

Deposition of Organochlorine Pesticides, PCBs (Aroclor 1268), and PBDEs in Selected Plant Species from a Superfund Site at Brunswick, Georgia, USA

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Abstract Deposition of organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) were measured in Loblolly pine needles (*Pinus taeda*) collected in and around a Linden Chemicals and Plastics (LCP) 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 to 0.05–3, ng/g wet wt, respectively in both plant species. Total OCPs concentrations in pine needles decreased from 10 to 2.3 ng/g; and total PCBs decreased from 28 to 9.3 ng/g between 1997 and 2006. To our knowledge, this is the first report on PBDEs concentrations in pine needles and red cedar foliage samples from the Superfund Site at Brunswick, Georgia, USA.

Keywords Pesticides · PCBs · Aroclor 1268 · PBDEs · Pine needles · Red cedar · LCP Superfund Site · Brunswick

Epicuticular wax of pine needles are known to accumulate organic pollutants from the atmosphere, therefore, pine needles have been used for monitoring both local and

regional distributions of semi-volatile organic air pollutants (Bacci et al. 1990). The Linden Chemicals and 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 (Kannan et al. 1997, 1998a, b). 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 (Kannan et al. 1997, 1998a, b). Aroclor 1268 is a high chlorinated PCB formulation that was applied to electrical equipment used in the chlor-alkali process at the LCP site (Kannan et al. 1997, 1998a, b; Loganathan et al. 2007, 2008; Senthil Kumar et al. 2007). Our earlier studies have shown presence of Aroclor 1268 congeners in street dust, soil, and pine needles collected near the Superfund Site; suggesting the escape of the PCB beyond the restricted area of the site (Loganathan et al. 1997, 2007, 2008). Present study was conducted to examine current levels of organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) contamination and to elucidate temporal variation in concentration of these contaminants using pine needles as a biomonitoring indicator. To understand possible temporal variation, the contamination levels obtained in the present study were compared with pine needles analyzed from this area during 1997.

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Materials and Methods

Loblolly pine (*Pinus taeda*) is common coniferous species in the state of Georgia, USA. One-year-old pine needles were collected from nine sites in and around LCP Superfund Site during 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*) foliage was also collected from two locations. Sampling sites were selected based on the Aroclor 1268 disposal area in side LCP Superfund Site. Nine sampling sites for pine needles were about 100 m east (site-1), ¼ mile east (site-2), ¼ mile north (site-3), ¼ mile north (site-4), ¾ mile west (site-5), 1 mile west (site-6), 3 mile west (site-7), 5 mile south (site-8) and about 12 mile south (site-9). Red cedar foliage was collected from sites 5 and 6. Collected plant samples were wrapped in pre-cleaned aluminum foil and transported to the laboratory in a cooler containing ice.

Organochlorine pesticides, PCBs, and PBDE congeners in the samples were analyzed following the procedures described by Loganathan et al. (2001, 2008). About 20-g of each sample was cut into small pieces then Soxhlet extracted for 16 h using 3:1 ratio of methylene chloride and hexane (325 mL). The sample extract was concentrated using RapidVap apparatus. An internal standard 4,4'-dibromooctafluorobiphenyl (DBOBF) was 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. Recovery of DBOFB in the blank and samples were $100\% \pm 30\%$. Eight OCPs, 41 predominant PCB congeners, 11 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, PBDE congeners and pesticides were identified in the sample by comparing the retention time from the standard mixture, and were 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 and 4.2–5.0 ng/g wet wt in pine and red cedar, respectively (Table 1). Maximum concentration of 10 ng/g OCP was recorded at ¼ mile east (site-2), while low levels of OCP were recorded at 1 mile west and 12 mile south (sites 6 and 9) from

Table 1 Concentrations (ng/g wet wt) of organochlorine pesticides in pine needle and red cedar foilage collected in and around a Superfund Site at Brunswick, GA, USA

Plant	Pine needle									Red cedar	
Sites	Site-1	Site-2	Site-3	Site-4	Site-5	Site-6	Site-7	Site-8	Site-9	Site-5	Site-6
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
Heptachlor 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
<i>o,p'</i> -DDE	<0.01	0.095	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
<i>p,p'</i> -DDE	0.02	5.1	0.14	0.02	0.12	0.04	0.14	0.19	<0.01	<0.01	0.78
<i>o,p'</i> -DDD	0.03	0.36	0.37	0.38	0.02	0.26	0.41	<0.01	0.04	1.32	<0.01
<i>p,p'</i> -DDD	<0.01	0.11	<0.01	0.02	0.04	<0.01	<0.01	<0.01	<0.01	2.03	<0.01
<i>o,p'</i> -DDT	0.01	1.1	0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.44	<0.01
<i>p,p'</i> -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

Aroclor discharge location in LCP Superfund Site. HCB, DDT, γ -HCH and chlordane residues were detected slightly higher than cyclodienes and mirex. No directional or distance gradient variation was observed when the current average total OCP concentrations were compared. The pine needles collected in LCP Superfund Site during 1997 were compared with this study. It is apparent that about 70% reductions in OCP concentration (Loganathan et al. 2008) have occurred from 1997 to 2006. Concentrations of OCPs in this study were also comparable to studies conducted in Croatia (Romanic and Krauthacker 2006), Sweden (Kylin and Sjodin 2003), and Finland (Sinkkonen et al. 1997) where OCP levels were observed to be decreasing over the years. In our study, OCPs were lower than PCBs; however, comparatively higher than PBDEs (Fig. 1).

Total PCB concentrations were 3.4–15 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 mile west side of the factory chimney,

while low levels were recorded at ¼-mile north of the factory chimney. The Aroclor-1268 mainly contains higher chlorinated PCBs (example 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 also indicated that Aroclor 1254 and Aroclor 1260 were used in the LCP Superfund Site since these congeners are present at fairly low amounts in Aroclor 1268. Presence of Aroclor 1254 and 1260 congeners in pine needles probably originated from transformers and capacitors used (Fig. 2) in LCP Superfund Site.

The Atlantic oceans winds would have transported PCBs from an east to west gradient, as Aroclor-1268 was discharged at Purvis Creek in the Atlantic Ocean. Lower chlorinated PCB congeners were abundant in pine, while one red cedar showed higher chlorinated PCB congeners (Fig. 2). This is in contrast to our earlier study where higher chlorinated PCBs were reported from 1997 pine

Fig. 1 Spatial difference in contamination of organochlorines

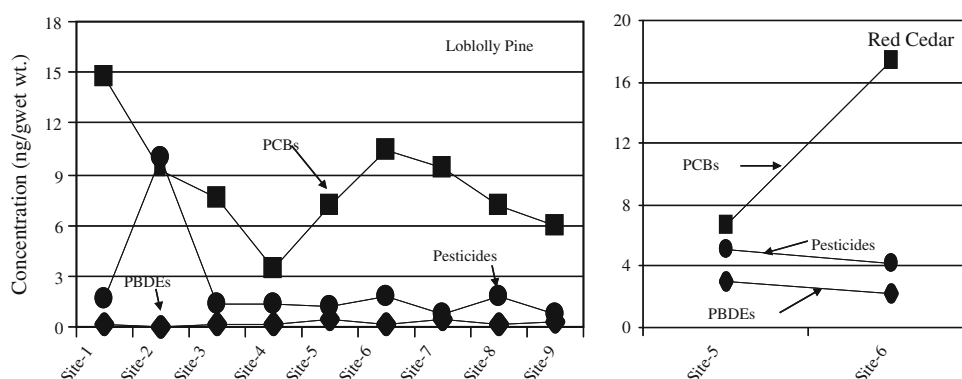
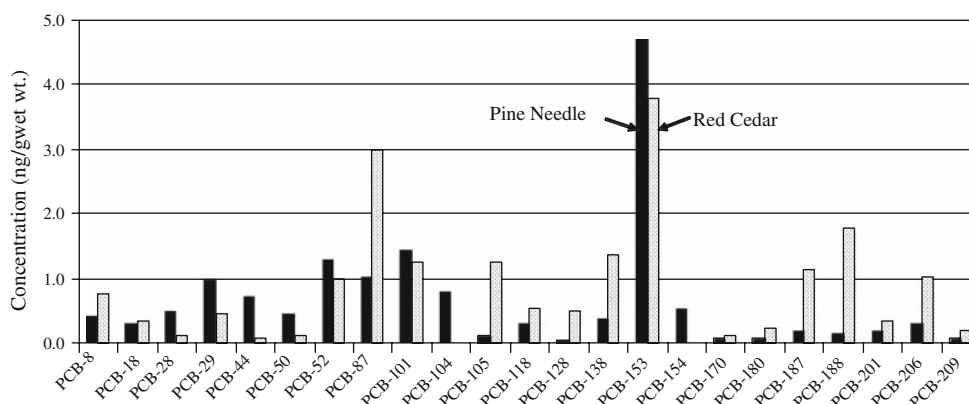


Table 2 Concentration (ng/g wet wt) of total PCBs in pine needle and red cedar

Plant	Pine needle									Red cedar	
Sites	Site-1	Site-2	Site-3	Site-4	Site-5	Site-6	Site-7	Site-8	Site-9	Site-5	Site-6
Total	15	9.2	7.6	3.4	7.1	9.3	10	7.2	6.0	6.6	17

Fig. 2 Congener profile of PCBs in pine needle and red cedar collected from Brunswick Superfund Site, GA



needles (Loganathan et al. 2007, 2008). The current average total of PCBs concentrations compared to pine needles collected from four sites in Superfund Site in 1997 revealed a 65% reduction in the PCBs 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 (Fig. 3). Pine needles collected 12-miles south of the Superfund Site, showed a 6.0-ng/g average which was 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 LCP Superfund Site, while pine needles collected from 12-miles away had lower chlorinated PCBs. Two studies conducted on sediment and biota collected at the LCP Superfund Site revealed a

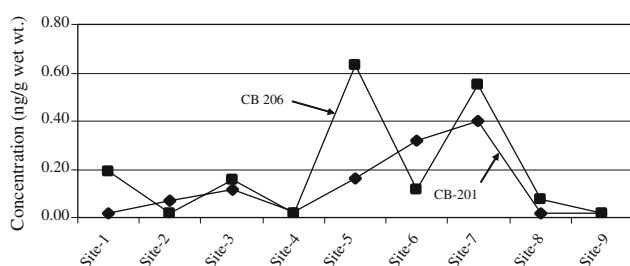


Fig. 3 Decrease of CB-201 and CB-206 with distance from discharge location of Brunswick Superfund Site

Fig. 4 Direction bound movement of PCBs from Aroclor discharge location

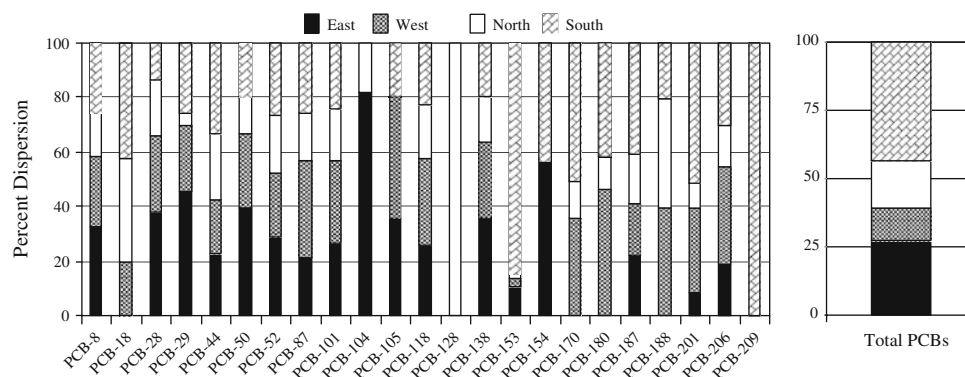


Table 3 Concentrations (ng/g wet wt) of PBDEs in pine needle and red cedar foilage collected from Brunswick Superfund Site

Plant	Pine needle									Red cedar	
Sites	Site-1	Site-2	Site-3	Site-4	Site-5	Site-6	Site-7	Site-8	Site-9	Site-5	Site-6
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

characteristic chlorobiphenyl congener pattern, with a greater proportion of hepta- CBs through deca-CBs; characteristics of the source Aroclor-1268 (Kannan et al. 1998a). Presence of lower chlorinated congeners in this study indicated a decline of PCB concentrations in atmospheric air samples, which would 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 (Romanic and Krauthacker 2006), Sweden (Kylin and Sjodin 2003), Finland (Sinkkonen et al. 1997), UK (Sinkkonen et al. 1997), Ireland (Tremolada et al. 1996), Poland (Wyrzykowska et al. 2006), China (Chen et al. 2006), Australia (Tausz et al. 2005), Korea (Choi et al. 2006), Spain (Grimalt and van Drooge 2006), Japan (Wyrzykowska et al. 2006; Hanari et al. 2004a, b), Germany (Kylin et al. 1994), Sweden (Kylin et al. 1996) and USA (Loganathan et al. 2007). The direction bound deposition of PCBs from the Aroclor 1268 discharge location showed mixed trend (Fig. 4). Higher chlorinated CBs mainly moved south followed by east, west and north (Fig. 4).

Among 11 PBDE congeners analyzed, only six congeners were detected. Total PBDE concentrations were 0.05–0.49 and 2.2–3.0 ng/g wet wt in pine needles and red cedar, respectively (Table 3). Maximum concentration of 3.0 ng/g was recorded in red cedar located 3/4-mile west side, while low levels were recorded in pine needles

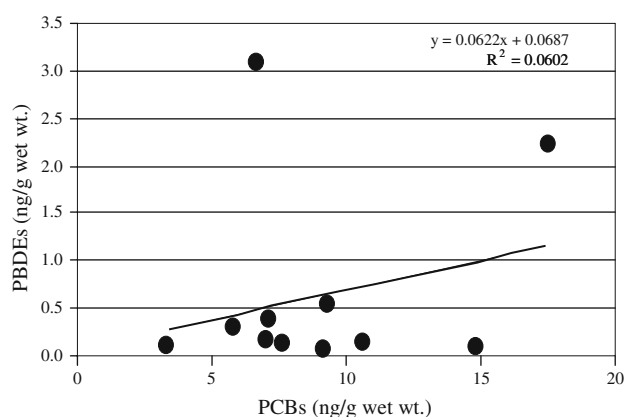


Fig. 5 Correlation of PCBs and PBDEs

collected about 100-m to the east and north. 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 but would have been transported through the atmosphere from the local residential areas. There was no good correlation between PCBs and PBDEs analyzed in this study (Fig. 5). Relatively higher levels of PBDEs in red cedar 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 low 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 be able to trap more volatile organic compounds than pine needles do. The red cedar could be used as an indicator species for studies dealing with atmospheric semi-volatile organic compounds.

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