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Contamination of Estuarine Water, Biota, and Sediment by Halogenated Organic Compounds: A Field Study

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■ Studies conducted in the vicinity of an industrial outfall in the Calcasieu River estuary, Louisiana, have shown that water, bottom and suspended sediment, and four different species of biota are contaminated with halogenated organic compounds (HOC) including haloarenes. A "salting-out" effect in the estuary moderately enhanced the partitioning tendency of the contaminants into biota and sediments. Contaminant concentrations in water, suspended sediments, and biota were found to be far below the values predicted on the basis of the assumption of phase equilibria with respect to concentrations in bottom sediment. Relative concentration factors of HOC between biota (catfish) and bottom sediment increased with increasing octanol/estuarine water partition coefficients (K_{ow*}), maximizing at log K_{ow*} of about 5, although these ratios were considerably less than equilibrium values. In contrast, contaminant concentrations in water, biota, and suspended sediments were much closer to equilibrium values. Bioconcentration factors of HOC determined on the basis of lipid content for four different biotic species correlated reasonably well with equilibrium triolein/water partition coefficients (K_{tw}).

Introduction

Discharge of industrial effluents containing organic contaminants into coastal inlets and estuaries is a relatively common practice, because the ocean generally is considered to be a disposal medium in which the adverse effects of hazardous organic compounds are minimized by infinite dilution. Estuaries, however, are fragile, yet dynamic, ecosystems and represent a transition zone for ocean-bound contaminants derived from terrestrial sources. Organic contaminants in estuarine systems are subject to a number of geochemical processes (*1–4*), many of which are not well understood. An understanding of these processes in different compartments of an estuarine system is essential, since these processes ultimately determine the geochemical transport and fate of organic contaminants in marine environments.

Distributions of organic compounds in various compartments of an estuarine system are determined by physicochemical properties of individual compounds as well as by the hydrodynamics of the system. Although water-soluble compounds tend to be associated mainly with the water column, sparingly soluble compounds show a greater tendency to partition into organic matter associated with suspended and bottom sediments or with lipid tissue of biota. Equilibrium studies of contaminant distributions between water, sediment, and biota phases under well-controlled laboratory conditions serve as a convenient basis for the assessment of bioconcentration potential (*5–8*) and sorption–desorption of organic compounds by sediments (*9–15*). In dynamic aquatic systems such as estuaries, however, maximum potential for bioconcentration and sorption by sediments may not be manifested fully because of a lack of equilibrium between different compartments in the system. For this reason, it is of interest to evaluate field data in relation to laboratory equilibrium measurements, for assessing the impact of system dynamics on the distributions of contaminants between these compartments.

The lower Calcasieu River, LA, is part of an estuarine ecosystem impacted by petrochemical and agrochemical industries (*16, 17*). The hydrologic environment south of Lake Charles and around the Calcasieu River is extremely complex. South of Lake Charles, the Calcasieu River enters a flat coastal environment of indeterminate drainage. Flow in the river mainly is confined to the ship-channel portion of the stream. However, numerous outlets occur from the channel into the marsh areas adjacent to the river. The flow is tidal and wind-affected. Chemical facilities in the area manufacture and process diverse materials, such as petroleum, sodium hydroxide, chlorine, Teflon, butadiene, and synthetic rubber. Wastes from these plants are stored in holding ponds, some of which may leach into the river.

A chemical plant, located in the Bayou d'Inde area of the Calcasieu River, manufactures trichloroethylene and perchloroethylene (*18*). Effluents from this plant are discharged into Bayou d'Inde, which drains into the Calcasieu River. Water- and bottom-sediment samples collected near the outfall were analyzed by gas chromatography–mass spectrometry (GC–MS); they were found to contain compounds such as petroleum hydrocarbons, chlorinated benzenes, naphthalenes, styrenes, and butadienes, volatile halogenated hydrocarbons, and polycyclic aromatic hydrocarbons (*16, 17*). Many of these compounds probably are condensation products formed during chlorination processes.

Haloarenes or halogenated aromatic compounds are a class of anthropogenic compounds that are toxic to aquatic species, such as algae and fish (*19*). Because of their relatively high K_{ow} (octanol–water partition coefficients) and bioavailability, they are sorbed strongly by sedimentary organic matter and bioconcentrate in lipid tissues of stream biota. In view of the hazardous nature of these compounds and the paucity of "real-world" data from bioconcentration and sorption studies, a field study was designed to investigate their environmental behavior and fate in an estuarine system and to compare these results with predictions from laboratory experiments. Sampling sites within the study area of the lower Calcasieu River estuary are shown in Figure 1.

Experimental Section

Sample Preparation. Biota species sampled for organic contaminants are shown in Table I. Blue crabs, spotted sea trout, and Atlantic croakers are migratory estuarine species; they are not present in the estuarine system during periods of large freshwater inflow or during the colder winter months. Blue catfish are primarily freshwater organisms capable of tolerating low to medium salinities; they are present all year (*20*). All these organisms are carnivorous; however, blue crab and blue catfish

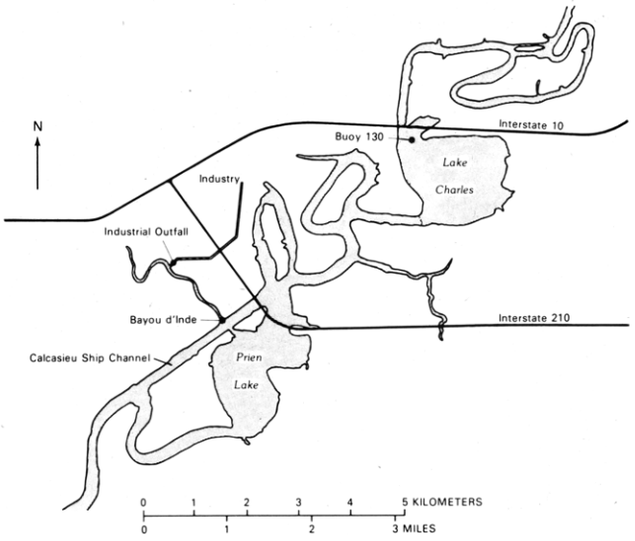

Figure 1. Location of sampling sites.

Table I. Species Selected for Field Study

common name	genus and species	no. of individuals for anal.	lipid content, %
Atlantic croakers	*Micropogonias undulatus*	6	2.2
blue crabs	*Callinectes sapidus*	6	0.5
spotted sea trout	*Cynoscion nebulosis*	4	2.3
blue catfish	*Ichtalurus furcatus*	6	3.3

(to a lesser extent) are opportunistic feeders, consuming both plant and animal tissue. Fish were collected by monofilament gill nets and hook and line. Blue crabs were collected in commercial-type crab traps. Upon capture, organisms were separated by species, wrapped in aluminum foil and stored at 5 °C, and transported to a mobile laboratory on shore. Species were measured (total length for fish, carapace width for crabs), weighed, and grouped by size and class. Intestinal contents of the fish then were removed either by flushing with deionized water or by physically removing the intestines and manually stripping them of their contents. The top carapace of the crabs was removed and discarded, although intestinal contents were not removed. The small size of the crab's intestines and their proximity to other fatty tissues made stripping impractical. Whole organisms then were placed in a stainless steel blender and blended at 10000 rpm. A small quantity of deionized water was added to facilitate blending. The blended samples then were transferred to clean glass jars, frozen, and shipped to the analytical laboratory for analysis. All equipment used in sample preparation was rinsed with methanol and deionized water prior to use. Control samples of methanol and deionizedwater also were analyzed for contaminants.

One hundred grams of tissue was saponified under reflux for 1 h with ethanolic KOH solution (5%). The mixture was cooled, and 100 mL of distilled water and 50 mL of glacial acetic acid were added. The solution was extracted with hexane (2 × 100 mL). The combined hexane extract was washed with saturated Na_2SO_4 solution (50 mL) and dried over anhydrous Na_2SO_4. After 1 mL of isooctane was added, the hexane extract was concentrated to a volume of approximately 10 mL in a Kuderna-Danish concentrator. The extract then was passed through a bed of Florisil (60–100 mesh; 2.5 × 10 cm), and the column was eluted with hexane (150 mL). The hexane eluate was concentrated in a Kuderna-Danish concentrator to a final volume of 1 mL. Prior to concentration, hexane extracts from catfish samples required an additional wash with dilute KOH solution to remove fatty acids. The extract was analyzed by GC–MS.

Determination of Lipid Content. Tissue samples (5 g) were weighed into a glass tissue homogenizer tube. Chloroform–methanol (1:2, 15 mL) was added and homogenized for 2 min. A total of 5 mL of $CHCl_3$ was added to the mixture and homogenized for 30 s. A total of 5 mL of distilled water was added to the mixture and homogenized for 30 s. The homogenate then was filtered in a Buchner filtration unit through a 5.5-cm, Whatman No. 4, filter paper into a preweighed glass centrifuge tube. The homogenizer tube and plunger were rinsed with $CHCl_3$ (5 mL), and the rinsings were filtered and collected in the centrifuge tube. The aqueous and organic layers were separated by centrifugation, and the aqueous layer was carefully removed by aspiration. The organic layer was evaporated under a stream of dry N_2, until the lipid residue achieved constant weight; the percent of lipid was then calculated.

Suspended Sediments. Suspended-sediment samples were collected by dewatering a large volume of river water with a Pelicon tangential-flow filtration system. River water continuously was pumped through a brass U.S. Standard 230 sieve into three 19-L glass bottles with a Johnson-Keck submersible pump. A Pelicon tangential-flow filtration unit then was used to dewater the suspended sediment collected in these bottles. The Pelicon filtration unit consisted of stainless steel fittings, plexiglass housing, linear channel–filter separators, and Durapore 0.4-μm filters. Flow rate through the filtration system was 7–8 L/min; a total of 570 L of water was filtered. Retentate was backflushed off the filters and concentrated to a final volume of approximately 0.5 L. All equipment was rinsed with reagent-grade methanol and deionized water prior to use. Organic carbon content of suspended sediment was 7.41%. Suspended-sediment solutions were centrifuged for 30 min, and the aqueous solutions were decanted. Suspended sediments were lyophylized to dryness. One gram of dry suspended sediment was extracted in a centrifuge tube on a vortex mixer with CH_2Cl_2 (5 mL), CH_2Cl_2 (4 × 3 mL), and hexane (2 mL). After each extraction, the mixture was centrifuged to facilitate separation of the organic phase. The organic extracts were combined and evaporated under a stream of dry N_2 to a final volume of 100 μL. The extract was analyzed by GC–MS.

Bottom Sediments. Bottom sediments were collected by a petite Ponar grab sampler. Samples were wet-sieved through a U.S. Standard sieve 230 (63 μm) to obtain fine (silt and clay) and sand fractions that were collected in wide-mouth glass jars with Teflon-lined screw caps. These samples were shipped to the laboratory on ice. Organic carbon content of the fine and sand fractions was 1.67 and 4.71%, respectively. The higher organic carbon content of the sand fraction was due to organic detritus associated with the sand. Supernatant water was decanted from each sample. Each sediment sample (75 g) was extracted for 24 h sequentially with 2-propanol and methylene chloride in a Soxhlet extractor. The organic extracts were combined and extracted with a Na_2SO_4 solution (2%, 900 mL), and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 100 mL). The organic extracts were combined and dried over anhydrous Na_2SO_4; 2 mL of isooctane was added as a keeper and concentrated in a Kuderna-Danish concentrator to a volume of approximately 10 mL. The sample was evaporated under a stream of dry N_2 to a volume of 5 mL. A total of 100 μL of each

extract was transferred to glass vials containing 10 mg of copper powder (to remove sulfur); the samples then were analyzed by GC–MS.

Water Samples. Water samples were collected in 4-L precleaned and baked amber glass bottles with air-tight, Teflon-lined screw caps. These samples were depth integrated from 1 to 11 ft. Water was continuously pumped into the bottle by a Johnson-Keck submersible pump with Teflon tubing. The sample container was flushed with 3 volumes of water, prior to collection of the 4-L samples for analysis. The sample was spiked with surrogate chloroalkane compounds in the field, capped to avoid air bubbles, chilled on ice, and shipped to the laboratory for analysis.

The closed-loop stripping (CLS) method of Grob (*21*, *22*) was used with some modification by Barber (*23*) and Coleman et al. (*24*) for the analysis of halogenated organic contaminants. In this study, 4-L water samples were heated to 40 °C and continuously purged for 2 h in an air-tight, glass–Teflon–nickel CLS device (Tekmar). Compounds were stripped from the water and trapped onto a 1.5-mg activated-carbon filter that then was eluted with 20 μL of distilled-in-glass methylene chloride (Burdick and Jackson, Muskegon, MI). The methylene chloride extract was collected in a calibrated glass vial and analyzed by GC–MS.

Instrumentation and Analyses. Analyses for volatile organic compounds in water were performed on a Hewlett-Packard 5985 GC–MS (*23*). Analyses for halogenated organic compounds (HOC) in sediments and biota were performed on a Finnigan TSQ-46B computerized capillary gas chromatograph–quadrupole mass spectrometer–mass spectrometer system (GC/MS/MS). The GC was equipped with a 30 m × 0.25 mm i.d. fused-silica capillary column with 0.25-μm bonded film of DB-5 (J & W Scientific). Linear velocity of helium was 30 cm/s. Splitless injections of 1 μL were made at 280 °C. The GC oven was held at 50 °C for 4 min, then increased at 6 deg/min to 300 °C. The MS was operated in electron impact mode with only the first quadrupole scanning from 45 to 450 amu in 1.0 s. Samples were spiked with 100 ng/μL internal standard, phenanthrene-d_{10}, immediately prior to analysis. A reverse-search library was generated, containing mass spectra, relative retention times of the internal standard, and compounds to be quantified.

Solutions of the standards at three different concentrations were analyzed to determine response factors for each compound relative to the internal standard. A computer quantitation routine (Autoquan) searched for each compound within an elution time window. If the library spectra matched a peak in the time window, the area of a preselected characteristic ion was quantified. The area of the peak was converted to a quantity, on the basis of the area of the internal standard base peak, by using the response factors determined previously. Throughout the study, at least one of the standard solutions was analyzed daily, and the new response factors were added to the response factor lists. All compounds quantified were confirmed by comparison of their mass spectra and Kovat's retention indexes with authentic standards analyzed under identical conditions. Because of interfering compounds in bed sediments, octachloronaphthalene and octachlorostyrene were quantitated by positive ion methane chemical ionization mass spectrometry. Because of the complexity of the sample matrixes, unknown exposure history to the contaminants, problems associated with uniformily spiking solid samples, and recoveries of contaminants from aged sediments, all of the interpretations in this report are based on the assumption that recoveries of compounds through the various analytical techniques are equivalent.

Table II. Partition Coefficients of Selected Halogenated Organic Compounds

compound	log K_{ow}[a]	log K_{ow*}[b]	K_{ow*}/K_{ow}
chlorobenzene	2.84	2.92	1.20
1,3-dichlorobenzene	3.50	3.58	1.20
1,4-dichlorobenzene	3.47	3.56	1.23
1,2-dichlorobenzene	3.49	3.56	1.17
1,3,5-trichlorobenzene	4.31	4.40	1.23
1,2,4-trichlorobenzene	4.02	4.09	1.18
1,2,3-trichlorobenzene	4.14	4.20	1.15
1,2,3,5-tetrachlorobenzene	4.59	4.67	1.20
1,2,4,5-tetrachlorobenzene	4.70	4.71	1.02
1,2,3,4-tetrachlorobenzene	4.60	4.67	1.18
pentachlorobenzene	5.20	5.27	1.18
hexachlorobenzene	5.50	5.59	1.23
hexachloro-1,3-butadiene	4.90	5.17	1.86

[a] K_{ow} = octanol/distilled water partition coefficient. [b] K_{ow*} = octanol/Bayou d'Inde water partition coefficient.

Results and Discussion

Partition Coefficients. To understand better the effect of salinity on the behavior of halogenated organic contaminants in the water column of the estuarine study area, octanol/water (K_{ow}) and octanol/Bayou d'Inde water (K_{ow*}) partition coefficients were determined in the laboratory by the method of Chiou et al. (*25*). Average Bayou d'Inde water salinity was 8.05 ‰ (parts per thousand); whereas, average seawater salinity was 33 ‰. Results of partition coefficient measurements are shown in Table II. Data in Table II show that, in general, K_{ow*} values are approximately 20% higher than K_{ow} values, suggesting that the solubility of these compounds in saline water is decreased by about 20% as a result of a salting-out effect. The enhancement of solute K_{ow*} over K_{ow} (i.e., the extent of solubility decrease in saline water) is comparable to the decrease of water solubility of phenanthrene in saline water, which also contains trace amounts of dissolved fulvic acid, 3.6 mg of carbon/L, as reported by Boehm and Quinn (*26*). At a salinity of 35 ‰ in water, phenanthrene shows a reduction of water solubility by approximately 30%, due to the combined effect of salt and dissolved fulvic acid. However, according to the recent work of Chiou et al. (*27*), trace levels of dissolved fulvic acid may be expected to have little effect on the water solubility of phenanthrene on the basis of its solubility in pure water or its octanol–water partition coefficient (log K_{ow} = 4.57). Therefore, the observed solubility reduction of the compound results mainly from the effect of salt. A similar effect on the water solubility of phenanthrene also has been noted by Eganhouse and Calder (*28*). The salting-out effect enhances partitioning of these compounds from water to sediments and lipid tissues of biota that serve as major sinks; thus, the salting-out effect may play a significant role in the fate and transport of these compounds in the estuary.

Bioconcentration Studies. These studies consisted of field data on four different species of biota in relation to three different estuarine compartments: (1) bottom sediment; (2) suspended sediment; and (3) the water column. To compare bioavailability of haloarenes in different species, concentrations were normalized to organic carbon content in the case of sediments and to lipid content for biota. Organic carbon and lipid are the major factors controlling the partitioning process (*6*, *9*, *12*) and they represent "sites-of-loss" from the water column.

Concentrations of HOC in sediments and water of the Calcasieu River near an industrial outfall located in Bayou d'Inde are shown in Table III. Concentrations of these

Table III. Concentrations of Halogenated Organic Compounds in Sediments and Water in Bayou d'Inde near the Industrial Outfall

compound	bottom sediments,[a] μg/g of organic carbon	suspended sediments, μg/g of organic carbon	water, ng/L
chlorobenzene	1.5	0.22	18.0
1,3-dichlorobenzene	101.0	0.98	48.0
1,4-dichlorobenzene	82.0	1.2	74.0
1,2-dichlorobenzene	7.1	*b*	9.0
1,3,5-trichlorobenzene	83.0	0.96	*b*
1,2,4-trichlorobenzene	306.0	4.9	40.0
1,2,3-trichlorobenzene	9.6	0.49	12.0
1,2,3,5-tetrachlorobenzene 1,2,4,5-tetrachlorobenzene	102.0	4.85	42.0
1,2,3,4-tetrachlorobenzene	48.0	2.5	9.0
pentachlorobenzene	1110.0	16.4	32.0
hexachlorobenzene	7544.0	33.7	8.0
hexachloro-1,3-butadiene	1148.0	23.5	1298.0
octachlorostyrene	56.0[c]	5.6	*b*
octachloronaphthalene	12.0[c]	0.81	*b*

[a] Values reported are for combined sand and fine fractions. [b] Values not detected. [c] Values determined by positive ion, methane chemical ionization.

compounds in suspended sediment are greater than those in the water column but substantially less than those in bottom sediment; hexachloro-1,3-butadiene (HCBD), pentachlorobenzene (5 Cl), and hexachlorobenzene (6 Cl) were the major contaminants identified. The finding that concentrations of contaminants in suspended sediment were much smaller than concentrations of contaminants in bottom sediments suggests that resuspension of bottom sediment in the water column in Bayou d'Inde was not significant and that contaminant exchange between the water column and bottom sediment was kinetically slow. This reasoning is partially in agreement with the observed average flow velocities in Bayou d'Inde (on the order of 0.2–2.4 cfs), which were apparently not high enough to cause large resuspension of the bottom sediment. Several isomers of chlorinated butadienes and styrenes also were identified by GC–MS (*17*); however, these compounds were not quantitated, because of lack of commercially available authentic standards.

Catfish were collected at three different locations: (1) near the industrial outfall, (2) 1 mi downstream from the outfall near the junction of Calcasieu River and Bayou d'Inde, and (3) at buoy 130 in Lake Charles, located approximately 5 mi upstream of Bayou d'Inde. Buoy 130 was selected to determine if HOC identified in the water column during an earlier reconnaissance study (*17*) were bioavailable. These compounds discharged into Bayou d'Inde appeared to have moved upstream with incoming tides to Lake Charles, an important fishing and recreational lake on the Calcasieu River, as substantiated by their positive identifications (although concentrations were much lower). Concentrations of HOC in lipid tissue of catfish collected at the three different locations are shown in Table IV. Concentrations in catfish collected at the junction of the Calcasieu River and Bayou d'Inde were greater than those collected at buoy 130 in Lake Charles but less than those collected near the industrial outfall; these differences could be explained in terms of lower contaminant concentrations in water as a result of dispersion and dilution of contaminants caused by the hydrodynamic effect. HOC signatures (compositions) in catfish, water, and bottom and suspended sediments also were different, suggesting different rates of uptake and elimination of individual isomers in these aquatic compartments.

Table IV. Concentrations of Halogenated Organic Compounds in Catfish (μg/g of Lipid)

compound	Bayou d'Inde (industrial outfall)	junction of Calcasieu River and Bayou d'Inde	Lake Charles (buoy 130)
chlorobenzene	*a*	0.05	*a*
1,3-dichlorobenzene	0.19	0.12	0.03
1,4-dichlorobenzene	0.47	0.24	0.17
1,2-dichlorobenzene	0.11	0.06	*a*
1,3,5-trichlorobenzene	0.48	0.25	*a*
1,2,4-trichlorobenzene	3.9	1.9	*a*
1,2,3-trichlorobenzene	0.77	0.37	*a*
1,2,3,5-tetrachlorobenzene 1,2,4,5-tetrachlorobenzene	7.2	3.4	0.07
1,2,3,4-tetrachlorobenzene	3.8	1.9	0.03
pentachlorobenzene	36.0	12.0	0.41
hexachlorobenzene	27.0	7.7	0.61
hexachloro-1,3-butadiene	120.0	46.0	1.0
octachlorostyrene	2.1	0.30	*a*
octachloronaphthalene	*a*	*a*	*a*

[a] Values not detected.

Table V. Concentrations of Halogenated Organic Compounds in Biota from the Calcasieu River at the Junction with Bayou d'Inde (μg/g of Lipid)

compound	Atlantic croakers	blue crabs	spotted sea trout	blue catfish
chlorobenzene	0.10	0.41	0.18	0.05
1,3-dichlorobenzene	0.19	0.35	0.09	0.12
1,4-dichlorobenzene	0.60	2.5	0.90	0.24
1,2-dichlorobenzene	0.08	0.26	0.06	0.06
1,3,5-trichloro-benzene	0.38	0.42	0.05	0.25
1,2,4-trichloro-benzene	2.3	3.2	0.14	1.9
1,2,3-trichloro-benzene	0.42	0.71	0.02	0.37
1,2,3,5-tetrachloro-benzene 1,2,4,5-tetrachloro-benzene	4.7	7.5	0.79	3.4
1,2,3,4-tetrachloro-benzene	2.6	4.5	0.43	1.9
pentachloro-benzene	27.0	42.0	2.9	12.0
hexachlorobenzene	21.0	41.0	7.3	7.7
hexachloro-1,3-butadiene	41.0	12.0	15.0	46.0
octachlorostyrene	*a*	1.0	0.16	0.30
octachloro-naphthalene	*a*	*a*	*a*	*a*

[a] Values not detected.

Concentrations of HOC in lipid tissue of four different biotic species collected from the Calcasieu River at the junction with Bayou d'Inde are shown in Table V. Major contaminants identified include hexachloro-1,3-butadiene, pentachlorobenzene, and hexachlorobenzene. Data in Table V indicate considerable species variability resulting from differences in biouptake of HOC, although analysis of such variability is not possible because of the dynamics of the system and the absence of records on the exposure history of the biotic species to each contaminant. In general, contaminant concentrations in biota (on a lipid basis) are orders of magnitude greater than corresponding concentrations in the water column. these results suggest that native stream biota not only are involved in the transport of hazardous organic compounds but may be used as sensors and concentrators of pollutants in water quality assessments.

To determine if contaminant concentrations in biota and sediments were in equilibrium through their individual

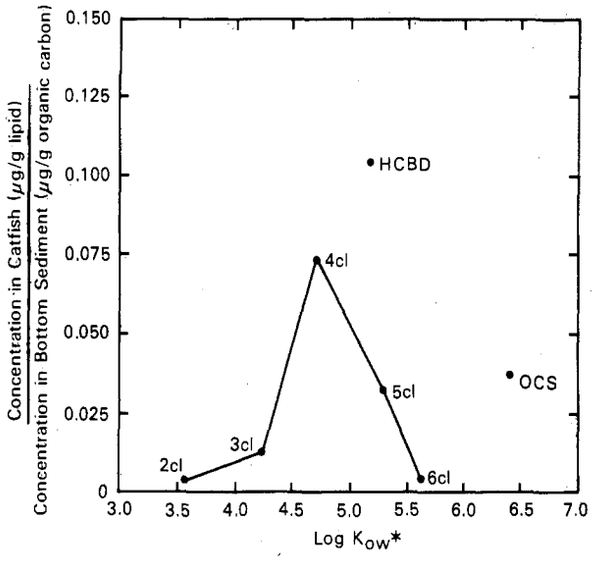

Figure 2. Relative concentration factors of halogenated organic compounds in blue catfish (blue catfish/bottom sediment) collected near the industrial outfall as a function of log K_{ow}*.

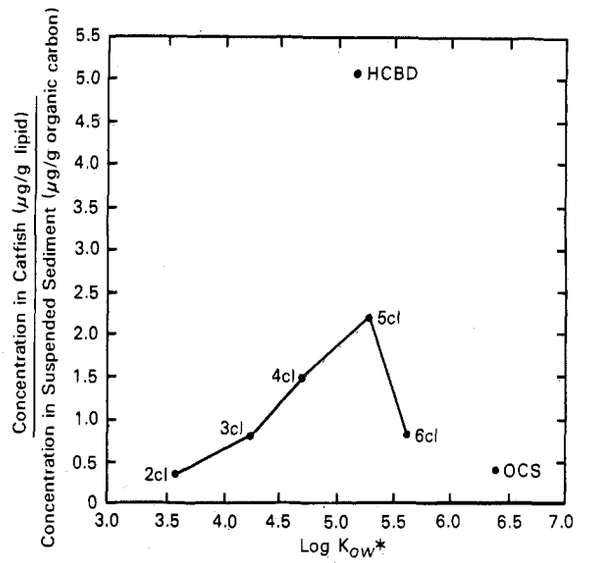

Figure 3. Relative concentration factors of halogenated organic compounds in blue catfish (blue catfish/suspended sediment) collected near the industrial outfall as a function of log K_{ow}*.

equilibria with the water column, relative concentration factors (ratio of the concentration in catfish to the concentration in bottom sediment) of HOC were determined (*15*, *29*). Relative concentration factors of HOC in catfish, collected near the industrial outfall (catfish/bottom sediment), as a function of log K_{ow}* are shown in Figure 2. In the case of chlorobenzenes, a slow increase in relative concentration factors is observed with di- and trichlorobenzenes, followed by a rapid increase for tetrachlorobenzenes and a subsequent rapid decrease for penta- and hexachlorobenzene. Hexachlorobutadiene (HCBD) and octachlorostyrene (OCS) are included for comparison. These results indicate that compounds with log K_{ow}* less than 5.2 show a greater tendency toward equilibrium with respect to lipid tissue of catfish than compounds with log K_{ow}* greater than 5.2. Although a similar finding has also been reported in laboratory studies with oligochaete worms (*15*), it is difficult to conclude whether such a result truly represents uptake and elimination rate differences of these compounds with bottom sediments and biotic species (such as catfish and worms) in the progression toward equilibrium. Since relative concentration factors at equilibrium state based on laboratory soil/sediment and bioconcentration studies are likely to be in the range of 3–6 (*6*, *15*), the small value observed (<1) in this study indicates that the contaminant concentrations in biota are far below the values to be expected under equilibrium conditions. While this observation manifests a rate-limiting slow desorption of the contaminants from bottom sediment as would be expected for a dynamic aquatic system, it also suggests that high levels of contaminants had been discharged into the water column contaminating the bottom sediments prior to sampling.

Relative concentration factors of HOC between catfish and suspended sediments collected near the industrial outfall as a function of log K_{ow}* are shown in Figure 3. An increase in concentration factors is observed for the chlorobenzenes, maximizing at pentachlorobenzene and decreasing for hexachlorobenzene. Octachlorostyrene and hexachlorobutadiene are included for comparison. In contrast to the results for the catfish/bottom sediment system, relative concentration factors between catfish and suspended sediments are markedly greater in magnitude, and they are reasonably close to equilibrium values. The fact that contaminant concentrations in suspended sediments and catfish are much closer to equilibrium appears to result from a more rapid exchange of contaminants between suspended sediment, the water column, and lipid tissue of fish. Hence, HOC associated with suspended sediments are more readily bioavailable to catfish, and probably to other aquatic species, although true equilibrium was not attained for all contaminants, with a possible exception of hexachlorobutadiene (HCBD). The concentration of HCBD in water was considerably greater than the rest of the contaminants (although still lower with respect to HCBD concentration in bottom sediment under the equilibrium conditions) for unknown reasons, thus giving a greater relative concentration factor between catfish and suspended sediments.

Bioconcentration factors [ratio of concentrations of HOC isomers in four species of biota (μg/kg lipid) to their concentrations in Bayou d'Inde water (μg/L)] are shown in Table VI. Despite the dynamics of the estuarine system and errors associated with sampling and analysis, calculated bioconcentration factors (BCFs) on a lipid-weight basis for the four species of biota are in reasonable agreement with values reported in the literature (*6*, *7*, *30*). Variability in bioconcentration factors for individual isomers with the same degree of chlorination, as well as for the same compound in different species, probably reflects nonuniformity of contaminant concentrations in the water column with time and possibly differences in the uptake/elimination rates and exposure times of the organisms.

Because of the recognized importance of lipids in aquatic bioconcentration, the relation between log BCF and log K_{tw} (triolein–water partition coefficients) was examined for HOC in four biotic species. Triolein has been shown to be a good model surrogate lipid in bioconcentration studies of lipophilic compounds (*6*). A plot of log BCF (on a lipid basis) for the four species of biota versus log K_{tw} for compounds listed in Table I is shown in Figure 4. A reasonably good linear correlation is seen between log BCF and log K_{tw} (r^2 = 0.57; n = 44) in accordance with the equilibrium finding that the lipid tissue of biota is the major component for bioconcentration. Although field BCF values show a certain degree of scattering in reflection of the dynamic nature of the system, most data points are within 1 order of magnitude to the equilibrium correlation line, assuming BCF = K_{tw}, with BCF normalized in terms

Table VI. Bioconcentration Factors of Halogenated Organic Compounds in Four Different Biota Species

compound	lipid-based log BCF				
	Atlantic croakers	blue crabs	spotted sea trout	blue catfish	rainbow trout[a]
1,3-dichlorobenzene	3.60	3.86	3.25	3.40	3.70–4.02
1,4-dichlorobenzene	3.91	4.53	4.09	3.51	3.64–3.96
1,2-dichlorobenzene	3.94	4.46	3.79	3.82	3.51–3.80
1,3,5-trichlorobenzene	4.40	4.45	3.51	4.22	4.34–4.67
1,2,4-trichlorobenzene	4.76	4.90	3.54	4.68	4.19–4.56
1,2,3-trichlorobenzene	4.54	4.77	3.13	4.49	4.15–4.47
1,2,3,5-tetrachlorobenzene 1,2,4,5-tetrachlorobenzene	5.05	5.20	4.27	4.90	4.86[b] 4.80–5.17
1,2,3,4-tetrachlorobenzene	5.46	5.70	4.68	5.30	4.80–5.13
pentachlorobenzene	5.93	6.12	4.96	5.57	5.19–5.36
hexachlorobenzene	6.42	6.71	5.96	5.98	5.16–5.37
hexachloro-1,3-butadiene	4.50	3.97	4.06	4.55	4.84–5.29

[a] Data from Oliver and Nimi (*7*). [b] Data (in guppies) from Konemann and van Leeuwen (*30*).

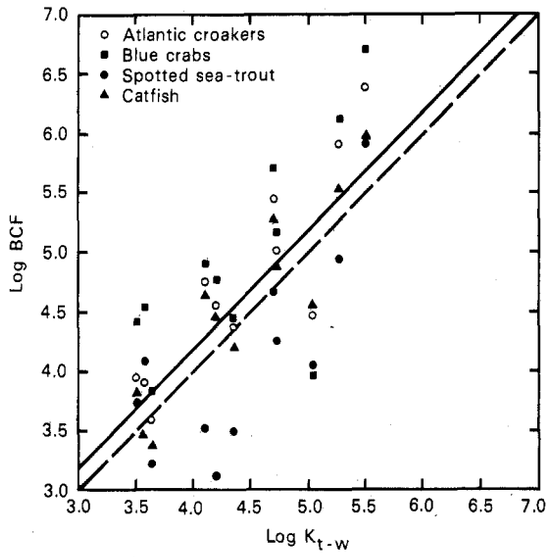

Figure 4. Correlation of log BCF (on a lipid basis) with log K_{tw} in four different species of biota.

of lipid content. The scattering of data points also appears to be random, showing no obvious relation to the biotic species. Results in Figure 4 also suggest that lipid tissue of biota and suspended sediments equilibrate more rapidly with the water column due to the hydrodynamics than do bottom sediments. In a dynamic estuarine system, true equilibrium among all compartments is probably rarely achieved.

Conclusions

Results presented in this study clearly indicate that several compartments of the Calcasieu River estuary are contaminated by anthropogenic halogenated organic compounds including haloarenes. Distributions of contaminants in water, in bottom and suspended sediments, and in four different species of biota indicate that sediments and biota are major sinks for these compounds.

Reasonably good agreement between BCF values determined in field samples and K_{tw} values determined in the laboratory suggest that exchange of contaminants between lipid tissues of biota suspended sediments and water is much more rapid than exchange between bottom sediments and water. Therefore, reasonable estimates of field BCF values can be made on the basis of the concentrations in water, the lipid of biota, and the equilibrium K_{tw} values.

Lack of equilibrium between contaminant concentrations in bottom sediments and the water column suggests a limited mixing action between bottom sediments and the bulk of the water body, resulting in slow desorption of contaminants from bottom sediments. Contaminant distributions between suspended sediments, biota, and water were much closer to equilibrium conditions, suggesting more intimate contact of suspended sediments and biota with the water column. Equilibrium distribution patterns provide a useful basis for assessing the impact of system dynamics on the fate and transport of organic contaminants in estuarine systems.

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Registry No. C_6H_5Cl, 108-90-7; 1,3-$Cl_2C_6H_4$, 541-73-1; 1,4-$Cl_2C_6H_4$, 106-46-7; 1,2-$Cl_2C_6H_4$, 95-50-1; 1,3,5-$Cl_3C_6H_3$, 108-70-3; 1,2,4-$Cl_3C_6H_3$, 120-82-1; 1,2,3-$Cl_3C_6H_3$, 87-61-6; 1,2,3,5-$Cl_4C_6H_2$, 634-90-2; 1,2,4,5-$Cl_4C_6H_2$, 95-94-3; 1,2,3,4-$Cl_4C_6H_2$, 634-66-2; C_6HCl_5, 608-93-5; C_6Cl_6, 118-74-1; $Cl_2C{=}CClCCl{=}CCl_2$, 87-68-3; $C_6Cl_5CCl{=}CCl_2$, 29082-74-4; octachloronaphthalene, 2234-13-1.

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Photoassisted Dissolution of a Colloidal Manganese Oxide in the Presence of Fulvic Acid

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■ The dissolution of a synthesized manganese dioxide by a well-characterized fulvic acid has been investigated over a range of reactant concentrations, pH, and illumination conditions, as have components of the overall dissolution process including fulvic acid and manganous ion adsorption to the oxide surface. The dissolution process is satisfactorily described by an initial rapid formation of a surface-located precursor complex followed by a slower intramolecular electron-transfer step resulting in Mn(II) formation at the oxide surface. Illumination by 365-nm light enhances the rate of electron transfer significantly, with an increase in first-order reduction rate constant from 0.31 min^{-1} (dark) to 0.55 min^{-1} (light) at pH 4.00 and from 0.53 min^{-1} (dark) to 1.23 min^{-1} (light) at pH 7.10. Depending on the affinity of the oxide surface for manganous ion, a portion of the Mn(II) produced at the oxide surface will be rapidly released to solution, resulting in dissolution of the oxide.

Introduction

In oxygenated natural waters, Mn(II) is thermodynamically unstable and tyically forms solid manganese(III) or manganese(IV) oxides. For example, the oxidation of manganous ion to the commonly occurring phases manganite, γ-MnOOH, and birnessite, γ-MnO_2, i.e.

$$Mn^{2+} + {}^1/_4O_2(g) + {}^3/_2H_2O \rightleftharpoons \gamma\text{-MnOOH}(s) + 2H^+ \quad (1)$$

$$Mn^{2+} + {}^1/_2O_2(g) + H_2O \rightleftharpoons \gamma\text{-}MnO_2(s) + 2H^+ \quad (2)$$

proceeds with Gibbs free energy changes of −4.5 and −3.8 kcal $(mol\ e^-)^{-1}$, respectively, for $P(O_2) = 10^{0.21}$ atm, pH 7.0, $[Mn^{2+}] = 10^{-6}$ M, and $T = 25$ °C [using standard electron activity (pe°) values of 25.3 and 21.5 for the Mn^{2+}/γ-MnOOH and Mn^{2+}/γ-MnO_2 half-reactions, respectively (*1*)]. The rate of oxide formation and type of phase produced are dependent on reaction conditions. Thus, the O_2 oxidation of Mn(II) from oversaturated solution leads, in most instances, to the slow formation of γ-MnOOH (*2*, *3*), whereas significantly higher rates of oxide formation can be attained through surface or bacterial catalysis resulting typically in the formation of relatively disordered manganese(IV) oxides (*4*, *5*).

Despite the tendency for solid manganese(III) and manganese(IV) oxides to form in oxygenated systems, significant steady-state concentrations of soluble Mn(II) may be generated as a result of the localized action of reductants at the oxide surface (*6*, *7*). Natural organic substances such as the humic and fulvic acids have been implicated in this oxide dissolution process in both freshwater and seawater (*6*, *7*) and certainly have the ability to reduce manganese(III) or manganese(IV) oxides to the soluble manganous state. Redox potential measurements on a variety of humic and fulvic acids indicate standard electron activities (pe°) in the region of 8.4 and consumption of two protons per electron transferred (*8*), i.e., for a fulvic acid (FA) the half-reaction may be schematically written as

$$FA(ox) + 2H^+ + e^- \rightleftharpoons FA(red) \quad (3)$$

As found for the reductive dissolution of iron oxides in the presence of a fulvic acid (*9*), the rate of dissolution of manganese oxides is significantly enhanced on illumination (*6*, *7*). In the case of iron oxides, the light enhancement has been associated with excitation of ligand to metal charge-transfer or internal ligand transitions within surface-located Fe(III) complexes (*10*, *11*) and similar mechanisms may well apply in the manganese oxide–fulvic acid system. A semiconductor mechanism in which valence band electrons of the metal oxide are photoexcited to the conduction band creating an $e^- - h^+$ pair capable of participating in redox reactions at the particle surface has also been proposed for iron oxides (*12*, *13*) and may be viable for some manganese oxides (*14*, *15*). In addition, the possible role of hydrogen peroxide (produced by the photoionization of natural organic matter) as reductant has been proposed (*16*), i.e.

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