ORGANOCHLORINE PESTICIDES, PCBS AND PBDEs IN SELECTED PLANT SPECIES FROM A SUPERFUND SITE AT BRUNSWICK, GEORGIA, USA

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Abstract

Levels of organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) were measured in loblolly pine needle (*Pinus taeda*) collected in and around a Superfund site at Brunswick, Georgia, USA. For the comparison, foliage of eastern red cedar (*Juniperus virginiana*) was also collected to monitor contaminant levels. This study revealed that concentrations of OCPs, PCBs and PBDEs ranged from 0.75-10, 3.4-15 and 0.05-3 respectively, on ng/g wet wt. basis. Temporal variation of total OCPs in pine needle declined from 10 to 2.3 ng/g, and total PCBs decreased from 28 to 9.3 ng/g between 1997-2006. To our knowledge, this is the first report on PBDE concentrations in pine needle samples from the Superfund site at Brunswick, Georgia.

Introduction

Epicuticular wax of pine needle accumulates organic pollutants from the atmosphere**,** and the pine needle have been used for monitoring both local and regional distributions of semi-volatile organic air pollutants[1]. The Linden Chemicals & Plastics (LCP) Superfund Site in Glynn County, Brunswick, Georgia, USA, had a chlor-alkali plant, which was established in 1955 and was operated until 1994, before it was designated as a Superfund Site[2-4]. As a result of multi-industrial operations, the site and the adjacent brackish water have been largely contaminated by organics such as PCBs, polycyclic aromatic hydrocarbons and phenolic compounds[2-4]. Aroclor 1268 is a highly chlorinated PCB formulation which was applied to electrical equipment used in the chlor-alkali process at LCP Site[2-4]. Our earlier study showed presence of Aroclor 1268 congeners in street dust, soil, and pine needle collected near the Superfund Site, suggesting the escape of the PCB beyond the restricted area of the site[5-6]. Present study was conducted to examine levels of OCPs, PCBs and PBDEs in this site based on distance and direction from the major chemical discharge area. To understand possible temporal variation, the contamination levels obtained were compared with the concentrations of the contaminants in pine needles analyzed from this region during 1997.

Materials and Methods

Loblolly pine (*Pinus taeda*) is common coniferous species in Georgia states. One year old pine needle samples were collected from 9 locations in and around LCP Superfund site's in October 2006. Using a telescoping pruner, a tip of a primary branch was cut from an accessible part of the tree. Foliage of 1-year old eastern red cedar (*Juniperus virginiana*) was also collected at 2 locations. The samples were then wrapped in pre-cleaned aluminum foil and transported to the laboratory in a cooler containing ice.

Organochlorine pesticides, PCB congeners and PBDEs in foliage, were analyzed using approved procedures[7,8]. About 25-g of each sample was cut into small pieces then Soxhlet extracted. Internal standards were spiked into sample prior to extraction. Silica-gel column chromatography was then carried out to remove interfering organic and polar species, and to separate the PCBs and PBDEs from the pesticides. First fraction containing

PCBs and some pesticides were eluted using 120 mL hexane. Second fraction containing other pesticides and PBDEs were eluted using 20% dichloromethane in hexane. Fractionated extracts were further subjected to concentrated sulfuric acid cleanup, then micro concentrated prior to injection into the Varian model CP-3380 gas chromatograph (GC), with Varian model CP-8410-auto injector equipped with 63^{Ni} electron capture detector (ECD). The concentration of analytes detected in the reagent blank, was less than the method detection limit. Eight OCPs, forty one predominant PCB congeners, eleven predominant PBDE congeners were analyzed. To determine the retention times of the individual PCB, PBDE congeners and OCPs, pure standards were injected into the GC-ECD. The retention times obtained were used to identify the congeners and pesticides in the standard mixtures. Five different concentrations of the standard mixtures were injected, in order to obtain calibration curves of the target compounds. The mean slope (response factors) and r^2 values were calculated for all the PCB, PBDE congeners, and pesticides. The PCB and PBDE congeners and pesticides were identified in the sample extract by comparing the retention time from the standard mixture, and quantified using the response factors. Concentrations of OCPs, PCBs and PBDEs were expressed on ng/g wet weight (fresh wt.) basis.

Results and Discussion

Total OCP concentrations were 0.75-10 ng/g wet wt. and 4.2-5.0 ng/g wet wt. in pine and red cedar, respectively (Table 1). Maximum concentration of 10 ng/g was recorded at about ½ km (¼ mile) east side of LCP factory, while low levels were recorded at 2 km and 18 km south to the factory and Superfund site, respectively. HCB, DDT, γ-HCH and chlordane residues were detected slightly higher than cyclodienes and mirex. No east-west, north-south and distance gradient variation was noticed when the current average total OCP concentrations compared to pine needles, were, collected from 4 Superfund sites in 1997[6] revealed 70% of reduction of the concentration. Concentrations of OCPs in this study were comparable to Croatia[9], Sweden[10], and Finland[11].

Table 1. Concentrations (ng/g wet wt) of organochlorine pesticides in pine needle and red cedar.

Plant	Pine Needle									Red Cedar	
Distance Direction & (age of tree)	100-Mt E (2 yr)	1/4-Mi E (2 yr)	1/4-Mi N (1 yr)	1/4-Mi N (4 yr)	3/4-Mi W (2 yr)	1-Mi S (1 yr)	3-Mi W (3 yr)	5-Mi S (5 yr)	12-Mi S (4 yr)	3/4-Mi W (1 yr)	1-Mi W (1 yr)
HCB	0.19	0.26	0.11	0.10	0.09	0.07	0.14	0.13	0.14	0.10	1.5
γ-HCH	0.36	0.02	0.02	0.03	0.23	0.03	0.05	0.01	0.17	<0.01	0.23
Aldrin	<0.01	0.05	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Dieldrin	0.03	0.01	0.14	0.07	<0.01	0.06	0.15	0.26	0.01	<0.01	0.26
Cis-chlordane	0.33	0.50	0.22	0.09	0.01	0.02	0.23	0.36	0.23	<0.01	0.36
Trans-nonachlor	0.50	0.43	0.29	0.21	0.29	0.02	0.41	0.38	<0.01	0.15	<0.01
Heptachlor	0.04	0.11	<0.01	0.06	0.16	0.13	<0.01	0.11	<0.01	0.14	0.15
H. Epoxide	0.03	0.05	<0.01	<0.01	0.26	0.11	0.22	0.30	<0.01	<0.01	0.23
MIREX	<0.01	0.02	0.01	0.01	<0.01	<0.01	<0.01	0.04	<0.01	<0.01	<0.01
o,p'-DDE	<0.01	0.95	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
p,p'-DDE	0.02	5.1	0.14	0.02	0.12	0.04	0.14	0.19	<0.01	<0.01	0.78
o,p'-DDD	0.03	0.36	0.37	0.38	0.02	0.26	0.41	<0.01	0.04	1.32	<0.01
p,p'-DDD	<0.01	0.11	<0.01	0.02	0.04	<0.01	<0.01	<0.01	<0.01	2.03	<0.01
o,p'-DDT	0.01	1.1	0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.44	<0.01
p,p'-DDT	0.08	0.94	0.04	0.07	<0.01	<0.01	<0.01	<0.01	0.05	0.86	0.56
Total	**1.6**	**10**	**1.4**	**1.3**	**1.2**	**0.75**	**1.7**	**1.8**	**0.81**	**5.0**	**4.2**

Total PCB concentrations were 3.4-15 ng/g wet wt. and 6.0-17 ng/g wet wt. in pine and red cedar, respectively (Table 2). Maximum concentration of 17 ng/g was recorded in red cedar located 1.6km west side of the chimney, while low levels were recorded a ¼-mile north of the factory. The Atlantic oceans wind would have transported PCBs from an east to west gradient, as Aroclor-1268 was discharged at Purvis Creek in the Atlantic

Table 2. Concentrations (ng/g wet wt) of PCBs in pine needle and red cedar.

Plant	Pine Needle									Red Cedar	
Distance Direction & (age of tree)	100-Mt E (2 yr)	1/4-Mi E (2 yr)	1/4-Mi N (1 yr)	1/4-Mi N (4 yr)	3/4-Mi W (2 yr)	1-Mi S (1 yr)	3-Mi W (3 yr)	5-Mi S (5 yr)	12-Mi S (4 yr)	3/4-Mi W (1 yr)	1-Mi W (1 yr)
PCB-8	0.79	0.30	0.36	0.19	0.31	0.61	0.53	0.29	0.38	0.79	0.75
PCB-18	<0.02	<0.02	0.35	<0.02	0.18	0.39	<0.02	<0.02	<0.02	<0.02	0.34
PCB-28	1.4	0.10	0.67	0.18	<0.02	0.27	0.58	<0.02	0.29	0.11	<0.02
PCB-29	3.0	0.20	<0.02	0.15	0.68	0.51	1.1	0.42	1.8	<0.02	0.44
PCB-44	1.1	0.17	0.51	0.85	0.60	1.2	0.52	0.70	<0.02	<0.02	0.07
PCB-50	1.1	0.44	0.35	0.16	0.25	0.17	0.78	0.36	0.59	0.09	0.16
PCB-52	1.9	0.94	1.0	<0.02	1.2	1.7	1.1	0.96	<0.02	0.91	1.0
PCB-87	0.37	1.5	1.2	0.28	<0.02	0.80	1.5	1.4	<0.02	4.8	1.2
PCB-101	2.4	0.73	1.7	0.53	1.7	0.63	1.8	1.9	1.7	<0.02	1.2
PCB-104	<0.02	1.3	<0.02	0.29	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
PCB-105	0.13	<0.02	<0.02	<0.02	0.08	0.09	0.26	0.08	0.05	<0.02	1.2
PCB-118	0.40	0.24	0.25	<0.02	0.29	0.25	0.49	0.33	<0.02	<0.02	0.52
PCB-128	<0.02	<0.02	<0.02	0.03	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.49
PCB-138	0.64	0.45	0.32	0.17	0.43	0.56	0.42	0.16	0.20	<0.02	1.4
PCB-153	0.49	2.7	0.27	0.24	0.37	37	0.36	0.30	0.47	<0.02	3.8
PCB-154	0.58	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.46	<0.02	<0.02
PCB-170	<0.02	<0.02	0.02	<0.02	0.05	0.08	0.07	0.09	<0.02	<0.02	0.11
PCB-180	<0.02	<0.02	0.03	0.03	<0.02	0.09	0.11	<0.02	<0.02	<0.02	0.23
PCB-187	0.17	0.13	0.12	<0.02	0.09	0.45	0.17	0.11	<0.02	<0.02	1.1
PCB-188	<0.02	<0.02	0.07	0.25	0.14	0.12	0.18	0.05	<0.02	<0.02	1.8
PCB-201	<0.02	0.07	0.12	0.02	0.16	0.40	0.32	<0.02	<0.02	<0.02	0.33
PCB-206	0.19	<0.02	0.16	<0.02	0.63	0.55	0.12	0.07	<0.02	<0.02	1.0
PCB-209	<0.02	<0.02	<0.02	<0.02	<0.02	0.10	<0.02	<0.02	0.06	<0.02	0.20
Total	**15**	**9.2**	**7.6**	**3.4**	**7.1**	**9.3**	**10**	**7.2**	**6.0**	**6.6**	**17**

Ocean. Lower chlorinated PCB congeners were abundant in pine, while one red cedar showed higher chlorinated PCB congeners. This is in contrast to our earlier study in which higher chlorinated PCBs were reported from 1997 pine needle[6]. The Aroclor-1268 mainly contains higher chlorinated PCBs (PCBs-196, 199 and 206) which was used in this site to lubricate graphite electrodes in the process equipment. The presence of congeners PCB-101, PCB-153 and PCB-138 in the LCP Superfund samples, indicate that Aroclor 1254 and Aroclor 1260 were used in the region since these congeners are present in very low amounts in Aroclor 1268. These Aroclors probably arose from transformers and capacitors used. The current average total of OCP concentrations compared to pine needles collected from the 4 Superfund sites in 1997[6] revealed, a 65% reduction in the concentration.

Due to the lower volatility of the highly chlorinated Aroclor 1268 congeners, their relative concentrations are expected to decrease with distance from the LCP Superfund Site. Pine needles collected 12-miles south of the Superfund site, showed a 6.0-ng/g average which is lower than rest of the samples (Table 2). Our earlier study exhibited higher chlorinated PCBs in pine needles collected within 50 feet to 4-miles of the site, while pine from 12-miles away had lower chlorinated PCBs[6]. Two studies conducted on sediment and biota collected at the LCP Superfund Site revealed a characteristic chlorobiphenyl congener pattern, with a greater proportion of hepta- CBs through deca-CBs; characteristics of the source Aroclor-1268[2,3]. Presence of lower chlorinated congeners in this study indicate a decline of PCB concentrations in atmospheric air samples, which will ultimately lead to less deposition of these compounds in this region. The current PCB concentrations were either comparable or lower than the available studies from Croatia[9], Sweden[10], Finland[11], UK[12], Ireland[12], Poland[13], China[14], Australia[15], Korea[16], Spain[17], Japan[13,18-19], Germany[20], Sweden[21] and USA[6].

Table 3. Concentrations (ng/g wet wt) of PBDEs in pine needle and red cedar.

Plant	Pine Needle									Red Cedar	
Distance Direction & (age of tree)	100-Mt E (2 yr)	1/4-Mi E (2 yr)	1/4-Mi N (1 yr)	1/4-Mi N (4 yr)	3/4-Mi W (2 yr)	1-Mi S (1 yr)	3-Mi W (3 yr)	5-Mi S (5 yr)	12-Mi S (4 yr)	3/4-Mi W (1 yr)	1-Mi W (1 yr)
PBDE-30	0.03	<0.01	0.01	0.02	0.02	<0.01	<0.01	<0.01	0.03	<0.01	0.34
PBDE-47	0.03	0.02	0.02	0.02	0.08	<0.01	0.03	0.03	0.05	<0.01	0.18
PBDE-66	<0.01	<0.01	<0.01	<0.01	0.09	<0.01	<0.01	<0.01	0.16	<0.01	<0.01
PBDE-99	0.02	0.03	0.03	0.02	0.11	0.36	0.04	0.06	0.06	1.8	1.7
PBDE-85	<0.01	<0.01	0.02	0.01	0.08	0.07	0.04	<0.01	<0.01	0.71	<0.01
PBDE-154	<0.01	<0.01	<0.01	<0.01	<0.01	0.06	<0.01	<0.01	<0.01	0.55	<0.01
Total	**0.08**	**0.05**	**0.08**	**0.08**	**0.37**	**0.49**	**0.10**	**0.09**	**0.30**	**3.0**	**2.2**

Among 11 PBDE congeners analyzed, only 6 congeners were detected. Total PBDE concentrations were 0.05-0.49 and 2.2-3.0 ng/g wet wt. in pine and red cedar, respectively (Table 3). Maximum concentration of 3.0 ng/g was recorded in red cedar located ¾-mile (1 km) west side of the factory, while low levels were recorded in pine needles collected about 100-meter to the east and north side of the factory. Only PBDE-99 was detected in all samples, while PBDE-47 and 99 were detected in 85% and 65% of samples, respectively. Contamination of PBDEs not from the Aroclor-1268 or 1260 source, may be transported through the atmosphere from the local residential areas. Relatively higher levels of PBDEs in Red Ceder which is generally grown in residential areas, supports our observation. To our knowledge, this is the first report that documents PBDEs in pine needles collected from this Superfund Site. It is apparent that deposition of PBDE in pine needles was minimum when compared to PCBs and OCPs. This may be due to less atmospheric transportability of PBDEs because of their higher molecular weight. The Red cedar's unique leaf is structurally different from that of the pine needles; therefore this species may able to trap more volatile organic compounds than pine needle does. This red cedar could be used as an indicator species for studies dealing with atmospheric semi-volatile organic compounds.

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