Chlorinated Hydrocarbons in Pine Needles: An Atmospheric Evaluation of Westernmost Kentucky, U.S.A.

B.G. Loganathan , J. Baust , J. Neale, S. White* and D.A. Owen

MSU Chemical Services Laboratory, Department of Chemistry,
Murray State University, Murray, KY 42071.
*Department of Biology, Murray State University, Murray, KY 42071.

Introduction

Pine needles have been demonstrated as a fixed site, regenerative, annual monitoring matrix for the evaluation of local and regional distribution of lipophillic air pollutants. Organochlorine compounds including polychlorinated biphenyls (PCBs), chlorinated hydrocarbon pesticides are among the most toxic man-made chemicals substances to a variety of animal species including humans. Although most of these compounds are banned or severely restricted production in many developed countries as early as 1970s, they are still considered 'priority pollutants' due to their chronic toxic effects on wildlife and humans [1,2]. In the USA, PCBs are continue to contaminate the environment by volatilization from the sites where they have been used/disposed, stored and incineration of PCB containing materials [3]. Similarly, several of the chlorinated pesticides input into the environment are also persists, due to their long-range atmospheric transport from other countries, where these pesticides are still in use. Westernmost Kentucky (Purchase Area) is endowed with variety of industries and moderate agricultural operations. In 1996, a Public Advisory Committee Report [4] identified diminished air quality due to high levels of release of toxic pollutants by industries in this area. However, very little is known on the atmospheric contamination levels of persistent and toxic organochlorine compounds. Accumulation of lipophillic organic compounds in the plant is attributed to uptake from the atmosphere. Root uptake followed by translocation within the plant is not significant for hydrophobic organic chemicals with octanol-water partitioning coefficient larger than 3 [5]. The present study is aimed at evaluating atmospheric contamination levels of PCB congeners and chlorinated pesticides in the westernmost Kentucky, using pine needles as passive diffusive bio-monitoring indicator. Organochlorine concentrations in pine needles from residential, recreational, industrial and undeveloped sites were used for understanding the regional atmospheric contamination in this area.

Sampling Locations: Pine needle sampling locations in the westernmost Kentucky are shown in Fig. 1. Most common pine species available in this region are Loblolly (*Pinus taeda*), White pine (*Pinus strobus*) and Virginia pine (*Pinus virginiana*). The sampling site # 1 represents city of Murray residential area. The site # 2 and # 3 are in the Land Between the Lakes (the land between Kentucky Lake and Lake Barkley, LBL), a national recreational area.

The sampling sites #4, #5 and #6 are near Calvert City Industrial Complex (CCIC) and its 'downwind' locations. The industries in this complex manufacture various chemicals including polymers, solvents, gases, heavy metals etc. The sampling location # 7 and # 8 are at the vicinity of Tennessee Valley Authority's (TVA) coal power plant located northwest of the city of Paducah, and a paper mill at the city of Wickliffe, respectively. Pine needle sampling were also done at the Columbus- Belmont State Park (site # 9) and near a steam power plant at New Johnsonville, Tennessee (site # 10).

Material and Methods

Since contaminant concentrations in pine needle wax reflect time-integrated air concentrations, we collected one year and two years old needles from the same tree. Age of the needles were determined by growth patterns of needles on a primary branch. The needles were cut using precleaned stainless steel scissors and packed in precleaned aluminum foil. The samples were stored under -20 °C until analysis. The needles were cut in to small pieces (<3 cm). Analytical protocol began with Soxhlet extraction, volume reduction, solvent exchange to hexane, silica gel column chromatography and cleanup with sulfuric acid, followed by quantitation using gas chromatographic separation and electron capture detection (GC-ECD). PCB congeners were analyzed using Shimadzu model GC-17A gas chromatograph (GC) with Shimadzu model AOC-17 autoinjector. The GC was equipped with DB-5 (30m; 0.25mm i.d.; 0.25μ film thickness) capillary column and a ^{63}Ni electron capture detector. The column oven temperature program was 90 °C (1.0 min^{-1}) ...@ 5 °C/ min^{-1} ...150 °C (0 min.) ...@ 2 °C/ min^{-1} ...260 °C (15 min.). Injector and detector temperatures were set at 270 °C and 330 °C respectively. Helium (2 mL/ min^{-1}) and nitrogen (28 mL/ min^{-1}) were used as carrier and makeup gases respectively. PCB calibration standard SRM-2262 obtained from National Institute of Standards and Technology (NIST) was used for quantitations of PCB congeners 8, 18, 29, 50, 28, 52, 104, 44, 66+95, 101+90, 87, 77, 154, 118, 188, 153, 105+132, 138+163+164, 126, 187+182+159, 128, 200, 180, 170+190, 195, 206 and 209 in the samples. Pesticide calibration standard, NIST-SRM-2261 was used for quantitations of pesticides. Quality control analysis included: reagent blank (<method detection limit), surrogate standard, 4,4'-dibromooctafluorobiphenyl spike recovery (100 ± 30% of known standard added prior to extraction), matrix spike recovery (100 ± 40% for all analytes of interest).

Results and Discussion

Total PCB (sum of the congeners quantitated) in the pine needles were in the range of 3 to 18 ng g^{-1} fresh wt. (Fig. 1, Table 1). Comparison of total PCB concentrations between the two year old needles of Virginia pine (*P. virginiana*) and loblolly (*P. taeda*) from the Land between the Lakes(site #3) revealed very little or no difference. Among the various sampling sites, needles from the vicinity of the CCIC and sites 'downwind' from CCIC showed relatively higher concentration (>15 ng g^{-1} fresh wt.) of total PCBs indicating a potential for atmospheric contamination from this area. Interestingly, the samples collected near Tennessee Valley Authority (TVA) (site #7) and New Johnsonville, Tennessee Power Plant area (site # 10) showed total PCB concentrations: < 5 ng g^{-1} fresh wt. which are in the similar range found in the needles from the reference sites (site # 1,2 and 9). The latter included needles taken from sites in the LBL, Columbus-Belmont State Park and Murray residential

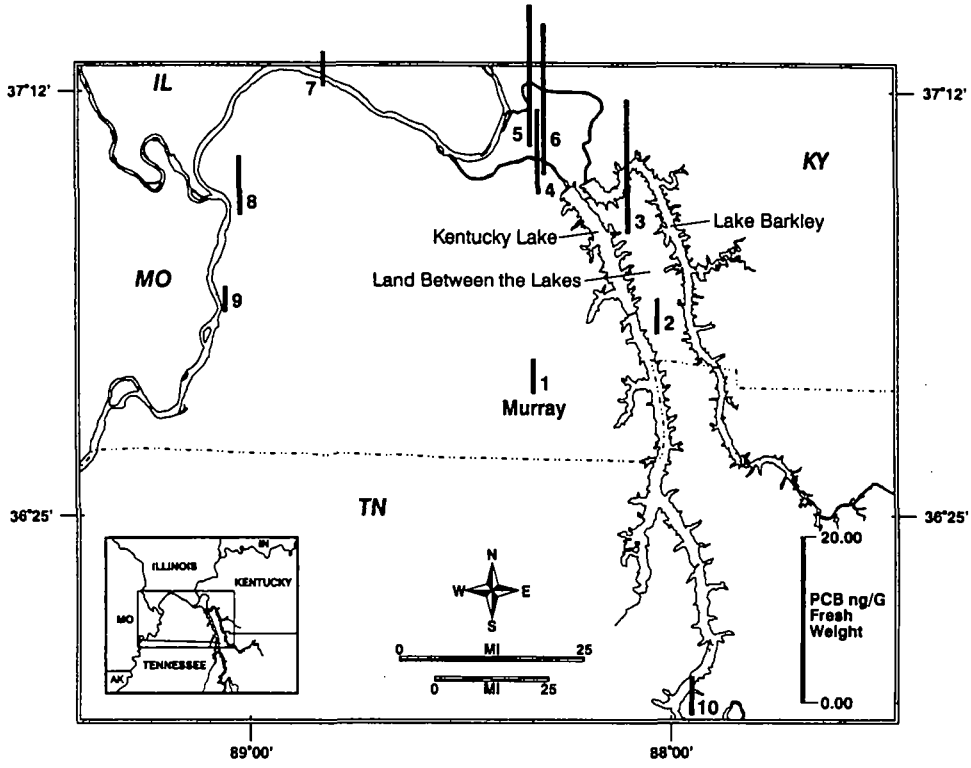

Fig. 1. Map showing pine needle sampling locations in the westernmost Kentucky and total PCB concentrations (solid bars) in pine needles collected at various sites. Details of the sites are given in Table 1.

Table 1. Details of sampling locations and samples.
PCB concentrations (ng g^{-1} fresh wt)

Site #	Date	Sampling Location	Species /Age	total PCBs*
1	3/21/97	Murray Residential	*P. strobus*/1	4.13
2	2/27/97	LBL Wrangler Camp Ground/Colson OL	*P. virginiana*/1	4.32
2	2/27/97	LBL Wrangler Camp Ground/Colson OL	*P.virginiana*/2	6.80
2	2/27/97	LBL Wrangler Camp Ground/Colson OL	*P.taeda*/2	6.83
3	2/27/97	LBL Old Ferry Road	*P. virginiana*/1	16.35
3	2/27/97	LBL Old Ferry Road	*P.taeda*/1	15.11
4	2/27/97	Hwy 62/1523 near Calvert City	*P.taeda*/1	9.67
5	3/21/97	Hwy 937 off of Hwy 453	*P.taeda*/1	16.85
6	3/21/97	1.2 Km from CCIC	*P.taeda*/1	18.05
7	5/15/97	near TVA Shawnee Power Plant	*P. strobus*/1	3.79
8	5/15/97	Wickliffe- near Westvaco Paper Mills	*P.taeda*/1	8.00
8	5/15/97	Wickliffe- near Westvaco Paper Mills	*P. strobus*/1	6.02
9	5/15/97	Columbus-Belmont State Park	*P. strobus*/1	3.25
10	8/1/97	Near New Johnsonville St. Power Plant	*P.taeda*/1	4.63

*: Sum of 35 PCB congeners quantitated.

area. Near background concentrations of PCBs in pine needles collected at TVA and New Johnsonville power plant area indicated the absence of any PCB sources (old electrical transformers). PCB Congener composition of pine needles revealed that the needles were exposed to both lower chlorinated and higher chlorinated PCBs. In general, lower chlorinated congeners. PCB-18 (2,2',5-T_3CB), PCB-28 (2,4,4'- T_3CB), PCB-52 (2,2',5,5'- T_4CB) and PCB-44 (2,2',3,5'- T_4CB) were more frequently encountered, and at comparatively greater concentrations than higher chlorinated congeners. Among the higher chlorinated congeners, PCB-101 (2,2',4,5,5'-P_5CB), PCB-87 (2,2',3,4,5'- P_5CB), PCB-118 (2,3'4,4',5- P_5CB) and PCB-153 (2,2',4,4',5,5'- H_6CB) were commonly detected. Hepta-, octa-, nona and decachlorobiphenyls were found below the detection limit or barely detectable. In contrast to the PCB levels, the chlorinated pesticide concentrations were low and several analytes were not detectable or close to the detection limits. Among the pesticides detected, hexachlorobenzene (HCB), lindane, 4,4'-DDE, trans-Nonachlor and cis-Chlordane were most frequently encountered in several samples. As observed for PCBs, HCB concentration was comparatively greater (5.66, 8.47 and 9.25 ng g^{-1} fresh wt.) at site #s 3, 5 and 6 respectively suggesting contributions from the industrial emissions [6].

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