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Zucheng Wang
Northeast Normal University

Zhanfei Liu
University of Texas at Austin

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The impact of drying on structure of sedimentary organic matter in wetlands: Probing with native and amended polycyclic aromatic hydrocarbons

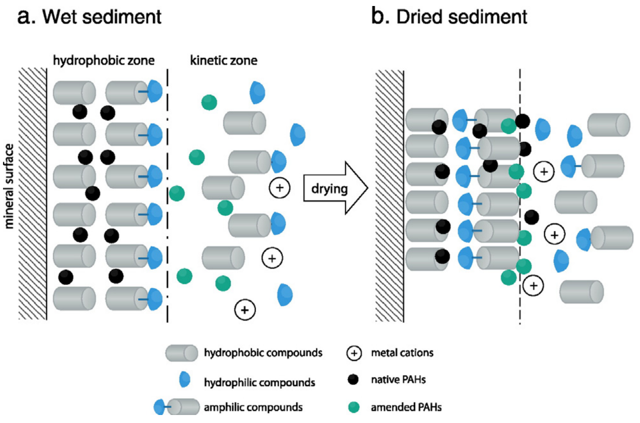
Zucheng Wang [a,b,c], Zhanfei Liu [a,*], Min Liu [b], Kehui Xu [d,e], Lawrence M. Mayer [f]

[a] *Marine Science Institute, The University of Texas at Austin, Port Aransas, TX 78373, USA*
[b] *Department of Geography, Key Laboratory of Geographic Information Science of the Ministry of Education, East China Normal University, Shanghai, China*
[c] *Institute for Peat and Mire, Northeast Normal University, Changchun, China*
[d] *Department of Oceanography and Coastal Sciences, Louisiana State University, Baton Rouge, LA 70803, USA*
[e] *Coastal Studies Institute, Louisiana State University, Baton Rouge, LA 70803, USA*
[f] *Darling Marine Center, University of Maine, Walpole, ME 04573, USA*

HIGHLIGHTS

- Native PAHs were released into solution after sediments suffering dry-wet cycles.
- Drying may expose hydrophobic interior of SOM, where native PAHs are concentrated.
- Drying enhanced the fresh PAHs sequestration in the sediments.

GRAPHICAL ABSTRACT



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ABSTRACT

Wetland sediments undergo dry-wet cycles that may change their structural properties and affect geochemical behavior of associated organic compounds. In this study, we examined the effect of drying on particle size distributions and the rapid (24 h) sorption reactions of polycyclic aromatic hydrocarbons (PAHs) with salt marsh sediments in Nueces Delta, South Texas. Drying reduced the fraction of fine particles in organically richer sediments, indicating structural rearrangement of organic matter and mineral aggregates. Among the 16 EPA priority PAHs examined, dried sediment preferentially released 1.0–7.5% of phenanthrene, fluoranthene and pyrene to added seawater (solid: water mass ratio of 1/100) - significantly greater than release from sediments maintained in the wet state. On the other hand, drying also increased the affinity of sedimentary organic matter (SOM) for experimentally amended (deuterated) phenanthrene relative to continually wet sediments. Further, deuterated phenanthrene was even more effectively retained when it was added to wet sediment that was subsequently dried and rewetted. These apparently contradictory results can be reconciled and explained by SOM having a heterogeneous distribution of hydrophobic and hydrophilic zones – e.g., a zonal model. We propose that drying

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[*] Corresponding author at: 750 Channel View Dr, Port Aransas, TX 78373, USA.
E-mail address: zhanfei.liu@utexas.edu (Z. Liu).

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Salt marsh
Sorption
Zonal assemblage

changed the orientation of amphiphilic SOM, exposing hydrophobic zones and promoting the release of some of their native PAHs to water. Freshly amended PAHs were only able to penetrate into the surface hydrophobic zone and/or deeper but rapidly accessible ("kinetic") zone in wet sediments due to the brief adsorption contact time. Subsequent drying presumably then induced structural changes in SOM that isolated these amended PAHs in sites inaccessible to water exchange in the next rewetting. These results provide insights into structural changes of SOM upon drying, and help predict the fate of compounds such as organic contaminants during drought/flood oscillations.

1. Introduction

Soils and wetland sediments are often subjected to dry-wet cycles in nature, and these cycles may change the structural properties of organo-mineral complexes and affect the distribution of associated chemicals (e.g., Horne and McIntosh, 2000; Liu and Lee, 2006). Soil organic matter becomes fragmented and more porous after being dried (White et al., 1998). Drying may also affect the orientation of non-polar and polar moieties of soil organic matter on mineral surfaces and change its apparent surface and/or bulk hydrophobicity (Doerr et al., 2000; Liu and Lee, 2007). Such behavior is consistent with proposed models of organic matter in soils or sediments that involve hydrophobic interiors and more hydrophilic exteriors – e.g., so-called "micelle" structures (Wershaw, 1993, 2004; Sutton and Sposito, 2005). Thus drying-rewetting can affect the partitioning of organic contaminants between water and solid phases in aquatic environments (Liu and Lee, 2006).

Understanding structural changes of SOM is key to deciphering association of organic contaminants, yet it is difficult to directly investigate the SOM structure due to limitations of available techniques. For example, electron microscopy can detect surface features of SOM, but current versions cannot probe the inner structure of solid samples and, furthermore, often require dried samples in vacuum (Ghosh et al., 2000; Arnarson and Keil, 2001; Liu and Webster, 2007). Because structural changes affect sorption behavior of various compounds onto SOM, these sorption reactions provide probes of 3-dimensional (3D) structural changes. For example, drying increases release of some SOM-sorbed compounds into solution (Liu et al., 2008). As an alternative, different types of amended sorbates can be used as probes to explore structure of SOM (White et al., 1998; Kottler et al., 2001; Liu and Lee, 2006, 2007). PAHs, as a group of hydrophobic organic compounds, are excellent sorbates due to their high affinity to SOM and widespread existence in natural environments (Wang et al., 2014).

Studies have shown that drying-rewetting increases the sequestration of organic contaminants in SOM, indicating that drying can distort pore networks and/or the hydrophobic zone of SOM, where organic contaminants such as PAHs are typically sorbed (Shelton et al., 1995; White et al., 1998). Most studies used amended PAHs and dried sediments (e.g., Chiou et al., 1998; Kottler et al., 2001; Wu and Sun, 2010), but how drying affects native, or aged, PAHs in sediments remains unclear. The comparison between partitioning of freshly amended vs. *native* PAHs, — i.e. those that have been in contact with SOM for longer time scales - can provide extra insight into interactions of PAHs with SOM. It also can provide tests of conceptual models of the structure of organo-mineral complexes, such as the one proposed by Kleber et al. (2007).

Using PAHs as the probe and drying as an experimental treatment, we address two questions in this study: (1) how does drying affect partitioning of native and amended PAHs between solid and solution phases, and (2) what are the implications for SOM structure from the PAH sorption reactions in dried or wet sediments? These questions are important, considering the widely-distributed PAHs in aquatic environments and the impacts of projected future increase of frequency and intensity of droughts/floods (Zakaria et al., 2002; Huntington, 2006). By comparing partition behaviors of both native and amended PAHs in marsh sediments, we demonstrate that drying causes structural changes of SOM and further affects distribution of organic contaminants.

2. Materials and methods

We used laboratory batch experiments to examine effects of drying-rewetting on the sorption/release of PAHs from salt marsh sediments, and to gain insights into structural properties of SOM. We studied the release of native PAHs from wet and dried sediments having different physical and chemical properties such as grain size distribution and total organic carbon contents. The release of native PAHs from different size fractions of marsh sediment was also compared, with the aim of testing the effects of grain size and associated SOM on the PAH release. We further tested the impact of drying on SOM, sorption and desorption of amended phenanthrene (deuterated Phe-d_{10}) among wet, dried, and dried/rewetted sediments.

2.1. Sample collection and pretreatment

We sampled salt marshes of the Nueces River Delta, South Texas (Fig. 1). Sediments in this area consist of mainly quartz (>90%), plus a small fraction of clay minerals including montmorillonite, illite and kaolinite in decreasing abundance order (White et al., 1983). Surface sediments (top 5 cm) were sampled during June–October 2011 using home-made core tubes. The sampling stations covered different types of wetland environment previously studied in this area (Dunton et al., 2001; Liu et al., 2013), including Nueces River riverbed at station LP (STLP), Nueces River mouth at station 104 (ST104), Nueces Bay at station 80 (ST80), and Nueces marsh at stations 450 and 451 (ST450, ST451). All cores were capped and stored in a freezer at −20 °C before processing. A portion of surface sediment (0–5 cm) was dried in an oven at 40 °C for at least 24 h until the sediment weight became constant. Drying at temperatures such as 40 °C has been shown to lead to inconsistent changes in water repellency, which is related to exposure of hydrophobic sites (Dekker et al., 1998; Doerr et al., 2000). However, little difference in lysine sorption was found between marsh sediments dried at 60 °C in the oven vs. a freeze-drier (Liu and Lee, 2006), indicating that different ways of drying do not significantly change sorptive properties of the SOM.

Portions of surface sediment were kept in a −20 °C freezer without drying. Seawater for making batch slurries was collected at each station and filtered through pre-combusted 0.7 μm GF/F filters (Whatman). Background concentrations of PAHs (total extractable PAHs) in seawater and sediments (the latter are termed "native" or "aged") were measured for each station (Fig. A1 in Appendix, Table 1).

2.2. Sediment characteristics

Black carbon (BC) contents in sediments were measured according to Gustafsson et al. (1997). Briefly, inorganic carbonates (IC) in dried sediments were removed by acid fuming in a sealed container with concentrated hydrochloric acid (Hedges and Stern, 1984). One fraction of the acidified sediment was measured by an elemental analyzer to obtain total organic carbon (TOC) content. The other fraction was placed in a

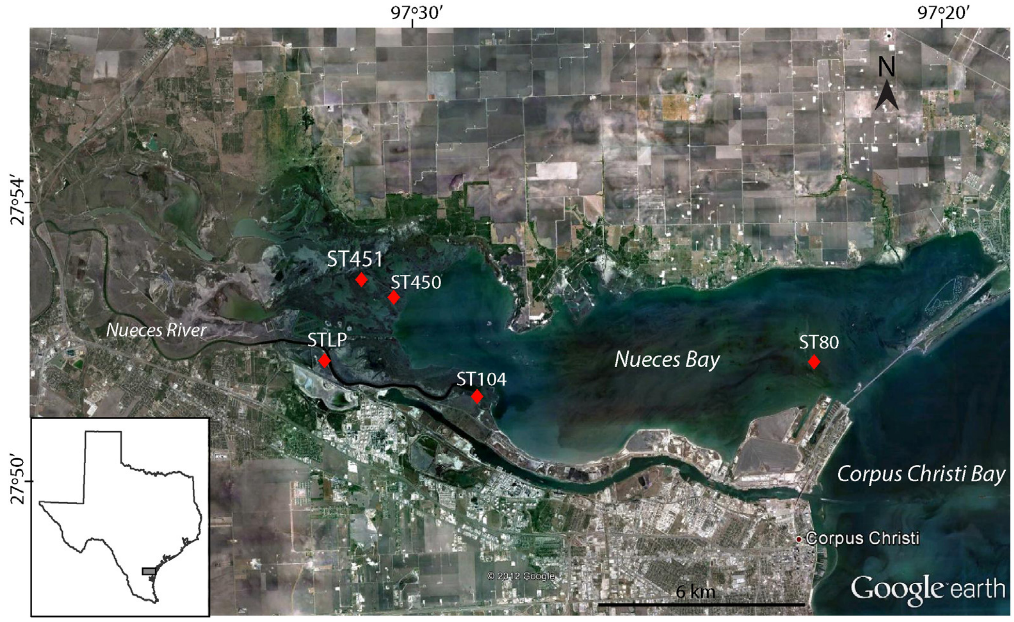

Fig. 1. Sampling stations in Nueces salt marshes and the adjacent area. ST80 is in Nueces Bay, ST451 and ST450 are in the Nueces marsh and STLP and ST104 are in the Nueces River. The inset shows the sampling area in Texas.

muffle furnace with controlled airflow at 375 °C for 24 h to remove organic carbon, and the residual BC measured by the elemental analyzer. The precision for C analysis is ± 2%. Dissolved organic carbon (DOC) in seawater was measured by a Shimadzu TOC-V analyzer, and duplicate analyses agreed within 10%. Specific mineral surface areas were measured after the sediment was muffled overnight at 350 °C, using the one-point BET method on a Quantachrome Monosorb analyzer (Mayer, 1994).

The grain size of wet and dried sediments in each station was measured using a Beckman-Coulter laser particle size analyzer (Model LS 13320) following the method of Xu et al. (2014). About 20 mL of deionized water were added to ~1 g of sediment in a beaker. After soaking for 24 h, the sediment was subjected to Vortex mixing for 5 min to ensure full disaggregation of loosely-attached aggregates. The high-strength sonication (100%) was turned on, while the samples were loaded and measured in the chamber of the laser analyzer, to maintain disaggregation. The size distribution was measured by polarization intensity differential scattering. The detection size range of this analyzer is from 0.02 to 2000 μm. The role of organic matter in controlling grain size distribution was examined further by measuring the particles with vs. without hydrogen peroxide (30%) pretreatment using sediments from ST450. All of the samples were measured in triplicate.

The PAH extraction from sediments followed the protocol of Rhind et al. (2009), which gives results similar to those of other extraction methods (Wang et al., 2014, Santschi et al., 2001). Briefly, ca. 1 g sediment (dry weight) was added with surrogate standards and 8 mL ethanoic potassium hydroxide (1 M), and then the slurry was heated to 90 °C for 8 h. Then the analytes in ethanoic potassium hydroxide were extracted by hexane and purified by passage through a column packed with activated silica gel and topped with 1 cm anhydrous sodium sulfate. The analytes on the column were eluted with 50 mL dichloromethane/hexane (1:4, *v*/v). Finally, the collected elution was reduced to 1 mL using a rotary evaporator and transferred to a 2 mL vial, and preserved in a freezer at −20 °C until gas chromatography–mass spectrometry (GC/MS) analysis.

2.3. Native PAHs released from dried and wet sediments

A fixed time (24 h) and solid/water ratio (1/100) were selected for the PAH release experiments based on our preliminary results (Fig. A2 in Appendix). We chose 24 h as a time that is long enough to approach to asymptotically maximum reaction extent but not so long as to allow other reactions to significantly affect the SOM matrix. For the wet sediment experiment, 20 g of thawed sediments (ca. 10 g dry weight) were added into a bottle containing 1 L filtered seawater. Our previous study showed that freezing and thawing does not affect sorption properties of sediments (Liu and Lee, 2007). Similarly, 10 g of dried sediment was added into a bottle, rewetted with 1 L filtered seawater, and then sealed. All bottles were shaken continuously in a rotary shaker (120 rpm) at room temperature (25 ± 1 °C) for 24 h, and the particles in slurries were allowed to settle for 2 h before the seawater was removed by pipet. The supernatant was filtered through a 0.7 μm Whatman GF/F filter, mixed with 5 μL of surrogates (Ace-d_{10}, Phe-d_{10}, BaP-d_{12}) in hexane with a final concentration level similar to those released from

Table 1
Characteristics of sediments and seawater used in this study. Grain size measurements were conducted on triplicate samples.

					% volume in grain size interval				
Station	PAHs in sediments (ng g^{-1})	PAHs in seawater (ng L^{-1})	[a]OC%	[b]SC%	<32 μm	32–63 μm	63–125 μm	125–300 μm	>300 μm
ST104	174.4 ± 16.7	20.2 ± 2.3	0.98	0.17	77.2 ± 0.6	11.3 ± 0.6	4.3 ± 0.1	6.7 ± 1.5	0.5 ± 0.9
STLP	90.6 ± 3.8	16.5	0.24	0.09	46.4 ± 1.9	9.2 ± 0.2	11.8 ± 0.4	25.6 ± 1.9	7.1 ± 0.3
ST80	173.9 ± 0.2	16.3 ± 3.6	0.13	0.04	11.7 ± 0.4	12.1 ± 0.4	36.0 ± 1.3	37.5 ± 1.0	2.7 ± 2.9
ST450	304.2 ± 82.8	23.5 ± 4.6	0.71	0.15	63.2 ± 0.9	12.5 ± 0.0	11.7 ± 0.1	10.8 ± 0.9	1.8 ± 1.6
ST451	74.6 ± 3.2	15.2	0.70	[c]nd	58.2 ± 6.2	11.1 ± 0.6	14.9 ± 3.0	10.9 ± 2.4	5.0 ± 0.3

[a] percentage of organic carbon.
[b] percentage of soot carbon.
[c] nd: not detected.

sediments. The seawater was extracted by 150 mL aliquots of dichloromethane three times. The extracts were combined and purified by passing through a column of 10 g anhydrous sodium sulfate, and replaced by hexane and condensed into 1 mL using a rotary evaporator before the PAH analysis. Seawater without sediments, but treated with the same procedure, served as control. The amount of PAHs released from the sediment was calculated by the concentration difference between the slurries and the control.

To examine the release mechanisms of PAHs, wet sediments from ST451 were also fractioned into different sizes (<32, 32–63, 63–125, and 125–300 μm) using stainless steel mesh sieves (Liu et al., 2013). Ten g of dried, size-fractioned sediment were mixed with 1 L filtered seawater. All bottles were shaken continuously at 120 rpm for 24 h and the particles allowed settling for 2 h before supernatants were collected by pipette. The supernatants were filtered through 0.7 μm GF/F filters and extracted with the procedure described above. The released PAHs from sediments were calculated as the difference between the concentrations of PAHs in slurries and the seawater controls without added sediment. All experiments were conducted on duplicate samples.

2.4. Adsorption and desorption of amended phenanthrene

2.4.1. Wet vs. dried sediments (ExpA)

Adsorption and desorption of freshly amended PAHs can provide further insights into structural changes of SOM caused by drying (Hung et al., 2012). We examined adsorption and desorption of deuterated phenanthrene (Phe-d_{10}) onto wet and dried sediments from ST451 (<300 μm fraction), respectively. Briefly, wet and dried sediments (0.6–1.0 g dry weight) were added respectively to pre-combusted 50 mL glass vials with Teflon-coated liners. The vials were filled with 40 mL of filtered seawater, containing 50 mg $HgCl_2$ L^{-1} to inhibit bacterial activities (Lee et al., 1992). Different amounts of Phe-d_{10} stock solution in HPLC-grade methanol were spiked into the vials with initial concentrations of 10, 20, 50, 80, 100 ng mL^{-1} for both the wet and dried sediment series. The methanol added to the slurry was less than 0.1% by volume, and thus the effect of methanol on sorption of Phe-d_{10} can be ignored (Huang et al., 2006). All vials were shaken for 48 h at room temperature (25 ± 1 °C) on a shaker table at 120 rpm, and then centrifuged at 3000 rpm (1811 g) for 20 min. The resulting supernatants were transferred to glass vials with a glass pipette to measure the Phe-d_{10} in the solution phase. Filtered seawater (40 mL) was added to the remaining rewetted sediments in the vial for the one-step desorption experiment with the same experimental procedure as the adsorption. Soaking times of 24 h for native released PAHs and 48 h for amended PAHs should not affect the results; previous work showed that sorption properties of rewetted marsh sediments did not change over 3 months of soaking (Liu et al., 2008).

After supernatants were transferred to other glass vials, Ace-d_{10} was added to them as a surrogate standard to examine the recovery efficiency of Phe-d_{10}. The procedure to extract Phe-d_{10} from supernatant followed the protocol for PAH extraction described above. The amount of Phe-d_{10} sorbed to sediments was calculated based on mass balance.

2.4.2. Drying impact on the release of amended phenanthrene from sediments (ExpB)

Desorption of Phe-d_{10} was further examined after Phe-d_{10} was first adsorbed to wet ST451 sediments and then subsequently dried and rewetted. This experiment allowed us to evaluate whether the sorbed PAHs in wet sediments can be further released when sediment is dried and rewetted, and provides further insights into structural changes of SOM. Briefly, the sorption procedure of Phe-d_{10} to wet sediments was same as described in ExpA. After the supernatant was removed and Phe-d_{10} was quantified at the end of the adsorption, the remaining sediment was dried in the oven at 40 °C until the sediment weight became constant. Filtered seawater was then added to the dried sediments in the vials to a volume of 40 mL for the one-step desorption experiment, using the same experimental procedure as the adsorption.

In ExpB we also evaluated the potential volatilization loss of sorbed Phe-d_{10} in wet sediments during the drying process in the oven. Wet sediments with sorbed Phe-d_{10} in an uncapped tube were placed in a sealed glass jar, with anhydrous sodium sulfate to sorb the water. The glass jar with the tube was put in an oven at 40 °C. After the sediment was dried and the jar cooled down to room temperature, the inner wall of the container and the anhydrous sodium sulfate were rinsed with hexane, and the hexane was concentrated in a rotary evaporator for Phe-d_{10} measurement. No Phe-d_{10} was detected in the hexane, suggesting that the volatilization loss of sorbed Phe-d_{10} in wet sediment was minimal during the oven drying.

2.5. PAH analysis

Sixteen priority PAHs listed by the US EPA were analyzed: naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*,*j*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3]pyrene, dibenzo[*a*,*h*]anthracene, and benzo[*ghi*]perylene. A mixture of targeted standards and three deuterated PAHs were used as surrogate standards, D_{10}-acenaphthene (Ace-d_{10}), D_{10}-phenanthrene (Phe-d_{10}) and D_{12}-benzo[*a*]pyrene (BaP-d_{12}) (Sigma). PAHs were analyzed by gas chromatography–mass spectrometry (GC–MS, Shimadzu QP2010 Plus) according to Liu et al. (2012). Briefly, the GC–MS was equipped with a RXi-1MS capillary column (20 m × 0.18 mm i.d., film thickness 0.18 μm), with helium as the carrier gas at 0.8 mL min^{-1} flow, and using selective ion monitoring mode to detect PAHs.

2.6. Quality assurance/quality control

All sorption and desorption experiments were conducted on duplicate samples. The average surrogate recoveries for sediments were 114 ± 4% ($n = 18$) and for seawater 92 ± 12% ($n = 60$). The method blank was analyzed by the same procedure as the samples, and the background contamination was negligible. The released native PAHs are expressed as %-released relative to the total amount of PAHs in the sediment. *T*-tests were used to evaluate the significance of differences in release of PAHs from dried vs. wet sediments, as well as the drying impact on sediment grain size distribution.

3. Results

3.1. Impact of drying on particle size distribution

For easier comparison, the grain size distributions of wet sediments are binned into size classes (Table 1). The <32 μm fractions dominated the sediments (>46%), except for ST80 with only 11.7%. The 32–63 μm fractions made up 9–13% across the four stations, while the amounts of >63 μm fractions varied greatly, with the highest in STLP (44.5%) and lowest in ST104 (11.5%).

The percentages of smaller size fractions decreased upon drying. For example, the <15 μm fraction was 10% lower in dried than wet ST450 sediments, whereas the 15–300 μm fractions increased by 10% (*t*-test, $p < 0.01$) (Fig. 2). Organic matter removal using hydrogen peroxide did not affect grain size distribution compared to wet sediments (Fig. 2). The size distributions of other sediments showed similar impacts of drying, except the ST80 sediment, which had the lowest TOC content (0.13%) (Fig. A3 in Appendix, Table 1).

3.2. Native PAHs released from wet and dried sediments

The levels of total extractable PAHs in Nueces marsh sediments ranged from 74.6 to 304.2 ng g^{-1}, with the highest concentration at

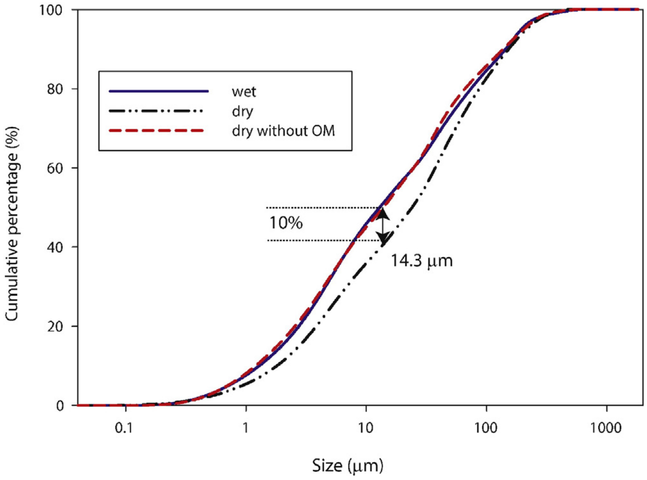

Fig. 2. Cumulative volume size distribution of ST450 sediments with different treatments ($n = 3$). Blue solid and black dash-dot lines represent wet and dry sediments, respectively. The red dotted line represents dried sediments with organic matter removed by hydrogen peroxide. The fraction <14.3 μm in wet sediments contained 10% more total cumulative volume than this size fraction in dry sediments (significance of difference, $p < 0.01$). The <32 μm fraction in dry sediments decreased significantly compared with wet sediments ($p < 0.05$), but no significant difference was found between wet and dry without organic matter ($p = 0.4$). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ST450 and lowest at ST451 (Fig. A1 in Appendix). These concentrations were in the range typically found in wetland sediments (e.g., Wang et al., 2012, 2014), and below ERL (Effects Range Low) (Long et al., 1995). PAHs with 3–4 rings made up more than 50% of the total by weight. The ratios of fluoranthene/(fluoranthene + pyrene) were above 0.5 in all stations, indicating that PAHs in this area are mainly from coal and/or biomass burning (Yunker et al., 2002). However, there might be additional biogenic PAHs formed during organic matter degradation because of the high proportions of naphthalene and phenanthrene in these sediments (Wakeham et al., 1980; Wilcke et al., 2003).

The release of PAHs within 24 h from wet vs. dried/rewetted sediments was compared using a solid/water ratio of 1/100. Among the 16 EPA priority PAHs examined, only phenanthrene, fluoranthene and pyrene were consistently released from dried sediments of all stations, and only a subset of these PAHs were released from wet sediments (Fig. 3). Phenanthrene and fluoranthene were released most readily from dried sediments, with highest release at STLP (7.0% and 10.5% of the total extractable concentrations, respectively) and lowest at ST450 (both about 1%). In contrast, less than 1% of each of these three PAHs was released from wet sediments. In addition to the STLP sample with the highest PAH release, other stations showed significant differences in released PAHs between wet and dried sediments for all three PAHs (t-test, $p < 0.05$). No such consistent patterns were observed for naphthalene between dried and wet sediments, perhaps because naphthalene is more soluble and volatile and has higher concentrations in ambient waters than other PAHs. Other PAHs in the supernatants from these suspensions were below the detection limit (<0.01 ppm).

3.3. PAH release from size-fractioned sediments

In size-fractioned ST451 sediments, the total PAH level was highest in the <32-μm fraction (94.5 ng g^{-1}), and decreased with increasing particle size, down to 13.1 ng g^{-1} in the 125–300-μm fraction (Fig. 4a). This pattern is expected because finer size fractions have higher specific mineral surface area and TOC contents (Table A1 in Appendix).

Phenanthrene, fluoranthene and pyrene were released to seawater consistently from all size fractions, similar to results from bulk sediment (Fig. 4b). However, the release percentages of these PAHs, relative to the total extractable amount, differed among the size fractions. The release percentages of total phenanthrene and pyrene from the 125–300-μm fraction were significantly higher than those from smaller size fractions (t-test, $p < 0.01$). For example, 47% of phenanthrene was released from the 125–300-μm fraction, compared to 10–12% in the finer fractions. Similarly, 15% of pyrene was released from the 125–300-μm fraction, compared to less than 1% in the finer fractions (Fig. 4b).

3.4. Adsorption and desorption of amended PAHs (ExpA)

The Freundlich model was applied to fit adsorption-desorption curves of Phe-d_{10} in both wet and dry sediments (Fig. 5) (Schwarzenbach et al., 2005):

$$C_s = K_F\, C_d{}^n$$

or

$$\mathrm{Log}C_s = \mathrm{Log}K_F + n\mathrm{Log}C_d$$

where C_s (ng g^{-1}) is sorbate concentration in sediment, C_d (ng mL^{-1}) is final sorbate concentration in solution, K_F [(ng g^{-1}) (ng mL^{-1})$^{-n}$] represents sorption affinity, and n is the nonlinearity factor, reflecting energy heterogeneity of the sorption sites. LogK_F for adsorption was higher in dried sediments than in wet sediments (1.93 ± 0.22 vs. 1.41 ± 0.51, Table 2), as well as the LogK_{oc} value at Cd = 10 ng mL^{-1} (3.9 vs. 3.6), indicating higher affinity of Phe-d_{10} to dried sediments than to wet sediments in both adsorption and desorption experiments. This higher affinity to dried sediments was especially strong at smaller amounts of amended Phe-d_{10} (Fig. A4 in Appendix). However, adsorption percentages of Phe-d_{10} in dried and wet sediments converged with increasing amount of amended Phe-d_{10}. Similarly, desorption percentages of Phe-d_{10} were higher in dried than in wet sediments with increasing amounts of amended Phe-d_{10} (Fig. A4). These results suggest that drying exposes only a limited number of high-energy sorption sites. In other words, adsorption sites were more heterogeneous in dried than wet sediments, as suggested by the n value of wet sediment (0.95 ± 0.18) being much closer to 1 (constant sorption free energy) as compared with that of dried sediment (0.79 ± 0.09).

Although higher affinity usually is associated with higher hysteresis during desorption (Wu and Sun, 2010), the desorption curve from dried sediments showed lower hysteresis than from wet sediments (Fig. 5). To compare the hysteresis of adsorption-desorption directly, we applied the hysteresis index (HI) of Huang et al. (1998):

$$\mathrm{HI} = \left(C_s{}^d - C_s{}^s\right)/C_s{}^s$$

where C_s^d and C_s^s are sorbate concentrations in sediments for the desorption and adsorption experiments, respectively. At constant room temperature (25 °C), HI was calculated at two concentration levels of C_d (1, 10 ng mL^{-1}) for wet and dried sediments using the Freundlich model parameters listed in Table 2. HIs were 2–3 times higher in wet sediments than in dried sediments, suggesting that sorption is more reversible in dried than in wet sediments. The hysteresis can be also attributed to slow sorption kinetics of adsorbed compounds (Altfelder et al., 2000), i.e., the fraction of slow sorption contributed more in wet sediments than in dried sediments.

3.5. Impact of further drying on the release of amended PAHs (ExpB)

To further explore the response of SOM structure to wet-dry cycles, we examined adsorption of Phe-d_{10} in wet sediments and its subsequent desorption after the sediments were dried and rewetted, with data fitted by the Freundlich model (Fig. 6, Table 2). The LogK_F calculated from desorption from dried sediments after one dried-rewetted cycle was much higher than that from wet sediments (2.85 ± 0.07 vs. 1.96 ±

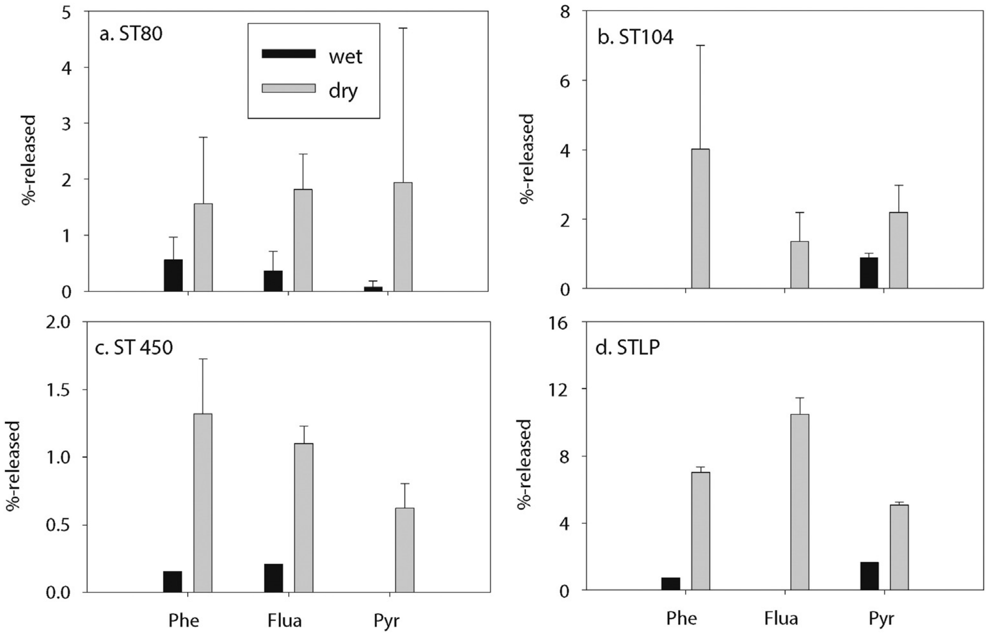

Fig. 3. The release of PAHs (as percentage of total extractable) from wet and dried sediments with solid/water ratios of 1/100 at 24 h. a: ST80, b: ST104, c: ST450, d: STLP. Error bars represent standard deviation of duplicate samples. In addition to STLP (the highest release), the percentage release of PAHs between dried and wet sediments was significantly different (*t*-test, $p < 0.05$).

1.64), and dried sediments (2.85 ± 0.07 vs. 2.36 ± 0.14) (Fig. 6, Table 2), indicating a much higher affinity of added Phe-d_{10} in sediments after one dried-rewetted cycle. Moreover, adsorption-desorption hysteresis, was greater in dried-rewetted sediments in ExpB ($HI = 28.4$ and 32.8 at $C_d = 1$ and 10 ng mL^{-1}, respectively) than in either wet or dried sediments in ExpA. These results agree with studies showing that wetting and drying enhance phenanthrene sequestration in terrestrial soils (White et al., 1998; Shchegolikhina et al., 2012).

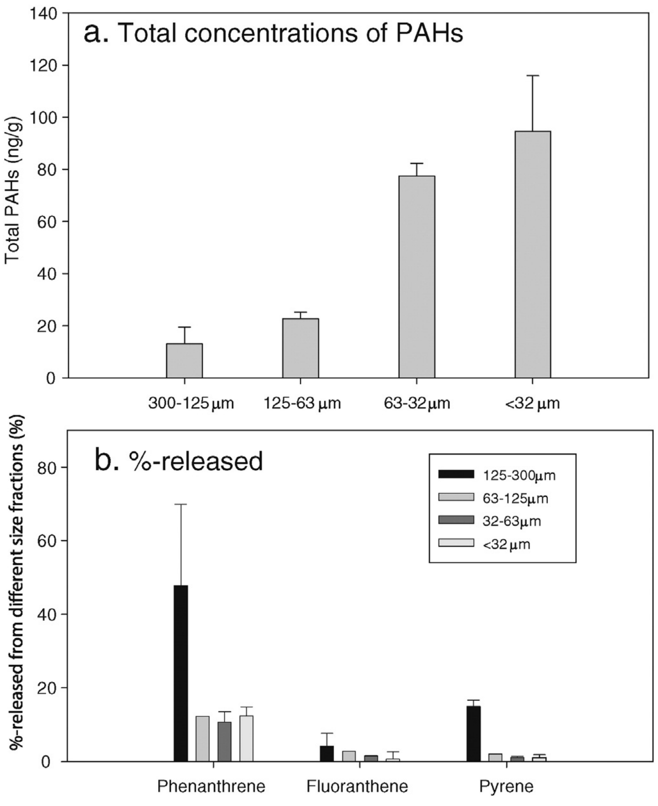

Fig. 4. (a) Total concentrations of PAHs for each size fraction of ST451 sediments (nonpolar solvent extraction), and (b) the release to water of three individual PAHs (% of the total individual PAH) from different size fractions of ST451 sediment at a solid/water ratio of 1/100. Error bars represent one analytical standard deviation of duplicate samples.

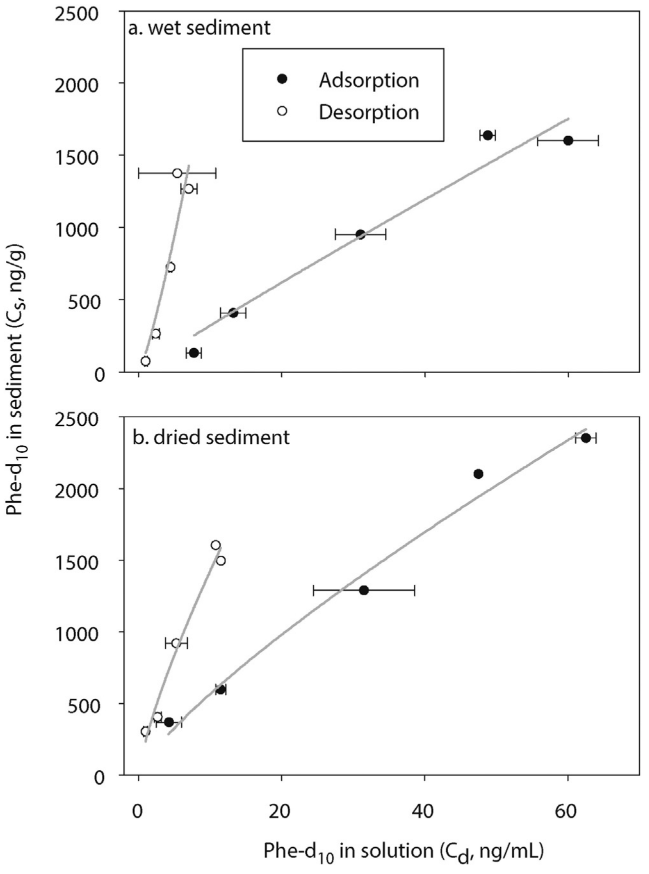

Fig. 5. Phe-d_{10} adsorption-desorption when Phe-d_{10} was added into wet and dried sediments from ST451. The curves were fitted by the Freundlich model. Error bars represent one standard deviation of duplicate samples.

Table 2
Parameters obtained by fitting adsorption and desorption curves to the Freundlich model for Exp A and Exp B (shown in Figs. 5 and 6, respectively). K_F (ng g^{-1}/(ng mL^{-1})^n) represents sorption affinity, and *n* is the nonlinearity factor, reflecting energy heterogeneity of the sorption sites. *HI* (hysteresis index) quantifies sorption hysteresis, and C_d is the final PAH concentration in solution. K_{oc}(mL g^{-1}) is calculated at $C_d = 10$ ng mL^{-1} to directly compare sorption affinity among experiments.

					K_{oc}	HI	
ST451		$LogK_F$	n	R^2	At $C_d = 10$ ng mL^{-1}	At $C_d = 1$ ng mL^{-1}	At $C_d = 10$ ng mL^{-1}
Wet sediments (Exp A)	Adsorption	1.41 ± 0.51	0.95 ± 0.18	0.96	4.6×10^3	2.6	5.8
	Desorption	1.96 ± 0.64	1.23 ± 0.44	0.98	1.6×10^4		
Dry sediments (Exp A)	Adsorption	1.93 ± 0.22	0.79 ± 0.09	0.98	8.1×10^3	1.6	1.5
	Desorption	2.36 ± 0.14	0.77 ± 0.11	0.95	2.1×10^4		
Dried and rewetted sediments (Exp B)	Adsorption onto wet	1.12 ± 0.84	0.99 ± 0.29	0.95	3.4×10^3	28.4	32.8
	Desorption from dried and rewetted	2.85 ± 0.07	1.05 ± 0.19	0.97	9.3×10^4		

4. Discussion

4.1. The rapid release of native PAHs from dry sediments

The percentages of total native, or aged, PAHs, mainly phenanthrene, fluoranthene and pyrene, released from dried sediments to solution within 24 h ranged from 1.0–7.5%, much higher than release from wet sediments. This finding is important to understanding the distribution of PAHs in coastal regions that undergo drought-flood fluctuations, especially contaminated areas such as the Mediterranean coast and Liaodong Bay (Men et al., 2009; Barakat et al., 2011). In particular, concentrations of PAHs in coastal waters may be greatly enhanced when dried marsh sediments are rewetted by a flood after a drought. The concentrations of PAHs (10s nM) released from these marsh sediments may not be high enough to cause acute toxic effects, but they may lead to sublethal and chronic impacts on aquatic larvae (Di Toro et al., 2000, Incardona et al., 2004). Even though a low percentage of PAHs was released from dried sediment, concentrations in slurries with higher solid/water ratios (e.g., at the sediment-water interface) may be high enough to be toxic to larvae. Further, the released PAHs, such as phenanthrene and fluoranthene, can be transformed to hydroxylated and carboxylated PAH products after aerobic exposure in the water column, which can be more toxic to organisms (Chibwe et al., 2015). Similarly, other hydrophobic contaminants, such as polychlorinated biphenyls, may also be released in greater amounts from dried sediments. More attention should be paid to the long term effects of low-concentration contaminants on organisms in aquatic environments with dry-wet cycles.

The types of PAHs released from dried sediment can provide insights into the binding mechanism of PAHs and organic matter particles. In desorption batch studies, the release rate and percentage of a given PAH desorbed from sediment depend on its K_{ow} (octanol-water distribution coefficient) and solubility (Helmstetter and Alden, 1994). For example, Qi et al. (2011) found that phenanthrene was released to a greater extent than pyrene from estuarine sediments due to its lower K_{ow} and higher solubility. However, of the 16 native PAHs examined, we found no correlation between K_{ow} and the percent released from dried sediments. For example, acenaphthylene and fluorene, with lower K_{ow}s (4.07 and 4.18, respectively) and higher solubilities (3.93 mg L^{-1} and 1.68 mg L^{-1}, respectively) than phenanthrene ($K_{ow} = 4.45$ and H_2O solubility = 1.20 mg L^{-1}), were not released from dried sediments in ST80, even though their concentrations in sediments were similar to those of phenanthrene or fluoranthene ($K_{ow} = 4.90$ and H_2O solubility = 0.20 mg L^{-1}) (Fig. A1 in Appendix). This result suggests that different PAHs associate with different types of organic matter. Natural organic matter is highly heterogeneous and contains binding sites with different energies (Weber et al., 2002). The role of minerals in sorbing hydrophobic PAHs is likely minimal, considering that sediments from this area are dominated by quartz (White et al., 1983). Previous studies have indicated that mineral sorption is usually negligible because of the significant competition of water for sorption sites (Chiou and Shoup, 1985; Birdwell et al., 2007).

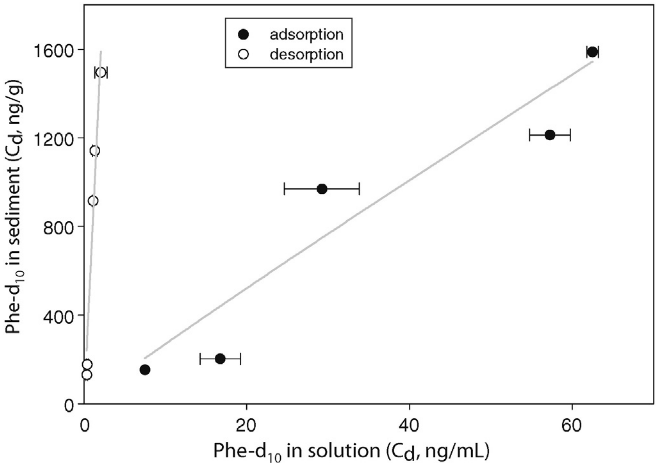

Fig. 6. Phe-d_{10} sorption when Phe-d_{10} was added into wet sediment and the subsequent desorption after the sediment was dried. The curves were fitted by the Freundlich model. Error bars represent one standard deviation of duplicate samples.

The degradation status of SOM may also affect the release of native PAHs, as indicated by K_{oc} values of PAHs in different size fractions. K_{oc} values of phenanthrene and pyrene in the 125–300-μm fraction were 4–8 and 11–14 times lower than those in the finer fractions, respectively (Table A2 in Appendix). Analysis of amino acids and *n*-alkanes suggested that the organic matter in the 125–300-μm fraction is the most labile, and least “aliphatic”, organic fraction in this sediment (Liu et al., 2013). This correlation is consistent with other studies showing that the K_{oc} value correlates with the proportion of aliphatic carbon among the size fractions (Ran et al., 2007; Sun et al., 2008). In addition, degradation can change the rigidity of organic matter; degraded organic matter, such as soot carbon, is more “glassy” while fresh organic matter is more “rubbery” (Leboeuf and Weber, 1997; Xing and Pignatello, 1997). The lower percentage of release from less-labile finer fractions might thus be explained by their more glassy nature, from which PAHs are more difficult to release than from more rubbery organic matter (Pignatello and Xing, 1996). Dominance of PAHs with 3–4 rings in the 125–300-μm fraction may also indicate biogenic origin for the PAH (Wakeham et al., 1980; Wilcke et al., 2003), which may be less strongly associated with fresher SOM.

One possible explanation for the PAH release from dried sediments is that enhanced DOC release in a slurry made from dried sediment may complex more PAHs (Gschwend and Wu, 1985). For example, the DOC concentration was 9.7 mg L^{-1} from ST450 in the wet sediment slurry, compared with 14 mg L^{-1} in the dried and rewetted sediment slurry. However, no strong correlation was found between DOC concentrations and the %-release of PAHs across all sediments tested. Although total DOC may not affect the PAH release, certain components in DOC may complex specific PAHs (Chiou et al., 2000). If this were true, however, equal amounts of added Phe-d_{10} would be expected in solutions from sediments after one dry-wet cycle (Phe-d_{10} was added in wet sediment then dried and rewetted) vs. dried sediments (Phe-d_{10} was added in rewetted dried sediment), because the same DOC components would be released from these two treatments that differed only in the sequence of trace-level Phe-d_{10} amendment. However, the Phe-d_{10} was adsorbed more by sediments subjected to one dry-wet cycle (Fig. A5 in Appendix), suggesting that structural changes of the particulate SOM, rather than released DOC components, are more important in controlling the partitioning of PAHs between solid and liquid phases. In any case, it is unlikely that the relatively small changes in DOC concentration would lead to the more dramatic differences in Phe-d_{10} release upon changed dry-wet cycles.

4.2. Structural change of SOM by drying

Our results on particle size changes during drying indicate that organic matter changes its structure in response to wet-dry cycles. Structural change in the organo-mineral complex is indicated by changes in particle size distribution, upon drying but not upon organic matter removal. For example, the < 15 μm fraction in the ST104 wet sediment decreased by 3.5% upon drying (Fig. A3 in Appendix), consistent with other studies on soils and sediments (Barbanti and Bothner, 1993). Morphology of wet sediment particles changes greatly upon drying, such as loss of gel-like structures, and these structural changes are irreversible on laboratory time scales (Liu and Lee, 2006; Liu et al., 2008). Upon dehydration, organic surfaces on fine mineral grains change their hydrophobic-hydrophilic character, and strongly bind each other via the hydrophobic effect or multiple hydrogen bonds (Ransom et al., 1998; Liu and Lee, 2006, 2007; Kleber et al., 2007). The dried organic glues seem to be strong enough to withstand vortex mixing and strong sonication in the laser analyzer during our laboratory grain-size analysis. The similar grain size distribution between the organic-rich wet sediment (ST-450, 0.71%) and the same sediment treated to remove organic matter (Fig. 2) indicates that minerals in wet sediments exist mostly as individual grains due to the low organic content in this area (<1%). Further, the sediment with the lowest organic content (ST80, 0.13%) showed minor change in grain size distribution (<2%) upon drying. In contrast, very organic-rich (4.5%) sediments from McGuill Lake, a nearby location, converted nearly all of its <63 μm materials to coarser fractions upon freeze-drying (Liu et al., 2013). These patterns indicate that drying affects SOM in ways that lead to changes in size distribution of mineral grains.

Our results clearly show that much more native phenanthrene was released from dried sediments to seawater than from fresh wet sediments, but the experimentally amended deuterated phenanthrene was adsorbed more to dried than to wet sediments. Slow sorption kinetics may explain some of our data, such as the hysteresis observed during the desorption (Figs. 5, 6) (Altfelder et al., 2000), but not the different patterns between wet and dried sediments. For example, if drying would only lead to compaction of particles or surface area, less release of PAHs, or less sorption of Phe-d_{10}, would be expected from dried sediment. These apparently contradictory results can be explained by the different distributions of native and amended PAHs in heterogeneous organo-mineral complexes. Consider, for example, the zonal model proposed by Kleber et al. (2007) that organizes this heterogeneity in layers of different depth, as shown in a modified version (Fig. 7). In this model, organically bound native, or aged, PAHs occur in a hydrophobic zone that consists of hydrophobic moieties of amphiphilic geopolymers, due to entropically-driven association (Alexander, 2000; Abu and Smith, 2006; Kleber et al., 2007). The hydrophobic zone is protected from exposure to solution by the hydrophilic moieties of the amphiphilic polymers and further by an outer, largely hydrophilic "kinetic" zone, where organic molecular fragments accumulate, probably mediated by multivalent cations. These hydrophilic zones partially inhibit transport of the buried PAHs, and hence reduce the fraction of the native PAHs desorbing from wet sediments (Northcott and Jones, 2001; Kottler et al., 2001). In other words, the exchange of PAHs between solution and the hydrophobic zone of wet sediment either did not occur or occurred very slowly within the 24 h experimental time scale (Altfelder et al., 2000).

Drying can expose some of the hydrophobic interior sites outside by rearrangement during dehydration, as often evidenced by increased hydrophobicity and water repellency in soils and sediments (Doerr et al., 2000; Liu and Lee, 2006). Likewise, drying can increase the external hydrophobicity of protein molecules by exposing the interior hydrophobic residual groups (Mine, 1997; Ju et al., 2001). This exposure of interior sites containing aged PAHs makes the latter more available for partitioning between solution and solid phases, resulting in rapid PAH release (Fig. 7). Such a structural change upon drying can also explain adsorption and desorption data of the freshly amended phenanthrene. The Freundlich n values in wet sediments are closer to 1 than that in dried sediments (Table 2), suggesting that free energies of the sorption sites in wet sediment were more uniform than those in dried sediment. The higher affinity (LogK_F) in dried sediments can be explained by the increased hydrophobicity of dried SOM due to rearrangement of amphiphilic compounds in the hydrophobic and kinetic zones (Fig. 7), providing access to adsorption of hydrophobic phenanthrene (Liu and Lee, 2006, 2007; Diehl et al., 2009). Moreover, drying can shrink SOM (White et al., 1998; Liu and Lee, 2006), reducing penetration of amended sorbates to micropores or channels within the SOM (Ghosh et al., 2000). Thus, the amended sorbates tend to accumulate in hydrophobic zones contained within the outer, or more accessible, kinetic zone of dried SOM (Diehl et al., 2009). During desorption, the PAHs on the hydrophobic surface of the dried SOM desorb more easily than those in inner regions.

This proposed interpretation is further supported by the considerably inhibited release of amended PAHs when Phe-d_{10} was added to wet sediment that was subsequently dried (Fig. 6). Unlike native PAHs that are residually concentrated in the interior hydrophobic zone, the freshly-amended Phe-d_{10} likely penetrates only to the kinetic or surface hydrophobic zones of SOM due to the short contact time. The partial collapse of these zones upon drying may seal the sorbed phenanthrene in a buried hydrophobic zone of SOM (White et al., 1998), thus inhibiting its diffusion back to the kinetic zone of SOM (Fig. 7) and hence release to solution. Overall, drying seems to change the physical forms (or conformations) of SOM by shrinking its three-dimensional networks (Xing and Pignatello, 1997), and simultaneously exposing hydrophobic zones to the solution. These data and interpretations are consistent with the zonal model proposed by Kleber et al. (2007), though other models of heterogeneous distribution of hydrophobic and hydrophilic regions might also serve.

5. Conclusion and implications

Adsorption/desorption of PAHs in aquatic environments has been well studied (e.g., Chiou et al., 1998; Altfelder et al., 2000; Hung et al., 2012), yet little is known how drying-rewetting would affect distribution of PAHs between solid and solution phases. Our adsorption-desorption experiments indicate that drying may lead to changes in the heterogeneous structure of SOM, such as shrinking and collapse of networks and reversing the orientation of amphiphilic compounds, resulting in greater release of aged PAHs from sediments and yet greater retention of freshly amended PAHs. These data are consistent with the "zonal model" of organo-mineral complexes proposed by Kleber et al. (2007). This finding indicates that concentrations of PAHs, or other types of organic contaminants, in natural waters may be greatly enhanced when dried sediments or soils are rewetted by a flood after a drought. Understanding these changes in SOM will be important to understanding the distribution and impacts of organic contaminants under the projected scenarios of increasing frequency of droughts in future. Freshly amended PAHs, as a probe, provide insights into the structure of organic-mineral complexes in salt marsh sediments, as well as

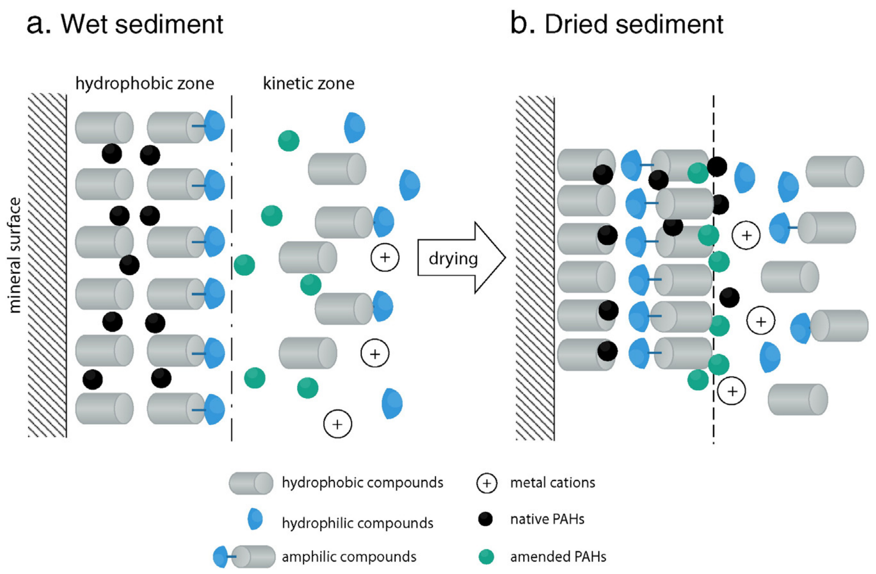

Fig. 7. A conceptual model, modified from Kleber et al. (2007), showing the drying impact on native and amended PAHs in SOM: (a) wet and (b) dried SOM. The hydrophobic zone is formed by the hydrophobic portions and covered by a second layer of amphiphilic molecules. In the kinetic zone, organic molecular fragments accumulate, probably largely mediated by multivalent cations. Drying exposes some native PAHs with hydrophobic compounds from the interior hydrophobic zone to the kinetic zone, enhancing release of native PAHs from SOM to water. In contrast, drying shrinks SOM and collapses pores and channels between the hydrophobic and kinetic zones, where fresh amended PAHs become adsorbed, sealing these amended PAHs. Drying also enhances the sorption of amended PAHs to hydrophobic groups of amphiphilic compounds.

how drying may change their structure and thus affect the distribution of organic contaminants in wetland environments.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2016.05.184.

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