Soil concentrations, occurrence, sources and estimation of air–soil exchange of polychlorinated biphenyls in Indian cities

Paromita Chakraborty [a], Gan Zhang [b], Jun Li [b], Sakthivel Selvaraj [a], Knut Breivik [c,d], and Kevin C Jones [e]*

[a] *SRM Research Institute and Department of Civil Engineering, SRM University, Kattankulathur, Tamil Nadu, India*

[b] *State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China*

[c] *Norwegian Institute for Air Research, Box 100, NO-2027 Kjeller, Norway*

[d] *University of Oslo, Department of Chemistry, Box 1033, NO-0315 Oslo, Norway*

[e] *Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, UK*

Corresponding author: Dr. Paromita Chakraborty

Tel: +91-44-27417909;

Fax: +91-44-27456702;

E-mail: paromita.c@res.srmuniv.ac.in

ABSTRACT: Past studies have shown potentially increasing levels of polychlorinated biphenyls (PCBs) in the Indian environment. This is the first attempt to investigate the occurrence of PCBs in surface soil and estimate diffusive air-soil exchange, both on a regional scale as well as at local level within the metropolitan environment of India. From the north, New Delhi and Agra, east, Kolkata, west, Mumbai and Goa and Chennai and Bangalore in the southern India were selected for this study. 33 PCB congeners were quantified in surface soil and possible sources were derived using positive matrix factorization model. Net flux directions of PCBs were estimated in seven major metropolitan cities of India along urban-suburban-rural transects. Mean Σ33PCBs concentration in soil (12 ng/g dry weight) was nearly twice the concentration found in global background soil, but in line with findings from Pakistan and urban sites of China. Higher abundance of the heavier congeners (6CB–8CB) was prevalent mostly in the urban centers. Cities like Chennai, Mumbai and Kolkata with evidence of ongoing PCB sources did not show significant correlation with soil organic carbon (SOC). This study provides evidence that soil is acting as sink for heavy weight PCB congeners and source for lighter congeners. Atmospheric transport is presumably a controlling factor for occurrence of PCBs in less polluted sites of India.

Key words: PCB, Levels, Sources, Fugacity Fractions, PMF Model

1. INTRODUCTION

High levels of polychlorinated biphenyls (PCBs) have been occasionally reported in developing regions at lower latitudes, despite a relatively limited historical usage of these chemicals (Breivik et al., 2011).Urban centers are the primary source regions for PCBs (Harner, 2004; Iwata, 1993; Jaward, 2004). PCBs were never manufactured in India but recently high atmospheric PCBs have been observed in the urban environment along the coastal length of India (Zhang, 2008) particularly in the metropolitan cities(Chakraborty et al., 2013). Chakraborty et al.(2013) reported profound influence of primary sources associated with cumulative growth of informal electronic waste recycling among the informal scrap dealers, ship breaking activities and secondary sources like open burning of municipal solid waste or biomass burning on the atmospheric PCBs in Indian cities. Soil represents an interesting archive of PCBs as these are influenced by past atmospheric deposition. PCBs have a strong affinity for soil organic matter (SOM) (Mackay, 2001) and their global distribution is retarded by soil (Ockenden et al., 2003). Studies conducted in developed nations e.g., in the urban residential soil of Iowa USA (Martinez et al., 2012) and urban areas of European cities (Cachada et al., 2009) reported heterogeneity in soil PCB distribution. Reported soil PCB concentrations in the developing countries of Southeast Asia are also highly variable. Average PCB concentration in Chinese surface soil (Ren et al., 2007) is one tenth of the global background soil concentration (Meijer et al., 2003). However, urban locations and electronic waste (e-waste) recycling sites in China reported much higher PCB concentrations in soil (Jiang et al., 2011; Tang et al., 2010). Recent studies reported elevated levels of PCBs in soil from Pakistan (Syed et al., 2013).PCB burden in soil has been reported from the north eastern states of India (Devi et al., 2014) and agricultural sites of New Delhi (Kumar et al., 2011). Following ratification of the Stockholm Convention, Ren et al.(2007) encouraged the need for more national level studies to assess contemporary PCB burden and emission sources. Despite clear evidence of increasing atmospheric PCBs in India from early 1990s (Iwata et al., 1994) very limited information is available on the soil PCBs concentration from the highly populated urban environment of

India and on the possible role of soils as a secondary source to the atmosphere. The main objectives of this study were to: (i) investigate the surface soil PCB concentration along urban-suburban-rural transect from seven major metropolitan cities of India viz., New Delhi and Agra from North, Kolkata from East, Mumbai and Goa from West and Chennai and Bangalore from Southern part of India (ii) estimate the net air-soil exchange of PCBs using previously published atmospheric data from all these cities (Chakraborty et al., 2013) (iii) identify potential sources using multivariate pattern analysis technique and receptor model and (iv) assess the regional variability and identify potential hotspots at local level within each metropolitan city.

2. MATERIALS AND METHODS

2.1. Sampling.

84 84 surface soil samples (0–20 cm) were collected from seven major cities of India along urban, suburban and rural transects (Fig. 1). Surface soil sampling was conducted during the same time frame of active air sampling in these cities (Chakraborty et al., 2013). Details of each site can be obtained from Supplementary Material. Five sub samples were collected from an approximated 100 square meter grid in zig-zag manner and mixed well to make one representative composite sample from each site. During the sample collection, gloves were worn, and surface soil samples collected were handled using acetone-rinsed stainless steel spatula. At the end of the collection, the soil samples were sealed in ziploc bags, and returned to the laboratory where they were stored in sealed, solvent-cleaned brown glass jars at −20 °C until extraction.

2.2. Extraction and Analysis

Soil samples were air dried, mixed and sieved through a 2mm sieve. Prior to extraction a mixture of surrogate standards (2,4,5,6-tetrachloro-m-xylene (TCmX), decachlorobiphenyl (PCB209), $^{13}C_{12}$-PCB138 and $^{13}C_{12}$-PCB180 were added to each of the samples. Soil samples (20 g each) were Soxhlet extracted for 18 h with dichloromethane (DCM). Activated copper granules were added to the collection flask to remove

potential elemental sulfur. The extract was rotary evaporated and transferred with hexane to a 15 ml amber vial. This was blown down under a gentle stream of nitrogen to about 0.5 ml and cleaned on a 8 mm i.d. chromatography column with 6 cm alumina (BDH neutral Alumina 3% deactivated), 10 cm of silica gel (Merck Silica 60 3% deactivated), 10 cm of 50% sulfuric acid silica and 1 cm of baked sodium sulfate (all baked at 450 °C overnight) and the column was eluted with 10 ml mixture of 50:50 hexane: DCM (v/v). The samples were reduced to a final volume of 25 µl after adding 25 µl of dodecane as solvent keeper and a known quantity of PCB-54 was added as an internal standard prior to GC–MSD analysis. PCBs analysis was carried out on a Finigan- TRACE GC-MS system with a CP-Sil 8 CB capillary column (50 m, 0.25 mm, 0.25 µm), operating under single-ion monitoring (SIM) mode. Helium was used as the carrier gas at 1.2 ml min−1 under constant-flow mode. The oven temperature began at 60 °C for 1 min and increased to 290 °C (10 min hold time) at a rate of 4 °C min^{-1}. Splitless injection of a 1 µl sample was performed with a 5 min solvent delay time. Injector temperature was at 250 °C. A total of 33 PCB congeners were detected and quantified. Congener details have been given in Supplementary Material.

2.3. QA/QC

Chemical standards were purchased from Accustandard Co. US. Method blanks were analyzed for every batch of 9 samples to provide an indication of the overall precision of the laboratory method. Limit of Detection (LOD) were derived from the blanks and quantified as the mean plus three times the standard deviation of the concentration in the blanks, based on surface soil sampling. LOD values varied between 0.0019-0.0023 ng/g dry weight (dw).Procedural blanks were below the instrument quantification limit. Surrogate recoveries were 91-135% (mean 97%) for PCB209, 72-81% (mean 77%) for TC*m*X, 87-91% (mean 89%) for $^{13}C_{12}$-PCB138 and 82-109% (mean 90%) for $^{13}C_{12}$-PCB180. Concentrations of the samples were corrected based on the recovery ratios and blank values.

2.4. Soil Organic Carbon

1 g of soil sample was mixed with 3 ml of 10 % HCl acid and kept for 8 h to remove inorganic carbon. Soil samples were then rinsed with doubled distilled water (three times) dried in oven at 45^0C. Weight of the soil samples were recorded before analysis by Elemental Carbon–Hydrogen–Nitrogen Analyzer (Elementar VARIO EL III).

2.5. Fugacity Fractions

Fugacity fractions (*ff*) were calculated for eight PCB congeners viz., PCB-28, 52, 101,105,118, 138, 153 and 180. The average concentration of atmospheric PCBs from each of the Indian cities measured by active air sampling during similar time frame (Chakraborty et al., 2013) were used to calculate the fugacity in the air (f_{AAS}). Measured soil concentrations from each site from this study were used to calculate the fugacity in soil (f_s) for each site. The following equations were used:

$$ff = f_s / (f_s + f_{AAS}) \quad (1)$$

$$fs = C_s RT / 0.411 \Phi_{OM} K_{OA} \quad (2)$$

$$f_{AAS} = C_{AAS} RT \quad (3)$$

where, C is the concentration in the medium (mol m^{-3}), R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature (K), Φ_{OM} is the fraction of the organic matter (1.7 times of the organic carbon fraction) in the soil and K_{OA} is the octanol-air partitioning coefficient. K_{OA} values at 25 ^{0}C (Li et al., 2003) were adjusted using the surface soil temperature for each city. The factor 0.411 improves the correlation between the soil-air partitioning coefficient and K_{OA} (Hippelein and McLachlan, 1998; Meijer et al., 2003a; RůŽičková et al., 2007).

2.6. Positive Matrix Factorization (PMF).

U.S. EPA positive matrix factorization (V5.0) was used to determine the optimal number of PCB sources in Indian soil. Details of the model are provided in the Supplementary document. PMF is a receptor model to identify and quantify the contribution of various sources of pollution by using a multivariate statistical method. By assuming that there is no degradation or selective retention in soils or other matrices on the way from sources to environmental samples (receptors), PMF can estimate how much each different source type contributes to different environmental samples (Hsu et al., 2003; Khairy et al., 2015; Stout and Graan, 2010; Wang et al., 2009). The data set used was an 84 × 33 matrix (sample number, number of PCB congeners) and the model was run in the default robust mode to decrease the influence of extreme values. All the variables were strong. Measured concentrations of PCB congeners were entered separately for each site. Since all the data were above the method detection limit (MDL), uncertainty was calculated using the following equation:

$$\sqrt{(Error\% * concentration)^2 + (MDL)^2}$$

To determine the PCB congeners that can be used for source profiles, the coefficient of determination (R^2) measuring the goodness of fit between the measured and modeled concentrations was used. In this application, the rotational freedom existed. The acceptable rotations were determined by trial and error. To achieve the optimal result, the PMF was run using different initial seeds for the iterative fitting process, and solutions with different numbers of sources were examined. The chemical fingerprints in this study are not individual in the sense that specific source can be identified. Instead, the fingerprints of plausible sources as identified by PMF have been used to identify a type of activity or process.

2.6. Statistical Analysis.

SPSS Version 19 were used for Principal Component Analysis and other statistical analysis.

3. Results and discussion

3.1. Soil PCB concentration.

Fig. 1 shows the concentration of Σ_{33}PCBs in soil (ng/g dw) for each site of seven major Indian cities. Detailed range of each PCB congener for each city has been provided in Table S1. Σ_{33}PCBs in Indian soil (ng/g dw) showed the highest range for urban locations (2–125, Avg ± SD, 16 ± 23) followed by rural (1–116) (Avg ± SD, 11±25) and suburban locations (2–15) (Avg ± SD, 6 ± 3).Majority of the measured indicator congeners were high mostly in the urban centers (Fig. 2A). Excluding the rural site in Bangalore (B-03), with maximum soil PCB concentration among all the rural sites, PCB distribution pattern for all other cities showed a decreasing trend along urban-suburban-rural transect. Dioxin like PCBs (dl-PCBs) ranged between 0.25-18 ng/g dw (Avg ± SD, 1.7 ± 0.9). Unlike B-03, dl-PCBs also showed a similar decreasing trend along urban-suburban-rural transect.

Average PCB concentration in Indian cities (12 ng/g) was higher than the average concentration reported for Chinese surface soil (0.5 ng/g) (Ren et al., 2007) but comparable to recent study from Pakistan (18 ng/g) (Syed et al., 2013). Relatively high soil PCB concentrations (7–4000 ng/g Avg, 390ng/g) were reported from southern part of China in Guangdong province where intensive informal recycling of electronic waste (e-waste) is practiced (Wang et al., 2011). In general, tetra homologue (4-CB) and hexa homologue (6-CB) dominated the overall PCB concentration followed by penta homologue (5-CB) contributing about 28 %, 27 % and 13 % respectively (Fig. S1). Such prevalence of 4-CB through 6-CB is comparable to informal e-waste recycling sites of China (Wang et al., 2011). Excluding B-03, most of the rural sites in India is dominated by tri homologue (3-CB) and tetra homologue (4- CB) as observed in Chinese rural and background soil (Ren et al., 2007). Elevated concentrations of heavier congeners particularly the octa homologue (8-CB) was prevalent mostly in the urban sites. Recently, heavier congeners were observed in agricultural soil of New Delhi (Kumar et al., 2011).

3.2. Effect of Soil Organic Carbon

Soil organic carbon (SOC) content is considered important for the binding of hydrophobic pollutants (Ribes

et al., 2002). Σ_{33}PCBs and SOC were examined statistically by evaluating the correlation between the two for each city. Excluding B-03, a strong correlation was observed between others sites of Bangalore and corresponding SOC ($p < 0.01$, $R^2 = 0.89$). Fair correlation was observed for soil samples from Goa ($p < 0.05$, $R^2 = 0.68$). For New Delhi the overall correlation was good ($R^2 = 0.60$, $p < 0.01$) but it further improved after excluding the site (D-03) with maximum soil PCB concentration. It is to be noted that Σ_{33}PCBs concentration in soil and corresponding SOC did not show any correlation for Chennai, Mumbai and Kolkata. Atmospheric transport is an efficient mechanism for SOC redistribution between contaminated and pristine soil (Wang et al., 2011). Lack of correlation between SOC and sites having high soil PCB concentration can be considered as an indicator for ongoing PCB sources. Similarly during 1950–1965, UK soil from agricultural regions did not show any correlation with total organic carbon in soil (Vane et al., 2014). But in 1993 a general decrease of PCB in the soils from the same sites showed a good correlation (Vane et al., 2014).

3.3. Estimation of Air-soil Exchange of PCBs

Fugacity fractions *(ff)* were used to estimate net diffusive exchange of eight PCB congeners between air and soil (Fig. 2B). In general, *ff* values showed net volatilization for lighter congeners like PCB-28 and PCB-52 in most of the sites particularly in urban centers. Excluding four sites (outliers), remaining sites showed net deposition of 5CB- 7CB congeners (Fig. 2B). Outliers in Fig. 2B are sites having elevated Σ_{33}PCBs concentration in soil with higher *ff* values (>0.5). Unlike other cities, the *ff* values of all the eight congeners displayed net deposition for New Delhi and Agra, consistent with other organochlorine compounds (Chakraborty et al., 2013). Net deposition of PCBs in Indian cities is presumably governed by the ongoing sources. Soil seems to act as sink for heavier PCB congeners even in the tropical cities. Volatilization of lighter congeners was evident mostly in the urban sites.

3.4. Source Profiling using PMF Model

Multivariate pattern analysis technique and receptor model, such as Principal Component Analysis (PCA)

and Positive Matrix Factorization (PMF), were used to trace PCB sources. PCA identified three broad factors viz., combustion of municipal solid waste or electronic waste or industrial waste, medical waste incineration or municipal waste incineration and atmospheric transport (Fig. S2 and Table S2). PMF analysis further clearly identified six factor profiles (sources) (Fig. 3) and fingerprints (Fig. 4) for PCBs, based on the congener distribution for each source type that exclusively or largely appeared in the factor. PMF analysis explained a better source profiling over PCA.

Factor profile A contributed 16 % with dominance of 4-CB (Figs. 3 and 4). In addition to 4-CB, 5-CB through 8-CBwere dominant in sites where informal e-waste recycling is prevalent (Fig. 1, SI Fig. 1) 6-CB and 7-CB were dominant in the atmospheric profile of e-waste recycling sites (Chakraborty et al., 2013). Various steps of informal electronic waste recycling are being carried out in and around those sites. Piles of waste containing electronic devices are set to fire for metal recovery. Most of the plastic parts of e-wastes are openly burnt in the informal e-waste recycling sites. Among dl-PCBs, PCB-105 is a major contributor for this profile. For every city PCB-105 was dominant near e-waste recycling sites. High dl-PCBs in the informal electronic waste recycling sites might be associated with burning of electric cables and components coated with polyvinyl chloride. Hence this factor is attributed to informal e-waste recycling in Indian cities.

Factor profile B accounted for 24 % with dominance of 5-CB. Among 5-CBs, PCB-126 was the dominant congener. Higher percentages of PCB-82, 77 and 126 were abundant in soil from the urban centers and certain suburban and rural sites close to the industrial belt. Expansion of industrial sector in the suburbs and rural locations particularly manufacturing units is increasing with the rapid growth of industrialization in India. Moreover during the National Implementation Program development in India, the power sector disposed at least 7700 tonnes of PCBs, PCB-containing equipment, PCB-containing mineral oil and wastes so as to create national capacity for proper management of PCBs (Pandit et al., 2006). Higher abundance and dominance of 8-CB primarily in the industrial belt (Fig. S1) could be associated with the power sector. Combustion of coal and industrial waste might have contributed to the measured concentration of non ortho

PCBs like PCB-77 and PCB 126 (Chi et al., 2007). Hence it can be inferred that this factor reflects mostly combustion of coal or industrial waste.

Factor profile C accounted for 19 % and nearly 50 % of this factor was loaded with 6-CB. PCB-128 is the dominant congener (Fig. 3). Similar concentrations and distribution patterns were observed for PCB-128 and PCB-118. PCB-118 is a major component of technical formulation. Significant correlation ($p < 0.01$) exists between PCB-118 and Σ_{33}PCB concentration in soil. PCB-118 is typically released during the municipal solid waste incineration (Dyke et al., 2003). For 44 % sites, PCB-118 contributed about 10 % of dl-PCBs and for another 35 % sites, PCB-118 contributed about 20 %, reflecting medical waste incineration (MWI) pattern and municipal solid waste incineration (MSWI) pattern, respectively (Liu et al., 2013). Unfortunately, in Indian cities, MSWI is not very much practiced but small incinerators are used for burning hospital waste (Chakrabarty et al., 1995; Dayal, 1994; Lal, 1996; Sharholy et al., 2005).
Hence this factor profile can be attributed to medical waste incineration (MWI) and municipal solid waste incineration (MSWI) as potential sources for PCBs in Indian cities.
Factor profile D is contributing 11% with the dominance of PCB-28. Such lighter congener might be reflecting fresh inputs. Indicator congener, PCB-28 was observed in the coastal sites located at close proximity from the ports, docks or ship dismantling area. Furthermore elevated concentrations of heavier congeners (5-CB and 6-CB) were observed in those coastal sites, consistent with atmospheric PCB profiles (Chakraborty et al., 2013). Hence, this factor has been attributed to ship breaking and port activities. We suspect PCB concentration at such sites have been influenced by very dense transportation activity of ferrous scrap trucks, ship dismantling activities, and busy ports with scrap iron dock yards.
Factor profile E contributed 16 %. This factor impacted all the PCB homologues. PCB-52 contributed about 77% of this factor. PCB-52 is the dominant and abundant PCB congener in Indian surface soil with elevated concentrations in and around the open dumpsites. PCB-52 has been mostly retained in soil possibly due to its higher half-life (15 years) combined with extensive global production (Breivik et al., 2002) and extensive usage of the associated technical formulation. Open burning of solid waste resulted in elevated PCB levels

in Indian cities and PCB-52 was the dominant congener in air (Chakraborty et al., 2013). Since open burning of solid waste is practiced all over India hence we speculate it represents this factor profile. Factor F contributed 14 % and was dominated by 3-CB and 4-CB. 96 % of PCB-30 has been contributed by this factor. Abundance of such lighter congeners in those rural sites where total soil PCB concentrations were comparatively low could be due to atmospheric transport from the emission source regions (Chakraborty et al., 2013). Hence, this factor has been mainly attributed to (short range) atmospheric transport.

3.5. Local and Regional Distribution

3.5.1. Northern India: New Delhi and Agra.

Highest Σ_{33}PCBs concentration in New Delhi was observed at an urban commercial site in the eastern part of New Delhi with dominance of 4-CB and 5-CB congeners (Fig. 1, SI Fig. 1). Eastern part of New Delhi houses several informal electronic waste recycling units. New Delhi alone generates 15,000 tonnes/year in addition to the electronic waste (e-waste) imported for recycling purpose. Elevated concentration of 6-CB congeners were observed in the sites located in the southern part of New Delhi. Relatively high dl-PCBs and maximum 6-CB was observed at Okhla (site, D-05) where a municipal waste incineration plant is gaining attention in the recent years due to dioxin emission. In New Delhi and Agra, deposition of the lighter congeners viz., PCB-28 and -52 (Fig. 2B) in all the sites was possibly due to lower winter time temperature under subtropical climate, consistent with other persistent organic pollutants (Chakraborty et al., 2013). 4-CB is the predominant homologue in Agra as observed in New Delhi but with much lower soil PCB concentration. This might have resulted due to atmospheric transport of PCBs, mostly from the point source regions especially from the eastern part of New Delhi (Chakraborty et al., 2015). It is noteworthy that factor profile F was the major contributor for 4-CB congeners in all the samples from Agra. Hence (short range) atmospheric transport seems to act as a major source for PCBs in Agra.

3.5.2. Eastern India: Kolkata.

Σ_{33}PCBs in urban sites of Kolkata is two folds higher than suburban and rural sites (Fig. 1). Maximum concentration was found in Dhapa, an urban dumpsite (K-18) with dominance of 4CB–7CB congeners.

Uncontrolled open burning of municipal solid waste including electronic waste and biomedical waste is in practice in Dhapa. In Kolkata, highest dl-PCB level was observed in this site. Earlier studies reported high dl- PCBs in human milk from this dumpsite (Someya et al., 2010). Similarly another site (K-08) close to K-18 also showed similar congener pattern t (Fig. S1). 70% of overall PCB contribution in Kolkata is due to low molecular weight congeners (3-CB and 4-CB). Also, 6-CB (PCB-138 & -158) were predominant within the city limit. Elevated PCB levels were observed along the Hooghly Dock in Howrah and sites near Calcutta port. Also Factor E had major contribution on samples from Kolkata. Hence port activities can be a potential source for PCBs in Kolkata. Fugacity fractions for lighter congeners from urban and suburban sites of Kolkata indicate their re-emission from soil whereas net deposition or close to equilibrium state was observed in the rural sites.

3.5.3. Western India: Mumbai and Goa.

Σ_{33}PCBs in Mumbai was found to be 2 folds higher than Goa (Fig. 1). Urban sites of Mumbai showed elevated level of PCBs. Maximum concentration was observed in an urban industrial site (M-05, Kurla), followed by an urban coastal site (M-06, 13 ng/gdw). 50 % sites in Mumbai showed dominance of 4-CB. 5CB–7CB were dominant mostly in the urban sites. Maximum PCB concentration in Goa was observed in a rural coastal site (G-04,Madgaon). Dominance of 5-CB congeners in Goa and coastal sites of Mumbai is consistent with the atmospheric PCB profile in the west coast along the coastal length of India (Zhang, 2008) as well as within the city limit of Mumbai and Goa (Chakraborty et al., 2013). Ship dismantling activities has been a major cause for PCB emission in the atmosphere of the Arabian Sea (Wurl et al., 2006). Highest level of 5-CB, contributing about 69 % of Σ_{33}PCBs concentration, was observed at M-05, consistent with atmospheric PCB profile of urban Mumbai (Chakraborty et al., 2013). Furthermore the ratio of PCB-118 to PCB- 77 for this site (3.8) reflects secondary metal smelting process (Liu et al., 2013). Informal e-waste shredding takes place at few locations close to this site (M-05). Hence this site was possibly impacted by both ship breaking activity and informal e-waste recycling leading to elevated dl-PCB concentration. Re-emission of lighter congeners was observed only in the hotspots within the city limit of Mumbai.

3.5.4. Southern India: Chennai and Bangalore:

Highest Σ_{33}PCB concentration in this study has been observed in an urban site of Chennai city (C-18; 125 ng/g dw) (Fig. 1). A nearby urban site also showed elevated PCB concentration (C-07; 82 ng/g dw). Informal e-waste recycling processes (shredding) is prevalent in these two sites. It is noteworthy that Chennai city being located at close proximity from the port, imports e-waste in addition to its domestic generation of nearly 47,000 tonnes of e-waste annually. C-18 contributed the maximum loading for the factor profile of informal e-waste recycling. Interestingly, the ratio of PCB-118 to PCB-77 at C-07 was 9.6, deviating from other sites. This deviation is suspected to be associated with informal e-waste recycling taking place at close proximity from this site. Second highest Σ_{33}PCBs concentration in this study was observed in a rural site namely Arudi village (B-03) with 10 folds higher concentrations compared to other sites in Bangalore. Arudi village was once an open solid waste dumping ground. Site B-03 contributed the maximum loading for the factor profile of open burning of dumped waste. It is to be noted that hotspots like B-03, C-06, C-07 and C-18 with high soil PCB concentration exhibited volatilization of all the indicator congeners excluding PCB-180 (Fig. 2B). Maximum range of dl-PCBs in India was observed in the hotspots of Chennai and Bangalore.

ACKNOWLEDGEMENT

This work was supported by the Chinese Academy of Sciences (No. KZCX2-YW-GJ02) and Natural Scientific Foundation of China (NSFC) (Project No. 41025020), and by the Fast Track Grant under Young Scientist Scheme by the Department of Science and Technology, Government of India (SR/FTP/EE-44/2012). KB was supported by the Research Council of Norway (213577). Authors are thankful to Mr. Elvis Dsouza, Managing Partner EDPC Polymer industries for his extensive support during sample collection.

REFERENCES

Breivik K, Gioia R, Chakraborty P, Zhang G, Jones KC. Are reductions in industrial organic contaminants emissions in rich countries achieved partly by export of toxic wastes? Environmental science & technology 2011; 45: 9154-9160.

Breivik K, Sweetman A, Pacyna JM, Jones KC. Towards a global historical emission inventory for selected PCB congeners—a mass balance approach: 1. Global production and consumption. Science of the Total Environment 2002; 290: 181-198.

Chakrabarty P, Srivastava V, Chakrabarti S. Solid waste disposal and the environment–a review. Indian Journal Of Environmental Protection 1995; 15: 39-43.

Chakraborty P, Zhang G, Eckhardt S, Li J, Breivik K, Lam PK, et al. Atmospheric polychlorinated biphenyls in Indian cities: levels, emission sources and toxicity equivalents. Environmental Pollution 2013; 182: 283-290.

Chakraborty P, Zhang G, Li J, Sivakumar A, Jones KC. Occurrence and sources of selected organochlorine pesticides in the soil of seven major Indian cities: Assessment of airâ€“soil exchange. ENVIRONMENTAL POLLUTION 2015; 204: 74-80.

Chi KH, Chang MB, Kao SJ. Historical trends of PCDD/Fs and dioxin-like PCBs in sediments buried in a reservoir in Northern Taiwan. Chemosphere 2007; 68: 1733-1740.

Dayal G. Solid wastes: sources, implications and management. Indian Journal of Environmental Protection 1994; 14: 669-677.

Devi NL, Yadav IC, Shihua Q, Chakraborty P, Dan Y. Distribution and risk assessment of polychlorinated biphenyls (PCBs) in the remote air and soil of Manipur, India. Environmental Earth Sciences 2014; 72: 3955-3967.

Dyke PH, Foan C, Fiedler H. PCB and PAH releases from power stations and waste incineration processes in the UK. Chemosphere 2003; 50: 469-480.

Harner T, Shoeib, M., Diamond, M., Stern, G., Rosenberg, B.,. Using passive air samplers to assess urban – rural trends for persistent organic pollutants. 1. Polychlorinated biphenyls and organochlorine pesticides. Environmental Science & Technology 2004; 38: 4474-4483.

Hippelein M, McLachlan MS. Soil/air partitioning of semivolatile organic compounds. 1. Method development and influence of physical-chemical properties. Environmental science & technology 1998; 32: 310-316.

Hsu Y-K, Holsen TM, Hopke PK. Locating and quantifying PCB sources in Chicago: receptor modeling and field sampling. Environmental science & technology 2003; 37: 681-690.

Iwata H, Tanabe S, Sakai N, Nishimura A, Tatsukawa R. Geographical distribution of persistent organochlorines in air, water and sediments from Asia and Oceania, and their implications for global redistribution from lower latitudes. Environmental Pollution 1994; 85: 15-33.

Iwata H, Tanabe, S., Sakai, N., Tatsukawa, R.,. Distribution ofpersistent organochlorines in the oceanic air and surface seawater and the role of ocean on their global transport and fate. Environmental Science and Technology 1993; 27: 1080-1098.

Jaward FM, Farrar, N.J., Harner, T., Sweetman, A.J., Jones, K.C.,. Passive air sampling of PCBs, PBDEs, and organochlorine pesticides across Europe. Environmental Science & Technology 2004; 38: 34-41.

Jiang Y, Wang X, Zhu K, Wu M, Sheng G, Fu J. Polychlorinated biphenyls contamination in urban soil of Shanghai: Level, compositional profiles and source identification. Chemosphere 2011; 83: 767-773.

Kannan K, Maruya KA, Tanabe S. Distribution and Characterization of Polychlorinated Biphenyl Congeners in Soil and Sediments from a Superfund Site Contaminated with Aroclor 1268. Environmental Science & Technology 1997; 31: 1483-1488.

Khairy M, Barrett K, Lohmann R. The changing sources of polychlorinated dibenzo-p-dioxins and furans in sediments and the ecological risk for nekton in the lower Passaic River and Newark Bay, New Jersey, USA. Environmental Toxicology and Chemistry 2015.

Kumar B, Kumar S, Goel G, Gaur R, Mishra M, Singh S, et al. Distribution of polychlorinated biphenyls in agricultural soils from NCR, Delhi, India. Annals Biol. Res 2011; 2: 247-254.

Lal A. Environmental status of Delhi. Indian Journal of Environmental Protection 1996; 16: 1-11.

Li N, Wania F, Lei YD, Daly GL. A Comprehensive and Critical Compilation, Evaluation, and Selection of Physical-Chemical Property Data for Selected Polychlorinated Biphenyls. Journal of Physical and Chemical Reference Data 2003; 32: 1545-1590.

Liu G, Zheng M, Cai M, Nie Z, Zhang B, Liu W, et al. Atmospheric emission of polychlorinated biphenyls from multiple industrial thermal processes. Chemosphere 2013; 90: 2453-2460.

Mackay D. Multimedia environmental models: the fugacity approach: CRC press, 2001.

Meijer SN, Shoeib M, Jones KC, Harner T. Air−Soil Exchange of Organochlorine Pesticides in Agricultural Soils. 2. Laboratory Measurements of the Soil−Air Partition Coefficient. Environmental Science & Technology 2003; 37: 1300-1305.

Ockenden WA, Breivik K, Meijer SN, Steinnes E, Sweetman AJ, Jones KC. The global re-cycling of persistent organic pollutants is strongly retarded by soils. Environmental Pollution 2003; 121: 75-80.

Pandit G, Sahu S, Sharma S, Puranik V. Distribution and fate of persistent organochlorine pesticides in coastal marine environment of Mumbai. Environment International 2006; 32: 240-243.

Ren, Que, Li Y-F, Liu, Wan, Xu, et al. Polychlorinated Biphenyls in Chinese Surface Soils. Environmental Science & Technology 2007a; 41: 3871-3876.

Ren N, Que M, Li Y-F, Liu Y, Wan X, Xu D, et al. Polychlorinated biphenyls in Chinese surface soils. Environmental science & technology 2007b; 41: 3871-3876.

Ribes A, Grimalt JO, Torres García CJ, Cuevas E. Temperature and Organic Matter Dependence of the Distribution of Organochlorine Compounds in Mountain Soils from the Subtropical Atlantic (Teide, Tenerife Island). Environmental Science & Technology 2002; 36: 1879-1885.

RůŽičková P, Klánová J, Čupr P, Lammel G, Holoubek I. An assessment of air− soil exchange of polychlorinated biphenyls and organochlorine pesticides across Central and Southern Europe. Environmental science & technology 2007; 42: 179-185.

Sharholy M, Ahmad K, Mahmood G, Trivedi R. Analysis of municipal solid waste management systems in Delhi–a review. Book of proceedings for the second International Congress of Chemistry and Environment, Indore, India, 2005, pp. 773-777.

Someya M, Ohtake M, Kunisue T, Subramanian A, Takahashi S, Chakraborty P, et al. Persistent organic pollutants in breast milk of mothers residing around an open dumping site in Kolkata, India: Specific dioxin-like PCB levels and fish as a potential source. Environment International; 36: 27-35.

Stout SA, Graan TP. Quantitative source apportionment of PAHs in sediments of little Menomonee River, Wisconsin: weathered creosote versus urban background. Environmental science & technology 2010; 44: 2932-2939.

Syed JH, Malik RN, Li J, Zhang G, Jones KC. Levels, distribution and air–soil exchange fluxes of polychlorinated biphenyls (PCBs) in the environment of Punjab Province, Pakistan. Ecotoxicology and environmental safety 2013; 97: 189-195.

Tang X, Shen C, Liu W, Zhang C, Chen Y. Levels, Distributions and Profiles of Polychlorinated Biphenyls in Paddy Fields from Two Towns in a Typical Electronic Waste Recycling Area of Eastern China. In: Xu J, Huang P, editors. Molecular Environmental Soil Science at the Interfaces in the Earth's Critical Zone. Springer Berlin Heidelberg, 2010, pp. 196-199.

Wang D, Tian F, Yang M, Liu C, Li Y-F. Application of positive matrix factorization to identify potential sources of PAHs in soil of Dalian, China. Environmental Pollution 2009; 157: 1559-1564.

Wang P, Zhang H, Fu J, Li Y, Wang T, Wang Y, et al. Temporal trends of PCBs, PCDD/Fs and PBDEs in soils from an E-waste dismantling area in East China. Environmental Science: Processes & Impacts 2013; 15: 1897-1903.

Wang Y, Luo C-L, Li J, Yin H, Li X-D, Zhang G. Characterization and risk assessment of polychlorinated biphenyls in soils and vegetations near an electronic waste recycling site, South China. Chemosphere 2011; 85: 344-350.

Wurl O, Potter JR, Obbard JP, Durville C. Persistent Organic Pollutants in the Equatorial Atmosphere over the Open Indian Ocean. Environ. Sci. Technol. 2006; 40: 1454-1461.

Zhang GC, Paromita Li, Jun Sampathkumar, Pichai Balasubramanian, Thangavel Kathiresan, Kandasamy Takahashi, Shin Subramanian, Annamalai Tanabe, Shinsuke Jones, Kevin C. Passive atmospheric sampling of organochlorine pesticides, polychlorinated biphenyls, and polybrominated diphenyl ethers in urban, rural, and wetland sites along the coastal length of India. Environmental Science & Technology 2008; 42: 8218-8223.

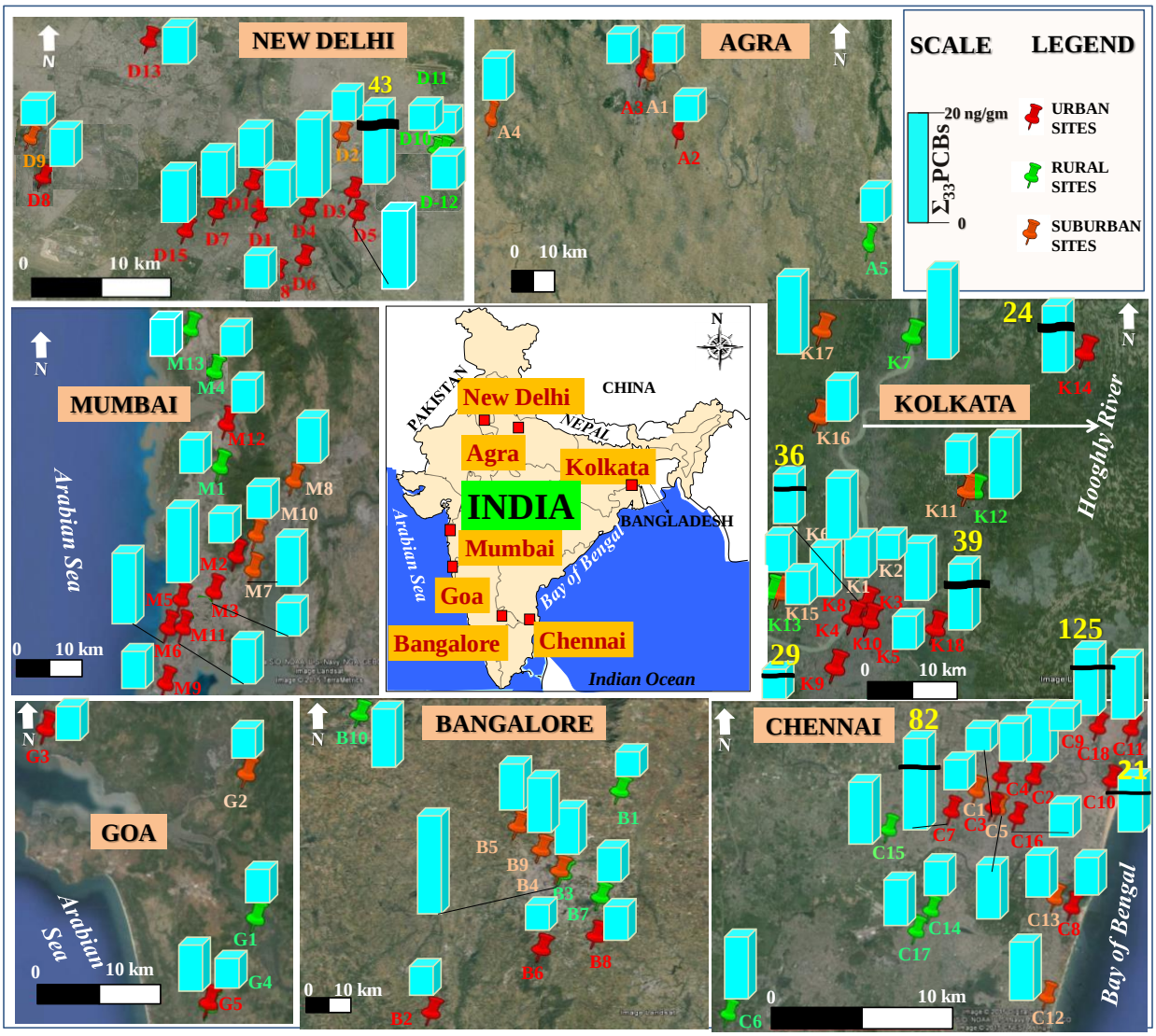
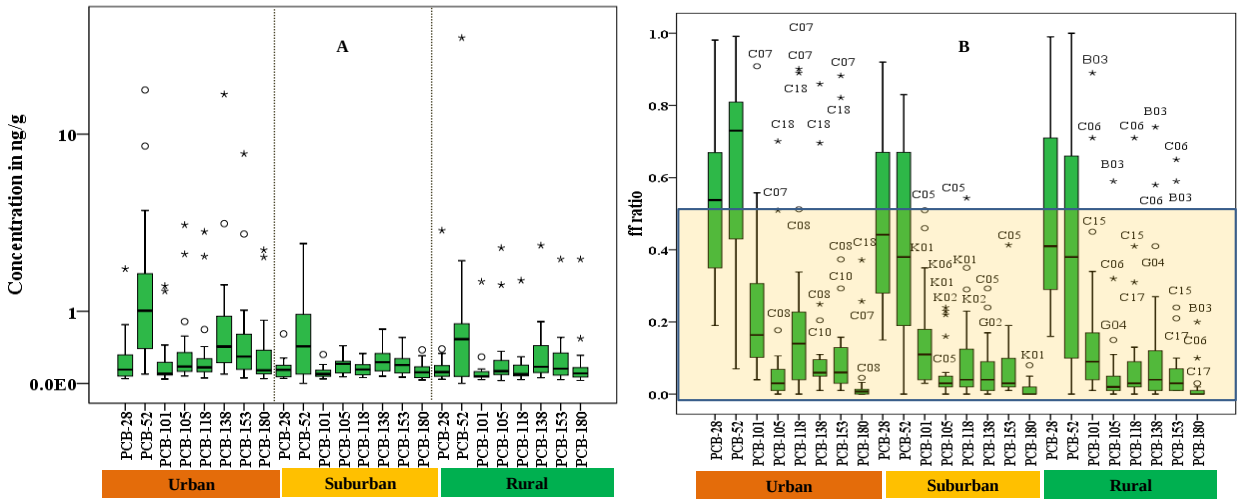


Figure 1: Sampling sites along urban-suburban-rural transect in seven major Indian cities showing Σ_{33}PCBs level for each site

481



482 **Figure 2A. Distribution of indicator PCB congeners along Urban, Suburban and Rural transect in**

483 **the seven major Indian cities. 2B. Fugacity fractions for indicator PCB congeners along Urban,**

484 **Suburban and Rural transect in the seven major Indian cities**

485

486

487

488

489

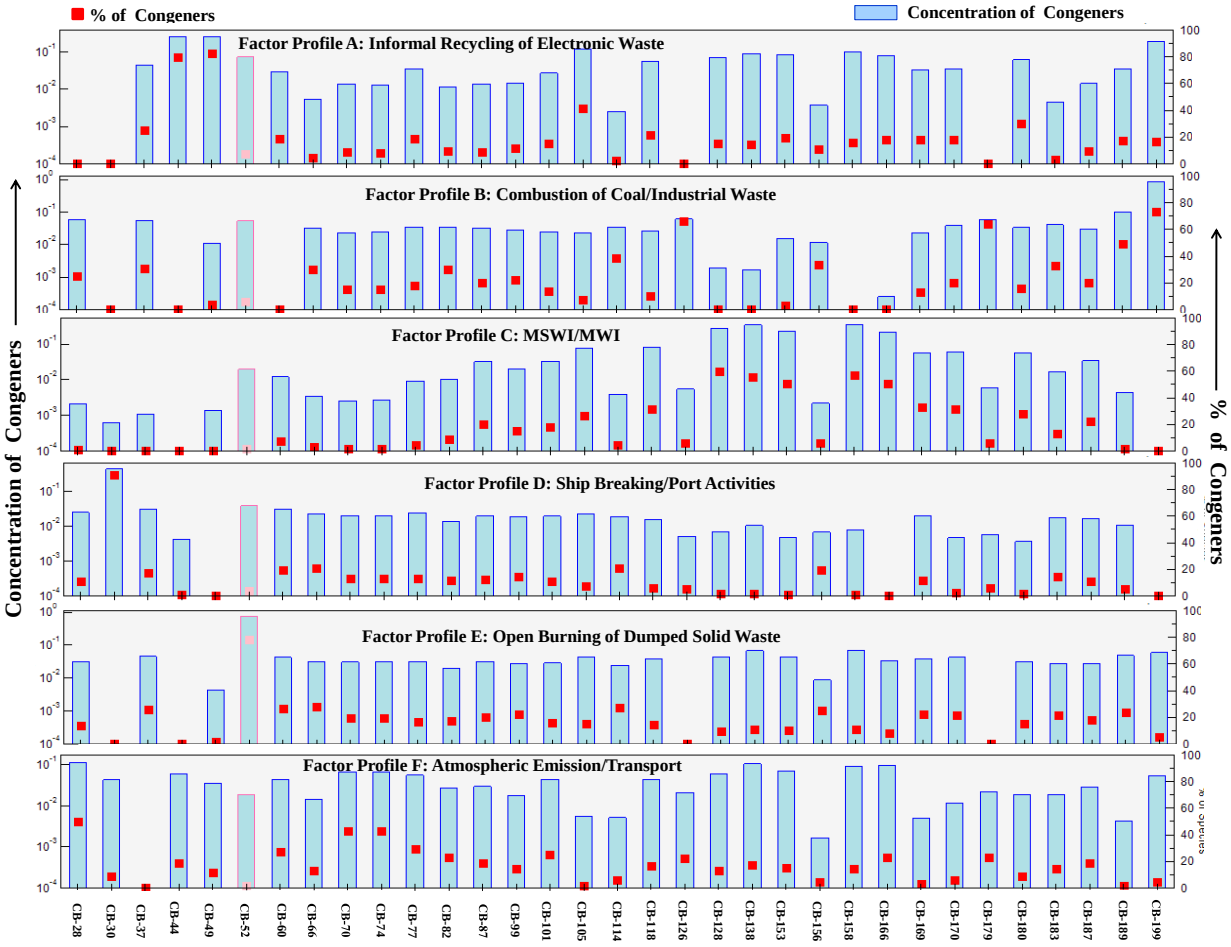


Figure 3. Factor profiles for PCB sources in India obtained from positive matrix factorization model

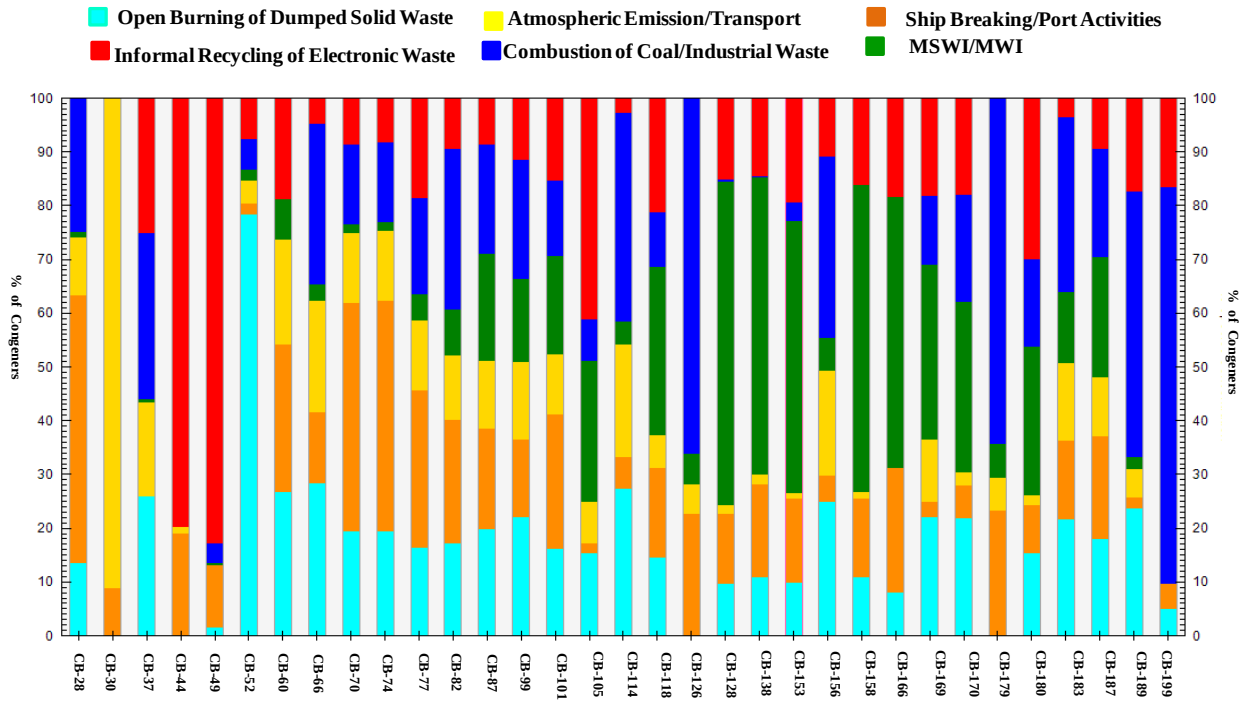


Figure 4. Percentage distribution of each factor profile affecting the source of each PCB congener in Indian cities.