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Journal of Contaminant Hydrology 72 (2004) 1–22
JOURNAL OF Contaminant Hydrology
www.elsevier.com/locate/jconhyd

Interaction of phenanthrene and its primary metabolite (1-hydroxy-2-naphthoic acid) with estuarine sediments and humic fractions

Sanjai J. Parikh[a], Jon Chorover[a,*], William D. Burgos[b]

[a] *Department of Soil, Water and Environmental Science, The University of Arizona, 429 Shantz Building, Tucson, AZ 85721, USA*
[b] *Department of Civil Engineering, The Pennsylvania State University, University Park, PA 16802, USA*

Received 17 April 2002; received in revised form 23 October 2003; accepted 31 October 2003

Abstract

Experiments were conducted to compare the sorption and desorption of phenanthrene and its primary degradation product, 1-hydroxy-2-naphthoic acid (HNA), in estuarine sediment, humic acid (HA) and humin. Ionic composition, ionic strength (0.4 M) and pH (7.6) were employed to mimic native estuarine pore water at the sediment–water interface. Sorption to whole sediment and organic matter (OM) fractions was significantly lower for HNA than for phenanthrene. Whereas HNA did not sorb to HA, uptake to sediment and humin was observed, suggesting that HNA does not bind directly to OM. Phenanthrene uptake was characterized by hysteretic behavior and exhibited slow desorption. In contrast, HNA initially was more readily desorbed from sediment and humic fractions, but a significant fraction was not recovered in repeated desorption runs. The lower sorption of HNA reflects its greater polarity and water solubility, but the consistent retention of a non-desorbing fraction suggests strong binding and/or chemical transformation reactions may be important. It was postulated that abiotic transformation of HNA may occur in estuarine sediments, in part due to the presence of redox active minerals (Fe(III) and Mn(IV) oxides). The presence of Fe and Mn solids in the estuarine sediment was verified by sequential extraction and studies were then conducted to investigate the transformation of HNA in the presence of synthetic goethite (α-FeOOH) and birnessite (δ-MnO_2) as model solids. Reaction with birnessite led to transformation of all HNA in solution within 24 h and resulted in the formation of partial oxidation products (POPs). Following reaction with goethite, HNA was present in solution and POPs were observed in the weakly bound fraction. This study indicates that degradation

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* Corresponding author. Fax: +1-520-621-1647.
E-mail address: chorover@cals.arizona.edu (J. Chorover).

doi:10.1016/j.jconhyd.2003.10.004

products of polycyclic aromatic hydrocarbons (PAHs) may have distinctly different sorption affinities and reactivities toward environmental surfaces than their parent compounds.

Keywords: Sorption; Phenanthrene; Oxidative transformation; Sediment; Humic acid; Humin; Hydroxynaphthoic acid

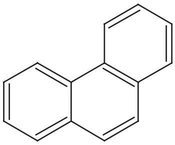
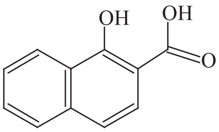
1. Introduction

Contamination of estuarine sediments by organic xenobiotics presents a threat to aquatic organisms. In particular, sediments tend to accumulate surface active pollutants as a result of depositional processes (Guerin, 1989). Sedimentary organic matter (OM) plays an important role in the sorption of contaminants, thus affecting bioavailability and toxicity. Common estuarine pollutants include polycyclic aromatic hydrocarbons (PAHs). PAHs are hydrophobic, causing them to accumulate in aquatic organisms, plants, and humic materials (Olsen et al., 1982; Swackhammer and Eisenreich, 1991). Phenanthrene, one of the most abundant PAHs in the environment (Cerniglia, 1993), is included in the U.S. EPA list of priority pollutants (Keith and Telliard, 1979). It is degraded microbially via a meta cleavage pathway resulting in the accumulation of 1-hydroxy-2-naphthoic acid (HNA) (Guerin and Jones, 1988; Menn et al., 1993). The reactivity and toxicity of this daughter compound are essentially unknown relative to phenanthrene, which has been studied much more extensively.

PAH sorption depends on solubility and size characteristics of the sorptive species, as well as composition of the solid phase. The affinity of hydrophobic organic contaminants for pristine mineral surfaces is often significantly lower than it is for humic substances (HS), but is important in low organic C environments (Hundal et al., 2001). Coating of mineral surfaces with HS can increase (Dexter and Pavlou, 1978; Murphy et al., 1990; Murphy et al., 1992) or decrease (Chorover et al., 1999) uptake of organic pollutants with the effect depending largely on functional group chemistry and hydrophobicity of the compound. Prior research indicates that HS are a major sink for hydrophobic organic compounds (HOCs) and sorption varies according to the structural properties of sorbate and sorbent (Rogers et al., 1980; Voice and Weber, 1983; Dzombak and Luthy, 1984; Karickhoff, 1984; Murphy et al., 1990; Schlautman and Morgan, 1993; Jones and Tiller, 1999). Non-polar domains of HS are postulated sites of HOC uptake, and both aliphatic and aromatic moieties are considered important (Gautheier et al., 1987; Chefetz et al., 2000). For example, significant sorption of PAHs to anthropogenic soot particles has also been observed (Gustafsson et al., 1997; Karapanagioti et al., 2000).

While there is a growing body of literature on the behavior of HOCs in soils and sediments, fewer analogous data are available on reactions of ionizable organic compounds (IOCs), including PAH metabolites. Sorption chemistry of IOCs is distinct from their hydrophobic counterparts: cation bridging (Wershaw, 1989), ligand exchange (Evanko and Dzombak, 1998) and site-specific binding to sorbent surfaces by polar or ionizable functional groups (Karickhoff, 1984; Senesi, 1993) are among the potential mechanisms. Compounds that are susceptible to abiotic oxidative transformation (e.g.

Table 1
Structure and molecular weight of compounds studied

Phenanthrene	1-Hydroxy-2-Naphthoic Acid (HNA)
 MW: 178.23 g mol^{-1}	 MW: 188.18 g mol^{-1} pK_a^*: 2.7 and 12.8

* pK_a values estimated by Evanko and Dzombak (1998).

phenols) may form covalent bonds with HS via coupling of reactive intermediates (Bollag et al., 1995) and polar compounds that exhibit low affinity for HS may bind strongly upon oxidation (Karthikeyan and Chorover, 2000). In addition to enzymatic catalysis, redox active minerals such as Fe(III) and Mn(IV) (hydr)oxides can also oxidize organic compounds abiotically (Huang, 1990). For example, numerous studies have documented the ability of birnessite to induce oxidative polymerization of phenolic compounds (Shindo and Huang, 1984; McBride, 1989; Ukrainczyk and McBride, 1992; Nadja et al., 1998; Majcher et al., 2000).

The toxicity and bioavailability of parent and daughter compounds likely differ in environmental systems. Therefore, it is essential to understand not only the behavior of the parent compound, but also that of its degradation products. The objective of the present study is to compare sorption/desorption behavior and reactivity of a parent PAH (phenanthrene) to its carboxylated phenolic metabolite (HNA) in estuarine sediments (Table 1).

2. Materials and methods

2.1. Sediment collection and porewater analysis

Sediment was collected from Carter's Creek, a tributary to the York River and part of the Chesapeake Bay watershed (37°19′ 42″ latitude, − 76°34′ 13″ longitude). Samples were obtained using a grab sampler (0–15 cm) while the boat was adrift. Sediment pore water was sampled and analyzed in triplicate to determine pH with a ROSS 81-02 combination electrode (Thermo Orion), total and dissolved organic carbon by high temperature combustion and infrared detection of CO_2 (Shimadzu TOC-5000A), anion (Cl^-, NO_3^-, SO_4^{2-} and HPO_4^{2-}) concentrations by ion chromatography (Dionex Ion Chromatograph DX500) and cation (Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe_T and Al_T) concentrations by atomic absorption (AA) spectrometry (Instrumentation Laboratory AA/AE Spectrophotometer Video 22).

2.2. Organic matter characterization

Humic fractions were extracted from the sediment using a modification of published protocol (Malcolm, 1991; Stevenson, 1994; Swift, 1996). After addition of NaOH and centrifugation, the insoluble "humin" was carefully collected as the discrete, organic-rich layer that sedimented on top of the mineral pellet. The HA fraction was obtained after its coagulation was induced by acidification of the supernatant solution, and it was de-ashed using a series of HF–HCl washes. The organic carbon content of each fraction was measured by TOC analyzer (Shimadzu TOC-5000A) after acidification to remove carbonates. The ash contents of the sediment, humic acid (HA) and humin were measured to determine the mass of mineral matter associated with each fraction (known mass of each fraction combusted at 450 °C for 6 h).

^{13}C cross-polarization (CP) magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra were obtained using the two-dimensional phase-adjusted spinning sidebands (2D PASS) method (Antzukin et al., 1995; Vogt et al., 2000). All fractions were de-ashed prior to collection of NMR spectra using a series of HF–HCl rinses to remove paramagnetic Fe. The acquisition parameters used were as follows: 6552 scans per row ($\times$ 243), ^{1}H frequency of 500 MHz, ^{13}C frequency of 125 MHz, contact time of 1.0 ms, relaxation delay of 1.3 s, sweep width of 75 kHz, spinning frequency of 8.0 kHz, π pulse duration of 7.8 μs and ^{1}H 90° pulse of 4.0 μs. Quantitative analysis of NMR spectra was based on spectral integration (using Microcal Origin 7.0) according to the following delimited regions (Malcolm, 1989; Bortiatynski et al., 1996): 0–50 ppm (alkyl C), 51–60 ppm (aliphatic esters and ethers), 61–85 ppm (CH(OH) groups), 86–111 ppm (O–C–O and anomeric C), 112–145 ppm (aromatic C), 146–163 ppm (O–aryl C) and 164–190 ppm (carboxyl C).

2.3. Sediment characterization

Sediment and humin clay mineralogy was determined by X-ray diffraction (XRD). Prior to XRD, the sediment and humin OM was removed by treatment with hydrogen peroxide (Kunze and Dixon, 1989), and the clay fraction was separated from the bulk sediment or humin by sedimentation (Gee and Bauder, 1986). XRD was performed on both oriented and randomly packed clay isolates (Whittig and Allardice, 1986). Diffraction patterns were obtained using a Scintag Pad V (Scintag) with a graphite monochromator, CuKα radiation (40 kV and 35 mA), a scan speed of $2^\circ\ 2\theta\ \mathrm{min}^{-1}$ and a step width of $0.01^\circ\ 2\theta$. A series of three sequential extractions, (i) 30% H_2O_2 (Kunze and Dixon, 1989), (ii) ammonium oxalate in the dark (Loeppert and Inskeep, 1996) and (iii) citrate–bicarbonate–dithionite (Loeppert and Inskeep, 1996), was performed in quadruplicate to obtain solid-phase Fe and Mn concentrations defined operationally as "complexed with OM", "amorphous" or "poorly crystalline" and "crystalline", respectively.

Mössbauer spectra were obtained on the sediment clay fraction, the humin clay fraction and the whole sediment with the OM intact. Spectra were collected at room temperature using an Austin 600 Mössbauer spectrometer with a 25 mCi ^{57}Co/Rh single-line thin source. The velocity transducer was operated in the constant acceleration mode and data were acquired on 1024 channel counters. Calibration spectra for zero-velocity position were obtained using a standard iron foil. Unfolded spectra obtained from the samples were folded and evaluated using the Recoil program (Lagarec and Rancourt, 1998).

2.4. Sorption and desorption experiments

A background electrolyte solution was synthesized for sorption experiments to mimic the natural pore water chemistry measured for Carter's Creek. A 0.4 M ionic strength solution, comprising 0.32 M NaCl, 0.02 M $MgCl_2$, 0.005 M $CaCl_2$ and 0.005 M KCl, was adjusted to pH 7.6 with 0.2 M NaOH prepared in the same 0.4 M background salt solution. Low solubility of phenanthrene (Table 1) necessitated use of ^{14}C-labeled compound. ^{14}C phenanthrene (specific activity = 10.6 mCi $mmol^{-1}$) was dissolved in methanol to make a 2 mmol l^{-1} stock solution. Separate stock solutions were made for each sorption experiment, with constant concentrations of stock ^{14}C phenanthrene and varied concentrations of ^{12}C phenanthrene. The 2 mmol l^{-1} stock solution of ^{14}C phenanthrene was diluted to 200 μmol l^{-1} with methanol and an aliquot of 0.0663 ml of that solution was mixed with varying amounts of ^{12}C phenanthrene stock. Duplicate samples of sediment, humic acid or humin were spiked with the appropriate stock solution (mix of ^{14}C and ^{12}C phenanthrene; between 0.0522 and 0.1045 ml) to give a desired initial contaminant concentration. Methanol was used as a cosolvent ($<0.5\%$) for ^{14}C phenanthrene experiments. At this concentration, methanol does not appear to affect the sorption of PAHs (Wauchope et al., 1983; Nkedi-Kizza et al., 1987). No cosolvent was needed for HNA studies.

Phenanthrene and HNA (Table 1) were reacted with Carter's Creek sediment, humin and HA fractions for time periods ranging from 15 min to 30 days in batch systems. Sediment and humic fractions were added to 25 ml Corex II centrifuge tubes at constant organic C concentrations (500 mg C kg^{-1} of suspension). Sodium azide was added to inhibit microbial activity (5 or 10 mg l^{-1} for reactions >48 h) (Karthikeyan and Chorover, 2000). Initial phenanthrene and HNA aqueous concentrations ranged from 0 to 5 μM for 24 h sorption experiments and 3 μM for kinetic studies. Aluminum lined caps were used and the total volume of each tube was brought to 28 ml to limit head space and volatilization. Reaction vessels were placed on an end-over-end shaker at 7 rpm, in the dark, at a constant temperature of 25 °C, and equilibrated for the appropriate time. HNA sorption to HA was measured using equilibrium dialysis (Spectra/por 7, MWCO 1000) in 250-ml jars as described in Karthikeyan and Chorover (2000).

After equilibration, sediment and humin samples were centrifuged (5633 RCF, 20 min, 25 °C) to separate solids from solution. ^{14}C phenanthrene concentrations were measured by liquid scintillation counting (Ecolume liquid scintillation cocktail, ICN Biomedicals; Beckman 8100 liquid scintillation counter). To measure ^{14}C phenanthrene sorption to HA, samples were acidified with concentrated HCl to pH <2 to induce coagulation of HA for 2 h prior to high-speed centrifugation. HNA concentrations in supernatant and dialysate solutions were measured via high-pressure liquid chromatography (HPLC) using a reverse phase (BetaBasic, C-18, Keystone Scientific) column with an eluent of methanol/Milli-Q water (73% methanol:27% Milli-Q water) flow rate of 1.0 ml min^{-1} and photodiode array (PDA) detection. Quantification was based on absorbance measured at 249 nm. Sorption data are reported in micromoles of compound sorbed per kilogram of sorbent carbon.

After determining solution phase analyte concentrations for 24 h sorption experiments, the masses of pellet and entrained solution were measured and contaminant-free background electrolyte solution was added. Samples were equilibrated for 24 h and concentrations measured as before (wash #1). The wash process was repeated twice (total of three washes) to measure desorption in each step, with additional equilibration times of 24 h (wash #2) and 5 days (wash #3).

Sorption data for phenanthrene and HNA were fitted to the Freundlich isotherm equation:

$$q_{\mathrm{s}} = KC_{\mathrm{eq}}^{n} \tag{1}$$

where q_{s} is sorbate mass (μmol kg^{-1} C), and K (Freundlich constant) and n (isotherm nonlinearity factor) are fit parameters. A plot of log q_{s} versus log C_{i} gives n as the slope and log K as the y intercept. The hysteresis index (HI), which provides a measure of sorption reversibility, was calculated for sorption and desorption data according to Huang and Weber (1997):

$$\text{Hysteresis Index} = \frac{q_{\mathrm{e}}^{\mathrm{d}} - q_{\mathrm{e}}^{\mathrm{s}}}{q_{\mathrm{e}}^{\mathrm{s}}} \Big|_{T}, C_{\mathrm{eq}} \tag{2}$$

where $q_{\mathrm{e}}^{\mathrm{s}}$ and $q_{\mathrm{e}}^{\mathrm{d}}$ represent the sorbate mass after sorption and desorption steps, respectively, and the subscripts T and C_{eq} represent constant temperature and solution concentration of sorptive compound (phenanthrene or HNA).

2.5. Reaction of HNA with Fe and Mn oxides

To study the potential for abiotic transformation of HNA in the presence of redox active oxides, experiments were conducted with synthetic goethite and birnessite. Goethite (α-FeOOH) was synthesized by adding KOH to a $\mathrm{Fe(NO_3)_3 \cdot 9H_2O}$ solution until the solution reached pH 12, followed by aging the solution at 60 °C for 24 h (Atkinson et al., 1967). Birnessite (δ-$\mathrm{MnO_2}$) was synthesized by adding concentrated HCl to a boiling solution of $\mathrm{KMnO_4}$ (McKenzie, 1971). HNA-oxide reactions were conducted in 25 ml Corex tubes with the same parameters as used in sorption experiments (Section 2.4). Initial concentration of HNA ranged from 0 to 160 μM. Birnessite and goethite were added at concentrations of 5 g kg^{-1} of suspension. $\mathrm{NaN_3}$ (5 mg kg^{-1}) was added to inhibit microbial activity and reaction kinetics were studied by varying time intervals of batch reaction (15 min, 2 h, 6 h, 1 day, 2 days, 4 days, 8 days). Concentrations of HNA remaining in solution were measured by HPLC. Solution pH was measured for each time interval. AA spectrometry (Instrumentation Laboratory AA/AE Spectrophotometer Video 22) was used to measure dissolution of Fe (goethite suspensions) and Mn (birnessite suspensions). Solutions were assayed for transformation products using HPLC–PDA, HPLC–mass spectrometry (MS) and gas chromatography (GC)–MS. HPLC–MS (Mariner, PerSeptive Biosystems) was performed in electrospray ionization (negative) mode using the same column and mobile phase conditions as for HNA quantification by HPLC–PDA. A post column split of 50 μl min^{-1} to the mass spectrometer was employed. GC–MS (Saturn 2000 GC/MS, Varian) employed an HP-5MS column (30 m length, 0.25 mm

ID, 0.25 μm film thickness) and a sample injection volume of 2 μl (250 °C injector temperature; oven temperature program 80 °C for 1 min, 20 °C min^{-1} increase to 300 °C, 5 min hold at 300 °C). Helium was used as the carrier gas at 1 ml min^{-1}. Mass spectra were collected using electron ionization. Samples were derivatized by using *N*-methyl-*N* (trimethylsilyl)trifluoroacetamide (MSTFA), 150 μl of sample was mixed with 50 μl MSTFA and heated to 60 °C for 10 min.

3. Results and discussion

3.1. Sorbent organic carbon and ash content

The organic carbon and ash content of each sorbent fraction is shown in Table 2. During fractionation and purification of OM, the HA fraction was de-ashed with a series of HF–HCl rinses so that contaminant-OM interactions could be studied in the absence of significant mineral matter. In order to preserve its intimate association with sediment clays, the humin fraction was not subjected to this treatment. Acid treatment of the humin would likely have altered the reactive surface of the mineral-organic complex. Therefore, a much higher inorganic (ash) content is reported for humin relative to HA (Table 2).

3.2. Mineral characterization

XRD patterns revealed the presence of smectite, mica or illite, and kaolinite in both sediment and humin clay fractions (data not shown). Chlorite was also found in the sediment clay fraction. Cation adsorption to expansible interlayers of smectite (Grim, 1968) could promote cation and water bridging interactions with dissolved anionic and polar organics (Senesi, 1993). Total mass of extractable Fe was 17 ± 1.4 g kg^{-1}; distributed among “OM bound” (4.0 ± 0.7 g kg^{-1}), “amorphous or poorly crystalline” (8.4 ± 1.3 g kg^{-1}) and “crystalline” (4.7 ± 0.6 g kg^{-1}) fractions. Total extractable Mn concentration was much lower (0.151 ± 0.005 g kg^{-1}). Most of the solid phase Fe and Mn is expected to be in the form of Fe(III) and Mn(IV), although some solid phase Fe(II) was noted in Mössbauer spectra (see below). The presence of both Fe and Mn in Carter’s Creek sediment indicates the potential for these hydroxylated solids to participate in abiotic oxidation and/or ligand exchange reactions with organic compounds.

Mössbauer spectra for all samples could be decomposed into two distinctive doublets (using Recoil software) that represent non-crystalline ferrihydrite and/or fine-grained goethite, and an unspecified ferrous mineral (data not shown). The relative intensity of the ferrous mineral doublet was greatest in the whole sediment sample indicating that the

Table 2
Total organic carbon and ash content

Sorbent	Carbon (%)	Ash content (%)
Sediment	2.06	81.02
Humic acid	36.9	0.1019
Humin	6.85	76.63

peroxide procedure to remove OM may have oxidized a portion of the ferrous mineral(s). The relative intensity of the ferrous mineral doublet was lowest in the humin clay fraction.

3.3. Organic matter characterization

^{13}C 2D-PASS NMR spectra provide structural information for OM in sediment, HA and humin. Peaks are assigned to specific carbon containing functional groups in accordance with Malcolm (1989). Comparison of the spectra shows that the fractions are structurally similar (data not shown). Spectral intensity deriving from aromatic moieties (chemical shift from 100 to 140 ppm) is slightly different for the various fractions. The HA fraction exhibited the highest relative aromaticity (28.5%), with humin (25.3%) and sediment OM (25.5%) showing slightly lower values. Humic substances exhibit variable composition depending on provenance and method of extraction. The distribution of aromatic to aliphatic moieties (as determined from NMR experiments) for the Carters Creek humic substances show some variation between the organic matter fractions, with aromaticity of HA higher than that of humin. This agrees with similar analysis of peat HA and humin studied by Xing (1998).

3.4. Sorption isotherms

The affinity of phenanthrene for estuarine materials followed the order HA > sediment > humin (Fig. 1) when data are normalized to organic C content. The high affinity

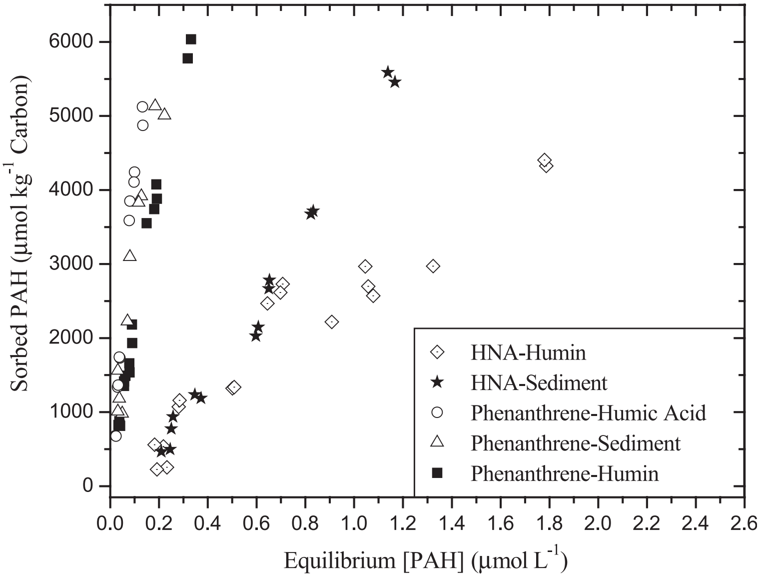


Fig. 1. Twenty-four-hour phenanthrene and HNA sorption to Carter's Creek humic fractions and sediment (0.4 mol l^{-1} background electrolyte solution at pH 7.6). No sorption of HNA to HA was detected. Phenanthrene measurements were based on LSC of ^{14}C-labeled compound.

of phenanthrene for HA is not surprising as HA is known to be an effective sink for HOCs (Murphy et al., 1992; Schlautman and Morgan, 1993). Given its low ash content, less of the HA surface is associated with mineral particles, relative to humin and sediment OM, thus enhancing the reactive area available for sorbate–sorbent interaction. The amount and accessible surface of HS are both important factors to the sorption of HOCs (Rogers et al., 1980; Voice and Weber, 1983; Karickhoff, 1984; Dzombak and Luthy, 1984; Murphy et al., 1990). Decreased sorption of HOCs to mineral-bound OM (vs. dissolved OM) is also consistent with previous reports (Karickhoff, 1984; Murphy et al., 1990).

As expected for an anionic, polar solute, HNA exhibited lower sorption affinity than phenanthrene for all sorbents (Fig. 1). The sorption of HNA to sediment and humin is approximately equal in the lower concentration range, but at higher equilibrium concentration, HNA sorption to sediment surpasses that of the humin. No sorption of HNA to HA was observed over the 24 h equilibrium period, indicating that cation bridging and water bridging between HNA and HA functional groups is not significant even in estuarine waters with high cation concentrations. Significant sorption of HNA to sediment and humin, therefore, suggests that HNA is not binding to OM, but rather to mineral surfaces associated with OM. From the sorption data we cannot rule out transformation of HNA on mineral surfaces. Products of phenol oxidation are known to bind strongly to OM (Bollag, 1983, Karthikeyan and Chorover, 2000) and mineral surfaces (Karthikeyan et al., 1999; Majcher et al., 2000), and this may also be the case for HNA.

The prevalence of bivalent cations and smectite clay in the humin and sediment systems suggest that cation and water bridging could promote weak sorption of HNA to mineral surfaces (Hayes and Mingelgrin, 1991). Similar experiments with 1-naphthylacetic acid showed no sorption to Carter's Creek humin, goethite, or montmorillonite under the same chemical conditions (Parikh, 2001), demonstrating that the specific number and arrangements of sorbate IOC functional groups is critical (Evanko and Dzombak, 1998).

3.5. Desorption of phenanthrene and HNA from sediment and humic fractions

Although a small mass of phenanthrene was released with each desorption step, sorption was not reversible (Fig. 2). Desorption isotherms exhibit steeper slopes and higher sorption values than adsorption isotherms at given aqueous concentrations of phenanthrene, reflecting hysteric behavior. Sorption/desorption hysteresis has been reported in numerous studies (Burgos et al., 1996; Huang and Weber, 1997; Yuan and Xing, 2001), but its assessment depends on how it is defined and quantified. When comparing the phenanthrene sorption isotherm to that for the first desorption wash (equivalent sorption and desorption time periods) there is no difference ($\alpha = 0.05$) between Freundlich parameters, log K and n (Table 3). In contrast, the HI values for phenanthrene do suggest hysteresis. Table 3 shows that for seven out of nine cases, the calculated range for phenanthrene HI is always greater then zero. According to Weber et al. (1998), if the range of the HI ± 1 standard deviation includes zero or a negative value, hysteresis is insignificant. The 95% confidence interval (which is larger than one

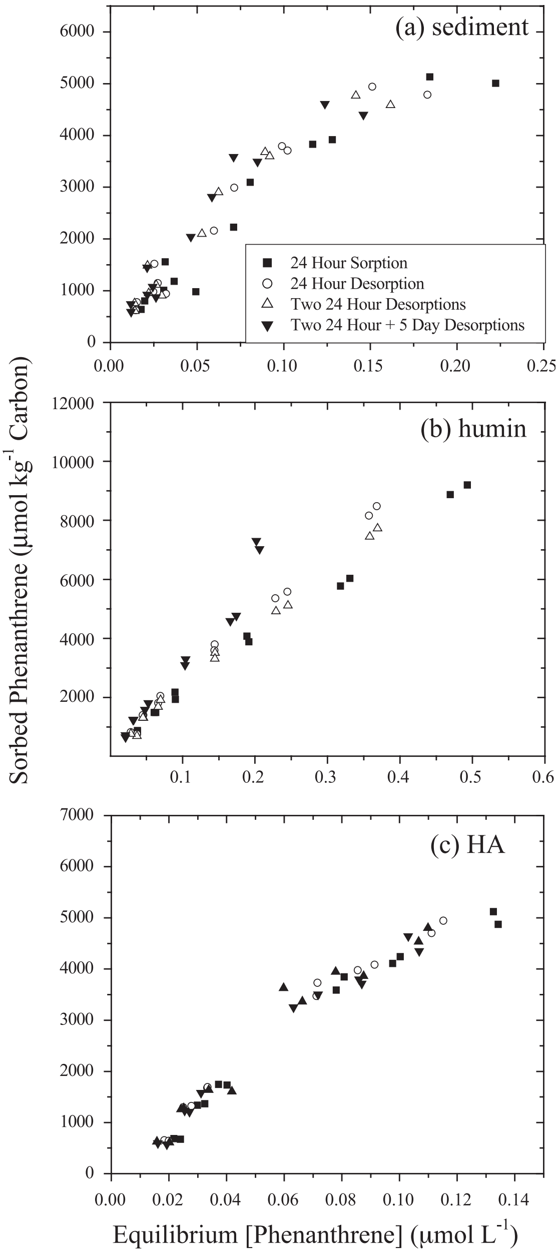


Fig. 2. Phenanthrene sorption and desorption from (a) sediment, (b) humin and (c) HA (0.4 mol l^{-1} background electrolyte solution at pH 7.6). Following each measurement, supernatant solution was removed and replaced with phenanthrene-free electrolyte solution for equilibration.

Table 3
Freundlich parameters and hysteresis index for sorption/desorption experiments

	Sorption ± 95% confidence intervals			Desorption ± 95% confidence intervals			Hysteresis index (at $C = x$ µg l^{-1})		
	Log K	n	r^2	Log K	n	r^2	1 µg l^{-1}	10 µg l^{-1}	100 µg l^{-1}
Sediment-P[a]	4.32 ± 0.22	0.85 ± 0.17	0.922	4.37 ± 0.19	0.83 ± 0.13	0.949	0.305 (0.218–0.398)	0.253 (0.066–0.472)	0.203 (−0.066–0.549)
Humin-P	4.24 ± 0.05	0.90 ± 0.05	0.995	4.33 ± 0.09	0.92 ± 0.09	0.983	0.237 (0.128–0.357)	0.293 (0.075–0.554)	0.351 (0.024–0.780)
Humic acid-P	4.71 ± 0.21	1.08 ± 0.16	0.957	4.73 ± 0.20	1.06 ± 0.15	0.962	0.136 (0.110–0.163)	0.092 (0.043–0.143)	0.049 (−0.0021–0.124)
Sediment-HNA	3.66 ± 0.05	1.38 ± 0.07[b]	0.970	4.14 ± 0.49	2.90 ± 1.15[b]	0.659	2.16 (0.147–7.70)	92.4 (2.34–3.63E+3)	2.76E+3 (8.56–1.51E+3)
Humin-HNA	3.44 ± 0.06	1.08 ± 0.25[b]	0.843	4.22 ± 0.92	4.34 ± 2.02[b]	0.584	0.672 (−0.769–11.1)	6.57 (0.012–574)	33.3 (3.44–2.73E+3)

( ) range of values within 95% confidence intervals.

[a] P = phenanthrene.

[b] Indicates significant difference between sorption/desorption isotherm parameters.

standard deviation) was used here for a more conservative test of the data. The HI results imply only slight hysteresis of phenanthrene sorption–desorption on all sorbents, since the values are consistently near zero.

Much higher hysteresis was observed for HNA; a significant fraction desorbed in the initial wash step (~ 5% at lowest initial concentration and ~ 70% at highest initial concentration), but subsequent desorption steps do not release additional HNA to solution (Fig. 3). The remaining sorbed fraction appears to be strongly retained and is, therefore, likely bound via a different mechanism. Given the evident key role of inorganic surfaces in HNA sorption, ligand exchange reactions, whereby dissociated HNA carboxyl and/or

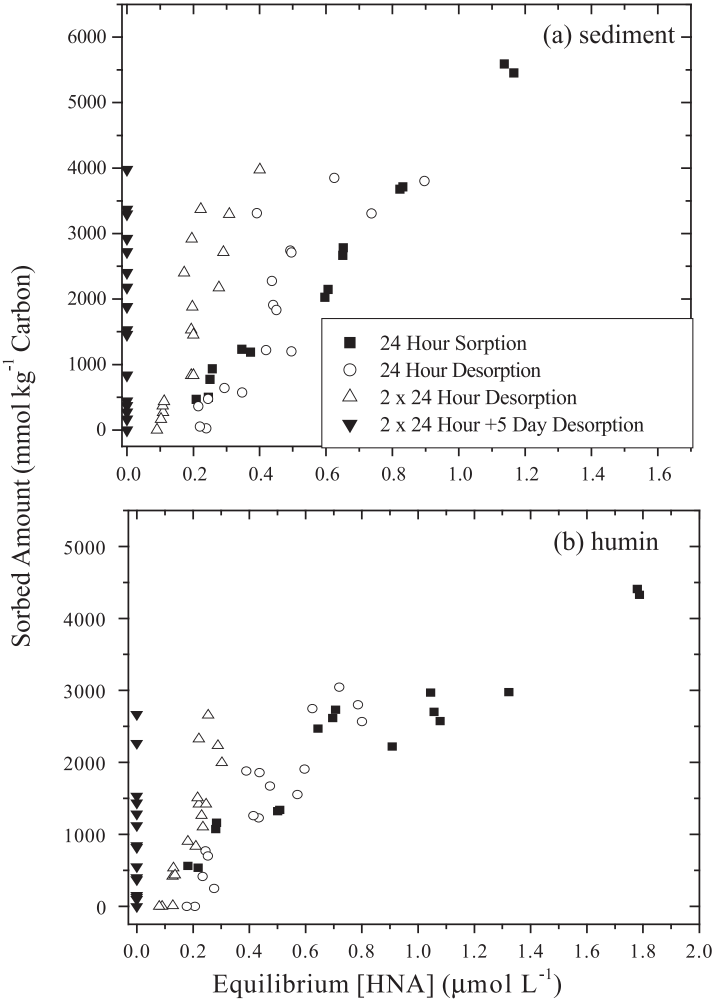


Fig. 3. HNA sorption and desorption on (a) sediment and (b) humin (0.4 mol l^{-1} background electrolyte solution at pH 7.6). Following each measurement, supernatant solution was removed and replaced with HNA-free salt solution for equilibration.

hydroxyl groups form direct bonds to Lewis acid sites (metal centers) on hydroxide surfaces, may be responsible for retaining HNA against desorption. Since 1-naphthylacetic acid was not strongly bound to the humin or sediment (Parikh, 2001), such a reaction for HNA may involve bidentate inner-sphere complexation of surface metal centers by the adjacent dissociated carboxyl and phenolate groups (Evanko and Dzombak, 1998). Sequential extractions indicate a significant fraction of crystalline Fe oxides in the Carter's Creek sediment. The Fe oxides contain surface hydroxyl groups that could serve as sites for high affinity ligand exchange (Sposito, 1984).

Another plausible explanation is that abiotic transformation of HNA has diminished desorption. Fe(III) and Mn(IV) (hydr)oxide surfaces can oxidize organic compounds (Stumm and Sulzberger, 1992), such as HNA to create partial oxidation products (POPs). The POPs, which comprise reactive intermediates such as semiquinones and free radicals, may then polymerize (Shindo and Huang, 1984; Stone and Morgan, 1984; Bollag and Myers, 1992; Whelan et al., 1995) and bind strongly to OM fractions or mineral surfaces (McBride, 1987; Majcher et al., 2000). This series of reactions can result in covalently bound HNA residues and diminished desorption.

A significant difference between HNA sorption and desorption isotherms is evident from inference on either Freundlich isotherm parameters (log K, n) or the HI (Table 3). The Freundlich n values for desorption are significantly higher than for sorption ($\alpha = 0.05$) Furthermore, HI values are much larger than zero. As noted above, simple sorption–desorption hysteresis may not be solely responsible for these results. Rather, we postulate that HNA may also be oxidized by redox active surfaces of the sediment and humin. This transformation would result in a diminished concentration of HNA as detected by HPLC, concave up slopes ($n > 1$) and "apparent" hysteresis.

3.6. Kinetic investigations

Phenanthrene sorption equilibrium was reached in less than 24 h (Fig. 4a). Phenanthrene sorption to sediment, humin and HA was very rapid and approximately 98.1%, 93.9% and 98.3% of the sorption maxima were reached within 15 min, respectively. HNA sorption equilibrium required much longer time scales (Fig. 4b), and kinetics of HNA sorption to humin was slower than for sediment. Only a fraction of the final sorbed value of HNA was attained at 15 min, equilibrium was nearly reached by 48 h, and apparent true sorption equilibrium was achieved at 10 days.

These kinetic data suggest that a fraction of HNA is bound rapidly (15 min) and then a slower sorbing fraction accumulates gradually over 10 days.

Cation and water bridging reactions are rapid due to the prevalence of sites on external clay surfaces. Ligand exchange reactions tend to be characterized by a slower approach to equilibrium (Stumm, 1992) and oxidative transformation reactions are expected to require even longer reaction times since they involve both complexation and electron transfer. The latter can lead to the formation of polymerized products that are recalcitrant to extraction. Karthikeyan and Chorover (2000) reported that abiotic oxidative transformation of 1-naphthol is a slow reaction (hours to days) and that POP concentration increases with time. Therefore, the longer time to reach apparent equilibrium for HNA is consistent with oxidative transformation.

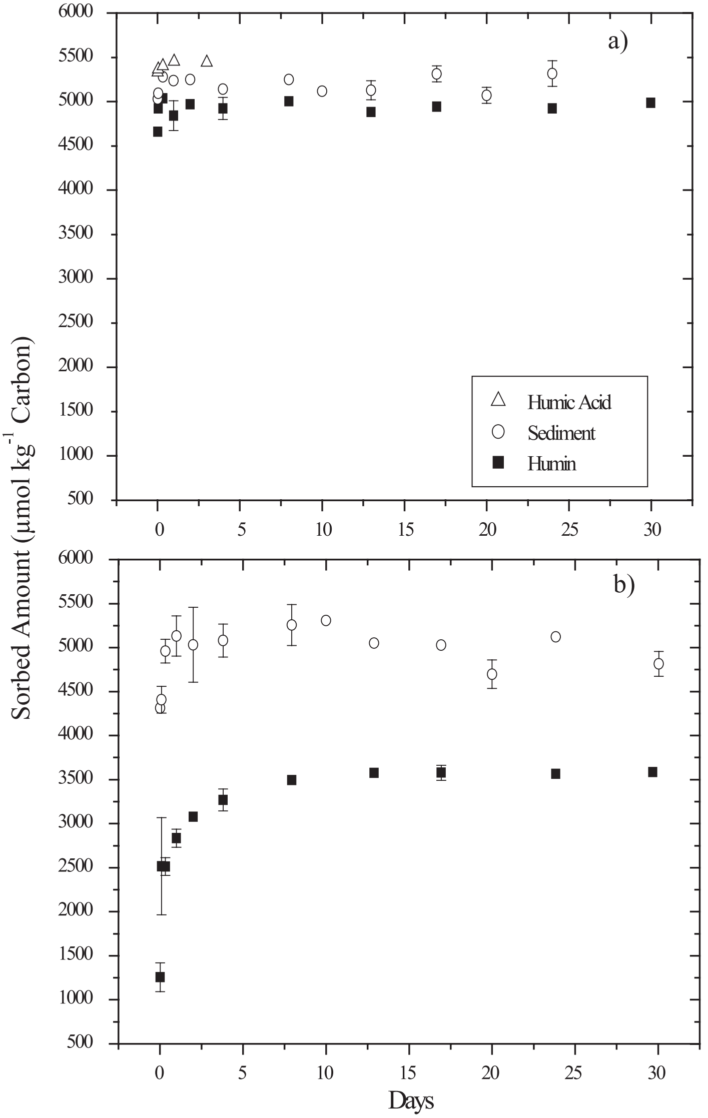


Fig. 4. Sorption kinetics for (a) phenanthrene on sediment, HA and humin; and (b) HNA on HA and humin (0.4 mol l^{-1} background electrolyte solution at pH 7.6). Duplicate means are shown and error bars indicate 95% confidence intervals. Confidence limits are not shown if they are smaller than the symbol size.

3.7. Chemical reaction of HNA with goethite (α-FeOOH) and birnessite (δ-MnO$_2$)

To test the hypothesis that HNA may be oxidized abiotically in the presence of Fe or Mn oxides, a separate set of experiments was conducted in aqueous suspensions with the same background electrolyte solution, but with synthetic goethite or birnessite sorbents in place of sediment or humic substances. In the absence of solids, the chromatogram of HNA is unchanged over a 24-h period and exhibits a peak at 2.48 min, with some tailing at longer elution times because of the high ionic strength of the background solution (Figs. 5a and 6a). Chromatograms of supernatant solutions (Figs. 5a and 6a) and aqueous extracts of the solid phase (Figs. 5b and 6b) after reaction of 100 μM HNA with goethite and birnessite show new peaks, suggesting that HNA does indeed undergo significant oxidative transformation under abiotic conditions. HPLC chromatograms revealed the presence of new peaks in supernatant solutions (3.26 min) and aqueous extracts (1.71 and 3.11 min) of the goethite solid (Fig. 5). The HNA chromatogram for supernatant solution after reaction with goethite is nearly identical to that of unreacted HNA (in the same background electrolyte), but with a slight growth in the shoulder at 3.26 min with increasing reaction time. The transformation effect is more evident following reaction with birnessite; new peaks are observed at several times including 2.20, 2.79 and 3.00 min for supernatant solutions and 1.76, 2.41, 2.95, 4.55, 6.74 and 7.92 min for aqueous extracts (Fig. 6). These new peaks clearly derive from HNA transformation, and not from impurities in the synthetic solids, since chromatograms of Milli-Q water extracts of

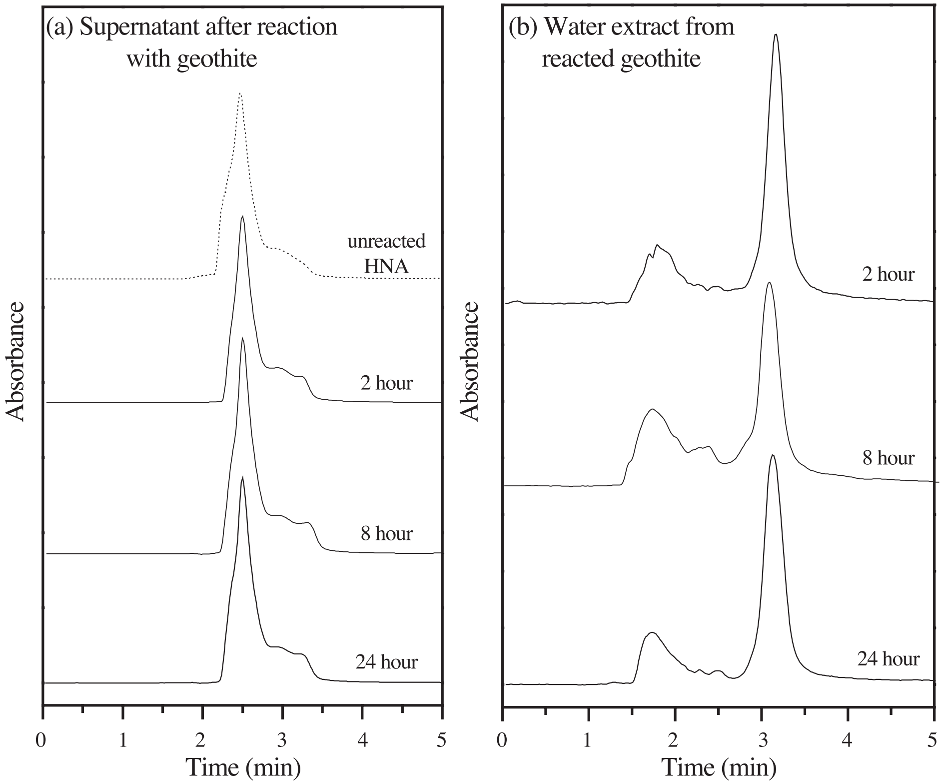


Fig. 5. HPLC chromatogram of (a) solution from 24 h reaction of 100 μmol l^{-1} HNA with goethite and (b) Milli-Q water extract of solid phase after 24 h reaction of 100 μmol l^{-1} HNA with goethite.

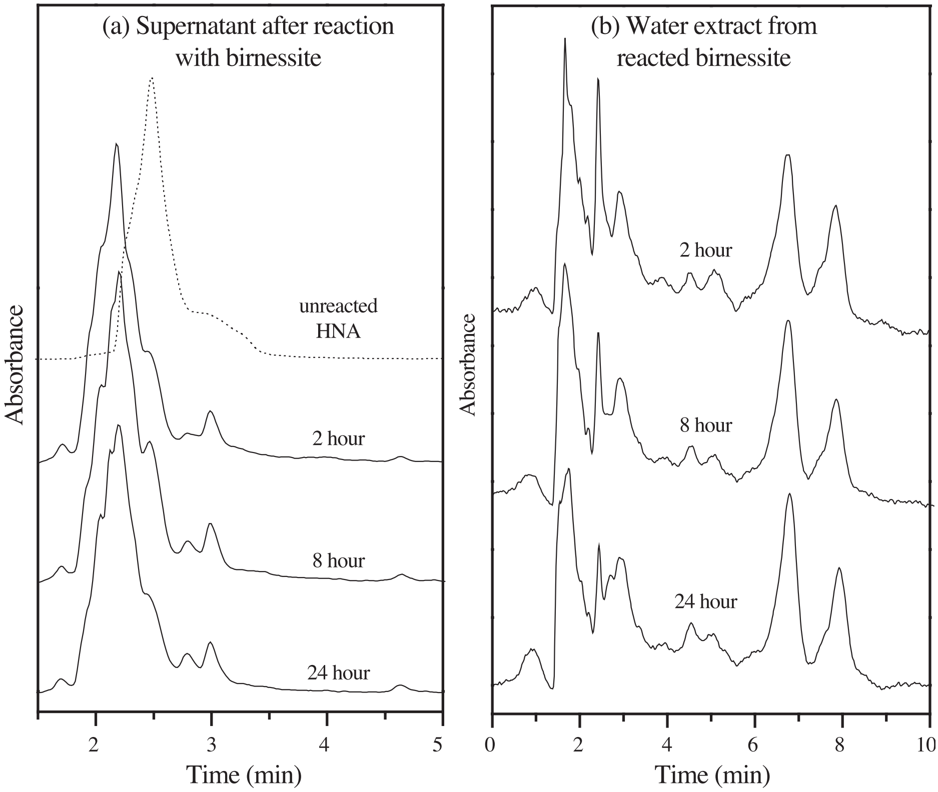


Fig. 6. HPLC chromatogram of (a) solution from 24 h reaction of 100 μmol l^{-1} HNA with birnessite and (b) Milli-Q water extract of solid phase after 24 h reaction of 100 μmol l^{-1} HNA with birnessite.

unreacted solids (goethite and birnessite) show no peaks beyond those of Milli-Q water itself (data not shown).

PDA detection of HPLC eluate permits evaluation of full UV–Vis spectra for each of the separate peaks depicted in Figs. 5 and 6. These spectra are shown for the 24-h reaction time with no solid added (Fig. 7) and following reaction with the two specimen minerals (Fig. 8). The UV spectrum of HNA reacted with background electrolyte alone (no solid phase) for 24 h (Fig. 7) is identical to that for HNA calibration standards prepared at the time of the HPLC analyses (not shown). Spectra for supernatant solutions of mineral suspensions show the presence of HNA and reaction products (POPs) following the goethite reaction (Fig. 8a), whereas only product peaks (no HNA peak) were detected in solution following reaction with birnessite (Fig. 8c). Spectra consistent with HNA and a reaction product are observed following extraction of the solid phase (Fig. 8b). UV spectra of the six major elution peaks arising in the extracted birnessite chromatogram (Fig. 6b) are shown in Fig. 8d. Many of the eluted fractions deriving from the birnessite reaction show featureless UV spectra consisting of decreasing absorbance with increasing wavelength, indicating significant transformation of the parent compound.

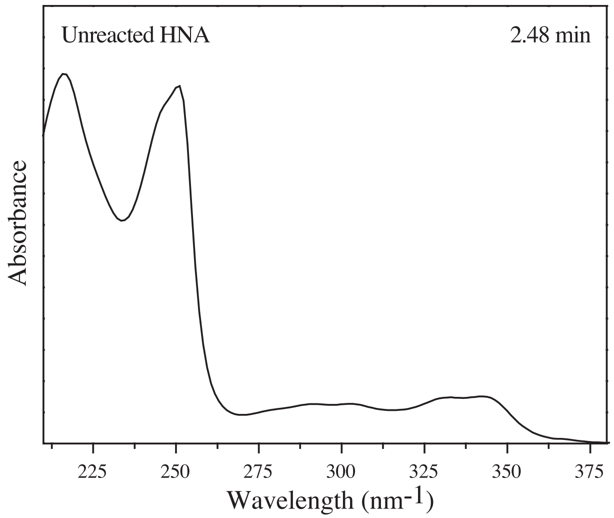


Fig. 7. UV spectrum of 24 h control of 100 μmol l^{-1} HNA (no solid phase present), corresponds to unreacted HNA chromatogram peak at 2.48 min and is identical to freshly prepared calibration standards.

The HPLC–PDA data indicate that after reaction with goethite, HNA is the most prevalent compound in solution (Figs. 5a and 8a). However, upon washing the goethite pellet with Milli-Q water, HNA and POPs are solubilized (Figs. 5b and 8b). This suggests that HNA is oxidized at the surface of goethite and the resulting POPs are sorbed preferentially to the solid. More extensive transformation was observed following reaction of HNA with birnessite. An array of several transformation products was observed both in solution and after washing the birnessite pellet with Milli-Q water (Figs. 6 and 8c,d), whereas the parent compound was not detected.

Mass spectra were compromised by the presence of chloride containing salts, associated with the background electrolyte, that eluted throughout the chromatograms and give salt cluster peaks at numerous masses. Therefore the resulting data did not reveal the identity of degradation products. Nonetheless, the HPLC–MS did clearly indicate HNA in the goethite supernatant solution, but not in the birnessite system, which is consistent with the HPLC–PDA data (Figs. 5–8), and gives further credence to the abiotic transformation of HNA. Furthermore, significant decreases in pH were observed during reaction of HNA with birnessite (from pH 7.6 to 6.0 in 7 days) and goethite (from pH 7.6 to 7.0 in 7 days). Proton production may be due to autocatalytic oxidation of Mn(II) and Fe(II) under oxic conditions as well as the formation of carboxylic acids. McBride (1989) showed a similar pH decrease during reaction of 1,4-dihydroxybenzene with birnessite in aerated 0.2 M NaCl suspensions.

Transformation mediated by Fe and/or Mn oxides could, therefore, be responsible for the strong binding of HNA observed in the sediment and humin systems. Surface-mediated oxidation of phenolic compounds produces reactive intermediates, such as semiquinone radicals that may bind covalently to other intermediates, to organic matter or to mineral surfaces (Stone and Morgan, 1984; Bollag and Myers, 1992; Nadja et al., 1998; Majcher et al., 2000). Thus, although there was no detectable sorption of HNA to

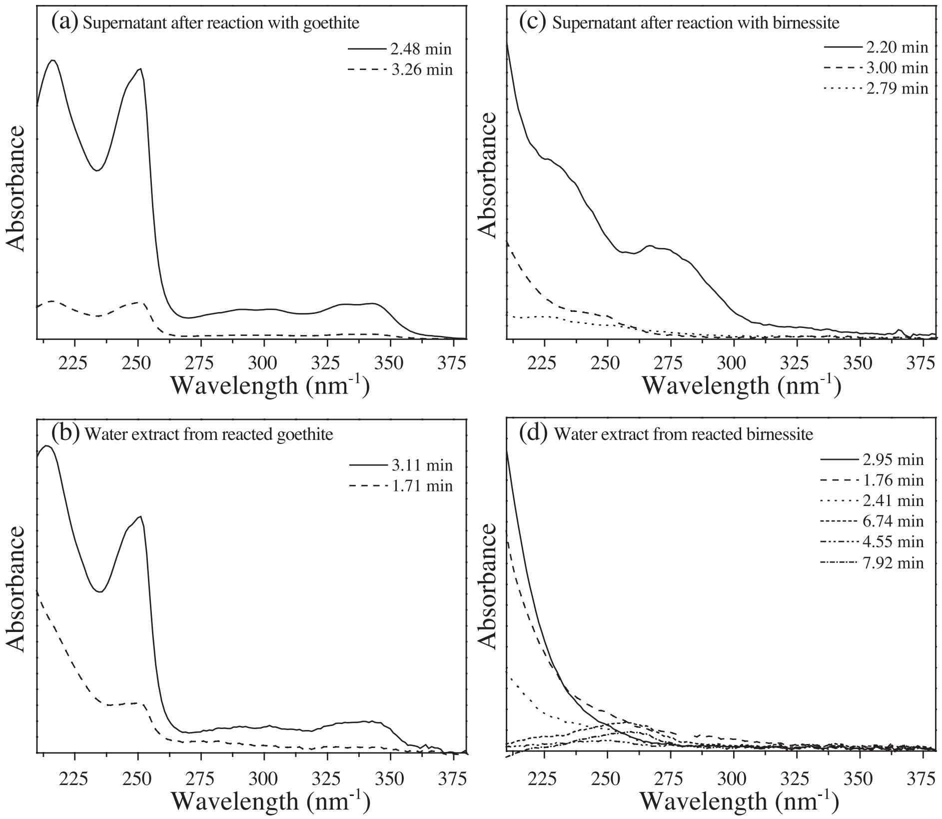


Fig. 8. UV spectra of (a) supernatant solution from 24 h reaction of 100 μmol l^{-1} HNA with goethite, (b) water extract 24 h reaction of 100 μmol l^{-1} HNA with goethite, (c) supernatant solution from 24 h reaction of 100 μmol l^{-1} HNA with birnessite and (d) water extract 24 h reaction of 100 μmol l^{-1} HNA with birnessite. Corresponding elution times are indicated in the legend.

HA, the presence of mineral oxidants such as birnessite or goethite (or HNA degrading microorganisms) could catalyze the binding of HNA POPs to HA. Majcher et al. (2000) observed oxidative transformation of catechol (1, 2-dihydroxybenzene) to a recalcitrant “humin-like” polymer in the presence of birnessite. The reaction pathway is comparable for Fe (hydr)oxides, but Fe(III) solids are weaker oxidizing agents. Microbially catalyzed oxidation could have the same or greater effect (i.e., binding of reactive intermediates) in biologically active sediments.

4. Conclusions

Affinity of phenanthrene for estuarine sediment fractions (normalized to their organic C content) followed the order HA > sediment > humin, whereas affinity of the primary phenanthrene metabolite, HNA, for the same sorbents was sediment > humin HA. HNA sorption was less reversible (larger non-desorbing fraction) than phenanthrene sorption. Despite elevated ionic strength, water and cation bridging reactions did not contribute significantly to sorption of HNA to estuarine OM. Weakly bound HNA sorbed to mineral surfaces via electrostatic interactions, or cation or water bridging, whereas a non-desorbing fraction likely binds via ligand exchange or oxidative coupling reactions. Fe and Mn oxides were shown to promote the oxidative transformation of HNA to surface active products, indicating the potential for redox-mediated uptake.

Acknowledgements

We acknowledge the assistance of Morris Roberts and George Vadas of the Virginia Institute of Marine Sciences in collecting the estuarine sediments. Thanks also to Dan Jones, Director of the Penn State Intercollegiate Center for Mass Spectrometry, and Arpad Somogyi (Supervisor) and Mark E. Malcomson of the University of Arizona Mass Spectrometry Facility for their assistance in conducting the MS analyses, and to Je-Hun Jang for Mössbauer data collection and analysis. This research was supported by the U.S. Department of Energy, Office of Biological and Environmental Research, Joint Bioremediation Program, Grant DE-FG02-97ER62356 and the National Science Foundation, Grant BES 9010112.

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