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

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Abstract

Concentrations 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 chlor-alkali facility. Concentrations of organohalogens were in the order of EOCl >>> EOBr > EOI. While EOCl concentrations measured in sediments were comparable to those reported for sediments from vicinities of bleached kraft pulp mill effluent discharges, concentrations of EOCl in biota were some of the greatest concentrations ever reported. Presence of considerable proportion of unidentified organochlorines in biota collected near the chlor-alkali facility suggests the need for further studies to characterize their toxic potential. Disposal of wastes from the chlor-alkali process can be an important source of chlorinated organic compounds in the environment.

Introduction

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) or as extractable organic halogens (EOX) for sediment and biota (1-3). 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) (4). While the release of EOX from bleached kraft pulp mills has been examined earlier, information regarding EOX concentrations in sediment and biota collected near chlor-alkali plants is less known. Several chlorinated organics may be formed during the process due to the reactions of chlorine with organic compounds used in the process. Sediment and biota collected in the vicinity of a former chlor-alkali plant near coastal Georgia, USA, 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 (5-8). Determination of EOX, especially EOCl, provided information on the total chlorinated organics present in these matrices, from which a mass balance between known and unknown organochlorines was estimated.

Materials and Methods

Samples of sediment and biota were collected near the discharge outfall of a former chlor-alkali facility at coastal Georgia, USA (called as LCP Chemicals Superfund site). Details regarding the study site have been provided earlier (5-8). Surficial sediments (0-5 cm) were collected from several locations during low tide in February 1996 from the intertidal marsh. Biota samples were collected during 1995 and 1997 and their details have been reported elsewhere (5-8).Samples were weighed (3 to 7 g for liver, 12-30 g for muscle and 10 g for dry sediment), homogenized and 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. Remaining extracts were taken to measure the concentrations of PCBs, organochlorine pesticides, PCDDs/PCDFs and PCNs, and the results of which have been reported elsewhere (5-8). Concentrations of EOCl, EOBr, and EOI were determined by Neutron Activation Analysis (4,9). Extracts for EOX analysis were sealed in an acid-washed polyethylene vial. Vials were washed with distilled water after an acid-rinse and then 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, 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 gamma ray spectrometry technique (9). The γ- energy spectra was recorded with two Ge solid-state detectors with associated electronics interfaced to 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 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. Coefficients of variation of three replicate analyses were 11% for EOCl, 5% for EOBr and 13% for EOI.

Results and Discussion

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. Sediment contained the highest EOCl concentration of 8220 μg/g, organic carbon. Concentration of EOCl observed in sediments was comparable to 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 (10,11). Presence of high concentrations of EOCl in sediments suggests that disposal of wastes from the chlor-alkali process has contributed to the sources of EOCl. Concentrations of known organochlorines such as organochlorine pesticides, PCBs, PCDDs/DFs and PCNs in sediments were 0.058, 375, 0.10 and 19.6 μg/g, dry wt, respectively (5-8). These known organochlorines accounted for about 48% of the EOCl measured in sediments. Thus, approximately 52% of the chlorinated organics present in sediments could not be identified. 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 wt basis (Table 1). The highest

EOCl concentrations were found in the carcass of a red-winged blackbird. EOCl concentrations of between 464 to 1300 μg/g, lipid wt, have been reported for herring gull eggs from Lake Ontario, Canada (3). The concentrations of EOCl found in fish samples were at least

TABLE 1. Concentrations of Organohalogens in Sediment (μg/g, organic carbon) and Tissues of Terrapins, Birds and Fish (μg/g, lipid wt) Collected near a Chlor-alkali Facility

Species	n	Length (cm)	Weight (g)	Tissue	Lipid (%)	EOCl	EOBr	EOI	EOX	Known OCs[c]
Diamond back terrapin	5	18 (16-19)[a]	797 (619-1030)	Liver	10 (7.3-14)	351 (245-507)	16 (4-34)	1.6 (0.91-2.2)	368 (250-521)	14.6
Clapper rail	1	NM	300	Muscle	2.5	560	5.6	ND	566	12.5
Clapper rail	1	NM	300	Liver	4.1	1150	12	ND	1160	11.7
Mottled duck	1	NM	1500	Muscle	1.9	1210	8.9	ND	1220	89.7
BT grackle	1	NM	177	Muscle	3.2	844	6.6	ND	851	104
BT grackle	1	NM	177	Liver	5.7	1140	5.1	ND	1150	NM
RW blackbird	1	NM	55	Carcass	2.6	3080	26	ND	3110	432
Striped mullet	2	25 (24-25)	354 (346-362)	Muscle	1.0 (0.8-1.2)	1360 (1210-1500)	20 (19-21)	24 (10-38)	1400 (1240-1560)	346
Yellow tail	1	18	92	Muscle	2.1	620	14	3.8	637	76
Yellow tail	1	20	113	Whole	3.7	595	8.6	2.7	606	NM
Seatrout	3	34 (31-36)	617 (570-710)	Muscle	1.3 (0.91-1.6)	1170 (800-1380)	15 (12-18)	5 (3.3-8.7)	1180 (827-1390)	59
Bluecrab	2	16 (14-18)[a]	NM	Hepat.	4.8 (2.1-7.4)	1400 (1030-1760)	49 (27-71)	3.2 (3-3.4)	1450 (1060-1840)	410
Atlantic croaker	1	NM	NM	Muscle	0.83	2170	24	7.2	2200	320
Sediment	1				10[b]	8220	ND	ND	8220	3950

[a]Refers to carapace length; NM- Not measured; ND-Not detected; EOX= EOCl+EOBr+EOI; Values in parentheses indicate range.
[b]Organic carbon (%);[c]From references 7 and 8; BT grackle = Boat-tailed grackle; RW blackbird = Red-winged blackbird; Hepat = Hepatopancreas
10-fold greater than those reported for fishes from the Great Lakes and carp from the Buffalo River, New York.

There was no correlation between concentrations of EOCl and EOBr or EOI (Figures 1A and 1B), which indicates that these three classes of organic halogens did not have a common source. The chlor-alkali process has been a major source for EOCl in sediment and biota, whereas naturally occurring brominated- and iodinated-organics appear to be the major sources of EOBr and EOI found in biota. Our results also suggest that the magnitude and accumulation pattern of EOX vary among species collected from the same location, which may be due to the influence of feeding habits.

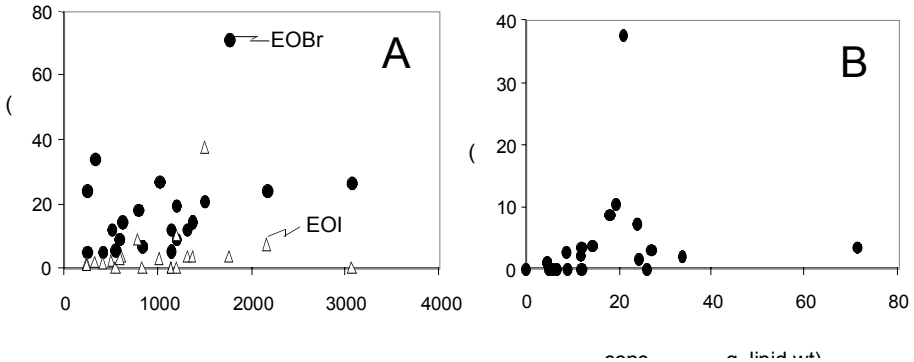

FIGURE 1. Relationship of EOCl to EOBr and EOI (A) and EOBr to EOI (B) in biota collected near a former chlor-alkali facility.

Measured concentrations of known (identified) organochlorines such as PCBs, organochlorine pesticides, PCDDs/DFs and PCNs in sediment, fishes, birds and terrapins were summed (Table 1). 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, suggesting the need for characterizing unidentified EOCl in samples near chlor-alkali facilities.

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