

POLYCHLORINATED BIPHENYLS IN SOILS FROM CROPLAND AREAS OF NORTH INDIA

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ABSTRACT

Polychlorinated biphenyls (PCBs) measured in agricultural soils from north India. The Σ PCBs were range between $<0.01 - 99.40 \text{ ng g}^{-1}$ (dry wt.) with the mean of $13.44 \pm 0.06 \text{ ng g}^{-1}$ (dry wt.). The concentration of DL-PCBs was ranged between $0.37 - 19.09 \text{ ng g}^{-1}$ (dry wt.) with an average of $6.26 \pm 0.03 \text{ ng g}^{-1}$ (dry wt.). PCB-105 (25%), PCB-114 (18%) and PCB-118 (18%), were the dominant congeners. Ortho PCBs account 61% and, non ortho PCBs contributed 18% to total DL-PCBs. The toxicity equivalent calculated using WHO 2005-TEFs and range from 0.01 to $105.40 \text{ pg WHO 2005-TEQ g}^{-1}$ (dry wt.) with the mean of $13.78 \pm 0.11 \text{ pg WHO 2005-TEQ g}^{-1}$ (dry wt.). PCBs contamination levels in soils from north India were lower than soil quality guidelines.

INTRODUCTION

Polychlorinated biphenyls (PCBs) are ubiquitous chemicals have been reported world-wide, affecting regions far from their original sources, such as the Arctic (AMAP, 1998). Their physico-chemical characteristics, which include hydrophobicity and resistance to degradation, make these chemicals to accumulate in soil, sediments, and biota. These compounds have a wide range of acute and chronic health effects (Van den Berg *et al.*, 2006).

As a party to the Stockholm Convention on POPs, India is legally obligated to abide by the objectives of the treaty, and is encouraged to support research on POPs. The occurrence of PCBs in various environmental matrices in India has been reported (Senthilkumar *et al.*, 2001b; Minh *et al.*, 2006; Kumar *et al.*, 2008; Zhang *et al.*, 2008; Chakraborty *et al.*, 2010). This study was focused on measuring PCBs concentrations in soils from variable cropland areas of north India.

MATERIALS AND METHODS

Study area & Sampling

The sampling area spread over around 30,242 sq. kms. The cultivated land is accounted a large proportion of 79.53%. The main crops grown in Delhi area are wheat, mustard, sugarcane, maize, paddy and commercial agricultural crops, such as, vegetables, flowers, mushroom etc.

49 samples collected from cropland areas in duplicate during April 2009-December 2009. Approximately 1 kg of soil sample was collected using stainless steel auger, and mixed thoroughly, then an aliquot was transferred to clean wide mouth amber glass bottle. After proper labeling, the sample bottles were transported to laboratory and kept at -4°C until further extraction.

Sample Extraction

Sample extraction was carried out as per USEPA Method No. 3545. Briefly, a homogenized 15 g wet sample was dried by mixing with diatomaceous earth (ASE prep DE, Dionex, USA) until a free-flowing powder was

obtained. The extraction was carried out with accelerated solvent extractor (ASE-350, Dionex, USA) using acetone: hexane (v/v, 1:1) in two cycles with 5 min. static time. The ASE was operated at 1500 psi and the oven was heated to 100⁰ C. The extracts were concentrated to 2.0 ml using Rotatory Vacuum evaporator (Eyela, Japan). Moisture content was determined to report data on dry weight basis.

Chromatographic Column cleanup

The sample extract clean-up was done with multilayered silica gel column chromatography on a tri-functional column with neutral, basic and acidic silica remove interfering organic and polar compounds. Briefly multilayered silica gel column (300 mm x 30 mm) was packed from bottom to up with 2.5 g silica gel, 4.0 g silver nitrate silica gel, 2.5 silica gel, 4.0 basic silica gel, 2.5 g silica gel, 12.0 g acid silica and 5.0 g anhydrous sodium sulphate. The column was pre-rinsed with 100 ml n-hexane before sample was loaded. The elution of pollutants was done with hexane. The eluted extract was concentrated using Rotatory Vacuum evaporator and under gentle stream of pure nitrogen using Turbo Vap (Caliper, USA) to 1.0 ml and transferred to auto sampler vial for quantification.

Instrumental quantification

The separation and quantification of polychlorinated biphenyls (PCBs) was performed by gas chromatography (Shimadzu 2010, Japan) attached with autosampler and equipped with an Electron Capture Detector (ECD, ⁶³Ni), on capillary column (HP-5MS, Agilent) 60 m x 0.25 mm x 0.25 μm film. The temperature program of the column oven was set to 170⁰ C for 1 min then increased with 3⁰C min⁻¹ to 270⁰C, kept for 1 min, then further ramped with 10⁰C min⁻¹ to 290⁰C at and kept for 3 min. The injector and detector temperature were maintained at 225⁰C and 300⁰C respectively. Purified nitrogen gas was used as carrier at the flow rate of 1.0 ml. min⁻¹.

Analytical quality control

Certified reference standards from Dr. Ehrenstorfer (GmbH, Germany) was used for the quantification of PCB congeners. The PCB congeners were identified in the sample extract by comparing the retention time from the standard mixture and quantified using the response factors from five level calibration curves of the standards. Appropriate quality assurance quality control (QA/QC) analysis was performed, including analysis of procedural blanks (analyte concentrations were <MDL 'method detection limit'), random duplicate samples (Standard deviation <5), calibration curves with the *r*² value of 0.999, and matrix spike recovery 100±20%. Each sample was analysed in duplicate and the average was used in calculations.

Toxic equivalent quantities (TEQ) for dioxin-like PCBs were calculated by multiplying the concentration of individual congener with the corresponding toxicity equivalent factors (TEFs). A reporting limit of > 0.01 ng g⁻¹ was taken for calculation. Levels below reporting limit or below MDL (<0.01 ng g⁻¹ dry wt.) were taken as zero (0) in the calculations. The results were reported as ng g⁻¹ and pg WHO₂₀₀₅-TEQ g⁻¹ dry wt. basis.

RESULTS AND DISCUSSION

The observed concentrations are presented in **Table 1**. The total concentration of PCBs were range between <0.01 – 99.40 ng g⁻¹ (dry wt.) with the mean of 13.44±0.06 ng g⁻¹ (dry wt.). The concentration of total non DL-PCBs was <0.01 – 99.40 ng g⁻¹ dry wt. (with the mean of 18.83±0.08 ng g⁻¹ dry wt.). The higher concentration of PCBs was detected in samples from the vicinities of industries. This indicates that PCB has been used in these industries

and the chemicals have found their way to the environment. Among the studied PCB congeners the mean concentration of PCB-74 was the highest (2.03 ± 0.18 ng g⁻¹ dry wt.), followed by PCB-151 (0.85 ± 0.19 ng g⁻¹ dry wt.), PCB-37 (0.77 ± 0.15 ng g⁻¹ dry wt.), PCB-187 (0.53 ± 0.09 ng g⁻¹ dry wt.), PCB-18 (0.46 ± 0.15 ng g⁻¹ dry wt.), and PCB-52 (0.45 ± 0.17 ng g⁻¹ dry wt.), other congener concentration were comparatively low (<0.01 to 0.3 ng g⁻¹ dry wt.).

Table 1: Levels (range & mean \pm SE*) of PCB congeners in soils (dry wt.) from north India (n=49)

PCB	PCBs		DL-PCB	DL-PCBs			
	Concentration (ng g ⁻¹)			Concentration (ng g ⁻¹)		pg WHO ₂₀₀₅ -TEQ g ⁻¹	
	range	mean		range	mean	range	mean
PCB - 18	<0.01-5.56	0.46 \pm 0.15	<i>Non ortho PCBs</i>				
PCB - 37	<0.01-3.81	0.77 \pm 0.15	PCB-77	<0.01-1.94	0.11 \pm 0.04	<0.01-0.19	0.01
PCB - 44	<0.01-0.91	0.10 \pm 0.03	PCB-81	<0.01-2.09	0.12 \pm 0.06	<0.01-0.63	0.03
PCB - 49	<0.01-1.08	0.08 \pm 0.03	PCB-126	<0.01-0.17	0.02 \pm 0.01	<0.01-17.47	2.15
PCB - 52	<0.01-5.49	0.45 \pm 0.17	PCB-169	<0.01-0.51	0.04 \pm 0.02	<0.01-15.42	1.14
PCB - 70	<0.01		<i>Mono ortho PCBs</i>				
PCB - 74	<0.01-5.01	2.03 \pm 0.18	PCB-105	<0.01-1.54	0.39 \pm 0.05	<0.01-0.05	0.01
PCB - 119	<0.01		PCB-114	<0.01-1.73	0.27 \pm 0.07	<0.01-0.05	0.01
PCB - 128	<0.01-0.95	0.10 \pm 0.04	PCB-118	<0.01-0.99	0.27 \pm 0.03	<0.01-0.03	0.01
PCB - 138	<0.01-1.44	0.15 \pm 0.03	PCB-123	<0.01-0.25	0.01 \pm 0.01	<0.01-	<0.01
PCB - 151	<0.01-4.64	0.85 \pm 0.19	PCB-156	<0.01-0.80	0.08 \pm 0.02	<0.01-0.02	<0.01
PCB - 168	<0.01-0.75	0.02 \pm 0.02	PCB-157	<0.01-0.28	0.02 \pm 0.01	<0.01-0.01	<0.01
PCB - 170	<0.01-0.76	0.17 \pm 0.03	PCB-167	<0.01-1.07	0.15 \pm 0.03	<0.01-0.03	<0.01
PCB - 177	<0.01-3.17	0.37 \pm 0.10	PCB-189	<0.01-0.36	0.06 \pm 0.01	<0.01-0.01	<0.01
PCB - 187	<0.01-2.86	0.53 \pm 0.09	-	-	-		
PCB - 207	<0.01-1.02	0.08 \pm 0.03	-	-	-		
Σ PCB	<0.01-99.40	18.83\pm0.08	Σ DL-PCB	0.37-19.09	6.26\pm0.03	0.01-105.40	13.78
Σ PCB+DL-PCB		Range (<0.01-99.40)		Mean (13.44\pm0.06)			-

Note: <0.01=below detection limit, *standard error=SD/ \sqrt{n} ,

The concentration of Σ DL-PCBs in this study was ranged between 0.37-19.09 ng g⁻¹ (dry wt.) with average of 6.26 \pm 0.03 ng g⁻¹ (dry wt.). Among DL-PCBs, congener -105 (19.09 \pm 0.05 ng g⁻¹ (dry wt.)) was the dominant congener followed by -114 (13.24 \pm 0.07 ng g⁻¹ (dry wt.)) and -118 (13.21 \pm 0.03 ng g⁻¹ (dry wt.)). The toxicity equivalent (TE) contribution calculated using WHO 2005-TEFs (Van den Berg *et al.*, 2006). Total TEQ levels of DL-PCBs, range from 0.01 to 105.40 pg WHO 2005-TEQ g⁻¹ (dry wt.) and, the mean was 13.78 \pm 0.11 pg WHO 2005-TEQ g⁻¹ (dry wt.). Mono ortho PCB-105 (25%), PCB-114 (18%) and PCB-118 (18%), were the dominant congeners and, account 61% and on the other hand, non ortho PCBs contributed only 18% for total DL- PCBs.

The PCBs contamination levels in soils from Delhi region were compared with guideline values (0.5 mg/kg) (CCME, 1999) and found far lower than soil quality guidelines. Contamination of PCBs in Indian environment is restricted to transformer oil rather than technical mixture that used for industries and electrical appliances. It seems likely that the main source of DL- PCBs in soils of agricultural fields from north India were from open biomass burning which is common in agricultural field after crop harvesting, and depositions of emissions from wood processing, paint and dyeing, chemicals and transformer manufacturing units and from electrical and electronic waste recycling units. These PCB sources also include off gassing from closed system such as older equipments (e.g. transformers that contain large quantities of PCB fluids), and PVC (polyvinylchloride) manufacture. It Soil contamination by PCB can occur in some point sources for PCB storage and usage, and their ambient areas, especially in the case where facilities for proper use and disposal of PCB are lacking.

CONCLUSION

The PCBs contaminations of soils are matter of concern but not alarming, because observed levels were lower than soil guidelines. The probably sources of PCBs pollution in this study may be from electronic waste recycling, open mass burning and, industrial depositions. It is recommended that more intensive for persistent organic pollutants to be conducted.

ACKNOWLEDGEMENTS

The authors express their sincere gratitude to the Member Secretary and Chairman of Central Pollution Control Board, Ministry of Environment & Forest Government of India for encouragement to conduct the study.

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