ACCUMULATION OF ORGANOCHLORINE PESTICIDES IN SELECTED FISH SPECIES COLLECTED FROM ST. SIMONS ESTUARY, BRUNSWICK, GEORGIA, USA

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Abstract

Concentrations of legacy organochlorine pesticides (OCPs) were determined in four selected fish species from St. Simons Estuary, Brunswick, Georgia, USA. Southern flounder (*Paralichthys lethostigma*), a large benthic species of flatfish feeding high in the food chain, had the highest concentrations of DDTs, chlordanes, and HCHs, which were 958 (ng/g lipid weight [lw]) at Towers of St. Simons, 1100 (ng/g^{-1} lw) at the Turtle River at Andrew Island and 219 (ng/g lw) at the Turtle River at Buffalo Swamp, respectively. Species specific accumulation was observed and is discussed in this study.

Introduction

Organochlorine pesticides (OCPs), such as DDTs and its metabolites, hexachlorocyclohexane isomers (HCHs), hexachlorobenzene (HCB), chlordane compounds (CHLs), cyclodiene compounds and mirex are classified as persistent organic pollutants (POPs), which are toxic to humans and wildlife[1]. Due to their ubiquitous nature, and peculiar chemical characteristics (e.g., persistence, long half-life, lipophilicity, and toxicity), OCPs ablility to diffused in all environments，including aquatic ecosystems[2-3]. Dichloro-diphenyl-trichloroethane compounds (DDTs) and HCHs were used extensively as an insecticide for agricultural purposes until the early 1970's, with a peak usage in 1959 for in the United States, and it may still be used illegally in developing countries, such as Mexico, India and China[4-6]. Chlordane compounds were used to control termite, grasshoppers, and cotton pests during the 1950s and 1970s. HCB was used as seed dressing fungicide and cyclodienes also been and being used in developed and developing countries. The Environmental Protection Agency (EPA) canceled all uses of chlordane except for subterranean termite control and on non-food plants in 1974[7].

Because of the ecological characteristics (type of diet, distribution in the biotope) and high economic interest, fish are a zoological group which are important for monitoring of aquatic ecosystems[8]. St. Simons Estuary is located in Brunswick, Glynn County, Georgia. Brunswick has a negative record of environmental protection. The brackish water was polluted by PCBs and mercury released by the LCP superfund site and Achlor-alkali plant[9]. There are also seventeen identified hazardous waste sites, six actively polluting industries in Brunswick[10]. According to the latest report from EPA, a Georgia-Pacific Brunswick gypsum plant, Hercules, Inc. and King and Prince Seafood Corp. released 391,806 pounds of organochlorine waste in 2007[11]. Although the Georgia Department of Natural Resources (GDNR) monitors the levels of contaminants in fish in the state[12], there is no report about the pollution condition of OCPs. Earlier studies focused mainly on the pollution of PCBs in fish and sediments[13-14], very limited information is available on the contamination of OCPs in fish[14-15] and pine needle[16]. The objective of the present study is to provide data on OCP concentrations in fish collected from eight sites in St. Simons Estuary, Brunswick, and to enumerate spatial and species-specific differences.

Materials and Methods

Eight different sites (Table 1) in the St. Simons Estuary were chosen, including Mouth of Frederica River, Back River, Mackay River South of Jove Creek, Towers of St. Simons, Lower Jekyll Cove, Turtle River at Andrew Island, Turtle River at Cowpen Creek, and Turtle River at Buffalo Swamp. Four fish species were collected using a single

40' otter trawl during July and October 2008, including southern flounder (*Paralichthys lethostigma*), a large benthic flatfish; weakfish (*Cynoscion regalis*), a pelagic sea trout; southern kingfish (also known as whiting, *Menticirris americanus*), a necto-benthic croaker; and hogchoker (*Trinectes maculatus*), a small benthic flatfish. Individuals of the same species from each site were combined into a composite sample and placed in a zip-lock bag. All fish were stored in a cooler with ice and transported to the laboratory. The samples were transferred to a -20^{o}C freezer and maintained at this temperature until sub-sampled.

All fish were thawed at 4^{o}C for 12 h, and individual fish were measured, weighed and dissected to obtain fillets. In later case fish fillet was cut into small pieces with a stainless steel knife and the entire composite was homogenized with a silver meat grinder. Twenty grams of wet tissue was homogenized with anhydrous sodium sulfate until a fine powder was obtained. This mixture was introduced into a Soxhlet apparatus and extracted with 300mL dichloromethane for 13hrs. All solutions were concentrated by a vacuum rotary evaporator (40^{o}C) to small volumes and transferred to hexane in 14mL polypropylene tubes. An aliquot of the extract (0.5mL) was used for lipid content determination with the gravimetric method. The remaining portion of the extract was concentrated to 5mL, which were cleaned with 5mL concentrated sulfuric acid to remove lipids. The acid layer was discarded and the procedure was repeated until a clear hexane extract was obtained. The hexane extracts were concentrated to about 1ml and then loaded onto an activated (12hrs at 120^{o}C) florisil column. In the first fraction (F_1), HCB, Aldrin, tran-Nonachlor and 4,4'-DDE were eluted with 120mL of hexane. Remaining OCPs were eluted subsequently with 100mL of 20% dichloromethane in hexane (F_2). Both fractions were concentrated using rotary vacuum evaporator to nearly 5mL, and further concentrated to 0.5mL using a gentle stream of nitrogen gas. The extract was transferred to auto sampler vial, and 1μL was injected into the GC-ECD for determination.

Seventeen organochlorine pesticides (α-BHC, β-BHC, γ-BHC, δ-BHC, HCB, heptachlor, aldrin, oxychlordane, heptachlor epoxide, trans-chlordane, cis-chlordane, trans-nonachlor, cis-nonachlor, 4,4'-DDE, 4,4'-DDD, 4,4'-DDT, and mirex) were analyzed in this study. Instrumental analysis was conducted using a Shimadzu GC-17A gas chromatograph with a Shimadzu AOC-17 auto injector. The GC was equipped with a DB-5 capillary column (30m×0.25-mm i.d., 0.25-μm film thickness) and a 63^{Ni} electron capture detector. Carrier gas and make-up gas were nitrogen. Retention time was used to identify the compounds of OCPs. A six calibration points (1, 5, 10, 20, 50 and 100ng/mL) calibration curves were derived from dilutions of certified PCBs and OCPs standards, and used to calculate the sample concentrations. Very good correlations (r^2 = 0.9990 to 0.9999) were achieved during different batch analyses for all the OCP compounds.

Quality control was implemented to insure acceptable levels of analytical accuracy and precision, including blank sample, matrix spikes, and replicate samples. Blank sample were analyzed with every set of six samples. Low levels of HCH isomers, heptachlor, oxychlordane were found in blanks. Results for individual OCPs were blank subtracted using values from each batch. One sample from each site was analyzed three times repeatedly. Matrix spike recoveries for all of these compounds were between 75% and 115%. Limit of detection ranged from 0.06ng/mL to 1.7ng/mL. All glassware was washed with liquid soap and rinsed properly with distilled water and then with pure acetone. All solvents used were pesticide-grade. Concentrations were given on a lipid weight basis, unless specified otherwise.

Results and Discussion

Fish collected at eight different sites (latitude and longitude) are shown in Table 1. Fish with similar size were used in order to reduce the possible effect of age related differences. The lipid percentage of analyzed fish species ranged from 0.45% to 4.96% which is reported in our other study[17].

The chlorinated pesticides analyzed in the present study were banned or restricted in United States almost 4 decades ago. DDTs including 4,4'-DDE, 4,4'-DDD, and 4,4'-DDT were found in all the fish species, except site 6 and site 8

(data is not shown). DDT can be biodegraded to more persistent DDE under aerobic conditions and to DDD under anaerobic conditions. DDD detected in the present study implicates sediment-feeding habit[18].The concentration of DDTs in southern flounder collected at site 4 Towers of St. Simons was the highest, which was 958 (ng/g lw). The concentration of DDTs in fish collected along the Turtle River in our study is consistent with a previous study that found the concentration of DDTs in sea trout to be 414 (ng/g lw) at LCP the superfund site[14].The concentration of chlordanes in southern flounder collected at site 6 Turtle River at Andrew Island was the highest, which was 1100 (ng/g lw). It is much higher than the concentration of chlordanes in sea trout, which was 228(ng/g lw)[14]. It is probably caused by recent use or release of these compounds. The concentration of HCHs in southern flounder collected at site 8 Turtle River at Buffalo Swamp was the highest, which was 219 (ng/g lw). The concentration of HCHs in southern flounder collected at site 6 the Turtle River at Andrew Island was the second highest, which was 167 (ng/g lw). Southern flounder collected at site 6 the Turtle River at Andrew Island also has the highest concentration of mirex and aldrin, which were 431 and 152 (ng/g lw), respectively (data not shown). Southern flounder are benthic (bottom dwelling) and generally rest on the bottom when inactive. They have large mouths with large and feed higher in the food chain Since marsh sediment is the major source of chemical contaminants, such as OCPs and PCBs, and since they feed higher in the food chain, direct contact with contaminated sediment and ingestion of food chain bioaccumulated contaminents may explain why they have the highest concentration of pesticides. Commercial fishing along the Turtle River has been banned[19]. Hogchokers collected at site 6 the Turtle River at Andrew Island had the second highest concentration of chlordane, which was 873 (ng/g lw). This is logical since they are a smaller species and proportionally have smaller, weaker mouths feeding lower on the food chain. Direct contact with contaminated sediments and less bio-magnification potential explains why it accumulated less OCPs than southern flounder. Whiting collected at the Back River (site 2) had the highest concentration of HCB, which was 48 (ng/g lw) (data not shown). Generally, there is no great difference among the eight sites, and benthic species southern flounder collected more OCPs than the other fish species.

Table 1. Details of sampling location.

Site	Name of sample site	Latitude & Longitude
1	Mouth of Frederica River	31.19767, -81.41422
2	Back River	31.15048, -81.44528
3	Mackay River South of Jove Creek	31.21227, -81.42635
4	Towers of St. Simons	31.15591, -81.42096
5	Lower Jekyll Cove	31.10067, -81.43227
6	Turtle River at Andrew Island	31.16875, -81.52657
7	Turtle River at Cowpen Creek	31.20963, -81.60789
8	Turtle River at Buffalo Swamp	31.21728, -81.55719

Table 2. Concentrations of OCPs (ng/g lw) in fish from eight sites.

No	Pesticide	Whiting	Weakfish	Southern flounder	Hog choker
Site 1	DDTs	199	249	199	126
	Chlordanes	536	781	805	484
	HCHs	82	91	73	54
Site 2	DDTs	360	212	NA	420
	Chlordanes	760	472	NA	693
	HCHs	83	44	NA	104

No	Pesticide	Whiting	Weakfish	Southern flounder	Hog choker
	DDTs	548	162	290	NA
Site 3	chlordanes	689	318	619	NA
	HCHs	83	45	117	NA
	DDTs	251	NA	958	165
Site 4	Chlordanes	489	NA	390	286
	HCHs	165	NA	91	73
	DDTs	270	NA	556	127
Site 5	Chlordanes	410	NA	626	108
	HCHs	84	NA	132	27
	DDTs	NA	NA	529	288
Site 6	Chlordanes	NA	NA	1100	873
	HCHs	NA	NA	167	122
	DDTs	NA	129	NA	NA
Site 7	Chlordanes	NA	211	NA	NA
	HCHs	NA	47	NA	NA
	DDTs	288	NA	733	NA
Site 8	Chlordanes	359	NA	739	NA
	HCHs	86	NA	219	NA

NA denotes not analyzed

Acknowledgements

The study was financially supported by United States Department of Energy and Environmental Protection Agency (contract number DE-FG09-96SR18558). The authors are thankful to Jim Page at the Georgia Department of Natural Resources, Captian Jay Rosenzweig and SSU marine science students Trey Mace, Mark Wagner and Devin Dumont for their help in field sampling.

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