

Statistical Implications of Pyrene and Phenanthrene Sorptive Phenomena: Effects of Sorbent and Solute Properties

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Abstract. A 3×2 factorial experiment in a generalized randomly complete block was conducted to assess the effects of soil type, soil preparation, and solute concentration on the sorptive behavior of pyrene (PYR) and phenanthrene (PHE). Three bulk soils were treated to remove the soil organic matter (SOM) or clay fractions, then spiked with an initial PYR/PHE concentration of either 3 or 15 mg/L. On average, 98.3% PYR and 91.3% PHE were sorbed to the bulk soils in 24 h, with 4.96 mg PYR kg⁻¹ soil and 22.48 mg PHE kg⁻¹ soil desorbed after three successive 24-h desorption steps. Both clay minerals and SOM greatly contributed to the sorptive behavior. For example, an average 95.1% and 96.1% of the initial PYR sorbed to the clay-removed and SOM-removed subsoils, respectively. Conversely, 16.5 mg/kg and 12.9 mg/kg of the sorbed PYR was desorbed from the clay-removed and SOM-removed subsoils, respectively.

Understanding the factors governing the environmental fate of contaminants is a key aspect for the eventual remediation of contaminated sites. Researchers have found sorption-desorption to be two of the critical factors controlling the fate and transport of polycyclic aromatic hydrocarbons (PAHs) (Luthy *et al.* 1997; Wilcke 2000). It is well known that the soil organic matter (SOM) is often the principal sorbent under hydrated conditions, whereas both SOM and clay minerals can significantly affect sorption when the SOM content is low (*i.e.*, <6% SOM) (Chiou 1989; Hassett and Banwart 1989).

Although PAH sorption studies dealing with natural clay minerals are rare, a few researchers have demonstrated that PAHs can sorb to soil clay minerals (Karimilofabad *et al.* 1996; Wefer-Roehl and Czurda 1997). The presence of clay minerals has accounted for the slow rates of PAH sorption (Huang *et al.* 1996). However, the majority of sorption studies still focus on the role of SOM in the partitioning of PAHs (Strangroom *et al.* 2000; Weber *et al.* 2001). A study on the role of the SOM and clay minerals in the PAHs sorption/desorption is necessary to garner a better understanding of the fate and transport of PAHs in soils.

The objective of this study was to assess sorption and desorption of pyrene (PYR) and phenanthrene (PHE) in natural soils. Specifically, the impact of the bulk soil type, the presence and absence of SOM and clays, and solute concentrations were investigated. Particular emphasis was given to the contribution of SOM and clays to PAH sorptive phenomena. To achieve the goals, statistical batch experiments were designed, performed, and analyzed in a generalized randomly complete block (GRCB) approach.

Materials and Methods

Bulk and Subsoil Sources

The clean soil samples were obtained from areas in Ohio, New Mexico, and Colombia (South America). The Ohio (OH) soil sample was collected at a depth of 0.9–1.5 m from an area representative of the predominant soil type in northeastern Ohio. The New Mexico (NM) soil was obtained from a site 50 km southwest of Albuquerque. The Colombia soil (CO) originated from a pristine area in Colombia, South America. The latter two soils were extracted from depths of 0.6 m and 3–6 m, respectively.

Sieved soil samples were used to obtain a particle size of less than 2 mm. The characteristics of each of the soil samples are given in Table 1. Based on the SOM content alone, it is believed that the NM soil will have a stronger partitioning potential, followed by the CO and OH soils. It is also hypothesized that the CO soil will have a stronger binding potential, followed by the OH and NM soils on the basis of the expandable clay minerals.

To investigate the contribution of SOM and clay minerals to the sorption and desorption of the model PAHs, two subsoils from each bulk soil were prepared: one without SOM and the other without clay minerals (< 2.0 μm diameter). Although clay minerals can be present in other size fractions, the largest portion is in the < 2 μm clay-size fraction (Christensen 1992; Wattel-Koekkoek *et al.* 2001).

Each bulk soil was repeatedly treated with hot 30% hydrogen peroxide to remove the SOM (Kunz and Dixon 1982). To verify that an acceptable SOM removal was achieved, the total organic carbon (TOC) content of the treated subsoil was measured via a TOC analyzer. The SOM removal efficiencies were 95% for the OH soil, 87% for the NM soil, and 90% for the CO soil. These values were in inverse relationship with the initial SOM content: a smaller SOM removal for the SOM-richer soil. These reduction efficiencies were well matched to the reported values by Hyeong and Capuano (2000) whose removal

Table 1. Characteristics of the bulk soil samples

Analysis	Ohio soil	New Mexico soil	Colombia soil
pH (in 0.01 M CaCl ₂) [†]	6.47	7.21	3.56
pH (in water) [†]	6.68	7.31	4.04
Moisture content (%wt) [‡]	5.23	4.08	2.24
Total organic carbon (%wt) [‡]	0.83	4.46	1.77
Cation exchange capacity (mEq 100 g ⁻¹) [†]	9.18	22.31	4.24
Soil organic matter (%wt) [†]	1.84	8.40	3.54
Soil classification (% wt) [§]	Sandy loam (sand 72.3, clay 11.1, silt 16.6)	Silty loam (sand 30.9, clay 10.5, silt 58.6)	Sandy clay loam (sand 57.3, clay 20.2, silt 22.5)
Clay mineralogy (%wt) [¶]			
	Smectite	5	15
	Vermiculite	15	0
	Kaolinite	10	6
	Chlorites	12	10
	Illites	38	35
	Interstratified	10	30
	Quartz	10	4
			5

[†] Methods are in Page *et al.* (1982).

[‡] Method is in Klute (1986).

[§] USDA textural classification system.

[¶] X-ray diffraction method (< 2 microns).

efficiency was 85–96% by using the same methodology. Although the use of hydrogen peroxide does remove the SOM, it is important to note that this method may alter the available surface area, thereby changing the sorption properties.

For the removal of clay minerals, the bulk soils were treated as outlined by Gee and Bauder (1982) and Jackson (1985). This method was less invasive than the other treatment. The only possible alteration of the clay-removed subsoil would be a slight swelling of the remaining SOM constituents. A standard hydrometer analysis (ASTM 1997) was then used to quantify the extent of clay removal. In all soil samples, the clay removal efficiency was as high as 99%. The total soil recovery during the SOM and clay mineral removals was 98% and 99% for the OH soil, 95% and 99% for the NM soil, and 96% and 99% for the CO soil, respectively. During the clay removal, there was 4–7% loss in silt fraction; however, these losses were not factored into the sorption-desorption results.

Chemical Sources

PYR was purchased in excess of 98% purity from Aldrich Chemical Company. PHE at 96% purity was obtained from Sigma Chemical Co. The physical and chemical characteristics of the compounds are shown in Table 2. Each stock solution of 100 mg/L was prepared in HPLC-grade hexane (Fisher Scientific). Background solution reagents, calcium chloride (CaCl₂) and sodium azide (NaN₃), were obtained from Fisher Scientific and dissolved in distilled water. CaCl₂ and NaN₃ were used to poise the ionic strength and prevent any microbial activity, respectively.

Statistical Approach and Analysis

Table 3 shows the statistical design matrix used for developing and analyzing the experiment. The experiment was initiated by randomly assigning 1/3 of soil samples from each of three locations to have SOM removed, 1/3 to have clay fractions removed, and 1/3 kept as is (*i.e.*, bulk soil). Therefore, soil location was a blocking factor with three levels (OH, NM, and CO soils) and soil preparation was a treatment factor with three levels: bulk, SOM-removed, and clay-removed. Next, half of the samples

were assigned to the lower level of contamination (30 mg/kg) and the remainder to the higher level (150 mg/kg). Thus, PAH concentration was another treatment factor containing two levels. Therefore, the replicate experiment was set up as a 3 × 2 factorial GRCB. The response variable was the normalized PAH sorption amount (*i.e.*, sorption ratio to 100% sorption) or the net PAH desorbed amount. The net desorbed amount is defined as the sorbed fraction minus the total amount desorbed after three successive 24-h desorption steps. The data was analyzed using a general linear analysis of variance (ANOVA) model. For multiple comparisons of data means, Tukey's honestly significant difference (HSD) test with an $\alpha = 0.05$ was performed.

Sorption and Desorption Experiments

The initial compound concentration in the solution phase was either 3 or 15 mg/L, which corresponded to 30 or 150 mg/kg soil if 100% sorption by soil was achieved. The rationale for spiking high concentrations was to evaluate the case when natural soils are subject to high PAH contamination. PYR or PHE concentration in natural soils was found to be 150 to 230 mg/kg soil of the 1,000 mg total PAH/kg soil (Braidia *et al.* 20001; Cornelissen *et al.* 1998).

For the sorption experiments, the appropriate volume of 100 mg PAH/L hexane stock solution was added to each reactor. After the hexane was evaporated, 4 g soil and 40 ml background solution were added. This approach resulted in an initial aqueous PAH concentration of 3 mg/L and 15 mg/L. The reactors were sealed, vortexed for 20 s, and then placed on a shaker bath operated at 24 ± 2°C and 125 rpm. After the 24-h sorption contact time, the reactors were centrifuged with IEC Centra-4B centrifuge at 1,070 g for 20 min. Thirty-five milliliters of supernatant were decanted and analyzed via a fluorescence spectrometry to determine the aqueous concentration. The amount sorbed to the soil was the difference between the amount added and the final aqueous concentration.

Desorption isotherm experiments were initiated immediately after the sorption isotherms had been determined. The 35 ml that had been decanted to ascertain the amount sorbed to the soil was replaced with the fresh background solution (0.5 mM CaCl₂ and 200 mg/L NaN₃). The reactors were resealed and returned to the shaker bath for 24 h.

Table 2. Physical and chemical properties of PHE and PYR

	Chemical Composition	Number of Rings	Molecular Weight	Solubility in H ₂ O (mg L ⁻¹ , 25°C)	Log <i>K</i> _{ow} [†]	Log <i>K</i> _{oc} [‡]
PHE	C ₁₄ H ₁₀	3	178	1.29 [§]	4.57 [¶]	4.36 [¶]
PYR	C ₁₆ H ₁₄	4	202	0.135 [§]	5.18 [¶]	4.92 [¶]

[†] Logarithm of octanol-water partition coefficient.

[‡] Logarithm of carbon-normalized partition coefficient.

[§] Value from Mackay and Shiu (1977).

[¶] Value from Karickhoff *et al.* (1979).

Table 3. Design matrix of 3×2 factorial in GRCB

Treatment	Location [†]	Preparation [‡]	Initial Concentration (mg L ⁻¹)			
			PYR		PHE	
1	OH	Bulk	3	15	3	15
2	OH	Bulk	3	15	3	15
3	OH	-SOM	3	15	3	15
4	OH	-SOM	3	15	3	15
5	OH	-clay	3	15	3	15
6	OH	-clay	3	15	3	15
7	COL	Bulk	3	15	3	15
8	COL	Bulk	3	15	3	15
9	COL	-SOM	3	15	3	15
10	COL	-SOM	3	15	3	15
11	COL	-clay	3	15	3	15
12	COL	-clay	3	15	3	15
13	NM	Bulk	3	15	3	15
14	NM	Bulk	3	15	3	15
15	NM	-SOM	3	15	3	15
16	NM	-SOM	3	15	3	15
17	NM	-clay	3	15	3	15
18	NM	-clay	3	15	3	15

[†] OH: Ohio soil; COL: Colombia soil; NM: New Mexico soil.

[‡] Bulk: not treated soil; -SOM: SOM-removed subsoil; -clay: clay-removed soil.

After 24 h, the solution was decanted for analysis (*i.e.*, the first desorption step). This was repeated for a total of three times, with a 24-h equilibration period for each experimental step. After centrifugation, the solution-phase PYR or PHE concentrations were analyzed by fluorescence spectrometry.

For both the sorption and desorption experiments, blank samples containing the target compound(s) 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.

Analytical Methods

A Perkin-Elmer LS-50B fluorescence spectrometer was used to detect the solution phase concentration of PYR or PHE. The optimal excitation and emission wavelengths determined were $\lambda_{\text{ex}} = 335$ nm and $\lambda_{\text{em}} = 378$ nm for PYR detection and $\lambda_{\text{ex}} = 253$ nm and $\lambda_{\text{em}} = 365$ nm for PHE detection. A concurrent study on the influence of dissolved organic matter (DOM) on desorption did not yield a fluorescence intensity. Therefore, DOM would not interfere with solute quantification.

The amount of PYR and PHE in soil phase was calculated by the difference in the solution phase concentrations between each experimental step. This approach assumes that the compound that disappeared from the solution was sorbed to the soil. The assumption was verified via a cursory mass balance analyses. The com-

pound sorbed to the soil was recovered via soxhlet extraction with methylene chloride over 15 h. The concentrated extracts were dissolved in hexane, and the concentrations were checked by the fluorescence spectrophotometer.

The mass balance between the compound in the solution- and in the soil-phase was within a $\pm 5\%$ error range. Each reactor was rinsed with solvent and 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 or PHE.

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 the manufacturer's guidelines.

Results

PYR Sorption and Desorption

The ANOVA *F*-test for PYR sorption indicated that soil location (test statistic = 51.64), soil preparation (85.9), and solute concentration (368.64) yielded a statistically significant difference ($p < 0.05$). The interactions between two factors also

produced substantial differences. The interactions among three or more factors were embedded in the error term in this study.

Figure 1a is the main effects plot for PYR sorption. In statistics, the main effects plot incorporates every value into one factor. For instance, the CO soil location sorption data (*i.e.*, Figure 1a) contained the sorption results for each and every CO soil combination (bulk soil, SOM-removed subsoil, clay-removed subsoil, 3 mg/L dosage, 15 mg/L dosage, and the respective duplicates). Similarly, the bulk preparation data included the sorption data for all three bulk soils at each PYR/PHE concentration. The asterisks in all the figures denote data that is statistically different ($p < 0.05$) based on the pairwise comparisons by Tukey's HSD. One asterisk was used to denote a statistical difference between soil location. Two and three asterisks were used to identify statistically significant results based on preparation (bulk versus clay or SOM removed) and PAH concentration, respectively.

Using Tukey's HSD, among levels of soil location CO soils (bulk and subsoils) produced the greatest PYR sorption affinity followed by the OH soils and NM soils, with each result being statistically different. Tukey's HSD tests also showed that the bulk soils had a substantially greater PYR sorption than the SOM- and clay-removed subsoils. Furthermore, the amount of PYR sorbed by the SOM-removed soils was statistically greater than that by the clay-removed soils ($p < 0.05$). This was a direct indication of the role of clay minerals in PYR sorption. In addition, when applied at a higher concentration (15 mg/L), PYR sorption was found to increase in regard to the absolute sorption magnitude.

More detailed simultaneous tests were conducted to assess the interaction effects. As seen in Figure 1b, the contribution of clay minerals and SOM to PYR sorption was varied in all cases. This indicated a greater PYR sorption affinity on both clay and SOM, depending on their quality (*i.e.*, SOM fraction and clay mineralogy) and quantity (*i.e.*, concentration). The clay contribution was more evident with the clay-removed NM subsoil than for the other two subsoils. For example, more PYR (97.5% of applied PYR) was sorbed to the bulk NM soil than to the clay-removed NM soil (93.1% PYR) ($p < 0.05$), but the sorbed PYR by the bulk NM soil was not different that that by the SOM-removed soil ($p > 0.05$). The soil characterization showed that the NM soil had an appreciable smectite content (15% of the 10.5% clays). Smectite is the most expandable clay on wetting and can provide an internal surface area as high as 570–660 m²/g (Brady and Weil 2000). Ghosh and Keinath (1994) also presented a significant impact of expandable clays on naphthalene sorption. Therefore, as this smectite group was removed along with other clays, the clay-removed NM subsoil would not have enough sites for PYR sorption, thereby resulting in 4.4% reduction in sorbed PYR.

In the SOM-removed CO soil, PYR sorption was not different from that in the bulk CO soil ($p > 0.05$), indicating a greater potential of clay minerals for PYR sorption. This result was also attributed to the clay mineralogy. The CO soil was characterized to have 20.2% clays, in which 20% was vermiculite. Like smectite, vermiculite is expanding and its internal surface area is 600–700 m²/g (Brady and Weil 2000). Moreover, it had an extraordinary amount of kaolinite (*i.e.*, 49% of the 20.2% clays) that could provide large external surface area for PYR binding. The presence of kaolinite afforded additional sorption sites, which overcame any loss of sorption sites from

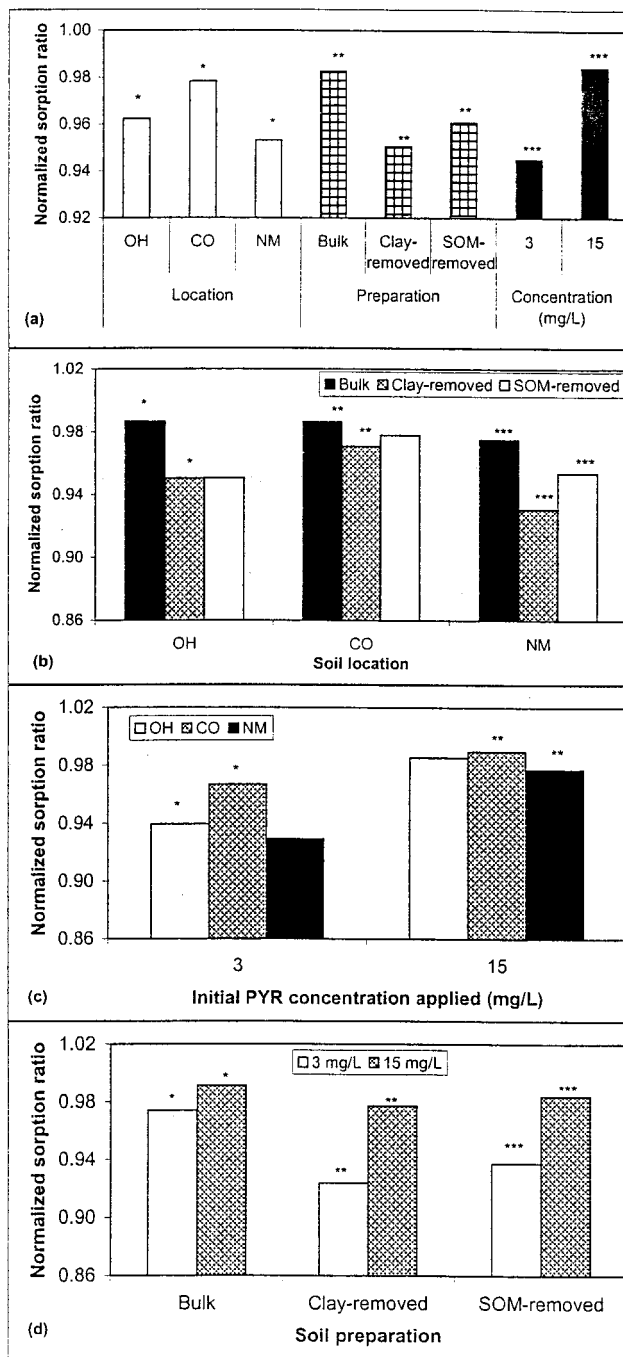


Fig. 1. PYR sorption normalized to the ratio of actual sorption to 100% sorption. (a) Main effect plot of soil location, soil preparation, and PYR concentration; (b) interaction plot between soil location and soil preparation; (c) interaction plot between soil location and PYR concentration; and (d) interaction plot between soil preparation and PYR concentration. Statistical significance based on * soil location, ** preparation, *** concentration

the SOM removal. The possibility may not be dismissed that more external surface area of kaolinite could be exposed by the removal of SOM complexed with kaolinite in the bulk soil.

Figure 1c showed that the OH and NM soils yielded a greater

increase in PYR sorption with an increase in applied PYR concentration than the CO soils. All increases were statistically significant. Furthermore, there was a similar trend of interactive effect between soil preparation and concentration. Generally, PYR sorption in the subsoils was increased to a greater extent with the increase of PYR concentration (Figure 1d). Therefore, it is believed that as the PYR concentration in the solution phase increased, the soil sorption capacity was increased by concentration gradient effects, which “drove” PYR molecules to less easily accessible sites, thereby giving the appearance of site increase.

The desorption experiment also found that each variation source yielded a statistical difference. As seen in Figure 2a, the main effects showed that there was not a significant difference in the amount of desorbed PYR between the CO and OH soils ($p > 0.05$). However, PYR desorption from the NM soils was substantially greater than that from the other two soils. This was attributed to the highest DOM content in the NM soils.

The contribution of clay and SOM to PYR sorption produced an expected desorption result. The desorbed PYR from both the clay- and SOM-removed subsoils, which was not different from each other ($p > 0.05$), was significantly greater than that from the bulk soils ($p < 0.05$). This result indicates that the subsoils didn't provide as tight a sorptive bond with PYR as the bulk soils did. In addition, less PYR was desorbed when PYR was applied at 3 mg/L than at 15 mg/L.

The interaction plots for PYR desorption yielded reasonable, anticipated results based on the sorption findings. For example, the NM soil that had the lowest sorption affinity showed the easiest desorption pattern among three soils (Figure 2b). For the CO soil systems, PYR desorption by the bulk soil was not different than that by SOM-removed soil ($p > 0.05$). As mentioned, this similarity for the CO soils was attributed to both the expandable vermiculite that formed strong sorptive bonds and the kaolinite that afforded more accessible external sorption sites.

The NM soils responded to the increase of PYR concentration in a very contrasting manner. Unlike the other two soils, the increase in desorbed PYR with an increase of initially applied PYR was phenomenal (Figure 2c). This remarkable increase was attributed to the extraordinarily large desorption amount in both SOM- (40.99 mg PYR/kg) and clay-removed (47.14 mg/kg) NM subsoils when PYR was initially applied at 15 mg/L. It is not clear at this moment why this abnormal desorption behavior occurred. However, it is believed that the great PYR desorption from the clay-removed soil was attributed to the substantial DOM content in that soil.

When either the SOM or clay minerals was removed, it was easier for PYR to desorb in conjunction with the increase of PYR concentration (Figure 2d), depicting the interconnected nature of total number of sorption sites and concentration gradient effect. The ease of desorption was greater in the clay-removed soils than in the SOM-removed soils, although the results were not significantly different ($p > 0.05$).

PHE Sorption and Desorption

The ANOVA *F*-test for PHE sorption also indicated that soil location (test statistic = 1,232.81), soil preparation (20.6), and solute concentration (275.27) were statistically different ($p < 0.05$). The interactions between two factors were also different.

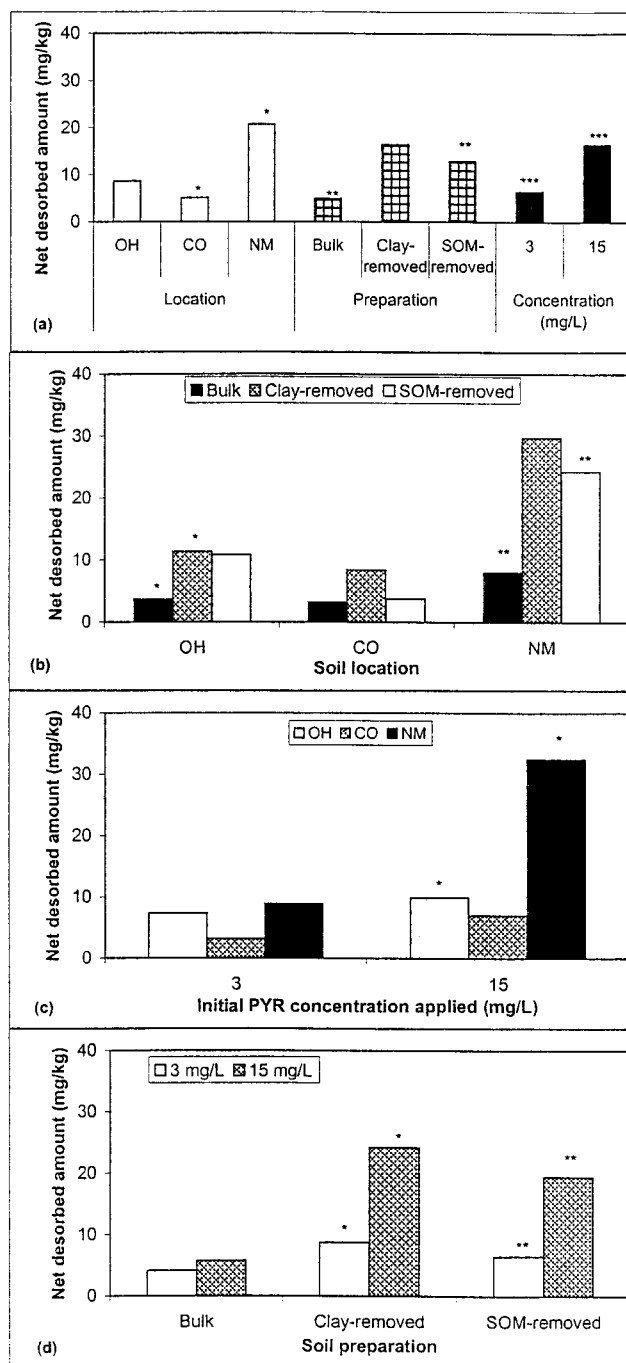


Fig. 2. Total PYR desorption after three sequential 24-h desorption steps. (a) Main effect plot of soil location, soil preparation, and PYR concentration; (b) interaction plot between soil location and soil preparation; (c) interaction plot between soil location and PYR concentration; and (d) interaction plot between soil preparation and PYR concentration. * Statistical significance between soil location; ** statistical difference based on preparation; *** statistical difference based on concentration

Tukey's HSD tests suggested that the NM soils had the greatest PHE sorption affinity followed by the CO soils and the OH soils (Figure 3a). Previously, the NM soil yielded the lowest

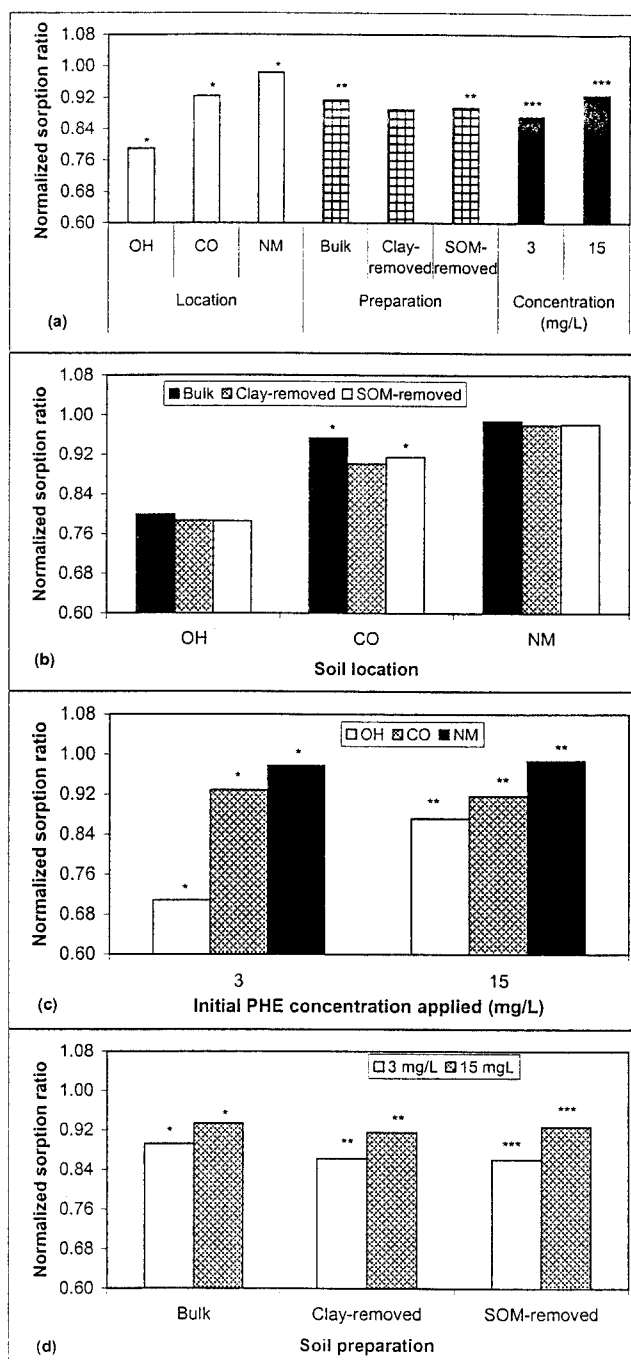


Fig. 3. PHE sorption normalized to the ratio of actual sorption to 100% sorption. (a) Main effect plot of soil location, soil preparation, and PHE concentration; (b) interaction plot between soil location and soil preparation; (c) interaction plot between soil location and PHE concentration; and (d) interaction plot between soil preparation and PHE concentration. * Statistical significance between soil location; ** statistical difference based on preparation; *** statistical difference based on concentration

PYR sorption affinity (PYR sorption CO > OH > NM). Although PHE sorption between the SOM- and clay-removed subsoils was not substantially different, their amount was sig-

nificantly less than that by the bulk soils. PHE also showed an increased sorbed amount with an increase in the applied PHE concentration; however, the extent was not as great as PYR sorption. This was due to a smaller PHE concentration gradient effect resulting from its ~ 10 times higher solubility (Table 2).

PHE sorption was relatively independent on soil constituents. For instance, PHE sorption showed a same intensity for the NM and OH soils, regardless of whether or not the clay or SOM was removed. The clay and SOM contribution to PHE sorption was noticeable only for the CO soil systems (Figure 3b). In these CO systems, 90.1% and 91.4% PHE was sorbed to the clay- and SOM- removed subsoils, respectively, whereas the bulk soil sorbed 95.4% PHE. Thus, both clay and SOM played key roles in PHE sorption for the CO soil.

Although the NM and CO soils weren't influenced by the increase of PHE concentration, the OH soils showed an appreciable sorption increase, from 70.8% to 87.2% (Figure 3c). Soil preparation and concentration showed a relatively weak interactive effect on PHE sorption (Figure 3d).

For PHE desorption, ANOVA analysis showed that all variation sources were statistically different ($p < 0.05$). Overall, the ease of PHE desorption was in the order of the OH > CO \gg NM soil (Figure 4a), which was the reverse order of the ease of PHE sorption (Figure 3a). This inverted trend was also found in the subsoil systems in which more PHE was desorbed when either clay or SOM were removed. Like the previous findings with PYR, more PHE was desorbed as the applied PHE concentration increased.

The interaction plot revealed that the clay minerals and SOM of the OH and CO soils greatly contributed to PHE desorption (Figure 4b). In other words, desorption enhancement was statistically significant in the clay- and SOM-removed subsoils. However, PHE desorption for the NM soils were approximately the same, regardless of what soil constituent was removed. Another interesting phenomenon was that the NM soils did not depict an increased desorption with an increase of PHE concentration (Figure 4c). Unlike PYR sorption, PHE exhibited an enhanced desorption from the bulk soils with increasing PHE concentration. However, the removal of either clay minerals or SOM made PHE desorption easier (Figure 4d).

Discussion

It was necessary to define why two PAHs yielded different sorptive results. First, PYR showed greater sorption and less desorption than PHE in the bulk soils. On average, 98.3% PYR and 91.3% PHE was sorbed, whereas 4.96 mg PYR/kg and 22.48 mg PHE/kg was desorbed. Sorption and desorption of hydrophobic compounds depend on their hydrophobicity and solubility. As seen in Table 2, PYR is more hydrophobic (*i.e.*, less water-soluble) than PHE. Therefore, it was natural that the more hydrophobic PYR sorbed more and desorbed to a lesser extent than the less hydrophobic PHE when the same solute concentration was provided. The solute concentration can also affect its behavior in soil (Chung and Alexander 1999; Schlebaum *et al.* 1999). For instance, DiVincenzo and Sparks (1997) documented that pentachlorophenol concentration affected not only the ratio of sorbed to solution-phase fraction but also the sorption kinetics and extent of desorption. In the present study, the increase in solute concentra-

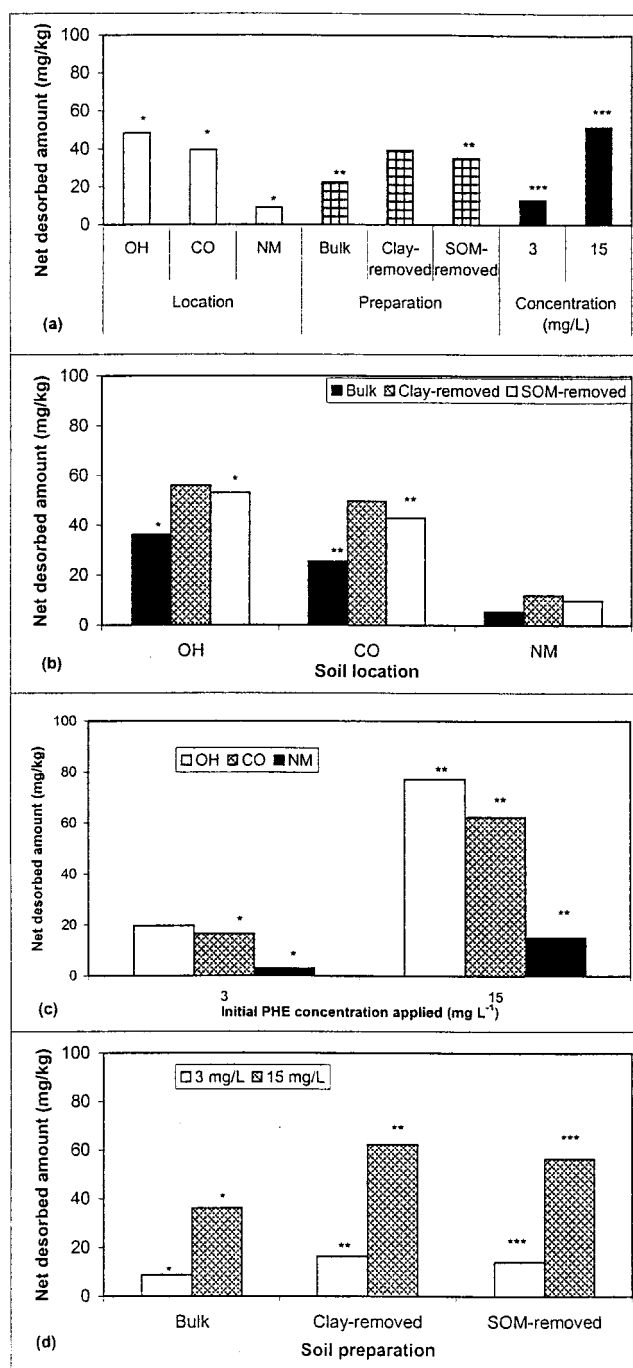


Fig. 4. Total PHE desorption after three sequential 24-h desorption steps. (a) Main effect plot of soil location, soil preparation, and PHE concentration; (b) interaction plot between soil location and soil preparation; (c) interaction plot between soil location and PHE concentration; and (d) interaction plot between soil preparation and PHE concentration. Statistical significance based on * soil location, ** preparation, *** concentration

tion (*i.e.*, from 3 to 15 mg/L) yielded a greater increase in both sorption and desorption of PHE than PYR. This indicates that the impact of solute concentration was a function of solute type.

It is also important to reiterate that for these experiments,

each of the three desorption steps were for 24 h, yielding a total desorption time of 3 days. Thus desorption equilibrium may not have been attained. A subsequent, concurrent study has determined the sorption and desorption equilibrium times were different for the bulk NM and OH soils and PAH compound. However, the sorption time and each desorption step for this manuscript was kept at 24 h.

Along with the solute properties, the sorbent characteristics also affect PAH sorptive behavior. Contrary to generally accepted beliefs that only SOM can provide sorption sites (Weber *et al.* 2001), both clay minerals and SOM greatly contributed to PAH sorption and desorption in this study. For example, it was found that sorbed PAH amount was significantly reduced when the clay materials were removed. The SOM also yielded a similar result, but its impact on sorption was less than that of clay minerals. Consequently, the amount of desorbed PAH was substantially increased when the clay minerals were not involved in the desorption mechanism. This is a direct indication of a stronger adsorption capability of clay minerals than the SOM, which is for a weak partitioning mechanism (Chiou *et al.* 1983; Murphy *et al.* 1990). Furthermore, the extent of their contribution relied on both the quantity (*i.e.*, concentration) and quality (*i.e.*, dominant clay and SOM fraction) (Chiou *et al.* 1998; Ghosh and Keinath 1994; Nam *et al.* 1998; Weber *et al.* 2001).

In terms of sorbent quality, the DOM should not be completely neglected. DOM could influence the sorptive behavior of PAH as the formation of a DOM-PAH complex would result in another solution subphase. This interaction was found to depend on the concentration and fractional characteristics of the DOM (Chefetz *et al.* 2000; Johnson and Amy 1995; Kogel-Knabner 2000). For the study presented here, the DOM was determined by placing 20 g NM soil in 200 ml distilled water and agitating for 2 days at 125 rpm and $28 \pm 2^\circ\text{C}$. The TOC analyzer measured the DOM in the supernatant. The NM bulk soil was found to have 17.87 mg/L of DOM. Because the NM bulk soil had the highest DOM, followed by CO soil (9.97 mg/L) and OH soil (4.14 mg/L), it seemed that the clay-removed NM soil, where the SOM content was higher than the bulk soil, would produce a greater DOM concentration, thereby decreasing the amount of sorbed PYR. However the DOM generation was not tracked during the desorption studies. At most, the sorption/desorption experiments would have generated 0.14 mg DOM for the NM, 0.07 mg for the CO, and 0.03 mg for the OH bulk soil. Although these quantities would not have yielded statistically different results, they probably would for systems utilizing more soil/water. For the OH and CO subsoils, the SOM and clay minerals showed an equal role in PYR sorption. In other words, the sorption amounts by the SOM-removed subsoils were not significantly different from those by the clay-removed subsoils.

Conclusions

The results of this statistical study show that soil type will greatly impact the sorption and desorption of PAHs. The extent of this influence depends on the specific soil-PAH combination. Compound concentration also affected the amount of the sorbed and desorbed fractions, which will directly influence the bioavailability of the compounds. In general, as a higher PAH

concentration was applied, the amount of sorbed and subsequent desorbed fractions were increased.

The most meaningful result of this study is that clay minerals, especially the expandable clays, played an important role in PAH sorptive interaction. Sorptive phenomena with PYR depicted a greater dependency on the clay minerals than PHE sorption and desorption. This observation can have significant implications from the viewpoint of remediation because sorption and desorption modeling often focus on the SOM, neglecting the potential effect of clay minerals.

Contaminants are released to the environment as multiple mixtures, rather than a single solute, so it is warranted to assess the different sorptive characteristics of PAHs in the presence of other PAHs as cosolutes. In addition, the contribution of clays and SOM to PAH sorptive behavior in those cosolute systems should be evaluated.

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References

- American Society for Testing and Materials (ASTM) (1997) Standard classification of soils for engineering purposes (Unified Soil Classification System), D2487-93. Annual book of ASTM standards, 04.08: Soil and rock (I). ASTM, Philadelphia, PA
- Brady NC, Weil RR (2000) Elements of the nature and properties of soils. Prentice-Hall, New Jersey
- Braida WJ, White JC, Ferrandino FJ, Pignatello JJ (2001) Effect of solute concentration on sorption of polycyclic aromatic hydrocarbons in soil: uptake rates. *Environ Sci Technol* 35(13):2765–2772
- Chefetz B, Deshmukh AP, Hatcher PG, Guthrie EA (2000) Pyrene sorption by natural organic matter. *Environ Sci Technol* 34:2925–2930
- Chiou CT (1989) Theoretical consideration of partition uptake of nonionic organic compounds by soil organic matter. In: Sawhney BL, Brown K: (eds) Reactions and movement of organic chemicals in soil. Soil Sci Soc Am, Madison, WI, pp 1–30
- Chiou CT, Porter PE, Schmedding DW (1983) Partition equilibria of nonorganic compounds between soil organic matter and water. *Environ Sci Technol* 17:227–231
- Christensen BT (1992) Physical fractionation of soil and organic matter in primary particle size and density separates. *Adv Soil Sci* 20:1–90
- Chung N, Alexander M (1999) Effect of concentration on sequestration and bioavailability of two polycyclic aromatic hydrocarbons. *Environ Sci Technol* 33:3605–3608
- Cornelissen G, Rigterink H, Ferdinandy MM, van Noort PCM (1998) Rapidly desorbing fractions of PAHs in contaminated sediments as a predictor of the extent of bioremediation. *Environ Sci Technol* 32:966–970
- DiVincenzo JP, Sparks DL (1997) Slow sorption kinetics of pentachlorophenol on soil: concentration effects. *Environ Sci Technol* 31:977–983
- Gee GW, Bauder JW (1982) Particle-size analysis. In: Methods of soil analysis. Part 1. Physical and mineralogical methods. American Soc Agronomy, Madison, WI, pp 383–411
- Ghosh DR, Keinath TM (1994) Effect of clay minerals present in aquifer soils on the adsorption and desorption of hydrophobic organic compounds. *Environ Prog* 13:51–59
- Hassett JJ, Banwart WL (1989) The sorption of nonpolar organics by soils and sediments. In: Sawhney BL, Brown K (eds) Reactions and movement of organic chemicals in soil. Soil Sci Soc of Am, Madison, WI, pp 31–44
- Huang W, Schlautman MA, Weber WJ Jr (1996) A distributed reactive model for sorption by soils and sediments. 5. The influence of near-surface characteristics in mineral domains. *Environ Sci Technol* 30:2993–3000
- Hyeong K, Capuano RM (2000) The effect of organic matter and the H₂O₂ organic matter-removal method on δD of smectite-rich samples. *Geochim Cosmochim Acta* 64:3829–3827
- Jackson ML (1985) Soil chemical analysis—advanced course. Published by author, Madison, WI
- Johnson WP, Amy GL (1995) Facilitated transport and enhanced desorption of polycyclic aromatic hydrocarbons by natural organic matter in aquifer sediments. *Environ Sci Technol* 29:807–817
- Karickhoff SW, Brown DS, Scott TA (1979) Sorption of hydrophobic pollutants on natural sediments. *Water Res* 13:241–248
- Karimilofabad S, Pickard MA, Gray MR (1996) Reactions of polynuclear aromatic hydrocarbons on soil. *Environ Sci Technol* 30:1145–1151
- Klute A (1986) Methods of soil analysis. Part 1. Physical and mineralogical methods, 2nd ed. American Soc Agronomy, Madison, WI
- Kogel-Knabner I, Raber B, Totsche KU (2000) Desorption of polycyclic aromatic hydrocarbon from soil in the presence of dissolved organic matter: effect of solution composition and aging. *J Environ Qual* 29:906–916
- Kunz GW, Dixon JB (1982) Pretreatment for mineralogical analysis. In: Methods of soil analysis. Part 1. Physical and mineralogical methods. American Society of Agronomy, Madison, WI, pp 91–100
- Luthy RG, Aiken GR, Brusseau ML, Cunningham SD, Gschwend PM, Pignatello JJ, Reinhard M, Traina SJ, Weber WJ Jr, Westall JC (1997) Sequestration of hydrophobic organic contaminants by geosorbents. *Environ Sci Technol* 31:3341–3347
- Mackay D, Shiu WP (1977) Aqueous solubility of polynuclear aromatic hydrocarbons. *J Chem Eng Data* 22:399–402
- Murphy EM, Zachara JM, Smith SC (1990) Influence of mineral-bound humic substances on the sorption of hydrophobic organic compounds. *Environ Sci Technol* 24:1507–1516
- Nam K, Chung N, Alexander M (1998) Relationship between organic matter content of soil and the sequestration of phenanthrene. *Environ Sci Technol* 32:3785–3788
- Page AL, Miller RH, Keeney DR (1982) Methods of soil analysis: part 2. chemical and microbiological properties, 2nd ed. American Society of Agronomy, Madison, WI
- Schlebaum W, Schraa G, van Riemsdijk WH (1999) Influence of nonlinear sorption kinetics on the slow-desorbing organic contaminant fraction in soil. *Environ Sci Technol* 33:1413–1417
- Strangroom SJ, Lester JM, Collins CD (2000) Abiotic behaviour of organic micropollutants in soils and the aquatic environment. A review: I. Partitioning. *Environ Technol* 21:845–863
- Wattel-Koekkoek EJW, van Genuchten PPL, Buurman P, van Lagen B (2001) Amount and composition of clay associated soil organic matter in a range of kaolinitic and smectitic soils. *Geoderma* 99:27–49
- Weber WJ Jr, Leboeuf EJ, Young TM, Huang W (2001) Contaminant interactions with geosorbent organic matter: insights drawn from polymer sciences. *Wat Res* 35:853–868
- Wefer-Roehl A, Czurda KA (1997) Adsorption of polycyclic aromatic hydrocarbons (PAH) on different clays and clay minerals. In: Kodama H, Mermut AR, Torrance JK (eds) Clays our future. Proc. Int. Clay Conf. 11th, pp 123–128
- Wilcke W (2000) Polycyclic aromatic hydrocarbons (PAHs) in soil — a review. *J Plant Nutr Soil Sci* 163:229–248