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DETERMINATION OF POLYCHLORINATED BIPHENILS IN THE SOIL, ATMOSPHERIC DEPOSITION AND BIOINDICATOR SAMPLES IN THE MERIC-ERGENE RIVER BASIN, TURKEY

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ABSTRACT

The Meric-Ergene Basin, located on the north-western part of Turkey, begins with the Istanbul provincial border in the east and covers the border area with Bulgaria and Greece borders in the west. The industry developed at a rapid race, especially in the last fifty years, despite the importance of agriculture in the basin. In the study, 15 types of Polychlorinated Biphenils (PCBs) were determined in 4 regions of in an intense industrialized area, industrial+residential area, an agricultural area and a background area in total of 12 points, in 2014-2015, representing 4 seasons, in soil, lichen, pine needles and bulk samples, in the basin.
In the study, spatial and seasonal changes in PCBs concentrations were set forth and "Incremental Lifetime Cancer Risk" were conducted. According to the results, increasing PCB values were observed in industrial areas and in soil samples. Generally heavier PCB species more abundant in the sampling area. PCB concentrations reached the highest values for all matrixes in the 2014 Spring and 2015 winter. According to the results of ILCR study, "Cancer Increase Rate" due to the PCB concentration was found to be over 10^{-4} and cancer risk assessment studies are needed in the area.

1. INTRODUCTION

Polychlorinated biphenils (PCBs) are a group of aromatic and synthetic compounds and have no natural sources. Due to their physical and chemical properties they are widely distributed in the environment and accumulated through the food web up to and including humans and influence human health [1]. PCBs were extensively used in various industrial applications like capacitors, transformers, and paints over the period of 1930–1975. However, their production was discontinued and their use was banned in many countries several decades ago. PCBs are emitted into the environment from PCB containing wastes, open burning, waste incineration, evaporation from PCB containing products and contaminated surfaces, and accidental spills to soil [2]. Soil and biological monitors have been used to evaluate environmental contamination, assessing the transfer of compounds from the natural environment to humans [3]. The Meric-Ergene River Basin, which is the area where the study is carried out, is located in the north-west of Turkey. 70% of the river basin consists of agricultural areas. Although agriculture maintains its importance in the region, the basin has faced to rapid development of the industry. There are approximately 1,300 industrial facilities in the textile, chemical, metal-automotive and food sectors, in the basin. In this study, 15 PCBs were sampled in 12 sampling points in soil, lichen and pine needle samples and in the total atmospheric deposition samples in the basin. The data obtained were evaluated on the basis of spatial and temporal variations, and cancer risk evaluation was conducted to the results.

2.Material and Methods

Study Area: In this study, 15 PCBs were measured in 4 periods representing the 4 seasons for 1 year (May 2014, July 2014, October 2014, February 2015) at 3 sampling points (at a total of 12 points) in 4 different regions consisting of industrial area (Ind), industrial+residential area (IndR), agricultural area (Agr) and background (Bg). PCB concentrations were determined in soil, lichen and pine needle samples and in the total atmospheric deposition samples. The characteristics of the sampling points are given in Table 1.

Sampling: Soil samples were taken from 0-5 cm depth of the surface to characterize the surface soil using the multiple sampling method. Lichen samples of *Xanthoria parietina* species and pine needles samples of *Pinus and Quercus* taxa were sampled in the region surrounding the sampling point. Total deposition sampling equipment consisting of 60 cm stainless steel funnel and 20 liter glass bottle which was designed to be placed about 1.5 m height was kept at the sampling point for 2 weeks.

Analysis Procedure: For pre-treatment procedure, soil, lichen or pine needle samples were weighed and dried with lyophilizator, and they were subjected to ultrasonic extraction. Clean up stage was made with alumina-silicic acid column [4]. The samples analyzed in GC-MS. Total deposition samples extracted by liquid-liquid extraction with hexane. The blank sample tests were conducted for each sample set. The instrumental detection limit and system performance measurements were conducted for the GC-MS device. Recovery of PCBs was found in 63-92% for all samples.

Table 1. Characteristics of the sampling points

Sampling Area	Sampling Point	Characteristics
Industrial Area (IND)	Ind1	Ind area in the south east of the basin was selected in order to represent the pollutants that may be introduced particularly by the industries and the settlements. Within this area there are a textile and chemistry oriented organized industrial zone (178 industries), a leather industry zone (110 industries), approximately 300 individual industries and a settlement with an approximate population of 350.000.
	Ind2	
	Ind3	
Industrial and residential Area (INR)	IndR1	IndR area has been selected in order to observe the effects of mixed industries such as textile, food, leather, chemicals and glass on the E-5 motorway at the center of the basin. The area consists of approximately 400 dense -yet not congested- industrial facilities and some freely spread residential areas.
	IndR2	
	IndR3	
Agricultural Area (AGR)	Agr1	The sampling points in Agr area, west of the basin, were selected in order to observe the effects of agricultural areas remote from industries. The agricultural activities conducted in the area are mostly focused on wheat, sun flower and canola.
	Agr2	
	Agr3	
Background Area (BG)	Bg1	Bg area located in the north eastern part of the basin is close to the source of the Ergene River and is remote from industrial facilities, agricultural areas and residential areas. The area that is in the windward zone of the basin was selected in order to represent a reference area.
	Bg2	
	Bg3	

3.Results

Descriptive statistics of the total PCB concentration values are presented in Table 2. As it is seen, the total PCB values varied between 10-63 ng/g for soil samples at all sampling points, and the highest values were determined in Ind areas. PCB values varied between 10-68 ng/g for lichen samples, and the highest concentrations were measured in the IndR area. It was measured between 11-33 ng/g for pine needle samples, and the highest values were determined in the Agr area. The values varied between 0-144 ng/m^2-day for the total deposition samples, and the highest values were measured in the IndR area. For the total PCB values, generally higher values were obtained in the soil samples and the lowest values were observed for pine needle samples. In general, the seasons in which the highest values are obtained for each matrix are Spring 2014 and Winter 2015.

PCB species are also evaluated according to their homolog groups. In Table 3, distributions of homolog groups of measured PCBs are given. The hepta and octa groups were evaluated together. Spatial distributions of determined homolog groups of PCBs are given in Figure 1. In general, heavy PCB species are predominantly determined for all sampling matrices. Maximum concentrations were measured for hepta-octa PCBs in all sampling areas Given the distribution of weights, it can be said that the heavier species are more abundant in industrial areas and the light species are dominant in background areas.

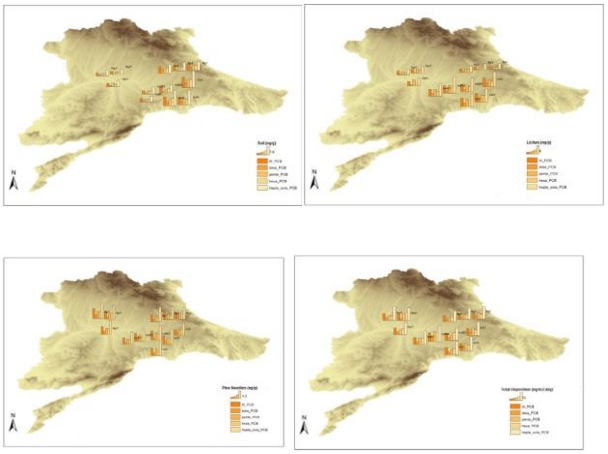

Table 2. Descriptive Statistics for total PCBs*

Sampling Area	Statistics	Σ_{15}PCB			
		Soil	Lichen	Pine Neddles	Total Deposition
		ng/g (dw)			ng/m^2-day
Ind n=12	Max.	62,85	48,97	25,24	75,16
	Min.	19,34	17,06	14,21	44,01
	Median	34,77	20,53	18,35	48,28
	Average	37,2	27,47	18,93	54,02
	Std. Dev.	15,55	12,65	3,5	11,09
IndR n=12	Max.	42,19	68,08	32,69	144,44
	Min.	10,39	10,03	13,62	41,08
	Median	13,8	22,64	16,24	47,50
	Average	16,48	25,94	18,65	57,93
	Std. Dev.	8,58	15,84	5,7	28,45
Agr n=12	Max.	16,12	18,95	32,25	87,85
	Min.	9,98	10,27	13,45	41,39
	Median	11,95	13,23	16,62	44,90
	Average	12,52	13,29	20,71	50,06
	Std. Dev.	2,09	2,57	8,08	13,04
Bg n=12	Max.	39,98	15,68	32,82	61,80
	Min.	10,96	6,78	11,35	0,00
	Median	22,97	11,57	13,56	39,78
	Average	23,86	11,24	17,79	39,62
	Std. Dev.	9,43	3,1	7,84	14,70

***Bolds are the highest values.**

Table 3. Homologue Groups of PCBs

Homologue Groups	Chlorine Number	PCB species
Tri-PCBs	3 Chlorines	PCB118, PCB20, PCB28, PCB31
Tetra-PCBs	4 Chlorines	PCB52, PCB44
Penta-PCBs	5 Chlorines	PCB101, PCB105, PCB118
Hexa-PCBs	6 Chlorines	PCB138, PCB149, PCB153
Hepta-Octa PCBs	7 and 8 Chlorines	PCB170-, PCB180, PCB194

3.1. Cancer Risk Calculation: In the study Incremental Lifetime Cancer Risk (ILCR) were used for evaluation cancer risk according to USEPA methods. ILCR values were calculated for direct ingestion, dermal contact and inhalation routes by these formulas [5, 6, 7].

$$ILCRs_{Ingestion} = \frac{CS \times (CSF_{Ingestion} \times \sqrt[3]{(BW/70)}) \times IR_{soil} \times EF \times ED}{BW \times AT \times 10^6}$$

$$ILCRs_{Dermal} = \frac{CS \times (CSF_{Dermal} \times \sqrt[3]{(BW/70)}) \times SA \times AF \times ABS \times EF \times ED}{BW \times AT \times 10^6}$$

$$ILCRs_{Inhalation} = \frac{CS \times (CSF_{Inhalation} \times \sqrt[3]{(BW/70)}) \times IR_{air} \times EF \times ED}{BW \times AT \times PEF}$$

The determination of carcinogenic slope factor was based on the cancer-causing ability of total

PCBs. $CSF_{Ingestion}$, CSF_{Dermal}, and $CSF_{Inhalation}$ of total PCBs were 2, 2,22 and 2 (mg kg^{-1} d^{-1})$^{-1}$, respectively [8, 9, 10]. The risks for children and adults were calculated separately. The total risks were the sum of risks associated with each exposure route. The variables used in the exposure calculation are given in Table 4. Calculated ILCR values are given in Table 5.

Table 4. Parameters used in the ILCR assessment [7]

Exposure variable	Unit	Child	Adult
Body weight (BW)	kg	15	60
Exposure frequency (EF)	day/year	350	350
Exposure duration (ED)	year	2	7
Inhalation rate (IR_{air})	m^3/day	5	20
Soil intake rate (IR_{soil})	mg/day	200	100
Dermal surface exposure (SA)	cm^2/day	1800	5000
Dermal adherence (AF)	mg/cm^2	0,2	0,2
Dermal adsorption (ABS)	unitless	0,1	0,1
Averaging life span (AT)	year	70	70
Soil dust produce factor (PEF)	m^3/kg	1,32	1,32

Tablo 4. ILCRs of three exposure routes for adult and child for total PCBs

Exposure pathways	Children			Adult		
	Ind	IndR	Agr	Ind	IndR	Agr
Direct ingestion	1,62636E-08	7,20495E-09	5,47366E-09	1,12949E-08	5,00375E-09	3,80139E-09
Dermal contact	3,24947E-09	1,43955E-09	1,09364E-09	1,25373E-08	5,55416E-09	4,21955E-09
Inhalation	0,000308023	0,000136457	0,000103668	0,001711344	0,000758144	0,000575968
Total	**3,1x10^{-4}**	**1,4x10^{-4}**	**1,0x10^{-4}**	**1,7x10^{-3}**	**7,6x10^{-4}**	**5,8x10^{-4}**

In regulatory terms, an ILCR of 10^{-6} or less denotes virtual safety and an ILCR of greater than 10^{-4} denotes potentially high risk [11]. Under calculated exposures, the estimated ILCRs for both adult and child are greater than 10^{-4}. It appeared that the PCBs are pervasive in the sampling areas and cancer risk assessment studies are needed in this sense.

4.Conclusions

In this study, it is aimed to compare pollutants that can come from industrial, residential and agricultural areas in comparison with the reference area in the basin where industrial pollution is known to have a very significant impact. Generally increasing PCB values were clearly observed in industrial areas in the study. PCB concentrations reached the highest values for all matrixes in the 2014 Spring and 2015 winter. The increasing values were clearly observed in soil concentrations. The lowest values in terms of averages were observed in pine needle samples. Generally heavier PCB species more abundant in the sampling area. In general, hepta-octa species (-7 and -8 rings) were predominantly determined for all sampling matrices,

and the average value of the total PCB concentration was 38%. It can be said that the concentrations found in industrial areas are heavier species and the light species are dominant in the background concentrations. ILCR were conducted for the observed values in the study. According to the information obtained, "Cancer Increase Rate" due to the PCB concentration was found to be over 10^{-4} and cancer risk assessment studies are needed in the area.

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