SPATIAL AND TEMPORAL TRENDS OF ORGANOHALOGEN POLLUTANTS IN PINE NEEDLES FROM WESTERN KENTUCKY, USA

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Introduction

Organohalogen compounds such as polychlorinated biphenyls (PCBs), polybrominated biphenyl ethers (PBDEs) and chlorinated pesticides are well known environmental pollutants[1-3]. Several studies have demonstrated that environmental exposure to these compounds lead to adverse health effects including hepatotoxicity, neurotoxicity, immunotoxicity, teratogenecity, endocrine disruption and carcinogenicity in aquatic and terrestrial animals including humans[4-10]. Although, most organochlorine compounds were banned/severely restricted production and use in the United States, due to its recalcitrant properties, organochlorines that are stockpiled and/or in contaminated sites continue to contaminate the environment and contribute to negative health effects[1,2,7,8]. Earlier studies have shown that contamination of these pollutants in environmental (air, water, sediment) and biological (fish, fresh water mussels) samples from Western Kentucky[11,13]. However, a spatial and temporal trend of organohalogen contamination of this region has not been adequately addressed. Since organohalogen compounds are persistent, bioaccumulative and toxic, understanding the contamination levels and long-term trends of these pollutants are essential in order to prevent further contamination, human exposure and harmful effects. The present study was conducted to describe spatial and temporal variation in organochlorine contamination levels in urban, undeveloped, industrial regions of Western Kentucky (Fig. 1) using pine needles as passive biomonitoring indicator.

Accumulation of organic compounds in the plant species is attributed to uptake from the atmosphere[14]. Root uptake followed by translocation within the plant is not significant for hydrophobic organohalogens with octanol-water partition coefficient >3. For long-term trend analysis, PCBs and chlorinated pesticide concentrations in pine needles were compared with literature data in pine needles collected from the same locations over ten years ago[11-13].

Materials and Methods

Sampling Locations, Samples and Sample Preparations

One year old pine needles samples (*Pinus taeda*,and *P.strobus*) were collected from urban, undeveloped and industrial regions of Western Kentucky (Fig. 1). Industrial sites included Paducah Gaseous Diffusion Plant and West Waco Paper Mill, undeveloped sites were Land Between the Lakes, Highway 937, Old Ferrie Road and Trace Intersection, and urban sampling sites were Murray City Park and Belmont State Park. The age of the pine needles was determined by their growth patterns on the primary branch. The needles were cut, packed in aluminum foil and stored at -20^{o}C until analysis. Standard analytical procedures were followed for analysis of organohalogens using GC-ECD[11-13]. Briefly, about 20g of pine needles were Soxhlet extracted for 17 h using 3:1 ratio of methylene chloride and hexane. The extract was K-D concentrated and concentrated sulfuric acid treatment was performed to remove interfering organic materials. Then the sample extracts were subjected to silica gel column chromatography to separate PCBs from chlorinated pesticides. Fraction 1 eluted with hexane contained all PCB congeners, hexachlorobenzene (HCB), 4,4'-DDE, trans-Nonachlor. Fraction 2 eluted with 20% methylene chloride in hexane contained all chlorinated pesticides. PCB congeners and chlorinated pesticides were analyzed using a gas chromatograph equipped with DB-5 capillary column and ^{63}Ni electron capture detector. PCB calibration standard SRM-2262 purchased from National Institutes of Standards and Technology (NIST) was used for GC calibration and quantitation of PCB congeners (representative congeners ranging from monochloro-decachlorobiphenyls). Pesticide calibration standard NIST-SRM 2261 was used for instrument calibration and quantitations of pesticides in the samples. Quality control analysis included: reagent blank(<MDL), surrogate standard, 4,4'-dibromooctafluorobiphenyl spike recovery (100±30% of known concentration standard added prior to extraction) and matrix spike recovery (100±40% for analytes of interest). Data were analyzed using repeated measures analysis (proc GLM, SAS ver 9.2). Two sites without matching samples from 1997 (sites 6 and 7) were not included in the analysis and undeveloped and residential sites were placed into a single group compared to the industrial sites.

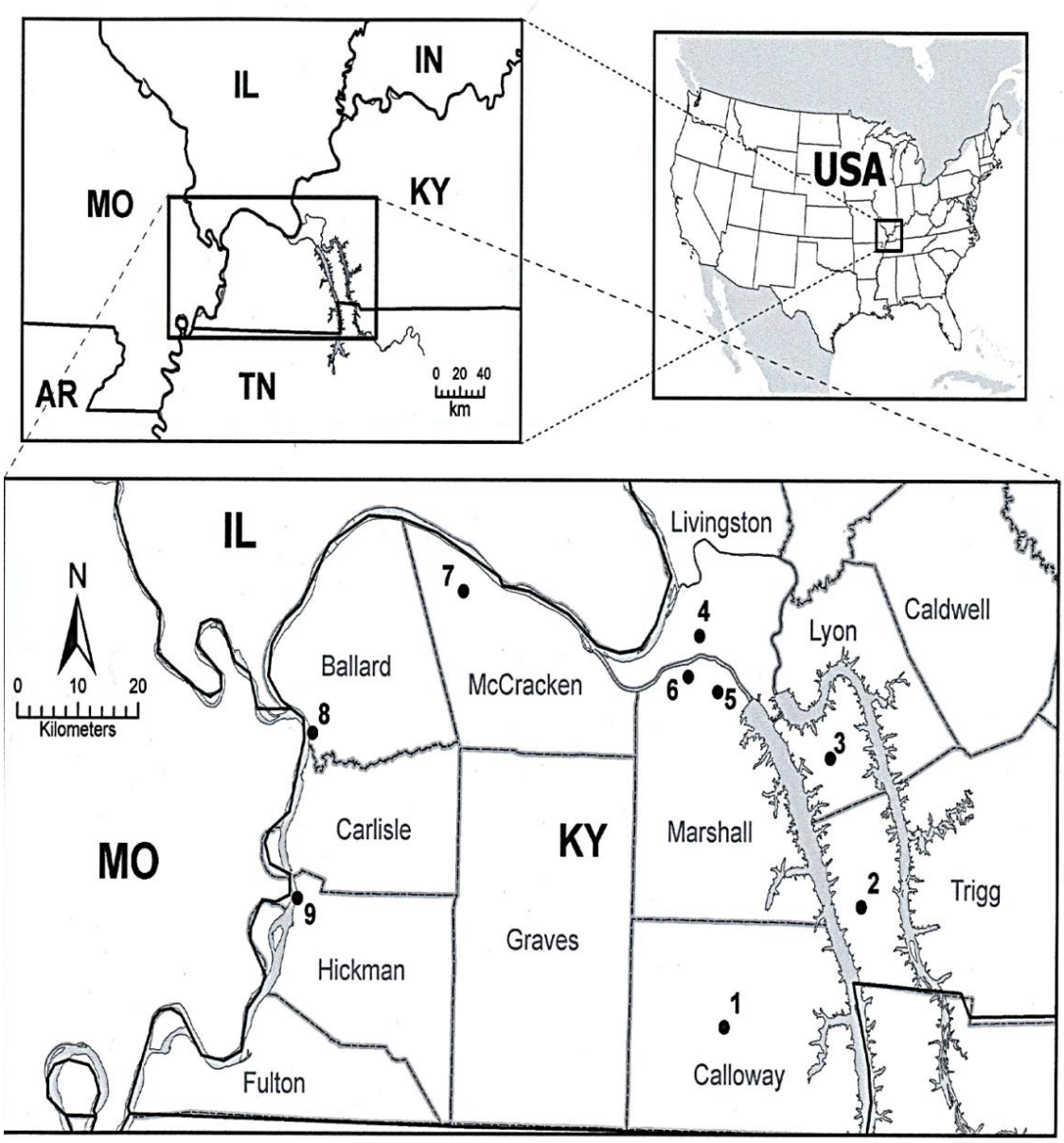

Figure 1. Map showing pine needle sampling locations in western Kentucky. Pine needles were collected from site numbers 1 through 9. Details of the sites: #1 and # 9 are adjacent to residential areas, #2 and #3 are undeveloped, #4 downwind location of Calvert City Industries, #5, #6, #7 and #8 are adjacent to industries.

Results and Discussion

Table 1 shows total PCB concentrations in pine needles collected from various locations in western Kentucky during 1997 and 2011. Total PCB concentrations data for pine needle samples collected during 1997 were obtained from the literature[11]. The same sampling locations, pine species and age of needles were chosen to collect pine needles in 2011[11]. In the 1997 pine needle samples, total PCBs ranged from 3.25 to 18.05 ng/g wet wt., whereas pine needles collected in the year 2011 contained total PCBs ranged from 0.44 to 7.18 ng/g wet wt. Variations in total PCB concentrations in pine needles indicate different levels of exposure of PCBs in residential and undeveloped compared industrial locations (Table 1). In general, downwind locations of industrial site (site #4) and industrial sites (sites #5 through #8) revealed comparatively higher total PCB concentrations than urban or undeveloped sites (sites 1, 2 and 9). Total PCB concentrations in pine needles collected in the year 2011 revealed approximately an order of magnitude lower than the total PCB concentrations in pine needles collected in 1997. Comparison of total PCB concentrations in pine needles from 1997 and 2011 revealed a clear declining trend, indicating effectiveness of regulations imposed on the production and use of PCBs. Detectable levels of HCB, lindane, 4,4'-DDE, trans-Nonachlor and cis-Chlordane

were found in pine needles collected during 1977[11]. Due to low concentrations of the pesticides, site to site differences were not discernible in those samples except HCB. HCB showed comparatively higher concentrations (5.66, 8.47 and 9.25 ng/g) at sites viz. downwind location of Calvert City and Calvert City Industrial sites respectively suggesting contributions from the industrial emissions[11]. In contrast, chlorinated pesticide concentrations were very low or barely detected in the pine needles collected in 2011.

Table 1. Comparison of total PCB concentrations in pine needle samples collected during 1997(Reference #11) and 2011. Site type indicates whether sites are adjacent to residential areas (R), undeveloped (U), or are adjacent to or downwind of Industrial sites(I).

Site Number	Site Type	Location	Species/Age(yr)	ΣPCBs ng/g wet wt.	
				Year 1997[11]	Year 2011
1	R	Calloway County Park	*P. strobus*/1	4.13	1.9
2	U	LBL Wrangler Camp	*P. taeda*/2	6.83*	6.13
3	U	LBL Old Ferry Road	*P. taeda*/1	15.11	7.18
4	I	Hwy 937off of Hwy 453	*P. taeda*/1	16.85	0.44
5	I	Calvert City	*P. taeda*/1	18.05	2.26
6	I	Calvert City Industrial Way	*P. taeda*/1	N/A	7.8
7	I	Near PGDP	*P. taeda*/1	N/A	4.91
8	I	Near Westvaco Paper Mill	*P. taeda*/1	8.00	0.9
9	R	Belmont State Park	*P. strobus*/1 and *P. taeda*/1	3.25	4.03**

LBL: Land between-the-Lakes; PGDP; Paducah Gaseous Diffusion Plant. N/A: Sample not available. *: ΣPCB in 2-yr old pine needles, and ** ΣPCB concentration from *P. taeda.*

Although there exists no significant difference overall in concentration of PCBs with respect to industrial versus non-industrial sites (P=0.549), the results did reveal a significant decline from 1997-2011 in PCB concentrations in the industrial sites compared to non-industrial sites (P=0.026) (Table 1). The present study provides evidence that pine needles are useful not only in evaluating atmospheric contamination of lipophilic organic contaminants, source identification, but also to trace the temporal trends of persistent organic pollutants[14]. Decreasing trends of total PCBs in pine needles indicate improving air quality with respect to PCB levels during the last decade and reduced exposure of PCBs to plants, animals and humans in the western Kentucky region. Further studies with additional sampling are warranted to confirm the decline in PCBs at industrial locations and to understand the spatial variation in PCB concentrations.

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