ~75 ppm. These peaks are most likely representative of the aliphatic carbons (0 to 50 ppm), oxygen-substituted aliphatic carbons (60 to 100 ppm), aromatic carbons (100 to 160 ppm), and carboxylic carbons (160 to 190 ppm). Thus, comparison of two ^{13}C-NMR spectra reveals that the DOM extracted from the SOM-rich, sandy lean clay soil (New Mexico soil) used by Ramirez and Cutright (2001) had a relatively higher aromatic carbon fraction (chemical shift 100 to 160 ppm) than the DOM produced from the silty-sand soil used for these experiments. Because the solute was forced to desorb by the co-solute in the binary system due to the site competition, the DOM-PAHs associates with the greater aromatic fraction increased co-sorption affinity to the soil matrix, which, in turn, decreased desorbed amount.

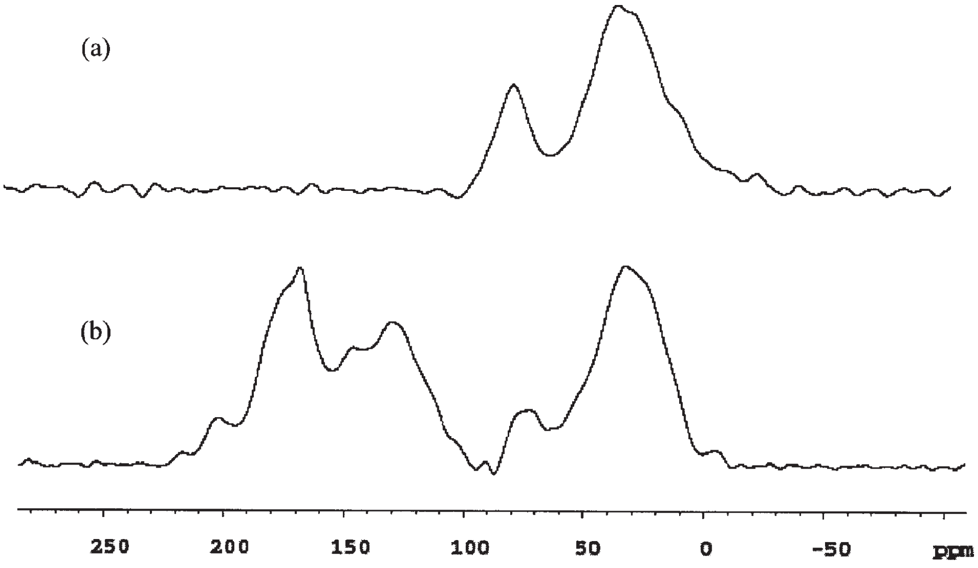


FIGURE 7

^{13}C-NMR spectra for DOM from model soil (a) and for DOM from the New Mexico soil (b).

CONCLUSIONS

This study was conducted to elucidate the sorptive phenomena of PYR and PHE in the single and binary solute systems. In both sorption and desorption processes, the presence of a co-solute modified the solute's sorptive characteristics, depending on the compounds concentration. This study also revealed that sorption should not be thought of as a unique interaction of compounds with the SOM without considering the effect of mineral constituents. No positive effect of DOM was found during the desorption step. Instead, co-sorption with DOM complexes occurred thereby reducing the desorption amount.

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