Environ. Sci. Technol. **1999**, *33,* 1004−1008

Extractable Organohalogens (EOX) in Sediment and Biota Collected at an Estuarine Marsh near a Former Chloralkali Facility

KURUNTHACHALAM KANNAN,*,† MASAHIDE KAWANO,‡ YUJI KASHIMA,§ MITSUAKI MATSUI,§ AND JOHN P. GIESY†

National Food Safety and Toxicology Center, Department of Zoology, Institute of Environmental Toxicology, Michigan State University, East Lansing, Michigan 48824, Department of Environment Conservation, Ehime University, Tarumi 3-5-7, Matsuyama 790, Japan, and Department of Hygiene, School of Medicine, Yokohama City University, 3-9 Fukuura, Kanazawa-ku, Yokohama 236, Japan

Extractable, organically bound chlorine (EOCl), which is determined by neutron activation analysis (NAA), has been used as a measure of pollution by chlorinated organics. In this study, the concentrations and distribution of extractable organohalogens (EOX = EOCl + EOBr + EOI) were measured in sediment, blue crab, fishes, birds, and terrapin collected at an estuarine marsh and a nearby creek contaminated by the disposal of wastes from a former chloralkali facility. The concentrations of the organohalogens were in the order of EOCl ≫ EOBr > EOI. The sediment EOCl concentration was comparable to those reported for sediments at sites that have been contaminated by the disposal of bleached kraft pulp mill effluents. The concentrations of EOCl measured in the tissues of blue crab, fishes, and birds were higher than any values previously reported. The absolute concentrations of EOCl coupled with its elevated proportions relative to the concentrations of EOBr or EOI in biota suggest that wastes from the chloralkali processes are a potential source of chlorinated organics present in the environment. The relative proportion of known [such as, polychlorinated biphenyls (PCBs), dibenzo-*p*-dioxins/dibenzofurans (PCDDs/PCDFs), polychlorinated naphthalenes (PCNs), and organochlorine pesticides] to unknown organochlorines in sediment, blue crab, fishes, birds, and terrapin was, on average, 48, 35, 5−25, 1−14, and 4.2%, respectively, which suggested that a major portion of the EOCl measured in biota remained uncharacterized. By assuming that the identities of unknown organochlorines in sediment and biota were similar, the estimated biota−sediment accumulation factor (BSAF) for the unknown EOCl fraction suggested that the components of this fraction have a tendency to bioaccumulate in the food chain.

Introduction

Due to their persistence, bioaccumulation, and toxicity, some organochlorine compounds have gained utmost attention as contaminants of the aquatic and terrestrial ecosystems. Polychlorinated biphenyls (PCBs) and pesticides such as DDT and HCHs are among the well-defined organochlorines. In addition to known man-made organochlorines, there are several unidentified chlorinated organics formed by the widespread use of chlorine and chlorination processes such as the bleaching of pulp and wastewater treatment (*1*−*3*). Furthermore, natural formation of chlorinated organics in water, sediments, and biota has been reported (*4*, *5*). Although several studies have examined the magnitude of chlorinated organics discharged in locations near bleached kraft pulp mills, there have been no reports on the distribution of halogenated organics found in sediments or biota collected near chloralkali facilities. The chloralkali process involves the production of chlorine and sodium hydroxide by the electrolysis of brine, which is constituted primarily of sodium chloride. During the process, several chlorinated organics such as polychlorinated dibenzofurans (PCDFs), polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated biphenyls (PCBs), and polychlorinated naphthalenes (PCNs) are reported to be either used or formed as side reactions (*6*, *7*). Due to the multitude of chlorinated organics that may be formed by the disposal of wastes from industrial processes involving chlorine, the total mass of organically bound chlorine can be estimated either as adsorbable organic halogens (AOX) for water samples (*8*) or as extractable organic halogens (EOX) for sediment (*9*) and biota (*10*). The parameters more closely related to EOX are extractable organic chlorine (EOCl), extractable organic bromine (EOBr), and extractable organic iodine (EOI). These groups of compounds are quantified in sediment and biota by extracting them with organic solvents followed by neutron activation analysis (NAA) (*11*).

Sediment and biota collected in the vicinity of a former chloralkali plant near coastal Georgia, USA (Figure 1), provided a unique opportunity to characterize the distribution and bioaccumulation of EOX. Our earlier studies have reported the occurrence of PCBs, PCDDs/PCDFs, PCNs, and organochlorine pesticides in soil, sediment, and biota collected at this site (*6*, *7*, *12*, *13*). The determination of EOXs, especially EOCl, would provide information on the total chlorinated organics present in these matrixes, from which a mass balance between known and unknown organochlorines can be estimated. The present study was undertaken to investigate the distribution pattern and accumulation characteristics of EOCl, EOBr, and EOI in sediment, blue crab, fishes, terrapins, and birds collected at the estuarine marsh near the site of a former chloralkali facility. EOCl concentrations were compared with the concentrations of known organochlorines such as PCBs, PCDDs/PCDFs, organochlorines pesticides, and PCNs, reported earlier (*6*, *7*, *12*, *13*). The measured concentrations of EOCl were compared with those from other locations to evaluate the significance of the chloralkali process as a source of chlorinated organics present in the environment.

Materials and Methods

Site and Sampling. Samples of sediment and biota were collected near the discharge outfall of a former chloralkali facility near coastal Georgia, USA (called the LCP Chemicals Superfund site; Figure 1). For over 40 years, wastes from the chloralkali plant were discharged into holding pits near the top of an intertidal marsh and also directly into Purvis Creek,

* Corresponding author. Phone: (517) 432-6321; fax: (517) 432-2310; e-mail: kuruntha@pilot.msu.edu.
† Michigan State University.
‡ Ehime University.
§ Yokohama City University.

10.1021/es9811142 CCC: $18.00
Published on Web 02/24/1999

TABLE 1. Concentrations of Organohalogens in Sediment (μg/g, Dry Weight) and Tissues of Terrapins, Birds, and Fish (μg/g, Wet Weight) Collected near a Chloralkali Facility

species	length, cm	wt, g	tissue	lipid, %	EOCl	EOBr	EOI	EOX[d]	EOCl:EOBr
				Terrapin					
terrapin	17[a]	659	liver	14	58(414)[e]	0.62(4.0)	0.17(1.21)	58.8(420)	100:1
terrapin	18.8	1033	liver	9.1	23(253)	2.2(24.2)	0.14(1.54)	25.3(278)	100:10
terrapin	18	876	liver	11	37(336)	3.7(33.6)	0.22(2)	40.9(372)	100:10
terrapin	15.8	619	liver	11	27(245)	0.49(4.5)	0.1(0.91)	27.6(251)	100:2
terrapin	NM[b]	NM	liver	7.3	37(507)	0.87(11.9)	0.16(2.19)	38(521)	100:2
				Birds					
clapper rail	NM	300	muscle	2.5	14(560)	0.14(5.6)	ND	14.1(566)	100:1
clapper rail	NM	300	liver	4.1	47(1150)	0.49(12)	ND	47.5(1160)	100:1
mottled duck	NM	1500	muscle	1.9	23(1210)	0.17(8.9)	ND	23.2(1220)	100:0.7
boat-tailed grackle	NM	177	muscle	3.2	27(844)	0.21(6.6)	ND	27.2(850)	100:0.8
boat-tailed grackle	NM	177	liver	5.7	65(1140)	0.29(5.1)	ND	65.3(1150)	100:0.5
red-winged blackbird	NM	55	carcass	2.6	80(3080)	0.68(26.2)	ND	80.7(3100)	100:0.9
				Fish					
striped mullet	24	346	muscle	0.78	9.4(1210)	0.15(19.2)	0.08(10.3)	9.63(1240)	100:2
striped mullet	25	362	muscle	1.2	18(1500)	0.25(20.8)	0.45(37.5)	18.7(1560)	100:1
yellow tail	18	92	muscle	2.1	13(620)	0.3(14.3)	0.08(3.81)	13.4(637)	100:2
sea trout	34	710	muscle	1.5	12(800)	0.27(18)	0.13(8.67)	12.4(827)	100:2
sea trout	31	570	muscle	0.91	12(1320)	0.11(12.1)	0.03(3.3)	12.1(1330)	100:0.9
blue crab	14.3[a]	NM	hepatopancreas	2.1	37(1760)	1.5(71.4)	0.07(3.33)	38.6(1840)	100:4
blue crab	18.3	NM	hepatopancreas	7.4	76(1030)	2(27)	0.22(2.97)	78.2(1060)	100:3
sea trout	36	570	muscle	1.6	22(1380)	0.23(14.4)	0.06(3.75)	22.3(1390)	100:1
yellow tail	20	113	whole fish	3.7	22(595)	0.32(8.6)	0.1(2.7)	22.4(606)	100:1
Atlantic croaker	NM	NM	muscle	0.83	18(2170)	0.2(24.1)	0.06(7.23)	18.3(2200)	100:1
				Sediment					
marsh sediment	NM	NM	sediment	10[f]	822(8220)	ND[c]	ND	822(8220)	100:0

[a] Refers to carapace length. [b] NM, not measured. [c] ND, not detected. [d] EOX = EOCl + EOBr + EOI. [e] Values in parentheses indicate the lipid (biota) or organic carbon (sediments) normalized EOX concentrations. [f] Organic carbon (%).

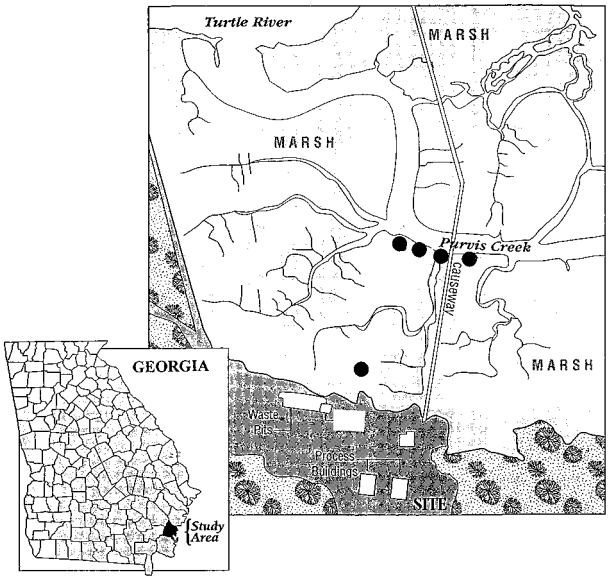

FIGURE 1. Map of study area (LCP Chemical Superfund site near coastal Georgia, USA) showing sampling locations (dots).

which drains into the Turtle River. Details regarding the study site have been provided earlier (*6*, *7*, *12*, *13*). Surficial sediments (0−5 cm) were collected from several locations during low tide in Feb 1996 from the intertidal marsh, using a clean stainless steel scoop. Sediments were pooled, air-dried, and passed through a 500-μm sieve. Adult female diamondback terrapins (*Malaclemys terrapin*) were collected from Purvis Creek in July 1995 by gill nets. All the terrapins were more than 5 years old. Birds—clapper rail (*Rallus longirostrus*), mottled duck (*Anas fulvigula*), boat-tailed grackle (*Quiscalus major*), and red-winged blackbird (*Agelaius phoeniceus*)—were collected from Purvis Creek during July−Aug 1995 by shooting them with steel shots. Blue crabs (*Callinectes sapidus*) were captured in traps. Striped mullet (*Mugil cephalus*), spotted sea trout (*Cynoscion nebulosus*), yellow tail (*Bairdiella chrysoura*), and Atlantic croaker (*Micropogonias undulatus*) were collected in Purvis Creek in March 1997 by using gill nets or by hook and line. The sampling points were within 1 km of the LCP Superfund site. Samples were placed in ice or dry-ice-filled portable containers and transported to the laboratory and stored at −20 °C until analysis. The samples analyzed included the muscle tissue from individual fish, the hepatopancreas from crabs, the liver and breast muscle from clapper rail and boat-tailed grackle, the breast muscle from mottled duck, the carcass of red-winged blackbird, and the liver from terrapin.

Analysis. Samples were weighed (3−7 g for liver, 12−30 g for muscle, and 10 g for dry sediment), cut into small pieces, and homogenized with anhydrous sodium sulfate (80−100 g). The samples were extracted with methylene chloride and hexane (3:1; 400 mL) in a Soxhlet apparatus for 16 h. The extract was reduced to 10 mL by rotary evaporation, and 1 mL was taken for EOX analysis. An aliquot of the extract was taken for lipid determination. The remaining extracts were taken to measure the concentrations of PCBs, organochlorine pesticides, PCDDs/PCDFs, and PCNs, and the results have been reported elsewhere (*6*, *7*, *12*, *13*). The concentrations of EOCl, EOBr, and EOI were determined by neutron activation analysis (*11*, *14*, *15*). The extracts for EOX analysis were sealed in an acid-washed polyethylene vial. The vials were washed with distilled water after an acid rinse, stored in hexane overnight, and dried in an oven at 60 °C. Activation was carried out at a neutron flux of 4.0×10^{13} (n/cm^2)/s for 2 min using JRR-4 research nuclear reactor of the Japan Atomic Energy Research Institute (JAERI), Ibaraki, Japan. The irradiated vials were transferred from the reactor to the laboratory, and aliquots were pipetted immediately into counting vials. The γ-rays from ^{38}Cl, ^{80}Br, and ^{128}I were measured by a γ-ray spectrometry technique (*16*). The γ-energy spectra were recorded with two Ge solid-state detectors with associated electronics interfaced to a EG&G Ortec Model GEM-15180 and Canbera Series 35 Plus 4096 channel for peak area calculations. The analyses were based on γ-peaks from ^{38}Cl ($t_{1/2}$ = 37 min, E_γ = 2167 keV), ^{80}Br ($t_{1/2}$ = 17.6 min, E_γ = 616 keV), and ^{128}I ($t_{1/2}$ = 25 min, E_γ = 443 keV). The count time was 3 min. Ammonium chloride, ammonium bromide, and ammonium iodide of known concentration, dissolved in hexane, were used as standards. Sodium sulfate (100 g) was extracted with methylene chloride and hexane, as described above, in a Soxhlet apparatus, and

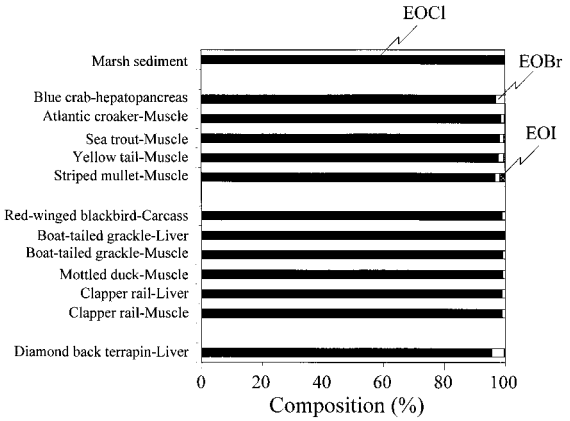

FIGURE 2. Relative distribution (%) of EOCl, EOBr, and EOI in total organohalogens (EOX) in the sediment and biota collected near a former chloralkali facility.

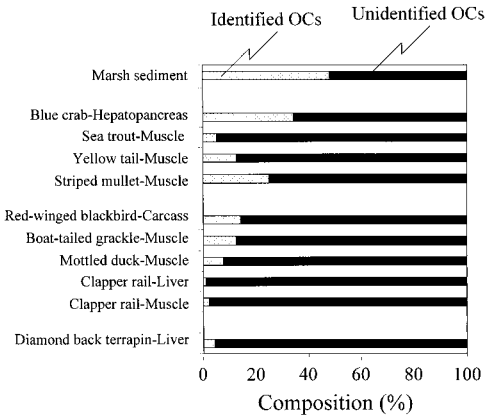

FIGURE 3. Relative contribution (%) of known and unknown organochlorines to EOCl in sediment and biota collected near a former chloralkali facility.

the extract was used as a procedural blank to correct sample values. Procedural blanks contained small amounts of EOCl, a maximum of about 6% of that found in the sample that contained the lowest concentration. However, EOBr and EOI were not detected in blanks. The coefficients of variation of three replicate analyses were 11% for EOCl, 5% for EOBr, and 13% for EOI. EOX values are presented both in terms of wet weight and lipid weight for biological tissues and dry weight and organic carbon normalized weight for sediments.

Results and Discussion

The concentrations of organohalogens measured in fish, bird, and terrapin tissues were in the order of EOCl ≫ EOBr > EOI (Table 1). EOCl accounted for >96% of the EOX measured in biota (Figure 2). Sediment contained the highest concentration of EOCl of 8220 μg/g, organic carbon (OC). The presence of an elevated concentration of EOCl in the sediment interfered with the quantification of EOBr and EOI, and therefore, they were not reported. The concentration of EOCl observed in the sediments was comparable to the values in the range of 6550−8220 μg/g OC, which have been reported for sediments in the vicinity of bleached kraft pulp mills in the Baltic Sea and Jackfish Bay, Canada (*17*−*19*). The sediment EOCl concentration was approximately 210-fold greater than the average background concentrations reported for Finnish lake sediments of 3.8 μg/g, dry weight (*17*). The presence of high concentrations of EOCl in the sediments suggests that disposal of wastes from the chloralkali process has contributed to the sources of EOCl, similar to that reported for bleached kraft pulp mills (*1*−*3*). The concentrations of known organochlorines such as organochlorine pesticides (DDTs + HCHs + CHLs + HCB), PCBs, PCDDs/DFs, and PCNs in sediments were 0.058, 375, 0.10, and 19.6 μg/g, dry weight, respectively (*6*, *7*, *12*, *13*). These known organochlorines accounted for about 48% (Figure 3) of the EOCl measured in the sediments. Thus, approximately 52% of the chlorinated organics present in sediments could not be identified. In sediments contaminated by the disposal of pulp mill effluents, only 8% of EOCl could be accounted for by known compounds (*20*). An elevated proportion of known organochlorines in the sediment in our study was contributed by PCBs, which were used as lubricants in graphite electrodes in the chloralkali process. In contrast, chlorinated organics present in pulp mill effluents are derived due to complex reactions involving chlorine and organic compounds present in wood (*20*), the identities of which are obscure.

In biota, EOCl concentrations were noticeably high, ranging from 595 to 2170 μg/g in fish, 560 to 3080 μg/g in birds, and 245 to 507 μg/g in terrapin, on a lipid weight basis (Table 1). The highest EOCl concentrations, both on a wet weight (80 μg/g) and lipid weight basis (3080 μg/g), were found in the carcass of a red-winged blackbird. Expressed on a lipid weight basis, the EOCl concentrations found in the liver tissues of birds were higher than those in the muscle. This pattern is similar to that observed for beluga whales (*21*), which was due to the presence of higher proportions of polar lipids such as phospholipids in liver tissues and preferential association of a major portion of EOCl with polar lipids. EOCl concentrations of between 33 and 107 μg/g, wet weight (464−1300 μg/g, lipid weight), have been reported for herring gull eggs from Lake Ontario, Canada (*10*), comparable to the range of values reported in this study.

The EOCl concentrations in the muscle tissues of birds were less than those observed in several fish species. Terrapins contained relatively lesser concentrations of EOCl than those of birds and fish. On a lipid weight basis, Atlantic croaker contained the highest EOCl concentrations, whereas yellow tail had the least. The concentrations of EOCl found in fish samples were at least 10-fold greater than those reported for fishes from the Great Lakes (*22*) and carp from the Buffalo River, NY (*15*).

The concentrations of EOBr in the tissues of blue crab, fishes, birds, and terrapins were 27−71, 8.6−24, 5.1−26, and 4−34 μg/g lipid weight, respectively (Table 1). The highest concentrations of EOBr were found in the livers of terrapins and the hepatopancreas of blue crabs. Similarly, detectable concentrations of EOI were observed in the livers of terrapin, whereas the tissues of birds did not contain measurable concentrations of EOI. Few studies have reported the concentrations of EOBr or EOI in biota. The concentrations of EOBr (0.56−1.4 μg/g, lipid weight) and EOI (0.11−0.81 μg/g, lipid weight) in carp from the Buffalo River, NY (*15*), were 10-fold less than those found in fishes in this study. The concentrations of EOBr in the eggs of herring gulls were in the range of 3.9−31 μg/g, lipid weight (*10*). The average concentrations of EOBr in the liver and muscle tissues of beluga whales were 39 and 27 μg/g, lipid weight, respectively (*21*), greater than those found in birds but comparable to those found in terrapins in this study. The EOBr concentrations in harbor porpoises from the Baltic Sea were 0.57−2.2 μg/g, lipid weight, whereas those in striped dolphin and Dall's porpoises were in the ranges of 31−54 and 5.5−19 μg/g, lipid weight, respectively (*23*). These results suggest a broader range of EOBr concentrations, which varies depending on species and location (*24*).

Ratios of EOCl to EOBr in bird tissues were greater than those found in fishes and terrapins. EOCl:EOBr ratios of the order of 100−200 were calculated in bird tissues, which were comparable to those reported for herring gull eggs from Lake Ontario, Canada (*10*). In general, ratios of EOCl to EOBr in the tissues of birds and fish were higher than those reported

TABLE 2. Concentrations of Known Organochlorines in Sediment (μg/g, OC) and Tissues of Terrapins, Birds, and Fish (μg/g, Lipid Weight) Collected near a Chloralkali Facility

species	tissue	fat, (%)	PCBs	HCB	HCHs[b]	CHLs[c]	DDTs[d]	PCNs	PCDDs/PCDFs	total known organochlorines
diamondback terrapin	liver	11	14.5	0.01	ND	0.029	ND	NA[e]	ND	14.6
clapper rail	muscle	2.5	12.0	ND[a]	ND	0.007	0.48	NA	ND	12.5
clapper rail	liver	4.1	10.2	ND	ND	0.009	1.44	NA	ND	11.7
mottled duck	muscle	1.9	89.5	ND	ND	0.002	0.23	NA	ND	89.7
boat-tailed grackle	muscle	3.2	103	0.15	ND	0.156	0.75	0.031	ND	104
red-winged blackbird	carcass	2.6	431	0.03	ND	0.003	0.65	NA	ND	432
striped mullet	muscle	0.99	343	0.05	0.02	0.242	1.92	0.606	ND	346
yellow tail	muscle	2.92	75.3	0.02	0.03	0.062	0.20	NA	ND	75.7
sea trout	muscle	1.34	59.0	ND	ND	ND	0.43	NA	ND	59.4
Atlantic croaker	muscle	0.83	320	0.03	ND	ND	ND	NA	ND	320
blue crab	hepatopancreas	4.75	408	ND	ND	0.884	0.80	0.274	ND	410
marsh sediment	sediment	10[f]	3750	0.08	0.05	0.100	0.35	196	1	3950

[a] ND: not detected. Detection limits for organochlorine pesticides, 1 ng/g, wet weight; PCDDs/PCDFs, 10 pg/g, wet weight. [b] HCHs = $\alpha + \beta + \gamma$ isomers. [c] CHLs = *trans*-chlordane + *cis*-chlordane + *trans*-nonachlor + *cis*-nonachlor + oxychlordane. [d] DDTs = *p,p′*-DDE + *p,p′*-DDD + *p,p′*-DDT. Values were taken from refs *6*, *7*, *12*, and *13*. [e] NA: not analyzed. [f] Organic carbon (%).

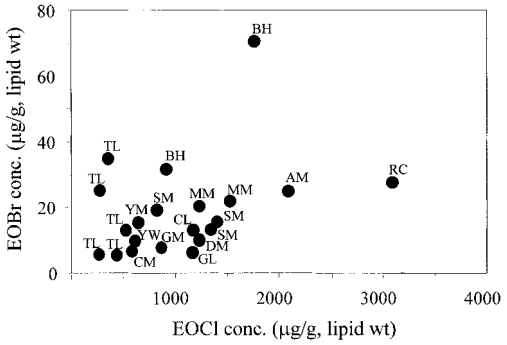

FIGURE 4. Relationship of EOCl to EOBr in biota collected near a former chloralkali facility (AM, Atlantic croaker muscle; BH, blue crab hepatopancreas; CM, clapper rail muscle; CL, clapper rail liver; DM, mottled duck muscle; GL, grackle liver; GM, grackle muscle; MM, striped mullet muscle; RC, red-winged blackbird carcass; SM, sea trout muscle; TL, terrapin liver; YM, yellow tail muscle; YW, yellow tail whole fish).

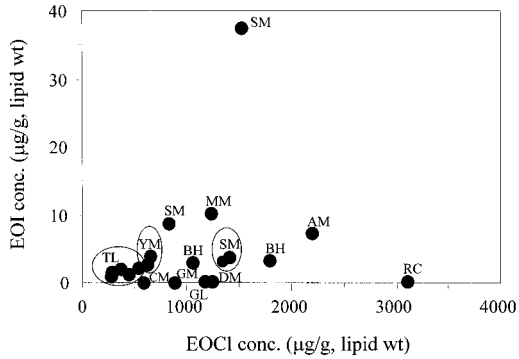

FIGURE 5. Relationship of EOCl to EOI in biota collected near a former chloralkali facility. For abbreviations, see Figure 4.

for beluga whales from the Canadian Arctic (*21*), carp from the Buffalo River (*15*), or striped dolphin and Dall's porpoises from the Pacific Ocean and harbor porpoises from the Baltic Sea (*23*). Relatively high concentrations of EOCl coupled with their elevated proportion in sediment and biota suggest the release/formation of chlorinated organics in chloralkali processes. The relative proportions of bromoorganics in fishes and terrapins were greater than those found in bird tissues. Marine biota, particularly algae, biosynthesize brominated organic compounds, which may concentrate in fish tissues and accumulate in food chains at high proportions (*25, 26*). EOBr and EOI present in biota collected near the chloralkali facility are thought to be primarily of natural/biogenic origin. Among known brominated compounds measured in sediments collected near the chloralkali facility, polybrominated diphenyl ethers (PBDE) were found up to 1.02 ng/g, dry weight, while brominated dioxins and furans were undetected (*6*).

There was no correlation between the concentrations of EOCl and EOBr or EOI (Figures 4 and 5), which indicates that these three classes of organic halogens did not have a common source. The chloralkali process has been a major source for EOCl in sediment and biota, whereas naturally occurring brominated and iodinated organics have been the major sources of EOBr and EOI found in biota. In addition, plots of EOCl to EOBr (Figure 4) and EOCl to EOI (Figure 5) suggested the segregation of data points by species. Few studies have measured EOX in several species collected at a single location. Our study suggests that the magnitude and accumulation patterns of EOX vary among species collected from the same location, which may be due to the influence of feeding habits.

The measured concentrations of known (identified) organochlorines such as PCBs, organochlorine pesticides, PCDDs/DFs, and PCNs in sediment, fishes, birds, and terrapins were summed (Table 2), and the values were subtracted from the average EOCl concentrations for individual species to estimate the concentrations of unknown (unidentified) organochlorines. In addition to those compounds, toxaphene in fish from the study area has been reported to occur at concentrations less than 1 μg/g, lipid weight, in the liver (*27*). On average, identified organochlorines accounted for 48% of the EOCl in sediments. In fishes (5−25%), blue crab (35%), birds (1−14%), and terrapin (4.2%), the relative proportions of identified organochlorines to unidentified organochlorines were less (Figure 3). Similarly, fishes collected near discharge sites of bleached kraft mill effluents contained <10% of the EOCl as known compounds (*28*). In general, the increase in the proportions of unidentified EOCl from sediments to biota suggests that certain unidentified chlorinated organics may have the tendency for bioaccumulation in the food chain. This does not preclude the possibility of trophic transfer of naturally occurring chlorinated organics in marine organisms such as chlorinated methanes or chlorinated fatty acids (*26, 29*). Although the origin of chlorinated fatty acids in fish lipids is primarily from anthropogenic sources such as bleached kraft mill effluents, natural formation is also suggested to be possible (*29, 30*).

Known organochlorine compounds are reported to account for 2−58% of the EOCl in North American and Japanese fish (*14, 15, 22*). The known compounds in herring gull eggs from Lake Ontario accounted for 25−50% of the EOCl (*10*). Approximately 45% of the EOCl measured in the blubber of

TABLE 3. Biota−Sediment Accumulation Factors (BSAF) for Known and Unknown Fractions of EOCl in Fish, Birds, and Terrapin Collected near a Chloralkali Facility

species	tissue	EOCl known	EOCl unknown	EOCl total
diamond back terrapin	liver	0.004	0.078	0.042
clapper rail	muscle	0.003	0.128	0.068
clapper rail	liver	0.003	0.266	0.140
mottled duck	muscle	0.023	0.262	0.147
boat-tailed grackle	muscle	0.026	0.173	0.103
boat-tailed grackle	liver	NA[a]	NA	0.139
red-winged blackbird	carcass	0.109	0.619	0.374
striped mullet	muscle	0.088	0.243	0.168
yellow tail	muscle	0.019	0.123	0.073
sea trout	muscle	0.015	0.255	0.140
Atlantic croaker	muscle	NA	NA	0.264
blue crab	hepatopancreas	0.104	0.182	0.145

[a] NA: not analyzed.

beluga whales from the Canadian Arctic was contributed to identifiable compounds (*21*, *31*), whereas 30−40% of the EOCl in striped dolphins and Dall's porpoises from the Pacific Ocean and the Baltic Sea were identifiable compounds (*23*). In comparison with these results, the relative proportion of unknown EOCl in terrapins and birds collected near the chloralkali facility was high.

Biota−sediment accumulation factors (BSAF = concentration in tissue normalized to lipid content divided by the concentration in the sediment normalized to total organic carbon) were estimated for known and unknown fractions of EOCl to evaluate their corresponding bioaccumulation potential (Table 3). This estimation is based on the assumption that the identities of unknown EOCl fractions in sediment and biota are similar. Although the overall BSAFs were less than unity, suggesting the preferential binding of EOCl to sediment organic carbon or interstitial pore waters instead of lipids or the lack of membrane permeability for high molecular size organchlorines (*13*), BSAFs for unknown EOCl were at least 10-fold greater than those for the identifiable portion of EOCl. This suggests the presence in the uncharacterized EOCl portion of compounds that have the potential for bioaccumulation. However, the number of sediment samples analyzed is small to provide further discussions about the bioaccumulation potential of the unknown EOCl fraction, which deserves further studies.

Disposal of wastes from the chloralkali process can be an important source of chlorinated organic compounds in the environment. While EOCl concentrations measured in sediments were comparable to those reported for sediments from vicinities of bleached kraft pulp mill effluent discharges, the concentrations of EOCl in biota were some of the greatest concentrations ever reported. The presence of a considerable proportion of unidentified organochlorines in the biota collected near the chloralkali facility suggests the need for further studies to characterize their toxic potential.

Acknowledgments

This research was supported by a grant from the National Institute for Health Superfund Basic Research Program (NIH-ES-04911), a cooperative agreement between the U.S. EPA Office of Water and Michigan State University (CR 822983-01-0), and a grant from the U.S. EPA Exploratory Research Program-Biology Panel (R825371-01-0). We thank Drs. R. Stafford (Georgia Environmental Protection Department) and G. R. Masson (U.S. Fish & Wildlife Service) for providing biological samples.

Literature Cited

(1) Neilson, A. H.; Allard, A.-S.; Hynning, P-C.; Remberger, M. *Toxicol. Environ. Chem.* **1991**, *30*, 3−41.
(2) Kankaanpää, H. T.; Laurén, M. A.; Saares, R. J.; Heitto, L. V.; Suursaar, Ü. K. *Environ. Sci. Technol.* **1997**, *31*, 96−104.
(3) Kahkonen, M. A.; Suominen, K. P.; Manninen, P. K. G.; SalkinojaSalonen, M. S. *Environ. Sci. Technol.* **1998**, *32*, 1741−1746.
(4) Grimvall, A. Evidence of Naturally produced and man-made organohalogens in water and sediments. In *Proceeding of the International Conference on Naturally-Produced Organohalogens: Formation, Occurrence, Characteristics and Environmental Significance*, 14−17 Sept 1993; pp 1−2.
(5) Gribble, G. W. *Environ. Sci. Technol.* **1994**, *28*, 310A−319A.
(6) Kannan, K.; Watanabe, S.; Giesy, J. P. *Toxicol. Environ. Chem.* **1998**, *67*, 135−146.
(7) Kannan, K.; Imagawa, T.; Blankenship, A. L.; Giesy, J. P. *Environ. Sci. Technol.* **1998**, *32*, 2507−2514.
(8) Asplund, G.; Grimvall, A.; Jonsson, S. *Chemosphere* **1994**, *28*, 1467−1475.
(9) Martinsen, K.; Kringstad, A.; Carlberg, G. E. *Wat. Sci. Technol.* **1988**, *20*, 13−24.
(10) Norstrom, R. J.; Gilman, A. P.; Hallett, D. J. *Sci. Total. Environ.* **1981**, *20*, 217−230.
(11) Gether, J.; Lunde, G.; Steinnes, E. *Anal. Chim. Acta* **1979**, *108*, 137−147.
(12) Kannan, K.; Maruya, K. A.; Tanabe, S. *Environ. Sci. Technol.* **1997**, *31*, 1483−1488.
(13) Kannan, K.; Nakata, H.; Stafford, R.; Masson, G. R.; Tanabe, S.; Giesy, J. P. *Environ. Sci. Technol.* **1998**, *32*, 1214−1221.
(14) Watanabe, I.; Kashimoto, T.; Kawano, M.; Tatsukawa, R. *Chemosphere* **1987**, *16*, 849−857.
(15) Loganathan, B. G.; Kannan, K.; Watanabe, I.; Kawano, M.; Irvine, K.; Kumar, S.; Sikka, H. C. *Environ. Sci. Technol.* **1995**, *29*, 1832−1838.
(16) Kawano, M.; Falandysz, J.; Tsiji, S.; Kitamura, S.; Wakimoto, T. *J. Environ. Chem.* **1997**, *7*, 7−13 (in Japanese)
(17) Håkansson, L.; Jonsson, P.; Jonsson, B.; Martinsen, K. *Wat. Sci. Technol.* **1988**, *20*, 25−36.
(18) Jonsson, P.; Rappe, C.; Kjeller, L.-O.; Kierkegaard, A.; Hakanson, L.; Jonsson, B. *Ambio* **1993**, *22*, 37−43.
(19) Sibley, P. K.; Dixon, D. G.; Barton, D. R. *Arch. Environ. Contam. Toxicol.* **1998**, *34*, 158−166.
(20) Remberger, M.; Hynning, P.-C.; Neilson, A. H. *J. Chromat.* **1990**, *508*, 159−178.
(21) Kiceniuk, J. W.; Holzbecher, J.; Chatt, A. *Environ. Pollut.* **1997**, *97*, 205−211.
(22) Newsome, W. H.; Andrews, P.; Conacher, H. B. S.; Rao, R. R.; Chatt, A. *J. AOAC. Int.* **1993**, *76*, 703−706.
(23) Kawano, M.; Falandysz, J.; Tanaka, Y.; Wakimoto T. *Organohalogen Compounds−Dioxin 97* **1997**, *33*, 328−332.
(24) Lunde, G.; Gether, J. *Ambio* **1976**, *5*, 180−182.
(25) Faulkner, D. J. *Tetrahedran* **1977**, *33*, 1421−1443.
(26) WesJn, C.; Carlberg, G. E.; Martinsen, K. *Ambio* **1990**, *19*, 36−38.
(27) Maruya, K. A.; Lee, R. F. *Environ. Sci. Technol.* **1998**, *32*, 1069−1075.
(28) Björn, H.; Sundin, P.; Wesén, C.; Mu, H.; Martinsen, K.; Kvernheim, A. L.; Odham, G. *Naturwissenschaften* **1998**, *85*, 229−232.
(29) Mu, H.; Wesén, C.; Sundin, P. *Trends Anal. Chem.* **1997**, *16*, 266−274.
(30) Sundin, P.; Wesén, C.; Mu, H.; Odham, G. Are chlorinated fatty acids in fish lipids of natural origin? In *Proceedings of the International Conference on Naturally-Produced Organohalogens: Formation, Occurrence, Characteristics and Environmental Significance*, 14−17 Sept 1993; pp 31−33.
(31) Muir, D. C. G.; Wageman, R.; Hargrave, B. T.; Thomas, D. J.; Peakall, D. B.; Norstrom, R. J. *Sci. Total Environ.* **1992**, *122*, 75−134.

Received for review October 29, 1998. Revised manuscript received January 13, 1999. Accepted January 20, 1999.

ES9811142