

BIOMONITORING THE SPATIAL VARIATIONS OF PCBs AND PBDEs IN AN INDUSTRIAL REGION

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Introduction

Persistent organic pollutants (POPs) are among the most widespread organic contaminants and their atmospheric concentrations have to be monitored closely due to their adverse effects on organisms. Monitoring POPs at several sites to determine their spatial variations has technical, physical and economical limitations when active air samplers are used. Biomonitoring the POPs via tree leaves, needles, and bark for routine spatial and temporal monitoring has been used as a low-cost alternative method^{1,2}.

A recent study showed that several industrial activities in Iskenderun region in Turkey are important local sources of several POPs and trace elements³. The main objective of this study was to investigate the spatial variation of air pollution in this region by measuring polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) sorbed in tree components. Ambient air samples by passive sampling, leaf litter, and soil samples were also collected at the sampling sites to investigate the relationships between the soil, tree components and ambient air in the area.

Materials and methods

Study area. The field studies were conducted in the forested areas of Iskenderun industrial region. The study area contain several pollutant sources: Scrap processing iron-steel plants with electric arc furnaces (EAFs), scrap storage and classification sites, steel rolling mills, heavy road traffic and busy ports, a large integrated steel plant (with a sintering plant, coke ovens, blast furnaces, a lime plant, and rolling mills), and a cement plant. Twenty seven sampling sites were selected in the study area to represent locations affected by industrial emissions and the background locations.

Sample collection. Ambient air samples were collected using polyurethane foam (PUF) disk passive air samplers (PAS). Before sampling, deuration compounds (DCs) (¹³C-PCB 3, ¹³C-PCB 9, ¹³C-PCB 15, PCB 30, PCB 107, and PCB 198, 17.5–20 ng per sample) dissolved in 10 mL hexane were spiked evenly onto PUF disks. Ambient air samples were collected during November, 2010-February, 2011 at 27 different sites. The soil samples were collected manually at 0–5 cm depth from the surface. The samples were sealed with an aluminum foil and stored at 4°C. Tree components (1 and 2-year pine needles, bark, branch, and trunk), leaf litter and soil samples were collected from all sampling sites during November, 2010. Collected samples were brought to the laboratory in their pre-cleaned containers (tightly closed glass jars and vials) and stored at 4°C until analysis.

Sample preparation and analysis. Prior to extraction, all samples were spiked with PCB and PBDE surrogate standards (PCB 14, 65, 166, PBDE 77, and ¹³C-PBDE 209). Ambient air PUFs were Soxhlet extracted for 12 hours with a mixture of 1:1 acetone:hexane. Five grams of soil samples were soaked in 40 mL of 1:1 acetone:hexane mixture overnight. Ten grams of tree component samples were soaked in 100 mL of 1:1 acetone:hexane mixture overnight. Then, they were ultrasonically extracted for 30 min. The extract volumes were reduced and were transferred into hexane using a rotary evaporator and a high purity N₂ stream. After concentrating to 2 mL, tree component samples were cleaned up using gel permeation chromatography. Then, soil, air and tree samples were cleaned up and fractionated on an alumina-silicic acid column. All samples were analyzed for 41 PCBs (18, 17, 31, 28, 33, 52, 49, 44, 74, 70, 95, 101, 99, 87, 110, 82, 151, 149, 118, 153, 132, 105, 138, 158, 187, 183, 128, 177, 171, 156, 180, 191, 169, 170, 199, 208, 195, 194, 205, 206, 209) and 7 PBDEs (28, 47, 100, 99, 154, 153, 209) with an Agilent 6890N gas chromatograph (GC) equipped with a mass selective detector (Agilent 5973 inert MSD). PCBs were analyzed using electron impact ionization (EI) while negative chemical ionization (NCI) mode was used for PBDEs. Compounds were identified based on their

retention times, target and qualifier ions, and were quantified using the internal standard calibration procedure. Further details for sample preparation and instrumental analysis could be found elsewhere^{4,5}.

Results and discussion

Σ_{41} PCB and Σ_7 PBDE concentrations measured in ambient air, soil, litter, and tree component samples are summarized in Table 1. Soil, litter, and tree component concentrations were reported on dry weight basis.

The average concentrations of Σ_{41} PCBs in ambient air ranged from 0.49 to 3.72 ng/m³ (average \pm SD, 1.6 \pm 0.9 ng/m³) while Σ_7 PBDEs ranged between 15 and 684 pg/m³ (average \pm SD, 181 \pm 196 pg/m³) in industrial/residential sites. The lowest concentrations in ambient air were found in background sites without specific local sources (0.18 \pm 0.14 ng/m³ for PCBs and 19 \pm 15.5 pg/m³ for PBDEs). Concentrations in 2-year needles were 2.4 and 17 times higher than 1-year needles for PCBs and PBDEs, respectively, as a result of longer exposure to polluted air. PCB and PBDE concentrations measured in tree components, soil, litter and ambient air samples were compared in Table 1. Among tree components, the highest PCB concentrations were measured in 2-year needles while highest concentrations for PBDEs were measured in the trunk samples.

Table 1. Summary of PCB and PBDE concentrations in the study area (air concentrations in ng/m³ for PCBs, pg/m³ for PBDEs, and all other concentrations in μ g/kg)

	Industrial		Background		Industrial		Background	
	AVG	SD	AVG	SD	AVG	SD	AVG	SD
	Σ PCBs				Σ PBDEs			
Air	1.6	0.9	0.18	0.14	181.0	195.9	19.2	15.5
Soil	26.6	61.6	0.90	0.56	9.7	13.0	0.8	0.6
Litter	54.4	37.8	4.7	4.7	16.0	18.8	2.4	2.3
Bark	8.6	14.2	1.3	0.69	5.0	8.0	1.1	0.6
1-Year	16.8	10.5	2.5	1.6	4.5	2.0	1.7	1.2
2-Year	41.0	25.6	4.3	4.2	7.6	4.3	2.0	0.8
Branch	3.3	1.9	1.2	0.57	2.5	1.3	1.4	0.3
Trunk	6.4	4.8	2.9	2.22	16.3	9.3	7.7	7.4

Ambient air PCB profile was dominated by low molecular weight compounds while PBDE profile was dominated by PBDE-209. Compound profiles were similar for ambient air and needle samples. However, medium to high molecular weight compounds dominated the PCB profiles in soil. No significant difference was observed for PBDE profiles, PBDE 209 being the dominating compound in all sample types.

Spatial variations of Σ_{41} PCBs and Σ_7 PBDEs in the study area are illustrated in Figures 1 and 2, using the measured concentrations in ambient air and in 2-year pine needles as examples. PCB and PBDE concentrations for air, soil and tree components decreased with distance from the major sources. Generally, substantially higher concentrations were measured near industrial sites and the lowest ones in background sites (see also Table 1). Spatial variations of the PCB and PBDE concentrations indicated that iron–steel plants were the major PCB emitters in the study area.

The relationship between PCBs and PBDEs measured in different samples were investigated by constructing correlation matrixes (Table 2). Statistically significant correlations ($p < 0.01$) were observed between PCBs and PBDEs in ambient air and tree components, soil and leaf litter. Statistically significant relationships between PCBs and PBDEs in ambient air and plant components, soil and leaf litter suggested that tree components could be used for biomonitoring and to assess the spatial variation of air pollution in a region.

PCB and PBDE amounts stored in different tree components and in environmental compartments were also inventoried. POP amounts per unit area (mg/ha) were calculated using the measured concentrations in tree components (mg/kg), litter and soil, and the amounts of these components per unit area (kg/ha). For tree components, generally, the highest amounts were stored in the trunk followed by needles or bark (Figure 3). For the overall inventory, the highest amounts were stored in soil followed by trees in the industrial area. Contribution of trees was substantially higher in the background area.

Table 2. Correlations between the measured PCB and PBDE concentrations (significant correlation coefficients in bold, $p < 0.01$)

PCBs	Air	Soil	Bark	Litter	1-Year needle	2-Year needle	Branch	Trunk
Air	1.00							
Soil	0.73	1.00						
Bark	0.67	0.94	1.00					
Litter	0.85	0.89	0.81	1.00				
1-Year needle	0.86	0.73	0.72	0.85	1.00			
2-Year needle	0.76	0.66	0.52	0.76	0.78	1.00		
Branch	0.52	0.71	0.66	0.61	0.50	0.54	1.00	
Trunk	0.62	0.44	0.14	0.54	0.45	0.70	0.31	1.00
PBDEs	Air	Soil	Bark	Litter	1-Year needle	2-Year needle	Branch	Trunk
Air	1.00							
Soil	0.66	1.00						
Bark	0.71	0.89	1.00					
Litter	0.78	0.76	0.76	1.00				
1-Year needle	0.63	0.64	0.59	0.68	1.00			
2-Year needle	0.52	0.58	0.64	0.62	0.67	1.00		
Branch	0.34	0.35	0.30	0.40	0.39	0.45	1.00	
Trunk	0.00	-0.12	-0.07	-0.05	0.29	0.09	0.03	1.00

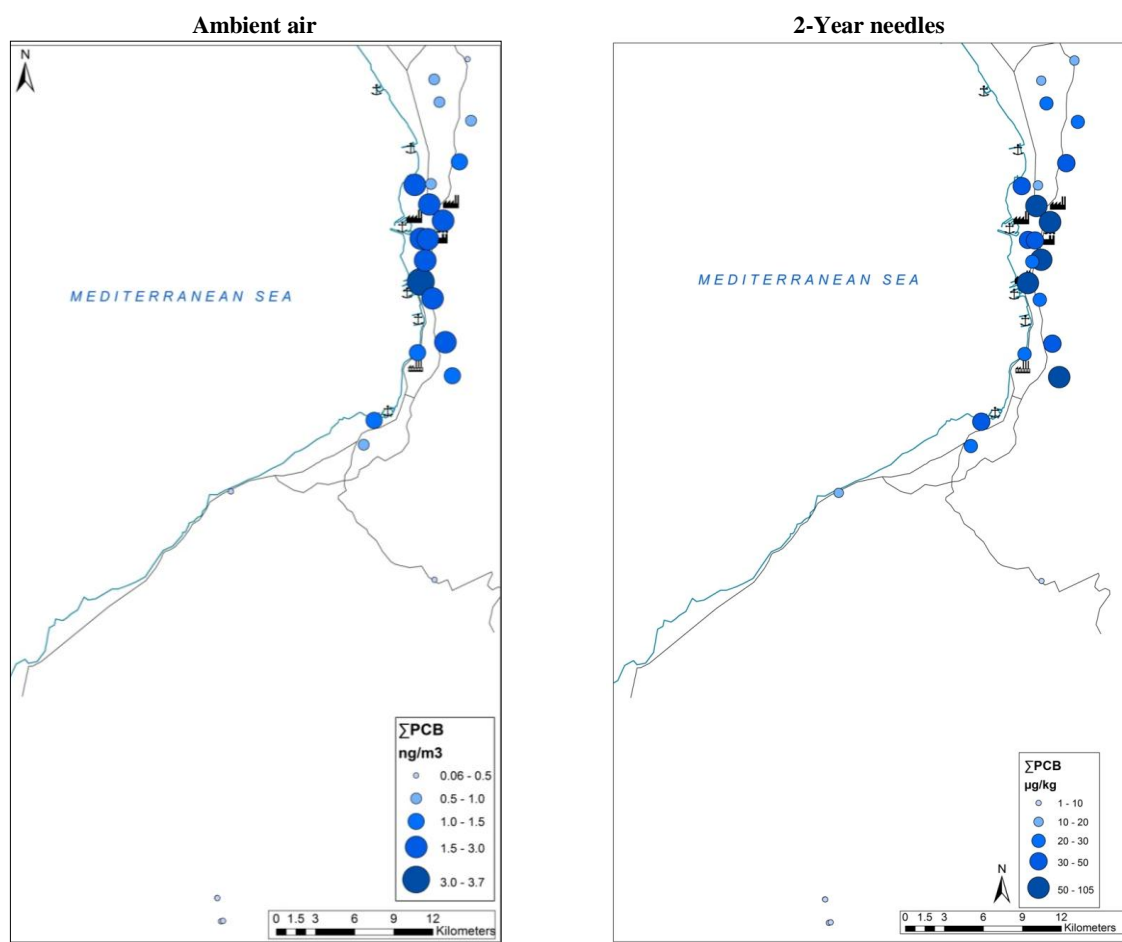


Figure 1. Spatial variation of PCB concentrations.

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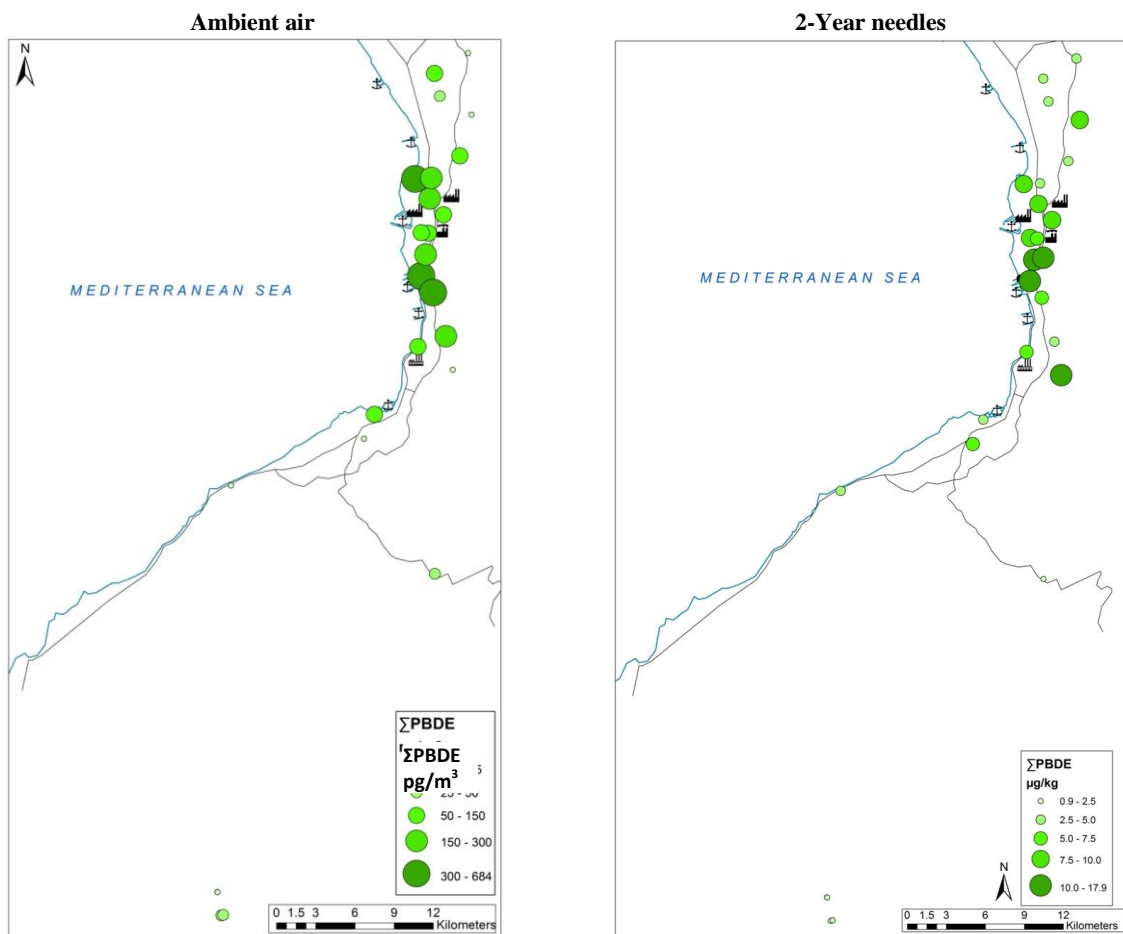


Figure 2. Spatial variation of Σ PBDE concentrations.

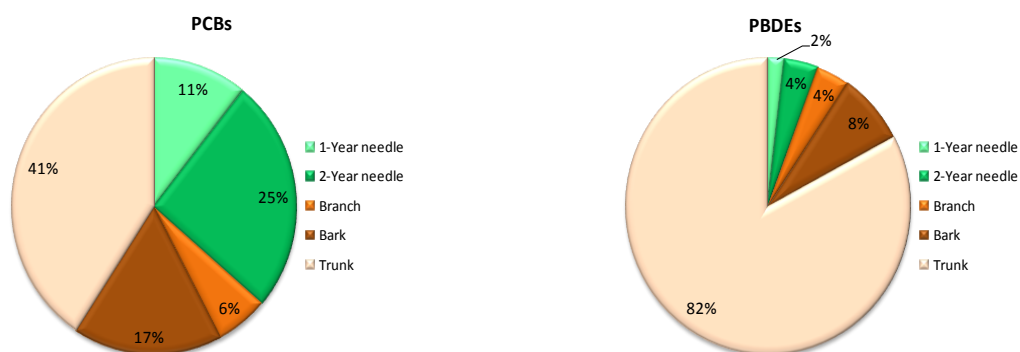


Figure 3. Inventory of PCBs and PBDEs in tree components (industrial sites).

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