ACCUMULATION OF POLYCHLORINED BIPHENYLS IN FISH COLLECTED FROM ST. SIMONS ESTUARY, BRUNSWICK, GEORGIA, USA

Hao L¹, Senthil Kumar K¹, Sajwan K S¹, Li P¹, Peck A², Gilligan M¹, Pride C¹

Department of Natural Sciences and Mathematics, Savannah State University, 3219 College Street, Savannah, GA 31404, USA; Skidaway Institute of Oceanography, #10 Ocean Science Circle, Savannah, GA 31411, USA

Abstract

Contamination profiles of 17 PCB congeners were determined in five fish species collected at eight sites in St. Simons Estuary, Brunswick, Georgia, USA (which is very close to an LCP Superfund Site). Pinfish collected at Turtle River at Buffalo Swamp had the highest PCBs concentration (143 ng/g wet weight [ww]). Whiting and southern flounder collected at Turtle River at Buffalo Swamp also had higher PCBs concentrations (57 ng/g and 73 ng/g ww, respectively) than the same fish species collected at the other sites (the Mouth of Frederica River, Back River, Mackay River South of Jove Creek, Towers of St Simons, Lower Jekyll Cove, Turtle River at Andrew Island, and Turtle River at Cowpen Creek). The current PCBs concentrations of fish in our study were lower than those reported in previous studies.

Introduction

Polychlorinated biphenyls (PCBs) are classified as persistent organic pollutants (POPs), which are toxic to humans and wildlife¹. PCBs are ubiquitous chemicals including in marine ecosystems, and posed potential harm to all kinds of living things²⁻³. St. Simons Estuary is located in Brunswick, Glynn County, Georgia. Brunswick has a poor record of environmental protection due to the negative impact of chemical pollution from Linden Chemicals and Plastics (LCP) Superfund Site. The LCP Superfund Site in Brunswick has been occupied by several industries, including an oil refinery, Georgia electrical power generating facility⁴. During various manufacturing activities, the adjacent brackish water has been severely contaminated with PCBs and mercury in the site sediment, plants in groundwater, and in the biota⁵⁻⁸. The Chlor-alkali plant was established on the site in 1955 and operated until 1994⁸. The company utilized Aroclor 1268, a chlorinated technical PCB mixture to lubricate graphite electrodes used in process equipment. Disposal of process wastes into holding pits near the top of the tidal marshlands and also directly into the adjacent marsh for over three decades has resulted in contamination of soils on-site and also of sediments in the coastal marsh⁶. It was reported that over 37 tons of PCBs have been released in the marsh and other nearby areas by the chlor-alkali plant between 1955 and 1994⁶. The concentration of PCBs in clapper rail (Rallus longirostris) collected at the LCP superfund site was up to 283 mg/g⁶, which is 566 times higher than the Food and Drug Administration (FDA) limit (500 ng/g ww) for PCBs in food items for human consumption⁹. Commercial fishing along the turtle river has already been banned¹⁰. Most of the reported studies focused on the PCBs accumulation in sediment and fish collected around the LCP superfund site, little study has been conducted on the accumulation of PCBs in fish collected in the overall estuary. In the present study, three sites along the Turtle River and five different marsh areas around the St. Simons Estuary were chosen as reference sites and the concentration of PCBs in five fish species were measured in these eight sites in order to compare the spatial differences between sites and species differences in PCBs accumulation.

Materials and Methods

Sampling

Eight different sites in the St. Simons Estuary were chosen, including the 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. Five fish species were collected using a single 40' otter

trawl during July and October 2008, including southern flounder (*Paralichthys lethostigma*), weakfish (*Cynoscion regalis*), southern kingfish (also known as whiting, *Menticirris americanus*), pinfish (*Lagodon rhomboides*) and hogchoker (*Trinectes maculatus*). All fish of the same species from each site were combined into a composite sample and placed in a zip-lock bag. Further fish were stored in a cooler with ice and transported to the laboratory. The samples were transferred to a -20°C freezer and maintained at this temperature until sub-sampled.

Cleanup

Prior to chemical analysis, fish samples were dissected to take fish fillets and freeze-dried. All fish were thawed at 4° C for 12 hours, and individual fish were measured and weighed. Fish fillets were cut into small pieces with a stainless steel knife and the entire composite was homogenized with a silver meat grinder. Fish of the same species and from the same site were combined. 20g of the 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 13 hours. All solutions were concentrated by a vacuum rotary evaporator (40° C) to small volumes and transferred with hexane into tubes. 0.5mL of the extract was used for lipid percentage with the gravimetric method. The extract was concentrated to 5mL, and 5mL concentrated sulfuric acid was added to remove the 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 1 ml and then charged onto a florisil column and PCBs were eluted with 120mL hexane. The fraction was concentrated to 0.5mL using rotary evaporator and a gentle stream of nitrogen gas. The extract was transferred to auto sampler vial, and 1μ L was injected into the GC-ECD for determination. Seventeen PCB congeners (PCB 1, 15, 28, 52, 105, 114, 123, 153, 156, 157, 167, 180, 189, 194, 206, and 209) were analyzed using GC-ECD.

Analysis

Instrumental analysis was conducted using a Shimadzu GC-17A gas chromatograph with a Shimadzu AOC-17 autoinjector. 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 PCB congeners. Six point (1, 5, 10, 20, 50 and 100ng/mL) calibration curves were derived from dilutions of certified PCBs standards, and used to calculate the sample concentrations. Significant correlation (r² = 0.9990 to 0.9999) were achieved during different batch analysis. Quality control was implemented by analyzing a blank sample in every batch of six samples. Low levels of PCB-1, and PCB-15 were found in blanks. Results for individual PCB congeners were blank subtracted using values from each batch. One sample from each site was analyzed three times repeatedly. Matrix spike recovery for all the congeners were between 85% and 128%. Limit of detection ranged from 0.10 to 0.73ng/mL. All glassware was washed with liquid soap and rinsed properly with distilled water and then with analytical grade acetone and hexane. Concentrations were given on a wet weight basis, unless specified otherwise.

Results and Discussion

Details of sampling location, sampling date, species collected, total length, weight and lipid percentage 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 ranged from 0.45% to 4.96%. Average concentrations of PCBs in whiting, weakfish, southern flounder, hogchoker, and pinfish collected from eight sites are presented in Table 2. Whiting collected at Turtle River at Buffalo Swamp had a higher concentration than the same species collected at other sites. Both the LCP superfund site and a chlor-alkali plant were located along the Turtle River and thus the fish from this river contained greater PCBs. Weakfish collected at the Turtle River at Cowpen Creek had a higher concentration of PCBs than the weakfish collected from the other sites. Turtle River at Cowpen Creek is about 300 yards away from LCP superfund site. A power station named Plant McManus, next to the Turtle River at Cowpen Creek is still active. PCBs concentration in southern flounder was higher in Turtle River at Buffalo Swamp followed by Turtle River at Andrew Island, Mackay River South of Jove Creek, Lower Jekyll Cove, Towers of St Simons, and Mouth of Frederica River. Hogchoker collected at the Turtle River at Andrew Island had the highest concentration, which was 82 ng/g ww.

Turtle River at Andrew Island is closely connected with pulp mill, which is a manufacturing facility that converts wood chips or other plant fiber source into a thick fiber board for paper production. PCBs concentration in Pinfish collected at the Turtle River at Buffalo Swamp had higher concentration than the pinfish at Turtle River at Cowpen Creek.

Table 1. Details of the fish samples collected from eight sites in St. Simons Estuary, Brunswick, Georgia, USA.

		nples collected from				nswick, Georgi	
Name of sample site	Collection date	Common name	Latitude & Longitude	Sample number	Total length (cm)	Weight (g)	Lipid (%)
Mouth of Frederica River	07/06/08	Whiting	31.19767, -81.41422	2	21.5-23.2	99.8-131.4	1.78
		Weakfish		4	17.0-25.8	45.1-145.5	0.98
		Southern flounder		2	19.0-26.2	69.5-193.9	0.72
		Hog choker		4	9.2-14.4	14.3-17.2	0.62
Back River	07/06/08	Whiting	31.15048, -81.44528	8	13.5-21.6	48.5-108.2	1.10
		Weakfish		3	14.5-20.4	36.7-79.7	1.76
		Hog choker		10	13.0-15.7	38.6-85.7	0.63
Mackay River South of Jove Creek	07/06/08	Whiting	31.21227, -81.42635	4	17.8-23.5	55.3-134.1	1.18
		Weakfish		27	18.0-25.2	50.4-139	1.74
		Southern flounder		4	15.4-25.5	50.4-174.7	0.95
Towers of St Simons	07/06/08	Whiting	31.15591, -81.42096	4	21.0-23.9	86.1-138.9	1.04
		Southern flounder		2	23.2-25.6	128.7-165	0.64
		Hog choker		16	10.2-16.0	20.4-77.8	1.39
Lower Jekyll Cove	07/06/08	Whiting	31.10067, -81.43227	7	18.2-24.1	58.8-147.4	1.38
		Southern flounder		1	25.4	184	0.68
		Hog choker		5	10.1-12.8	27.8-74.4	2.91
Turtle River at Andrew Island	10/07/08	Southern flounder	31.16875, -81.52657	3	22.6-24.2	129.5-155.7	0.95
		Hog choker		7	9.6-11.3	18.8-25.1	0.84
Turtle River at Cowpen Creek	10/07/08	Weakfish	31.20963, -81.60789	1	25.6	161.9	1.16
		Pinfish		2	15.8-16.9	67.3-80.1	1.52
Turtle River at Buffalo Swamp	10/07/08	Whiting	31.21728, -81.55719	2	23.5-25.4	119.8-130.5	0.81
		Southern flounder		2	20.7-21.8	92-105.6	0.45
		Pinfish		10	12.2-14.1	36-49.9	4.96

Whiting collected at the mouth of Frederica River had a higher concentration of PCBs than the other three species collected at the same site. Weakfish collected at Back River had higher PCB concentration (43 ng/g ww) than whiting (31 ng/g ww) and hogchoker (24 ng/g ww). Weakfish collected at Mackay River South of Jove Creek had higher PCB concentration (41 ng/g ww) than whiting (37 ng/g ww) and southern flounder (27 ng/g ww). Hogchoker

collected at Lower Jekyll Cove had a higher PCB concentration (62 ng/g ww) than whiting (27 ng/g ww) and southern flounder (26 ng/g ww). Pinfish collected at Turtle River at Buffalo Swamp had a higher concentration (143 ng/g ww) than whiting (57 ng/g ww) and southern flounder (73 ng/g ww). The chemical characteristics of PCBs, such as lipophilicity, make PCBs easily accumulated in lipid-rich organs. Whiting collected at the Mouth of Frederica River, weakfish collected at Back River, weakfish collected at Mackay River South, hogchoker collected at Lower Jekyll Cove and pinfish collected at Turtle River at Buffalo Swamp had the highest lipid percentages among the species collected at the same site (1.8%, 1.8%, 1.7%, 2.9%, and 5.0%, respectively). The PCB concentrations in southern flounder and hogchoker collected at Turtle River at Andrew Island were 47 and 82 ng/g ww, respectively. Since the contaminated marsh sediment was the major source of exposure to PCBs along the Turtle River, benthic species such as hogchoker and flounder collected had higher PCBs concentrations^{6, 11}. However, the PCBs concentrations of fish collected at Turtle River at Cowpen Creek in our study were lower than in previous studies. Possible reasons could be the cleanup during the past several decades by USEPA decreased the pollution in the estuary.

Table 2. Average concentrations of total PCBs (ng/g ww) in fish from eight sites in St. Simons Estuary.

No	Site name	Whiting	Weakfish	Southern flounder	Hog choker	Pinfish
Site 1	Mouth of Frederica River	52.9	22.8	16.3	13.5	N/A
Site 2	Back River	30.9	42.9	N/A	23.8	N/A
Site 3	Mackay River South of Jove Creek	37.2	41.3	29.0	N/A	N/A
Site 4	Towers of St Simons	30.5	N/A	22.9	26.5	N/A
Site 5	Lower Jekyll Cove	26.9	N/A	26.3	62.2	N/A
Site 6	Turtle River at Andrew Island	N/A	N/A	46.8	82.3	N/A
Site 7	Turtle River at Cowpen Creek	N/A	45.3	N/A	N/A	43.9
Site 8	Turtle River at Buffalo Swamp	57.1	N/A	73.2	N/A	143.1

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 of the Georgia Department of Natural Resources, Caption Jay Rosenzweig and SSU marine science students Trey Mace, Mark Wagner and Devin Dumont for their help in field sampling.

References

- USEPA. Georgia NPL/NPL Caliber Cleanup Site Summaries: LCP Chemicals Georgia Inc. Report # GAD099303182. 2002a.
- 2. Verwejj F., Booij K., Satumalay K. Molen N.V.D. and Oost R.V.D. 2004. Chemosphere 54:1675.
- 3. Perugini M., Giammarino A., Olivieri V., Nardo W.D. and Amorena M. 2006. J of Food Protection 69:1144.
- 4. USEPA, 1995. Analytical Report- LCP Chemical Site Brunswick, Georgia; Washington DC, 72pp.
- 5. Kannan, K., Maruya, K., Tanabe, S., 1997. Environ Sci Tech 31: 1483.
- 6. Kannan K., Nakata H., Stafford R., Masson G.R., Tanabe S. and Giesy J.P. 1998. Environ Sci Tech 32:1214.
- 7. Senthil Kumar K., Sajwan K.S., Weber-Goeke M.A., Weber-Snapp S., Kelly S., Sanya S.C., Loganathan B.G., 2007. *Organohalogen Compd* 68: 1341.
- 8. Sajwan K.S., Senthil Kumar K., Goeke M.A.W., Gibson C. and Loganathan B.G. 2008. Mar Pollut Bull 56:1353.
- 9. Loganathan B.G., Sajwan K.S., Richardson J.P., Chetty C.S. and Owen D.A. 2001. Mar Pollut Bull 42:246.
- 10. USEPA. Persistent organic pollutants: a global issue, a global response. 2002b. 26 pp.
- 11. Maruya K. and Lee R.F. 1998. Environ Sci Tech 32:1069.