ELEVATED AROCLOR 1268 CONGENERS AND RESIDUES OF POLYBROMINATED DIPHEYL ETHERS IN SEDIMENT FROM A SUPERFUND SITE AT BRUNSWICK, GEORGIA, USA

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Abstract

In 1994, a former chlor-alkali plant located at Brunswick, Georgia, USA disposed a huge amount of Aroclor 1268 in creek/marsh of Atlantic coast, which resulted in PCB contamination of soils, sediment and biota[1-3]. This site has been designated as Superfund site by the United States Environmental Protection Agency (US EPA). The US EPA conducted enormous remediation work and monitoring of toxic contaminants. The objective of this study was to understand the current status of contamination by Aroclor 1268 and polybrominated biphenyls in sediment collected from ten selected sites in the Superfund site. Total Aroclor-1268 concentrations was 4.1-111,000 ng/g dry wt. and PBDEs was less than detection limit to 150 ng/g dry wt. To our knowledge, this is the first report on PBDE concentrations in sediment samples from the Superfund site at Brunswick, Georgia.

Introduction

Linden Chemicals and Plastics (LCP) Superfund site is located at Ross Road in Brunswick (Glynn County), Georgia. The site is bordered by the Purvis Creek, Turtle River and salt marshes to the west, mixed residential and commercial areas to the north, and mixed residential and industrial areas to the east and south. This roughly includes an 80-acre industrialized upland portion, and over 550 acres of salt marsh and tidal creeks. Various industries operated on the site include, an oil refinery, 1919–1935, an electrical power generating facility, 1935–1955, a paint and varnish manufacturer, 1941–1955, and a chlor-alkali chemical manufacturing facility, 1955–1994. The chlor-alkali process continued with modification following the purchase. Part of the modification included the production of hydrochloric acid, by reacting chlorine and hydrogen. Manufacturing operations continued until February 1994, when LCP notified site personnel that it would cease operation due to the revocation of the facility's water and air permits by the Georgia Environmental Protection Division (GA EPD)[4].

Polychlorinated biphenyls (PCBs) became a historic problem in Brunswick GA after the 1994 discharge. LCP released hazardous substances including Aroclor 1268, mercury, polynuclear aromatic hydrocarbons (PAHs), lead, and other phenolic compounds. Natural resources that may have been injured and may continue to be adversely affected include surface water, groundwater, soils, sediments, birds, fish, shellfish, mammals, and other biota. Aroclor 1268 is a highly chlorinated PCB formulation, which was applied to electrical equipment used in the chlor-alkali process at LCP Site[1-3]. Our earlier study showed presence of Aroclor 1268 congeners in street dusts, soil and pine needle collected near the Superfund Site, suggesting the escape of the PCB beyond the restricted area of the site[5-6] soil/sediment[1] and biota[2-3]. Present study was conducted to examine levels of Aroclor 1268 and PBDEs in some selected locations at the Superfund site.

Materials and Methods

Surface sediments (0-5 cm) were collected by Environmental Planning Specialists, Inc. Group in October 2006. Samples were collected with a pre-cleaned stainless steel scoop, homogenized, and immediately placed in I-Chem glass jars and transported to the laboratory in ice, and stored at -20 °C until further analysis. Details of the

sampling locations have been illustrated in Figure 1. Sites-1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 are identified as SDMC-AET-5, SDWC-AET-38, SDME-AET-10, SDMC-AET-1, SDEC-AET-30, SDWC-AET-46, SDMC-AET-20, SDEC-AET-36, SDWC-AET-6 and SDWC-AET-13, respectively.

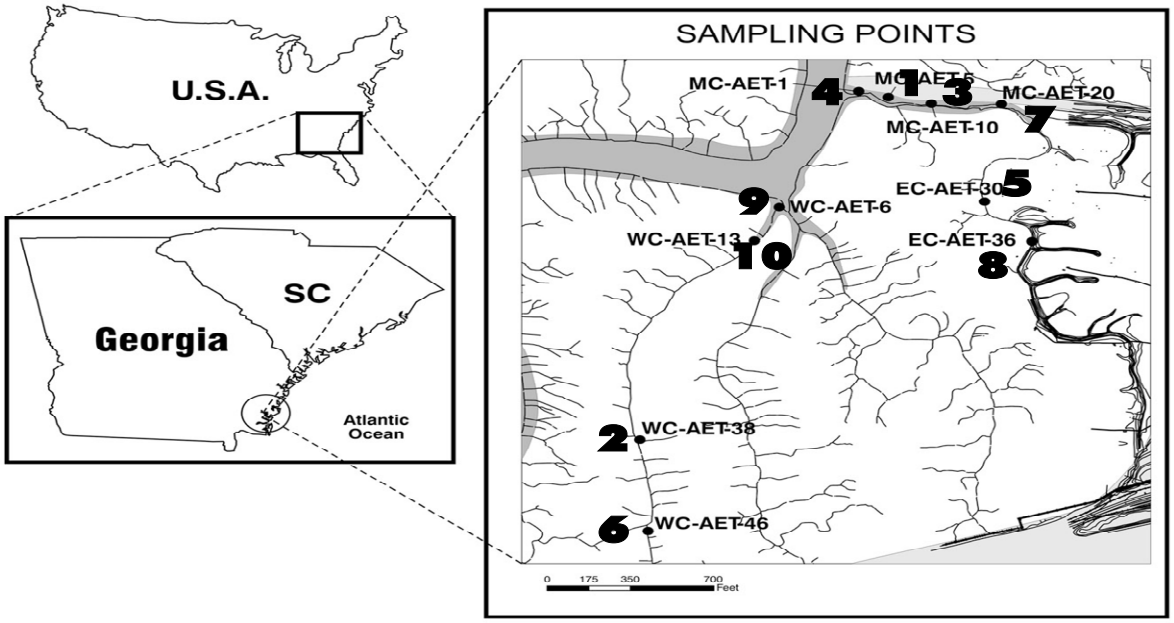

Figure 1. Map showing sampling locations (1-10).

About 5 gram of sediment was Soxhlet extracted for 16 h using 3:1 ratio of methylene chloride and hexane. The sample extract was concentrated using RapidVap apparatus. Silica gel column chromatography was performed for clean-up and separation of PCB congeners and pesticides. Fraction 1 was eluted with 120-mL of hexane (Aroclor 1268), and PBDEs were eluted using 100-mL of 20 methylene chloride in hexane. Concentrated sulfuric acid treatment was done to remove interfering compounds. Freshly activated Cu-treatment was done to remove elemental sulfur. Fractionated extracts were concentrated at 5 mL, and injected in Varian model CP-3380 gas chromatograph (GC) equipped with 63^{Ni} electron capture detector (ECD), and Varian model CP-8410-auto injector. DB-5 capillary column (60 m; 0.25 mm i.d. 0.25 micron film thickness) was used for chromatographic separation of the analytes.

Forty one predominant PCB congeners and eleven predominant PBDE congeners were analyzed. To determine the retention times of the individual PCB, PBDE congeners, pure standards were injected into the GC-ECD. The retention times obtained were used to identify the congeners in the standard mixtures. Five different concentrations of the standard mixtures were injected in order to obtain calibration curves of all the PCB congeners and PBDEs. The mean slope (response factors) and r^2 values were calculated for all the PCBs and PBDE congeners. The PCB and PBDE congeners were identified in the sample, by comparing the retention time from the standard mixture, and quantified using the response factors. Concentrations of Aroclor 1268 and PBDEs were expressed in ng/g dry weight (dw) basis.

Results and Discussion

Concentrations of Aroclor 1268 in sediments from 10 selected sites are shown in Table 1. Due to elevated concentration from site-7, this sample was analyzed twice, and the percent difference was less than 10%.

Concentrations of Aroclor 1268 congeners ranged from were 4.1 to 111,000 ng/g (ppm). PCB-196 2,2',3,3',4,4',5,6'-octachlorobiphenyl was the predominant congener in all of the samples analyzed. PCB-87 2,2',3,4,5'-pentachlorobiphenyl was detected in 2 samples. Six PCB congeners such as 87, 187, 200, 198, 206 and 209 belong to penta-to decachlorobiphenyls were found comparatively lower concentration than PCB-199 (2,2',3,3'4,5,5',6'-octachlorobiphenyl), PCB-196 (2,2',3,3',4,4',5,6'-octachlorobiphenyl), and PCB-208 (2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl) congeners. Kannan et al.[1] Takasuga et al[7] reported congener profiles of Aroclor 1268 which predominated by octa- and nonachlorobiphenyls. Our earlier studies[8-9] with pine needles collected from LCP Superfund site showed higher chlorinated PCBs, however, very recent study[9] showed lower chlorinated PCBs, and this data revealed decline of PCB contamination levels in this area.

Information on the environmental fate of Aroclor 1268 is scarce. Despite its relatively low toxic potential, as suggested from the previous computation of TCDD equivalents, the predominance of higher chlorinated congeners may have different implications as to its ecotoxicity. Whereas the predominant congeners in Aroclor 1268 might be predicted to be (i) less mobile from a physicochemical standpoint (very low aqueous solubilities and vapor pressures) and (ii) highly resistant to biotransformation (high degree of chlorine substitution, including ortho locations), their potential for bioaccumulation by benthic organisms and biomagnifications in the estuarine food web, may be high. Moreover, once taken up, little is known about the chronic effects of these congeners. Isomer-specific examination of Aroclor 1268-contaminated media from our study site may provide baseline information on the pattern of accumulation, in situ biotransformation, and ecological effects of these highly chlorinated congeners. Concentrations of total PCBs in excavation soil, marsh left and right transect sediments, and tidal creek sediments were 567, 481, 276, and 9.6 μg/g dry wt, respectively[1], which is several orders of magnitude grater than this study.

Table 1. Concentrations of (ng/g dry weight) Aroclor 1268 in sediment samples

Site	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-7 duplicate	S-8	S-9	S-10
PCB-87	<0.05	0.39	<0.05	<0.05	<0.05	0.22	1.0	3.3	<0.05	<0.05	<0.05
PCB-187	58	0.26	29	54	7.7	0.05	1100	1200	31	6.3	58
PCB-200	110	<0.05	50	79	12	<0.05	1700	1600	52	10	97
PCB-198	46	<0.05	21	32	5.2	<0.05	680	660	24	4.9	40
PCB-199	2100	3.9	940	1500	220	0.66	16000	15000	990	190	1900
PCB-196	3600	6.9	1600	2600	380	1.7	38000	38000	1600	320	3200
PCB-208	1800	2.4	810	1300	180	0.60	17000	16000	830	160	1600
PCB-207	980	0	450	690	100	<0.05	18000	17000	450	88	850
PCB-194	610	4.4	260	370	86	0.5	12000	11000	200	76	630
PCB-206	880	1.4	370	590	78	0.29	4000	88	370	71	740
PCB-209	20	<0.05	89	140	19	0.06	3100	3000	91	17	170
Total (ng/g)	**10000**	**20**	**4700**	**7400**	**1100**	**4.1**	**111000**	**104000**	**4700**	**940**	**9200**

Concentrations of PBDEs were several orders magnitude lower than PCB congeners (Table 2). Among the ten sediment samples analyzed, PBDE congener concentrations in 4 sediment samples (S-2, S-5 and S-10 were below the detection limit (<0.02). PBDE congener concentrations in other samples ranged from 1.7-150 ng/g dw. To our knowledge, this is the first report on PBDE concentrations in sediment samples from the Superfund site at Brunswick, Georgia. PBDE-47, PBDE-99, PBDE-85 and PBDE-153 were the predominant congeners found in sediment samples and concentrations varied with the sampling location.

Table 2. Concentrations of (ng/g dry weight) PBDEs in sediment samples from LCP Superfund Site.

Site	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	S-9	S-10
PBDE-30	1.2	BDL	0.90	<0.02	BDL	<0.02	<0.02	BDL	<0.02	BDL
PBDE-28	<0.02	BDL	<0.02	<0.02	BDL	<0.02	5.8	BDL	<0.02	BDL
PBDE-47	0.24	BDL	0.69	2.4	BDL	0.49	41	BDL	1.69	BDL
PBDE-66	<0.02	BDL	<0.02	<0.02	BDL	<0.02	<0.02	BDL	<0.02	BDL
PBDE-100	<0.02	BDL	<0.02	<0.02	BDL	<0.02	<0.02	BDL	<0.02	BDL
PBDE-99	2.8	BDL	1.0	1.4	BDL	<0.02	<0.02	BDL	<0.02	BDL
PBDE-85	<0.02	BDL	<0.02	5.0	BDL	1.6	24	BDL	<0.02	BDL
PBDE-154	1.7	BDL	0.32	2.3	BDL	0.88	<0.02	BDL	<0.02	BDL
PBDE-153	10	BDL	<0.02	<0.02	BDL	<0.02	80	BDL	<0.02	BDL
PBDE-138	4.4	BDL	<0.02	<0.02	BDL	<0.02	<0.02	BDL	<0.02	BDL
PBDE183	<0.02	BDL	<0.02	<0.02	BDL	<0.02	<0.02	BDL	<0.02	BDL
Total	**21**	**BDL**	**2.9**	**11**	**BDL**	**3.0**	**150**	**BDL**	**1.7**	**BDL**

BDL=below than detection limit of 0.2 ng/g dry weight

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