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University of Alaska  
**Coastal Marine Institute**



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**Interaction Between Marine Humic Matter and  
Polycyclic Aromatic Hydrocarbons  
in Lower Cook Inlet and Port Valdez, Alaska**

David G. Shaw, Principal Investigator  
University of Alaska Fairbanks

**Final Report**

September 1998

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by

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## Abstract

Humic acid is a major component of naturally occurring organic matter; it interacts strongly with organic pollutants including polycyclic aromatic hydrocarbons (PAH), a class of organic pollutants present in petroleum and associated with significant long-term environmental and human health problems. The chemical associations resulting from the interaction between humic acid and PAH influence the fate and effects of PAH which are of great concern in coastal regions such as Cook Inlet, Alaska, where petroleum production and transportation coexist with renewable resources and environmental values. Better understanding of biogeochemical processes that influence the degradation and bioavailability of petroleum can lead to improvements in environmental management for such systems.

This project investigated the interaction of PAH and marine humic acid from sediments of Lower Cook Inlet and Port Valdez, Alaska, in an attempt to understand how and to what extent the molecular character of humic acid from these sediments influences their ability to adsorb PAH. Geochemical characterization of sediments and humic acids from the study area showed that their chemical composition is non-uniform, probably reflecting differences in both source materials and post-depositional alterations. This result indicates that the measured concentrations of PAH are largely unrelated to the properties of the humic acid from the same sediments. It is more likely that the amounts of PAH to which the sediments are exposed control observed concentrations. Experiments which measured the ability of humic acid extracted from these sediments to adsorb phenanthrene showed marked differences among sediments. Humic acid from subtidal sediments showed a greater tendency to adsorb phenanthrene than did humic acid from intertidal sediments.

Based on this study and the CMI-sponsored studies of J. F. Braddock and S. M. Henrichs, it appears likely that humic acid is involved in the adsorption of PAH in sediments of Lower Cook Inlet and Port Valdez, Alaska. The variability of adsorption and its implications for corresponding variability in bioavailability suggest that management tools (e.g., ecotoxicological models) that depend on a single value for adsorption of PAH by marine sediments should be used with caution.



## 1.0 Introduction

### 1.1 Background

Petroleum contamination of the oceans is a continuing public concern both nationally and globally (NRC, 1985) and is of great concern in coastal regions such as Cook Inlet, Alaska, where petroleum production and transportation co-exist with productive fisheries as well as other renewable resources and environmental values. While the most intense public concern has focused on catastrophic accidents such as the *Exxon Valdez* oil spill, a larger quantity of petroleum enters the ocean from small spills, from permitted discharges, and from non-point sources, than from relatively rare large spills. Thus, effective management of marine environments requires attention to chronic, low-level inputs as well as catastrophic accidental releases. Since neither major spills nor chronic releases will be totally eliminated in the foreseeable future, it is important to have as much information as possible so management attention can be focused on the sources of pollution and the waters most likely to have pronounced adverse effects.

In the marine environment petroleum is subject to a wide variety of physical, chemical, and biological processes which, taken together, determine its fate and effects. The relative importance of the many contributing factors which influence fate and effects is a complex function of both the chemical characteristics of petroleum and the physical and biological characteristics of the environment into which the petroleum enters. Although a very large body of scientific work now exists for examining the processes which control the fate and effects of petroleum in the marine environment (Frankel, 1995; Kennish, 1997), many factors remain incompletely understood—especially in their quantitative aspects.

Polycyclic aromatic hydrocarbons (PAH) are generally considered to be among the petroleum constituents of most concern because of their toxicity (including carcinogenicity) and their resistance to chemical breakdown under many conditions. PAH have very low solubilities in seawater (Shaw et al., 1989) and therefore tend to concentrate in sediments rather than remain in the water column. Within sediments, PAH associate with organic matter and organic coatings of mineral particles of low polarity (Luthy et al., 1997). The extent of this association is known to vary depending on the character of the organic matter present (Means et al., 1980; Garbarini and Lion, 1986).

It appears to be generally true (although exceptions are known) that biological uptake of petroleum, leading either to biodegradation, bioaccumulation, or toxicity, occurs from solution (Landrum et al., 1985; Efroymson and Alexander, 1995). Sorption of PAH to organic matter in the sediments often reduces the bioavailability of PAH (Luthy et al., 1997). Consequently, knowledge of the concentrations of PAH on sediments, expressed in the usual units (micrograms of hydrocarbon per kilogram of dry sediment), may not by itself be a reliable guide to the fate and effects of PAH in those sediments.

Humic acid is the fraction of organic material that when isolated from natural waters, soils, and sediments, is soluble in aqueous base but insoluble in aqueous acid (Parsons, 1988). Thus, humic acid is a class of organic compounds defined by solubility characteristics. A considerable body

of work has shown that humic acid isolated from soil differs in structure and reactivity from humic acid isolated from marine sediments (Sastre et al., 1994). The sources of marine humic acid are generally understood, although many of the details are unclear (deLeeuw and Largeau, 1993). Large amounts of detrital plant and other organic material are released to the aquatic environment during normal physiological processes and on the death of organisms. Once in the environment, most of these materials reenter the biological cycle directly, as substrates for other organisms (Fenchel and Blackburn, 1979). However, a portion undergoes a wide variety of chemical condensation reactions with other organic materials (Tissot and Welte, 1978). In the condensation process, reactive portions of the molecules combine, usually without enzymatic control. This gradually leads to large organic molecules with few reactive sites remaining for further condensation and little chance of being consumed by other organisms.

The resulting humic acid molecules have variable structures, reflecting the structural characteristics and origin of the initial constituent molecules as well as the extent of condensation. In natural systems humic acid tends to coat mineral particles. This converts the surface of sediment particles from high polarity to low polarity and thereby makes them sites for the sorption of low polarity contaminants such as PAH (Boehm and Farrington, 1984). The time scale over which these processes occur may be years to decades or even longer, depending on environmental conditions. Sediments receiving greater fluxes of organic detritus can be expected to have more, but “younger,” less-condensed humic acid, on average, compared with sediments with lower carbon input.

Seawater and marine sediments contain considerable amounts of organic material, mostly of natural origin. This organic material has a much greater affinity for organic compounds such as PAH than does water itself or the mineral portion of sediments. The particular chemical nature of the organic matter strongly influences the fate and effect of pollutants, including petroleum and petroleum-related compounds. Humic acid, whether dissolved in the water column or associated with mineral particles in the sediment, often shows a marked tendency to associate chemically with other organic molecules, including organic pollutants (Piccolo, 1994; Karickhoff and Morris, 1985; Karickhoff et al., 1979).

Characteristics of the sediment that are thought to influence the binding of PAH to sediments include the amount of organic matter present, the fraction of that organic matter that is humic acid, and the aromaticity (the proportion of benzene-like rings relative to other organic structures) of the humic acid present (Gauthier et al., 1987). Aromaticity may be important because of possible binding interactions between the ring systems of the humic acid and those of the PAH. This humic acid-PAH association appears to result from weak dipole interactions between aromatic rings of the PAH and similar rings which are part of many humic acids, particularly those derived from lignins and related materials from woody terrigenous plants (Chin et al., 1994). This chemical association influences the chemical properties and biological availability of pollutants (Guerin and Boyd, 1992). Strong binding between humic acid and pollutants can result in lower bioavailability, and thus, lessened environmental toxicity (Weissenfels et al., 1992).

One widely used method for the characterization of humic acid is E4/E6, the ratio of two absorption bands in the visible region of the electromagnetic spectrum (465 nm and 665 nm).

Ratios for humic acids are usually less than 5.0 and decrease with increasing molecular weight and aromatic condensation. Thus the E4/E6 ratio has been proposed as an index of humification (Stevenson, 1994). A low ratio indicates a relatively high degree of condensation, while a high ratio implies the presence of smaller, possibly more aliphatic structures. An inverse relationship has been observed between the ratio and age of humic material. This leads to the suggestion that the older material is more highly condensed and aromatic in nature. In practice the E4/E6 ratio can be difficult to interpret because several factors contribute to an observed value. The ratio can be useful when applied with other indicators to separate the effects of source material from post-depositional alteration.

Two recently completed CMI-sponsored projects have investigated the fate of petroleum hydrocarbons in Lower Cook Inlet, Alaska (one of the two environments studied in the present work). Henrichs and co-workers (1997) studied the adsorption of aromatic hydrocarbons (benzene, naphthalene and phenanthrene) by formaldehyde-poisoned intertidal sediments from Jakolof Bay on the western margin of Kachemak Bay. They found that all three compounds were strongly adsorbed, although adsorption was neither rapid nor fully reversible. Adsorption was approximately linear with hydrocarbon concentration, indicating that all surface adsorption sites were equivalent. The investigators concluded that these and other characteristics of phenanthrene adsorption were most consistent with rapid adsorption to sediment particle surfaces, followed by relatively slow diffusion into sediment organic matter or micropores.

Braddock and Richter (1998) also investigated potential rates of microbial degradation of aromatic hydrocarbons (naphthalene and phenanthrene) in intertidal sediments from Jakolof Bay, Lower Cook Inlet. They found that naturally occurring populations of phenanthrene-degrading microbes tended to be low in these sediments and that degradation of both compounds was inhibited in the presence of sediment. This inhibition increased with increasing sediment load and with increasing sediment organic content.

Taken together, these two studies indicate that marine sediments of Lower Cook Inlet can interact with aromatic hydrocarbons in ways that influence the bioavailability of the hydrocarbons. The inhibition of hydrocarbon degradation in the presence of sediment, as observed by Braddock and Richter, is most likely the result of sediment adsorption of hydrocarbons, as observed by Henrichs and co-workers. Braddock and Richter's finding that the inhibition of degradation increases with increasing organic content of the sediment strongly suggests that hydrocarbon adsorption by sediments involves a molecular association between hydrocarbons and sediment organic matter.

## **2.0 Objectives**

This project investigated the interaction between petroleum hydrocarbons (specifically PAH) and humic acid associated with marine sediments from Lower Cook Inlet and Port Valdez, Alaska, in order to determine the influence of this interaction on the fate and effects of petroleum in these marine systems. This work extended the line of investigation carried forward by Henrichs, who investigated PAH adsorption and desorption by Lower Cook Inlet sediments, and by Braddock, who studied the biodegradation of PAH in seawater-sediment systems from Lower Cook Inlet. The present work sought understanding of how and to what extent the molecular character of

humic acid from these sediments influences their ability to adsorb PAH. The following two hypotheses were examined:

1. There is a direct correlation between the amount of sediment humic acid and the concentration of PAH in marine sediments of lower Cook Inlet and Port Valdez.
2. There is a direct correlation between the aromatic character of sediment humic acid and the concentration of PAH in marine sediments of lower Cook Inlet and Port Valdez.

The study areas were chosen because they presented a contrast between an area of present oil industry operations (Port Valdez) and possible future offshore petroleum exploration (Lower Cook Inlet). In each area, petroleum and humic acid were isolated from sediments. The chemical characteristics of humic acid associated with sediment were compared with the kinds and amounts of PAH present. Experiments were performed to measure the ability of humic acid extracted from the sediments to adsorb phenanthrene.

## **3.0 Methods**

### **3.1 Field**

Subtidal sediments were collected using a HAPS corer, which is a small stainless steel box corer (Kannevorff and Nicolaisen, 1973). Sediment cores were allowed to settle and overlying water was removed by siphon. A 0- to 2-cm subsample from the core was placed in an 8-oz. glass jar with an aluminum cap liner. The entire container had been previously cleaned by washing and baking in a muffle furnace at 450°C for eight hours. The transfer of the subsamples was done using metal implements that had been heated to redness before use. Samples were stored frozen at -50°C.

Intertidal sediment samples were taken near the mean lower-low water level. These sediments were collected from the oxic upper 1 cm during low tide using metal implements that had been heated to redness before use. In the field, some samples were temporarily stored on ice in sterile plastic bags. The sediments were later transferred to 8-oz. glass jars with aluminum cap liners, both of which had been previously cleaned by washing and baking in a muffle furnace at 450°C for eight hours. Samples were stored frozen at -50°C.

### **3.2 Procedures Using Bulk Sediment**

Sediment samples were removed from the freezer, allowed to thaw, and homogenized by stirring. Subsamples of homogenized sediment were taken as needed for analytical procedures. The remaining homogenized samples were stored frozen when not in use. Sediment subsamples were dried, acidified, redried, ground to a powder, and submitted for combustion analysis to determine total organic carbon (TOC) and total organic nitrogen (TON) (Feder and Shaw, 1996). PAH concentrations were determined as described by Feder and Shaw (1996). Subsamples were extracted using Soxhlet apparatus and fractionated by column chromatography. An aromatic fraction was isolated by high-performance liquid chromatography and quantified by flame ionization gas chromatography.

Humic acid was obtained using an extraction procedure based on Anderson and Schoenau (1983). Approximately 30 g of weighed wet sediment were added to a 250-mL centrifuge bottle with a sealing cap and shaken on a wrist-action shaker for 10 minutes with 150 mL of 0.5M HCl to remove floating plant debris and acid volatile inorganic forms of C, N, P, and S. The sample was then centrifuged for 20 minutes at 9000 RPM. The sediment was washed with 150 mL of double-distilled H<sub>2</sub>O and centrifuged again as described above. The supernatant solutions from both washes were discarded. A 150-mL portion of freshly prepared 0.5M NaOH was added to the washed sediment sample and the headspace flushed with ultra-high-purity nitrogen gas (UHP-N<sub>2</sub>) to minimize hydrolysis and oxidation of humic acid. The sample was then shaken for 20 hours. After shaking, the sample was centrifuged as above; the supernatant was decanted into a tared centrifuge bottle, and the residual sediment was discarded. The humic acid portion of the supernatant was precipitated by adding 6M HCl until a pH of 1.5 was obtained. Approximately 23 mL of acid were required. The precipitated extract was allowed to stand for 15 minutes and then centrifuged for 30 minutes as described above. The precipitated humic acid was lyophilized at -85°C for 24 hours. The resulting dry humic acid was weighed and stored in a glass vial. Water content of sediment was determined by drying a weighed aliquot of sediment and reweighing. Each sample was extracted in duplicate and the mean percentage of humic acid was reported.

### **3.3 Characterization of Humic Acid**

Subsamples of humic acid were submitted to the Stable Isotope Laboratory at the University of Alaska Fairbanks for isotopic analysis of  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ . Analysis was performed using a Europa 20/20 mass spectrometer equipped with Roboprep. Ultraviolet–visible light spectroscopy was performed on humic acid (2–4 mg) dissolved in 10 mL of 0.05 N sodium bicarbonate (Chen et al., 1977).

Cross-polarized magic angle spinning  $^{13}\text{C}$  nuclear magnetic resonance spectroscopic data on selected humic acid extracts were obtained from Florida State University in Tallahassee. From these data, aromaticity was calculated by integrating the area between 100 and 160 ppm (aromatic region) and dividing it by the area between 0 and 200 ppm (entire spectrum) minus the area between 160 and 190 ppm (carbonyl region). This gives carbonyl-free aromaticity as a percent of the entire humic acid fraction. Aromaticity was then multiplied by percent humic acid found in the sediment to give aromatic abundance.

Fourier-transformed infrared spectra were obtained using a Nicolet model 560 FT spectrometer with an infrared source, a potassium bromide (KBr) beamsplitter, and an MCT/B detector. Signals were averaged from 200 scans, with a resolution of  $0.121\text{ cm}^{-1}$ , and processed against a background of KBr. Humic acid samples were prepared as KBr pellets (0.200 g KBr and 0.005 g humic acid) and spectra obtained between  $4000\text{ cm}^{-1}$  and  $400\text{ cm}^{-1}$ . After baseline correction, a ratio of peak heights corresponding to aliphatic carbon deformation modes ( $1535\text{ cm}^{-1}$ ) and aromatic carbon stretching ( $1658\text{ cm}^{-1}$ ) was determined. By plotting these ratios against aromaticity data from nmr, an empirical relationship was obtained and used to estimate aromaticities for humic acid samples not analyzed by  $^{13}\text{C}$  nuclear magnetic resonance.

### 3.4 Sorption Experiments

Organic free water was prepared by distilling deionized water over potassium permanganate. Into approximately 300 mL of this water was dissolved: 11.630 g sodium chloride, 5.318 g magnesium chloride hexahydrate, 1.959 g anhydrous sodium sulfate, 0.551 g calcium chloride, 0.332 g potassium chloride, 0.096 g sodium bicarbonate, 0.048 g potassium bromide, 0.013 g boric acid, and 0.250 g of mercuric chloride. The final volume of solution was adjusted to 500 mL in a volumetric flask by the addition of organic free water (Lyman and Fleming, 1940).

A saturated solution of humic acid was prepared in an Erlenmeyer flask by adding 0.050 g of lyophilized humic acid to 40.0 mL of artificial seawater; the headspace was flushed with UHP-N<sub>2</sub> to prevent oxidation. The flask was shaken on an orbital table shaker for seven days. The solution was allowed to stand for 24 hours so that undissolved humic acid could settle. The supernatant was drawn off and used to make various concentrations of humic acid ranging from 50% to 1% by dilution with artificial seawater. The headspaces over these solutions were flushed with UHP-N<sub>2</sub>.

A stock solution of phenanthrene in artificial seawater was prepared. To a 200-mL volumetric flask were added 4.1 mL of a 0.867 g/L solution of [9-<sup>14</sup>C]phenanthrene in acetonitrile (5–15 mCi/mmol; Sigma Chemical Company) and 1.05 mL of a 0.002 g/L solution of non-labeled phenanthrene in acetonitrile. The acetonitrile was removed by evaporation with a stream of UHP-N<sub>2</sub>. The flask was then filled to the mark with artificial seawater to give a final phenanthrene concentration of 300 mg/L (1.68 μM/L; 1.40 × 10<sup>-5</sup> mCi/mL). The solution was stored in a refrigerator until needed.

Chlorite for use in sorption experiments was prepared by grinding in a glass mortar and pestle and then passing the resulting powder through a USA Standard Sieve Series 230 mesh sieve. All particles were 63 μm or less in size. To remove any organic coatings on the ground chlorite, approximately 75 mL of 30% hydrogen peroxide were added and the sample was warmed in a 65°C oven for 24 hours. The chlorite was centrifuged at 9000 RPM for 20 minutes and the supernatant discarded. This treatment was repeated, after which the chlorite was washed with 25 mL of organic free water. The chlorite was centrifuged as above and the wash discarded. Washing was repeated twice more.

Sorption experiments were carried out in 10-dram glass vials with Teflon-lined screw caps, both of which had been cleaned with chromic acid and rinsed with organic free water. Contact of the solutions with the liners was avoided.

Treated chlorite (0.05 g) was weighed into a vial and 5.0 mL of humic acid solution were added by pipette. The headspace was flushed with UHP-N<sub>2</sub> and the contents of the vial were vortex-mixed for 10 seconds. The vial was placed on an orbital table shaker for 24 hours and then centrifuged at 9000 RPM for 25 minutes; the supernatant was discarded. Radiolabeled phenanthrene solution (5.0 mL) was added to the vial containing the humic acid-treated chlorite, and the headspace was again flushed with UHP-N<sub>2</sub> and vortex-mixed for 10 seconds. The vial was placed on the table shaker for another 24 hours, after which it was again centrifuged as above. A 1.00 mL sample of the supernatant was removed by Eppendorf pipette and transferred to a scintillation vial containing 15 mL of counting fluid (ICN Biomedicals' UniverSol

biodegradable scintillation cocktail). The vial was shaken and allowed to stand for one hour before liquid scintillation counting.

## 4.0 Results

### 4.1 Site Descriptions

The sampling sites in Port Valdez (Figure 1; Table 1) include locations that were expected to be influenced by oil tanker loading operations (PV-16, PV-25, PV-33, PV-51, PV-77, PV-80, and PV-82: Feder and Shaw, 1996), by commercial fish processing plants (PV-2, PV-5, PV-7, and PV-8: Feder and Shaw, 1994), by locations several kilometers distant from these and other likely anthropogenic carbon sources (PV-11, PV-37, PV-45, PV-50, and PV-91: Feder and Shaw, 1996). Locations were all subtidal and ranged in depth from 20 m to 240 m. Sediments collected were all fine silts. Sample sites located in Lower Cook Inlet (Figure 2; Table 1) were all intertidal or shallow subtidal (< 2 m) and were chosen to include those of Henrichs et al. (1997) (Jakolof-1, Jakolof-2) and Braddock and Richter (1998) (Jakolof-3, Jakolof-4), and to provide a greater range of organic material types and concentrations than the Port Valdez sediments. All samples from Lower Cook Inlet were muddy except Bishop Beach which was sand. The geographic separation of intertidal and subtidal sediments was necessitated by logistic and cost-matching requirements. While not ideal, this separation probably had little or no effect on the results of this study. The two study sites are generally similar: both are coastal areas with substantial inputs of glacially derived sediment material. None of the locations sampled for this project were contaminated during the *Exxon Valdez* oil spill.

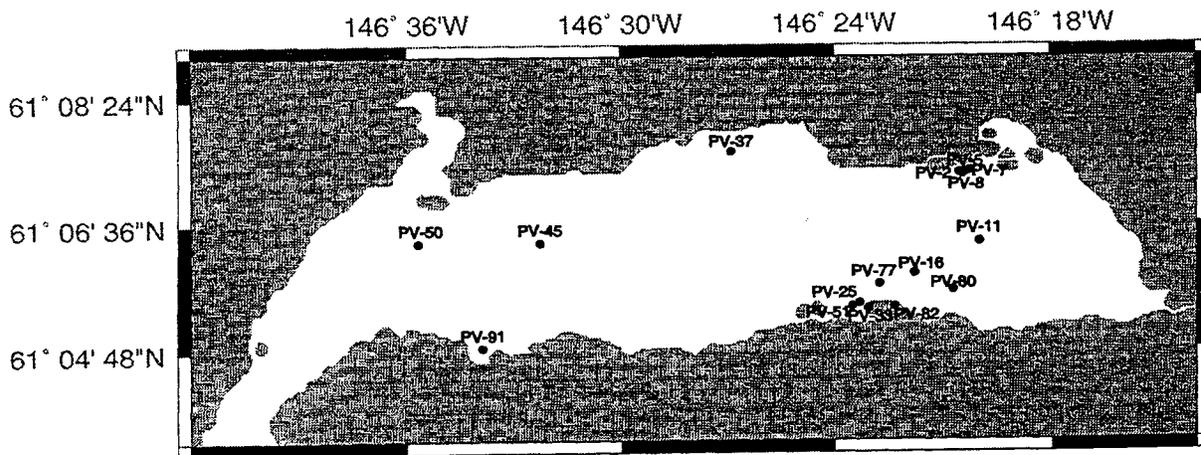


Figure 1. Sampling locations at Port Valdez, Alaska, used in this study.

Table 1. Coordinates of sediment sampling stations used for this study.

Station	Latitude, °W	Longitude, °N
PV-2	61.122	146.342
PV-5	61.122	146.340
PV-7	61.123	146.338
PV-8	61.122	146.341
PV-11	61.106	146.333
PV-16	61.098	146.363
PV-25	61.091	146.389
PV-33	61.090	146.385
PV-37	61.128	146.449
PV-45	61.106	146.538
PV-50	61.106	146.595
PV-51	61.090	146.392
PV-77	61.096	146.379
PV-80	61.094	146.345
PV-82	61.090	146.372
PV-91	61.081	146.565
Anderson Bay	61.080	146.564
Bishop Beach	59.639	151.554
Homer boat harbor	59.606	151.417
Homer mud flat	59.638	151.489
Jakolof-1	59.451	151.494
Jakolof-2	59.452	151.488
Jakolof-3	59.451	151.494
Jakolof-4	59.452	151.488
Jakolof-5	59.451	151.494
Tutka Bay	59.447	151.342

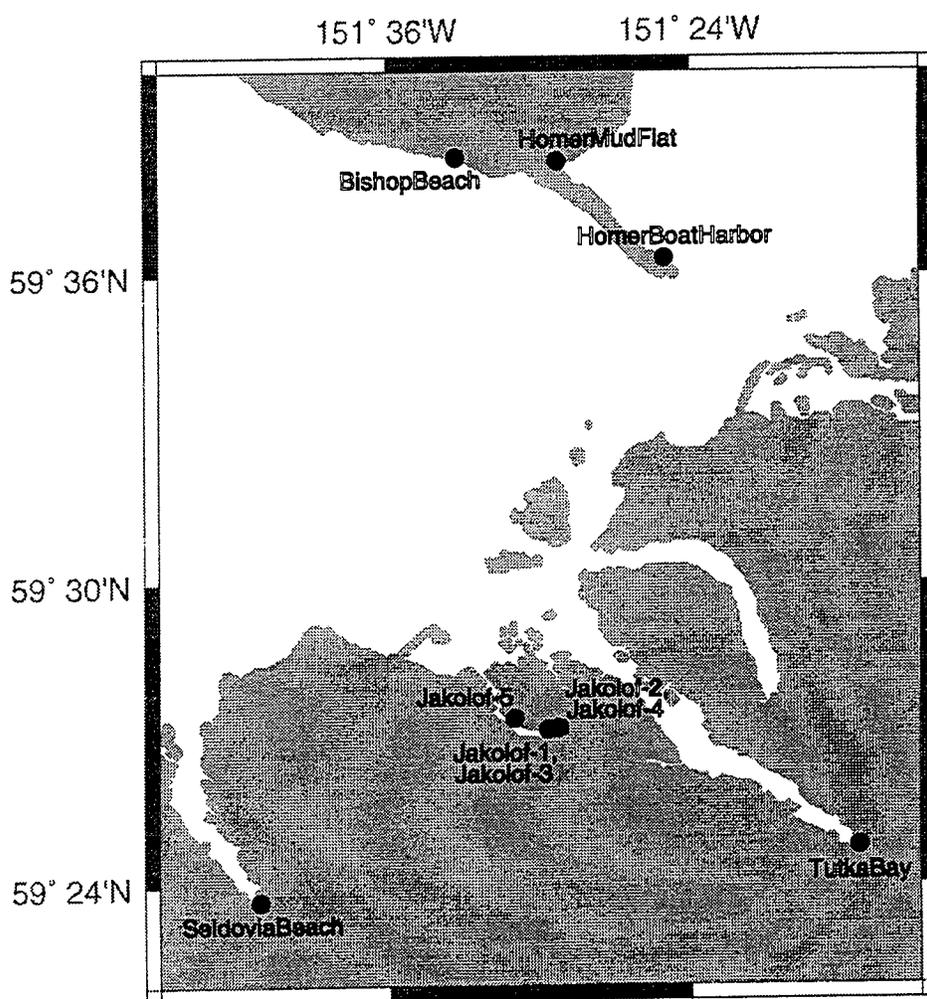


Figure 2. Sampling locations at Lower Cook Inlet, Alaska, used in this study.

#### 4.2 Bulk Sediment Properties

Geochemical measurements (Table 2) were made to characterize the relationship of PAH and humic acid in a suite of 32 sediment samples (22 from Port Valdez and 10 from Lower Cook Inlet). The sediments were representative of those occurring widely in coastal marine areas of south-central Alaska, including sands and glacially derived silt-clay mixtures which are low in organic material (less than 1.0% TOC), as well as higher organic intertidal muck (1.8–5.7% TOC). Most of the sediment sampling locations have relatively low human impact, but two (the Homer boat harbor and PV-33, the discharge site for treated ballast water for Alyeska) were adjacent to identifiable sources of petroleum contamination. Lower Cook Inlet sediments also contain PAH from detrital coal sources in the area (Shaw and Wiggs, 1980; Boehm, 1998). The carbon/nitrogen ratios (C/N) were all less than 12.3 and generally in the range 6.5 to 10.0, indicating that the predominant source of organic matter for most of these sediments is marine algae, but that vascular plants (probably including both sea grasses and terrigenous plants) also contribute to the accumulating organic matter.

Table 2. Bulk characteristics of sediments studied in this project. The percentages of humic acid (HA, %) and organic carbon (TOC, %) are expressed relative to sediment dry weight. The weight ratio of carbon to nitrogen (C/N) is a dimensionless number and the concentrations of aromatic hydrocarbons (naphthalene, phenanthrene, and total [TARO]) are expressed as ng of hydrocarbon per gram of dry sediment (ppb).

Station	HA, %	TOC, %	C/N	Napthalene	Phenanthrene	TARO
PV-2	0.61	0.65	6.69	1.7	31.1	156.7
PV-5	0.44	0.52	7.59	1.1	17.5	88.2
PV-7	0.49	0.60	7.94	<1.0	11.2	49.4
PV-8	0.46	0.57	7.08	1.2	12.4	38.2
PV-11a	0.24	0.39	8.98	<1.0	3.0	18.2
PV-11b	0.21	0.36	7.68	<1.0	1.6	13.0
PV-16	0.20	0.37	7.52	<1.0	2.7	18.3
PV-25a	0.55	0.77	11.06	<1.0	18.3	308.6
PV-25b	1.49	0.64	9.65	<1.0	6.9	91.9
PV-33a	0.54	0.71	10.97	3.4	80.2	517.4
PV-33b	0.60	0.65	9.77	1.0	16.6	137.3
PV-37	0.45	0.47	8.15	<1.0	5.4	23.8
PV-45	0.44	0.56	8.01	1.9	5.7	30.2
PV-50a	0.61	0.59	9.09	1.1	7.1	68.1
PV-50b	0.71	0.63	7.92	1.2	8.1	40.9
PV-51	0.53	0.6	9.28	<1.0	5.7	56.1
PV-77	0.30	0.41	8.07	<1.0	2.4	17.9
PV-80	0.53	0.55	8.72	<1.0	4.1	108.9
PV-82a	0.67	0.61	11.56	2.0	15.5	80.1
PV-82b	0.60	0.62	10.13	<1.0	8.1	73.1
PV-91	0.89	0.69	8.49	<1.0	6.5	36.3
Anderson Bay	0.70	0.68	8.61	<1.0	7.3	41.5
Bishop Beach	0.17	0.09	6.78	<1.0	<1.0	10.8
Homer Boat Harbor	3.75	1.76	10.35	1.7	12.3	707.5
Homer Mud Flat	2.79	2.42	10.95	<1.0	4.2	128.1
Jakolof-1	5.30	2.85	8.07	1.3	<1.0	66.5
Jakolof-2	4.80	3.20	8.78	2.1	8.0	112.2
Jakolof-3	4.07	2.70	8.08	3.1	10.3	358.6
Jakolof-4	7.29	5.66	8.76	1.8	8.7	489.3
Jakolof-5	3.30	4.48	7.59	3.3	228.6	914.4
Seldovia Beach	3.72	3.03	12.21	<1.0	12.1	109.2
Tutka Bay	1.60	1.99	6.68	2.4	4.0	52.8

The percentage of TOC ranged from 0.09% in sand from Bishop Beach in Cook Inlet to 5.66% in an intertidal sediment from Jakolof Bay. Values between 0.4 and 0.8 were common for subtidal sediments of glacial origin. The percentages of humic acid ranged from 0.17 to 7.29 with humic acid exceeding TOC at 14 of the 32 locations. This is not unexpected, as humic acids typically contain substantial quantities of oxygen. In the humic acids isolated from these sediments, carbon never exceeded 25% of the total weight. In all samples the amount of carbon in the humic acid fraction was less than the TOC value.

Concentrations of 18 PAH were determined for each sediment sample. All of the PAH concentrations were low. The highest total aromatic concentration (TARO) was 914 ng g<sup>-1</sup> at Jakolof-5. The concentrations of naphthalene and phenanthrene were also low. At 16 of the 32 sites, naphthalene was below 1.0 ng g<sup>-1</sup>, the limit of quantification. Phenanthrene was below the same quantification limit at two of the sites.

#### 4.3 Characterization of the Humic Acids

Chemical characterization of the humic acid extracts from the 32 sites was made in order to assess properties that might influence their ability to associate with and sequester PAH. The results of these characterizations are shown in Table 3.

Table 3. Characteristics of humic acid isolates studied in this project. The quantities and their units are discussed in the text.

Site	Aromaticity by nmr	Aromaticity by ir	Aromatic Abundance	$\delta^{15}\text{N}$	$\delta^{13}\text{C}$	E4/E6
PV-2		29.9	0.18	8.9	-23.8	1.31
PV-5		36.3	0.16	8.6	-24.0	1.26
PV-7		30.4	0.15	7.6	-23.7	1.28
PV-8		28.3	0.13	9.2	-23.8	1.32
PV-11a		46.0	0.11		-24.9	1.40
PV-11b		34.0	0.07		-24.9	1.37
PV-16		38.1	0.08		-24.2	1.37
PV-25a		39.4	0.22	7.1	-24.2	3.27
PV-25b	21.69	24.0	0.36	1.3	-27.6	1.99
PV-33a		30.6	0.17	5.3	-24.6	3.29
PV-33b		24.9	0.15	6.6	-24.0	1.50
PV-37		28.4	0.13	8.6	-24.1	1.32
PV-45		33.0	0.15	7.8	-23.5	1.98
PV-50a		33.4	0.20	6.5	-22.9	1.92
PV-50b		28.8	0.21	7.2	-23.0	1.37
PV-51		15.1	0.08	8.0	-23.9	1.42
PV-77		39.2	0.12		-24.0	1.35
PV-80		22.7	0.12	5.2	-23.4	1.86
PV-82a		34.0	0.23	4.7	-24.2	1.55
PV-82b	27.06	27.6	0.17	4.3	-24.4	1.62
PV-91	24.06	21.7	0.19	5.5	-22.6	1.42
Anderson Bay		36.6	0.26	5.4	-22.7	2.42
Bishop Beach		15.3	0.03			4.17
Homer boat harbor	33.86	29.8	1.11	8.6	-21.0	2.87
Homer mud flat		21.6	0.60	7.9	-21.9	3.01
Jakolof-1		22.5	1.19	7.1	-20.2	3.90
Jakolof-2		19.8	0.95	7.2	-21.1	4.03
Jakolof-3		20.5	0.83	6.9	-21.1	3.83
Jakolof 4	19.07	21.5	1.57	6.9	-17.4	3.30
Jakolof-5		23.3	0.77	9.4	-18.6	3.20
Seldovia Beach		22.1	0.82	5.6	-20.5	3.30
Tutka Bay	14.64	21.6	0.35	5.7	-18.2	2.52

The determination of percent aromaticity (the percentage of humic acid carbon atoms in aromatic rings) by nmr spectroscopy is generally thought to be more accurate than by ir spectroscopy since the peak area in nmr spectroscopy is proportional to the number of carbon atoms present; this is not the case for ir spectroscopy. However, because measurement of aromaticity by nmr consumes relatively large quantities of humic acid, nmr was used for only six samples.

Aromaticity gives information about the fraction of the humic acid in a sediment which is aromatic (an intensive property) without consideration of whether humic acid is abundant or depleted in that sediment (an extensive property). To obtain information about the relative amounts (as opposed to fractions) of aromatic humic acid carbon in the sediments, the percentage of humic acid was multiplied by the aromaticity (expressed as a decimal fraction) to give a quantity we called "aromatic abundance," which is the percentage of humic aromatic carbon in the sediment. Although the aromatic abundance was low, typically in the parts per thousand range, it was much higher than the concentration of PAH, which was always less than one part per million.

Carbon and nitrogen isotope ratios were measured in the humic acid extracts to determine the source of organic matter. Values of  $\delta^{13}\text{C}$  ranged from -17.4 to -27.6 and the  $\delta^{15}\text{N}$  values ranged from 1.3 to 9.4. These values are consistent with the C/N data for the bulk sediment and suggest that the major source of organic matter from which the humic acids were derived was marine (Parker et al., 1972; Schell, 1997). However, vascular plants also contributed. The mean values of both isotopes in sediments from Port Valdez were isotopically lighter ( $\delta^{13}\text{C} = -24.0$ ,  $\delta^{15}\text{N} = 6.5$ ) than for Cook Inlet sediments ( $\delta^{13}\text{C} = -20.0$ ,  $\delta^{15}\text{N} = 7.3$ ). These isotopic differences probably reflect different sources of humic acid for the two areas and may also depend on the degree of condensation the materials have undergone. These source differences may give rise to structural differences and differences in the ability of the humic acid to associate with PAH.

Further support for structural differences in humic acid, in comparisons of Port Valdez and Cook Inlet sediments, comes from their E4/E6 ratios. Chen and co-workers (1977), in experiments with a suite of humic acid samples isolated from terrestrial soils, showed that lower values of E4/E6 are associated with higher molecular weight humic acid particles but are not directly related to the concentration of condensed aromatic rings. Chin et al. (1994) found that for aquatic humic materials only a weak relationship existed between E4/E6 and percent aromaticity. The mean E4/E6 value for sediments from Port Valdez was significantly lower than that from Cook Inlet. This suggests that the humic acid from Port Valdez is more highly condensed, older, and possibly more aromatic than the humic acid from Cook Inlet. All of the sediments from Port Valdez used in this study are subtidal; the sediments from Cook Inlet include intertidal and shallow subtidal sediments collected with the intent of studying sediments with higher amounts of organic matter. It is possible, even likely, that subtidal sediments from Cook Inlet contain humic acid similar to the material found in Port Valdez. In any case, it is clear that there exist significant differences in the character of humic acid from different locations in south-central Alaska.

#### **4.4 Sorption Experiments**

A series of sorption experiments was carried out to assess the ability of humic acid extracted from three Lower Cook Inlet and two Port Valdez sediments to adsorb phenanthrene. The work

of Henrichs and co-workers (1997) has shown that the sediments of Lower Cook Inlet have the ability to adsorb aromatic hydrocarbons. The present work has focused on the role of sediment organic matter—specifically humic acid—in bringing about that adsorption:

In these sorption experiments a saturated solution of the humic acid to be tested was prepared in artificial seawater. Serial dilutions of the saturated solution (generally 1% to 50% of saturation) were added to portions of the clay mineral chlorite to give humic-coated mineral preparations. These were then exposed to artificial seawater solutions of radiolabeled phenanthrene. After 24 hours a sample of the solution was assayed for phenanthrene, and its reduction in concentration attributed to adsorption by the humic acid-treated chlorite. Most determinations were carried out in triplicate. Chlorite was used as the mineral phase because it is a common clay mineral constituent (generally 30–40% of coastal marine sediments of south-central Alaska), and it is readily available in reasonably pure form. Phenanthrene was chosen as the aromatic hydrocarbon for study because it (and naphthalene) were used by Henrichs et al., (1997) and Braddock and Richter (1998) in their studies of PAH fate and effects in Lower Cook Inlet sediments. Phenanthrene was preferred to naphthalene because the latter is more water soluble and more volatile, making it less likely to persist as a chronic contaminant in marine systems. The distribution coefficients ( $K_d$ ) obtained from these experiments are shown in Table 4.

Table 4. Result of experimental determinations of distribution coefficients ( $K_d$ , mL/g) for phenanthrene between seawater and chlorite which had been treated with solutions of humic acid extracts from Lower Cook Inlet and Port Valdez sediments. Percent saturation refers to the humic acid solution used to treat the calcite. Columns A through D are replicate determinations of  $K_d$ .

Sediment	% Saturation	A	B	C	D	Mean	Std Dev
Homer Boat Harbor							
	0.00	42.9	32.3	19.5		31.6	11.7
	0.99	1.1	13.6	15.7		10.1	7.9
	9.09	-7.8	5.8	0.5		-0.5	6.8
	25.00	91.3	122.8	66.5		93.5	28.2
	33.33	493.5	452.5	414.4		453.5	39.6
	50.00	306.9	375.2	245.5		309.2	64.9
Jakolof Bay-4							
	0.00	1.8	17.3	19.1		12.7	9.5
	0.99	33.5	18.2			25.8	10.9
	9.09	26.9	3.5			15.2	16.5
	25.00	59.5	-10.3	-15.2		11.3	41.8
	33.33	75.2	43.8			59.5	22.3
	50.00	78.8	83.1	-9.0		51.0	52.0
Tutka Bay							
	0.00	2.6	28.0	16.2	15.6	15.6	10.4
	0.10	15.4	-0.3	28.4	-9.8	8.4	16.9
	0.99	26.5	22.6	31.1	14.1	23.6	7.2
	9.09	135.5	83.3	31.1	76.3	81.5	42.7
	50.00	1144.6	1002.3	514.1	679.3	835.1	289.3
PV82							
	0.00	-121.1	891.1	-107.5		220.8	580.5
	0.99	1071.3	-10.1			530.6	764.6
	9.09	-506.2	795.3	628.1		305.7	708.1
	25.00	4807.6	2135.8	-545.8		2132.5	2676.7
	33.33	3246.1	2247.4			2746.8	706.2
	50.00	-206.9	3255.6	5673.5		2907.4	2955.6
PV91							
	0.00	-47.7	-334.4	-88.8		-157.0	155.0
	0.99	833.9	672.0	621.8		709.2	110.8
	9.09	583.3	190.3	373.4		382.3	196.7
	25.00	816.5	547.7	693.7		686.0	134.6
	33.33	717.8	2853.4	2276.4		1949.2	1104.8
	50.00	1935.8	2677.0	3539.6		2717.5	802.7

## 5.0 Discussion

Correlations (Table 5) were performed to investigate relationships among the sediment and humic acid properties reported in Tables 1 and 2. There is a strong correlation ( $r^2 = 0.88$ ) between the percentage humic acid (%HA) and total organic carbon (TOC) in sediment. This, together with the abundance of humic acid in these sediments, indicates that humic acid is, on a mass basis, an important constituent of the total organic matter. Consequently, any study of the interaction of humic acid with PAH can be expected to provide a reasonable approximation of the interaction of sediment organic matter as a whole with PAH. The good correlation coefficient between total aromatic hydrocarbons (TARO) and phenanthrene ( $r^2 = 0.74$ ) supports the choice of phenanthrene as a reasonable choice as a proxy for PAH in experimental work.

Table 5. Correlation coefficients ( $r^2$ ) and numbers of samples correlated (N) for a selection of properties of bulk sediments and humic acid extracted from those sediments.

First variable	Second variable	N	$r^2$
Percent humic acid	Total organic carbon	32	0.88
Phenanthrene	Total aromatics	32	0.74
Percent humic acid	Phenanthrene	30	0.14
Percent humic acid	Total aromatics	32	0.50
Total organic carbon	Phenanthrene	30	0.39
Total organic carbon	Total aromatics	32	0.61
Aromatic abundance	Phenanthrene	30	0.16
Aromatic abundance	Total aromatics	32	0.56
Aromatic abundance, nmr	Phenanthrene	6	0.73
Aromatic abundance, nmr	Total aromatics	6	0.95
E4/E6	Phenanthrene	30	0.21
E4/E6	Total aromatics	32	0.46
Aromaticity, nmr	Phenanthrene	6	0.85
Aromaticity, nmr	Total aromatics	6	0.52
$\delta^{13}\text{C}$	Phenanthrene	30	0.29
$\delta^{15}\text{N}$	Phenanthrene	27	0.26

Most of the correlations in Table 5 are between measures of the concentration of PAH in sediment (either phenanthrene concentration or the TARO) and measures which characterize the humic acid present in the sediment. Both extensive properties (percentage humic acid, aromatic abundance, total organic carbon) and intensive properties (E4/E6,  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , aromaticity) of humic acid were included although stronger correlations with extensive properties were expected. Most of these correlations are poor ( $r^2 < 0.5$ ). The only strong correlations ( $r^2 > 0.7$ ) are between aromatic abundance (as determined by nmr) and phenanthrene ( $r^2 = 0.73$ ); between aromatic abundance (as determined by nmr) and total aromatics ( $r^2 = 0.95$ ); and between aromaticity (as determined by nmr) and phenanthrene ( $r^2 = 0.85$ ). The general absence of correlation between PAH concentrations and the properties of the humic acid (other than the two measures of aromatic character in Port Valdez and Lower Cook Inlet sediments) indicates that these properties are not controlling the concentrations of PAH presently associated with these sediments. This, and the low concentrations of PAH, are consistent with the idea that the availability of hydrocarbons to the sediments is more important than the character of sediment-

associated organic matter in determining hydrocarbon concentrations. Nevertheless, it is still possible that the character of sediment-associated organic matter, particularly aromatic character, may influence the strength of binding between sediments and PAH and thus affect the bioavailability or residence time of PAH.

Another factor which may confound the relationship between humic acid and PAH concentration is that detrital coal is an important source of PAH in Lower Cook Inlet (Shaw and Wiggs, 1980; Boehm, 1998), but not in Port Valdez (Shaw and Hameedi, 1988). PAH which enter the marine environment associated with coal particles may be chemically bound to the coal organic matrix to a degree that prevents adsorption by humic acid. Thus, PAH which enter the marine environment associated with coal may remain bound to coal particles and not be available for adsorption by humic acid on clay particles.

For each of the humic acid extracts used in the sorption experiments the measured distribution coefficient was plotted against the percentage saturation of the humic acid solution that had been used to coat the chlorite (Figures 3–7). In every case the distribution coefficient rises with increasing percentage saturation (positive slope of least squares best fit line in each figure) indicating that more phenanthrene was adsorbed to mineral particles which had been exposed to more humic acid and presumably had more humic acid on their surfaces.

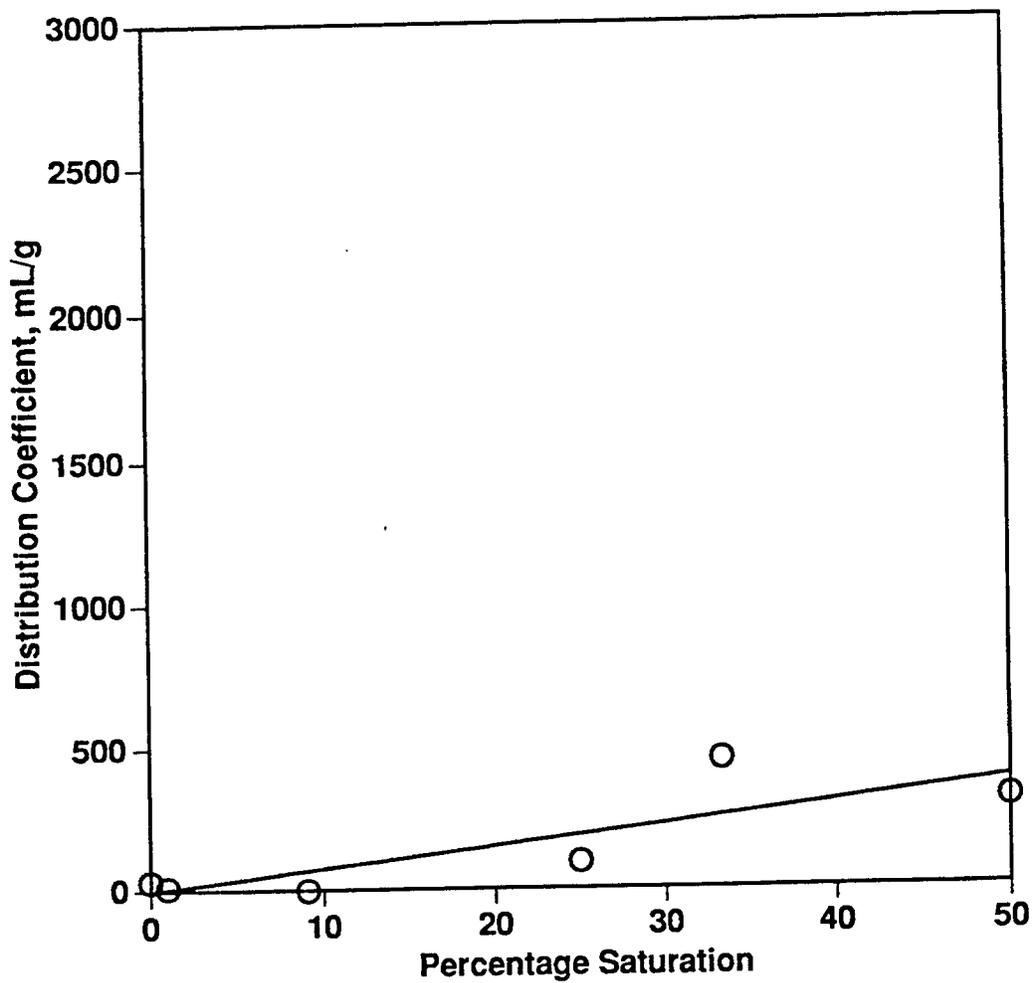


Figure 3. Distribution coefficient ( $K_d$ , mL/g) of phenanthrene on humic acid extracted from intertidal sediment from the Homer boat harbor. Humic acid was coated onto chlorite from serial dilutions of a saturated solution in artificial seawater.

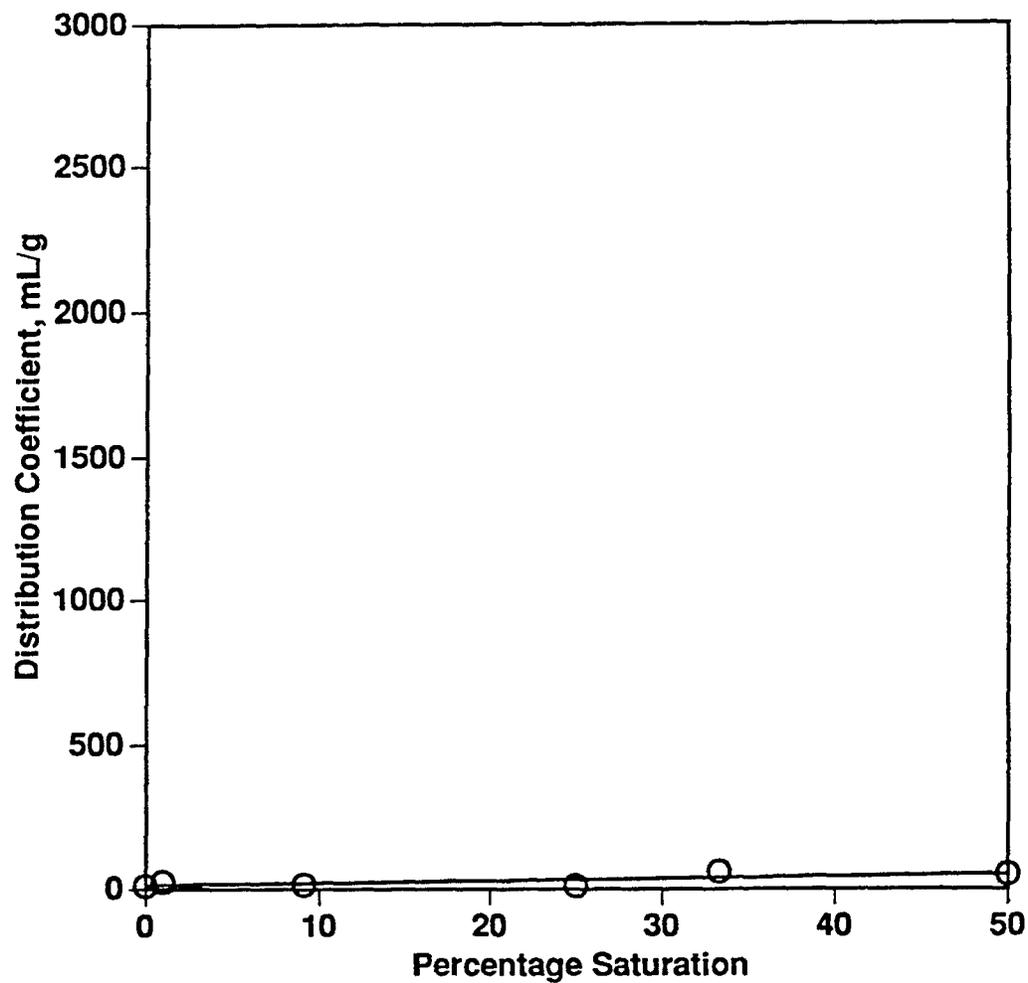


Figure 4. Distribution coefficient ( $K_d$ , mL/g) of phenanthrene on humic acid extracted from intertidal sediment from Jakolof Bay-4. Humic acid was coated onto chlorite from serial dilutions of a saturated solution in artificial seawater.

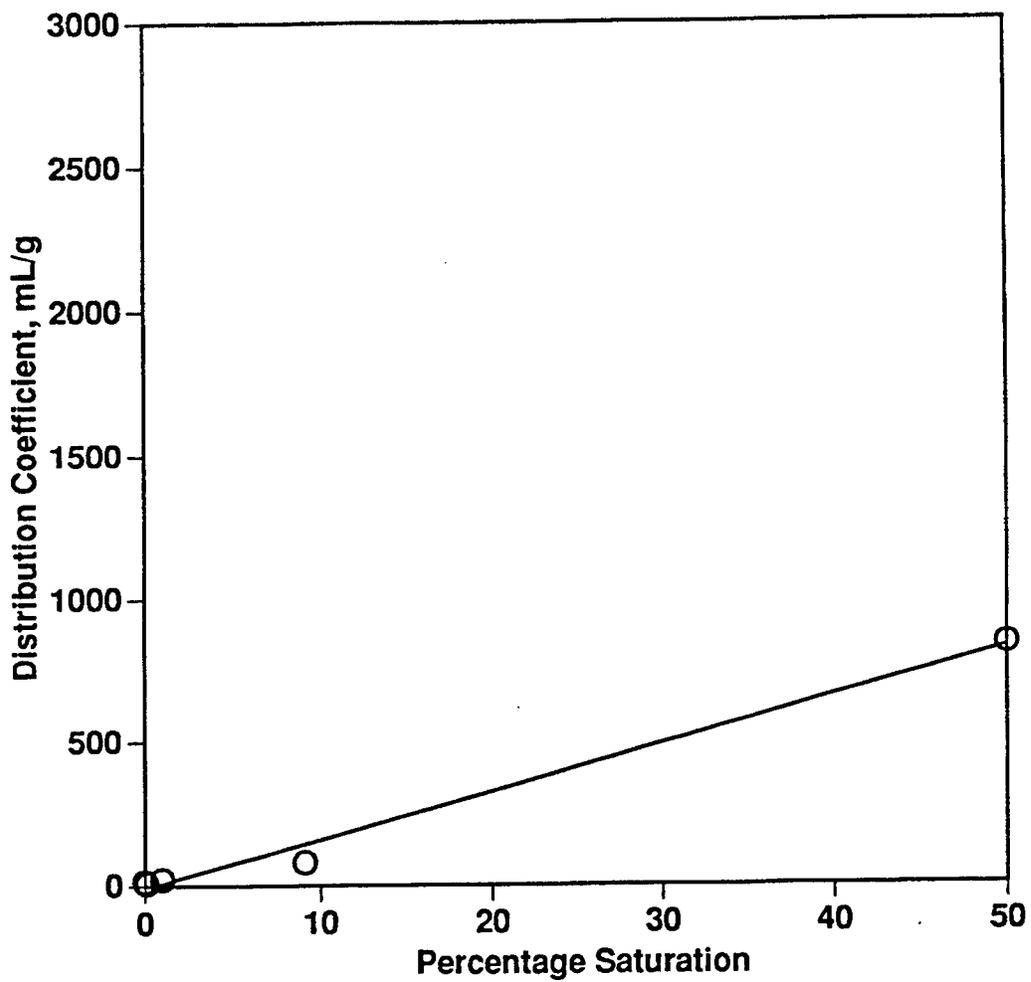


Figure 5. Distribution coefficient ( $K_d$ , mL/g) of phenanthrene on humic acid extracted from intertidal sediment from Tutka Bay. Humic acid was coated onto chlorite from serial dilutions of a saturated solution in artificial seawater.

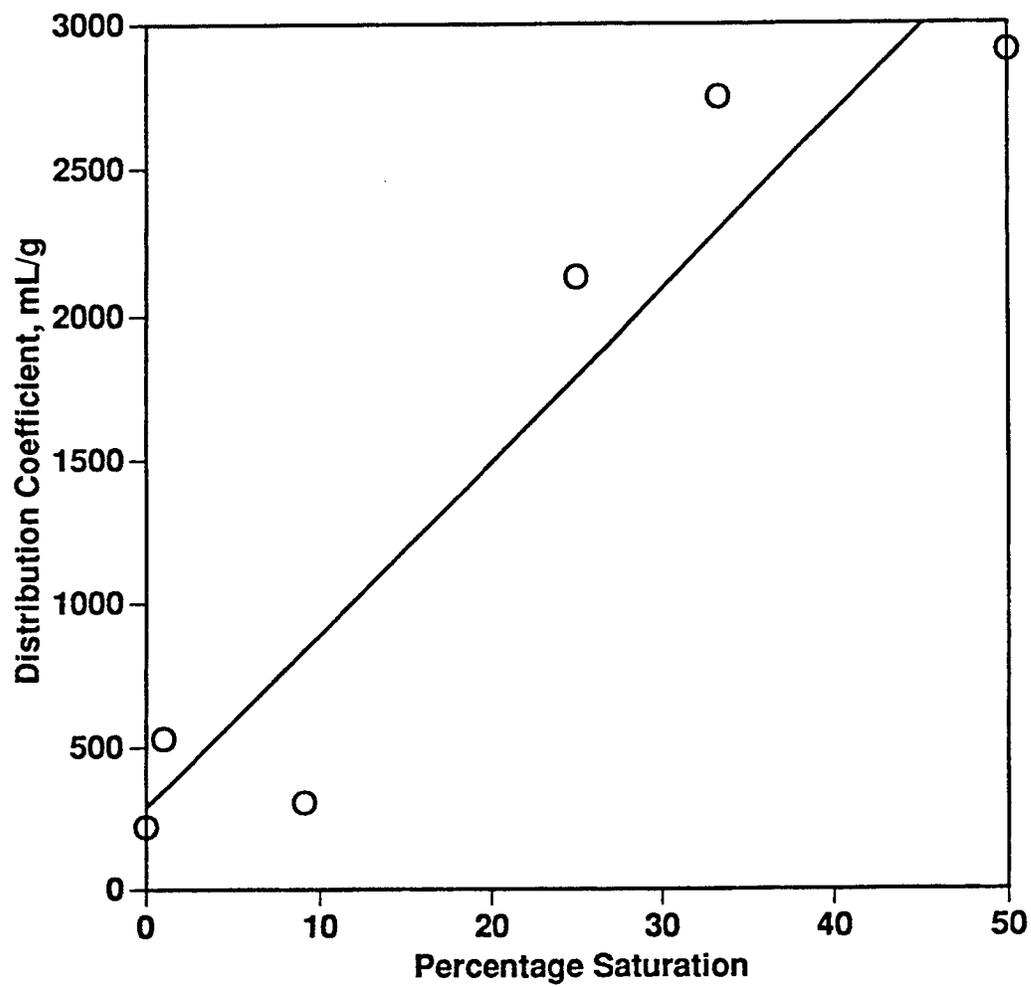


Figure 6. Distribution coefficient ( $K_d$ , mL/g) of phenanthrene on humic acid extracted from intertidal sediment from PV-82 in Port Valdez. Humic acid was coated onto chlorite from serial dilutions of a saturated solution in artificial seawater.

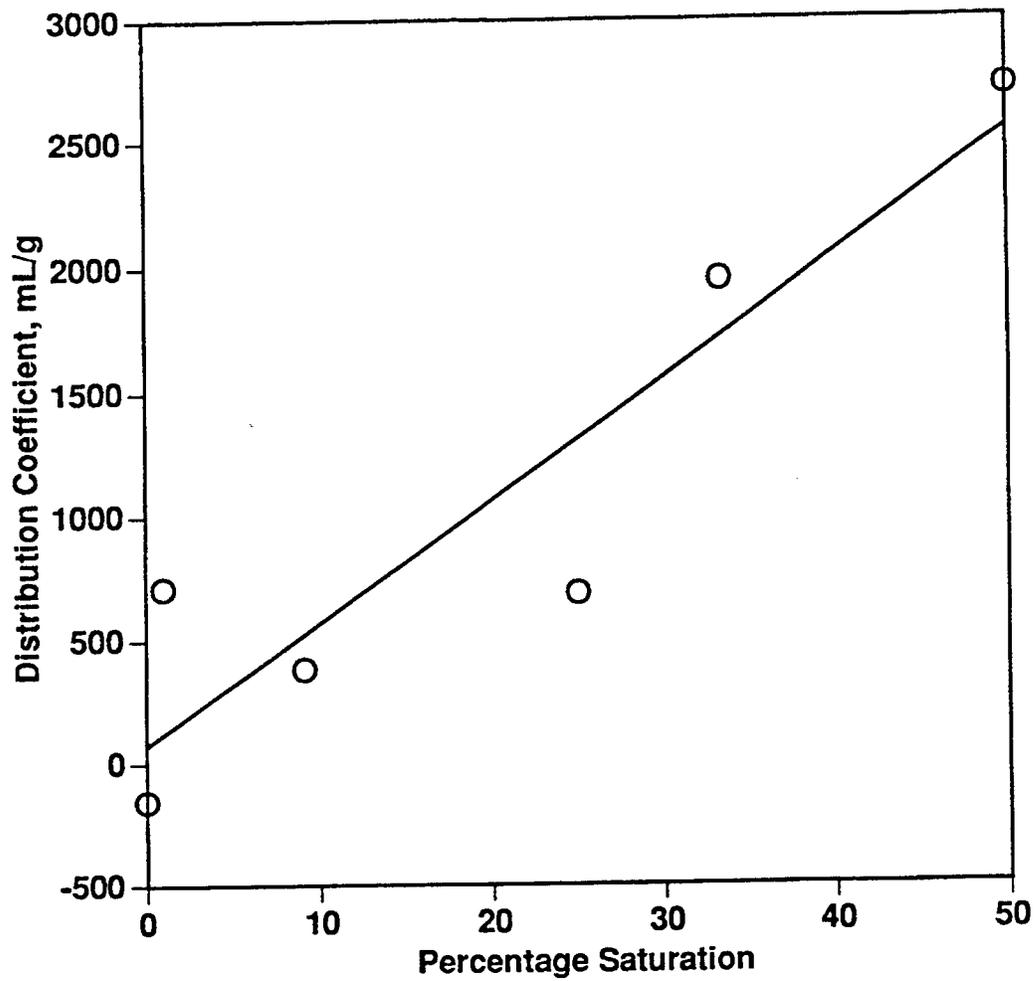


Figure 7. Distribution coefficient ( $K_d$ , mL/g) of phenanthrene on humic acid extracted from intertidal sediment from PV-91 in Port Valdez. Humic acid was coated onto chlorite from serial dilutions of a saturated solution in artificial seawater.

Although the concentration of humic acid that associated with the chlorite particles under the various treatments was not directly determined, the results strongly indicate that the presence of humic acid enhances the ability of mineral particles to adsorb phenanthrene and that this enhancement increases with the concentration of humic acid. Since PAH are generally thought to be bioavailable to most organisms only from solution, this finding is consistent with Braddock's observation that microbial degradation of phenanthrene in Lower Cook Inlet sediments is inhibited by the presence of sediments and that inhibition increases with increasing sediment organic content. These results are also consistent with Henrichs' conclusion that slow and only partially reversible adsorption of phenanthrene to Lower Cook Inlet sediments is likely associated with the hydrocarbon's diffusion into sediment organic matter.

Figures 3–7 also show that the humic acid extracts are not equally effective in adsorbing phenanthrene. The humic acid extracted from the three intertidal sediments from Lower Cook Inlet (Homer boat harbor, Jakolof Bay-4, and Tutka Bay) showed lower distribution coefficients (most notably at higher percentage saturations) than the two humic acid extracts from subtidal sediments from Port Valdez (Table 4). Similarly, differences in the sources of sediment organic matter have been associated with differences in ability to bind small nonpolar molecules. Kile and co-workers (1995) showed that the partition coefficients for carbon tetrachloride and 1,2-dichlorobenzene were similar in organic matter from numerous soils, but differed from the values for bedded sediments. Grathwohl (1990) found that organic matter in shales and coal had greater sorption affinity than organic matter from soils. Rutherford and co-workers (1992) showed that sorption was greater when sediment organic matter contained fewer polar groups. These prior studies, as well as the work reported here, suggest that the ability of humic acid to adsorb PAH increases with age and degree of condensation of the humic acid.

To investigate whether this variability in adsorption can be related to the measured properties of the humic acid extracts, correlations were calculated. For this analysis,  $K_d$  values at 40% saturation were found from least squares best fit lines derived from all available experimental data (Table 4). Calculated values were preferred to measured data since the calculated values incorporate information from all measurements made for a particular humic acid, and therefore are expected to be more accurate than any single data point. The choice of 40% saturation was arbitrary, but avoids possible confusion with measured data.

Correlation coefficients between  $K_d(40)$  and intensive properties of humic acid were: aromaticity (nmr),  $r^2 = 0.19$ ;  $\delta^{15}\text{N}$ ,  $r^2 = 0.81$ ;  $\delta^{13}\text{C}$ ,  $r^2 = 0.88$ ; E4/E6,  $r^2 = 0.95$ . Intensive properties were expected to be more appropriate for these correlations than extensive properties since intensive properties do not depend on the amount of humic acid present. Since the design of the sorption experiment (particularly the way in which humic acid was coated onto the calcite) should have made the amounts of humic acid nearly the same in each experimental run, observed differences were expected to depend on differences in intensive properties among the humic acid samples.

Strong correlations with  $K_d(40)$  were observed for carbon and nitrogen isotopic ratios and for E4/E6, but not for aromaticity. Surprisingly, aromatic abundance (an extensive property) also showed a good correlation ( $r^2 = 0.80$ ) with  $K_d(40)$ . However, the fact that this correlation was negative (i.e., the distribution coefficient rose as the aromatic abundance declined) is nonsensical; the correlation is regarded as an artifact. The correlations of  $K_d(40)$  with the isotope

ratios and E4/E6 are also negative. Falling E4/E6 (Stevenson, 1994) and depletion of  $^{13}\text{C}$  and  $^{15}\text{N}$  (Schell, 1997) all indicate a trend toward more terrigenous input or toward more highly condensed humic acid or both. These results can be interpreted as indicating that more highly condensed, “more humified” humic acid is more enriched in terrigenous carbon either because of the character of the original source material or due to selective removal of more labile moieties from marine sources during formation. This may explain why subtidal sediments such as PV-82 and PV-91 contain humic acid that has a greater potential to adsorb phenanthrene than do intertidal sediments from the Homer boat harbor, Jakolof, or Tutka Bay. Of course correlation does not necessarily imply causation; some other mechanism may be at work in causing the observed correlation.

Based on these findings it is possible to evaluate the two hypotheses originally proposed for this work. Neither of the hypotheses—that there is a direct correlation between the amount of humic acid and the concentration of PAH in a sediment, or that there is a direct correlation between the aromatic character of a humic acid and the concentration in a sediment, is fully supported. Correlations between percent humic acid and phenanthrene or TARO are positive but weak (Table 4). The differences in phenanthrene distribution coefficients suggest that the differing adsorption tendencies of the humic acid samples preclude a simple correlation between the amount of humic acid and PAH. Simply put, the quality of the humic acid is more important than the quantity. A second factor may contribute to the low correlations between the amount of humic acid and the concentration of PAH. All of the Lower Cook Inlet and Port Valdez sediments investigated in this study have low, but not equally low, concentrations of PAH. It is probable that the PAH-adsorbing capacity of the humic acid of these sediments is utilized to low but varying extents. Thus, even if the PAH adsorbing *potential* of the sediments were proportional to the percentage of humic acid, the *observed* correlation could be weak.

The correlations between aromatic abundance (nmr) and phenanthrene or TARO are good, although the corresponding correlations using aromatic abundances estimated from ir measurements are weak (Table 4). In addition, the correlation between  $K_d(40)$  and aromaticity (nmr) is poor. Again, it appears that other structural factors of the humic acid samples, probably related to the original source of the organic matter and the age and degree of condensation of the humic acid, are important in determining the tendency of the humic acid to adsorb PAH.

This work indicates that humic acid extracts from different Alaska coastal marine sediments differ in their ability to adsorb phenanthrene (and, presumably, other PAH) and that E4/E6 is a good predictor of this difference. More broadly, this work suggests that marine environmental management tools that incorporate single distribution coefficients (such as the commonly used  $K_{ow}$ ) are, at best, of limited applicability to actual marine systems where distribution coefficients vary. Care should be exercised when applying such tools.

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