DISTRIBUTION OF POLYCHLORINATED BIPHENYLS INCLUDING DIOXIN-LIKE PCBs IN SOILS FROM AGRICULTURAL FIELDS IN NEW DELHI, INDIA

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Introduction

Polychlorinated biphenyls (PCBs) are ubiquitous chemicals and long range atmospheric transport pollutants (LRAT), transported world-wide, affecting regions far from their original sources such as the Arctic and Antarctic[1]. Their characteristics of hydrophobicity and resistance to degradation make these chemicals to accumulate in soil, sediments and biota[1-2]. PCB compounds have a wide range of acute and chronic health effects, including cancer, neurological damage, reproductive disorders, immune suppression, birth defects, and are also suspected endocrine disruptors[3] and are classified as probable human carcinogens. Even if air represents the dominant medium of global transport and the site of important degradation loss, soil and sediment are important reservoirs of PCBs globally, and vegetation acts as an efficient scavenging medium from the atmosphere and as a major vector of PCB into terrestrial food chain[4].

Recent studies in India, reported PCBs contaminations with various environmental matrices, including water, soil, sediment and air[5-9]. In continuation of support research on POPs in India, this study was aimed to evaluate polychlorinated biphenyls (PCBs) including dioxin like PCBs (dl-PCBs) concentrations in soils from roadside agricultural fields of National Capital Region (NCR), India. The NCR with the population of ~22.157 million comprises by the National Capital Territory (NCT) New Delhi and the delineated area of the surrounding states of Haryana, Uttar Pradesh, and Rajasthan. The entire NCR spread over around 30,240 km^2, where cultivated land is accounted a large proportion of 79.53%. Consequently, in this study we report distribution of PCBs in roadside agricultural fields of New Delhi, India for the first time.

Materials and Methods

Sample Collection and Processing: Sampling locations were selected in agriculture dominance areas of New Delhi and adjoining districts of Uttar Pradesh and Haryana states in NCR. A total 83 soil samples collected from roadside agricultural lands during November 2011 to January 2012. Approximately 1 kg of soil sample was collected in duplicate using stainless steel auger. The pebbles and wood sticks were removed immediately after collection and then sample was mixed thoroughly to ensure that the soil collected was truly representative of each location. Further, sub-samples was subsequently taken and transferred to clean wide mouth amber glass bottle. After proper labeling the sample bottles were transported to laboratory and kept at -4^{0}C until further chemical treatment.

Sample extraction was carried out after EPA Method No. 355^{0}C. Briefly, a homogenized 15 g wet sample was dried by mixing with sodium sulfate until a free-flowing powder was obtained. Approximately 1 g of copper powder was added to remove the sulfur. The sample was then extracted with 3 cycles (50, 25, 25 ml) of hexane/acetone (1/1v/v) solvent mixture by ultra-sonication for 30 min each cycle. The extract was then concentrated to approximately 2.0 ml using Rotatory Vacuum evaporator (Eyela, Japan) for further cleanup. The sample extract clean-up was done with multilayered silica gel column chromatography on a tri-functional column with neutral, basic and acid silica to remove interfering organic and polar compounds.

Instrumental Analysis and Quality Control: The separation and quantification of PCBs was performed by gas chromatography (Shimadzu 2010, Japan) attached with auto sampler and equipped with an Electron Capture Detector (ECD, ^{63}Ni), on capillary column (HP-5MS, Agilent) 60 m × 0.25 mm × 0.25 µm film. The temperature program of the column oven was set to 170^{o}C for 1 min then increased with 3^{o}C min^{-1} to 270^{o}C, kept for 1 min, then further

ramped with 10°C min^{-1} to 290°C at and kept for 3 min. The injector and detector temperature were maintained at 225°C and 300°C respectively. Purified nitrogen gas was used as carrier gas at the flow rate of 1.0 ml. min^{-1}.

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.

Dioxin-like PCBs are assigned with the toxic equivalent factors based on the relative toxicity with 2,3,7,8-tetrachloro dibenzo-*p*-dioxin (TCDD)[3]. Toxic equivalent quantities (TEQ) were calculated by multiplying the concentration of individual dl-PCB congener with the corresponding 2,3,7,8-TCDD substituted toxicity equivalent factors (TEFs).

Soil moisture was determined separately to report data on dry weight basis. The results were reported as ng g^{-1} and pg WHO_{2005}-TEQ g^{-1} dry-weight (dw). 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} dw) were taken as zero (0) in the calculations.

Results and Discussion:

The observed concentrations of PCBs in soils of roadside agricultural lands are presented in Table 1. The total concentration of PCBs were range between <0.01 – 38.32 ng g^{-1} (dw) with the mean value of 8.40±1.27 ng g^{-1} (dw). The concentration of PCBs in soils from Uttar Pradesh was comparatively higher than soils from New Delhi and Haryana states. The average concentration of PCBs in soils from New Delhi, Uttar Pradesh and Haryana was 0.86±0.15 ng g^{-1}, 20.77±1.82 ng g^{-1} and 3.97±3.33 ng g^{-1} with the range of <0.01-4.69 ng g^{-1}, 0.26-38.32 ng g^{-1} and <0.01-30.58 ng g^{-1}, respectively. Earlier studies reported significant levels in of PCBs in different environmental matrices from New Delhi and adjoining areas[6-9]. The PCBs contamination levels in soils from National Capital Region (NCR) were lower than soil quality guideline value of 500 ng g^{-1} by CCME [10].

Table 1: ∑PCBs and ∑dl-PCBs (ng/g) in roadside agricultural soils from NCR, India

Study area (n)*	PCBs	Range	Mean	SE*	%
New Delhi (44)	PCBs	<0.01-4.30	0.67	0.14	77.86
	dl-PCBs	<0.01-0.66	0.19	0.03	22.14
	∑PCBs	<0.01-4.69	0.86	0.15	100
Uttar Pradesh (30)	PCBs	0.26-24.72	13.5	1.21	64.98
	dl-PCBs	<0.01-13.59	7.27	0.70	35.02
	∑PCBs	0.26-38.32	20.77	1.82	100
Haryana (9)	PCBs	<0.01-22.48	2.80	2.46	70.41
	dl-PCBs	<0.01-8.09	1.18	0.87	29.59
	∑PCBs	<0.01-30.58	3.97	3.33	100
All area (83)	PCBs	<0.01-24.72	5.54	0.84	65.96
	dl-PCBs	<0.01-13.59	2.86	0.46	34.04
	∑PCBs	<0.01-38.32	8.40	1.27	100

*n=number of samples, <0.01=below detection limit, **SE=standard error (SD/√n)

Among the 28 PCB congeners, PCB-44 was the dominant congener (1.58±0.27 ng g^{-1}), followed by PCB-49 (1.19±0.20 ng g^{-1}), PCB-81 (0.77±0.17 ng g^{-1}), PCB-151 (0.62±0.11ng g^{-1}), PCB-156 (0.47±0.09 ng g^{-1}), PCB-77 (0.45±0.11 ng g^{-1}), and PCB-74 (0.44±0.12 ng g^{-1}), other congener concentration were comparatively low (<0.01 to 0.30 ng g^{-1}). The group homolog of PCBs dominated by tetra- and hexa- chlorinated biphenyls. Tetra-CB (56%) homolog was the major contributors to the total PCB homologue profiles followed by hexa-CBs (23.6%). Overall,

the homolog pattern was observed as tetra-CBs > hexa-CBs > penta-CBs > tri-CBs > hepta-CBs. Figure 1 shows that the percentage (average >60% for tri- to tetra-PCBs) of lighter-weighted molecular PCBs (LWM-PCBs) were higher than those higher-molecular weight PCBs (HMW-PCBs) (penta to hepta-CBs). It is reported that LMW-PCBs were primarily used in power capacitors and transformers, while HMW-PCBs were mainly used as an additive[11]. This indicates that PCBs used in heat transfer equipments and as additives found their way to the environment of national capital region.

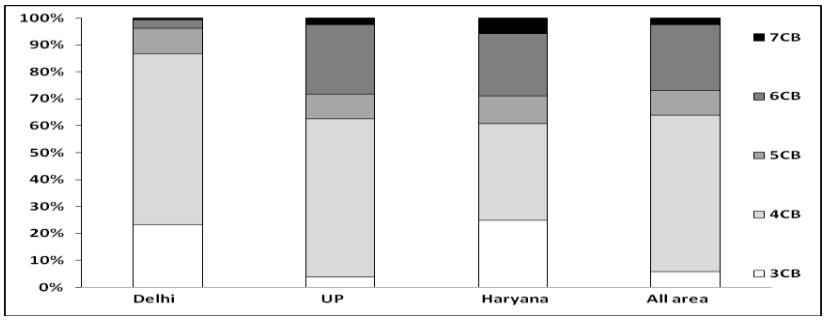

Figure 1: Percent homolog distribution in roadside agricultural soils from NCR, India

The concentration of ∑dl-PCBs in this study was ranged between <0.01-13.59 ng g^{-1} with an average of 2.86±0.46 ng g^{-1}. In this study, the quantity of of 12 dioxin-like PCBs accounts for 34.04% of total 28 PCBs. The toxicity equivalency (TEQ) for 12 dl-PCBs was presented in Table 2. Total TEQ levels ranged from <0.01 to 140.24 pg WHO_{2005}-TEQ g^{-1} with the mean of 31.86±5.25 pg WHO_{2005}-TEQ g^{-1} (Table 2). The TEQ of non-ortho-PCBs (CB-77, CB-81, CB-126 and CB-169) were higher and contributed 92-99% for total TEQ, while the TEQ of mono-ortho PCBs (CB-105, CB-114, CB-118, CB-123, CB-156, CB-157, CB-167 and CB-189) were <1. CB-126 and CB-169 congeners represent the higher TEQ values which both had the high toxic potency (toxic equivalency factor proposed WHO-TEF=0.1 and 0.03 respectively) thus significantly increasing the ∑dl-PCBs with the contribution of 99% for ∑TEQ. On the whole, concentration of 12 dl-PCBs TEQ in agricultural soils from New Delhi roadside agricultural soils were lower than environmental quality standard (1000 pg WHO-TEQ g^{-1})[12].

Table 2: Toxic Equivalent of dl-PCBs (range and mean) (pg WHO-TEQ g^{-1}) in roadside agricultural soils from NCR, India

Study area (N)*	dl-PCBs	Range	Mean	SE	%
New Delhi (44)	non-ortho	<0.01-0.18	0.03	<0.01	92.7
	mono ortho	<0.01-0.02	<0.01	<0.01	7.1
	total	<0.01-0.18	0.03	0.01	100
Uttar Pradesh (30)	non ortho	<0.01-140.07	84.36	7.29	99.9
	mono ortho	<0.01-0.21	0.09	0.01	0.1
	total	<0.01-140.24	84.45	7.30	100
Haryana (9)	non ortho	<0.01-108.69	12.11	12.07	99.8
	mono ortho	<0.01-0.11	0.02	0.01	0.2
	total	<0.01-108.80	12.13	12.08	100
All area (83)	non ortho	<0.01-140.07	31.82	5.25	99.9
	mono ortho	<0.01-0.21	0.04	0.01	0.1
	total	<0.01-140.24	31.86	5.25	100

*N=number of samples

PCBs have never been produced in India but used as transformer oil rather than technical mixture that used for industries and electrical appliances. The data on the transformers containing PCBs were inventoried and showed that around 9837 tons of PCBs exist in India[13]. Other possible PCBs sources to the environment in India include biomass burning, depositions of emissions from wood processing, paint and dying, chemicals, transformer and polyvinylchloride (PVC) manufacturing units and also from electrical and electronic waste recycling[14]. The agricultural open biomass burning is common in agricultural field after crop harvesting. These PCB sources also include off gassing from closed system such as older equipments (e.g. transformers that contain large quantities of PCB fluids). The PCBs contaminations in soils are considered to a great concern however, not alarming, due to lower than soil quality guideline values. The probably sources of PCBs pollution in this study may be from electronic waste recycling, open mass burning and from industrial depositions. An intensive study is recommended for PCBs and persistent organic pollutants due to human health and environment concerns.

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References:

1. Senthil Kumar K, Kannan K, Corlsolini S, Evans T, Giesy JP, Nakanishi J, Masunaga S. (2002); *Environ. Pollut*. 119:151-161
2. Alison LS, Jason DW. (2008); *Rev. Biol. Trop*. (*Int. J. Trop. Biol*.), 56 (4):1-9
3. den Berg M, Linda SB, Denison M et al. (2006); *Toxicol. Sci.* 93 (2): 223-241
4. Zhao X, Zheng M, Zhang B, Zhang Q, Liu W. (2006); *Science of Total Environment* 368: 744–752
5. Senthil Kumar K, Kannan K, Subramanian AN, Tanabe S. (2001); *Environ, Sci. Pollut. Res.* 8: 35-47
6. Chakraborty P, Zhang G, Li, J, Xu Y, Liu X, Tanabe S, Jones KC. (2010); *Environ. Sci. Technol*. 44: 8038-8043
7. Kumar B, Kumar S, Gaur R, Goel G, Mishra M, Singh SK, Prakash D, Sharma CS. (2011); *Soil & Water Research* 6 (4): 190–197
8. Kumar B, Mishra M, Goel G, Gaur R, Singh SK, Prakash D, Kumar S, Sharma CS. (2011); *Adv. Life Sci. Technol*. (1): 1-8
9. Kumar B, Singh SK, Kumar S, Sharma CS. (2012); *J. Natural Sci. Research* 2 (1):26-37
10. Canadian Council of Ministers for the Environment. (1999); Health branch, Ottawa, Canada
11. You H, Ding J, Zhao XS, Li YF, Liu LY, Ma WL, Hong QH, Shen JM. (2011); *Geochem. Health*, 33: 291–299
12. Government of Japan. (2009); Brochure Dioxin, www.env.go.jp/en/chemi/dioxins/brochure2009.pdf
13. Stockholm Convention. (2012); National Implementation Plan for POPs, India. www.pops.int/
14. Senthil Kumar K, Kannan K, Paramsivan ON, Shanmugasundaram VP, Nakanishi J, Giesy JP, Masunga S. (2001); *Environ. Sci. Technol*. (35): 3448 -3455