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Distribution of polychlorinated biphenyls in agricultural soils from NCR, Delhi, India

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ABSTRACT

Twenty eight polychlorinated biphenyls (PCBs) congeners including twelve dioxin-like PCBs were measured in agricultural soils. Σ PCBs ranged 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 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 accounted for 61% and, non ortho PCBs contributed only 18% to the total DL- PCBs. The toxicity equivalent calculated using WHO 2005-TEFs 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 in soils from Delhi region was lower than Canadian guideline values. The contamination source of PCBs in soils possibly comes from open waste burning, electronic waste recycling and depositions from industrial emissions.

Keywords: polychlorinated biphenyls (PCBs), dioxin-like PCBs, agricultural soil, accelerated solvent extraction (ASE).

INTRODUCTION

Polychlorinated biphenyls (PCBs) are ubiquitous chemicals and their environmental contamination was recognized more than 45 years ago. These are long range transport pollutants, and have been transported world-wide, affecting regions far from their original sources, such as the Arctic [1-3]. Their physico-chemical characteristics, which include hydrophobicity and

resistance to degradation, make these chemicals to accumulate in soil, sediments, biota [4-5], and in human body through dietary intake, inhalation and other indirect exposure [6]. These are toxic and, well known for their carcinogenic potential. These 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 [7].

In May 2004, Stockholm Convention on POPs entered into force with the intention of reducing, and ultimately eliminating these pollutants. As a party to the Convention, India is legally obligated to abide by the objectives of the treaty, and is encouraged to support research on POPs. In India, some studies have been conducted into distributions of POPs, such as intentionally released insecticide DDT, little known about the unintentionally released POPs, such as PCBs. The contamination of PCBs in soils, sediments, air and biota has been extensively studied worldwide [8-13]. This study was focused on measuring PCBs concentrations in soils from National Capital Region, Delhi (India).

MATERIALS AND METHODS

Description of study area

The National Capital Region (NCR), Delhi comprises by the National Capital Territory (NCT) Delhi and the delineated area of the surrounding states of Haryana, Uttar Pradesh, and Rajasthan. The entire NCR Delhi region spread over an area of around 30,242 sq. kms. The cultivated land is accounted a large proportion of 79.53 per cent area in the NCR, Delhi region [14-15]. The main crops grown in Delhi area are wheat, mustard, sugarcane, maize, jawar, bajra, paddy and commercial agricultural crops, such as, vegetables, flowers, mushroom etc.

Sampling

The sampling sites are localized in the agricultural area with different cropping pattern. 49 samples were randomly collected in duplicate during April 2009-December 2009. Approximately 1 Kg. of soil sample was collected using stainless steel auger, and after removing pebbles and wood sticks the sample was mixed thoroughly to homogenized, 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 -4⁰C until further chemical treatment.

Chemicals

Chemicals and solvents were purchased from Merck India. Silica gel 60 (0.063 – 0.100 mm) was from Sigma-Aldrich. Prior to use, silica gel and anhydrous sodium sulphate was cleaned separately with methanol, dichloromethane and acetone in Soxhlet extractor and, stored air tight at 130 ⁰C. PCBs congener mixture standard solutions were purchased from Dr. Ehrenstorfer (GmbH, Germany).

Extraction

Sample extraction was carried out as per validated methods [16-17]. Briefly, a homogenized 15-20 g sample was mixed 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 top 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, ^{63}Ni), 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 170°C for 1 min then increased with 3°C min⁻¹ to 270°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 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.

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) [7]. Toxic equivalent quantities (TEQ) were calculated by multiplying the concentration of individual DL-PCB congener with the corresponding toxicity equivalent factors (TEFs).

The results were reported as ng g⁻¹ and pg WHO₂₀₀₅-TEQ g⁻¹ dry -weight (dry wt.) basis. A reporting limit of > 0.01 $\mu\text{g kg}^{-1}$ dry wt 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.

RESULTS AND DISCUSSION

The observed concentrations of non DL-PCBs and DL-PCBs in soils 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.). Levels of PCBs from Delhi and adjoining areas were reported [12-14;18-19].

PCBs are not used as single compounds but as technical mixtures. 70% of PCBs produced globally were tri-, tetra-, and penta-chlorinated biphenyls, with trichlorinated ones as dominating homologues [20]. In present study range of concentration sum of 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.).

Table 1: Range and mean \pm SE* of PCB congeners concentrations (ng g⁻¹ dry wt.) in agricultural soils.

PCBs congeners			DL-PCBs congeners		
No.	Range	Mean \pm SE	No.	Range	Mean \pm SE
PCB - 18	<0.01-5.56	0.46 \pm 0.15	PCB-77	<0.01-1.94	0.11 \pm 0.04
PCB - 37	<0.01-3.81	0.77 \pm 0.15	PCB-81	<0.01-2.09	0.12 \pm 0.06
PCB - 44	<0.01-0.91	0.10 \pm 0.03	PCB-105	<0.01-1.54	0.39 \pm 0.05
PCB - 49	<0.01-1.08	0.08 \pm 0.03	PCB-114	<0.01-1.73	0.27 \pm 0.07
PCB - 52	<0.01-5.49	0.45 \pm 0.17	PCB-118	<0.01-0.99	0.27 \pm 0.03
PCB - 70	<0.01		PCB-123	<0.01-0.25	0.01 \pm 0.01
PCB - 74	<0.01-5.01	2.03 \pm 0.18	PCB-126	<0.01-0.17	0.02 \pm 0.01
PCB - 119	<0.01		PCB-156	<0.01-0.80	0.08 \pm 0.02
PCB - 128	<0.01-0.95	0.10 \pm 0.04	PCB-157	<0.01-0.28	0.02 \pm 0.01
PCB - 138	<0.01-1.44	0.15 \pm 0.03	PCB-167	<0.01-1.07	0.15 \pm 0.03
PCB - 151	<0.01-4.64	0.85 \pm 0.19	PCB-169	<0.01-0.51	0.04 \pm 0.02
PCB - 168	<0.01-0.75	0.02 \pm 0.02	PCB-189	<0.01-0.36	0.06 \pm 0.01
PCB - 170	<0.01-0.76	0.17 \pm 0.03	-	-	-
PCB - 177	<0.01-3.17	0.37 \pm 0.10	-	-	-
PCB - 187	<0.01-2.86	0.53 \pm 0.09	-	-	-
PCB - 207	<0.01-1.02	0.08 \pm 0.03	-	-	-
Σ PCBs	<0.01-99.40	18.83\pm0.08	Σ DL-PCBs	0.37-19.09	6.26\pm0.03
Σ PCBs+ Σ DL-PCBs					
Range			Mean+SE		
<0.01-99.40			13.44\pm0.06		

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

The higher concentration of PCBs was detected in samples from the vicinities of industries which are the emission sources of PCBs. This indicates that PCB has been used in these industries and the chemicals have found their way to the environment. Congener profiles PCBs in agriculture soils from Delhi region were depicted in **Figure 1**.

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.). The results of this study were in agreement with the observations from urban Kathmandu soils [21], and soil from Tibetan Plateau, China [22]. However, the concentrations of PCBs were lower than those PCBs in soils from Switzerland [23], Romania [24], China [25], San Felipe, Nuevo Mercurio, Zacatecas, Mexico [26] but, higher than soils from Turkey [27] and Antarctica [3]. 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 ± 0.03 ng g⁻¹ (dry wt.).

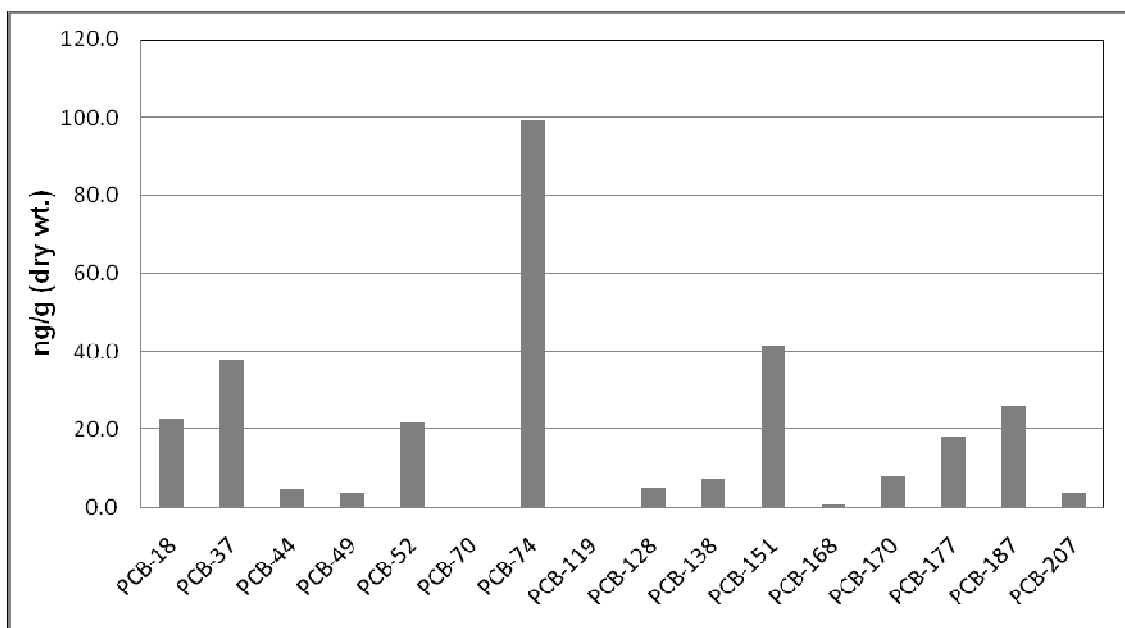


Figure 1: Distribution of Σ PCBs congeners in agricultural soils (ng g^{-1} dry wt.)

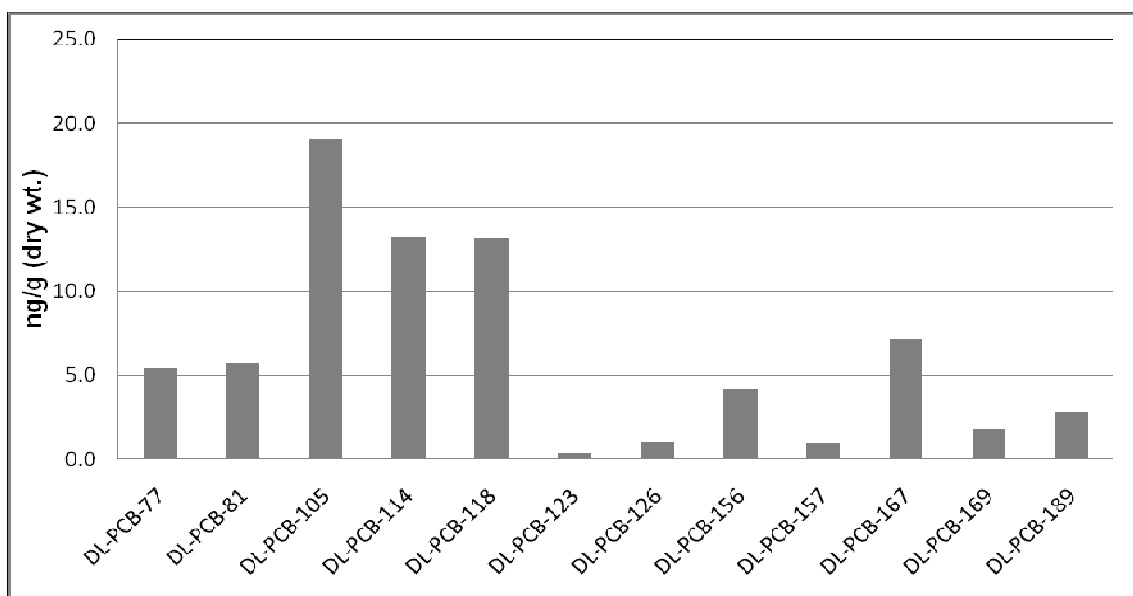


Figure 2: Distribution of Σ DL-PCBs congeners in agricultural soils (ng g^{-1} dry wt.)

The total concentration profile of Σ DL-PCB congeners was shown in **Figure 2**, and reveals that congener -105 ($19.09 \pm 0.05 \text{ ng g}^{-1}$ (dry wt.)) was the dominant congener followed by -114 ($13.24 \pm 0.07 \text{ ng g}^{-1}$ (dry wt.)) and -118 ($13.21 \pm 0.03 \text{ ng g}^{-1}$ (dry wt.)).

Table 2: Range and mean \pm SE* of DL-PCB congeners TEQs (pg WHO₂₀₀₅-TEQ g⁻¹ dry wt.) in agricultural soils from Delhi region, India

DL-PCB Congeners	WHO 2005-TEF**	Range	Mean \pm SE
Non ortho - PCB			
DL-PCB – 77	0.0001	<0.01-0.19	0.01
DL-PCB – 81	0.0003	<0.01-0.63	0.03
DL-PCB – 126	0.1	<0.01-17.47	2.15
DL-PCB – 169	0.03	<0.01-15.42	1.14
Mono ortho - PCB			
DL-PCB – 105	0.00003	<0.01-0.05	0.01
DL-PCB – 114	0.00003	<0.01-0.05	0.01
DL-PCB – 118	0.00003	<0.01-0.03	0.01
DL-PCB – 123	0.00003	<0.01	<0.01
DL-PCB – 156	0.00003	<0.01-0.02	<0.01
DL-PCB – 157	0.00003	<0.01-0.01	<0.01
DL-PCB – 167	0.00003	<0.01-0.03	<0.01
DL-PCB – 189	0.00003	<0.01-0.01	<0.01
ΣDL-PCBs	-	0.01-105.40	13.78\pm0.11

<0.01=below detection limit, *standard error=SD/ \sqrt{n} , ** Van den Berg *et al.*, 2006

The toxicity equivalent (TE) contribution, calculated using WHO 2005-TEFs (Van den Berg *et al.*, 2006) values, are reported in **Table 2**. 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. Congener specific concentration of DL-PCBs in Delhi region were in agreement with other reports [25,28]. Municipal solid waste incinerations typically release PCB-118 into the atmosphere [29]. Emissions from coal combustion and industrial waste incineration sources contributed non ortho PCBs and do not solely come from commercial PCB mixtures [30]. The observed concentrations of Σ DL-PCBs in agricultural soils from North India were lower than Tailake region and Southern Jiangsu region of China [28,31], Pancevo, Serbia [32] but, higher than Yellow river delta, China [25], Switzerland [23], Tailke region, China [31]. The average WHO-TEQ were comparable with other study [33].

Contamination of PCBs in Indian environment is restricted to transformer oil rather than technical mixture which were used for industries and electrical appliances. It seems likely that the main source of DL- PCBs in soils of agricultural fields 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. 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 usage and disposal of PCB are lacking.

CONCLUSION

PCBs contamination levels in soils from Delhi region were compared with guideline values (0.5 mg/kg) [34] and found lower than soil quality guidelines. PCBs contaminations in soils are

matter of concern but not alarming, because observed levels are far lower than soil quality guidelines. The probable sources of PCBs pollution in this study might have arisen from electronic waste recycling, open mass burning and, industrial wastes. It is recommended that more intensive assessment for persistent organic pollutants to be conducted, due to human health and environment concerns.

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