Final Report

Phenanthrene Adsorption and Desorption by Melanoidins and Marine Sediment Humic Acids

by

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Abstract

Sediments are major reservoirs of persistent petroleum contamination in marine environments. Petroleum hydrocarbons associate with the sediment organic matter, of which humic acids are an important constituent. This study examined the role that humic acids and their structures play in the kinetics and mechanisms of polycyclic aromatic hydrocarbon (PAH) interactions with sediments. Natural humic acids, with a wide range of properties, were isolated from Alaska coastal marine sediments. Melanoidins were synthesized and used as humic acid analogs. The humic acids were characterized by elemental and isotopic analyses, Fourier transform infrared spectroscopy, and cross-polarized magic angle spinning ^{13}C nuclear magnetic resonance spectroscopy. The humic acids were coated onto a standard montmorillonite clay, and the adsorption and desorption of phenanthrene was measured using a radiotracer.

Adsorption required about one week to reach steady state, indicative of slow diffusion of PAH within the humic acid. The composition of the humic acids had a greater effect on phenanthrene adsorption than their concentrations on the clay. Organic carbon normalized adsorption partition coefficients were closely correlated with the sum of amide and carboxylic carbons, a measure of the polarity of the humic acids, but were independent of initial phenanthrene concentration, indicating that the binding sites were unlimited and uniform in strength. This explains the fact that the initial adsorbed concentration of phenanthrene had no effect on subsequent phenanthrene adsorption.

Desorption of phenanthrene was not related to any of the humic acid structural characteristics measured. The initial desorption rate was linearly related to the initial adsorbed concentration, as expected for a diffusive process, and was negatively correlated with the carbon content of the humic acid coated clay. Under most conditions, desorption was complete after one to seven days; there was little evidence for irreversible adsorption.

Because of the substantial variability of adsorption and desorption behavior with organic matter characteristics, interactions of aromatic hydrocarbons with marine sediments cannot be predicted based on total organic matter concentration alone. Information on aspects of organic matter composition is needed in order to make accurate predictions.

Chapter 1. Introduction

Background

Hydrocarbon contamination of the coastal marine environment results from both acute and chronic anthropogenic sources. Catastrophic accidents such as the *Exxon Valdez* oil spill are widely publicized, while smaller spills, permitted discharges, and non-point sources, which in sum contribute a larger quantity of petroleum to the environment, receive much less public scrutiny. The fate and effects of petroleum are a complex function of both the chemical characteristics of the petroleum and the physical and biological characteristics of the marine environment that is contaminated. Although polycyclic aromatic hydrocarbons (PAH) (see p. 10 for a list of abbreviations and acronyms) make up only about 10% of petroleum, they are of special concern because, in addition to being resistant to biological and chemical breakdown under many conditions, they are toxic, mutagenic, and carcinogenic [Black et al. 1983; White 1986; Pahlman and Pelkonen 1987]. In addition to petroleum, combustion is an important and widespread source of PAH to the environment [Wakeham and Farrington 1980; Gschwend and Hites 1981].

PAH have very low solubilities in seawater [Shaw et al. 1989] and therefore tend to concentrate in sediments rather than remaining in the water column. The adsorption of PAH onto particulate matter

is an important process affecting their movement and fate in the environment. For example, the observed trapping of PAH and other hydrophobic pollutants in estuarine and coastal marine environments has been commonly attributed to adsorption to sediments. Bates et al. [1987] and Murphy et al. [1988] examined suspended sediment concentrations of PAH in a fjord-like estuary near Seattle, Washington. Bates et al. [1987] concluded that vertical rather than horizontal transport dominated, and Murphy et al. [1998] found that greater than 90% of sediment-bound PAH remained within the estuary. Although sedimentary contamination decreases markedly with time after a spill, due to biodegradation and other processes, aromatic hydrocarbons can persist for at least 20 years in contaminated sediments [Teal et al. 1992]. A likely factor in this persistence is a decrease in biodegradability associated with adsorption [Guerin and Boyd 1992; Luthy et al. 1997]. The effect of desorption on bioavailability has been noted in laboratory studies, in that freshly added hydrophobic organic compounds (HOC) are metabolized, while they persist in "aged" environmental samples, even though they contain the appropriate degrading microorganisms [Braddock and Richter 1998].

Biological uptake of petroleum occurs mainly from solution, leading to biodegradation, bioaccumulation, or toxicity [Landrum et al. 1985; Efroymson and Alexander 1995]. There is evidence that petroleum associated with sediments can be a major source of polycyclic aromatic hydrocarbons and other hydrophobic organic compound pollutants for marine and lacustrine organisms [reviewed in McElroy et al. 1989], and exposure of benthic invertebrates can result in subsequent transfer to higher trophic levels [Long et al. 1998; Thompson et al. 1999; Valette-Silver 1999; Krantzberg et al. 2000]. Harmful effects of contaminated sediments have been found for polychaetes [Knauss and Hamdy 1991; Weston 1990; Weston and Mayer 1998], bacteria [Moll and Mansfield 1991], amphipods [Daan et al. 1994], echinoids [Daan et al. 1994], and bivalves [Knauss and Hamdy 1991; Daan et al. 1994], among other groups of organisms. Strong binding of pollutants to sediments can result in lower bioavailability, and thus, lessened environmental toxicity [Weissenfels et al. 1992]. On the other hand, weak and reversible binding can result in greater dispersal and availability of pollutants, and therefore higher effective toxicity.

Many studies have found non-equilibrium (or rate-limited) adsorption of organic chemicals, including aromatic hydrocarbons and hydroxy- and carboxy-substituted aromatic compounds, by sediments and soils [Brusseau et al. 1991; Hatzinger and Alexander 1995]. Specifically, desorption is often slower than adsorption and is biphasic, with the rate decreasing over time [Brusseau et al. 1991; Isaacson and Frink 1984]. Henrichs et al. [1997] reported that Lower Cook Inlet sediments strongly adsorbed phenanthrene, naphthalene, and benzene, and that this adsorption was not completely reversible using their experimental conditions. Their desorption experiments were carried out for a maximum of three days and used water:particle concentration ratios equal to those in the adsorption experiments. They recognized that adsorption could be reversible under more favorable conditions. For example, Means [1995] found that pyrene adsorption by sediments was reversible, but he exhaustively eluted sediments with seawater, which would allow even slow desorption of strongly adsorbed hydrocarbons to proceed to completion. Observations of slow or apparently irreversible adsorption are most consistent with slow diffusion of the hydrocarbons into a three-dimensional organic structure; reversal of this process would also be slow [Brusseau et al. 1991; Isaacson and Frink 1984]. Although adsorption of aromatic hydrocarbons at several types of sites (with varying partition coefficients) on the particle surface did not explain the observations as well, this remains a possible interpretation [Henrichs et al. 1997].

Another observation which is not consistent with a simple, reversible adsorption process is that partition coefficients (K_p) sometimes decrease with decreasing particle concentrations, an effect that could be due to binding of hydrocarbons by dissolved or colloidal organic matter [Voice and Weber 1985]. Complexation of nonpolar organic compounds by dissolved or colloidal organic matter in soil solutions or sediment pore waters increases their mobility [Brownawell and Farrington 1986; Chin and Gschwend 1992; Hebert et al. 1993]. Bacterial extracellular polymers are one category of soluble compounds that have been shown to enhance pore water transport of phenanthrene [Dohse and Lion 1994].

Within sediments, PAH associate with organic matter and organic coatings of mineral particles of low polarity [Luthy et al. 1997]. The adsorption of hydrophobic compounds by sediments and soils is positively correlated with their organic matter content [Means et al. 1980; Schwarzenbach and Westall 1981; Shaw and Terschak 1998]. The extent of the association is known to vary depending on the character of the organic matter present [Means et al. 1980; Garbarini and Lion 1986]. Adsorption of aromatic hydrocarbons is positively correlated with the nonpolar-to-polar functional group ratio [Garbarini and Lion 1986; Rutherford et al. 1992] and the proportion of the organic structure that is composed of aromatic rings (aromaticity) [Gauthier et al. 1987]. This specific organic matter–PAH association appears to result from weak dipole interactions between aromatic rings of the PAH and similar rings which are part of many organic compounds, particularly those derived from lignins and related materials of woody terrigenous plants [Chin et al. 1994]. Terrigenous organic matter has, on average, greater aromaticity and lower oxygen content (polarity) than marine sediment organic matter, which would tend to increase the affinity for aromatic hydrocarbons. Adsorption of phenanthrene on natural soils is also related to the extent of diagenetic alteration of soil organic matter [Young and Weber 1995].

Humic acid is the fraction of naturally occurring dissolved, sedimentary, or soil organic material that is soluble in aqueous base but insoluble in aqueous acid [Parsons 1988]. Humic acid associates strongly with other organic molecules, including organic pollutants [Piccolo 1988; Karickhoff and Morris 1985; Karickhoff et al. 1979]. Despite their similarity in solubility behavior, soil and marine sediment humic acids differ in structure and reactivity [Sastre et al. 1994], reflecting the structural characteristics of the original detrital organic material as well as the extent and pathways of biological and chemical transformation. Terrestrial humic material includes structural components derived from lignin, a component of all vascular plants, but not algae or other nonvascular plants. The sources of marine humic acid are generally understood, although many of the specific transformation processes leading to these materials are not. Organic material is released to the marine environment mainly by plankton, and by macroalgae in some coastal areas. Once in the environment, most of these materials are consumed as food by detritivores and bacteria [Fenchel and Blackburn 1979]. However, it appears that a fraction undergoes chemical condensation reactions [Tissot and Welte 1978] in which the reactive portions of the molecules combine, usually without enzymatic control. This gradually leads to large organic molecules with few reactive sites and low biodegradability. An alternate hypothesis on the origin of humic substances is that they represent a largely unmodified residue of the decomposition process, composed of certain natural products of organisms that are inherently resistant to decay [DeLeeuw and Largeau 1993].

Lignin degradation products can react with proteins and amino acids to form humic substances [Flaig 1964], and evidence suggests that natural humic substances can also be produced by condensation reactions between reducing sugars and free amino acids [Maillard 1913; Enders and Theis 1938; Hodge 1953; Abelson and Hare 1971]. The evidence includes chemical similarities between natural humic substances and sugar–amino acid condensation products (melanoidins) produced in the laboratory [Hoering 1973; Ertel and Hedges 1983]. Also, in marine environments, carbohydrates, because of their much greater abundance, are more likely precursors of humic substances than lignin [Nissenbaum and Kaplan 1972; Hedges and Parker 1976].

Ishiwatari [1985] found that artificial kerogen, a highly refractory product of further condensation and other transformations of humic substances, formed rapidly in a reaction between glucose and casein. Yamamoto and Ishiwatari [1989] hypothesized that proteins are the more probable reactants with carbohydrates than free amino acids in the natural environment. Their kinetic study indicated that kerogen could form in 11 years at 20°C and 140 years at 5°C, not unrealistic for the natural environment. Other investigations show substantial similarities between humic substances synthesized from a variety of starting materials and naturally occurring humic substances [Haider et al. 1975; Martin and Haider 1980; Gilam and Wilson 1985; Taguchi and Sampei 1986]. Using cross-polarized magic angle spinning [13]C

nuclear magnetic resonance (CPMAS/^{13}CNMR), Ikan et al. [1990] found that melanoidins synthesized with higher initial proportions of sugar than amino acids yielded products with considerably greater aromaticity compared with those prepared from higher proportions of amino acids.

Although there have been a number of investigations of the role of sediment organic matter in aromatic hydrocarbon adsorption, there is reason to believe that these are not entirely applicable to Alaska sediments. The terrestrial vegetation that supplies a substantial fraction of the organic matter to coastal sediments is substantially different from that in temperate climates, especially on the North Slope of Alaska. Decomposition processes, which affect the properties of sediment organic matter, are influenced by lower temperatures and greater seasonality of organic matter inputs. The physically-weathered lithogenic minerals of high-latitude sediments probably have different adsorptive properties from those derived from chemical weathering regimes, potentially leading to differences in the type and quantity of natural organic matter adsorption to the sediment surface, which is thought to be an important mechanism of sediment organic matter preservation [Hedges and Keil 1995].

The following hypotheses were tested:

1. Aromatic hydrocarbon adsorption that was apparently irreversible in the experiments of Henrichs et al. [1997] and Braddock and Richter [1998] is reversible with longer desorption times. The kinetics of desorption largely controls the persistence of petroleum-derived aromatic hydrocarbons in sediments.

2. Interactions of aromatic hydrocarbons with sediment organic matter are responsible for adsorption that appears to be irreversible, at least under some conditions.

   • Diffusion into the three-dimensional structure of organic matter slows desorption.

   • Binding to a variety of adsorption sites with different partition coefficients causes differences in the apparent, experimental partition coefficient under conditions of adsorption and desorption.

3. Variations in organic matter properties influence the rate and extent of adsorption and desorption processes. In particular, there is a direct correlation between the aromatic character of sediment humic acid and the adsorption partition coefficient of phenanthrene.

   • Model organic substances similar to those occurring in sediments, but with well-controlled composition and properties, will show a systematic relationship between adsorption and desorption properties and organic structure.

   • The aspects of organic structure identified as important to adsorption properties using model compounds will also show a systematic relationship to adsorption and desorption of aromatic hydrocarbons by natural sediment organic matter.

4. Previous phenanthrene adsorption of sediments affects subsequent adsorption.

Both natural humic acids representing a wide range of organic matter properties and synthetic humic acids (melanoidins) were used in the experiments. Melanoidins were used because of the ability to control various aspects of their structural components during synthesis, such as the degree of aromatic constituents, and their initial lack of PAH.

Included within this report are three manuscripts that address the major hypotheses of this investigation. The first (Chapter 2), "Effects of Humic Acid Properties on Phenanthrene Adsorption", looks closely at PAH partition coefficients and how they are related to the molecular structures of organic coatings. The second manuscript (Chapter 3), "Phenanthrene Adsorption to Mineral-Bound Humic Acid: Kinetics and Influence of Previous Phenanthrene Adsorption", reports on investigations of the processes of PAH

adsorption—more specifically, the rates and the effect initial sediment phenanthrene concentration has on subsequent PAH adsorption. The final paper (Chapter 4), "Observed Desorption Kinetics of Phenanthrene from Mineral-Bound Humic Acids: Consequences of Conformational Changes", examines biphasic patterns seen in the rates of PAH desorption and offers explanations for incomplete desorption.

Site Descriptions

Sediment samples were taken from three distinct regions within Alaska (Figure 1). These regions included portions of the Beaufort Sea, Lower Cook Inlet, and Port Valdez. It was expected that characteristics of the sediments and the humic acids associated with those sediments would vary due to differences in physical and chemical weathering processes, terrestrial run-off, marine influences, and anthropogenic inputs within the selected areas.
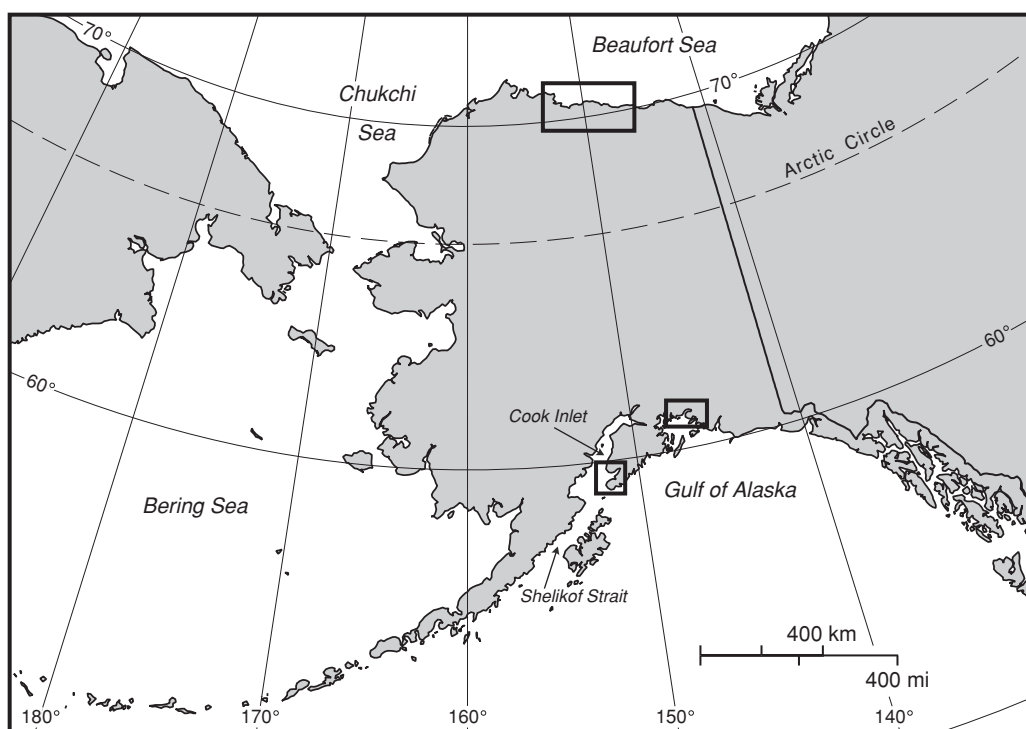
Figure 1. Sample regions within Alaska. The northernmost box is the Beaufort Sea region, the southernmost box is the Lower Cook Inlet region, and the easternmost box is the Port Valdez region.

Beaufort Sea

Offshore exploratory drilling in the Beaufort Sea began in 1973, with 15 exploratory wells drilled by the end of 1981 [Norton and Weller 1984]. A total of 57 wells had been drilled in the Alaskan Beaufort Sea by 1986 [Boehm et al. 1987]. The sample locations (Figure 2, Table 1) were originally selected for a trace metal contaminant study under the Outer Continental Shelf Environmental Assessment Program (OCSEAP) [Crecelius et al. 1991]. Naidu et al. [2001] also used these sites in a study of trace metal and hydrocarbon contamination.

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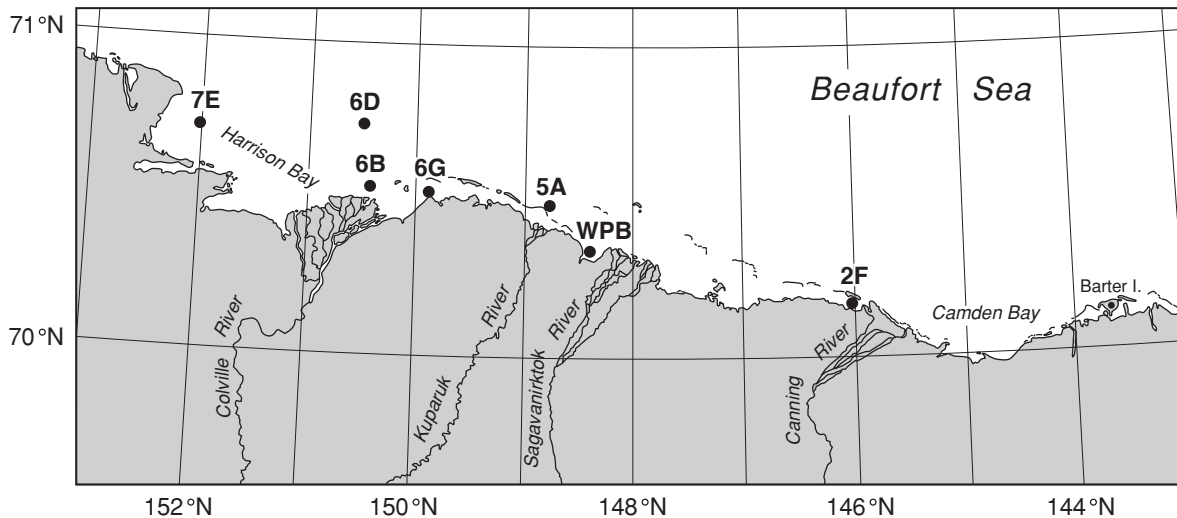
Figure 2. Sample sites within the Beaufort Sea region.

Table 1. Sample sites – Beaufort Sea region. Site denoted with an asterisk (*) indicates sample used in the adsorption and desorption experiments.

Station	Latitude (N)	Longitude (W)	Depth (m)
2F	70° 10.3′	146° 02.0′	1.9
5A*	70° 29.7′	148° 46.0′	11.4
6B	70° 33.4′	150° 24.6′	5.5
6D	70° 44.9′	150° 28.5′	18.4
6G	70° 31.3′	149° 53.9′	2.1
7E	70° 43.6′	152° 04.4′	3.3
WPB	70° 20.6′	148° 23.2′	2.5

The bordering terrestrial coastal plains consist of nearshore marine, fluvial, and aeolian deposits of mid- to late-Quaternary age [Black 1964]. The uppermost soils of the seasonal thaw layer, ranging from 0.5 to 2.5 m in thickness, are made up of silts and fine sands and often have high organic matter content, including both finely divided material and larger plant fragments [Everett and Parkinson 1977]. Tundra vegetation is low in species diversity. The lichens *Collema fuscovirens* (present nomenclature; *C. tunaeforme* in the referenced report), *Evernia perfragilis*, and *Fulgensia bracteata*, and the vascular plants *Carex atrofusca*, *C. membranacea* and *C. misandra* are common [Webber and Walker 1975]. Average air temperatures at Barter Island range from 4.4 °C in July to –28.6 °C in February [Brown et al. 1975]. The ground is frozen to depths greater than 625 m [AEIDC 1975] and only surface thawing (15 cm to 1 m) occurs in the summer. Nearshore bottom water averages –1.3 °C and the sediment temperatures in waters shallower than 2 m range between –2.2 °C and –4.6 °C [Reimnitz and Barnes 1974].

The input of sediments is highly seasonal. In spring the large quantity of water tied up in snow is released over a short period. Approximately 80% of the total discharge into the Beaufort Sea occurs in June via the

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Colville, Kuparuk, Sagavanirktok, and Canning rivers [Sharma 1979]. In summer, coastal bluffs suffer thermoerosion due to melting permafrost and are a locally important source of terrigenous material for coastal sediments. Sedimentation on the shelf is controlled by wave- and current-related processes. There is a general westward movement of sediment resulting from the nearshore current [Sharma 1979] driven by the prevailing easterly winds. Sea ice covers the shelf from mid-September through early July [Sharma 1979]. Ice-related sedimentary processes occur during the 8–10 months of shorefast ice in winter, but sediment transport during ice cover is minimal [Sharma 1979]. The thickness of Recent sediments on the shelf is generally <5 m [Reimnitz and Barnes 1974]. Surface sediments are generally poorly sorted gravel, moderately sorted silt and sand, and well-sorted clays. Naidu and Mowatt [1974] found that the fine clay fraction consists mostly of illite (56–69%), with smaller amounts of chlorite (14–30%) and kaolinite (5–10%), and trace amounts of smectite (<9%).

Lower Cook Inlet

Offshore oil exploration and production in Cook Inlet (Figure 3) have occurred since the mid-1960s. Since construction of the Trans Alaska Pipeline, tankers have carried Prudhoe Bay crude oil from Port Valdez to refineries located near Kenai. In Lower Cook Inlet, merchant and fishing vessels are sources of small but constant inputs of fuel and combustion products. Additional hydrocarbons come from erosion of coastal and submarine coal outcrops and natural oil seeps [Shaw and Wiggs 1980]. The sampling locations in Lower Cook Inlet are given in Figure 4 and Table 2. The samples were all collected from the intertidal zone near mean low-low water.
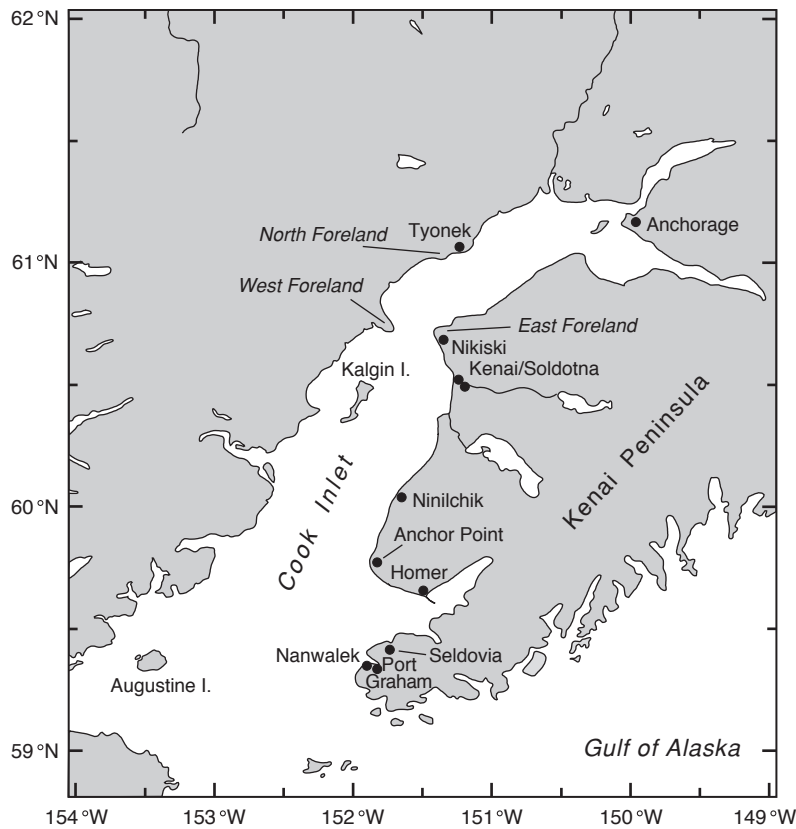
Figure 3. Cook Inlet.
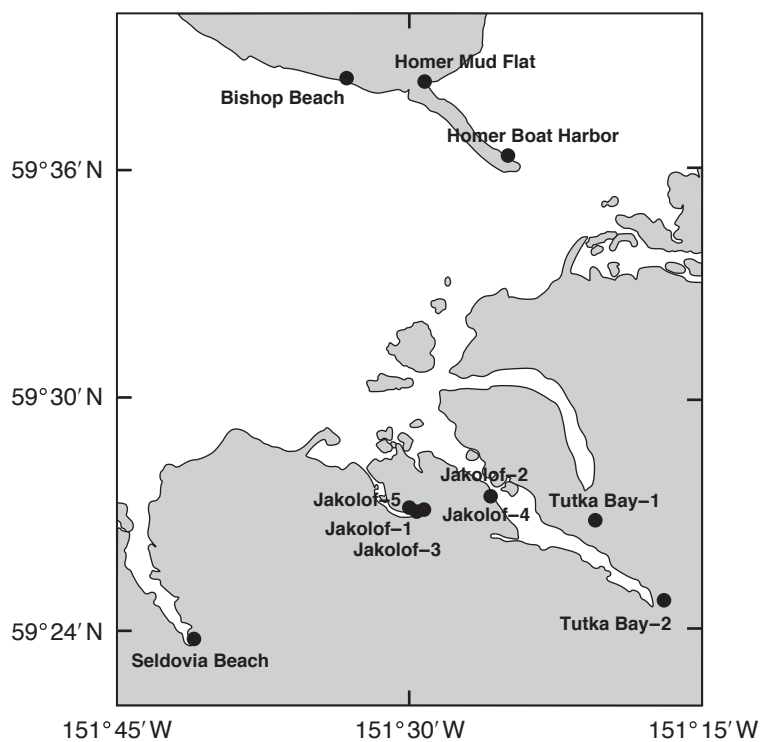
Figure 4. Sample sites within the Lower Cook Inlet region.

Table 2. Sample sites – Lower Cook Inlet region. Sites denoted with an asterisk
(*) indicate samples used in the adsorption and desorption experiments.

Station	Latitude (N)	Longitude (W)
Bishop Beach	59° 38.3′	151° 33.3′
Homer Boat Harbor* (HBH)	59° 36.3′	151° 25.0′
Homer Mud Flat	59° 38.3′	151° 29.3′
Jakolof-1	59° 27.1′	151° 29.6′
Jakolof-2 (JB2)	59° 27.1′	151° 29.3′
Jakolof-3	59° 27.1′	151° 29.6′
Jakolof-4	59° 27.1′	151° 29.3′
Jakolof-5	59° 27.1′	151° 29.7′
Seldovia Beach	59° 23.8′	151° 41.0′
Tutka Bay-1	59° 26.8′	151° 20.5′
Tutka Bay-2* (TB2)	59° 24.8′	151° 17.0′

Feely et al. [1980] and Larrance and Chester [1979] studied the distribution and dynamics of Cook Inlet sediments. Concentrations of suspended matter, largely rock flour input by streams draining surrounding glaciers, are high in upper Cook Inlet, ranging from about 50 to 100 mg L^{-1} near the Forelands to 1 g L^{-1} near the mouths of some rivers. These materials tend to have low organic content, 0.5 to 1% by weight. Suspended sediment concentrations in Lower Cook Inlet are much lower, often near the 1 mg L^{-1} typical of the adjacent Gulf of Alaska waters. The organic content of suspended particles is higher than in the upper inlet, averaging 4% in surface waters, due to seasonally high phytoplankton productivity and to fluvial inputs of terrigenous organic matter. The change in suspended sediment concentration does not appear to be largely due to deposition in the central area of the inlet. Feely et al. [1980] theorized that much of the sediment is either carried out into Shelikof Strait or deposited in small embayments along the coastline. There are also substantial cross-channel gradients in suspended sediment concentrations, which are generally lower on the eastern side due to water circulation patterns. The available information suggests that any sediments contaminated by petroleum in the upper or lower sections of Cook Inlet might ultimately be deposited in bays of the lower inlet or outside the inlet.

Port Valdez

Port Valdez is the terminus of the Trans Alaska Pipeline, where major oil-related activities have been ongoing since 1977. In addition to the oil terminal operations, tanker movements, merchant shipping, and fisheries activities all contribute petroleum to the marine environment [Hameedi 1988]. Sampling locations for this study in Port Valdez (Figure 5 and Table 3) are a subset of sites originally selected for initial environmental impact studies and long-term monitoring of petroleum operations within the area [Feder and Shaw 1996].
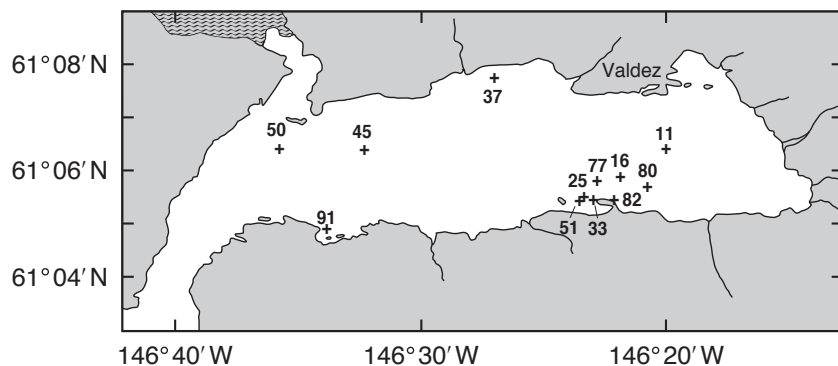
Figure 5. Sample sites within the Port Valdez region.

The region is characterized by glaciated, steep, high mountains (150 to 1000 m) which create a fjord that is 21 km long and 4.5 km wide. Port Valdez is a flat-bottomed, steep-sided, glacially-carved trough, with two sills near the mouth of the port [Feder et al. 1976]. Surface waters range from less than 2.5 °C in the winter to greater than 11 °C in the summer, but temperatures below 75 m remain in the 3 to 6 °C range. Typical precipitation in the area is in on the order of 158 cm yr^{-1} [Hood et al. 1973], causing surface salinities to be extremely low in the summer (<1.0‰), but during the winter, freezing air temperatures and limited freshwater runoff allow salinities to increase to about 32‰ and result in mixing of the entire water column within Port Valdez.

Table 3. Sample sites – Port Valdez region. Sites denoted with an asterisk (*)
indicate samples used in the adsorption and desorption experiments.

Station	Latitude (N)	Longitude (W)	Depth (m)
PV11	61° 06.4′	146° 20.0′	198
PV16	61° 05.9′	146° 21.8′	239
PV25*	61° 05.5′	146° 23.3′	73
PV33	61° 05.4′	146° 23.1′	55
PV37	61° 07.7′	146° 26.9′	51
PV45	61° 06.4′	146° 32.3′	241
PV50	61° 06.4′	146° 35.7′	241
PV51	61° 05.4′	146° 23.5′	79
PV77	61° 05.8′	146° 22.8′	231
PV80	61° 05.7′	146° 20.7′	79
PV82*	61° 05.4′	146° 22.3′	79
PV91	61° 04.9′	146° 33.9′	45

Much of the sediment within tidal flats, outwash deltas, and alluvial fans consists of poorly sorted debris ranging from gravels to muddy sands, with anoxic conditions existing 3 cm below the surface of the mud flats. The sedimentary clay minerals are composed mainly of chlorite and illite which have undergone little in the way of chemical weathering [Feder et al. 1976].

Summary

This report describes an experimental investigation of the adsorption and desorption of PAH from Lower Cook Inlet, Port Valdez, and inner Beaufort Sea shelf sediments, including an examination of the reasons that desorption of aromatic hydrocarbons from sediments is often slow and incomplete. The work is built upon that of Henrichs et al. [1997], who investigated PAH adsorption and desorption by Lower Cook Inlet sediments, and Braddock and Richter [1998], who studied the biodegradation of PAH in seawater–sediment systems from Lower Cook Inlet. The goal of the research was to improve the ability to predict the persistence and fate of these compounds in slightly- to moderately-contaminated sediments.

Acronyms and Abbreviations

CHN	carbon–hydrogen–nitrogen
CPMAS/^{13}CNMR	cross-polarized magic angle spinning ^{13}C nuclear magnetic resonance
DOM	dissolved organic matter
dpm	disintegrations per minute
E_4/E_6	ratio of absorbances at 465 and 665 nm
EPA	Environmental Protection Agency
FTIR	Fourier transform infrared
GC	gas chromatography
HBH	Homer Boat Harbor
HOC	hydrophobic organic compounds
IRMS	isotope ratio mass spectrometry
K_{OC}	organic carbon normalized partition coefficient
K_p	partition coefficient
MCT-B	mercury/cadmium/telluride detector at the 400–4000 cm^{-1} wavenumber range
N/C	nitrogen to carbon ratio
NIST	National Institute of Standards and Technology
NMR	nuclear magnetic resonance
OC	organic carbon
PAH	polycyclic aromatic hydrocarbons
PCB	polychlorinated biphenol
PCP	pentachlorphenol
PDB	PeeDee Belemnite (reference standard for δ^{13}C values)
TARO	total aromatics
TOC	total organic carbon
UHP-N$_2$	ultra high purity nitrogen gas

Chapter 2. Effects of Humic Acid Properties on Phenanthrene Adsorption[1]

Abstract

This study examined the role humic acid and its structure plays in the adsorption of organic pollutants in coastal sediments. Humic acids were extracted from intertidal and subtidal Alaska coastal marine sediments, representing a variety of organic matter sources. Melanoidins, used as model humic acids, were synthesized via the Maillard reaction between glucose and bovine casein. The natural and synthetic humic acids were characterized by elemental and isotopic analyses, as well as ultraviolet/visible, Fourier transform infrared, and cross-polarized magic angle spinning ^{13}C nuclear magnetic resonance spectroscopies. Adsorption of phenanthrene to the humic substances was investigated using a radiotracer. Concentrations of humic materials on clay were not related to partition coefficients (K). The percent nonpolar carbon of humic material, but not aromaticity alone, was weakly correlated to the organic carbon normalized K (K_{OC}). However, K_{OC} was more closely negatively correlated with the sum of amide and carboxylic carbons, a measure of the polarity of the humic acids.

Introduction

Aromatic hydrocarbons make up only about 10% of the complex mixture of compounds in petroleum, but are a special concern as environmental contaminants, because they are among the most toxic, mutagenic, and carcinogenic constituents [Black et al. 1983; White 1986; Pahlman and Pelkonen 1987]. They are also the most soluble constituents, and thus the most likely to be transported in solution, to affect organisms from the dissolved phase, and to be affected by adsorption–desorption reactions in the marine environment. However, in absolute terms, aromatic hydrocarbons have low to very low aqueous solubilities and high affinities for surfaces in aquatic ecosystems [Farrington and Westall 1986]. Their adsorption is usually not rapidly or completely reversible, indicating that this process is probably a factor in polycyclic aromatic hydrocarbon (PAH) retention by contaminated sediments [Brusseau and Rao 1991; Hatzinger and Alexander 1995]. Adsorption may decrease the availability of contaminants to microbial degraders [Weissenfels et al. 1992; Manilal and Alexander 1991; Braddock and Richter 1998]. Sediments are important reservoirs for aromatic hydrocarbons in the marine environment [Wakeham and Farrington 1980; Gschwend and Hites 1981].

Weissenfels et al. [1992] concluded that biodegradability and biotoxicity of PAH were decreased by adsorption and migration into an organic matter matrix. It has been suggested by some that the concentration is less important in determining the pollutant's biological hazard than is the ratio of PAH to total organic matter [Hansen et al. 1991]. Proponents of this hypothesis reason that there is a characteristic partition ratio of PAH in organic matter, and only when this is exceeded do substantial amounts of pollutant become bioavailable. This hypothesis was the basis for the U.S. Environmental Protection Agency (EPA) to write "Proposed Sediment Quality Criteria for the Protection of Benthic Organisms", in which acceptable concentrations of pollutants in sediments were related to the concentration of organic materials in those sediments [Hansen et al. 1991].

For uncharged organic pollutants, organic matter is considered the primary sorbent component [Karickhoff and Morris 1985]. The adsorption partition coefficient, K_p, increases with increasing organic content of sediments and soils [Means et al. 1980; Schwartzenbach and Westall 1981; Shaw and Terschak 1998]. Organic matter properties also influence adsorption. Adsorption of various aromatic hydrocarbons has correlated positively with the nonpolar–polar functional group ratio [Rutherford et al. 1992; Garbarini and Lion 1986] and aromaticity [Gauthier et al. 1987]. The mechanisms for binding of PAH to organic

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matter have not been completely elucidated [Ragle et al. 1997 and references therein]. Interactions between PAH and humic acids result, at least in part, from weak dipole interactions between aromatic rings of the PAH and those of humic acids, particularly humic acids derived from lignins and related materials of woody terrigenous plants [Chin et al. 1997; Chin et al. 1994]. The adsorption of neutral hydrophobic organic compounds (HOC) to organic matter is generally considered to involve rapid van der Waals type interactions [Brusseau and Rao 1991].

Organic matter, of which humic acid is a part, is a flexible, cross-linked, branched, amorphous, polyelectrolytic, polymeric substance within which organic pollutants can diffuse [Brusseau et al. 1991]. Schnitzer and Khan's [1972] theory is that humic acid is an open structure with hydrophobic cavities [Schlautman and Morgan 1993 and references therein]. Direct confirmation of the "porous" nature of organic matter has been reported [Brusseau et al. 1991 and references therein]. While the pores of sediment mineral particles are fixed and rigid, organic matter pores are dynamic and ephemeral [Brusseau et al. 1991]. The size, shape, and hydrophobicity of the pores within organic matter are sensitive to variations in solution chemistry, and, therefore, changes in the ability to bind HOC occur [Schlautman and Morgan 1993]. The hydrophobicity of PAH suggests that PAH association is governed by diffusion into nonpolar environments of organic matter [Gauthier et al. 1987; Ragle et al. 1997; Uhle et al. 1999].

A number of authors have reported evidence for irreversible adsorption of organic compounds to particles and organic matter [Brusseau and Rao 1991; Hatzinger and Alexander 1995; Karickhoff and Morris 1985; Brusseau et al. 1991; Carmichael et al. 1997; Kan et al 1994; Di Toro and Horzempa 1982; Pavlostathis and Mathavan 1992], but differ over the exact causes for the observations. Hypothesized mechanisms include adsorption to the particle's surface [Mingelgrin and Gerstl 1983], diffusion into tortuous particle micropores [Brusseau et al. 1991; Wu and Gschwend 1986; Steinberg et al. 1987], and diffusion into the organic matrix [Brusseau and Rao 1991; Karickhoff and Morris 1985; Brusseau et al. 1991; Schlautman and Morgan 1993; Kan et al. 1994]. Intraorganic matter diffusion is thought to be the most likely mechanism for HOC [Brusseau and Rao 1991; Brusseau et al. 1991]. Adamson [1990] suggests that irreversible adsorption is probably due to a mechanical or structural rearrangement of the adsorbent, that is, the matrix from which desorption takes place is different from that during adsorption.

This study was conducted to examine the role that humic acids play in the adsorption of PAH by the sediments of coastal marine environments. This chapter addresses the effects of humic acid structure and other characteristics on the extent and rate of phenanthrene adsorption. Both natural humic substances and an artificial analog, melanoidins [Gagosian and Stuermer 1977; Nissenbaum and Kaplan 1972; Hedges and Parker 1976], were investigated. These organic substances represent a wide range of properties potentially affecting associations with PAH.

Experimental Section

Sampling sites and sample collection
Samples were taken from three separate coastal locations in Alaska (Table 4). In Port Valdez, natural petroleum seeps [Page et al. 1996], oil terminal operations, tanker movements, general shipping, and fisheries activities all contribute petroleum to the marine environment [Hameedi 1988]. In Lower Cook Inlet, shipping and fisheries activities contribute petroleum and additional PAH come from natural oil seeps and erosion of coastal and submarine coal outcrops [Shaw and Wiggs 1980]. Although the Beaufort Sea is a site of petroleum exploration and extraction, the main contributors of PAH to the marine environment are non-anthropogenic sources such as natural oil seeps and tundra vegetation [Naidu et al. 2001; Yunker et al. 1991; Steinhauer and Boehm 1992; Yunker and MacDonald 1995].

Intertidal sediment samples from Lower Cook Inlet were collected in July 1995, July 1996, and May 1999. Sampling occurred during spring tides below the mean lower-low water level. Subtidal sediment samples were collected from the Port Valdez region in August 1996 using a Haps corer and from the Beaufort Sea region during September 1997 using a Kynar-coated van Veen grab sampler. Any overlying debris was removed and then sediment was collected from the oxic layer (upper 2 cm) with metal implements that had been heated to redness before use. All samples were stored until needed at –50 °C in pre-combusted glass jars.

Table 4. Site locations of sediments discussed in this study; n/a – not applicable, as Lower Cook Inlet samples were intertidal and collected during low tide.

Location	Station	Latitude (N)	Longitude (W)	Depth (m)
Port Valdez	PV25	61° 05.5′	146° 23.3′	73
Port Valdez	PV82	61° 05.4′	146° 22.3′	79
Lower Cook Inlet	HBH	59° 36.3′	151° 25.0′	n/a
Lower Cook Inlet	JB2	59° 27.1′	151° 29.3′	n/a
Lower Cook Inlet	TB2	59° 24.8′	151° 17.0′	n/a
Beaufort Sea	5A	70° 29.7′	148° 46.0′	11.4
Beaufort Sea	6G	70° 31.3′	149° 53.9′	2.1

Sediment organic matter and humic acid characterization

Table 5 lists the characteristics examined in the sediment organic matter and humic acids used in this study. The methods associated with each are described below.

Sediment organic carbon and nitrogen determination by combustion and isotope ratio mass spectrometry

Approximately 2 grams of each thawed sediment were weighed into pre-combusted glass vials and oven dried for 48 hours. The dry sediment was acidified with 1 N HCl and homogenized. Samples were redried and ground to a powder. The analyses of Port Valdez and Lower Cook Inlet sediments were performed by the MSI Analytical Lab (Marine Science Institute, University of California, Santa Barbara), which uses one of two automated CHN analyzers (CE 240 X and Leeman Lab CE 440). Orchard leaves (NIST [National Institute of Standards and Technology] standard reference material) and previously characterized marine sediments were the standards. Total organic carbon (TOC) and nitrogen analyses of the Beaufort Sea sediments and all humic acids were performed at the University of Alaska Fairbanks using a Finnigan MAT Delta Plus mass spectrometer with a Conflo II interface and a Carlo Erba elemental analyzer.

Table 5. The measured properties of sediment organic matter, natural humic acids, and synthetic humic acids evaluated in this study and the methods by which they were obtained. IRMS – isotope ratio mass spectrometry, GC – gas chromatography, CPMAS/^{13}CNMR – cross-polarized magic angle spinning ^{13}C nuclear magnetic resonance, N/C – nitrogen to carbon ratio, E_4/E_6 – ratio of absorbances at 465 and 665 nm.

Organic Constituent	Characteristic	Method
Sediment organic matter	% C	Combustion & IRMS
	% N	Combustion & IRMS
	N/C	Combustion & IRMS
	Phenanthrene	Extraction & GC
	Total aromatics	Extraction & GC
Humic acid	% Extractable humic acid	Gravimetric
	% C	Combustion & IRMS
	% N	Combustion & IRMS
	N/C	Combustion & IRMS
	δ^{13}C & δ^{15}N ratios	Combustion & IRMS
	E_4/E_6	UV/Visible spectroscopy
	% Aromaticity (carboxyl-free, aromatic carbon)	CPMAS/^{13}CNMR
	% Aliphatic carbon	CPMAS/^{13}CNMR
	% Oxygen bound alkyl carbon	CPMAS/^{13}CNMR
	% Carboxyl + amide carbon	CPMAS/^{13}CNMR
	% Carbonyl carbon	CPMAS/^{13}CNMR
	% Non-polar carbon (aromatic + aliphatic carbon)	CPMAS/^{13}CNMR
	% Polar carbon (O-alkyl + carboxyl + amide + carbonyl carbon)	CPMAS/^{13}CNMR
	Partition coefficient	Radiotracer

Sediment hydrocarbon analyses by extraction and gas chromatography

Hydrocarbon analyses of Port Valdez and Lower Cook Inlet sediment samples were done as described by Feder and Shaw [1996]. Beaufort Sea samples were analyzed by M.I. Venkatesan's laboratory at the University of California Los Angeles following a similar method [Naidu et al. 2001]. The sum of 18 individual PAH (naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, biphenyl, 2,6-dimethylnaphthalene, acenaphthene, fluorene, phenanthrene, anthracene, 1-methylphenanthrene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[e]pyrene, benzo[a]pyrene, perylene, and dibenz[a,h]anthracene) are reported as total aromatics (TARO) in µg PAH kg^{-1} dry sediment.

Humic acid extraction

Humic acid was obtained using the alkali (0.5 M NaOH) extraction procedure of Anderson and Schoenau [1983]. After extraction from approximately 30 g of wet sediment, humic acid was precipitated by the addition of 6 M HCl until a pH of 1.5 was obtained. The precipitated extract was allowed to stand for 15 minutes and was then centrifuged for 30 minutes at 14,000 g. The precipitated humic acid was

lyophilized at –85 °C for 24 hours. The resulting dry humic acid was stored at room temperature in a glass vial under N_2.

Synthetic humic acid preparation

Artificial humic acids were prepared in the laboratory by refluxing several ratios of glucose and bovine casein (1:1, 10:1, and 1:10) in buffered solutions for 24 to 48 hours as described by Yamamoto and Ishiwatari [1989]. The buffer (50%/30%/20%) was composed of 125 ml 0.1 M KH_2PO_4, 75 ml 0.1 M NaOH and 50 ml of glass-distilled water to give a final pH of 7.0. After the prescribed reaction time, the mixture was allowed to cool with stirring, then transferred to 250-ml Nalgene® centrifuge bottles and the artificial humic acid was isolated using the extraction procedure described in the previous paragraph.

UV/Visible spectroscopy

The ratio of absorbance at 465 and 665 nm (E_4/E_6 ratio) of the extracted humic acids was determined using ultraviolet/visible light spectroscopy. A Milton Roy Spectronic 21D UV/visible spectrometer was used to measure light absorbance characteristics of the humic acids. Humic acid (2–4 mg) was dissolved in 10 ml of 0.05 N $NaHCO_3$ [Chen et al. 1977] and light absorbance readings were taken.

FTIR spectra acquisition

Fourier transform infrared (FTIR) spectra were obtained using a Nicolet Magna 560 FT spectrometer with an infrared source, KBr beam splitter, and an MCT-B detector. Sixty milligrams of a ground mixture of 0.200 g KBr and 0.005 g humic acid were made into a pellet. Signals were averaged from 200 scans at a resolution of 0.121 cm^{-1}. Spectra were obtained between 4000 cm^{-1} and 400 cm^{-1} and processed against a background of KBr.

CPMAS/^{13}CNMR spectra acquisition

Cross-polarized magic angle spinning ^{13}C nuclear magnetic resonance (CPMAS/^{13}CNMR) spectroscopic data were obtained from the NMR Laboratory at Florida State University in Tallahassee using the standard methods described by Hatcher et al. [1981]. The NMR spectrometer was a Bruker/IBM WP200SY with a solid state accessory package. A 7-mm standard Doty Scientific multifrequency CPMAS probe was employed. Sample weights of approximately 225–300 mg were used and spun at 3.5–4.3 kHz. The frequency for ^{13}C on this instrument was 50.325 MHz. Five major regions of chemical shifts between 0 ppm and 300 ppm were assigned. These corresponded to carbons associated with aliphatic (0–50 ppm), aromatic (110–160 ppm), oxygen bound alkyl (50–110 ppm), carboxylic and amide (160–190 ppm), and carbonyl (190–240 ppm) functional groups [Malcolm 1990]. Carboxyl-free aromaticities were reported by subtracting the integrated area of carboxylic and amide carbon peaks from those assigned to the aromatic carbons. The nonpolar fraction was calculated by adding the fractions of aliphatic and aromatic carbons.

Adsorption experiments

Radiolabeled phenanthrene was used to examine adsorption [Henrichs et al. 1997]. All glassware and Teflon® liners used in this study were treated to remove any hydrocarbon contamination before use. Glassware was baked in a muffle furnace at 450 °C for at least 8 hours. Teflon® cap liners were soaked in chromic acid for 20 minutes and then rinsed 3 times with organic-free water. A stock solution was prepared by dissolving [9-^{14}C] phenanthrene (5–15 mCi $mmol^{-1}$; Sigma Chemical Co.) and nonlabeled phenanthrene in acetonitrile. After evaporation of the acetonitrile, artificial seawater was added to aliquots of the stock solution to produce 50, 300, and 700 µg L^{-1} phenanthrene solutions. Previous experiments within this laboratory have shown that for concentrations of phenanthrene ranging

from 10 to 750 μg L^{-1}, there was no loss of hydrocarbon due to evaporation or adhesion to the walls of the container [Henrichs et al. 1997]. In addition, all experiments had control vials containing no sediment.

Artificial seawater was prepared from organic-free water that had been glass distilled over a saturated solution of potassium permanganate. To each liter of water the following salts were added: 23.260 g NaCl, 10.636 g MgCl$_2$·6H$_2$O, 3.918 g anhydrous Na$_2$SO$_4$, 1.102 g CaCl$_2$, 0.664 g KCl, 0.192 g NaHCO$_3$, 0.096 g KBr, and 0.026 g H$_3$BO$_3$ [Lyman and Fleming 1940]. Also, 0.500 g HgCl$_2$ was added as an antibiologic agent.

A montmorillonite standard (A.P.I. # 26, 49 E 2600 from Clay Spur, Wyoming; Ward's Natural Science Establishment, Inc.) was ground for 2 minutes using a shatter box equipped with carbide rings. The resulting powder was passed through a 270 mesh (53 μm) sieve using a Ro-Tap® apparatus. Organic material was removed from the clay by oxidizing it with 30% hydrogen peroxide.

Humic acids were coated onto inorganic substrate for use in the adsorption experiments. Approximately 1 g of lyophilized humic acid was dissolved in 100 mL of organic-free water, maintained at a pH of 10 by additions of 0.5 M NaOH, and mixed under an atmosphere of ultra high purity nitrogen gas (UHP-N$_2$) for 3 to 7 days. The humic acid solution was then added to the washed clay and mixed for 24 hours. The suspension was transferred to a centrifuge bottle containing the salts resulting from the evaporation of an equal volume of artificial seawater and mixed for 48 hours, then centrifuged at 14,000 g for 2 hours and the supernatant discarded. A sample of the humic acid coated clay was dried and submitted for TOC analysis. The remaining humic acid coated clay was stored in a refrigerator at 5–10 °C in a container flushed with UHP-N$_2$.

Adsorption experiments began by weighing 0.1 g of wet, humic-coated clay into each of a number of 2-dram vials with Teflon® lined caps and adding 5 ml of a radiolabeled phenanthrene/seawater solution. After mixing for 15 seconds using a vortex mixer, the vials were placed on a table shaker at 150–200 rpm. After 14 days, the vials were centrifuged at 2400 g for 30 minutes. A 1.0 mL aliquot of each of the radiolabeled reaction solutions was removed and the ^{14}C activity was measured by liquid scintillation counting. Partition coefficients, K$_{OC}$, were reported as the ratio of adsorbed phenanthrene to dissolved phenanthrene, normalized to organic carbon (Equation 2–1).

$$K_{OC} = \left. \frac{\dfrac{100 - \dfrac{a}{b} \times 100}{c}}{\dfrac{\dfrac{a}{b} \times 100}{d}} \right/ f_{OC} \qquad (2\text{–}1)$$

where a is the measured dpm of the sample, b is the measured dpm of the control, c is the dry sediment weight of the sample, d is the solution volume, and f_{OC} is the sediment weight fraction of organic carbon.

Statistical treatments

A Microsoft® Excel 2000 spreadsheet was used to calculate linear correlation coefficients (r^2) between pairs of variables. The statistical significance of correlations was determined using a two-tailed t-test with ($n - 2$) degrees of freedom at both the 5% and 10% significance levels ($p = 0.05$ and $p = 0.10$, respectively) [Miller and Miller 1988; Mendenhall and Sincich 1996]. All correlations are reported at the $p = 0.05$ significance level unless otherwise noted.

Results

Humic acid properties

The $\delta^{13}C$ (PDB standard) of the extracted sediment humic acids averaged –24.00 ± 0.99‰ in Port Valdez, –19.82 ± 1.36‰ in Lower Cook Inlet, and –26.01 ± 0.72‰ in the Beaufort Sea. The $\delta^{15}N$ (air standard) of the extracted sediment humic acids averaged 6.46 ± 1.99‰ in Port Valdez, 7.71 ± 1.37‰ in Lower Cook Inlet, and 5.42 ± 2.21‰ in the Beaufort Sea.

Nitrogen/carbon ratios (N/C) of natural humic acids ranged from 0.026 to 0.14 with a mean of 0.088 ± 0.027; they were correlated with, but consistently lower than, those of the total sediment organic matter. The synthetic humic acids had greater N/C, ranging from 0.16 to 0.27 with a mean of 0.22 ± 0.041. The N/C of laboratory prepared humic acids increased as the casein/glucose in the reaction mixture increased.

Spectral results of CPMAS/^{13}CNMR showed that natural humic acids and melanoidins were similar (Figure 6). As indicated by ^{13}CNMR data, the carboxyl-free aromaticities ranged from 15 to 34% for natural humic acids and 10 to 18% for the synthetic humic acids. The percentage of carbon atoms involved in carboxyl and amide bonds ranged from 10 to 14% for natural humic acids and 16 to 22% for the synthetic humic acids. As expected, increasing N/C ratios corresponded to an increase in the relative proportions of carbon atoms associated with amide bonds ($r^2 = 0.90$, $t = 10.091$) (Figure 7). The trend was similar for natural and synthetic humic acids, although the natural humic acids were consistently lower in amide carbon and N/C. Increasing N/C ratios also correlated with a decrease in carboxyl-free aromaticity, but this trend was caused by the difference between natural and synthetic humic acids and did not exist within the natural humic acids. Negative correlations existed between aromaticity and the degree of polarity, as measured by N/C ($r^2 = 0.55$, $t = 3.649$), and fraction carboxyl and amide C ($r^2 = 0.44$, $t = 2.914$), but aromaticity did not correlate significantly with the aliphatic fraction ($r^2 = 0.05$, $t = 1.718$) in the humic acids of this study. E_4/E_6 ratios showed no relationship to the other measured properties of the humic acids, including carboxyl-free aromaticity ($r^2 = 0.10$, $t = 1.120$).

Fourier transform infrared spectra of the natural and synthetic humic acids were similar to each other [cf. Ertel and Hedges 1983], with some minor differences (Figure 8). All showed absorbance bands for hydrogen-bonded OH at about 3400 cm^{-1} [Ertel and Hedges 1983; Goh and Stevenson 1971; Stevenson and Goh 1971]; aromatic C–H stretch as a shoulder between 3100 and 3000 cm^{-1} [Silverstein et al. 1991]; aliphatic C–H stretch between 3000 and 2850 cm^{-1} [Ertel and Hedges 1983; Goh and Stevenson 1971; Stevenson and Goh 1971; Rubinsztain et al. 1984]; C=O stretch of aldehydes, ketones, and acids as a shoulder at 1710 cm^{-1} [Ertel and Hedges 1983; Rubinsztain et al. 1984; Kononova 1966]; amide linkages of proteins at 1650 cm^{-1} [Ertel and Hedges 1983; Goh and Stevenson 1971; Stevenson and Goh 1971]; C–O stretch of ethers, esters, and phenols at 1230 cm^{-1} [Ertel and Hedges 1983; Goh and Stevenson 1971; Stevenson and Goh 1971]; COO– stretching at 1532 and 1386 cm^{-1} [Stevenson and Goh 1971]; C–O stretch of carbohydrates at 1040 cm^{-1} [Ertel and Hedges 1983; Goh and Stevenson 1971; Stevenson and Goh 1971]; and possible NH_3^+ torsional vibrations at 530 and 470 cm^{-1} [Silverstein et al. 1991]. The Beaufort Sea 5A humic acid showed stronger absorption bands associated with ethers, esters, and phenols than the other natural and synthetic humic acids, including a sharp phenolic and alcoholic OH stretch at 3622 cm^{-1} [Silverstein et al. 1991]. The Lower Cook Inlet samples all showed pronounced absorption bands associated with amide linkages, while the same bands in other humic acids were less prominent. The synthetic humic acid, 1:10–24, produced a more defined peak in the aromatic C–H stretching band than any of the other humic acids.

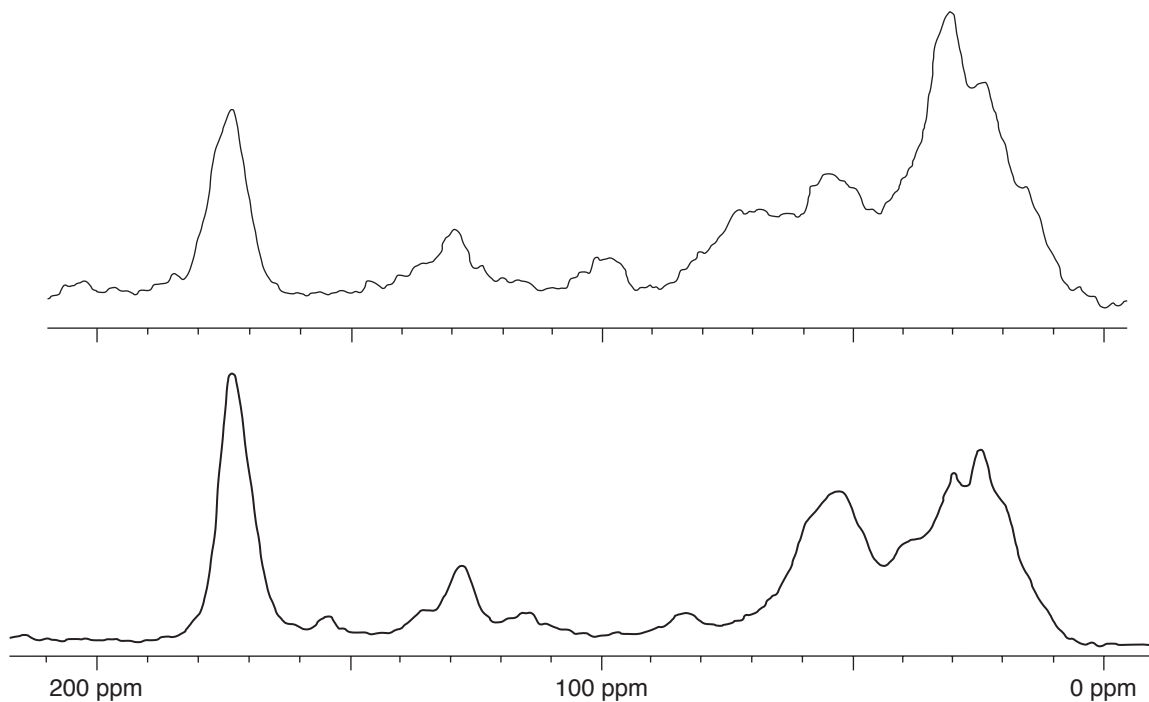Figure 6. Cross-polarized magic angle spinning/^{13}C nuclear resonance spectroscopy. The figure compares spectral bands of a natural humic acid (TB2, top) and a melanoidin (1:10–24, bottom).
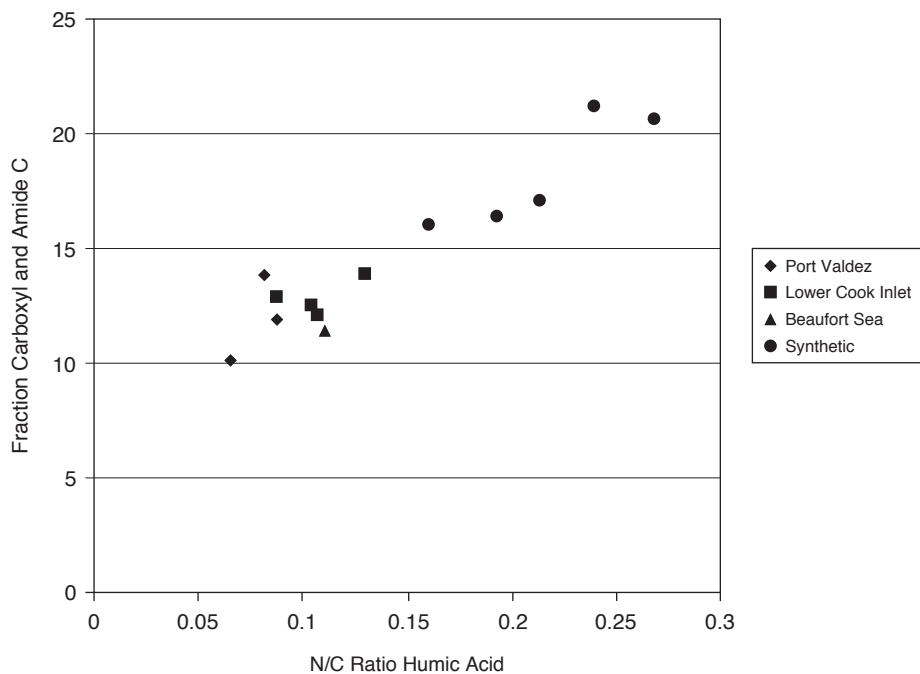

Figure 7. Increasing nitrogen to carbon ratios of humic acid were associated with an increase in the fraction of carbon atoms associated with oxygen and nitrogen bonds in natural and synthetic humic acids.
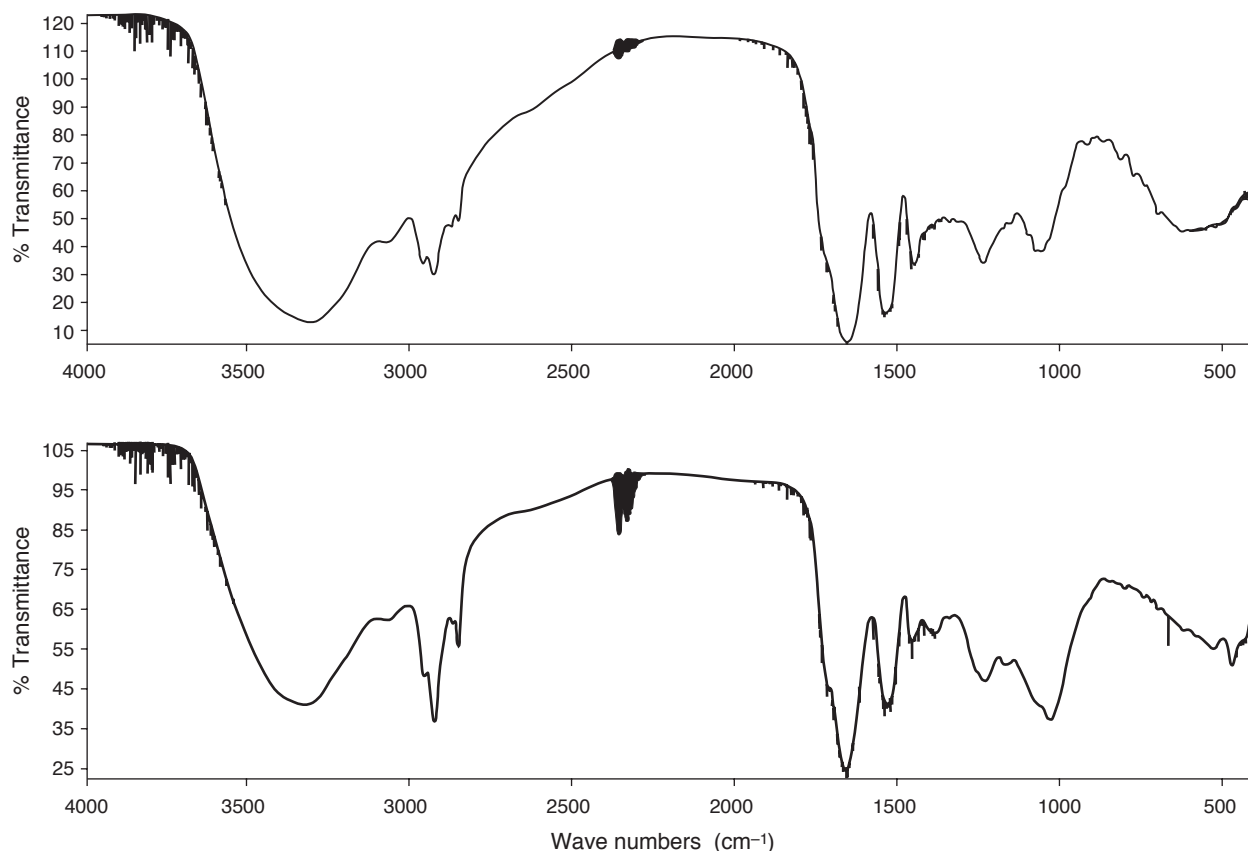
Figure 8. Fourier transform infrared spectroscopy. The figure compares spectral bands of a natural humic acid (TB2, top) and a melanoidin (1:10–24, bottom).

The humic acids of this study, both natural and synthetic, had major ^{13}CNMR peaks corresponding to terminal methyl groups (~24 ppm), methylene carbon (~31 ppm), aliphatic esters and ethers, methoxyl and ethoxyl carbons (~55 ppm), ring carbons of polysaccharides and ether bonded aliphatic carbons (~70 ppm), carbon singly bonded to two oxygen atoms and anomeric carbon in polysaccharides, acetal or ketal groups (~100 ppm), unsubstituted and alkyl substituted aromatic carbons (~129 ppm) [cf. Ikan et al. 1992], and mostly carboxyl with some esters and amide carbon (~173 ppm) [Malcolm 1990].

TARO ranged from values of less than 100 µg PAH kg^{-1} sediment to larger values, such as 708 µg PAH kg^{-1} sediment at the Homer Boat Harbor (HBH) in Lower Cook Inlet, a site with substantial anthropogenic contaminants. The high Beaufort Sea sample (5A), with 632 µg PAH kg^{-1} sediment, contained mainly natural TARO derived from tundra vegetation on the nearby coast [Naidu et al. 2001]. Environmental TARO correlated neither with sediment organic carbon content nor with humic acid N/C ratios ($r^2 = 0.00$, $t = 0.385$). In fact, there was no trend for environmental TARO concentrations with any of the humic acid properties assessed in this study.

Adsorption measurements

While all of the humic acids investigated showed strong adsorption of phenanthrene, the synthetic humic acids' partition coefficients averaged about 50% less than those for the natural humic acids. The montmorillonite clay alone adsorbed phenanthrene at a much reduced level, with the average partition

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coefficients for the montmorillonite clay being three times smaller than those for the humic acid coated clay with the smallest partition coefficients.

Neither aromaticity ($r^2 = 0.15$, $t = 1.121$) nor aliphaticity ($r^2 = 0.03$, $t = 0.456$) appeared to control measured partition coefficients in the laboratory (Figures 9a and 9b). An increase in humic acid nonpolar carbons (i.e., those only involved in aliphatic or aromatic bonds) weakly correlated with an increase in the partition coefficient ($r^2 = 0.38$, $t = 2.091$, $p = 0.10$) (Figure 9c). However, partition coefficients decreased as nitrogen increased relative to carbon (Figure 10a); this trend was mainly due to the difference between natural and synthetic humic acid properties. The combined effects of nitrogen and oxygen, measured as the percent carboxyl and amide carbon, correlated with a decrease in the partition coefficient ($r^2 = 0.78$, $t = 4.982$) (Figure 10b). The natural humic acids showed this trend clearly, and it was also seen in the comparison of natural and synthetic humic acids (Figure 6). Partition coefficients (K_p; not normalized to organic carbon content) did not correlate with the amount of organic carbon coated on the clay particles (mg OC g^{-1} clay) used in the laboratory experiments ($r^2 = 0.03$, $t = 0.429$).
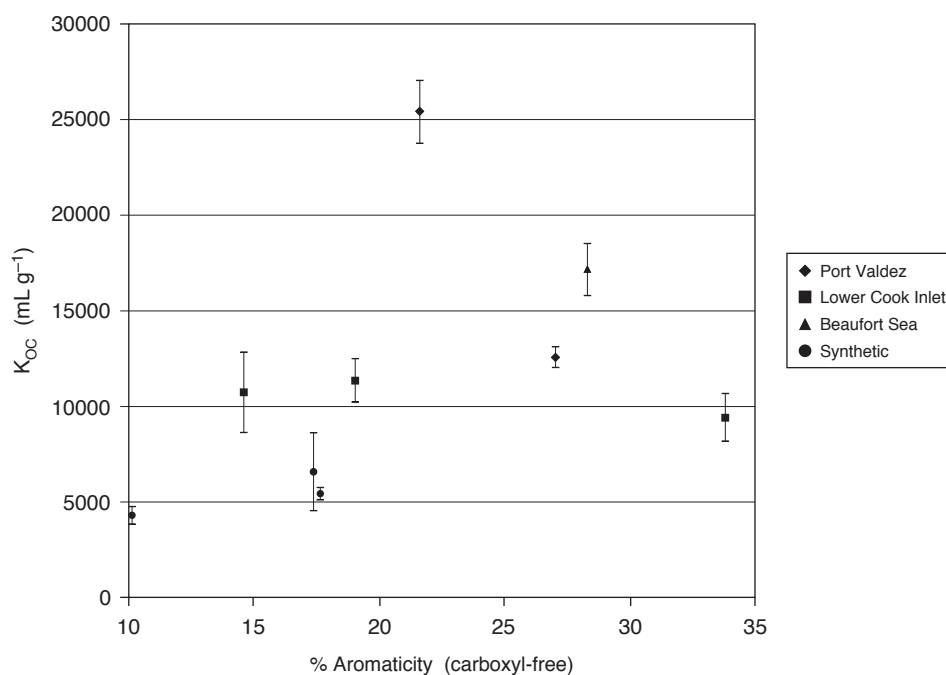
Figure 9a. Partition coefficients (K_{OC}) and percent aromaticity of humic acids were not significantly correlated.
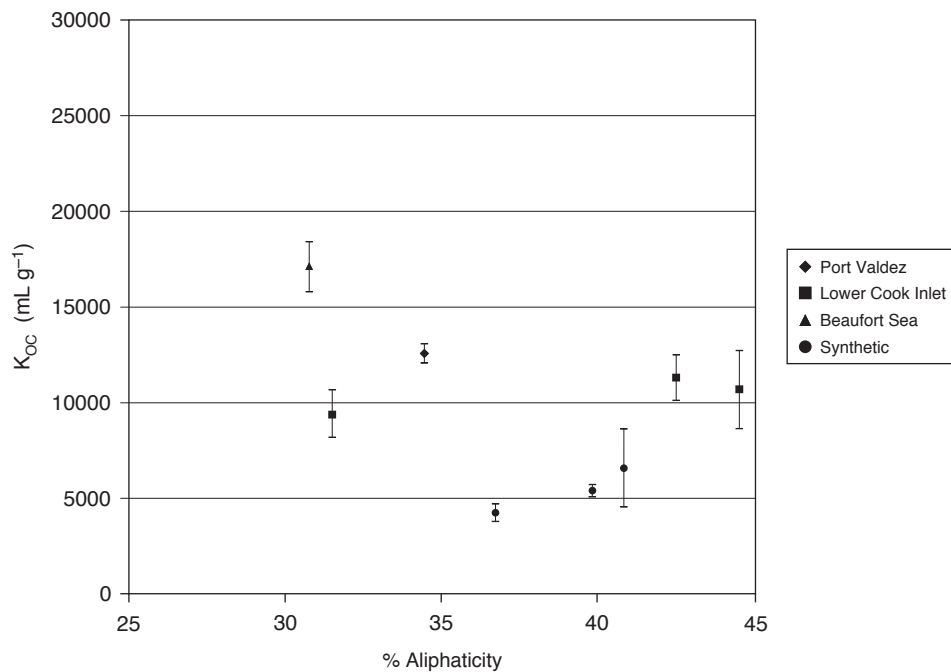
Figure 9b. Partition coefficients (K_{OC}) and percent aliphaticity of humic acids had no significant correlation.
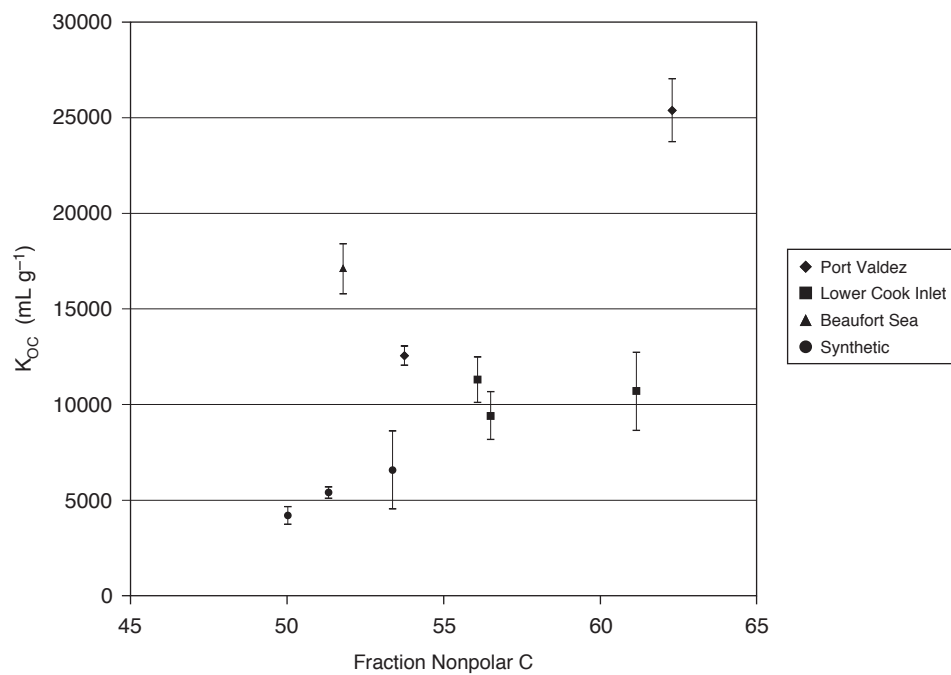
Figure 9c. Partition coefficients (K_{OC}) increased with the fraction of nonpolar carbons (the sum of those carbons involved with aromatic and aliphatic bonds).
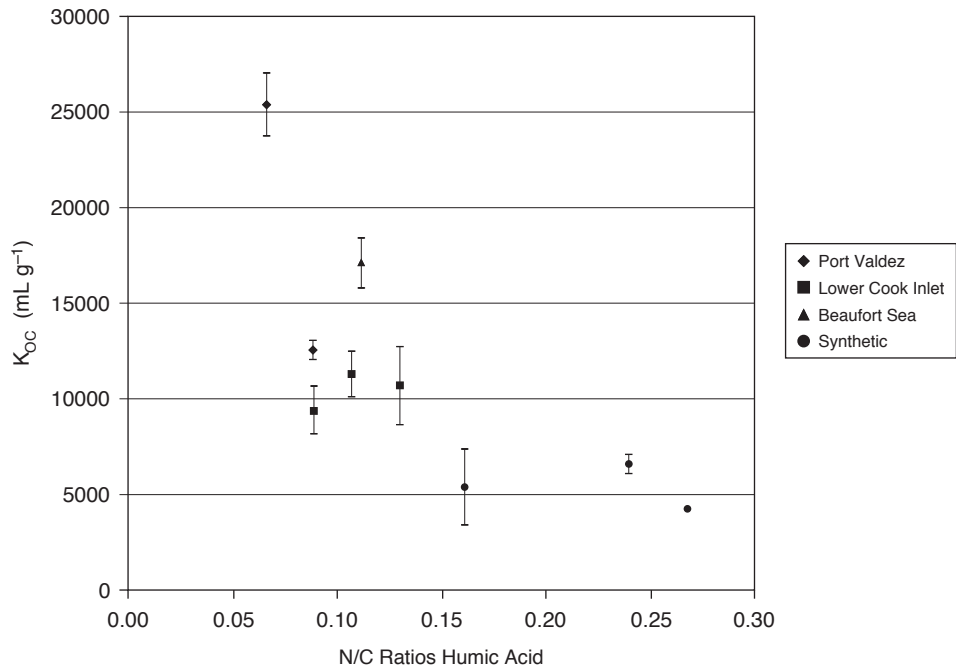
Figure 10a. Partition coefficients (K_{OC}) decreased with increasing nitrogen to carbon (N/C) ratios of humic acid.
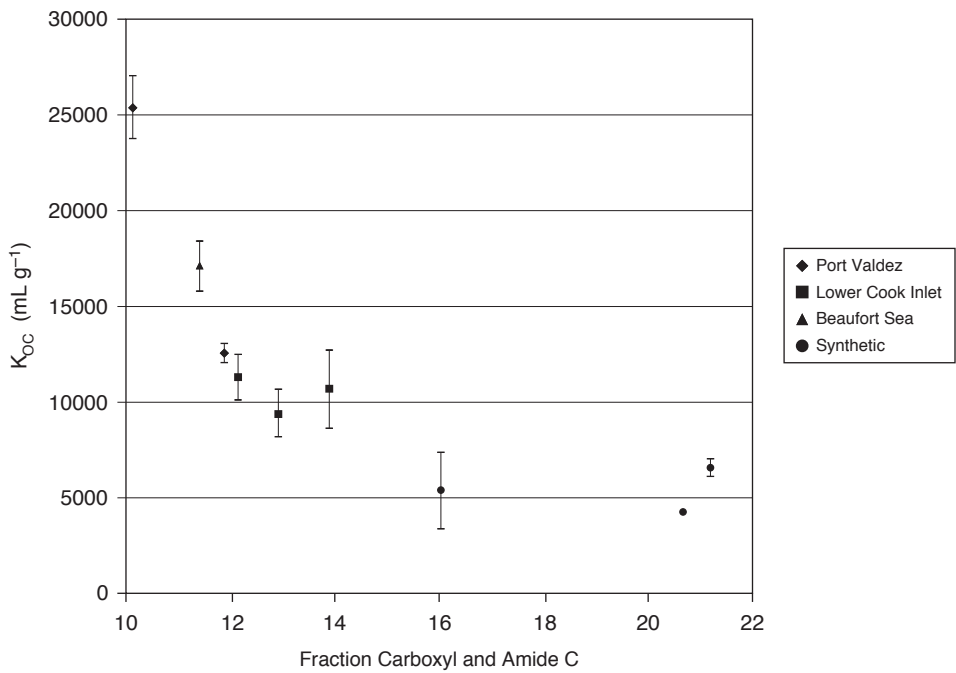
Figure 10b. Partition coefficients (K_{OC}) decreased as the number of carbons in O and N bonds (fraction carboxyl and amide C) increased.

Discussion

The organic matter examined in earlier studies on hydrophobic organic compound adsorption to humic acids was isolated from a variety of sources (e.g., river dissolved organic matter [Chiou et al. 1987], river sediment [Means et al. 1980; Karickhoff et al. 1979], estuarine sediment [Gundersen et al. 1997], coastal marine sediment [Maruya et al. 1996]), but was not usually very diverse in its properties within each study. This project sought to broaden the range of organic matter properties examined within a single investigation. Although this study used marine humic acids possessing a wide variety of properties, the characteristics were within the range of those seen in previous studies. The melanoidins, used as synthetic, model humic acids, were also similar to the natural marine derived humic acids in many respects, but had greater average N/C, a greater fraction of amide and carbonyl carbon, and negligible TARO. These synthetic humic acids are condensation products of reducing sugars and amino acids [Maillard 1913]. One hypothesis on the origins of naturally formed humic acids in the marine environment is that they are produced by the same types of browning reactions [Ertel and Hedges 1983; Enders and Theis 1938; Hodge 1953], based upon chemical similarities between melanoidins and natural marine humic acids [Gagosian and Stuermer 1977; Nissenbaum and Kaplan 1972; Hedges and Parker 1976].

Sediment isotope ratios tend to reflect the sources of organic carbon, namely photosynthetic organisms [Nissenbaum and Kaplan 1972 and references therein; Ikan et al. 1990]. Several investigations have used stable isotopic ratios of carbon to help determine the source material of marine humic acids [Gagosian and Stuermer 1977; Nissenbaum and Kaplan 1972; Malcolm 1990; Ikan et al. 1992; Ikan et al. 1990]. Biomolecules formed in the marine environment usually have isotopic signatures around –20 to –23‰. Terrestrially derived biomolecules from C_3 plants have $\delta^{13}C$ values around –25 to –27‰. Literature values for marine humic acids range between –19 and –23‰ [Gagosian and Stuermer 1977; Nissenbaum and Kaplan 1972; Malcolm 1990; Ikan et al. 1992; Ishiwatari 1992]. Humic acids from coastal and littoral sediments have a larger range, –19 to –27‰, indicating mixed marine and terrestrial inputs [Nissenbaum and Kaplan 1972]. Nitrogen isotopic signatures in the marine environment are usually in the range of 6–10‰, reflecting the sources of inorganic nitrogen in the form of ammonium and nitrate in the ocean, while terrestrial plant $\delta^{15}N$ values are closer to that of atmospheric nitrogen (0‰).

N/C ratios can be used in conjunction with isotopic studies to make a clearer distinction between marine and terrestrial humic acids. Organic matter of most Recent soils and sediments has N/C ratios of about 0.083 to 0.1 [Stevenson 1994]. A similar range was found for extracted humic acids from most marine sediments [Ertel and Hedges 1983; Ikan et al. 1992; Ishiwatari 1992; Rashid et al. 1972; Gauthier et al. 1987], while some authors have reported lower marine humic acid N/C values [Nissenbaum and Kaplan 1972; Sastre et al. 1994]. Terrestrial plants contain nitrogen deficient lignin and cellulose, and have low N/C [Goodell 1972], while marine phytoplankton is richer in protein, leading to higher N/C (~0.167) [Muller 1977]. N/C ratios of the synthetic humic acids were significantly higher than those previously reported in the literature [Ertel and Hedges 1983; Rubinsztain et al. 1984; Ikan et al. 1992], perhaps due to the use of a protein (bovine casein) as opposed to an amino acid reactant. Synthetic humic acid N/C is very dependent upon the reactants and the amino acid/carbon ratio of starting materials [Rubinsztain et al. 1984].

The values of $\delta^{13}C$, $\delta^{15}N$ and N/C, shown in Table 6, indicate that Lower Cook Inlet sediment humic acids are mostly of marine origin, even with the surrounding steeply sloping, forested coast. Like Lower Cook Inlet, Port Valdez is also a fjordal environment. Port Valdez humic acids, however, show greater terrestrial input. Beaufort Sea humic acids have a marine $\delta^{15}N$ signature and N/C similar to Lower Cook Inlet. The $\delta^{13}C$, however, is relatively light. Zooplankton in the Beaufort Sea have light $\delta^{13}C$, indicating that marine primary producers there are isotopically light [Schell et al. 1998]. Hence isotopic and N/C ratio data suggest that Beaufort Sea humic substances are mainly of marine origin. However, spectroscopic data indicate a significant terrigenous component.

Intercomparison of FTIR spectra is limited to qualitative identification of functional groups. The bands result from the absorption of energies required for vibrational modes of functional groups and provide no quantitative means of assessing the number or distribution of chemical bonds within a sample. To overcome this limitation, the use of peak ratios has been explored [Johnston et al. 1994], but was not successful as a method in this study. Both natural and synthetic humic acid FTIR spectra of this study were similar to those previously reported in the literature [Ertel and Hedges 1983; Goh and Stevenson 1971; Hedges 1978]. The natural humic acids from all sites showed strong adsorption bands characteristic of marine derived humic acids [Ertel and Hedges 1983]. A strong phenolic signal in the Beaufort Sea 5A sample suggests lignin-derived structures.

Similar to the humic acids of this study, Hatcher et al. [1980] reported major ^{13}CNMR peaks in extracted marine sediment humic acids at 30 ppm, 130 ppm, and 175 ppm, and weak or absent peaks (compared to terrestrial humic acids) at 75 ppm and 150 ppm. No statistically significant differences in ^{13}CNMR spectra could be found when comparing the integrated peak areas of the humic acids from Port Valdez and Lower Cook Inlet, when examined as separate geographical groups. The Beaufort Sea spectra (5A and 6G) were of very low resolution even after 30,500 and 49,800 scans, respectively. Low resolution for marine humic acids at up to 182,000 scans has been previously reported [Malcolm 1990]. The Beaufort Sea 5A humic acid was found to be paramagnetic, probably due to iron content, which interferes with NMR spectral acquisition.

The synthetic humic acids displayed a larger and sharper ^{13}CNMR peak in the carboxylic region and smaller integrated aliphatic areas than the natural humic acids. Rubinsztain et al. [1984] showed these trends to be indicative of sugar rich synthetic humic acids. Gauthier et al. [1987] questioned whether amide carbon was insignificant in the 160–190 ppm region for marine humic acids. However, the high N/C ratios of the humic acids of this study, coupled with the fact that the ^{13}CNMR carboxylic region (160–190 ppm) also includes amide carbons, and the strong presence of amide groups, as determined by FTIR, indicate that amide carbon is probably responsible for a larger portion of the "carboxylic" ^{13}CNMR signal than originally assumed.

The remainder of the discussion addresses relationships among humic acid properties and phenanthrene adsorption. Simple linear correlation coefficients are reported, since the sample size is insufficient for multivariate techniques. The results of this study suggest that several humic acid properties influence aromatic hydrocarbon adsorption, but don't allow a quantitative assessment of the contribution of each factor. The results do indicate which properties should be the focus of further study.

Table 6. N/C ratios and carbon and nitrogen stable isotope values versus PDB and air, respectively. n/a – not available

Sample	Humic Acid δ^{13}C	Humic Acid δ^{15}N	Humic Acid N/C	Humic Acid N/C
PV25 humic acid	−27.57	1.27	0.0657	0.1036
PV82 humic acid	−24.37	4.35	0.0878	0.0987
HBH humic acid	−21.04	8.56	0.0879	0.0966
JB2 humic acid	−17.38	6.95	0.1067	0.1142
TB2 humic acid	−18.21	5.72	0.1297	0.1497
5A humic acid	−25.94	5.72	0.1109	n/a

No significant correlations were found between E_4/E_6 and aromaticity, any of the other humic acid characteristics examined, or adsorption of phenanthrene. The E_4/E_6 ratio has been used to measure the degree of condensation of aromatic groups [Ertel and Hedges 1983], with smaller ratios of E_4/E_6 being found with humic acids of higher aromaticity [Kononova 1966]. However, most studies investigating E_4/E_6 as a proxy for aromaticity of humic acids have been unable to support its use [Chin et al. 1994; Nissenbaum and Kaplan 1972; Johnston et al. 1994; Chen et al. 1977], and the more specific ^{13}CNMR data presented here provide clear evidence that this measure should not be used.

Environmental TARO were unrelated to sediment TOC, N/C and aromaticity of humic acids, or other organic matter properties. All environmental TARO values, ranging from 10.8 to 914.4 µg PAH kg^{-1} sediment, were much less than the sediments' capacities for PAH adsorption. After 14 days of laboratory adsorption, the adsorbed quantities for phenanthrene were between 46 and 81 mg kg^{-1} sediment (46,000 and 81,000 µg kg^{-1} sediment). There were large variations in TARO from sediments of similar origin with the same percent organic carbon; for example, TARO values ranged from 36.3 to 517 µg PAH kg^{-1} sediment with 0.7% OC. Variations in TARO were clearly due to variations in anthropogenic and natural sources of PAH at the different sampling locations, rather than variations in sediment sorptive properties.

Partition coefficients measured in the laboratory are a better method of determining sorptive properties of organic matter than bulk TARO measurements, since dissolved PAH concentrations are controlled. In this study, extracted humic acids were coated onto a uniform clay mineral before use in phenanthrene adsorption experiments. This procedure reduced variability due to the mineral phase or particle size that can be present with natural sediments. Clay with no added organic matter showed much less phenanthrene adsorption than the clay with added humic acids, and so the humic acids were clearly the major adsorbent.

Partition coefficients of phenanthrene determined by this research ($14,000 \pm 6000$ mL g^{-1} C) are consistent within the range found by others. For example, Kopinke et al. [1995] determined phenanthrene K_{OC} for coal wastewater sediment to be 15,000 mL g^{-1} C. Karickhoff et al. [1979] found K_{OC} to be 23,000 mL g^{-1} C for coarse silt fractions of two ponds of northern Georgia. This is comparable to the partition coefficient of $19,800 \pm 954$ mL g^{-1} C found for Boston Harbor sediments by Chin and Gschwend [1992]. Partition coefficients for intact Jakolof Bay sediments were about $50,000 \pm 20,000$ mL g^{-1} C [Henrichs et al. 1997]; this is larger but of similar magnitude to values for the extracted humic substances reported here.

Although a positive correlation between organic matter concentration and partition coefficients was found in several earlier studies [Means et al. 1980; Schlautman and Morgan 1993; Chiou et al. 1987; Karickhoff et al. 1979; Gundersen et al. 1997; Maruya et al. 1996], it was absent here, probably because of the wide range of organic matter properties present. This correlation is more likely where organic matter properties are fairly uniform over the range of organic matter concentrations. Samples used in previous studies were usually from small geographical regions and characterization of the organic matter was limited. For example, Karickhoff et al. [1979] sampled two ponds and one small river in northern Georgia. Although the ponds were associated with different terrestrial vegetation (grass watershed vs. wooded watershed), other aspects of their environments were similar (lignin, pH, temperature, and weathering regime) and the structural properties of the organic matter were not characterized. Gundersen et al. [1997] limited their study to a single estuary in Virginia. Sediment grain size varied, but organic matter differences were not characterized. Maruya et al. [1996] sampled a very small section of a marsh on San Francisco Bay. Characterization of their samples was limited to PAH, grain size analysis, and total organic carbon. While Means et al. [1980] did cover a larger region, by investigating sediments and soils in the Great Lakes area of the United States, the sampling still took place within an area of similar weathering and parent materials. Their soils and sediments showed a range in carbon and nitrogen values, but no other characterizations of the organic matter were done. The results of the present study show that sediment

TOC alone is not necessarily the best indicator of sorptive properties. More information on organic matter properties, selected based on understanding mechanisms of adsorption, is needed.

Hydrophobic adsorption to humic acids is thought to be a pH-independent mechanism of binding between aliphatic chains and aromatic moieties with non-ionic HOC [Senesi 1992]. A number of laboratory studies have shown a positive correlation between humic substance aromaticities and measurements of PAH adsorption such as partition coefficients [Gauthier et al. 1987; Chin et al. 1997; Maruya et al. 1996], PAH solubility [Uhle et al. 1999], and Freundlich exponents [Xing 2001]. Aromaticity, however, did not predict partition coefficients in this study. The sum of both the aromatic and aliphatic fractions (as the nonpolar fraction) predicted partition coefficients better than either alone. The data suggest that phenanthrene adsorbs equally well to aliphatic and aromatic parts (hydrophobic parts) of the humic molecule.

Partition coefficients for phenanthrene decreased with increasing polarity of the humic acid and increased with increasing nonpolar fractions [cf. Kile et al. 1999]. Humic acid polarity, although not measured directly, was inferred from increasing N/C, increasing fraction of carboxyl and amide carbon, and decreasing fraction of nonpolar carbon (the sum of aliphatic and aromatic carbons by ^{13}CNMR). The polarity of the overall structure should increase based on the non-symmetrical addition of nucleophilic atoms such as nitrogen and oxygen. Similar to the results of this study, Rutherford et al. [1992] showed a correlation between partition coefficients of aromatic hydrocarbons and polar-to-nonpolar group ratios (quantified as (O+N)/C) of soil organic matter. More recently, Kile et al. [1999] demonstrated that polarity (determined by ^{13}CNMR) was a significant factor in the binding of carbon tetrachloride to soil and sediment organic matter. This is not surprising, following the concept that "like dissolves like". It has been proposed that humic acids, being amphiphilic, form regions similar to detergent micelles. These "pseudomicelles" are considered to have a hydrophobic interior into which nonpolar compounds can partition [Ragel et al. 1997 and references therein].

The relationship between K_{OC} and the fraction of carboxyl and amide carbon is tighter than the relationship of K_{OC} and nonpolar carbon. Carboxyl and amide carbons constitute only 10–20% of the carbon, and it is not obvious why small changes in this fraction have a strong effect on K_{OC}. One possibility is that when adsorbed on the clay, the polar functional groups of the humic acid are positioned outward, so that they have an especially strong influence on the particle surface properties.

The sediments with the highest partition coefficients had humic acid structural characteristics indicating mixed terrestrial and marine organic matter input (PV25, PV82, and 5A). While it has been suggested that terrestrial humic acids bind aromatic hydrocarbons better due to their lignin precursors, and therefore greater aromaticity, it was shown that aromaticity is not a predictor in this study. Rather, the data suggest that the precursors to humic acids in these mixed environments are lower in polarity, that is, have less carboxylic and amide carbon and lower N/C, contributing to the low polarity of these humic acids and greater affinity for phenanthrene. However, another characteristic shared by natural humic acids with greater partition coefficients was origin in subtidal sediments. The intertidal sediments of Lower Cook Inlet probably contained more living organisms and fresh detritus than the subtidal sediments of Port Valdez and the Beaufort Sea, and this could have contributed to their greater content of amide and carboxylic acid functional groups.

Overall, the results of this work indicate that sediment organic content alone is not a reliable predictor of phenanthrene adsorption when a broad range of sediment organic matter types are examined. The differences in adsorption appear to be best explained by a measure of polar functional group content (fraction carboxyl and amide carbon), but the ^{13}CNMR data required for this parameter are costly and not readily available in most laboratories. A simple N/C ratio captures much of the variability in humic acid properties in this sample set, and may be a better candidate for routine assessments of sediment adsorptive properties.

Chapter 3. Phenanthrene Adsorption to Mineral-Bound Humic Acid: Kinetics and Influence of Previous Phenanthrene Adsorption[2]

Abstract

This study was comprised of two related components. One was an investigation of the kinetics of phenanthrene adsorption to mineral-bound humic acids. The other focused on the effects previous phenanthrene contamination of sediments had on subsequent phenanthrene adsorption. Natural humic acids were isolated from coastal Alaska sediments, and represented a wide range of organic matter properties. Several synthetic melanoidins were used as humic acid analogs. These humic acids or melanoidins were coated onto a standard clay, and adsorption of phenanthrene was measured using a radiotracer. Adsorption isotherms were linear up to a concentration of 5500 µg phenanthrene per gram organic carbon. Isotherm slopes, interpretable as organic carbon normalized partition coefficients, K_{OC}, and initial adsorption rates were negatively correlated to the polarity of the organic matter. Partition coefficients were found to be independent of initial phenanthrene concentration, indicating that the binding sites were unlimited and uniform in strength. Initial rates were rapid, but the approach to steady state was slow, requiring approximately one week, consistent with a slow diffusion within the sorbent. Finally, the comparison of rates and partition coefficients for pristine sediments with those of sediments already having adsorbed phenanthrene showed that previous phenanthrene adsorption had no effect.

Introduction

Sediments are a major reservoir of persistent environmental contamination by hydrophobic substances such as polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB) and pesticides [Chin and Gschwend 1992; Hatzinger and Alexander 1995] because of the low aqueous solubility and high surface affinity of these compounds. Adsorption has been investigated as a key process leading to sediment contamination and its persistence in the environment. For uncharged organic pollutants, organic matter is considered the primary sorbent component [Karickhoff and Morris 1985]. The adsorption partition coefficient, K_p, increases with increasing organic content of sediments and soils [Means et al. 1980; Schwartzenbach and Westall 1981; Shaw and Terschak 1998]. The adsorption of neutral hydrophobic organic compounds (HOC) to organic matter is generally considered to involve rapid van der Waals type interactions [Brusseau and Rao 1991], although mechanisms for the binding of PAH to organic matter have not been completely elucidated [Ragle et al. 1997].

Organic matter properties influence adsorption. Adsorption of various aromatic hydrocarbons has correlated positively with the nonpolar–polar functional group ratio (Rutherford et al. [1992], Garbarini and Lion [1986], and see Chapter 2) and aromaticity [Gauthier et al. 1987]. Adsorption of PAH to humic acids is thought to result, at least in part, from weak dipole interactions between aromatic rings of the PAH and those of humic acids, particularly humic acids derived from lignins and related materials of woody terrigenous plants [Chin et al. 1997; Chin et al. 1994].

The sediment or soil organic matter, of which humic acid is a part, is a flexible, cross-linked, branched, amorphous, polyelectrolytic, polymeric substance within which organic pollutants can diffuse [Brusseau et al. 1991]. Schnitzer and Khan [1972] theorize that humic acid is an open structure with hydrophobic cavities. The organic matter is porous as are clay mineral surfaces, but while the pores of sediment mineral particles are fixed and rigid, the organic matter pores are dynamic and ephemeral [Brusseau et al. 1991]. The size, shape, and hydrophobicity of the pores within organic matter are sensitive to variations

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in solution chemistry, and, therefore, changes in the ability to bind HOC can occur [Schlautman and Morgan 1993]. The hydrophobicity of PAH suggests that PAH association is governed by diffusion into the nonpolar environments of organic matter [Ragle et al. 1997; Gauthier et al. 1987; Schlautman and Morgan 1993].

Investigations into the adsorption kinetics of HOC to natural organic matter have shown a rapid initial uptake of the HOC followed by a slow approach to steady state. Wu and Gschwend's [1986] adsorption kinetics data of four congeners of chlorobenzene (pentachlorobenzene, 1,2,3,4-tetrachlorobenzene, 1,2,4-trichlorobenzene, 1,4-dichlorobenzene) to North River sediments showed that adsorption processes were complete at times longer than two days. Their results for pentachlorobenzene adsorption to Charles River sediments reached steady state around 16 hours. Chin and Gschwend [1992] examined pyrene adsorption to Fort Point Channel sediments and found that it reached steady state sometime after 24 hours. The results from these studies indicate that HOC adsorption to natural organic matter generally takes a minimum of one to two days to reach steady state.

Preliminary studies of this laboratory on PAH adsorption to natural humic acids found that previous exposure to PAH may alter subsequent PAH binding (unpublished data). Hypothetically, the nonpolar environments described above could increase in hydrophobic character when PAH are bound to the organic matter, and further PAH adsorption could be enhanced by dipole–dipole interactions as proposed for PAH–lignin interactions. Existing PAH contamination enhancing further PAH adsorption has been observed by Boyd and Sun [1990], who reported that pentachlorophenol (PCP) adsorption to petroleum contaminated environmental soils was greater than that estimated via modeled octanol–water partition coefficients and soil organic content. In contrast, PCP adsorption to a Capac soil that was assumed to be uncontaminated was consistent with the model, so they concluded that the petroleum contamination was enhancing PCP adsorption. The effect of prior HOC contamination was also used to explain high K_{OC} in environmental samples by Chin and Gschwend [1992] and Kile et al. [1995].

On the other hand, partition coefficients would be expected to decrease with increasing PAH-loading if there was very strong adsorption to a limited number of sites, with further adsorption having lower binding energies, or if saturation of binding sites occurred. Several adsorption sites of varying strength is one explanation for the common observation that PAH adsorption is partly irreversible [Hatzinger and Alexander 1995; Yonge et al. 1985; Kan et al. 1994]. Other hypothesized mechanisms of irreversible adsorption include slow diffusion into tortuous mineral particle micropores [Brusseau et al. 1991; Wu and Gschwend 1986; Steinberg et al. 1987] and diffusion into the organic matrix [Karickhoff and Morris 1985; Brusseau and Rao 1991; Brusseau et al. 1991; Schlautman and Morgan 1993; Kan et al. 1994]. Intraorganic matter diffusion is thought to be the most likely mechanism for HOC adsorption [Brusseau and Rao 1991; Brusseau et al. 1991]. Adamson [1990] suggests that irreversible adsorption is probably due to a mechanical or structural rearrangement of the adsorbent, that is, the matrix from which desorption takes place is different from that during adsorption.

This research was conducted as part of an examination of the role humic acids play in the adsorption and desorption of PAH by the sediments of coastal marine environments. The adsorbents investigated were extracted humic acids bound to a standard clay mineral, in order to eliminate variability due to the mineral phase. This study addresses the rates and mechanisms of phenanthrene adsorption to humic acid and melanoidin-coated clay, and is the first to specifically test the effects of previous PAH contamination on subsequent binding. Melanoidins were used as model marine humic acids because of their lack of initial PAH contamination relative to their natural counterparts. The melanoidins were compared with natural humic acids isolated from coastal Alaska sediments. These organic substances represent a wide range of properties potentially affecting associations with PAH.

Experimental Section

Substrate preparation

A montmorillonite standard (A.P.I. # 26, 49 E 2600 from Clay Spur, Wyoming; Ward's Natural Science Establishment, Inc.) was ground for 2 minutes using a shatter box equipped with carbide rings. The resulting powder was passed through a 270 mesh (53 µm) sieve using a Ro-Tap® apparatus. Organic material was removed from the clay by oxidizing it with 30% hydrogen peroxide. A slurry of clay and H_2O_2 was prepared in an open Pyrex container. The clay was mixed for 12 hours at room temperature. Low heat was then applied, bringing the slurry to 35–40 °C. Fresh H_2O_2 was added as needed. Stirring was continuous until no evolution of CO_2 gas was evident. The slurry was then centrifuged at 14,000 g for 2 hours and the clear supernatant was discarded. A wash of organic-free, glass-distilled water was used and the clay was again centrifuged as above. A small sample of the organic-free clay was submitted for total organic carbon analysis and the remaining material was stored under ultra high purity nitrogen gas (UHP-N_2) gas at 5–10 °C.

Sediment subsamples were analyzed for size distribution of particles using the sieve-pipette method [Jackson 1965]. The sediment was divided into six fractions: fine sand > 63 µm, very fine sand (63–50 µm), coarse silt (50–20 µm), medium silt (20–5 µm), fine silt (5–2 µm), and clay (< 2 µm). Fine sand and larger particles were removed from the sediment by sieve. In a 1-L graduated cylinder, a suspension of the material that passed through the sieve was made in 1 L of distilled water and allowed to settle for a prescribed time based on Stokes' Law [Jackson 1965]. Particle size distribution was calculated as a percentage of the recovered material (99.99% recovery).

Humic acid sources

Natural humic acids were taken from sediment samples collected at three separate coastal locations in Alaska (Table 7). Intertidal sediment samples from Lower Cook Inlet were collected in July 1995, July 1996, and May 1999. Sampling occurred during spring tides below the mean lower-low water level. Subtidal sediment samples were collected from the Port Valdez region in August 1996 using a Haps corer and from the Beaufort Sea region during September 1997 using a Kynar-coated van Veen grab sampler. Any overlying debris was removed and then sediment was collected from the oxic layer (upper 2 cm) with metal implements that had been heated to redness before use. All samples were stored until needed at –50 °C in pre-combusted glass jars.

Table 7. Site locations of sediments discussed in this study; n/a – not applicable, as Lower Cook Inlet samples were intertidal and collected during low tide.

Location	Station	Latitude (N)	Longitude (W)	Depth (m)
Port Valdez	PV25	61° 05.5′	146° 23.3′	73
Port Valdez	PV82	61° 05.4′	146° 22.3′	79
Lower Cook Inlet	HBH	59° 36.3′	151° 25.0′	n/a
Lower Cook Inlet	JB2	59° 27.1′	151° 29.3′	n/a
Lower Cook Inlet	TB2	59° 24.8′	151° 17.0′	n/a
Beaufort Sea	5A	70° 29.7′	148° 46.0′	11.4

Humic acid was isolated using the alkali (0.5 M NaOH) extraction procedure of Anderson and Schoenau [1983]. After extraction from approximately 30 g of wet sediment, humic acid was precipitated by the addition of 6 M HCl until a pH of 1.5 was obtained. The precipitated extract was allowed to stand for 15 minutes and was then centrifuged for 30 minutes at 14,000 g. The precipitated humic acid was lyophilized at –85 °C for 24 hours. The resulting dry humic acid was stored at room temperature in a glass vial under $N_{2(g)}$.

Artificial humic acids were prepared in the laboratory by refluxing various ratios of glucose and bovine casein in buffered solutions for 24 to 48 hours as described by Yamamoto and Ishiwatari [1989] The buffer was composed of 125 ml 0.1 M KH_2PO_4, 75 ml 0.1 M NaOH and 50 ml of glass-distilled water to give a final pH of 7.0. After the prescribed reaction time, the mixture was allowed to cool with stirring, then transferred to 250 ml Nalgene® centrifuge bottles. The artificial humic acid was isolated using the extraction procedure above.

Substrate coating

Humic acids were coated to the montmorillonite substrate for use in the adsorption/desorption experiments. Approximately 1 g of lyophilized humic acid was dissolved in 100 mL of organic-free water and brought to a pH of 10 with sodium hydroxide. The solution was mixed under an atmosphere of UHP-N_2 for 3 to 7 days with adjustments made daily to maintain the pH. Once dissolved, the humic acid solution was added to the washed clay and mixed for 24 hours. The suspension was transferred to a centrifuge bottle containing the crystallized salts resulting from the evaporation of an equal amount of artificial seawater and mixed for 48 hours. The suspension was then centrifuged at 14,000 g for 2 hours and the supernatant was discarded. A sample of the humic acid coated clay was dried and submitted for TOC analysis to determine the extent of humic acid adhesion. After flushing the headspace with UHP-N_2 gas, the humic acid coated clay was stored in a refrigerator at 5–10 °C.

Total organic carbon measurements

Total organic carbon analyses of the clay substrates were performed by Donald Schell's laboratory at the University of Alaska Fairbanks using a Delta Plus mass spectrometer equipped with a Finnigan MAT Conflo II interface and a Carlo Erba elemental analyzer.

Adsorption experiments

All glassware and Teflon® liners were treated to remove any hydrocarbon contamination before use. Glassware was baked in a muffle furnace at 450 °C for at least 8 hours. Teflon® cap liners were soaked in chromic acid for 20 minutes and then rinsed 3 times with clean organic-free water.

Artificial seawater was prepared from organic-free water that had been glass distilled over a saturated solution of potassium permanganate. To each liter of water the following salts were added: 23.260 g NaCl, 10.636 g $MgCl_2 \cdot 6H_2O$, 3.918 g anhydrous Na_2SO_4, 1.102 g $CaCl_2$, 0.664 g KCl, 0.192 g $NaHCO_3$, 0.096 g KBr, and 0.026 g H_3BO_3 [Lyman and Fleming 1940]. Also, 0.500 g $HgCl_2$ was added as an antibiologic agent.

A stock phenanthrene solution was prepared by dissolving 0.0060 g of phenanthrene in a 100-mL volumetric flask with acetonitrile. This solution was then used to prepare the various phenanthrene solutions required for the adsorption experiments. After evaporation of the acetonitrile, aliquots of the phenanthrene stock solution were diluted with the required amount of artificial seawater to make final concentrations of 50, 300, and 700 µg L^{-1}. Radiolabeled phenanthrene solutions were prepared using a similar technique. However, 10% of the phenanthrene was replaced with [9-^{14}C] phenanthrene (5–15 mCi mmol^{-1}; Sigma Chemical Co.) dissolved in acetonitrile. All solutions were prepared 24 hours in advance

and stored in a refrigerator (5–10 °C). Previous experiments within this laboratory have shown that for concentrations of phenanthrene ranging from 10 to 750 µg L^{-1}, there was no loss of hydrocarbon due to evaporation or adhesion to the walls of the container [Henrichs et al. 1997]. In addition, all experiments had control vials containing no sediment.

Adsorption experiments began by weighing 0.1g of wet, humic-coated clay into 2-dram vials with Teflon[®] lined caps. Five milliliters of artificial seawater solutions containing either phenanthrene (for adsorption experiments with PAH-loaded sediments) or radiolabeled phenanthrene (for adsorption experiments with pristine sediments) at several concentrations (50, 300, or 700 µg L^{-1}) were added to the vials. A 15-second agitation on a vortex mixer thoroughly mixed the clay and solution. The vials were then placed on a table shaker at 150–200 rpm. After adsorption for 1 h, 1 d, 3 d, 7 d, or 14 d, the vials were centrifuged at 2400 g for 30 minutes and a 1.0 mL aliquot of each of the radiolabeled reaction solutions was removed and scintillation counted to determine phenanthrene adsorption to pristine sediments. The remaining supernatant, including that from all vials containing phenanthrene without radiolabel, was discarded. The second adsorption segment of the experiment began with the replacement of the nonlabeled supernatant with fresh radiolabeled 300 µg L^{-1} phenanthrene solution to determine the adsorption of phenanthrene to sediments previously loaded with phenanthrene. The vials were vortex mixed as above and returned to the table shaker at 150–200 rpm. The second adsorption was carried out for 1, 3, 7, 14, 30, 60, or 90 days. After the adsorption time was completed, a group of vials was centrifuged as above and a 1.0 mL aliquot was taken from each supernatant and scintillation counted.

Upon the completion of the second adsorption, the supernatant was discarded and the sediments were placed in a 65 °C oven until dry. Sediment dry weights were measured and pore water volumes were calculated from the weight loss upon drying.

The calculation to determine dissolved concentrations of phenanthrene remaining in solution after prescribed reaction times with pristine sediments is shown in Equation 3–1, where [*diss*] is the amount of phenanthrene remaining in solution in µg L^{-1}, *dpm* is the disintegrations per minute of the radiolabeled phenanthrene solutions by scintillation counting, and [*phen*]$_i$ is the initial phenanthrene concentration.

$$[diss] = \frac{dpm_{dissolved}}{dpm_{control}} [phen]_i \qquad (3–1)$$

As shown in Equation 3–2, the adsorption of phenanthrene to pristine sediments was calculated as the amount of the phenanthrene removed from the initial solution as a function of dissolved phenanthrene activity, where [*ads*] is the amount of phenanthrene adsorbed to the sediment in µg·g OC^{-1}, *a* is the solution volume, *b* is dry weight of the clay substrate, and *OC* is the fraction of organic carbon in grams of carbon per 1 g of clay.

$$[ads] = \frac{dpm_{control} - dpm_{dissolved}}{dpm_{control}} [phen]_i \left(\frac{a}{b}\right) OC^{\pm 1} \qquad (3–2)$$

The adsorption of phenanthrene to PAH-loaded sediments was calculated assuming reversible adsorption using Equations 3–1 and 3–2 for dissolved and adsorbed concentration, respectively. However, [phen]$_i$ becomes the total amount of phenanthrene in the system, expressed as [phen]$_t$ (Equation 3–3), that is, the second phenanthrene solution (300 µg L^{-1}) together with the amount of phenanthrene adsorbed in the first step ([ads]$_1$).

$$[phen]_t = 300\,\frac{\mu g}{L} + [ads]_1\,OC\left(\frac{b}{a}\right) \tag{3–3}$$

In both situations (phenanthrene adsorption to pristine sediments and adsorption to PAH-loaded sediments), the ratio of adsorbed to dissolved phenanthrene concentrations was reported as a partition coefficient normalized to organic carbon content (K_{OC}), as shown in Equation 3–4.

$$K_{OC} = \frac{dpm_{control} - dpm_{dissolved}}{dpm_{dissolved}}\,OC^{\pm 1}\left(\frac{a}{b}\right) \tag{3–4}$$

Results

The particle size distribution for the montmorillonite clay used in the adsorption experiments is shown in Figure 11. The particles were predominantly clay, followed by lesser quantities of medium silt, fine silt, and coarse silt. The organic carbon content of the clay after hydrogen peroxide treatment was ≤ 0.095 wt %.
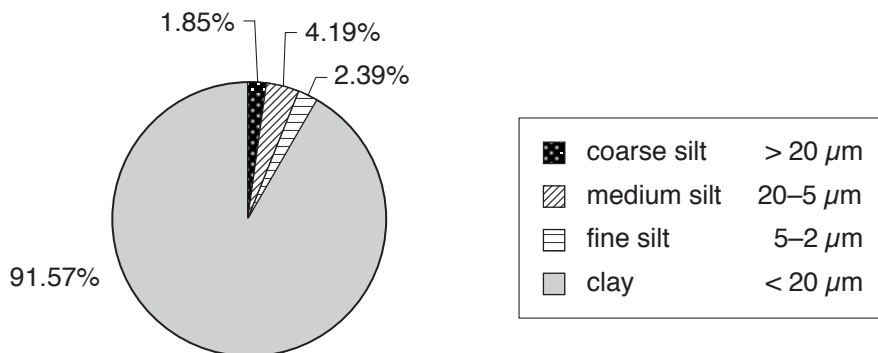
Figure 11. Montmorillonite particle size distribution.

Analyses were performed to confirm that humic acid was, indeed, bound to the clay after the coating process and that humic acid was not removed from the clay during the course of the adsorption experiments. Initial concentrations of organic matter were similar to those found naturally in marine sediments. The organic carbon contents of the clays after the adsorption experiments were not statistically different from those measured before the experiments.

Fourteen-day adsorption isotherms were found to be linear up to 5500 μg phenanthrene·g OC^{-1} ($r^2 > 0.97$) (Figure 12). Intercepts of the y-axis were not significantly different from 0 μg phenanthrene· gram sediment^{-1}, so linear regressions were forced through the origin. Slopes (interpretable as partition coefficients, K_{OC}) were found to range from 5872 to 17,699 mL·g OC^{-1}. Slopes associated with natural humic acids ($m \geq 10{,}750$ mL·g OC^{-1}) were consistently larger than those for synthetic humic acids ($m \leq 8370$ mL·g OC^{-1}).

Figure 12. Linear adsorption of phenanthrene to pristine sediments (without Port Valdez
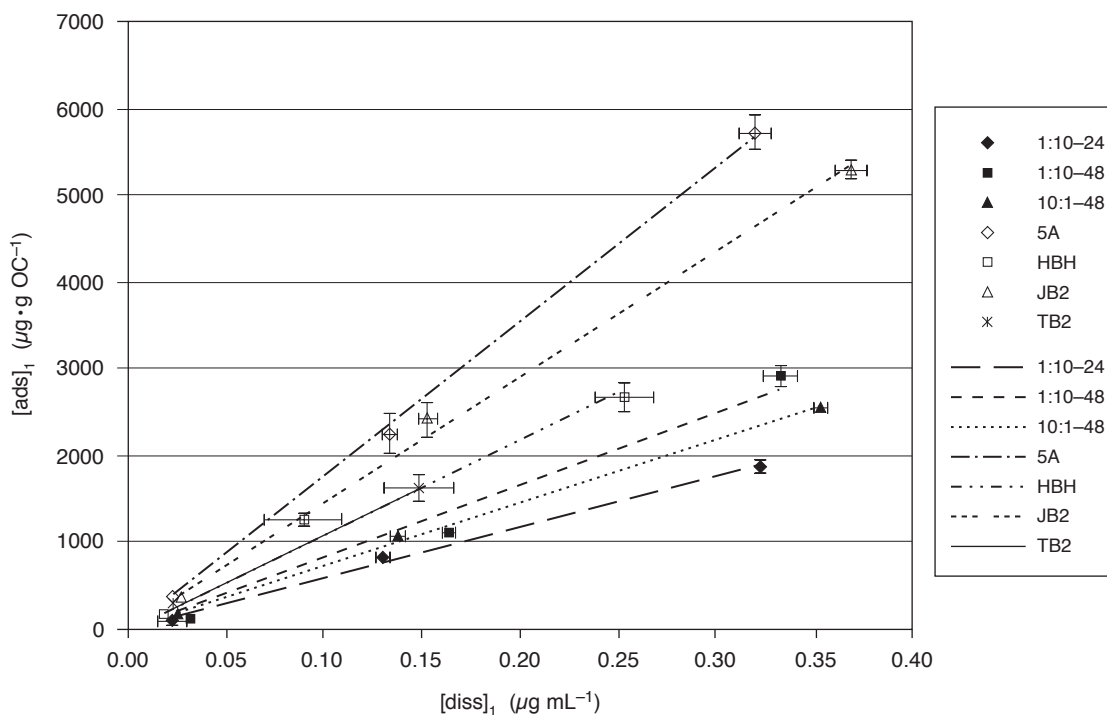samples). Initial adsorption time was 14 d. Initial phenanthrene concentrations
were 50, 300, and 700 µg L^{-1}.

A comparison between phenanthrene adsorption to pristine sediment ([ads]$_1$) and adsorption to PAH-loaded sediment ([ads]$_2$) can be seen in Figure 13. Adsorption coefficients for pristine sediments measured at 1 hour, and at 1, 3, 7, and 14 days for initial phenanthrene concentrations of 50, 300, and 700 µg L^{-1}, range from 99.5 to 5722.4 µg·g OC^{-1}. Corresponding adsorption coefficients for PAH-loaded sediments after 14 days at 300 µg L^{-1} phenanthrene concentration, were larger, especially at lower values of [ads]$_1$, ranging from 786.3 to 5292.9 µg·g OC^{-1}.

Initial rates of phenanthrene adsorption to pristine sediments (Rate$_1$) were calculated for 1 hour and 1 day of reaction time (Tables 8a and 8b). Figure 14 shows the initial rate to be directly proportional to the initial dissolved concentration of phenanthrene. Overall, the rates ranged from 122 µg·g OC^{-1}·d^{-1} for a synthetic humic acid, 1:10–24, at 50 µg L^{-1} phenanthrene to 4656 µg·g OC^{-1}·d^{-1} for a natural humic acid, 5A, at 700 µg L^{-1} phenanthrene. Mineral particles coated with natural humic acids generally displayed faster initial rates of adsorption than did synthetic humic acids (PV82 > JB2 > PV25 > 5A > TB2 > 1:10–48 > HBH > 10:1–48 > 1:10–24), corresponding to their greater K$_{OC}$. Initial rates, evaluated after 1 day and at 300 µg L^{-1} phenanthrene concentration, were found to be significantly negatively correlated with proxies for humic acid polarity (N/C: $r^2 = 0.54$, $t = 2.867$, $n = 9$; fraction carboxyl and amide carbons: $r^2 = 0.59$, $t = 3.174$, $n = 9$) (see Chapter 2). The rate of phenanthrene adsorption at 50, 300, and 700 µg L^{-1} to sediment with previously adsorbed phenanthrene (14 day reaction time) was greater (Figure 15) than that to pristine sediment, as was seen for [ads]$_2$, above.
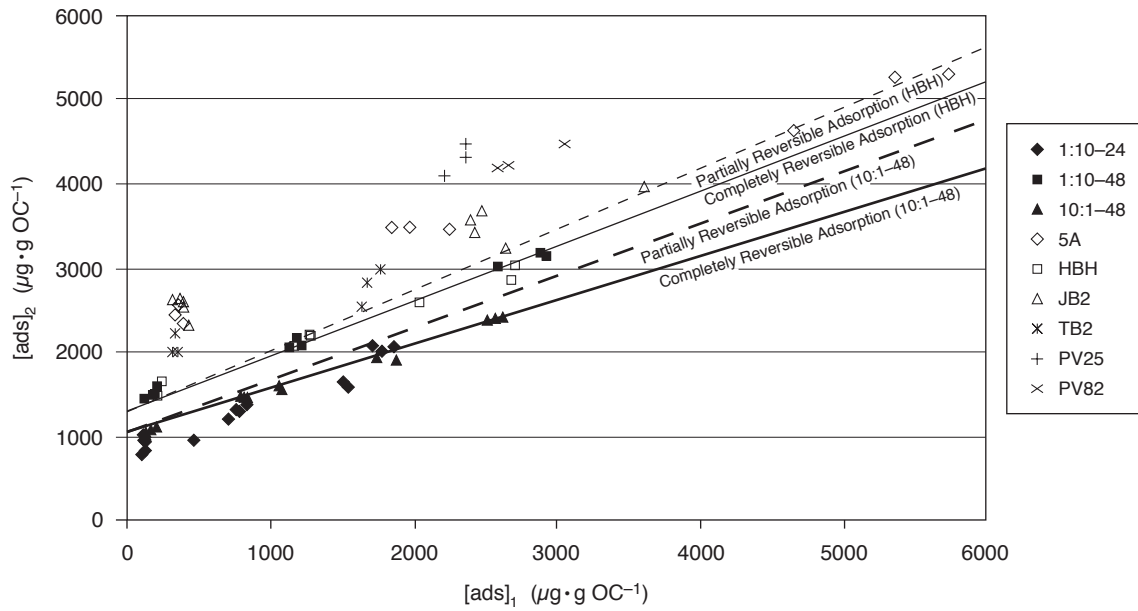
35

Figure 13. Phenanthrene adsorption to pristine sediments ($[ads]_1$, contact time of 1 h, and 1, 3, 7, and 14 d) and to PAH-loaded sediments ($[ads]_2$, reaction time of 14 d).
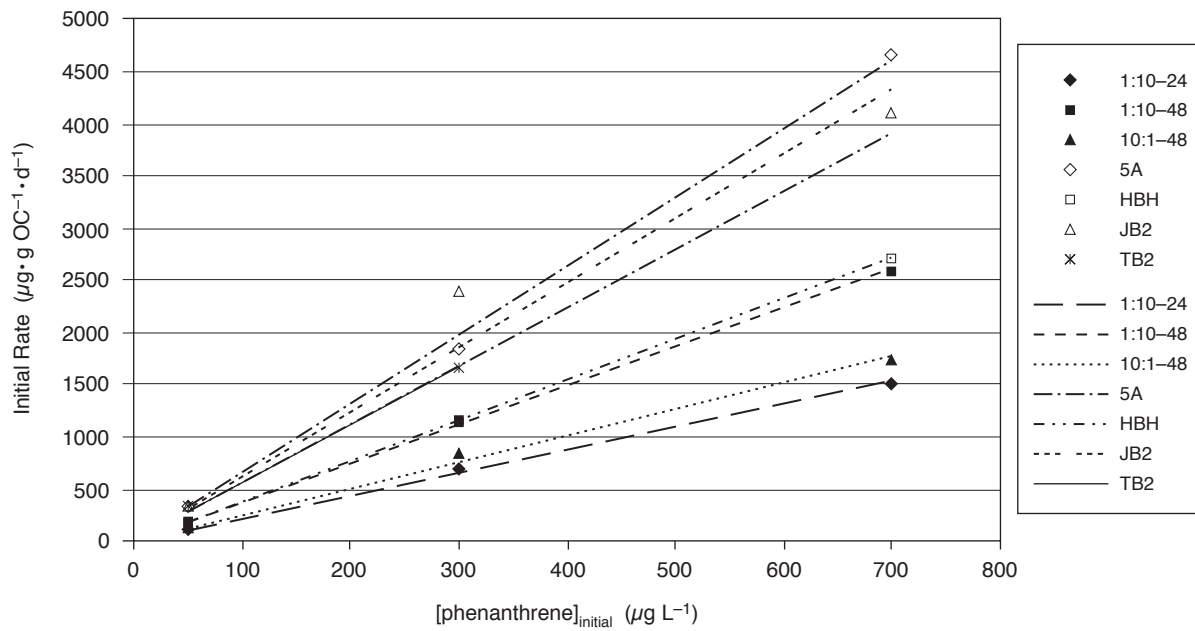

Figure 14. Initial rate of phenanthrene adsorption as a function of initial phenanthrene concentration to pristine sediment (without Port Valdez samples). Reaction time was 1 day.

Table 8a. Initial rates of phenanthrene adsorption at various concentrations based on 1 hour initial time increments. Initial rates at 1 hour were determined only for those sites listed, since adsorption was not measured at 1 hour for the others. Concentrations are for micrograms of phenanthrene per liter of solution at the start of the reaction. Rates of adsorption are on a per gram of organic carbon basis (g OC).

Sample	Initial Rate 50 µg L^{-1} (µg·g OC^{-1}·d^{-1})	Initial Rate 300 µg L^{-1} (µg·g OC^{-1}·d^{-1})	Initial Rate 700 µg L^{-1} (µg·g OC^{-1}·d^{-1})
1:10–24	99.5	461.4	1542.7
10:1–48	127.3	805.7	1874.4
JB2	306.9	1543.8	3599.3

Table 8b. Initial rates of phenanthrene adsorption at various concentrations based on 1 day initial time increments. Concentrations are for micrograms of phenanthrene per liter of solution at the start of the reaction. Rates of adsorption are on a per gram of organic carbon basis (g OC). n/d – not determined

Sample	Initial Rate 50 µg L^{-1} (µg·g OC^{-1}·d^{-1})	Initial Rate 300 µg L^{-1} (µg·g OC^{-1}·d^{-1})	Initial Rate 700 µg L^{-1} (µg·g OC^{-1}·d^{-1})
1:10–24	121.6	706.3	1512.5
10:1–48	131.0	838.1	1739.6
1:10–48	188.4	1173.3	2593.1
HBH	177.6	1156.1	2711.6
TB2	343.4	1665.9	n/d
PV25	n/d	2361.4	n/d
JB2	358.5	2386.2	4102.0
PV82	n/d	2386.6	n/d
5A	334.9	1845.2	4655.7
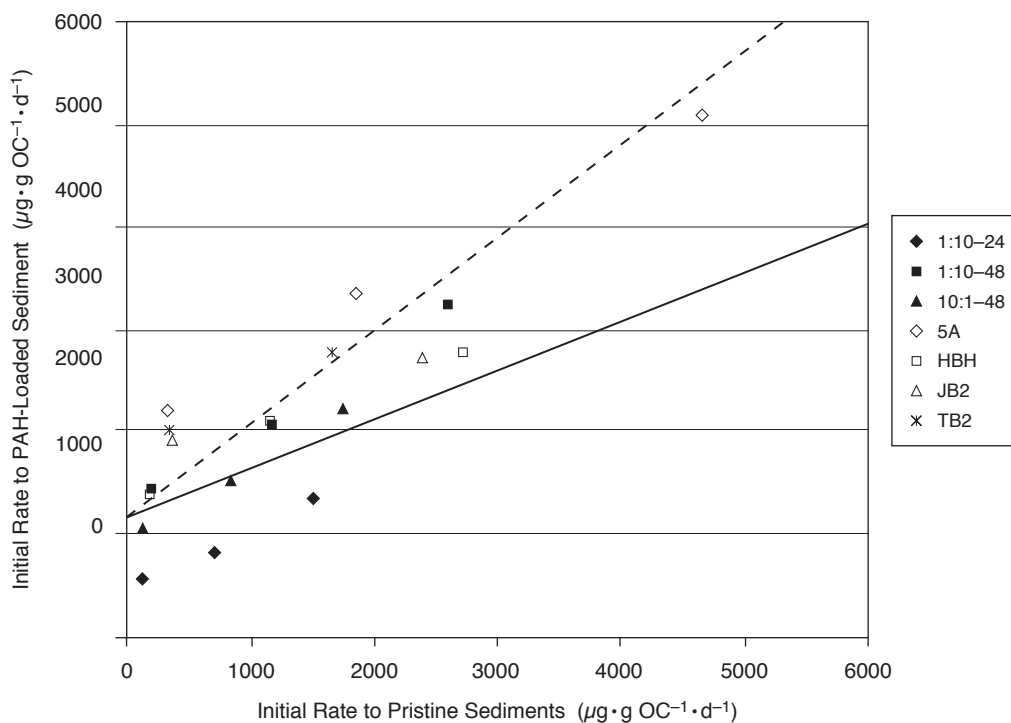
Figure 15. Comparison of initial rates of phenanthrene adsorption to pristine sediments and to PAH-loaded sediments. Reaction times were 1 day. The solid line describes completely reversible adsorption, and the dashed line describes partially reversible adsorption.

Organic carbon-normalized partition coefficients (K_{OC}) did not vary significantly for the different initial phenanthrene concentrations (50, 300, and 700 µg L^{-1}). Eighty percent (60 of 75) of the pairings were statistically the same at $p = 0.05$. In cases where K_{OC} differed, there was no consistent pattern with increasing concentration.

Figure 16a shows the variation in time of partition coefficients for both pristine and PAH-loaded sediments of sample 5A. This sample is typical in that 7 samples of 9 (5A, HBH, 10:1–48, 1:10–48, TB2, PV25, PV82) display the same trend, with K_{OC_2} being greater than K_{OC_1} at early time points. In 4 of the 7 cases (5A, HBH, 10:1–48, PV82), the partition coefficients become approximately equal at 7 to 14 days. Figure 16b, for the artificial humic acid 1:10–24, shows results contrary to most of the samples, with K_{OC_1} > K_{OC_2} initially, and is presented for contrast and comparison. In 6 of 9 cases (5A, HBH, 10:1–48, JB2, 1:10–24, PV82), there are large changes in K_{OC_1} within the first 7 days of adsorption, but most reactions reach steady state by 1 week. A few (TB2, 1:10–48, PV25) appear to reach steady state after only 1 day, and their partition coefficients did not vary significantly from that point on.

Figure 16a. Partition coefficients for phenanthrene adsorption to JB2. K_{OC_1} and K_{OC_2} describe partition coefficients for pristine and PAH-loaded sediments, respectively. K_{OC_2} was determined for sediments after 14 d of PAH-loading.

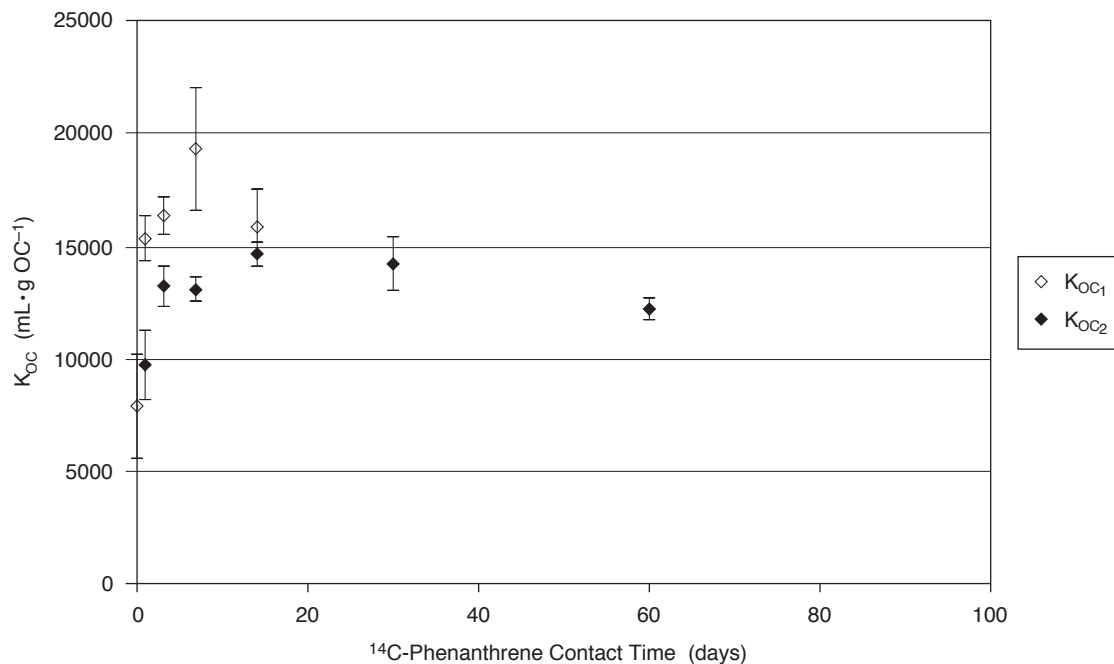Figure 16b. Partition coefficients for phenanthrene adsorption to 1:10–48. K_{OC_1} and K_{OC_2} describe partition coefficients for pristine and PAH-loaded sediments, respectively. K_{OC_2} was determined for sediments after 14 d of PAH-loading.
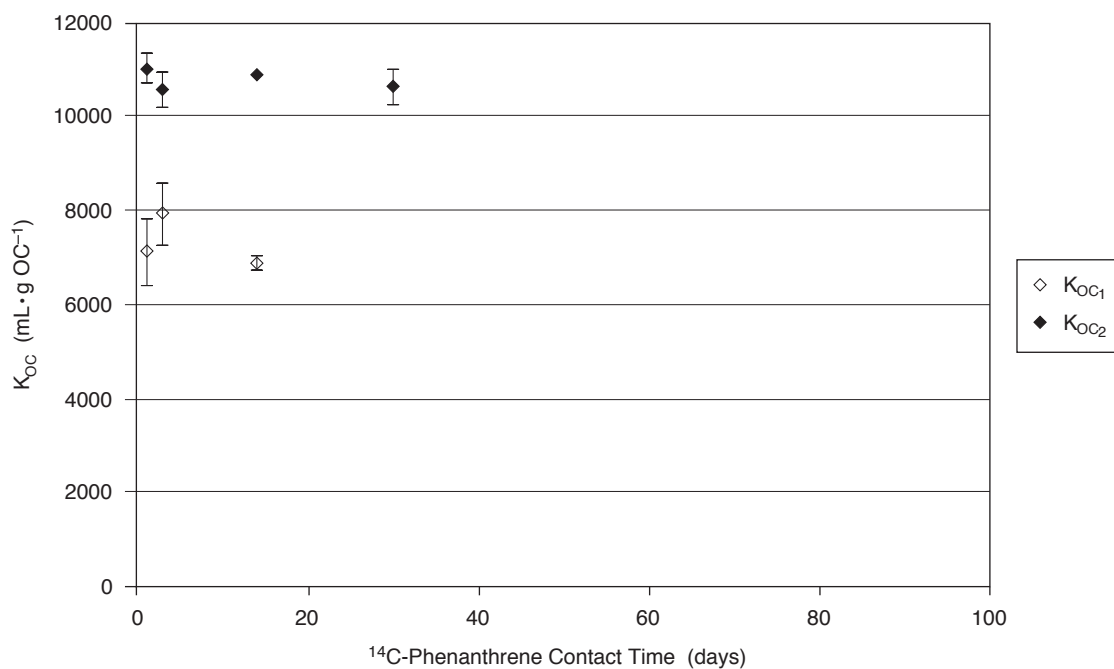
Discussion

The particle sizes of the ground montmorillonite were mostly clay, giving a large surface area-to-volume ratio. Montmorillonite was chosen as the standard material matrix because of its uniformity and its ability to adsorb humic acid. By removing the variability due to different substrate (i.e., natural sediment) properties, the intrinsic phenanthrene-adsorptive characteristics of the humic acid, alone, could be elucidated. The analyses of clays after the humic adsorption step indicated the carbon contents were comparable to those of normal marine sediments. Further, the humic clay association was stable under the experimental conditions employed, since percent OC did not change over time. Hence, the sorbents used in this study were good analogs of natural sediments, but controlled the variability of the mineral phase present in natural sediments and soils.

Reaction time was a minor factor in controlling the amount of phenanthrene adsorbed by pristine sediment on an organic carbon content normalized basis, while the initial concentrations of phenanthrene in solution (50, 300, or 700 $\mu g \ L^{-1}$) were the primary controlling factor. Linear adsorption was found for both the natural and synthetic humic acids of this study. Chiou et al. [1998] also found phenanthrene adsorption, up to 600 mg kg^{-1} substrate, to be linear in soils from Oregon and Illinois and oxic sediments of the Lower Mississippi River and Massachusetts Bay. Similarly, Kan et al. [1994] found linear adsorption for phenanthrene in sediments from a small river flood plain in Oklahoma. If phenanthrene adsorption sites were limited in number and the adsorbed phenanthrene saturated these sites within the experiments' concentration ranges, higher concentrations of phenanthrene would have lower partition coefficients. A similar result would be expected if there were a limited number of strong sites, even though weaker adsorption sites were numerous. However, K_{OC} varied little with concentration, leading to the inference that the organic matrix contained an unlimited number of sites with uniform strength.

The slopes of the individual linear adsorption isotherms were related to the properties of the humic acids discussed in Chapter 2. Generally, lower K_{OC} were found for humic acids with high N/C and fraction of carboxyl and amide functional groups. Rutherford et al. [1992] found similar relationships between adsorption isotherm slopes of benzene and carbon tetrachloride and the properties of organic matter extracted from natural soils. The phenanthrene K_{OC} values for natural humic acids in this study are of the same magnitude as those found by Chiou et al. [1998] using various North America sediment sources (21,000 to 44,000 $mL \cdot g \ OC^{-1}$) and those found by Kan et al. [1994] using Oklahoma flood plain sediment (12,000 $mL \cdot g \ OC^{-1}$).

In Figure 13, which compares adsorption properties of pristine sediments to those of sediments that were pre-loaded with phenanthrene, two pairs of theoretical lines are presented. The lines shown are for the HBH humic acid sample (see Chapter 2), chosen because it had the median adsorption of natural sediments in terms of partition coefficient as well as rate constant (expressed as $L \cdot g \ OC^{-1} \cdot d^{-1}$), and for sample 10:1–48, which was typical of the melanoidins. Both lines in each pair assume that $K_{OC_1} = K_{OC_2}$. One line (solid), for complete reversibility, is based on the premise that phenanthrene adsorbed to the sediment is freely able to dissociate from the organic matrix, limited only by the rate of diffusion. The other line (dashed), describing partial reversibility, is based on the premise that only a portion of the phenanthrene adsorbed to the sediment is free to redissolve, while 20% of the phenanthrene is irreversibly bound. That phenanthrene could either be trapped within the organic matrix, due to changes in the conformational structure of the matrix, or be associated with sites having unusually large binding energies for phenanthrene. However, the linear adsorption isotherms indicate that the second possibility is unlikely. In either the wholly reversible or partly reversible case, some phenanthrene desorbed from the organic matrix and was added to the total dissolved phenanthrene pool in the second experiment, in which an aliquot of 300 $\mu g \ L^{-1}$ ^{14}C-phenanthrene was added to the PAH-loaded sediments. This, in turn, caused the adsorbed phenanthrene concentration after the second phenanthrene addition to be greater, even in the absence of any change in K_{OC} or any irreversible adsorption. For total phenanthrene adsorbed to the

sediments on a per unit organic carbon basis, the influence of reversibility can be seen by comparing the theoretical lines to the observed data for HBH. Most of the humic acids were similar, in that the theoretical line describing complete reversibility fitted the data better than the line for partial reversibility.

In this study, the possibility was considered that the greater $[ads]_1$ of humic acids could be due, in part, to their previous exposure to environmental PAH. Even though the extraction of humic acids from natural sediments was a fairly vigorous process, natural PAH may have been retained by the humic acid and carried over into the laboratory controlled experiments. The environmental phenanthrene could affect $[ads]_1$ much like $[ads]_1$ influenced $[ads]_2$. Total aromatic content (TARO) of the natural sediments (see Chapter 2) was weakly correlated with $[ads]_1$ ($p = 0.10$, $n = 92$, $\alpha = 1.665$, $t = 0.17779$). However, the concentrations of TARO in natural sediments were small, and should not influence $[ads]_1$ because the potential desorbed phenanthrene concentration was much less than concentrations used in the experiments. The effect seen may, in fact, be due to just the greater partition coefficient and, hence, a greater affinity for environmental PAH.

The initial rates of PAH adsorption in this study were rapid, with a slow approach to steady state occurring after 24 hours (Figures 14 and 16a). The linear relationship between phenanthrene concentration and initial adsorption rate (Figure 14) for each humic acid is consistent with a diffusion process. Adsorption was nearly complete only after three days in most cases, as opposed to time scales on the order of minutes or hours, which would be expected of a process occurring solely at the particle surface. Similar patterns of nonionic organic compound adsorption have been observed by others [Wu and Gschwend 1986; Leenheer and Ahlrichs 1971; Karickhoff 1980]. The slow approach to steady state is indicative of diffusion of HOC into a three-dimensional organic matrix. Kan et al. [1994] reported phenanthrene adsorption to Oklahoma flood plain sediment reaching equilibrium in one to four days, while Allen-King et al. [1995] reported perchlorethene adsorption to sediments of Ontario, Canada, reached equilibrium by three days. Wu and Gschwend [1986] described a diffusion model in which initial rapid HOC diffusion into pore fluids of the interstitial spaces between particle aggregates is followed by much slower microscale partitioning into the organic matter. It is interesting that, in this study, the pattern was seen in the sediments coated with reconstituted humic acids, and argues that the phenomenon is a general characteristic of a three-dimensional structure that humic acids acquire when adsorbing to clay minerals. It is not only true of associations that form in the environment.

In Figure 15, initial rates of adsorption of phenanthrene to sediments pre-loaded with PAH are compared to the initial rates of phenanthrene adsorption to pristine sediments. On the figure, two theoretical lines are plotted; one represents complete reversibility of phenanthrene adsorption (solid), and the other represents partially reversible adsorption of phenanthrene (dashed). The partially reversible line is based on an average of desorption partition coefficients for HBH, as was done earlier for the $[ads_2]$ calculations. As illustrated by the HBH example, most data points fall near, but slightly above, theoretical lines describing completely reversible adsorption. This indicates that a small fraction of the initial phenanthrene adsorption was not reversible under the conditions of these experiments.

The points in Figure 16a also show evidence of slow adsorption. As seen, K_{OC_2} was greater than K_{OC_1} initially for most of the humic acids, but the two became similar later. This is expected, since the initially adsorbed phenanthrene takes some time to exchange with the solution during desorption from the organic matter, according to its diffusion rate. In the two cases where K_{OC_1} was initially greater than K_{OC_2} (samples JB2 and 1:10–24), an examination of their desorption from pristine sediments over 14 days (Figure 16b) shows that it took much longer to achieve steady state (possibly greater than 14 days) than for the other humics. The diffusion of adsorbed phenanthrene back into the solution phase would likewise be slow. So, at the initial time points of the investigation into adsorption to PAH-loaded sediments, the previously adsorbed phenanthrene contributes less to the available phenanthrene pool in solution as it desorbs, leading to smaller apparent K_{OC_2}.

The range of organic matter properties and loadings examined in this study spans a large part of the natural variability seen in the environment. The rates of adsorption, ranging from 100 to 4700 $\mu g \cdot g\ OC^{-1} \cdot d^{-1}$ are not different from those found for intact sediments [Henrichs et al. 1997]. From this, it follows that the conclusions drawn from this data may be applied to natural sediments and other environmental samples. The slow approach to steady state indicates that the rate of adsorption is primarily controlled by diffusion within the organic matrix, and investigations into PAH adsorption may need to last at least seven days for steady state to be reached. Once within the organic matrix, phenanthrene binding is almost entirely reversible, but this too is a slow process requiring one to more than 14 days for completion.

Finally, the earlier reports [Chin and Gschwend 1992; Boyd and Sun 1990; Kile et al. 1995] that subsequent adsorption is enhanced in previously contaminated sediments is not supported by the findings of this study. Except for the synthetic humic acid 1:10–48, the adsorption of phenanthrene to humic acids previously contaminated with PAH was not affected by the adsorbed PAH already present in the organic matrix.

Chapter 4. Observed Desorption Kinetics of Phenanthrene from Mineral-Bound Humic Acids: Consequences of Conformational Changes [3]

Abstract

This study addresses the rates and mechanisms of phenanthrene desorption from marine humic acids and melanoidins coated onto clay. The humic acids were extracted from Alaska coastal sediments and the melanoidins synthesized from glucose and bovine casein. These organic substances represent a wide range of properties potentially affecting associations with polycyclic aromatic hydrocarbons. Montmorillonite was used as a common mineral substrate in order to eliminate variability due to the mineral phase. The desorption of phenanthrene was measured using a radiotracer. The extent of desorption was less for both increasing phenanthrene concentrations used in the initial adsorption phase of the experiment and shorter adsorption reaction time. Desorption steady state was reached after three to seven days for all of the humic acids studied in this experiment, reflecting slow diffusion processes within the organic matrix. Initial rates were found to be directly proportional to the initial concentration of phenanthrene used during the adsorption phase, and decreased with the carbon content of the humic acid coated clay. Desorption was not related to humic acid structural characteristics such as aliphaticity, aromaticity, percent carboxylic, amidic, or carbonyl carbons measured by ^{13}C nuclear magnetic resonance spectroscopy. Decreased desorption with increasing adsorbed phenanthrene concentration was consistent with the interpretation that conformational changes to the humic acid structure occurred during the adsorption and diffusion of phenanthrene into the organic matrix.

Introduction

Sediments are a major reservoir of persistent environmental contamination by hydrophobic substances such as polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB) and pesticides [Chin and Gschwend 1992; Hatzinger and Alexander 1995], because of the low aqueous solubility and high surface affinity of these compounds. Adsorption has been investigated as a key process leading to persistent sediment contamination in the environment. It is believed that hydrophobic organic compounds (HOC) can either become entrapped within the solid micropores or between the silicate layers of montmorillonite [Lahlou and Ortega-Calvo 1999] or partition into the organic matter [Karickhoff and Morris 1985; Brusseau et al. 1991]. For uncharged organic pollutants, organic matter is considered the primary sorbent component [Karickhoff and Morris 1985].

Desorption processes have a significant bearing on the redistribution of hydrocarbon pollutants and their uptake by marine organisms. They have, however, received less attention than adsorption processes [Kan et al. 1994]. While theories exist to explain adsorption of hydrophobic organic compounds to organic matter [Karickhoff and Morris 1985; Brusseau et al. 1991], understanding of desorption presents many challenges that are only just beginning to be explored. The reversibility of HOC adsorption is the subject of much debate in the literature, with reports of adsorption/desorption hysteresis [Kan et al. 1994 and references therein] due to the sequestration of HOC into a non-labile fraction. There are also reports that adsorption of HOC is completely reversible [Wu and Gschwend 1986; Borglin et al. 1996], with the appearance of hysteresis actually being an artifact of slow sorption kinetics [Kan et al. 1994 and references therein].

Studies have attributed slow sorption kinetics to the complex pore geometry of particle matrices [Pavlostathis and Mathavan 1992]. The sediment or soil organic matter, of which humic acid is a part, is a flexible, cross-linked, branched, amorphous (noncrystalline), polyelectrolytic, polymeric substance

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[3] Terschak, J.A., and S.M. Henrichs. Observed Desorption Kinetics of Phenanthrene from Mineral-Bound Humic Acids: Consequences of Conformational Changes. In preparation for submission to Environmental Science and Technology.

within which organic pollutants can diffuse [Brusseau and Rao 1991]. Humic acid has been described as an open structure with hydrophobic cavities [Schnitzer and Khan 1972]. The organic matter is porous, and in contrast to the fixed, rigid pores of sediment mineral particles, the organic matter pores are dynamic and ephemeral [Brusseau and Rao 1991]. The size, shape, and hydrophobicity of the pores within the organic matter are sensitive to variations in solution chemistry (e.g., ionic strength), and, therefore, changes in the ability to bind HOC can occur [Schlautman and Morgan 1993]. The hydrophobicity of PAH suggests that PAH association is governed by diffusion into nonpolar environments of the organic matter [Schlautman and Morgan 1993; Ragle et al. 1997; Gauthier et al. 1987].

Investigations into the adsorption kinetics of HOC to natural organic matter have shown a rapid initial uptake of the HOC followed by a slow approach to steady state [Chin and Gschwend 1992; Wu and Gschwend 1986]. Slow adsorption kinetics have been shown to be correlated with humic acids possessing more rigid structural components [Schlebaum et al. 1998]. This leads to the conclusion that the labile fraction of humic acids is composed of relatively open humic structures while the non-labile fraction is composed of more condensed, rigid humic structures [Schlebaum et al. 1998 and references therein].

This chapter addresses the rates and mechanisms of phenanthrene desorption from humic acids and melanoidin-coated clay. This study was conducted as part of an examination of the role humic acids play in the adsorption and desorption of PAH by sediments of coastal marine environments. The sorbents investigated were humic acids that were extracted from Alaska coastal sediments, then bound to a standard clay mineral, in order to eliminate variability due to the mineral phase. Melanoidins were used as model marine humic acids because of their lack of initial PAH contamination (see Chapter 2), and because they extend the range of structural properties within this set of humic acids. These organic substances represent a wide range of properties potentially affecting associations with PAH.

Experimental Section

Substrate preparation

A montmorillonite standard (A.P.I. # 26, 49 E 2600 from Clay Spur, Wyoming; Ward's Natural Science Establishment, Inc.) was ground for 2 minutes using a shatter box equipped with carbide rings. The resulting powder was passed through a 270 mesh (53 µm) sieve using a Ro-Tap® apparatus. Organic material was removed from the clay by oxidizing it with 30% hydrogen peroxide. A slurry of clay and H_2O_2 was prepared in an open Pyrex container. The clay was mixed for 12 hours at room temperature. Low heat was then applied, bringing the slurry to 35–40 °C. Fresh H_2O_2 was added as needed. Stirring was continuous until no evolution of CO_2 gas was evident. The slurry was then centrifuged at 14,000 g for 2 hours and the clear supernatant was discarded. A wash of organic-free, glass-distilled water was used and the clay was again centrifuged as above. A small sample of the organic-free clay was submitted for TOC analysis and the remaining material was stored under ultra high purity nitrogen gas (UHP-N_2) gas at 5–10 °C.

Sediment subsamples were analyzed for size distribution of particles using the sieve-pipette method [Jackson 1965]. The sediment was divided into six fractions: fine sand > 63 µm, very fine sand (63–50 µm), coarse silt (50–20 µm), medium silt (20–5 µm), fine silt (5–2 µm), and clay (< 2 µm). Fine sand and larger particles were removed from the sediment by sieve. In a 1-L graduated cylinder, a suspension of the material that passed through the sieve was made in 1 L of distilled water and allowed to settle for a prescribed time based on Stokes' Law [Jackson 1965]. Particle size distribution was calculated as a percentage of the recovered material (see Chapter 3, Figure 11).

Humic acid sources

Natural humic acids were taken from sediment samples collected at three separate coastal locations in Alaska (see Chapter 3, Table 7). Intertidal sediment samples from Lower Cook Inlet were collected in July 1995, July 1996, and May 1999. Sampling occurred during spring tides below the mean lower-low water level. Subtidal sediment samples were collected from the Port Valdez region in August 1996 using a Haps corer and from the Beaufort Sea region during September 1997 using a Kynar-coated van Veen grab sampler. Any overlying debris was removed and then sediment was collected from the oxic layer (upper 2 cm) with metal implements that had been heated to redness before use. All samples were stored until needed at $-50\,°C$ in pre-combusted glass jars.

Humic acid was isolated using the alkali (0.5 M NaOH) extraction procedure of Anderson and Schoenau [1983]. After extraction from approximately 30 g of wet sediment, humic acid was precipitated by the addition of 6 M HCl until a pH of 1.5 was obtained. The precipitated extract was allowed to stand for 15 minutes and was then centrifuged for 30 minutes at 14,000 g. The precipitated humic acid was lyophilized at $-85\,°C$ for 24 hours. The resulting dry humic acid was stored at room temperature in a glass vial under $N_{2(g)}$.

Artificial humic acids were prepared in the laboratory by refluxing various ratios of glucose and bovine casein in buffered solutions for 24 to 48 hours as described by Yamamoto and Ishiwatari [1989] The buffer was composed of 125 ml 0.1 M KH_2PO_4, 75 ml 0.1 M NaOH and 50 ml of glass-distilled water to give a final pH of 7.0. After the prescribed reaction time, the mixture was allowed to cool with stirring, then transferred to 250-ml Nalgene® centrifuge bottles. The artificial humic acid was isolated using the extraction procedure above.

Substrate coating

Humic acids were coated to the montmorillonite substrate for use in the adsorption/desorption experiments. Approximately 1 g of lyophilized humic acid was dissolved in 100 mL of organic-free water and brought to a pH of 10 with sodium hydroxide. The solution was mixed under an atmosphere of UHP-N_2 for 3 to 7 days with adjustments made daily to maintain the pH. Once dissolved, the humic acid solution was added to the washed clay and mixed for 24 hours. The suspension was transferred to a centrifuge bottle containing the crystallized salts resulting from the evaporation of an equal amount of artificial seawater and mixed for 48 hours. The suspension was then centrifuged at 14,000 g for 2 hours and the supernatant was discarded. A sample of the humic acid coated clay was dried and submitted for TOC analysis to determine the extent of humic acid adhesion. After flushing the headspace with UHP-N_2 gas, the humic acid coated clay was stored in a refrigerator at $5-10\,°C$.

Total organic carbon measurements

Total organic carbon analyses of the clay substrates were performed by Donald Schell's laboratory at the University of Alaska Fairbanks using a Delta Plus mass spectrometer equipped with a Finnigan MAT Conflo II interface and a Carlo Erba elemental analyzer.

Desorption experiments

All glassware and Teflon® liners were treated to remove any hydrocarbon contamination before use. Glassware was baked in a muffle furnace at $450\,°C$ for at least 8 hours. Teflon® cap liners were soaked in chromic acid for 20 minutes and then rinsed 3 times with clean organic-free water.

Artificial seawater was prepared from organic-free water that had been glass distilled over a saturated solution of potassium permanganate. To each liter of water the following salts were added: 23.260 g NaCl, 10.636 g $MgCl_2 \cdot 6H_2O$, 3.918 g anhydrous Na_2SO_4, 1.102 g $CaCl_2$, 0.664 g KCl, 0.192 g $NaHCO_3$,

0.096 g KBr, and 0.026 g H_3BO_3 [Lyman and Fleming 1940]. Also, 0.500 g $HgCl_2$ was added as an antibiologic agent.

A stock phenanthrene solution was prepared by dissolving 0.0060 g of phenanthrene in a 100-mL volumetric flask with acetonitrile. This solution was then used to prepare the various phenanthrene solutions required for the experiments. Aliquots of the phenanthrene stock solution, along with [9-^{14}C] phenanthrene (5–15 mCi mmol^{-1}; Sigma Chemical Co.) dissolved in acetonitrile were added to vials. The acetonitrile was evaporated, and the required amount of artificial seawater was added to make final concentrations of 50, 300, and 700 μg L^{-1}, in which 10% of the final phenanthrene concentration was radiolabeled. All solutions were prepared 24 hours in advance and stored in a refrigerator (5–10 °C). Previous experiments within this laboratory have shown that for concentrations of phenanthrene ranging from 10 to 750 μg L^{-1}, there was no loss of hydrocarbon due to evaporation or adhesion to the walls of the container. In addition, all experiments had control vials containing no sediment.

Experiments began by weighing 0.1 g of wet, humic-coated clay into 2-dram vials with Teflon$^®$ lined caps. Controls were treated exactly as experimental vials from this point forward, but did not have sediment added. Five milliliters of artificial seawater solutions containing radiolabeled phenanthrene at several concentrations (50, 300, or 700 μg L^{-1}) were added to the vials. A 15-second agitation on a vortex mixer thoroughly mixed the clay and solution. The vials were then placed on a table shaker at 150–200 rpm. After adsorption for 1 h, 1 d, 3 d, 7 d, or 14 d, the vials were centrifuged at 2400 g for 30 minutes and a 1.0 mL aliquot of each of the radiolabeled reaction solutions was removed and scintillation counted to determine phenanthrene adsorption to pristine sediments. The remaining supernatant was discarded and replaced with a 300 μg L^{-1} phenanthrene solution, without radiolabel, to begin the desorption phase of the experiment.

Vials containing the previously adsorbed sediment and the fresh phenanthrene solution were vortex mixed for 15 seconds and then placed on a table shaker at 150–200 rpm. After desorption for 1, 3, 7, 14, 30, 60, or 90 days, the vials were centrifuged at 2400 g for 30 minutes and a 1.0 mL aliquot of the supernatant was removed and scintillation counted to determine the amount of labeled phenanthrene desorbed from the sediment.

Upon the completion of each desorption experiment, the remaining supernatant was discarded and the sediments were placed in a 65 °C oven until dry. Sediment dry weights and pore water volumes were calculated from these dried sediments.

Results

The organic carbon content of the clay after hydrogen peroxide treatment was ≤ 0.095 wt %. Analyses were performed to confirm that humic acid was, indeed, bound to the clay after the coating process and that humic acid was not removed from the clay during the course of the adsorption and desorption experiments. Initial concentrations of organic matter were similar to those found naturally in marine sediments. The organic carbon contents of the clays after the adsorption and desorption experiments were not statistically different from those measured before the experiments (data not shown).

Radiolabeled phenanthrene concentrations remained constant over time in the controls, indicating that there were no significant losses due to adsorption to vessel walls of the Teflon$^®$ cap liner, nor to volatilization. Desorption plots similar to Figures 17a (melanoidins) and 17b (natural humic acids) were constructed. For each humic acid coated sediment, radiolabeled phenanthrene was allowed to adsorb for a prescribed number of days (7 days for sample 10:1–48 in Figure 17a), after which the solution was replaced with non-labeled 300 μg L^{-1} phenanthrene. The desorption of adsorbed radiolabeled phenanthrene was measured at 1, 3, 7, 14, 30, 60, and 90 days and reported as a fraction of what was

expected based on 100% reversibility, that is, partition coefficients associated with adsorption were assumed to be the same as those associated with desorption [Wu and Gschwend 1986].
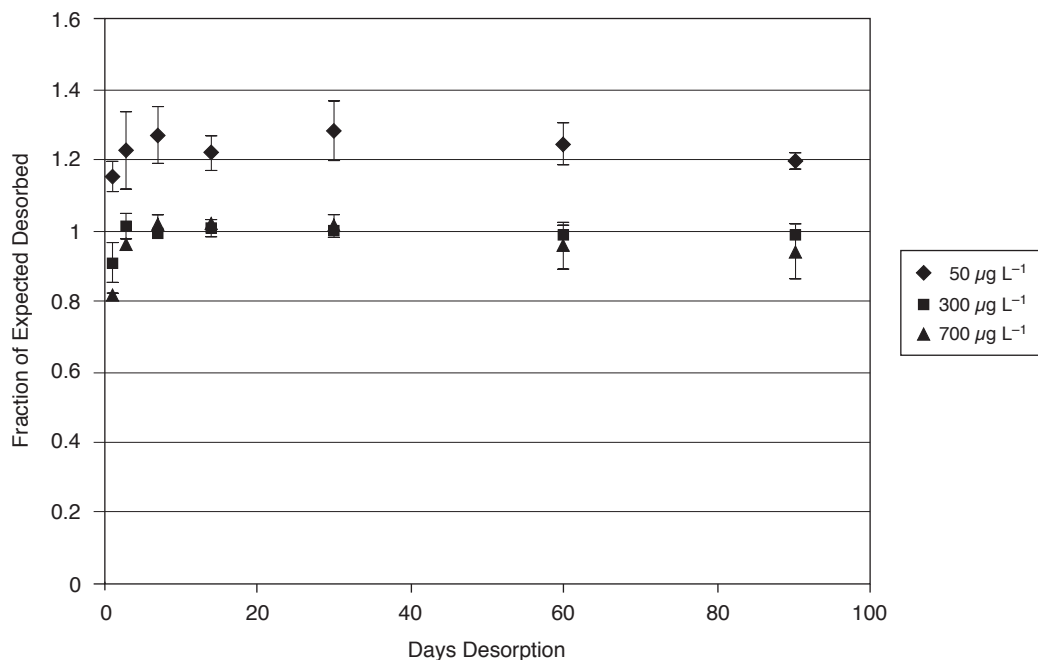

Figure 17a. Desorption plot for a synthetic humic acid (10:1–48). Radiolabeled phenanthrene (50, 300, and 700 µg L^{-1}) was adsorbed for 7d, then replaced with non-labeled phenanthrene (300 µg L^{-1}). Desorption was measured after 1, 3, 7, 14, 30, 60, and 90 d.

Figure 17a is typical of these plots, in that desorption decreases with increasing concentrations of phenanthrene adsorbed to the sediment. In general, desorption required 3 to 7 days to reach steady state. The observed fraction of expected phenanthrene desorption ranged from 0.6 to 1.6 for all of the humic acids investigated, with most values lying between 0.8 and 1.2. Note that the expected (calculated) desorption is much less than 100% of the phenanthrene adsorbed initially, because of the very strong phenanthrene adsorption. So, fractions of expected phenanthrene adsorption >1 still reflect incomplete desorption.

A second series of desorption plots (Figures 18a and 18b, melanoidins and natural humic acids, respectively) was constructed to investigate the influence adsorption time had on desorption. In these plots, the percent of expected phenanthrene desorption after a fixed time (7 days for sample 10:1–48 shown in Figure 18a) was compared to adsorption times of 1 hour, and 1, 3, 7 and 14 days for a particular humic acid. While 20 of 44 samples approached steady state after approximately 3 to 7 days of adsorption time, 24 of 44 continued a trend of increasing desorption with increasing days of adsorption, but to varying degrees (from 10% to 40% increase). The magnitude of these slow increases in fraction of expected desorbed phenanthrene was not correlated with any of the humic acid structural properties studied (see Chapter 2).

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Figure 17b. Desorption plot for a natural humic acid (TB2). Radiolabeled phenanthrene (50, 300, and 700 µg L^{-1}) was adsorbed for 14 d, then replaced with non-labeled phenanthrene (300 µg L^{-1}). Desorption was measured after 1, 3, 7, 14, 30, 60, and 90 d.

Figure 18a. Extent of desorption for a synthetic humic acid (10:1–48). Radiolabeled phenanthrene (50, 300, 700 µg L^{-1}) was adsorbed for 1 h, 1, 3, 7, and 14 d. The solution was replaced with non-labeled phenanthrene (300 µg L^{-1}) and allowed to desorb for 90 d.
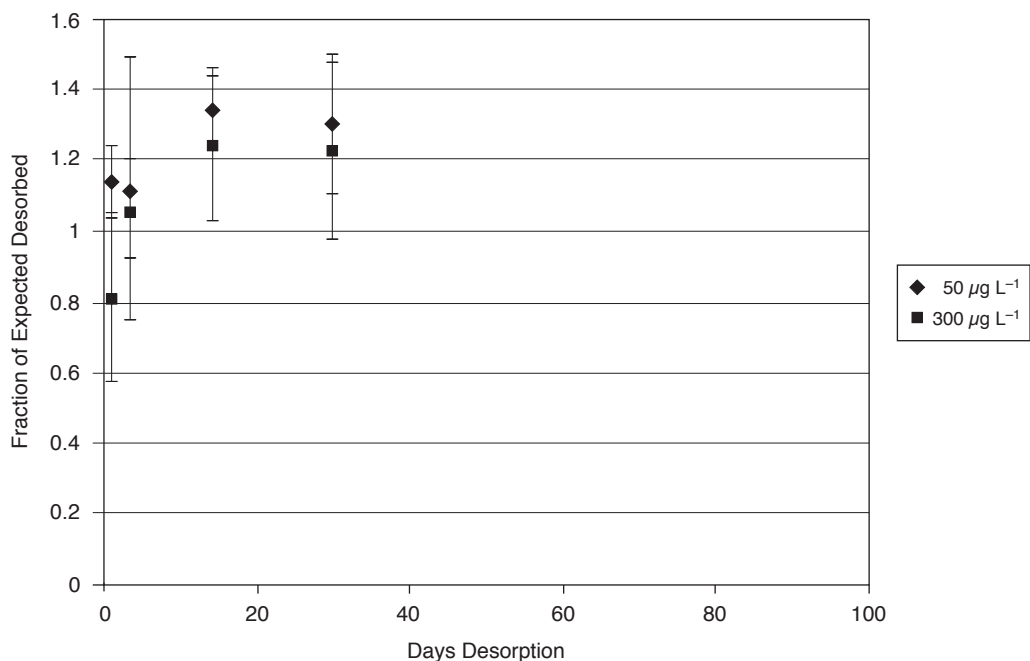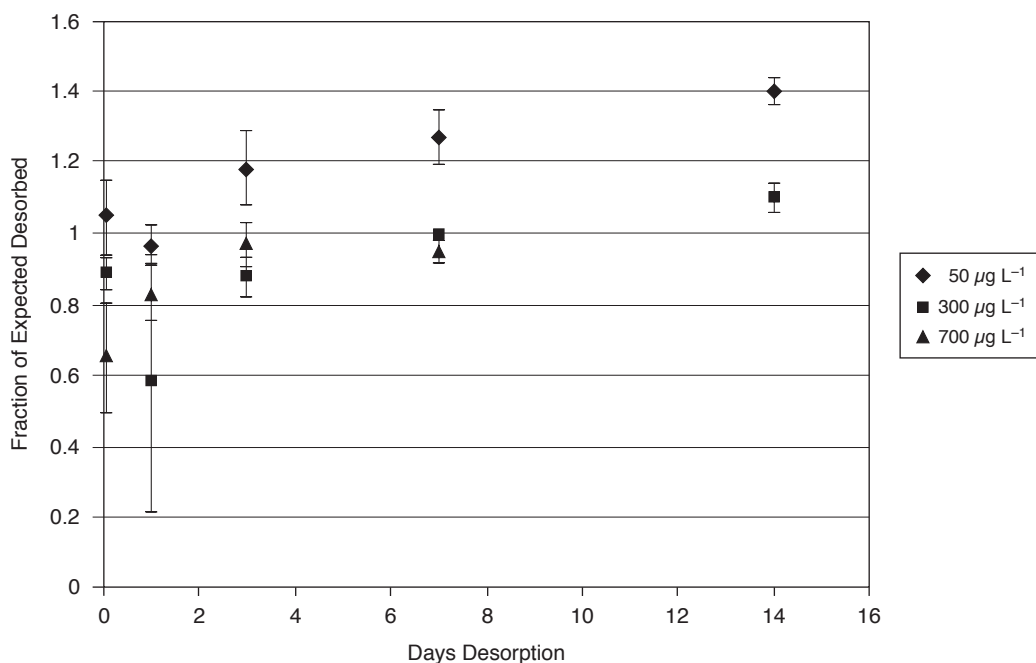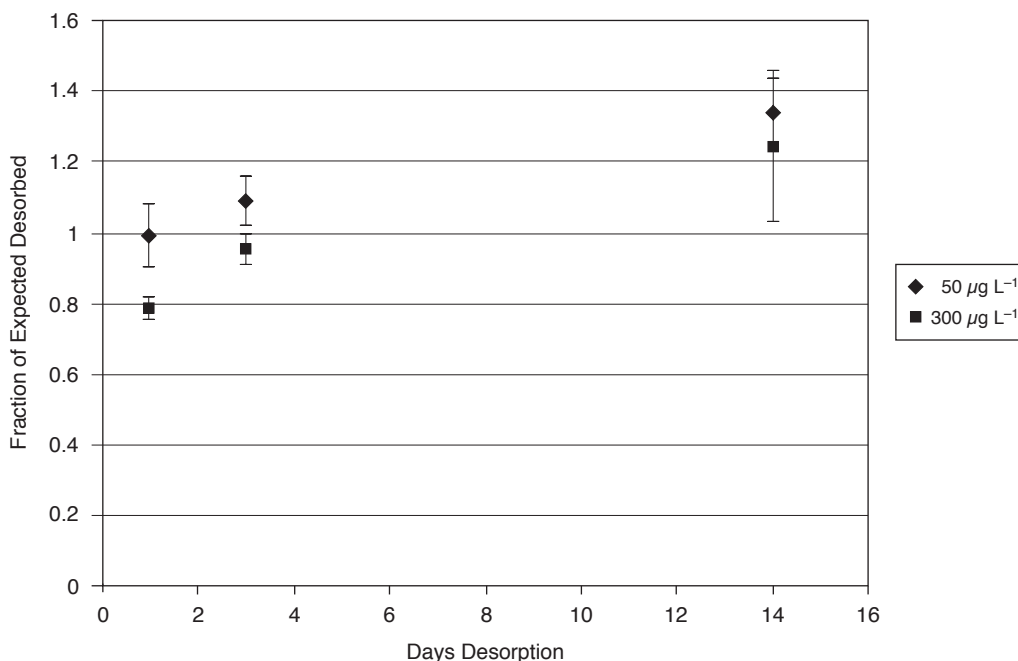
Figure 18b. Extent of desorption for a natural humic acid (TB2). Radiolabeled phenanthrene (50, 300, 700 µg L^{-1}) was adsorbed for 1 h, 1, 3, 7, and 14 d. The solution was replaced with non-labeled phenanthrene (300 µg L^{-1}) and allowed to desorb for 14 d.

Initial rates of phenanthrene desorption from sediments were calculated for 1 day of desorption after 1 day of adsorption time (Table 9). Figure 19 shows the initial rate to be directly proportional to the dissolved concentration of phenanthrene during the prior adsorption reaction. Overall, the rates ranged from 169 µg·g OC^{-1}·d^{-1} for a synthetic humic acid, 1:10–24, at 50 µg L^{-1} phenanthrene to 7800 µg·g OC^{-1}·d^{-1} for a natural humic acid, JB2, at 700 µg L^{-1} phenanthrene. Mineral particles coated with natural humic acids generally displayed faster initial rates of desorption than did synthetic humic acids (JB2 > 5A >> 10:1–48 = TB2 > 1:10–48 > HBH > 1:10–24), corresponding to their greater partition coefficients (see Chapter 3). Initial rates, evaluated after 1 day of desorption and at 300 µg L^{-1} phenanthrene concentration, were found to be significantly negatively correlated with both the carbon content of the humic acid coated clay ($r^2 = 0.52$, $t = 1.714$, $n = 9$) and the percent carbon of the humic acid itself ($r^2 = 0.62$, $t = 3.409$, $n = 9$).

Table 9. Initial rates of phenanthrene desorption after 1 day of adsorption at various concentrations based on 1 day time increments. Concentrations are for micrograms of phenanthrene per liter of solution at the start of the adsorption phase. Rates of desorption are on a per gram of organic carbon basis (g OC). n/d – not determined

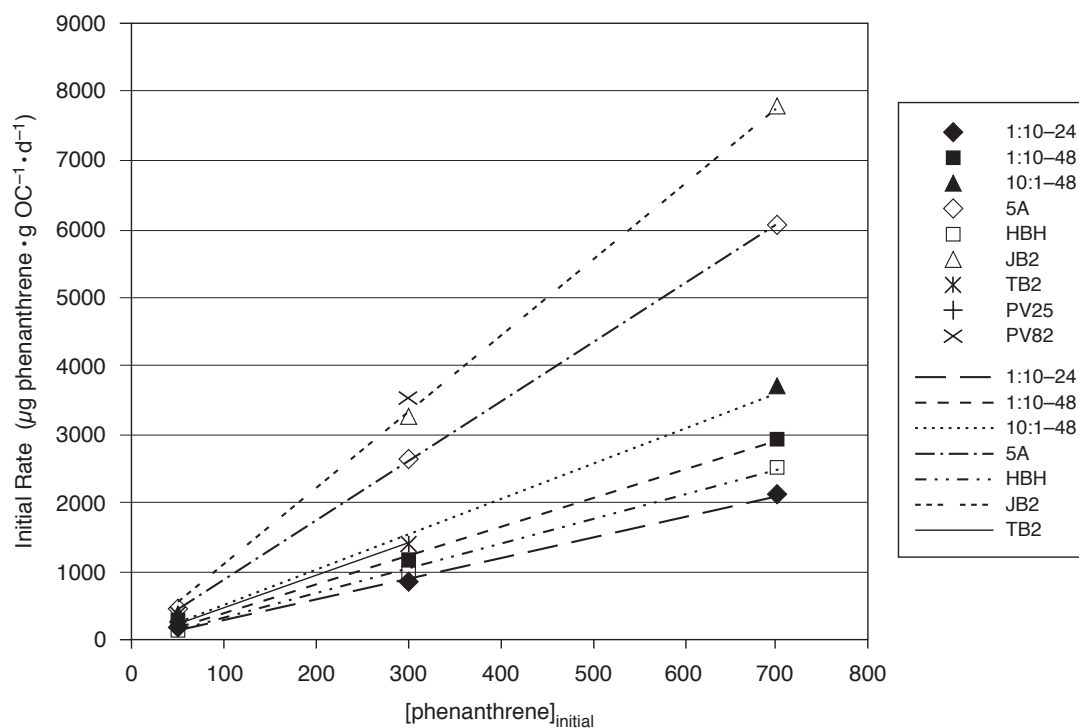| Sample	Initial Desorption Rate 50 µg L^{-1} (µg·g OC^{-1}·d^{-1})	Initial Desorption Rate 300 µg L^{-1} (µg·g OC^{-1}·d^{-1})	Initial Desorption Rate 700 µg L^{-1} (µg·g OC^{-1}·d^{-1})
1:10–24	169	838	2110
1:10–48	317	1210	2940
10:1–48	257	1250	3710
5A	501	2660	6050
JB2	370	3250	7800
HBH	185	974	2530
TB2	441	1410	n/d
PV25	n/d	1090	n/d
PV82	n/d	3540	n/d

Figure 19. Initial desorption rates after 1 day of desorption time. Radiolabeled phenanthrene was in contact with the sediments for 1 day before desorption began.

Discussion

In previous work, phenanthrene adsorption was found to be dependent upon the degree of nonpolar character of the humic acids (see Chapter 2), but desorption trends of the current study were not explained by humic acid structural characteristics such as aliphaticity, aromaticity, or percent carboxylic, amidic, or carbonyl carbons as measured by ^{13}C nuclear magnetic resonance spectroscopy. Other studies have been unable to link the observed extent of desorption to additional characteristics of the organic matter such as cation exchange capacity, organic carbon content, surface area, and solubility [Pavlostathis and Mathavan 1992].

Contact time is a minor factor in controlling the amount of phenanthrene adsorbed to sediments on a normalized to organic carbon content basis, while the initial concentration of phenanthrene in solution is the primary factor (see Chapter 3). The extent of phenanthrene desorption was found to decrease for both increasing initial phenanthrene concentrations used in the adsorption phase of the experiment and decreased reaction time. The reduction in the proportion of desorbed phenanthrene with increasing concentrations is consistent with other studies [Schlebaum et al. 1998] which attributed this pattern to increasing partitioning of phenanthrene into more structurally rigid portions of the humic acid matrix. However, decreased desorption was also expected with increasing adsorption times, but this was not observed. Numerous studies in the literature report that decreased reversibility of hydrocarbon adsorption is a function both of increasing initial concentrations [Borglin et al. 1996; Pavlostathis and Mathavan 1992; Schlebaum et al. 1998] and increasing adsorption times [Karickhoff and Morris 1985; Borglin et al. 1996; Pavlostathis and Mathavan 1992; Schlebaum et al. 1998].

One potential explanation for changes in desorption with phenanthrene concentration is conformational changes in the humic acid structure. A possible cause of conformational change is the concentration of salt. The humic substances used in this study were first dissolved in fresh water, but then artificial seawater salts were added before the material was coated onto humic substances for 48 hours. Subsequent experiments took place in artificial seawater. The addition of salt causes negative sites on the humic acid to become neutralized and the intramolecular repulsions to decrease, allowing for the humic acid molecule to fold and coil upon itself [Ragle et al. 1997]. This conformational change has been observed to take place within two hours of the addition of salt [Engebretson and von Wandruszka 1998] for dissolved humic substances, and, unless the process was much slower for the particle associated humics, it should have been complete long before the experiments began. Large anions such as bromide and chloride were found to be unable to penetrate the pseudomicellar domains of a folded humic acid in the studies conducted by Ragle et al. [1997]. If increasing conformational change took place during longer adsorption times, the more compact structure could have excluded phenanthrene from tortuous paths within the organic matter, making desorption more likely. However, this salt effect is unlikely to explain most of the results, because it should have been largely complete before experiments began.

A related interpretation would be that conformational change was caused by mercuric chloride added as an antibiological agent. The mercuric ion has a radius similar to that of sodium and calcium ions, which were present in the artificial seawater in greater concentration than the mercuric ion. Any conformation effect of mercuric ion should have been complete on a time scale similar to that for the other cations. It could have had a proportionally greater effect because of its strong association with humic acid, but it constituted a small fraction of total ion concentration (1.24% by wt).

Finally, hydration of the humic acid coating could have changed, most likely beginning at the time the moist humic acid coated clay was first suspended in the artificial seawater at the beginning of the adsorption phase of the experiment. Again, this would be expected to occur more quickly than the adsorption of phenanthrene owing to the smaller size of the water molecule. In addition, conformational changes due to sea salts, mercuric ion, or water would not be expected to vary with phenanthrene concentration, but desorption decreased as phenanthrene concentration increased.

The decrease in phenanthrene desorption with increasing phenanthrene concentration is contrary to the pattern expected if equally accessible strong and weak adsorption sites were present in the humic structure. That situation could explain apparently irreversible adsorption; phenanthrene adsorbed at stronger sites would appear to be irreversibly adsorbed under conditions that readily desorbed it from weaker sites. However, more phenanthrene would be adsorbed at the stronger sites at lower phenanthrene concentrations. This would result in increasing apparent K_{OC} with decreasing concentration, which was not observed (see Chapter 3). It would also result in decreased desorption at lower concentrations, opposite to the observed pattern. Decreased desorption with increasing initial dissolved and adsorbed concentration could be caused by the phenanthrene itself affecting the humic structure, reducing its porosity. At most, the phenanthrene would comprise only 1% of the mass of the humic substance, so it could exert an observable effect only if a small proportion of the material was accessible to adsorbing phenanthrene molecules.

Possible phenanthrene effects on humic acid structure are less helpful in explaining why desorption increased with increasing initial adsorption time. Since adsorbed phenanthrene concentration increased with adsorption reaction time, decreased adsorption would be the expectation. Rather, that result can be best explained by the fact that for short adsorption times, adsorption had not yet reached steady state. For the longest reaction times, presumably all accessible regions of the humic acid coating have a quantity of adsorbed phenanthrene described by the steady state partition coefficient. At earlier times, however, the amount of adsorbed phenanthrene in less accessible regions could be lower. So, redistribution of phenanthrene during the desorption step could include diffusion into those less accessible regions as well as desorption into the solution.

Desorption steady state was reached between three and seven days for all of the humic acids studied in this experiment. These results are comparable to those found in other studies (two to four days) using radiolabeled phenanthrene desorbing from humic acid coated montmorillonite clays [Lahlou and Ortega-Calvo 1999]. The approach to steady state slowed after relatively fast initial desorption within the first 24 hours. These biphasic patterns of desorption have been observed in the literature, with the fast stage lasting from a few hours [Karickhoff and Morris 1985; Schlebaum et al. 1998] to one day [Pavlostathis and Mathavan 1992]. As with slow adsorption, biphasic patterns of desorption are indicative of diffusion within the organic matrix.

Initial rates of desorption were found to be directly proportional to the initial concentration of phenanthrene used during the adsorption phase. The pattern in initial desorption rates may simply be due to concentration effects on diffusion rates, since the concentration of adsorbed phenanthrene was correlated with initial solution concentration. In a study by Borglin et al. [1996], it was also found that increasing initial concentrations of hexachlorobenzene led to faster initial desorption rates from natural sediments. The observation that humic acids with larger organic normalized partition coefficients were associated with faster initial rates of desorption could also be related to the concentration gradient driving outward diffusion, since, of course, more phenanthrene associated with humic acids having higher partition coefficients. However, this result differs from those of previous studies [cf. Borglin, et al. 1996; Schlebaum et al. 1998], where desorption rate decreased with increasing partition coefficient. Schlebaum et al. [1998] suggested that larger partition coefficients increase the amount of a hydrocarbon bound to a non-labile fraction, resulting in significantly lower desorption rates, but points out that this has not been observed experimentally.

The negative correlation of initial desorption rate with the organic carbon concentration of the coated clay is also consistent with the interpretation that desorption rate is controlled by slow diffusion within the organic matrix. In the absence of major differences in the tortuosity of the pores within the structure of the different humic acids, thicker coatings should lead to longer diffusive paths and slower desorption.

The humic acids with lower organic carbon content had higher rates of desorption. Folding and coiling may be limited due to a decrease in flexibility of the humic acid resulting from fewer long carbon chains. This would produce a more open structure through which molecules would have a less tortuous path to follow as they diffuse both in and out of the organic matrix. Alternatively, humic substances with less carbon per gram generally have more oxygen, which was not measured. Higher oxygen content would make them more hydrophilic, leading to a more open structure with greater water content. This would result in faster rates of adsorption as well as desorption.

Slow desorption is clearly a contributing factor in the phenomenon of irreversible adsorption. Desorption increased for up to a week, and at steady state was near 100% for most of the experiments. However, shorter reaction times would have led to the conclusion that adsorption was partly irreversible. In some experiments, more than the expected amount of phenanthrene desorbed. The most likely explanation is a change in the conformation of the humic acid—due to salt, phenanthrene concentration, or simply time —that decreased the phenanthrene partition coefficient. Most experiments with greater than expected desorption were those with the smallest initial phenanthrene concentration in the adsorption reactions, indicating that phenanthrene concentration is the most likely factor.

While there was little evidence for irreversible adsorption in the results of the experiments described here, this is a widely observed phenomenon in sediments and soils [Hatzinger and Alexander 1995; Lahlou and Ortega-Calvo 1999; Kan et al. 1994]. Adsorption that is irreversible over much longer time scales could occur for materials more complex than the deliberately simplified model sediments prepared for this work. In particular, the model sediments included only the base extractable portion of the sediment organic matter. Other sediment organic constituents could exhibit different interactions with phenanthrene.

Chapter 5. Conclusion

At present it is impossible to accurately predict the ecotoxicological effects of any specific combination of pollutant and sedimentary organic material. The goal of the research was to improve our ability to predict the persistence and fate of polycyclic aromatic hydrocarbons in contaminated sediments, through elucidation of the role sediment organic matter has in adsorption and desorption processes. The project investigated the interaction between an aromatic hydrocarbon, phenanthrene, and humic acids obtained from marine sediments from Lower Cook Inlet, Port Valdez, and the inner Beaufort Sea, Alaska, and from laboratory synthesized homologs (melanoidins). The work sought understanding of how the structural characteristics of humic acids influence the rate and extent of phenanthrene adsorption.

The first hypothesis tested was that aromatic hydrocarbon adsorption that was partly irreversible in experiments lasting a few days would be reversible with longer desorption times. The results described in Chapter 4, were consistent with this hypothesis in general. Adsorbed phenanthrene was completely desorbed within one week under most experimental conditions. While the rate of desorption was directly proportional to the initial concentration of phenanthrene adsorbed to the sediments, the extent to which the bound phenanthrene desorbed was negatively correlated with the initial phenanthrene concentration. Desorption was biphasic, with a slow approach to steady state again taking approximately one week. These facts, when taken together, indicate that desorption is not governed solely by slow diffusion within the three-dimensional structure of humic acid. In addition, the adsorbed phenanthrene appears to influence the adsorptive or diffusive properties of the humic acid, leading to the concentration effects observed.

The results were therefore consistent with the second hypothesis, that interactions of aromatic hydrocarbons with sediment organic matter are responsible for adsorption that appears to be irreversible, at least under some conditions. A subhypothesis, that binding to a variety of adsorption sites with different partition coefficients causes differences in the apparent, experimental partition coefficient, was rejected. A mixture of strong and weak adsorption sites in the humic acid would lead to decreasing adsorption partition coefficients with increasing concentration, which was not observed (see Chapter 3). It would also lead to decreases in percentage of expected desorption with decreasing phenanthrene concentration adsorbed, opposite to the trend actually found (see Chapter 4).

The third hypothesis was that variations in organic matter properties influence the rate and extent of adsorption and desorption processes. The tests of this hypothesis were described in Chapter 2. It was found that the partitioning of phenanthrene to the sediments was not related to the concentration ($g\ OC \cdot g\ clay^{-1}$) of humic acid coating the mineral substrate. Adsorption, however, was found to be negatively correlated with the polarity of the humic acid. This indicates that it is the nature of the organic matter and not the quantity alone that governs the extent of hydrophilic organic carbon adsorption to sediments. Desorption, on the other hand, was found to be inversely related with the amount of humic acid coating the mineral substrate (see Chapter 4), probably because thicker coatings result in longer diffusion paths out of the organic matrix. Structural characteristics of the humic acids were not found to influence the desorption of phenanthrene. The subhypothesis that there is a direct correlation between the aromatic character of sediment humic acid and the adsorption partition coefficient of phenanthrene was rejected (see Chapter 2). There was no relationship between aromaticity and adsorption within our sample group. The subhypothesis that the synthetic humic substances would show clearer relationships between organic matter composition and adsorption was rejected; trends for natural sedimentary humic acids and melanoidins were similar.

Finally, the hypothesis that previous phenanthrene adsorption of sediments affects subsequent adsorption was rejected, as discussed in Chapter 3. The investigation was comprised of two related components—the kinetics of phenanthrene adsorption to mineral-bound humic acids and the effects previous phenanthrene contamination of sediments had on subsequent phenanthrene adsorption. Organic normalized partition

coefficients (K_{OC}) were determined by using the slopes of linear adsorption isotherms. These K_{OC} were found to be negatively correlated with the polarity of the organic matter, as was seen in Chapter 2. Initial rates of adsorption were also found to be negatively correlated with the polarity of humic acids coating the mineral substrate. The observation that the initial uptake of phenanthrene was rapid, but the approach to steady state required approximately one week, was consistent with hydrocarbon diffusion into a three-dimensional organic matrix. The initial concentration of phenanthrene in solution had no effect on the partitioning of the hydrocarbon into the sediment, indicating that binding sites within the organic matter are both uniform in strength and unlimited. This, again, supports the idea that rates of hydrocarbon adsorption are controlled by intraorganic matter diffusion. If there existed only a finite number of sites to which phenanthrene could bind, hydrocarbons from previous contamination would be expected to occupy these sites, thus hindering additional uptake of phenanthrene. This was not observed experimentally.

The results presented in Chapter 2 showed that humic acids with properties indicating a mixed terrestrial and marine origin adsorbed phenanthrene to a greater extent than those of a wholly marine origin. However, this was not attributable to greater aromaticity derived from lignin, but rather to a relative lack of amide and carboxylic acid functional groups. Another characteristic shared by humic acids exhibiting stronger PAH adsorption and lower polarity was a subtidal sediment source, while the less adsorptive Lower Cook Inlet samples were all from intertidal sediments. The intertidal sediments were probably richer in living organisms and fresh detritus than the subtidal sediments, potentially another factor contributing to the greater polarity of their humic acids. Although the number of samples studied was not sufficient to conclusively identify geographic patterns in adsorptive properties of humic acids, the results do suggest that terrigenous inputs and, possibly, extent of diagenetic alteration of organic matter should be investigated as potential predictors of adsorptive properties.

The conclusions reached should serve to warn against applying results regarding adsorption of pollutants by sediments from one study to another. Policies and predictions need to be made on a case-by-case basis, because of the clear dependence of adsorption/desorption processes on sediment organic matter structures. Additional work, however, is required to further define the role the organic matrix has on the processes of adsorption and diffusion. The body of work shows that hydrocarbon associations with organic matter in marine sediments are controlled by diffusion processes, regulated by the structural characteristics of the organic matrix. Additional desorption studies that focus on both the initial hydrocarbon concentrations, and the hydrocarbon concentrations within the organic matrix once adsorbed, are needed. Supplemental investigations of the adsorption process would be desirable to complement that research focus. These include investigations of HOC other than phenanthrene and organic matter of a greater variety of types or origins.

Acknowledgments

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