Congener specific distribution and health risk assessment of polychlorinated biphenyls in urban soils

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Abstract
Polychlorinated biphenyls (PCBs) are a group of 209 congeners and have been designated as persistent organic pollutants by the Stockholm Convention. PCBs were primarily used in transformers and capacitors as dielectric and coolant fluids and in lubricants, flame retardants, plasticizers, paint, etc. Even though the production has been banned since the 1970s and usage of these contaminants are restricted in many countries, PCBs continue to be detected in environmental samples from around the world.

PCBs are toxic, bioaccumulative, and can undergo long-range atmospheric transport world-wide to regions such as the Arctic, Antarctic and high altitude regions of Mount Everest. PCBs are characterized by high thermal and chemical stabilities, low vapor pressures, high dielectric constants, hydrophobicity, high lipophilicity, and extreme resistant to degradation. Because of these characteristics, PCBs accumulate in soil, sediments and biota.

Soils of urban areas are usually known as the source as well as sink for environmental pollutants, where cumulative effects of long-range atmospheric transport and local sources are the important factors. As a result, comparatively higher concentrations of PCBs have been reported in urban soils than suburban or rural soils.

Human health risk estimates through the soil ingestion pathway were made in terms of lifetime average daily dose (LADD), incremental lifetime cancer risks and non-carcinogenic hazard quotient (HQ). The LADD for Delhi adults and children was 3.02×10⁻⁸ mg kg⁻¹ d⁻¹, which was lower than the acceptable limit of 1. The study found lower concentrations of PCBs than guideline values and low health risk estimates through the soil ingestion pathway within acceptable levels, indicating a minimum risk for Delhi residents.

Introduction
Polychlorinated biphenyls (PCBs) are toxic, bioaccumulative, and can undergo long-range atmospheric transport world-wide to regions such as the Arctic, Antarctic and high altitude regions of Mount Everest. PCBs are characterized by high thermal and chemical stabilities, low vapor pressures, high dielectric constants, hydrophobicity, high lipophilicity, and extreme resistant to degradation. Because of these characteristics, PCBs accumulate in soil, sediments and biota.

Soils of urban areas are usually known as the source as well as sink for environmental pollutants, where cumulative effects of long-range atmospheric transport and local sources are the important factors. As a result, comparatively higher concentrations of PCBs have been reported in urban soils than suburban or rural soils.

Humans are exposed to PCBs mainly through the consumption of contaminated food, and occupational exposure to PCBs occurs mainly via the inhalation and dermal routes. Higher amount of PCBs in soils, especially dioxin-like PCBs (dl-PCBs), may cause toxicological health risks to urban residents through ingestion, inhalation and skin contact. This paper presents the PCB distribution in soils from Delhi, India, and exposure risk estimates for human health through soil ingestion. The concentration of ∑PCBs ranged between 1.08-100.67 ng g⁻¹ (mean 21.16 ng g⁻¹±5.24 ng g⁻¹), which was much lower than the Canadian soil quality guideline value of 1.3 mg/kg or 1300 ng g⁻¹.

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Materials and Methods
Study area and sampling
The sampling area was the national capital region of India (NCT), Delhi, which is the capital of India with a population of 1.67 million. The total area of NCT, Delhi, is approximately 1483 km² and is located in northern India between 28°24'17"N to 28°53'00"N and between 76°50'24"E to 77°20'37"E. Average annual rainfall is 714 mm. The climate in Delhi is hot and humid. During summer, temperatures rise up to 40-45°C and in winters temperatures fall to 4-5°C.

The soil sampling was conducted from 14 urban locations on streets and roads near residential areas in Delhi. Approximately 1/2 kg of soil sample was collect-
ed from each sampling location, and after removing pebbles, sticks and leaves the sample was mixed thoroughly until homogenized. One part was then transferred to clean, wide-mouthed amber glass containers that were then labeled. After collection, samples were transported to the laboratory and kept at 4°C until analysis.

Chemicals and solvents
Chemicals (sodium sulfate, potassium hydroxide and sulfuric acid) and solvents (high performance liquid chromatography grade acetonitrile, hexane and dichloromethane) were purchased from Merck India. Pre-cleaned silica gel 60 (0.063-0.100 mm) was obtained from Supelco (Sigma-Aldrich Corp., St. Louis, MO, USA) and used as adsorbent in column chromatography. Prior to use, anhydrous sodium sulfate was cleaned separately with methanol, dichloromethane and acetone in Soxhlet extractor for 8 h each, and stored in air-tight conditions at 130°C. Reference standard solutions of PCBs were purchased from Dr. Ehrenstorfer (Dr. Ehrenstorfer GmbH, Augsburg, Germany) and used for the instrument calibration and quantification.

Sample extraction, clean up and analysis
Sample extraction and clean up was carried out according to validated methods.2 Briefly, a homogenized 20 g sample was dried by mixing with diatomaceous earth (ASE prep DE, Dionex Corp., Sunnyvale, CA, USA) until a free-flowing powder was obtained. The extraction was carried out with accelerated solvent extractor (ASE-350, Dionex Corp.) using acetonitrile/hexane (9:1) solvent mixture in two cycles with 5 min static time. The ASE was operated at 1500 psi and the oven temperature was maintained at 100°C. The extracts were concentrated to 2.0 mL using a rotatory vacuum evaporator (Eyela, Tokyo, Japan). Multilayered silica gel column chromatography on a tri-functional column with neutral, basic and acidic silica was performed to remove interfering organic and polar compounds. Details of methodology for clean up and instrumental analysis are reported elsewhere.

Quality control analysis
Appropriate quality assurance quality control analysis was performed, including analysis of procedural blanks (analyzed concentrations-method detection limit, MDL), random duplicate samples (standard deviation, SD<5%), calibration standard verification (SD<15%) and matrix spike recovery (100±20%).20 PCB congeners were identified in the sample extract by comparing the accurate retention time from the standard mixture and quantified using the response factors from multi-level calibration curves of the standards (r2 value 0.999).

A signal to noise ratio of 3:1 was used to calculate instrument detection limits by using a valid quantifiable peak. Each sample was analyzed in duplicate and the average was used in calculations. Method detection limits were established by processing 8 aliquots of a sample spiked with a quantity sufficient to produce a detectable response (s/n>3) and multiplying the standard deviation by the t0.05,99 value (3.0 for 8 replicates). For statistical calculations the non-detect values of PCB congeners have been reported as <0.01 ng g−1 (MDL of all 28 individual congeners being less than 0.01ng g−1).

Furthermore, it may be noted that our laboratory is ISO 17025 accredited and had been participating in proficiency testing exercises conducted by international agencies, including the Centre d’expertise en analyse environnementale du Québec, and performance scores were satisfactory for PCBs.

Toxic equivalent quotients (TEQ) of each congener were calculated by multiplying the concentration of individual dl-PCB congener with the toxic equivalent factors (TEFs)11 with reference to 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and reported as pg WHO01 TEQ g−1 dry-weight (dw).

Health risk assessment for polychlorinated biphenyls exposure
In this study, assessment of human health risk is discussed as the calculated estimates of the upper-bound exceed probabilistic lifetime cancer risk and non-carcinogenic hazards. Hazard is the exact measure of the magnitude of exposure potential or a quantifiable potential for developing non-carcinogenic health effects after averaged exposure period. Risk is the probability of cancer development in a lifetime after a uniform exposure.23 We estimated the human exposure to PCBs through soil ingestion and the consequent health risk by using equations presented by United States Environmental Protection Agency.24-26 For this purpose, the LADD (lifetime average daily dose), non-cancer risk HQ (hazard quotient) and probabilistic incremental lifetime cancer risks (ILCR) were calculated. LADD is an amount a person takes in as a result of exposure to a chemical in contaminated air, water, soil or food. The input parameters used in the health risk estimation for PCBs are given in Table 1. The equations used for estimating LADD, HQ (non-cancer risk) and probable cancer risk were as follows:

\[
\text{LADD (mg kg}^{-1} \text{day}^{-1}) = (C_s \times IR \times F \times EF \times ED)/(BW \times LT) \\
\text{HQ=LADD/RID} \\
\text{ILCR=LADD x cancer slope factor oral (3)}
\]

where:
- \(C_s\) is the total PCBs concentration in soil (µg kg−1);
- \(IR\) is the soil ingestion rate (mg day−1);
- \(F\) is the unit conversion factor (10−5);
- \(EF\) is exposure frequency (days/year);
- \(ED\) is the exposure duration (year);
- \(BW\) is the body weight (kg);
- \(LT\) is the lifetime which is equal to exposure duration x 365 days (days);
- \(RID\) is the reference dose for individual dl-PCB congener (mg kg−1 day−1).

An RID is a daily intake rate that is estimated to cause no adverse health effects over a specific exposure duration. Non-carcinogenic risks (HQ) were assessed by comparing exposure with RID of each dl-PCB and the total was reported for each sampling location. Cancer risk for dioxin-TEQ was calculated for each of the 12 dl-PCB congeners from LADD by multiplying slope factor for dioxin (150,000/mg kg−1 day−1) and the total was reported. Cancer risk for non-dl-PCBs was calculated from LADD of 28 PCBs by multiplying the upper bound cancer slope factor (2/mg kg−1 d−1). The upper

Table 1. Summary of input parameters used in calculations for health risk assessment.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
<th>Unit</th>
<th>Point estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs</td>
<td>PCB concentration</td>
<td>µg kg−1</td>
<td>Data from this study</td>
</tr>
<tr>
<td>CTEQ</td>
<td>TEQ concentration</td>
<td>µg TEQ kg−1</td>
<td>Data from this study</td>
</tr>
<tr>
<td>IR</td>
<td>Soil ingestion rate</td>
<td>mg day−1</td>
<td>100 (adults), 200 (children)</td>
</tr>
<tr>
<td>EF</td>
<td>Exposure frequency</td>
<td>Days/year</td>
<td>365 days</td>
</tr>
<tr>
<td>ED</td>
<td>Exposure duration</td>
<td>Years</td>
<td>70 (adults), 12 (children)</td>
</tr>
<tr>
<td>BW</td>
<td>Body weight</td>
<td>Kg</td>
<td>70 (adults), 27 (children)</td>
</tr>
<tr>
<td>LT</td>
<td>Life time</td>
<td>Days</td>
<td>70×365=25,550 (adults)</td>
</tr>
<tr>
<td>CSF</td>
<td>Cancer slope factor</td>
<td>Per mg kg−1 day−1</td>
<td>Dioxin-TEQ: 150,000 Non-dl-PCBs: 2 (upper bound)</td>
</tr>
<tr>
<td>F</td>
<td>Unit conversion factor</td>
<td>-</td>
<td>10−5</td>
</tr>
</tbody>
</table>

Cs, concentration in soil; dl-PCBs, dioxin-like polychlorinated biphenyls; TEQ, toxic equivalent quantities.
bound slope factor is used for those exposure pathways for which environmental processes are likely to increase health risk, such as exposure from consumption of foods, sediment or soil ingestion, and dust or aerosol inhalation.

Results

Polychlorinated biphenyl concentrations in soil

The concentrations of $\sum$PCBs and individual 28 congeners in urban soils from Delhi, India, are presented in Table 2. The observed levels of total PCBs ranged between 1.08-100.67 ng g$^{-1}$ (dw) with the mean and median of 21.16 ng g$^{-1}$ and 10.16 ng g$^{-1}$ ($\pm$5.24 ng g$^{-1}$), respectively, which is at par with those of other cities around the world. The most common congener numbers among studied PCBs were CB-44, CB-52 and CB-138. The concentration range of 12 dl-PCBs was 0.10-22.57 ng g$^{-1}$ (mean 5.33 ng g$^{-1}$$\pm$0.55 ng g$^{-1}$, median 2.00 ng g$^{-1}$$\pm$0.55 ng g$^{-1}$) and accounted for approximately 25% of total PCBs. TEQ of 12 dl-PCBs, calculated using WHO 2005-TEFs, ranged from less than 1 to 387 pg-TEQ g$^{-1}$ (mean 73$\pm$28 pg-TEQ g$^{-1}$). Non-ortho-PCBs (CB-77, CB-81, CB-126 and CB-169) were the sole contributors and accounted for over 99% of total TEQ (Table 3). Tetrachlorinated, pentachlorinated and hexachlorinated biphenyls were the dominant homologues groups of PCBs (Table 4, Figure 1).

Health risk assessment

Adults and children may be exposed to contaminants in soil and may also take chemicals from soil through different intake pathways, such as ingestion, inhalation and dermal contact. Figure 2 shows average of $\sum$PCBs in urban soil at different locations in Delhi, India. The calculated average daily intake of PCBs through soil ingestion by adults and children in Delhi was 3.02$\times$10$^{-8}$ mg kg$^{-1}$ d$^{-1}$ and 1.57$\times$10$^{-7}$ mg kg$^{-1}$ d$^{-1}$, respectively (Table 5), for a soil PCB concentration of 21.2 µg kg$^{-1}$. With respect to RfD, the average LADD for adults and children was less than 1% and less than 5%, respectively, of the RfD. The calculated value of TCDD substituted WHO-TEQ daily intake for adults and children was 1.05$\times$10$^{-10}$ mg TEQ kg$^{-1}$ d$^{-1}$ when soil TEQ was 0.073 µg kg$^{-1}$ (Table 5). The calculated probability cancer risk estimate for PCB exposure from ingestion of soil was 6.04x10$^{-6}$ ($\sum$PCBs) to 1.57x10$^{-5}$ ($\sum$TEQ) and 3.13x10$^{-5}$ ($\sum$PCBs) to 8.15x10$^{-5}$ ($\sum$TEQ) for Delhi adults and children, respectively (Table 5). The quantified non-carcinogenic HQ for soil ingestion pathway of PCBs was 0.105 and 0.330 for Delhi adults and children, respectively (Figure 3).

Table 2. Polychlorinated biphenyl congener concentrations (ng/g dw) in urban soils from Delhi, India.

<table>
<thead>
<tr>
<th>Congeners</th>
<th>Range</th>
<th>Mean</th>
<th>Median</th>
<th>SE*</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCB-18</td>
<td>0.17-4.31</td>
<td>1.02</td>
<td>0.51</td>
<td>0.18</td>
<td>3.8</td>
</tr>
<tr>
<td>PCB-37</td>
<td>0.21-7.07</td>
<td>1.38</td>
<td>0.76</td>
<td>0.27</td>
<td>5.1</td>
</tr>
<tr>
<td>PCB-44</td>
<td>0.24-15.60</td>
<td>2.78</td>
<td>1.13</td>
<td>0.61</td>
<td>11.2</td>
</tr>
<tr>
<td>PCB-49</td>
<td>0.22-10.20</td>
<td>1.96</td>
<td>1.01</td>
<td>0.36</td>
<td>7.9</td>
</tr>
<tr>
<td>PCB-52</td>
<td>0.18-11.2</td>
<td>2.56</td>
<td>1.00</td>
<td>0.52</td>
<td>11.3</td>
</tr>
<tr>
<td>PCB-70</td>
<td>0.08-6.30</td>
<td>1.30</td>
<td>0.43</td>
<td>0.28</td>
<td>5.3</td>
</tr>
<tr>
<td>PCB-74</td>
<td>0.16-5.11</td>
<td>1.35</td>
<td>0.59</td>
<td>0.23</td>
<td>5.5</td>
</tr>
<tr>
<td>PCB-119</td>
<td>&lt;0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCB-128</td>
<td>0.09-2.62</td>
<td>0.55</td>
<td>0.34</td>
<td>0.10</td>
<td>2.2</td>
</tr>
<tr>
<td>PCB-138</td>
<td>0.06-12.80</td>
<td>2.54</td>
<td>1.02</td>
<td>0.55</td>
<td>11.1</td>
</tr>
<tr>
<td>PCB-151</td>
<td>0.12-2.66</td>
<td>0.70</td>
<td>0.21</td>
<td>0.12</td>
<td>1.9</td>
</tr>
<tr>
<td>PCB-168</td>
<td>0.08-9.68</td>
<td>1.61</td>
<td>0.49</td>
<td>0.37</td>
<td>7.6</td>
</tr>
<tr>
<td>PCB-170</td>
<td>&lt;0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCB-177</td>
<td>0.09-0.76</td>
<td>0.36</td>
<td>0.22</td>
<td>0.04</td>
<td>1.1</td>
</tr>
<tr>
<td>PCB-187</td>
<td>0.11-0.70</td>
<td>0.41</td>
<td>0.41</td>
<td>0.06</td>
<td>0.3</td>
</tr>
<tr>
<td>PCB-207</td>
<td>0.05-0.55</td>
<td>0.32</td>
<td>0.32</td>
<td>0.03</td>
<td>0.5</td>
</tr>
<tr>
<td>$\sum$PCBs</td>
<td>0.77-78.93</td>
<td>15.83</td>
<td>7.30</td>
<td>3.29</td>
<td>74.8</td>
</tr>
</tbody>
</table>

Table 3. Toxic equivalent quotients of dioxin-like polychlorinated biphenyl congeners in urban soils from Delhi, India.

<table>
<thead>
<tr>
<th>dl-PCBs (pg WHO 2005-TEQ g$^{-1}$)</th>
<th>Range</th>
<th>Mean</th>
<th>SE</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non ortho-PCBs</td>
<td>&lt;1-387</td>
<td>73</td>
<td>28</td>
<td>99</td>
</tr>
<tr>
<td>Mono ortho-PCBs</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>$\sum$dl-PCBs</td>
<td>&lt;1-387</td>
<td>73</td>
<td>28</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 4. Polychlorinated biphenyl homologues (3-7 CB) in urban soils from Delhi, India (ng/g dw).

<table>
<thead>
<tr>
<th>Homolog</th>
<th>Tri-CB</th>
<th>Tetra-CB</th>
<th>Penta-CB</th>
<th>Hexa-CB</th>
<th>Hepta-CB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>1.88</td>
<td>9.03</td>
<td>4.94</td>
<td>4.52</td>
<td>0.53</td>
</tr>
<tr>
<td>Median</td>
<td>1.05</td>
<td>3.55</td>
<td>1.63</td>
<td>1.31</td>
<td>0.22</td>
</tr>
<tr>
<td>Range</td>
<td>&lt;0.01-11.38</td>
<td>0.23-48.93</td>
<td>&lt;0.01-31.30</td>
<td>0.06-24.31</td>
<td>&lt;0.01-2.05</td>
</tr>
<tr>
<td>% of $\sum$PCBs</td>
<td>10.3</td>
<td>49.0</td>
<td>17.3</td>
<td>18.8</td>
<td>4.7</td>
</tr>
</tbody>
</table>
Discussion

Concentrations and possible sources

The PCBs contamination levels in soils from Delhi were much lower than soil quality guidelines (1.3 mg/kg or 1300 ng g⁻¹).²⁷ The results of this study were similar to observations reported for urban soils from Kathmandu,⁷ urban soils of Beijing²⁸ and from Tibet.²⁹ However, the concentrations of PCBs in Delhi soils were lower than those of Vietnam,³⁰ Switzerland,³¹ Romania,³² China,³³ San Felipe, Nuevo Mercurio, Zacatecas, Mexico,³⁴ Moscow³⁵ and Guangdong Province, South China,³⁶ but higher than PCBs reported in soils from Turkey.³⁷

The PCB patterns show that the low molecular weighted PCBs were major contributors (60%) compared to high molecular weight PCBs (with 40%). Low molecular weight PCBs were primarily used in electrical equipments while high molecular weight PCBs were mainly used as additives in various applications.³⁸ PCBs had never been produced in India, but are used in industrial applications.³⁹ Possible sources of PCBs releases in the study area may be from electronic and electrical waste recycling and industrial emission depositions. During the burning of different mixtures of waste content, garden waste, paper, plastics, PVC (polyvinyl chloride) and painted wood may produce relatively large amounts of dioxin like-PCBs.⁴⁰-⁴²

Risk estimates

To ensure public health safety, a tolerable daily intake (TDI) has been set by international agencies. The TDI is the amount of intake per kg of body weight per day of a chemical substance suspected of having adverse health effects when absorbed into the body over a long period of time. The joint FAO/WHO Expert Committee on Food Additives⁴³ recommended a TDI of 1.0 pg TEQ kg⁻¹d⁻¹ for acute, sub-chronic and chronic exposures to dioxins. The European Commission⁴⁴ established an acceptable weekly intake of 14 pg WHO-TEQ/kg body weight for dioxins and 12 pg dioxin-like PCBs. The Japanese government⁴⁵ established the TDI of dioxins at 4 pg-TEQ kg⁻¹d⁻¹.

The observed LADD of TEQ intake for adults (1.05×10⁻¹⁰ mg TEQ kg⁻¹d⁻¹) and children (3.02×10⁻¹⁰ mg TEQ kg⁻¹d⁻¹) are much lower than recommended acceptable daily intake. The acceptable risk distribution is equal or lower than 10⁻⁶ for carcinogens and may be up to 10⁻⁴. The observed ILCR (10⁻⁴-10⁻⁵) and HQ values less than the acceptable risk level (HQ=1) (Figure 3) suggests minimum risk to the adults and children due to exposure to PCBs through urban soils in Delhi.

Table 5. Calculated polychlorinated biphenyl exposure from urban soil and risk for adults and children.

<table>
<thead>
<tr>
<th>Soil ingestion</th>
<th>Concentration (µg/kg)</th>
<th>Adults</th>
<th>Children</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LADD</td>
<td>Risk</td>
<td>LADD</td>
</tr>
<tr>
<td>Dioxin-TEQ</td>
<td>0.073</td>
<td>1.05×10⁻¹⁰</td>
<td>1.57×10⁻⁸</td>
</tr>
<tr>
<td>Non-dl-PCBs</td>
<td>21.2</td>
<td>3.02×10⁻⁸</td>
<td>6.04×10⁻⁸</td>
</tr>
</tbody>
</table>

LADD, lifetime average daily dose (mg/kg bw/d); dl-PCB, dioxin-like polychlorinated biphenyls; TEQ, toxic equivalent quotients.

Figure 1. Polychlorinated biphenyl homologs in soil at different locations in Delhi, India.

Figure 2. Average of ∑polychlorinated biphenyls in urban soil at different locations in Delhi, India.

Figure 3. Health risk hazards of polychlorinated biphenyls for adults and children through soil ingestion.
Conclusions

Low concentrations of PCBs in Delhi soils, and subsequently their intake values, were lower than those established in international guidelines. Therefore, estimates of cancer and non-carcinogenic risk through soil ingestion were low, indicating no harmful effects on the population of Delhi. In future, it may be useful to conduct more intensive assessments for persistent organic pollutants, in response to human health and environmental concerns.

References

30. Kishida M, Imamura K, Maeda Y, Lan TTN, Thao NTP, Viet PH. Distribution of persistent organic pollutants and polycyclic aro-


