



Sorption of naphthoic acids and quinoline compounds to estuarine sediment

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Abstract

The sorption of 16 ionizable organic compounds (IOCs) to an estuarine sediment was measured in synthetic estuarine water as a function of IOC concentration (1–100 μM) at fixed ionic strength (0.4 M), pH (7.6), and sediment concentration (0.018 g sediment kg^{-1} suspension). Of the 16 IOCs, 11 were naphthoic acids and five were quinoline compounds. The linear sorption distribution coefficient (K_d) was used to correlate sorption to IOC physicochemical and molecular characteristics. With respect to naphthoic acid, sorption increased with the addition of *ortho*-substituent groups and with increasing chain length of the 1-acid group, and the greatest increase occurred with *ortho*-hydroxyl, carbonyl, and carboxyl groups. With respect to quinoline, sorption decreased with substituent group addition (except for nitro group) and with additional heterocyclic N atoms. For the naphthoic acids, $\log K_d$ exhibited a positive correlation with water solubility ($\log S_w$) indicative of sorption primarily to mineral surfaces under the solution chemistry. For the quinoline compounds, $\log K_d$ exhibited a negative correlation with $\log S_w$ and a positive correlation with *n*-octanol/water partition coefficient ($\log K_{OW}$) indicative of sorption primarily to organic matter. For both compounds, poor or no correlations were established between $\log K_d$ and acid dissociation constant ($\text{p}K_{a1}$), and between $\log K_d$ and a variety of molecular connectivity indexes. The results from this study demonstrate that the sorption of IOCs differ depending on their backbone structure and may differ between parent compound and ionizable degradation product.

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1. Introduction

Estuaries are vital habitats for thousands of aquatic organisms living in either the water column or the sediment. More than 76% of all commercially and recreationally important fish and shellfish species are estuarine-dependent (Lewis, 2000). When toxic pollutants (e.g., heavy metals, synthetic organic chemicals) enter estuaries they tend to associate with particles suspended in the water column and subsequently settle into the sediment. Sediment contamination can harm organisms both in the sediment and in the overlying water column. Benthic organisms can be exposed to sediment contaminants by direct dermal contact, ingestion of sediment particles, and/or uptake of dissolved contaminants present in interstitial water. Pelagic organisms can be exposed to sediment contaminants released to the overlying water. Contaminant uptake by lower-level trophic species can directly harm those organisms while contaminant biomagnification can subsequently harm higher-trophic level species in aquatic food chains.

Comprehensive nationwide surveys of sediments provided convergent assessments that approximately 10% (12 billion cubic yards) of sediments are contaminated with priority pollutants (EPA, 1997) and 11% of sediments are toxic based on sediment amphipod survival tests (Long et al., 1996). The most common contaminants found in estuarine sediments include polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), heavy metals, pesticides, and mercury (EPA, 1997). The primary anthropogenic sources of PAHs in the environment result from incomplete combustion of fossil fuels and vehicle emissions. PAHs typically enter estuaries through the atmospheric fallout of particulate matter (e.g., soot), polluted surface water runoff (Hoffman et al., 1984), and point-source discharges from industrial and municipal wastewater treatment facilities (Guerin and Jones, 1989). PAHs exert both acute toxic and sub-lethal effects on some aquatic organisms and, due to their lipophilic nature, have high potential for biomagnification.

Most PAHs detected in the environment are homocyclic aromatic structures, neutrally charged and hydrophobic. However, PAHs that contain basic or acidic functional groups, referred to as ionizable organic compounds (IOCs), are also environmentally relevant contaminants. Basic IOCs include aromatic amines and *N*-substituted heterocyclic aromatic compounds (NHCs). Aromatic amines are synthetic components of textile dyes and agrochemicals, and NHCs are generated from energy development technologies (e.g., coal gasification, shale oil extraction) (Weber et al., 2001). Acidic IOCs include azo dyes and anthraquinone acid dyes (sulfonic acids). Acidic IOCs such as naphthoic acids are common intermediates in the biodegradation of high molecular weight PAHs such as anthracene (Menn et al., 1993), phenanthrene (Guerin and Jones, 1988) and pyrene (Gibson and Subramanian, 1984). In addition, the accumulation of naphthoic acids has been reported in both liquid media with pure bacterial cultures (Guerin and Jones, 1988) and in contaminated sediments with native microbial communities (Mahaffey et al., 1988; MacGillivray and Shiaris, 1994; Stringfellow and Aitken, 1994).

Sorption plays a dominant role in the fate, transport, bioavailability and toxicity of organic contaminants in natural systems. Sorption of nonionic, hydrophobic organic compounds (HOCs) is envisioned to occur primarily with sediment organic matter via hydrophobic partitioning based on numerous studies that have shown that HOC sorption is strongly correlated to the organic carbon content of the sediment (i.e., f_{OC}) and the hydrophobicity of the HOC (e.g., K_{OW}) (Means et al., 1980; Karickhoff, 1981; Dzombak and Luthy, 1984; Hong et al., 1996; Luthy et al., 1997). HOCs do not tend to associate with sediment minerals (e.g., clays and metal oxides) because of the polar, charged nature of these minerals. Sorption of charged IOCs to sediment components is

comparatively more complex due to potentially multiple operative sorption mechanisms. For example, IOC sorption may involve electrostatic interactions or ligand exchange reactions with charged surface minerals (Zachara et al., 1986; Evanko and Dzombak, 1998; Schwarzenbach et al., 2003), or hydrophobic interactions with organic matter. Solution pH and ionic strength directly affect mineral surface charge and sorbate ionization and, therefore, strongly influence IOC sorption to sediments.

Because of this complexity, few predictive relationships between IOC sorption and adsorbate properties have been established. In comparison, quantitative structure–activity relationships (QSARs) have been established for the sorption of HOCs based on *n*-octanol/water partition coefficients (K_{OW}) and water solubilities (S_w) (Means et al., 1980; Briggs, 1981; Karickhoff, 1981; Chiou et al., 1983; Baker et al., 2001), and molecular connectivity indexes (Grover et al., 1984; Sabljic, 1984, 1987; Meylan and Howard, 1992). The goal of a QSAR is to predict the activity of a chemical that has not been experimentally measured from a well-established reliable model. The premise of this study was that biological or chemical degradation of “parent” PAHs and NHCs produces more polar metabolites that may be more or equally toxic than the parent compounds. In general, PAH (Gibson and Subramanian, 1984; Guerin and Jones, 1988; Menn et al., 1993) and NHC (Shukla, 1986; Kaiser et al., 1996) degradation will progress through carboxylated and hydroxylated aromatic intermediates. Therefore, test compounds for this study were selected to resemble these degradation intermediates. In addition, test compounds were selected so that the effects of different structural features (specifically, number and type of substituent groups, *ortho*- vs. non-*ortho*-substituent groups, and PAH vs. NHC backbone) on IOC sorption to estuarine sediments could be evaluated. The objectives of this study were to: (1) measure the sorption of a series of IOCs in estuarine sediment under conditions designed to mimic the sediment collection site (0.4 M, pH 7.6), (2) elucidate the influence of the IOC chemical structure on sorption behavior, and (3) develop IOC sorption QSARs to predict sorption from readily obtainable chemical and molecular descriptors.

2. Experimental

All solutions were prepared using distilled water that was passed through a MilliQ UV-plus water purification system (Millipore, Inc., Bedford, MA). All glassware and Teflon containers were copiously rinsed with MilliQ water, rinsed in a 50% MilliQ water–50% methanol solution, and rinsed again with MilliQ water prior to use.

2.1. Estuarine sediment

Sediment was collected from Carter’s Creek, Virginia (37°19′ 42″ latitude, –76°34′ 13″ longitude), a tributary to the York River and part of the Chesapeake Bay watershed. Samples were collected using a grab sampler (0–15 cm) while the boat was adrift. The sediment collection site was uncontaminated and routinely used for collecting sediment amphipods. The sediment was 7.9% sand (0.05–2 mm), 54.1% silt (0.002–0.05 mm), and 37.6% clay (<0.002 mm) (mass %) as determined by the pipette method (Gee and Bauder, 1986). Total organic carbon (TOC) content of the sediment was 2.06 mass %. Sediment samples were extracted in 0.1 M NaOH to solubilize the organic matter and the TOC content of the acidified extract was measured using the solid phase module of a Shimadzu TOC-5000A carbon analyzer. Ash content of the sediment was 81.0 mass %, and was determined by combustion at 450 °C for 6 h. Total extractable Fe in the sediment was 17 g kg⁻¹ and total

extractable Mn was 0.15 g kg^{-1} . The mineralogy of the sediment clay fraction was characterized by X-ray diffraction (XRD) patterns and Mössbauer spectroscopy (Parikh et al., 2004). XRD patterns revealed the presence of kaolinite, smectite and mica (in likely order of mass prevalence). Mössbauer spectra revealed non-crystalline ferrihydrite and/or fine-grained goethite and an unspecified ferrous mineral. After transport to Penn State, sediment was stored at $-4 \text{ }^\circ\text{C}$. Frozen sediments were thawed at room temperature and centrifuged at 7000 g and $20 \text{ }^\circ\text{C}$ for 10 min to remove excess water. The supernatant was added back until a uniform paste was formed, and the sediment paste was adjusted to pH 7.6 with 0.4 M NaOH . Sediment paste was sterilized by autoclaving twice for 1 h ($121 \text{ }^\circ\text{C}$, 14 psig) with a 1 day interval between heat treatments (Wolf et al., 1989). Sediment sterility was tested by spreading a small portion of the twice autoclaved sediment on Luria-Bertani agar and no growth occurred after a 48 h incubation at $30 \text{ }^\circ\text{C}$ (Sambrook et al., 1989). Sediment sterilization by successive autoclaving was selected because it has been demonstrated to effectively kill soil microbes and not greatly affect soil physical and chemical properties (Wolf et al., 1989).

2.2. Synthetic Estuarine Water (SEW)

Synthetic Estuarine Water (SEW) was designed to mimic the major ions measured in the natural pore water of Carter's Creek sediment (Parikh, 2001). In addition, certain components and preparation procedures were modified from an artificial seawater recipe (Dyksterhouse et al., 1995). The solution had an ionic strength equivalent to 0.4 M NaCl and pH 7.6. To avoid precipitation of salts during autoclaving, the SEW was prepared separately as three stock solutions. The final SEW constituent concentrations were (μM): $43,800 \text{ NaCl}$; $6780 \text{ MgCl}_2 \cdot 6\text{H}_2\text{O}$; $3150 \text{ Na}_2\text{SO}_4$; 1480 CaCl_2 ; 1090 KCl ; $568 \text{ NH}_4\text{Cl}$; 91 NaBr ; $49 \text{ H}_3\text{BO}_3$; $37 \text{ Na}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$; 41 NaHCO_3 ; $10 \text{ Sr}_2\text{Cl} \cdot 6\text{H}_2\text{O}$; 7.0 NaF ; $2.8 \text{ 3-[N-tris(hydroxymethyl)methylamino]-2-hydroxypropanesulfonic acid (TAPSO)}$; and $0.95 \text{ FeCl}_2 \cdot 4\text{H}_2\text{O}$.

2.3. Ionizable organic compounds

The 16 test compounds (Fig. 1) used in these experiments included: 1-hydroxy-2-naphthoic acid (1H2NA); 1,8-naphthaldehydic acid (1,8NDA); 3-hydroxy-7-methoxy-2-naphthoic acid (3H7M2NA); 2,3-naphthalenedicarboxylic acid (2,3NDCA); 1-methoxy-2-naphthoic acid (1M2NA); 6-amino-2-naphthoic acid (6A2NA); 6-methoxy-2-naphthoic acid (6M2NA); 4-fluoro-2-naphthoic acid (4F2NA); 1-naphthoic acid (1NA); 1-naphthaleneacetic acid (1NAA); 1-naphthoxyacetic acid (1NOA); quinoline (Q); 5-nitroquinoline (5NQ); quinoxaline (QX); 2-quinoxalinecarboxylic acid (2QXCA); and 3-hydroxy-2-quinoxalinecarboxylic acid (3H2QXCA). The following compounds were purchased from Sigma-Aldrich, Inc. (St. Louis, MO): 1H2NA; 1,8NDA; 3H7M2NA; 2,3NDCA; 1M2NA; 6A2NA; 6M2NA; 5NQ; QX; 2QXCA; and 3H2QXCA. The following compounds were purchased from Avocado Research Chemical, Inc. (Ward Hill, MA): 4F2NA and 1NAA. The following compounds were purchased from Alfa Aesar Co. (Ward Hill, MA): 1NOA and Q. The following compound was purchased from Acros Organics (Morris Plains, NJ): 1NA. All test compounds were greater than 95% purity and used without further purification. IOC stock solutions were gravimetrically prepared to desired concentrations in SEW and filtered ($0.45 \mu\text{m}$) into amber glass bottles.

Physical, chemical, and molecular properties of the test compounds are summarized in Table 1. When test compound properties were not published, molecular fragment methods were used for their estimation. A complete description of the estimation methods are presented

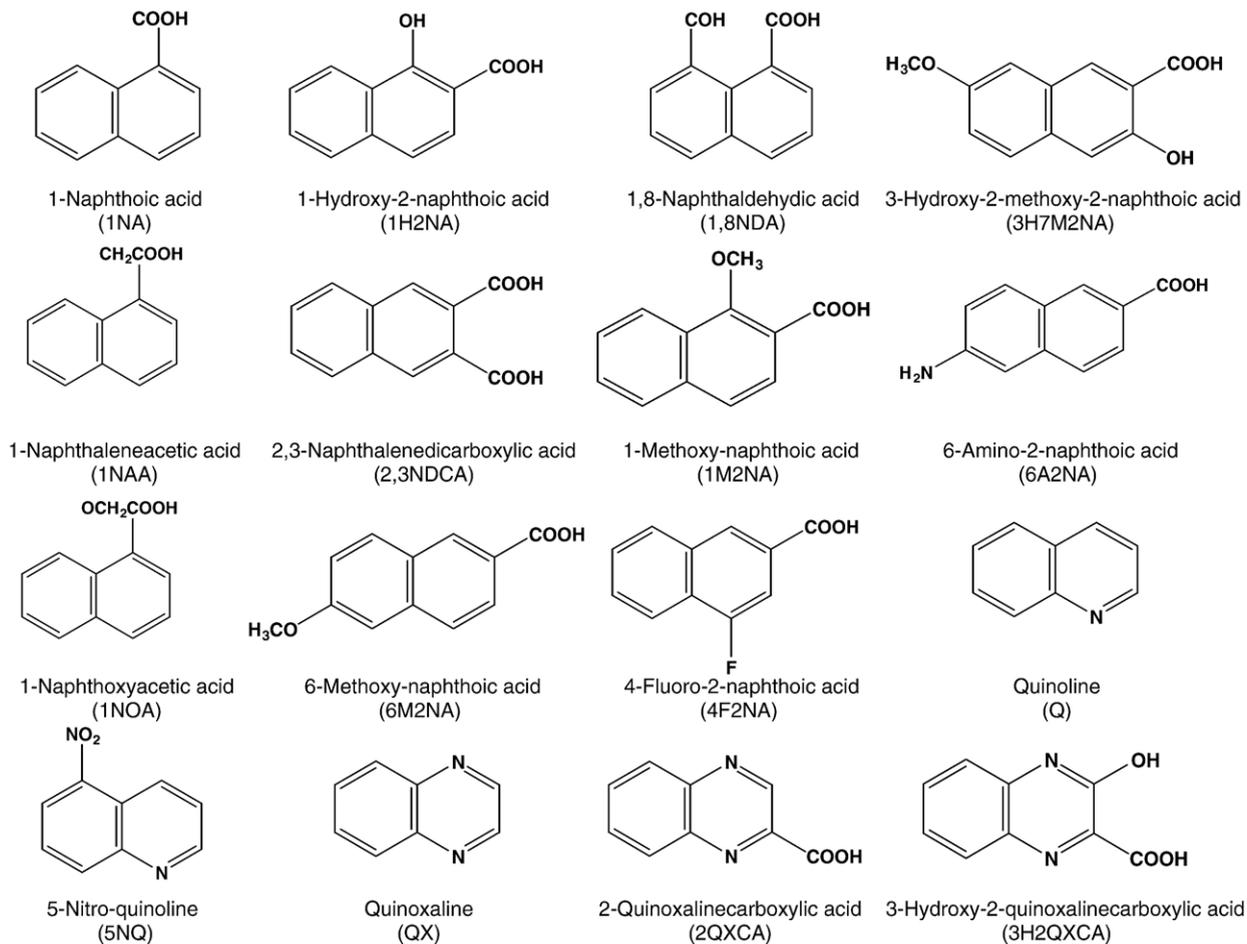


Fig. 1. Chemical structures of the series of ionizable organic compounds (IOCs) tested to develop quantitative structure activity relationships (QSARs) for IOC sorption. Test compounds included 11 naphthoic acids and 5 quinoline compounds.

Table 1

Physical and chemical properties of the ionizable organic compounds (IOCs) tested

Compound	MW	log K_{OW}^a	log S_w^b	pK_{a1}^c	${}^1X^d$	${}^4X_{vpc}^d$
1-hydroxy-2-naphthoic acid (1H2NA)	188.2	3.42	0.769	2.94	6.70	0.721
1,8-naphthaldehydic acid (1,8NDA)	200.2	2.77	0.248	3.34	7.24	0.781
3-hydroxy-7-methoxy-2-naphthoic acid (3H7M2NA)	202.2	3.97	0.228	2.97	7.61	0.830
2,3-naphthalenedicarboxylic acid (2,3NDCA)	216.2	2.25	-0.028	3.21	7.59	0.821
1-methoxy-2-naphthoic acid (1M2NA)	202.2	2.79	-0.293	4.04	7.24	0.756
6-amino-2-naphthoic acid (6A2NA)	190.2	3.25	0.296	3.82	6.68	0.689
6-methoxy-2-naphthoic acid (6M2NA)	202.2	3.13	-0.293	4.15	7.20	0.727
4-fluoro-2-naphthoic acid (4F2NA)	187.2	2.13	-0.498	3.93	6.66	0.667
1-naphthoic acid (1NA)	172.2	3.05 (3.10)	-0.197	3.70 (3.59)	6.29	0.619
1-naphthaleneacetic acid (1NAA)	186.2	2.66 (2.24)	-0.717	NE ^c	6.77	0.656
1-naphthoxyacetic acid (1NOA)	202.2	2.50 (2.60)	0.248	NE ^c	7.27	0.548
Quinoline (Q)	129.1	2.14 (2.03)	-0.349	4.92	4.97	0.331
5-nitroquinoline (5NQ)	174.2	1.96 (1.86)	-0.765	NE ^c	6.29	0.519
Quinoxaline (QX)	130.1	1.12 (1.32)	-0.332	2.08	4.97	0.281
2-quinoxalinecarboxylic acid (2QXCA)	174.2	1.00	-0.164	2.80	6.27	0.439
3-hydroxy-2-quinoxaline carboxylic acid (3H2QXCA)	190.2	-0.08	0.802	2.58	6.68	0.513

^a n -octanol/water coefficient ($\{\text{mol L}^{-1} \text{ octanol}\} \{\text{mol L}^{-1} \text{ water}\}^{-1}$) for neutral species (K_{OW}^{neutral}) estimated using K_{OW} WIN software (Syracuse Research Corporation, 2005). Experimental values shown in parentheses (Lide, 2003).

^b Water solubility (mM) for neutral species (S_w^{neutral}), estimated using ChemSW software (ChemSW, 2005).

^c First acid dissociation constant, estimated using fragment data provided by Perrin et al. (1981). Experimental value shown in parentheses (Serjeant and Dempsey, 1979).

^d First-order simple path molecular connectivity index (1X) and fourth-order valence path cluster index (${}^4X_{vpc}$) estimated using ADAPT software (ADAPT, 2005).

^e Not estimated due to insufficient correlation information.

elsewhere (Pisutpaisal, 2003). Briefly, log K_{OW}^{neutral} values were calculated using the log K_{OW} WIN software (Syracuse Research Corporation, 2005) and log S_w^{neutral} values were calculated using the ChemSW, Inc. (Fairfield, CA) software (ChemSW, 2005). K_{OW}^{neutral} and S_w^{neutral} values were calculated for neutral species with no exact value specified for the pH of property estimations. No adequate estimation method was available for test compound melting points and, therefore, aqueous activity coefficients of the subcooled liquids (γ_w^{sat}) could not be determined. Molecular connectivity indexes, including first-order simple path molecular connectivity (1X), first-order valence path molecular connectivity (1X_v), third-order valence path molecular connectivity (3X_p), fourth-order valence path molecular connectivity (4X_p), and fourth-order valence path cluster (${}^4X_{vpc}$), were calculated using the ADAPT software (ADAPT, 2005), and pK_{a1} values were calculated based on Hammett constants (Perrin et al., 1981). 1-Naphthoic acid and quinoline, respectively, were used as the backbone structures for property estimations of naphthoic acids and quinoline compounds. For pK_{a1} estimations, naphthoic acids were treated as corresponding benzoic acids with an annealed aromatic ring. Due to insufficient correlation information, pK_{a1} values could not be estimated for certain compounds.

2.4. Sorption isotherm experiments

Sorption of each IOC to the Carter Creek sediment was measured as a function of IOC concentration (5 to 8 duplicated values between 1 and 100 μM) in 50 mL PTFE centrifuge

tubes. Each tube contained 1.45 g sediment paste (equivalent to 0.72 g dry sediment), a measured mass of IOC stock solution, and a measured mass of SEW for a total suspension mass of 40.0 g. Tubes were sealed with threaded PTFE caps and suspensions were equilibrated at room temperature (20–23 °C) by end-over-end rotation at seven revolutions per min (rpm) for 24 h. Sorption kinetic experiments were conducted with all IOCs (at single IOC concentration of 80 µM) to determine the contact time required for equilibrium (samples collected after 4 to 360 h). For all IOCs, sorption extent reached a constant value in less than 24 h. Following 24 h equilibration, suspensions were centrifuged at 7000 g and 20 °C for 10 min. Supernatant solutions were aspirated into amber glass threaded high performance liquid chromatography (HPLC) autosampler vials (triplicate for each tube), and into glass vials where final pH was measured immediately using a combination glass electrode (single measurement for each tube). The final pH values for all IOC supernatants were within 7.6 ± 0.20 pH units. Following aspiration of supernatant, tubes were re-weighed, 25 mL of 0.1 M potassium phosphate buffer (pH 7.6) was added, tube contents were re-suspended, and the sediment pellets were extracted for 24 h on a reciprocal shaker (7 rpm). Following phosphate extraction, suspensions were centrifuged at 7000 g and 20 °C for 10 min, and aspirated extractant was collected for HPLC analysis. Sediment-free controls were prepared for all IOCs to account for any abiotic losses. IOC-free sediment controls were prepared and confirmed that no IOCs were initially present in the sediment.

The quantity of IOC sorbed (q_e , µmol IOC kg⁻¹ sediment) was calculated on the basis of loss from solution and accounted for any loss to the reaction vessel:

$$q_e = (m_0 - m_{eq}) * M_w \quad (1)$$

where m_0 and m_{eq} are, respectively, the molinities of the IOC (µmol IOC kg⁻¹ solution) in the supernatant solution of a sediment-free control and the experimental suspension following 24 h

Table 2

Summary of high performance liquid chromatography (HPLC) conditions for ionizable organic compounds (IOCs) tested

Test compound	Mobile phase ^a		Flowrate (mL min ⁻¹)	Retention time (min)	Extracted wavelength (nm)
	%A	%B			
1H2NA	80	20	0.70	2.8	250
1,8NDA	75	25	0.80	2.6	300
3H7M2NA	80	20	1.00	1.8	250
2,3NDCA	75	25	0.70	2.3	250
1M2NA	80	20	1.00	2.2	240
6A2NA	80	20	0.90	2.0	250
6M2NA	80	20	0.90	3.1	254
4F2NA	80	20	0.70	4.1	280
1NA	80	20	0.70	4.1	270
1NAA	75	25	0.70	2.5	250
1NOA	70	30	1.00	3.5	230
Q	80	20	0.90	2.9	315
5NQ	80	20	0.90	2.8	280
QX	40	60	0.90	3.0	300
2QXCA	40	60	0.90	2.5	300
3H2QXCA	60	40	1.00	2.2	270

Test compound acronyms defined in Table 1, and chemical structures shown in Fig. 1.

^a A=Methanol, B=10 mM phosphate buffer pH 3.0.

equilibration time, and M_w is the gravimetric water content of the suspension ($\text{kg solution kg}^{-1}$ sediment). The quantity of total IOC recovered was calculated from:

$$\text{Total recovery (\%)} = [(V_{24\text{ h}} * C_{24\text{ h}} + V_{\text{extract}} * C_{\text{extract}}) / V_c * C_{c,0\text{ h}}] * 100 \quad (2)$$

where $V_{24\text{ h}}$ and $C_{24\text{ h}}$ are, respectively, the total volume (L) of supernatant and IOC supernatant concentration ($\mu\text{mol IOC L}^{-1}$) after 24 h equilibration; V_{extract} and C_{extract} are, respectively, the total volume of phosphate extractant and IOC concentration ($\mu\text{mol IOC L}^{-1}$) in the extract; V_c and $C_{c,0\text{ h}}$ are, respectively, the total solution volume (L) and IOC concentration ($\mu\text{mol IOC L}^{-1}$) at $t=0$ h for the sediment-free control. Recovery values ranged from 90.1% to 101% and are presented in Table 3.

2.5. Analytical procedures

IOC concentrations in the supernatants and phosphate extraction solutions were measured with a HPLC (Waters 2695, Milford, MA) equipped with a 150×4.6 mm reverse-phase column (LC-PAH, Supelco, Bellefonte, PA) and a photodiode array detector (PDA, Waters 996). The mobile phase consisted of methanol (HPLC grade) and 10 mM potassium phosphate buffer at pH 3.0. The mobile phase mixture ratio, flow rate, integration interval, and specific PDA wavelength were optimized for each analyte (Table 2).

3. Results and discussion

The major findings of this research are that, under the estuarine solution chemistry tested, anionic naphthoic acids sorb primarily to sediment mineral surfaces, and that neutral or anionic quinoline compounds sorb primarily to sediment organic matter. Support of these findings will be made throughout the following presentation of experimental data. The current findings are also consistent with a previous study on the sorption of phenanthrene and 1-hydroxy-2-naphthoic acid to the same estuarine sediment, and humin and humic acid extracted from the sediment (Parikh et al., 2004). 1-Hydroxy-2-naphthoic acid sorbed to the sediment and humin, both of which contained significant mineral content, but did not sorb at all to humic acid. In comparison, phenanthrene sorbed to sediment, humin and humic acid to essentially equal extent when normalized to sediment organic C content. These previous results highlighted important differences between the surface reactivity of HOCs and IOCs.

Several sorption isotherm models were tested, including linear and Freundlich isotherms. The linear sorption isotherm can be written as:

$$q_e = K_d * C_e \quad (3)$$

where q_e is the sorbed concentration at equilibrium ($\mu\text{mol IOC kg}^{-1}$ sediment), C_e is the corresponding aqueous concentration at equilibrium ($\mu\text{mol IOC L}^{-1}$), and K_d is the linear distribution coefficient (L kg^{-1} sediment). The Freundlich isotherm can be written as:

$$q_e = K_F * C_e^n \quad (4)$$

where K_F is the Freundlich constant ($\{\mu\text{mol IOC kg}^{-1} \text{ sediment}\} \{\mu\text{mol IOC L}^{-1}\}^{-n}$), and n is the Freundlich exponent (dimensionless). These sorption isotherm models are used to determine adsorbate sorption capacity to sediment under specific solution chemistry conditions.

When considering all 16 IOCs, sorption data were best fit using the Freundlich isotherm (Table 3), whereas the linear sorption isotherm gave poorer fits based on correlation coefficients (R^2). Adsorption isotherms can be broadly categorized into four characteristic shapes, designated as S (sigmoidal), L (non-linear), H (strong/steep) and C (linear) (Sposito, 1984). At low dissolved adsorbate concentrations for an S-type isotherm, n values can be >1 . Thus, the five IOCs (1-hydroxy-2-naphthoic acid; 3-hydroxy-7-methoxy-2-naphthoic acid; 2,3-naphthalenedicarboxylic acid; 6-amino-2-naphthoic acid; and 4-fluoro-2-naphthoic acid) with n values >1 may display S-type behavior. For non-linear L-type isotherms, n is typically <1 and the maximum sorbed concentration becomes relatively independent of the dissolved adsorbate concentration. For all other naphthoic acids and all quinoline compounds, n values were always <1 .

For presentation and correlation purposes, IOCs have been divided into two major groups based on their different backbone structures (i.e., homocyclic naphthoic acids and N -substituted heterocyclic quinoline compounds). Naphthoic acids have been further divided into compounds with two *ortho*-substituent groups, two non-*ortho*-substituent groups, and single 1-substituents. The series of *ortho*-substituted naphthoic acids have been grouped together because the proximity of two groups allows these compounds to associate with the sediment in specific ways (e.g., multidentate multinuclear coordination) not possible with mono-substituted adsorbates (Evanko and Dzombak, 1998) (Fig. 2). The series of non-*ortho*-bi-substituted naphthoic acids have been grouped together to evaluate the effect of substituent groups that have little interaction with one another (Fig. 3). The series of single 1-naphthoic acids have been grouped together to demonstrate

Table 3
Linear and Freundlich adsorption isotherm coefficients for the ionizable organic compounds (IOCs) tested

Compound	Linear isotherm ^a		Freundlich isotherm ^b			N^c	Recovery ^d
	K_d	R^2	K_F	n	R^2		
1-hydroxy-2-naphthoic acid (1H2NA)	12.9	0.892	7.53	1.15	0.909	6	95.4 ± 0.5
1,8-naphthaldehydic acid (1,8NDA)	6.76	0.928	17.1	0.739	0.953	8	91.5 ± 2.5
3-hydroxy-7-methoxy-2-naphthoic acid (3H7M2NA)	4.60	0.658	0.587	1.52	0.867	6	99.1 ± 2.5
2,3-naphthalenedicarboxylic acid (2,3NDCA)	2.01	0.605	.00181	2.79	0.992	5	98.3 ± 5.8
1-methoxy-2-naphthoic acid (1M2NA)	1.23	0.953	1.67	0.920	0.978	7	93.3 ± 0.1
6-amino-2-naphthoic acid (6A2NA)	3.68	0.763	.0166	2.41	0.948	6	94.8 ± 0.3
6-methoxy-2-naphthoic acid (6M2NA)	2.60	0.857	5.39	0.822	0.965	6	90.1 ± 0.3
4-fluoro-2-naphthoic acid (4F2NA)	0.696	0.683	.00779	2.14	0.973	6	90.0 ± 0.3
1-naphthoic acid (1NA)	1.65	0.741	7.22	0.603	0.973	6	92.1 ± 0.7
1-naphthaleneacetic acid (1NAA)	2.03	0.534	23.0	0.384	0.960	7	93.1 ± 0.2
1-naphthoxyacetic acid (1NOA)	3.38	0.795	8.99	0.752	0.903	6	94.1 ± 0.1
Quinoline (Q)	6.87	0.908	33.4	0.663	0.962	7	93.0 ± 0.1
5-nitroquinoline (5NQ)	11.2	0.839	34.0	0.685	0.980	7	90.9 ± 1.3
Quinoxaline (QX)	4.20	0.857	21.9	0.589	0.915	8	94.1 ± 0.1
2-quinoxalinecarboxylic acid (2QXCA)	3.11	0.793	11.2	0.653	0.934	8	101 ± 0.1
3-hydroxy-2-quinoxaline carboxylic acid (3H2QXCA)	2.15	0.407	23.5	0.376	0.959	6	99.2 ± 0.2

^a $q_c = K_d C_e$ (Eq. (3)).

^b $q_c = K_F C_e^n$ (Eq. (4)).

^c Number of data points in isotherm regression.

^d Total recovery = ([Total mass in supernatant] + [Total mass from phosphate extraction]) / [Total mass in sediment-free control] * 100% (Eq. (2)).

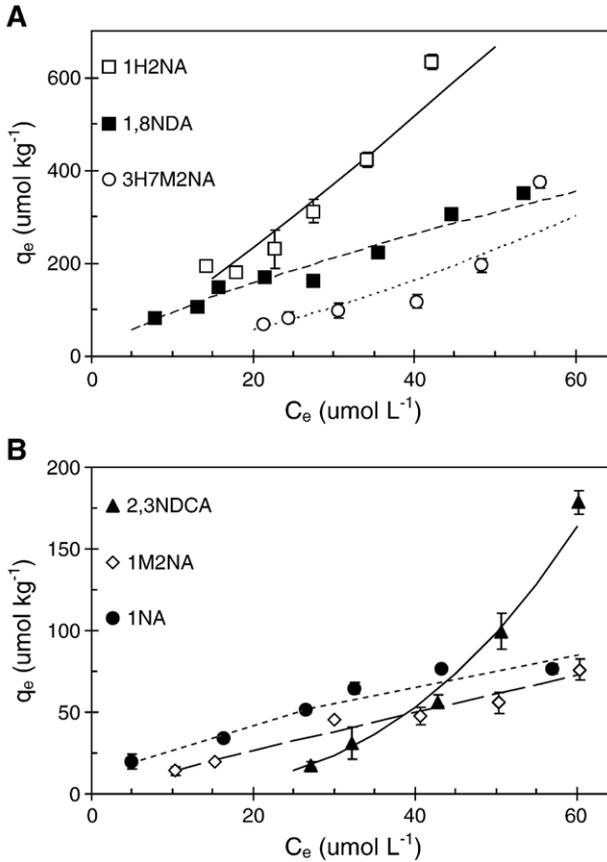


Fig. 2. Sorption of *ortho*-substituted naphthoic acids and 1-naphthoic acid to estuarine sediment. All experiments were conducted with $0.018 \text{ g sediment kg}^{-1}$ suspension and variable test compound concentrations in synthetic estuarine water (0.4 M , $\text{pH } 7.6$) and measured after 24 h equilibration. Symbols represent mean values of duplicate measurements, error bars represent one standard deviation, and adjacent lines represent Freundlich isotherm model (Eq. (4)) results using K_F and n values from Table 3.

the effect of adsorbate hydrophobicity (Fig. 4). The series of quinoline compounds have been grouped together to demonstrate the effect of substituent addition on NHC adsorption (Fig. 5).

3.1. Sorption of naphthoic acids

The sorption of 1-naphthoic acid (1NA) is included as a reference point for comparison with the *ortho*-substituted naphthoic acids (Fig. 2). Linear distribution coefficients decreased in the following order: 1-hydroxy-2-naphthoic acid > 1,8-naphthaldehydic acid > 3-hydroxy-7-methoxy-2-naphthoic acid > 2,3-naphthalenedicarboxylic acid > 1NA > 1-methoxy-2-naphthoic acid. These results indicate that the presence of an adjacent hydroxyl, carbonyl, or carboxyl functional group to another carboxyl group (Fig. 1) enhanced sorption relative to the 1NA backbone structure. By comparison, the presence of an *ortho*-methoxy group (i.e., 1M2NA) slightly decreased sorption. The current results are consistent with the sorption of substituted benzoic acids onto metal oxide surfaces. Evanko and Dzombak (1998) reported that hydroxyl or carboxyl

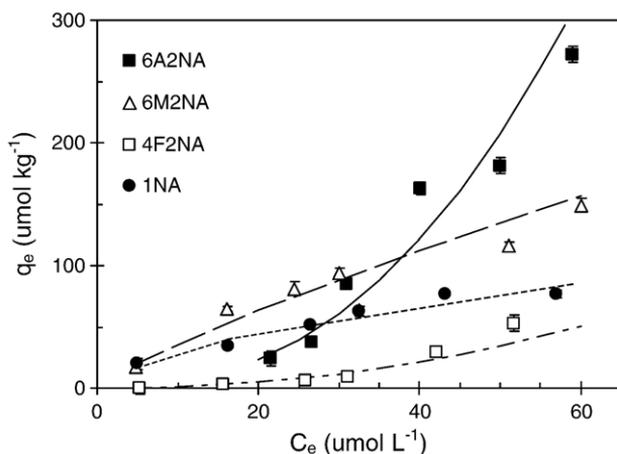


Fig. 3. Sorption of non-*ortho*-substituted naphthoic acids and 1-naphthoic acid to estuarine sediment. All experiments were conducted with $0.018 \text{ g sediment kg}^{-1}$ suspension and variable test compound concentrations in synthetic estuarine water (0.4 M , $\text{pH } 7.6$) and measured after 24 h equilibration. Symbols represent mean values of duplicate measurements, error bars represent one standard deviation, and adjacent lines represent Freundlich isotherm model (Eq. (4)) results using K_F and n values from Table 3.

groups adjacent to another carboxyl group in benzoic acids enhanced sorption to goethite, and proposed several possible structures for surface complexes between substituted benzoic acids and ferric oxides. Other studies have also reported that *ortho*-substituted aromatic acids (e.g., salicylic acid) adsorb more strongly to iron and aluminum oxides than mono-substituted benzenes (Schnitzer and Khan, 1972; Davis and Leckie, 1978; Kummert and Stumm, 1980).

Differences in the *ortho*-pair of functional groups influenced sorption. Sorption extent corresponding to the *ortho*-pairs decreased in the following order: OH/COO^- (1H2NA) > COH/COO^- (1,8NDA) > $\text{COO}^-/\text{COO}^-$ (2,3NDCA) > $\text{OCH}_3/\text{COO}^-$ (1M2NA). Greater sorption of 1-hydroxy-2-naphthoic acid compared to 2,3-naphthalenedicarboxylic acid is in agreement with

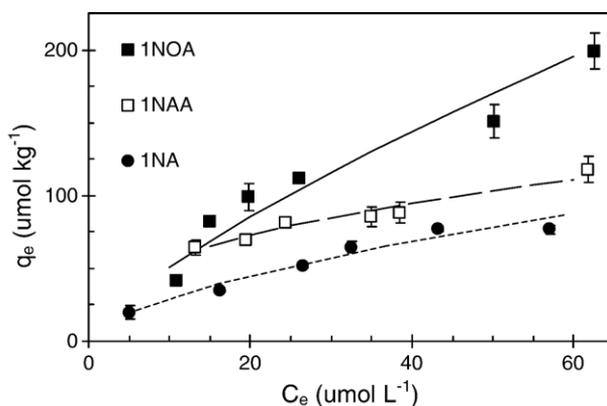


Fig. 4. Sorption of 1-substituted naphthoic acids to estuarine sediment. All experiments were conducted with $0.018 \text{ g sediment kg}^{-1}$ suspension and variable test compound concentrations in synthetic estuarine water (0.4 M , $\text{pH } 7.6$) and measured after 24 h equilibration. Symbols represent mean values of duplicate measurements, error bars represent one standard deviation, and adjacent lines represent Freundlich isotherm model (Eq. (4)) results using K_F and n values presented in Table 3.

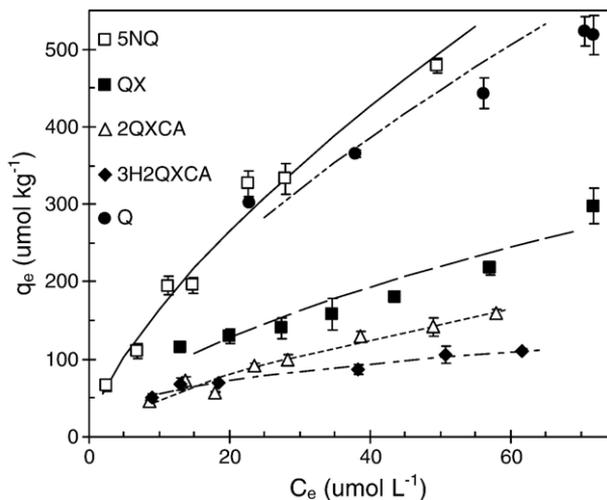


Fig. 5. Sorption of quinoline compounds to estuarine sediment. All experiments were conducted with 0.018 g sediment kg^{-1} suspension and variable test compound concentrations in synthetic estuarine water (0.4 M, pH 7.6) and measured after 24 h equilibration. Symbols represent mean values of duplicate measurements, error bars represent one standard deviation, and adjacent lines represent Freundlich isotherm model (Eq. (4)) results using K_F and n values from Table 3.

greater sorption of salicylic acid (OH/COO^- substituted benzene) compared to phthalic acid ($\text{COO}^-/\text{COO}^-$ substituted benzene) to soluble aluminum complexes in soil (Hue et al., 1986). Hue et al. (1986) reported that OH/COO^- substituted benzene rings can form a 6-membered ring structure with soluble aluminum complexes, and that $\text{COO}^-/\text{COO}^-$ substituted benzene rings can form a 7-membered ring structure with Al. Based on quantum mechanics calculations, Kubicki and Apitz (1999) also illustrated that phthalate–Al complexes in the 7-membered ring structure were energetically less stable than salicylate–Al complexes in the 6-membered ring structure. Formation of the 6-membered ring structure is more energetically stable because all atoms in the complex are within the plane of the benzene ring (Biber and Stumm, 1994; Kubicki et al., 1997). Due to repulsion of the two adjacent carboxyl groups, all atoms in the 7-membered ring structure are not in the same plane as the benzene ring. Opposite results were reported where phthalic acid sorbed more than salicylic acid to goethite (Evanko and Dzombak, 1998) and highlight differences with different sediment minerals.

The additional $-\text{OCH}_3$ group of 3-hydroxy-7-methoxy-2-naphthoic acid decreased sorption compared to 1-hydroxy-2-naphthoic acid (both adsorbates contain *ortho*- OH/COO^- groups). The additional weight of this substituent group did not increase sorption, e.g. via hydrophobic interactions. Instead, the relatively non-reactive $-\text{OCH}_3$ group apparently decreased the *ortho*- OH/COO^- groups' ability to specifically interact with sediment minerals. In a similar but less pronounced manner, the $-\text{OCH}_3$ group of 1-methoxy-2-naphthoic acid may have decreased the reactivity of the adjacent $-\text{COO}^-$ group and decreased sorption of 1-methoxy-2-naphthoic acid compared to 1-naphthoic acid.

The sorption of non-*ortho*-bi-substituted naphthoic acids is shown in Fig. 3. Based on linear distribution coefficients, sorption of 6-amino-2-naphthoic acid and 6-methoxy-2-naphthoic acid increased while sorption of 4-fluoro-2-naphthoic acid decreased compared to 1-naphthoic acid. Increased sorption due to addition of $-\text{NH}_2$ or $-\text{OCH}_3$ in the 6-position (i.e., 6A2NA vs. 6M2NA, respectively) was likely caused by distinctly different mechanisms.

The addition of $-\text{NH}_2$ increased hydrophilicity so that enhanced sorption was likely caused by increased electrostatic interactions between 6-amino-2-naphthoic acid and sediment minerals. The addition of $-\text{OCH}_3$ increased hydrophobicity so that enhanced sorption was likely caused by nonspecific hydrophobic interactions with hydrophobic components of the sediment. Greater sorption of 6-methoxy-2-naphthoic acid ($-\text{OCH}_3$ in 6-position) compared to 1-methoxy-2-naphthoic acid ($-\text{OCH}_3$ in 1-position) reinforces the interpretation that proximity of the $-\text{OCH}_3$ group decreased the reactivity of the adjacent $-\text{COO}^-$ group. The addition of $-\text{F}$ increased hydrophobicity, however, the strong electron-withdrawing ability of this group may reduce electrostatic interactions with sediment minerals.

The sorption of mono-substituted 1-naphthoic acids are shown in Fig. 4. Based on linear distribution coefficients, sorption extent decreased in the following order: 1-naphthoxyacetic acid (NOA) > 1-naphthaleneacetic acid (NAA) > 1-naphthoic acid, and indicate that addition of $-\text{OCH}_2$ or $-\text{CH}_2$ into the carboxylic side chain enhanced sorption. Previous studies have reported that increasing the side chain length by addition of $-\text{CH}_2$ groups enhanced the hydrophobic interactions between organic acids and oxide surfaces. Evanko and Dzombak (1998) found that the sorption of benzoic acids with aliphatic side chains onto goethite increased with increasing chain length. Ulrich et al. (1988) also reported that the sorption of straight-chain fatty acids ($>C_8$) onto alumina increased as chain length increased. In the current study, however, the measured $\log K_{\text{ow}}^{\text{neutral}}$ values of the adsorbates (Table 1) increased in the following order NA > NOA > NAA, which is opposite of the sorption order. Based on the finding that hydrophobicity decreases sorption, we speculate that naphthoic acids interact with polar mineral surfaces in these sediments.

3.2. Sorption of quinoline compounds

The sorption of quinoline compounds are shown in Fig. 5. Based on linear distribution coefficients, sorption extent decreased in the following order: 5-nitroquinoline > quinoline > quinoxaline > 2-quinoxalinecarboxylic acid > 3-hydroxy-2-quinoxalinecarboxylic acid. Two high quinoline sorption data points and one high quinoxaline data point are not shown in Fig. 5 for clarity of scale. At pH 7.6, 5-nitroquinoline, quinoline, and quinoxaline would be predominantly neutral molecules, while 2-quinoxalinecarboxylic acid and 3-hydroxy-2-quinoxalinecarboxylic acid would be predominantly anionic molecules. These results demonstrate that quinoline sorption increased as hydrophobicity increased, i.e. the exact opposite trend compared to naphthoic acids. Based on the finding that hydrophobicity increases sorption, we speculate that quinoline compounds interact primarily with organic matter in these sediments.

3.3. Quantitative Structure Activity Relationships (QSARs) for IOC sorption

The sorption of HOCs to sediments is often well described by linear sorption isotherms (Eq. (3)). When linear distribution coefficients (K_d , L kg^{-1}) are normalized to sediment organic C content, a relatively constant distribution coefficient is obtained for each HOC (K_{OC} , L kg^{-1} sediment organic C). Since HOC sorption is envisioned as a hydrophobic partitioning process to sediment organic matter, HOC hydrophobicity (e.g., K_{OW}) can be used to predict K_{OC} . This predictive relationship is an example of a QSAR. The superposition of multiple sorption processes, namely hydrophobic partitioning into condensed organic matter and specific adsorption onto mineral surfaces, has also been used to model the sorption of HOCs to soils and sediments (e.g., Weber et al., 1992; Allen-King et al., 2002). In a similar manner, the sorption of

anionic organic acids to soils has been modeled as hydrophilic sorption to anion exchange sites plus hydrophobic sorption to organic matter (Hyun and Lee, 2005). Sorption QSARs can be developed from these more sophisticated models but require additional characterizations of the sorbents (e.g., H/C and O/C ratios of organic matter; anion and action exchange capacities).

IOC sorption data were best fit using the Freundlich isotherm (Eq. (4)), however, the Freundlich equation is empirical and has two adjustable parameters (K_F and n) in which the units of K_F ($\{\text{mol kg}^{-1} \text{ sediment}\} \{\text{mol L}\}^{-n}$) are related to n . Because n values were different among the test compounds (Table 3), the units of the Freundlich constants were correspondingly different. Sorption parameters of different units are not readily comparable. Establishing a predictive QSAR based on K_F or n is also problematic because these two coefficients are coupled. Instead, the linear sorption isotherm (Eq. (3)) was used to establish IOC sorption QSARs (Figs. 6 and 7) allowing speculative mechanistic interpretations of the results of this study.

Correlations between linear sorption coefficients ($\log K_d$) and water solubility ($\log S_w^{\text{neutral}}$), water solubility calculated at pH 7.6 ($\log S_w^{\text{pH } 7.6}$), n -octanol/water partition coefficients ($\log K_{\text{OW}}^{\text{neutral}}$), and n -octanol/water partition coefficients calculated at pH 7.6 ($\log K_{\text{OW}}^{\text{pH } 7.6}$) were all examined. As noted above, S_w and K_{OW} values were calculated for neutral test compounds. The pH-adjusted property estimates were calculated for the experimental pH of 7.6 by the following equations (Schwarzenbach et al., 2003):

$$\alpha_a = 1 / \left(1 + 10^{(\text{pH} - \text{p}K_{\text{a}1})} \right) \quad (5)$$

$$S_w^{\text{pH } 7.6} = S_w^{\text{neutral}} / \alpha_a \quad (\text{for organic acids}) \quad (6)$$

$$S_w^{\text{pH } 7.6} = S_w^{\text{neutral}} / (1 - \alpha_a) \quad (\text{for organic bases}) \quad (7)$$

$$K_{\text{OW}}^{\text{pH } 7.6} = \alpha_a * K_{\text{OW}}^{\text{neutral}} \quad (\text{for organic acids}) \quad (8)$$

$$K_{\text{OW}}^{\text{pH } 7.6} = (1 - \alpha_a) * K_{\text{OW}}^{\text{neutral}} \quad (\text{for organic bases}) \quad (9)$$

where α_a is the fraction of an organic acid present in its protonated, neutral, acidic form; $(1 - \alpha_a)$ is the fraction of an organic base in its deprotonated, neutral, basic form; and, $\text{p}K_{\text{a}1}$ is the first acid dissociation constant of the IOC.

Correlations between linear sorption coefficients ($\log K_d$) and acid dissociation constants ($\text{p}K_{\text{a}1}$), first-order simple path molecular connectivity (1X), first-order valence path molecular connectivity (1X_v), third-order valence path molecular connectivity (3X_p), fourth-order valence path molecular connectivity (4X_p), and fourth-order valence path cluster (${}^4X_{\text{vpc}}$) were also examined. For both naphthoic acids and quinoline compounds, poor correlations were established between $\log K_d$ and $\text{p}K_{\text{a}1}$ (R^2 values < 0.52). A number of molecular connectivity indexes were tested to account for branching, substitution, heteroatom content, and structural conformation. For both naphthoic acids and quinoline compounds, poor or no correlations were established between $\log K_d$ and 1X ($R^2 < 0.18$), 1X_v ($R^2 < 0.13$), 3X_p ($R^2 < 0.06$), 4X_p ($R^2 < 0.02$), or ${}^4X_{\text{vpc}}$ ($R^2 < 0.22$). Correlations between Freundlich sorption coefficients ($\log K_F$ and n) were also tested. For both naphthoic acids and quinoline compounds, poor correlations were established between $\log K_F$ and $\log S_w^{\text{pH } 7.6}$ ($R^2 < 0.29$), between $\log K_F$ and $\log K_{\text{OW}}^{\text{pH } 7.6}$ ($R^2 < 0.33$), between n values and $\log S_w^{\text{pH } 7.6}$ ($R^2 < 0.36$), and between n values and $\log K_{\text{OW}}^{\text{pH } 7.6}$ ($R^2 < 0.39$).

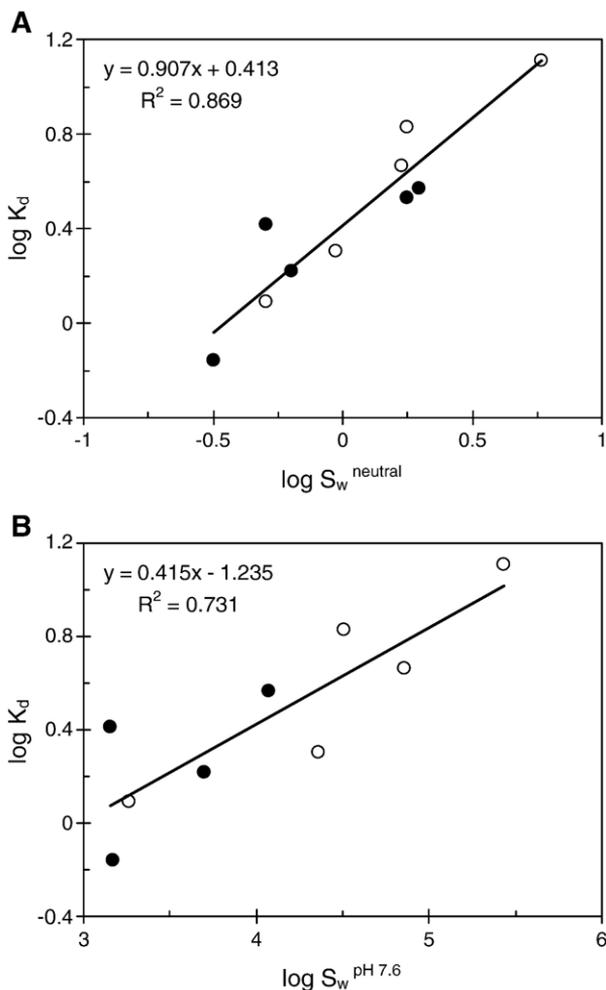


Fig. 6. Correlations between linear sorption coefficients ($\log K_d$) and (A) water solubility ($\log S_w^{\text{neutral}}$), and (B) water solubility calculated at pH 7.6 ($\log S_w^{\text{pH } 7.6}$) for naphthoic acids: *ortho*- (closed circles) and *non-ortho*- (open circles) substituent groups. Regression line and equation are for all data in each panel.

From a thermodynamic standpoint, a sorption QSAR should be based on the aqueous activity coefficient of the subcooled liquid (γ_w^{sat}) instead of the saturated solubility of the solid compound ($C_w^{\text{sat}}(s)$) (Schwarzenbach et al., 2003). However, no adequate method was found for estimating test compound melting point which is required to calculate free energy of fusion and γ_w^{sat} . Nonetheless, the sorption of naphthoic acids was shown to have a positive correlation with both neutral IOC water solubility ($R^2=0.869$, $N=10$), and with water solubility calculated at pH 7.6 ($R^2=0.731$, $N=9$) (Fig. 6). Correlation coefficients may have been affected by the combined uncertainty of property estimates for neutral compounds being extended to ionized species. 1-Naphthaleneacetic acid was rejected from the $\log S_w^{\text{neutral}}$ regression because its sorption isotherm was highly nonlinear (Table 3) and its low solubility significantly leveraged the correlation ($R^2=0.704$, $N=11$). Both 1-Naphthaleneacetic acid and 1-naphthoxyacetic acid were excluded from the $\log S_w^{\text{pH } 7.6}$ regression because $\text{p}K_{\text{a}1}$ values were not available for calculation

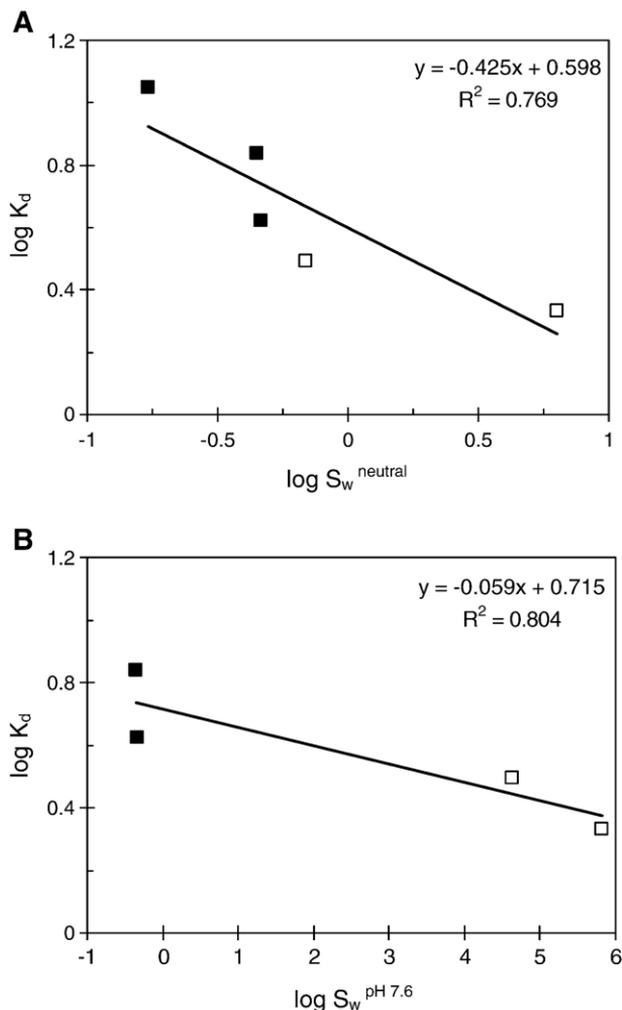


Fig. 7. Correlations between linear sorption coefficients ($\log K_d$) and (A) water solubility ($\log S_w^{\text{neutral}}$), and (B) water solubility calculated at pH 7.6 ($\log S_w^{\text{pH } 7.6}$) for quinoline compounds: neutral (closed squares) and anionic (open squares) species at pH 7.6. Regression line and equation are for all data in each panel.

purposes. The sorption of naphthoic acids ($\log K_d$) had poor correlations with both $\log K_{OW}^{\text{neutral}}$ ($R^2=0.354$, $N=11$) and $\log K_{OW}^{\text{pH } 7.6}$ ($R^2=0.006$, $N=9$). These data are consistent with the interpretation that naphthoic acids sorb preferentially to sediment mineral surfaces. Naphthoic acid sorption to polar mineral surfaces first requires the displacement of surface-associated water. As the solubility (i.e., hydrophilicity) of the naphthoic acid increases, the thermodynamic “cost” to displace this vicinal water decreases and, therefore, sorption increases (Schwarzenbach et al., 2003). This correlation and its mechanistic interpretation are strongly dependent on the estuarine solution chemistry tested.

In contrast, the sorption of quinoline compounds was shown to have a negative correlation with both neutral IOC water solubility ($R^2=0.769$, $N=5$), and with water solubility calculated at pH 7.6 ($R^2=0.804$, $N=4$) (Fig. 7). 5-Nitroquinoline was excluded from the $\log S_w^{\text{pH } 7.6}$ and \log

$K_{OW}^{pH\ 7.6}$ correlations because its pK_{a1} value was not available for calculation purposes. It should be noted that there are no neutral forms of the zwitterions 2-quinoxalinecarboxylic acid and 3-hydroxy-2-quinoxalinecarboxylic acid (open squares in Figs. 7 and 8). Instead, there is a pH region above the pK_{a1} of the carboxylic acid group and below the pK_{a2} of the *N*-heteroatom (which could not be estimated) where the net charges of the ionized species are neutral. However, pH-adjusted property estimates for 2QXCA and 3H2QXCA simply considered acid ionization above pK_{a1} (i.e., used Eqs. (5), (6), (8)), and this should be noted when considering correlations shown in Figs. 7B and 8B.

The sorption of quinoline compounds was also shown to have a positive correlation with both neutral IOC *n*-octanol/water partition coefficients ($R^2=0.839$, $N=5$), and with *n*-octanol/water partition coefficients calculated at pH 7.6 ($R^2=0.878$, $N=4$) (Fig. 8). These data are consistent

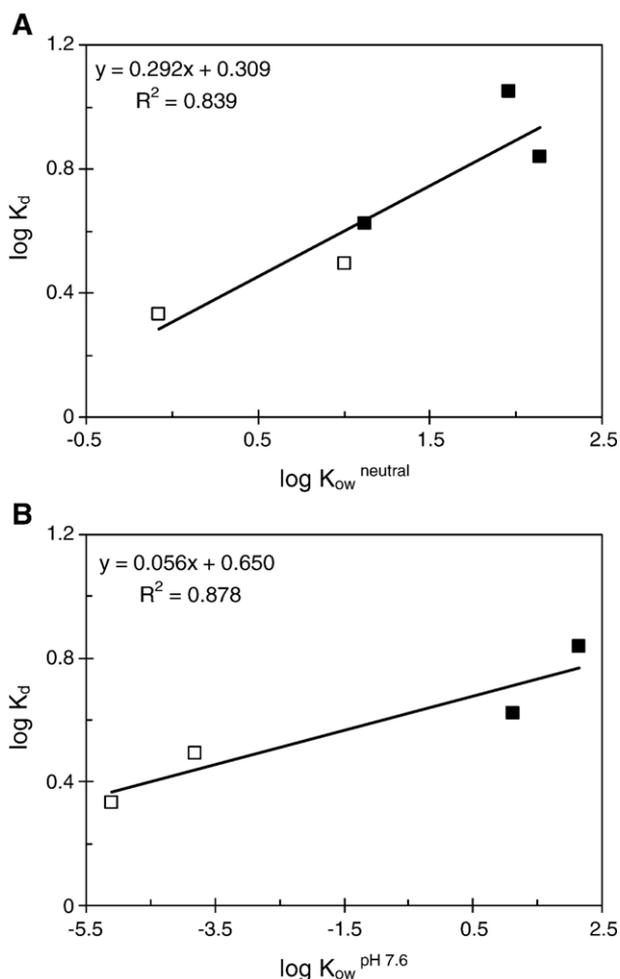


Fig. 8. Correlations between linear sorption coefficients ($\log K_d$) and (A) *n*-octanol/water partition coefficients ($\log K_{OW}^{neutral}$), and (B) *n*-octanol/water partition coefficients calculated at pH 7.6 ($\log K_{OW}^{pH\ 7.6}$) for quinoline compounds: neutral (closed squares) and anionic (open squares) species at pH 7.6. Regression line and equation are for all data in each panel.

with the interpretation that quinoline compounds do not strongly associate with sediment mineral surfaces but instead preferentially sorb to sediment organic matter. While the sorption of the quinolinium cation can occur at pH values well above its pK_a (Zachara et al., 1986; Ainsworth et al., 1987; Zachara et al., 1990; Chorover et al., 1999), the estuarine solution chemistry tested could suppress quinolinium sorption to mineral surfaces due to relatively high Ca^{2+} and Mg^{2+} concentrations and promote quinoline sorption to organic matter. The overall trend with all quinoline compounds suggests that hydrophobic interactions with organic matter are predominant. This interpretation is supported by sorption studies of apolar and slightly monopolar organic compounds to aluminum oxides (Schwarzenbach and Westall, 1981; Mader et al., 1997) that show a strong negative correlation between sorption and hydrophilicity (Schwarzenbach et al., 2003). It should be noted that a definitive conclusion is difficult to make from only four or five data points, and that this mechanistic interpretation is dependent on the estuarine solution chemistry tested.

One motivation for this study was to examine if the sorption of ionizable degradation products of PAHs were substantially different than the sorption of their parent compounds. The results from this study demonstrate that the sorption of ionizable organic compounds differ depending on their backbone structure (e.g., homocyclic naphthoic acid vs. *N*-substituted heterocyclic quinoline). Interestingly, the sorption mechanism of more polar substituted ionizable quinoline compounds appeared to remain hydrophobic partitioning into sediment organic matter. In contrast, the sorption mechanism of ionizable naphthoic acids appeared to change to sorption to sediment mineral surfaces while parent PAHs would partition into sediment organic matter.

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