

Sorption–desorption behavior of polycyclic aromatic hydrocarbons in upstream and downstream river sediments

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Abstract

Sorption and desorption behaviors of phenanthrene and naphthalene were studied with the whole sediment, humic acid (HA) and humin samples from downstream and upstream sites along the Kishon River, Israel. The ^{13}C nuclear magnetic resonance spectra and the sorption coefficients suggest that sorption occurs to both aromatic and aliphatic moieties of the sedimentary organic matter and that rigid paraffinic domains probably contribute to the sorption non-linearity. The carbon-normalized Freundlich affinity values for the two sorbates were significantly higher for the whole sediment and humin samples from the downstream region of the river than for the upstream sediment samples. On the basis of the measured affinity values, the sorbents can be arranged in the following order: humin > HA > whole sediment. Phenanthrene exhibited the lowest desorption from the whole sediment samples compared with the other sorbents. For naphthalene, the desorption hysteresis obtained with the whole sediment and humin samples were similar: both exhibited a decrease in desorption with decreasing solute concentration. The higher sorption affinities observed for all the organic fractions from the downstream sediment are suggested to be related to the low levels of polar domains and humin content. It is concluded that in bulk sediment samples, the overall contribution of the HA fraction to short-term sorption is of high importance, but the sorption non-linearity is controlled mainly by the humin complexes. The low desorption potential recorded for the whole sediment samples could affect the natural attenuation of the sorbed hydrophobic organic compounds.

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1. Introduction

Sorption and desorption are the major processes influencing the overall fate of hydrophobic organic com-

pounds (HOCs) such as pesticides, petroleum hydrocarbons and polychlorinated biphenyls in marine and river sediments. Many studies have shown that the soil and sedimentary organic matter (SOM) are the major sorbents for HOCs. The role of SOM in the sorption of HOCs depends on the composition and physico-chemical nature of the SOM (Huang et al., 1997; Luthy et al., 1997; Chiou et al., 1998; Chefetz et al., 2000).

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Overall, sorption processes consist of at least two steps: forward (sorption) and reverse (desorption). Solid-phase dissolution (partitioning) is widely used for predicting the sorption of organic compounds in soils and sediments. Sorption of HOCs to gel-like (rubbery) sorbents has been traditionally described as a partition-type process where desorption hysteresis is not expected. However, recent findings have shown significant deviations between sorption and desorption lines in many cases (Huang and Weber Jr., 1997; Huang et al., 1998; Weber Jr. et al., 1998; Ran et al., 2002). The reasons for sorption–desorption hysteresis are not yet fully understood; they can result from irreversible chemical binding or sequestration of the solute, entrapment of the sorbate in meso- or micropores of the inorganic structures or organic matrices, and structural changes (deformation) of the sorbent (Weber Jr. et al., 1998). Sorption–desorption hysteresis can also be explained in the context of polymer theory (LeBoeuf and Weber Jr., 1997). Sorption to the rubbery domain of SOM is characterized as linear, non-competitive and fully reversible. In contrast, sorption to the glassy fraction of SOM occurs by both dissolution and hole-filling processes, making it typically non-linear. A positive correlation between sample aromaticity and isotherm non-linearity has been drawn in many sorption studies, which concluded that the condensed domains of the SOM are constructed mainly from aromatic moieties (Chin et al., 1997; Perminova et al., 1999; Johnson et al., 2001; Xing, 2001; Kulikova and Perminova, 2002). However, other studies have shown that the sorption of HOCs by aliphatic-rich sorbents also exhibits high sorption capacities and non-linear isotherms (Chefetz et al., 2000; Mao et al., 2002b; Salloum et al., 2002). The role of these two SOM domains in the sorption of HOCs is still under debate.

The desorption process has significant environmental effects during the remediation of contaminated rivers and streams, where the rate and level of sorbed pollutants which can be released to the water phase (when the solid–liquid phase equilibrium is changed) are determined mainly by this process. Therefore, understanding the mechanisms that cause sorption-irreversibility is of interest from both a scientific and technological viewpoint. The desorption data can increase our mechanistic understanding of the type of sorbate–sorbent interactions involved and can provide further insight into the structural composition of the sorbent. From a technological point of view, it can reveal different remediation strategies based on the desorption hysteresis. The objective of this study was to evaluate the sorption–desorption interactions of polycyclic aromatic hydrocarbons (PAHs) with river sediments from upstream and downstream regions of a polluted coastal river (Kishon) in Israel.

2. Materials and methods

2.1. Sampling site, samples and extraction procedures

Sediments were sampled from upstream and downstream sites along the Kishon River. This river drains an area of about 1100 km² in the northern part of Israel. It is perennial for most of its course (70 km) to the Mediterranean Sea. Upstream, where the water quality is affected by the flow of semi-treated municipal wastewater and agricultural runoff, the river is relatively clean. The last 7 km of the river (downstream region) were heavily contaminated for dozens of years by nearby heavy industry—including oil refineries, fertilizer and chemical factories, and by untreated municipal wastewater. In the last decade, there has been a significant reduction in the pollution level of this part of the river due to the enforcement of new environmental regulations.

Sediments were sampled from two sites along the river: (1) downstream, about 4 km from where the river enters the sea, and (2) about 25 km upstream. At each site, samples were collected from the surface of the sediments (0–20 cm), at least 1 m away from the riverbank. A composite 10-kg sample was prepared in each sampling area by mixing five 2-kg subsamples collected randomly over 50 m length strip of the riverbank. Upon reaching the laboratory, samples were immediately dried, ground, sieved through a 2-mm sieve and stored dry at room temperature. General sediment characteristics are presented in Table 1. Humic acid (HA) and humin were isolated from the sediment samples according to the protocol outlined by Swift (1996). Briefly, the sediments were extracted three times with 0.1 M NaOH for 24 h under N₂. The alkaline supernatant was decanted

Table 1
Selected properties of the Kishon sediments

	Upstream sediment	Downstream sediment
Sand (%)	30	30
Silt (%)	30	20
Clay (%)	40	50
Texture type	Clay loam	Clay
Total organic carbon (%)	1.63	1.25
N (%)	0.16	0.09
Calcium carbonate (%)	13.8	12.8
pH ^a	7.1	6.8
Cation-exchange capacity (meq/100 g)	24.4	18.5
Specific surface area (m ² /g) ^b	294	213
Humic acid (HA) ^c	30	60
Humin ^c	61	34

^a Measured in a saturated paste.

^b Measured using ethylene glycol monoethyl ether as described in Carter et al. (1965).

^c % of sedimentary organic matter.

and then acidified to pH 2 with 6 M HCl to obtain the HA fraction. The HA was then purified with a 0.3 N HF/0.1 N HCl mixture. The non-extractable fraction (i.e., the humin fraction) was treated with the HF/HCl mixture for a week and then rinsed several times with deionized water, centrifuged and freeze-dried. Percent of HA and humin in SOM was determined by monitoring the amount of carbon during all steps of the extraction procedure. This provided us with a complete carbon mass-balance for the humic fractions. Carbon, hydrogen and nitrogen were measured with an 1108 Elemental Analyzer (Fisons Instruments, Milan, Italy). The samples (whole sediment, HA and humin) were classified according to sampling site (i.e., upstream and downstream).

2.2. ^{13}C NMR analysis

The ^{13}C nuclear magnetic resonance (NMR) spectra were acquired on a Bruker DSX-300 spectrometer at the University of Massachusetts, using cross-polarization magic-angle spinning with total sideband suppression (Mao et al., 2000, 2002a). Prior to the NMR analysis, the sediment and humin samples were de-ashed with 1 M HF according to the method suggested by Preston and Newman (1995). No additional purification treatments were performed for the HAs. Freeze-dried samples were packed into a 7-mm rotor and spectra were acquired using the following acquisition parameters: spectral frequency of 75 MHz for ^{13}C and 300 MHz for ^1H , spinning rate of 5 kHz, contact time of 1 ms, recycle delay of 1 s and line broadening of 30 Hz. The spectra (about 30,000 scans per sample) were integrated into the following chemical-shift regions: paraffinic carbon (0–50 ppm); methoxyl carbon (50–60 ppm); O-alkyl carbon (60–108 ppm); aromatic and phenolic carbon (108–162 ppm); carboxyl and amide carbon (162–190), and carbonyl carbon (190–220 ppm). Aromaticity was calculated by expressing the level of aromatic carbon (108–162 ppm) as a percentage of the aliphatic plus aromatic carbons (0–162 ppm).

2.3. Batch sorption–desorption experiments

Preliminary experiments were conducted to determine the time needed for each sorbent–sorbate pair to reach apparent equilibrium. Statistical analysis of the resultant data indicated that both phenanthrene and naphthalene (>98% purity; Sigma-Aldrich, St. Louis, MO) reached sorption equilibrium within 2–3 d (phenanthrene sorption rates are presented in Fig. 1). All batch-sorption experiments were therefore performed for 4-d periods (Chiou et al., 1998; Lu and Pignatello, 2004). Aqueous solutions were prepared by adding aliquots from concentrated HPLC-grade methanol stocks of the PAHs to a background solution containing 5 mM CaCl_2 and 1×10^{-5} M HgCl_2 to maintain a con-

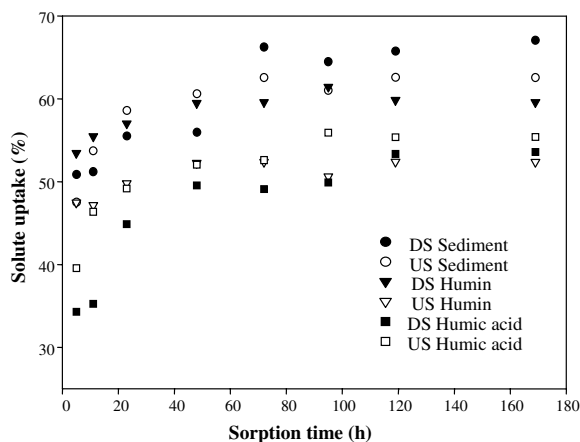


Fig. 1. Sorption uptake rates of phenanthrene by the downstream (DS) and upstream (US) bulk sediments, humic acid and humin samples (all values represent the mean of triplicate measurements with a coefficient of variation less than 5%).

stant ionic strength and to inhibit microbial activity, respectively. The pH of the solution was 7.5 and the methanol concentration was maintained at less than 0.1% (v/v). To prevent any potential dissolution of the sorbent, the background solution was adjusted to pH 4.0 for all sorption–desorption experiments with HAs (Xing et al., 1994). The maximal amount of HA dissolved at pH 4 was measured in blank experiments (without solute) and found to be smaller than 0.1% of the total mass of HA used in the sorption experiments. For each sorbent–sorbate pair, solid-to-solution ratios were selected to achieve 40–60% sorption.

PAH solutions, covering a range of 0.05–1.0 mg/l (for phenanthrene) and 0.1–10 mg/l (for naphthalene), were added to samples previously weighed into 30-ml glass screw-cap centrifuge tubes with Teflon-backed silicon septa (Kimble/Kontes, Vineland, NJ). Sorption of the PAHs to the tubes was found to be negligible (<1%). To ensure that volatilization losses of naphthalene were negligible relative to sorption, the liquid phase was adjusted to keep the headspace below 0.5 ml. The tubes (three replicates and a blank for each concentration) were agitated end-over-end at 25 °C in the dark at 250 rpm for 4 d and then centrifuged for 20 min at 12000g. Next, 10 ml of the supernatant were removed using a glass pipette and replaced with fresh background solution, and the tubes were further agitated under the same conditions. Four sequential desorption steps were performed. Supernatants collected after the sorption and each of the desorption steps were diluted (1:1, v:v) with methanol into 1.5-ml HPLC vials. The methanol was added to prevent PAH sorption to the vials. Quantitative HPLC analyses were performed using an L-7100 LaChrom HPLC (Merck-Hitachi, Darmstadt, Germany) with a LiChroCART® column (25 cm × 4 mm)

packed with spherical particles of silica with an octadecyl derivative (particle size, 5 μm ; pore size, 100 nm). A 10- μl sample was injected to the HPLC column and the PAHs were eluted using isocratic conditions of water/acetonitrile (15/85). The flow was maintained constant at 1 ml/min. The PAHs were detected with a fluorescence detector (L-7485, Merck-Hitachi) using the following excitation and emission wavelengths: 244 nm (ex) and 360 nm (em) for phenanthrene and 270 nm (ex) and 335 nm (em) for naphthalene. All solutes were quantified using external standards prepared in a background solution. Because of negligible sorption to the vials, minimal headspace and no biodegradation, sorption was calculated by mass differences.

2.4. Data analysis

The Freundlich parameters (K_F and N) were calculated from the logarithmic form of the equation: $q = K_F C^N$, where q is the total sorbed concentration (mg/kg), C is the solution-phase concentration (mg/l), K_F (mg/kg) (mg/l) $^{-N}$ is the Freundlich affinity coefficient and N is the non-linearity factor. Isotherms were plotted ($\log q$ vs. $\log C$), and $\log K_F$ and N were obtained from the fitting. The K_F values from different isotherms were compared after normalizing C by the super-cooled liquid-state solubility (S_{scf}) of the sorbate (Carmo et al., 2000). This method generates a modified Freundlich parameter (K'_F) which enables a comparison of K_F values from isotherms having different N values. The K'_F data were normalized to the carbon level of each sorbent to obtain the K'_F OC values. A single-point organic carbon-normalized distribution coefficients (K_{OC}) were calculated at an equilibrium concentrations of $C_e/S_w = 0.05, 0.1$ and 0.5 where C_e and S_w are the equilibrium aqueous phase concentration and aqueous solubility, respectively. The ratio of the Freundlich exponents for desorption and sorption (N_D/N_S) was calculated and used as the desorption apparent hysteresis index (AHI), where a lower index value indicates increased difficulty of the sorbed analyte to desorb from the matrix (Gunasekara and Xing, 2003). Statistical analysis (All Pairs, Tukey Kramer, $P = 0.05$) was performed by JMPIN software, version 4.0.4 (SAS Institute Inc., Cary, NC).

3. Results and discussion

3.1. ^{13}C NMR characterization of the sorbents

^{13}C NMR spectroscopy provided useful information on the chemical properties of the various tested samples and their effects on sorption. The major peaks in the ^{13}C NMR spectra (Fig. 2) were at 18, 21 and 33 ppm (methyl

and methylene carbons), 56 ppm (methoxyl carbon), 72 and 105 ppm (hexose ring carbons and anomeric carbon of polysaccharides, respectively), 128 ppm (carbon-substituted aromatic carbon), 147 and 153 ppm (phenolic carbon) and 174 ppm (carboxyl/amide carbon). The major differences between the spectra of the whole sediment samples were: (i) the spectrum of the downstream sample exhibited more pronounced peaks assigned to lignin structures at 150 and 56 ppm; (ii) the spectrum of the sediment from the upstream site exhibited well-resolved peaks related to both CH_2 in simple aliphatics (21 ppm) and CH_2 , CH and C in complex aliphatics (33 ppm), whereas the 21- and 25-ppm peaks were significantly reduced in the downstream spectrum; (iii) the spectrum of the downstream sample exhibited a higher aromaticity value (24% vs. 15%) than the upstream sample, and (iv) the upstream sediment exhibited a higher level of carbohydrate (29%, vs. 21% calculated for the downstream sediment sample).

The spectra of the HA samples were characterized by a considerable amount of aromatic carbon and a low level of O-alkyl carbon, as seen by the small peak at 72 ppm. Similar to the sediment sample, the HA from the downstream sample exhibited a higher level of aromatic carbon (47%, vs. 32% in the upstream HA). In addition to the aromatic peaks, the HA spectra exhibited a sharp peak at 29 ppm which is assigned to an amorphous (mobile) polymethylenic carbon (Hu et al., 2000; Sachleben et al., 2004). The peak at 33 ppm (long crystalline polymethylenic chains) was not seen in either HA spectrum.

The spectrum of the humin from the downstream sample was characterized by dominant paraffinic carbon peaks at 25 and 33 ppm. Similar to the sediment sample, the humin from the upstream sample exhibited a higher content of polysaccharides (31% vs. 23%, in the downstream humin). The humin samples exhibited a similar aromaticity level (28–31%) but the downstream humin exhibited higher aliphatic content (31% vs. 24% for the upstream humin). The spectra of the humin samples exhibited only the peak assigned to rigid polymethylenic $(\text{CH}_2)_n$ chains at 33 ppm while the amorphous polymethylenic peak at 29 ppm was absent. The presence of a rigid polymethylenic $(\text{CH}_2)_n$ domain within the humin samples and the amorphous polymethylenic domain in the HA structure suggests that the humin samples are richer in condensed aliphatic domains than the HA structures. This could have a significant influence on the sorptive capacities of the samples.

3.2. Sorption

Isotherm non-linearity values (N) for phenanthrene were lower than for naphthalene with the whole sediment and humin samples; however with the HAs, the N values were similar for both sorbates (Table 2).

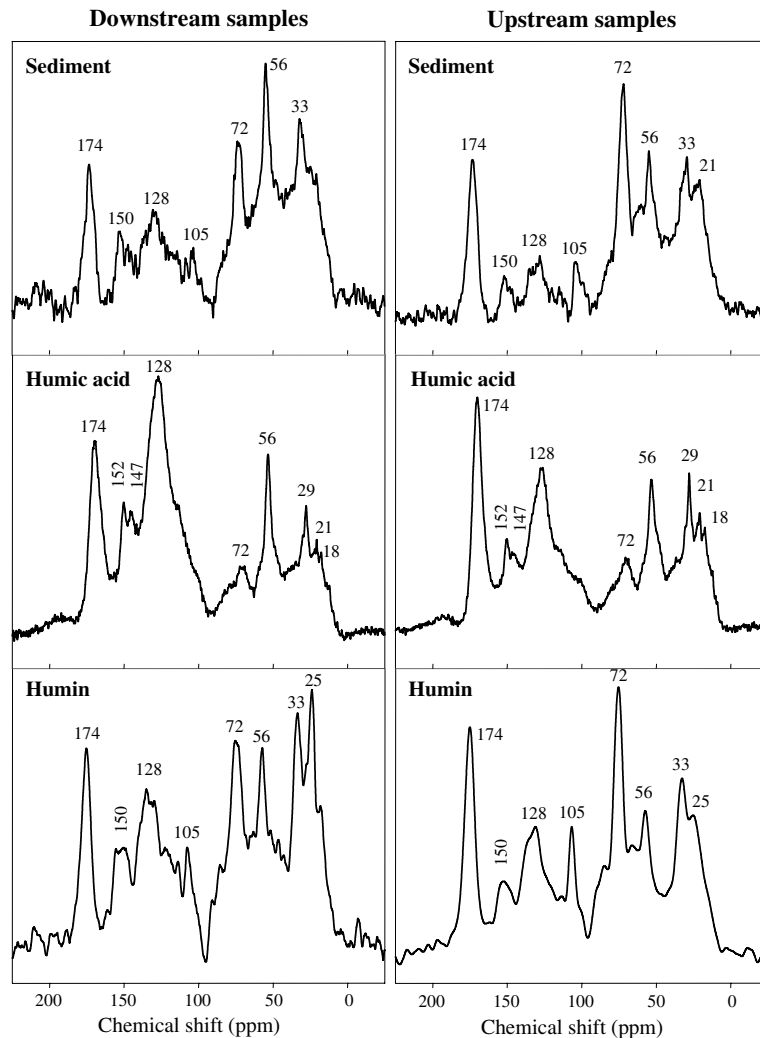


Fig. 2. ^{13}C nuclear magnetic resonance (NMR) spectra of the Kishon River samples (whole sediment, humic acid and humin). The downstream samples are presented in the left column and the upstream samples in the right column.

The higher N values exhibited for phenanthrene by the HAs compared to the humin samples are consistent with previous studies showing that humin from peat and soil exhibits a higher degree of non-linearity relative to HAs extracted from the same samples (Xing, 2001; Gunasekara and Xing, 2003). It is assumed that the more non-linear sorption isotherms exhibited by the humin samples are related to the more condensed and rigid structure of the humin fraction as compared to the HA macromolecule. Another interesting observation is that the phenanthrene N values obtained for the upstream whole sediment and humin samples were significantly lower than those calculated for the corresponding samples from the downstream site. All naphthalene sorption isotherms were also non-linear (N values between 0.86 and 0.92) but did not show

statistical differences between the two sediments or their organic matter fractions. A high degree of non-linearity has been reported to correlate with the level of aromaticity of the sorbent (Johnson et al., 2001; Simpson et al., 2003). However, within the measured concentration range, the samples containing the highest level of aromatic moieties (i.e. HAs) exhibited lower isotherm non-linearity for phenanthrene and similar non-linearity for naphthalene relative to the other samples. This data suggests that the non-linear sorption behavior is not solely governed by the aromatic sorption domains but can also be influenced by the presence of condensed paraffinic sorption domains, as suggested by the 33-ppm peak in the NMR spectra of the humin samples.

Concentration-independent K_{OC} values could not be calculated because of the non-linear sorption isotherms

Table 2

Sorption coefficients and Freundlich model parameters. N values for each sorbate followed by different letters are significantly different at $P < 0.05$

	Phenanthrene			$\log K_F$ (mg/kg) (mg/l) ^{-N}	N	K'_F OC (mg/kg OC)
	$\log K_{OC}$ $C_e/S_w = 0.05$	$\log K_{OC}$ $C_e/S_w = 0.1$	$\log K_{OC}$ $C_e/S_w = 0.5$			
<i>Downstream samples</i>						
Whole sediment	4.15	4.11	4.02	2.09 (±0.02)	0.87ab	46200
Humic acid	4.14	4.11	4.04	3.76 (±0.01)	0.90a	51400
Humins	4.58	4.53	4.42	2.28 (±0.01)	0.84ab	110000
<i>Upstream samples</i>						
Whole sediment	4.27	4.17	3.92	2.07 (±0.02)	0.65c	22800
Humic acid	4.13	4.10	4.03	3.76 (±0.01)	0.92a	51000
Humins	4.44	4.37	4.22	2.24 (±0.01)	0.78d	61600
	Naphthalene			$\log K_F$ (mg/kg) (mg/l) ^{-N}	N	K'_F OC (mg/kg OC)
	$\log K_{OC}$ $C_e/S_w = 0.05$	$\log K_{OC}$ $C_e/S_w = 0.1$	$\log K_{OC}$ $C_e/S_w = 0.5$			
<i>Downstream samples</i>						
Whole sediment	2.80	2.77	2.69	0.92 (±0.01)	0.89a	42100
Humic acid	2.93	2.90	2.81	2.57 (±0.01)	0.88a	55100
Humins	3.05	3.02	2.95	0.95 (±0.02)	0.91a	80500
<i>Upstream samples</i>						
Whole sediment	2.60	2.58	2.52	0.83 (±0.01)	0.92a	29700
Humic acid	2.85	2.81	2.76	2.55 (±0.01)	0.91a	50100
Humins	2.89	2.85	2.75	0.97 (±0.02)	0.86a	45900

obtained for all sorbents. Therefore, single-point (concentration-dependent) K_{OC} values were calculated for both solutes at reduced concentrations of 0.05, 0.1 and 0.5. Phenanthrene K_{OC} values obtained for the whole sediments were within the range of values reported for sediments (Chiou et al., 1998; Jonker et al., 2003), but were slightly lower than the values reported for $C_e/S_w = 0.5$ by Ran et al. (2002) for river sediments from China. The K_{OC} values for the HAs were within the range reported for soil HAs (Yuan and Xing, 2001) but were lower than the values reported for black shale HAs (Salloum et al., 2002). Our recorded K'_F OC values for both sorbents were in the range of values reported for soils (Carmo et al., 2000) and river sediments (Ran et al., 2002).

The overlapping isotherms of the two studied PAHs (on a C_e/S_w -normalized basis, Fig. 3) for the whole sediment samples suggest that both solutes were sorbed to these sorbents by the same mechanism and probably onto the same domain in each sorbent. However, a larger deviation between the isotherms of phenanthrene and naphthalene was observed for the HA samples, and between the sampling sites for the humin samples. This suggests that the upstream and downstream sorbents differ in their sorption capabilities and furthermore, that the sorbates may have been taken up by different domains within the same sorbent.

The naphthalene K'_F OC data of all sorbents from the downstream site exhibited higher values than the corresponding upstream samples. The same trend was observed for phenanthrene, except with the HAs from both sites, which exhibited similar values. It is important to note that the K'_F OC values of the downstream whole sediment and humin samples were about twice the values for their upstream counterparts. For phenanthrene, the K'_F OC values of the different SOM fractions can be arranged as follows: humin > HA > whole sediments. For naphthalene, the K'_F OC values of the sorbents from the downstream site showed the same trend, but for the upstream site the sorbents are arranged as HA > humin > whole sediment. It is worth noting that the differences between the K'_F OC values of the upstream and downstream HAs were relatively low (<10%) considering the significant differences obtained between the whole sediments and between the humin samples from the two sites. These findings suggest similar sorptive properties for the two HAs (although they exhibit different distributions of carbon functionalities), but different sorptive capacities for the whole sediment and humin samples from the two sites.

High sorption affinities were exhibited by the humin samples, even though they are composed of less aromatic structures than the corresponding HAs. Moreover, the downstream HA which was characterized by the highest aromaticity level (59%) exhibited only 10%

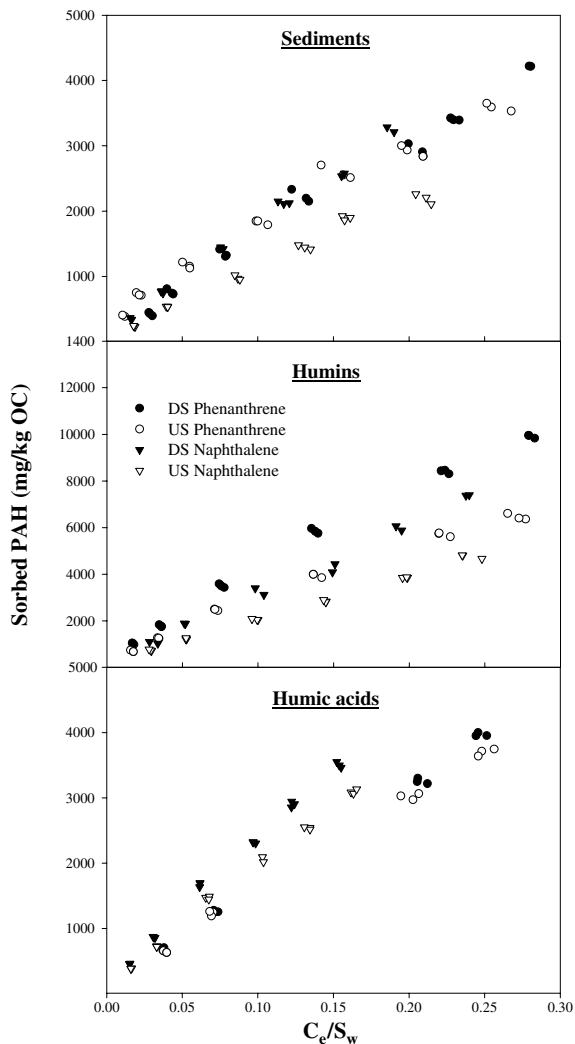


Fig. 3. Sorption isotherms of phenanthrene and naphthalene by downstream (DS) and upstream (US) whole sediment, humic acid and humin samples.

higher K'_F OC values for naphthalene, and similar values for phenanthrene, relative to the upstream HA, which showed a significantly lower aromaticity level (43%). These data confirm the notion that sorption affinity does not solely depend on the level of aromatic domains in the sorbent. Correspondingly, Mao et al. (2002b) suggested that PAH partitioning into amorphous aliphatic domains controls their sorption by SOM. In our study, the phenanthrene sorption isotherms with the humin samples exhibited non-linear characteristics, suggesting that partitioning was not governing the sorption interactions. The humin samples were also characterized by a crystalline $(CH_2)_n$ domain—a 33-ppm peak in the ^{13}C NMR spectra (Sachleben et al., 2004). The paraffinic crystalline domain is expected to facilitate non-linear

Langmuir-type surface adsorption of the PAHs, probably onto the surface of the nanocrystals. Gunasekara and Xing (2003) suggested that nonlinearity of PAHs sorption on to humin could be explained by the interactions of PAHs with complexes of mineral matter with amorphous or crystalline carbon paraffinic matrix. This kind of aliphatic structures (complexed or non-complexed with mineral matter) are probably present in the Kishon River humin fractions. In contrast to the non-linear sorption behavior obtained with the humin samples, more linear sorption isotherms were found with the HAs, which exhibited a characteristic mobile $(CH_2)_n$ peak at 29 ppm in the NMR spectra. This mobile paraffinic region is expected to assist with the linear partitioning of the solute.

The higher sorption coefficients observed for the downstream sediment are in agreement with its higher aromatic content relative to the upstream sediment (24% vs. 15%, respectively). However, the higher aromaticity of this sample did not result in lower N values. Similar to the humin spectra, the spectra of the whole sediment samples exhibited a crystalline polyethylene-like peak at 33 ppm. Therefore, we can suggest that both aliphatic and aromatic moieties of SOM contribute to PAH sorption and, based on their structural conformation, both can contribute to the non-linear sorption behavior. In our study, the crystalline aliphatic-mineral complexes may be governing the non-linear behavior.

3.3. Desorption

Sorption reversibility provides additional information on the sorbate–sorbent interactions, as well as insight into the structural properties of the sorbent. The sorption–desorption isotherms for phenanthrene and naphthalene are presented in Figs. 4 and 5, respectively. All desorption isotherms for phenanthrene show hysteresis. The most significant hysteresis was observed for the whole sediment samples, where desorption decreased with decreasing phenanthrene loading. At high solute concentration, the sorbed phenanthrene molecules were more readily desorbed compared with the molecules sorbed at lower concentrations. Less pronounced hysteresis, which nevertheless followed a similar trend, was exhibited for the humin samples. The opposite trend was observed for the HAs: phenanthrene desorption decreased from low to high solution concentrations (solutes were readily released at low sorbed-phase concentration), resulting in an increase in sorption–desorption hysteresis at higher phenanthrene loading levels. An increased ratio of low- to high-energy occupied sorption sites results in increased desorption with increasing solute concentrations, as observed for the whole sediment and humin samples. This mechanism can explain the desorption trend observed for the whole sediment and humin samples, but not the opposite trend

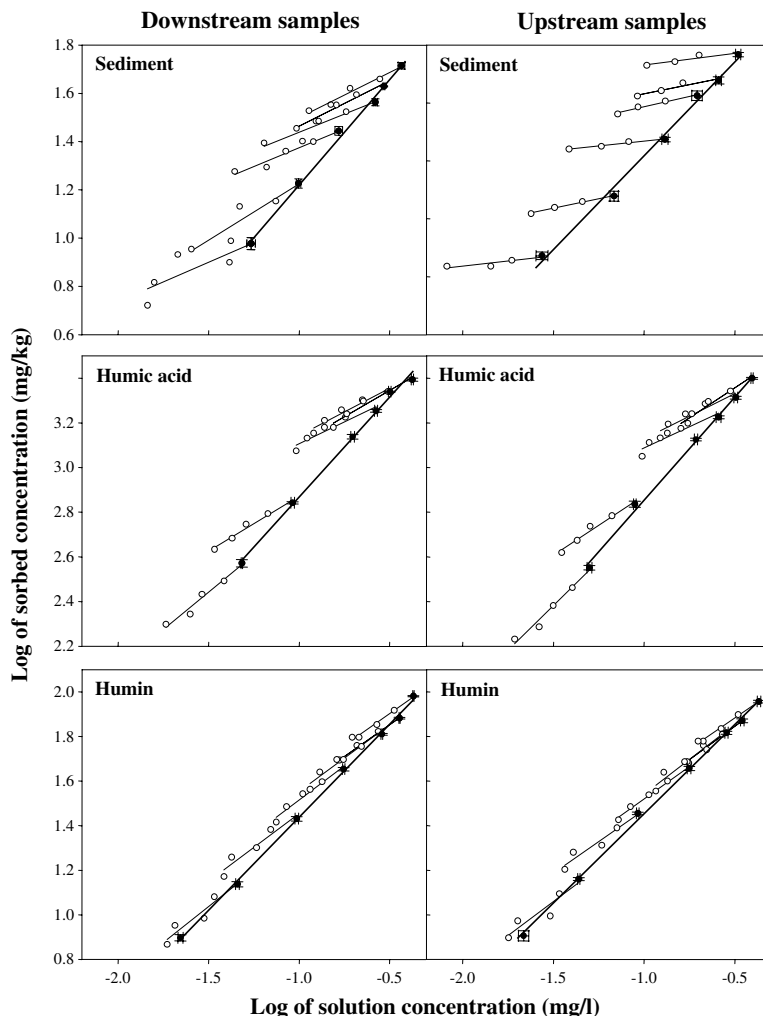


Fig. 4. Sorption (filled symbols) and desorption (open symbols) isotherms of phenanthrene by downstream and upstream whole sediment, humic acid and humin samples (downstream samples, left column; upstream samples, right column).

exhibited for phenanthrene with the HAs. We hypothesize that for the HAs at high phenanthrene levels, a concentration gradient forces the sorbed molecules to penetrate deeper into the HA micropores, resulting in deformation of the micropores which in turn leads to lower desorption. At low solute concentration, the gradient is less pronounced, and therefore fewer molecules deform the HA matrix, resulting in more readily reversible sorption behavior. Similar conclusions have been reported by Chefetz et al. (2004) for the sorption–desorption behavior of triazine herbicides with the same set of samples.

The sorption and desorption isotherms of naphthalene with the HAs showed no deviation, suggesting that this sorbate is less active in the meta-stability of the HA during sorption, thereby eliminating sorption–

desorption hysteresis. Although both sorbates belong to the same group of compounds (PAHs), it seems that internal micropores are deformed mainly by phenanthrene during sorption, such that desorption occurs from a different microenvironment. Similar conclusions were drawn by Braida et al. (2003) who observed a pronounced hysteresis in the sorption of benzene to charcoal materials. Moreover, the S_w -normalized sorption isotherms of the two PAHs with HAs did not overlap (Fig. 3), suggesting that the two compounds were not necessarily sorbed by the same domains. Similar observations of low desorption hysteresis of naphthalene with HA and significant sorption–desorption hysteresis for phenanthrene have been reported by Yuan and Xing (2001). These latter authors also concluded that naphthalene is primarily sorbed through partitioning. It is

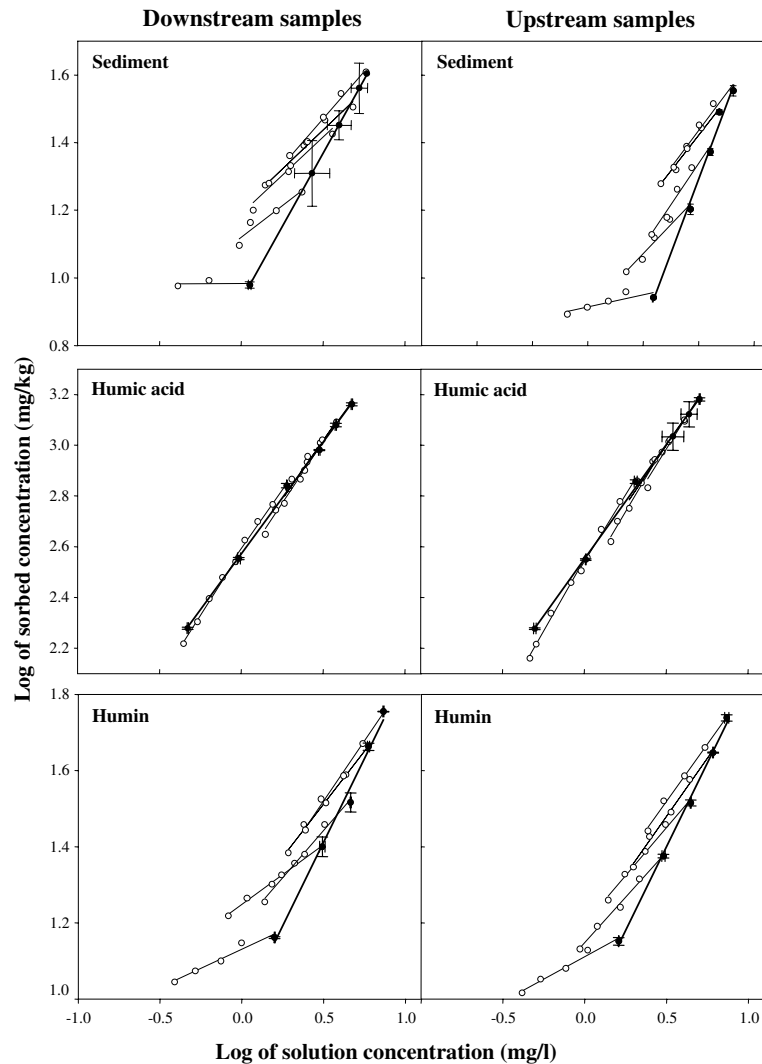


Fig. 5. Sorption (filled symbols) and desorption (open symbols) isotherms of naphthalene by downstream and upstream whole sediment, humic acid and humin samples (downstream samples, left column; upstream samples, right column).

worth noting that the two HAs exhibited similar sorptive capabilities (K'_F OC) and desorption behavior, probably due to their similar physico-chemical properties resulting from the isolation and purification procedure.

The upstream whole sediment sample exhibited the lowest N values (0.65), suggesting that partitioning was not governing the sorption mechanism. The desorption hysteresis observed for this sample was indeed very pronounced, as evidence by the low AHI values (AHI < 0.2) obtained for all phenanthrene concentrations. These values were lower than the AHI values recorded for the downstream sample (ranging between 0.37 and 0.43), suggesting that sorbed solutes were strongly bound to the upstream sediment, or that the structure

of this sorbent (both organic and inorganic) was significantly deformed during sorption, resulting in lower desorption. Similarly, naphthalene desorption from the whole sediment samples was relatively low, but exhibited higher AHI values than for phenanthrene at high solute loading levels (0.56 and 0.44 vs. 0.37 and 0.18 for the downstream and upstream samples, respectively). The humin samples exhibited non-linear isotherms, but for phenanthrene the desorption hysteresis was less pronounced than for the whole sediment samples. A higher level of desorption hysteresis was observed for naphthalene with these samples. This suggests that the non-linear sorption obtained with the humin samples does not necessarily result from a hole-filling mechanism

and could result from a surface interaction, as suggested by the presence of a crystalline paraffinic sorption domain (33-ppm peak in the ^{13}C NMR spectra; Fig. 2). The surface-sorbed molecules probably desorb more readily. Similar observations of non-linear sorption and negligible desorption hysteresis have been reported for phenanthrene with peat (Ran et al., 2002). Gunasekara and Xing (2003) also reported significant naphthalene desorption hysteresis for soil and humin samples and less pronounced hysteresis for a HA sample. Although the downstream humin and whole sediment samples exhibited significantly higher K'_F OC values than the corresponding samples taken from the upstream, the trends of desorption hysteresis for the humins and whole sediments were the same for both sites.

4. Conclusions

This study demonstrates that SOM isolated from upstream and downstream sites in the Kishon River exhibits different structural characteristics and that this diversity has a significant impact on the sorption affinity of PAHs, and probably of other HOCs as well. The ^{13}C NMR spectra and the sorption coefficients suggest that sorption occurs to both aromatic and aliphatic moieties of the SOM and that crystalline paraffinic domains probably contribute to the sorption non-linearity. The humin samples exhibited a higher degree of non-linearity than the HAs; this is assumed to be related to the more condensed and rigid structure of the former. The higher sorption affinities observed for all the organic fractions from the downstream sample are suggested to result from their relatively low content of polar domains (i.e., polysaccharides). Moreover, the higher sorption coefficient recorded for the downstream sediment is suggested to relate to its lower humin content (34% vs. 61% of the SOM in the upstream sediment). Although the humin sample exhibited high sorptive capacity, it is suggested that in the whole sediment, the humin exhibits less available sorption sites due to its association with minerals. Therefore, a larger content of humin results in a lower sorption potential of the upstream whole sample relative to that exhibited by the downstream sediment. The humin–mineral complex contributes to sorption non-linearity, and therefore the N values recorded for the sample with the larger humin content (upstream) were low. We may conclude that in bulk sediments, the HA fraction is responsible for the linear and fast sorption and the humin contributes to the sorption non-linearity. The humin fraction can be considered as an efficient sorbent for PAHs over a long period of time of interactions, allowing the sorbate molecules to diffuse into the humin macrostructure and the humin–mineral complexes. Finally, the low recorded desorption of PAHs from the whole sediments has to be taken into

consideration when evaluating the efficiency of remediation approaches for the river.

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