Environmental Pollution 182 (2013) 283–290

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Atmospheric polychlorinated biphenyls in Indian cities: Levels, emission sources and toxicity equivalents

Paromita Chakraborty [a,b,*], Gan Zhang [a], Sabine Eckhardt [c], Jun Li [a], Knut Breivik [c,d], Paul K.S. Lam [e], Shinsuke Tanabe [f], Kevin C. Jones [g]

[a] State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
[b] SRM Research Institute, SRM University, Kattankulathur, Tamil Nadu, India
[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] State Key Laboratory in Marine Pollution, Department of Biology and Chemistry, City University of Hong Kong, Hong Kong
[f] Centre for Marine Environmental Studies (CMES), Ehime University, Matsuyama 790-8577, Japan
[g] Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, UK

ARTICLE INFO

Article history:
Received 27 April 2013
Received in revised form
13 July 2013
Accepted 17 July 2013

Keywords:
Polychlorinated biphenyls
Air
India
FLEXPART
HYSPLIT
Toxicity equivalents

ABSTRACT

Atmospheric concentration of Polychlorinated biphenyls (PCBs) were measured on diurnal basis by active air sampling during Dec 2006 to Feb 2007 in seven major cities from the northern (New Delhi and Agra), eastern (Kolkata), western (Mumbai and Goa) and southern (Chennai and Bangalore) parts of India. Average concentration of Σ_{25}PCBs in the Indian atmosphere was 4460 (±2200) pg/m^{-3} with a dominance of congeners with 4–7 chlorine atoms. Model results (HYSPLIT, FLEXPART) indicate that the source areas are likely confined to local or regional proximity. Results from the FLEXPART model show that existing emission inventories cannot explain the high concentrations observed for PCB-28. Electronic waste, ship breaking activities and dumped solid waste are attributed as the possible sources of PCBs in India. Σ_{25}PCB concentrations for each city showed significant linear correlation with Toxicity equivalence (TEQ) and Neurotoxic equivalence (NEQ) values.

1. Introduction

Tropics have been evidenced with significant emission source regions for polychlorinated biphenyls (PCBs) and associated global atmospheric distribution of PCBs (Iwata et al., 1994; Watanabe et al., 1996). Exposure to PCBs can cause a wide variety of health effects, often at very low exposure levels and are highly toxic compounds with carcinogenic and mutagenic effects (Ruiz et al., 2008). PCBs have been widely used as plasticizers, as coolants and lubricants in transformers and capacitors, and as hydraulic and heat exchange fluids, and may be present in the electronic waste (e-waste) stream (Wong et al., 2007). It has even been hypothesized that there has been a shift in primary emission regions of PCBs on a global scale with high emission continuing in some sub-tropical and tropical regions implicated as recipients of wastes, paralleled by significant reductions in atmospheric burdens within former use regions (Breivik et al., 2011). Furthermore due to the tropical climate in India, PCBs can readily enter the atmosphere from some sources such as volatilization from or incineration of PCB containing materials and products, vaporization from landfills, air–water/soil exchange, vaporization from contaminated surfaces and sludge dewatering beds contaminated with PCBs (Totten et al., 2004; Biterna and Voutsa, 2005). Inhalation exposure is an important route and is of substantial concern for the urban environment. Very limited data is available on the atmospheric emissions and concentrations of PCBs in Indian cities although high levels were reported in 1994 (Iwata et al., 1994) and recently elevated levels have been reported in our previous work (Zhang et al., 2008) and also by the global atmospheric passive air sampling study from New Delhi in India (Pozo et al., 2008) and from agricultural regions of India (Pozo et al., 2011). An international mandate under the Stockholm Convention (UNEP, 2001) aims to identify and quantify ongoing PCB sources and the continued presence and distribution of these chemicals in the environment. Some dioxin-like PCBs (dl-PCBs) are of particular toxicological concern. 4 coplanar PCBs and 8 mono-

* Corresponding author.
E-mail addresses: paromita.c@res.srmuniv.ac.in, parochakraborty@gmail.com (P. Chakraborty).

0269-7491/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.envpol.2013.07.032

ortho-PCBs share a similar chemical structure and common mechanism of toxic action as that of 7 polychlorinated dibenzo dioxins (PCDDs) and 10 polychlorinated dibenzo furans (PCDFs) (Mandal, 2005; Van den Berg, 2006). dl-PCBs are never found as individual congeners but occur as complex mixtures in air and other environmental media. Corresponding to 12 dioxin-like PCB congeners, the remaining congeners are referred to as the non-dioxin-like congeners (ndl-PCB). These congeners exert weak or no effect on Ah-receptors; however, they interfere with intracellular signaling pathways that are regulated and modulated by Ca^{2+}, such as those involving ryanodine receptors, protein kinase C, inositol triphosphate or arachidonic acid, and, thus, cause neurotoxicity (Simon et al., 2007). This paper reports (i) occurrence of PCBs in the atmosphere of seven major Indian cities, (ii) evaluates potential source regions of measured PCBs using two different Lagrangian transport models (HYSPLIT and FLEXPART), (iii) estimates toxicity equivalents associated with inhalation exposure to PCBs.

2. Material and methods

2.1. Air samples

The details of the sampling protocol is the same as the active air sampling reported earlier (Chakraborty et al., 2010). Precisely, short-term high resolution samples of 12 h duration (day, 8:00 a.m.–8:00 p.m.; night, 8:00 p.m.–8:00 a.m.) were collected. Altogether 91 active air samples were obtained between Dec 3 2006 and Feb 24 2007 from the seven major cities of India: New Delhi and Agra in the north, Kolkata in the east, Mumbai and Goa in the west and Bangalore and Chennai in the south. Sampling sites are shown in Fig. 1.

Air volumes of 72 m^3 in 12 h was drawn through quartz microfiber filter (QFF) (Grade GF/A, 8.9 cm diameter, Whatman, Maidstone, England), and subsequently through 6.5 cm in diameter-7.5 cm in thickness (density of 0.030 g/cm^3) polyurethane foam (PUF) plugs using a high-volume sampler at a flow rate of 0.1 m^3/min. Prior to sampling, QFFs were baked at 450 °C for 12 h to remove any organic contaminants, and PUF plugs were Soxhlet extracted for 48 h with methanol and then acetone for 24 h, followed by two overnight extractions using dichloromethane (DCM). PUF plugs were dried overnight in a vacuum desiccator and stored in solvent-rinsed glass jars with Teflon lined lids before use. During the sample collection, gloves were worn, and QFFs and PUF plugs were handled using acetone-rinsed stainless steel tongs. At the end of the deployment period, the QFFs and PUFs were re-sealed in their original transport containers, and returned to the laboratory where they were stored at −20 °C until extraction.

Fig. 1. Sampling sites in India.

2.2. PCB analysis

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 was added to each of the samples. The samples were Soxhlet extracted for 18 h with 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 an 8 mm i.d. 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 30 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 pentachloronitrobenzene (PCNB) and PCB-54 was added as an internal standard prior to GC-MSD analysis. PCB 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 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. 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 25 PCB congeners (PCB-28, -37, -44, -49, -52, -60, -66, -70, -74, -77, -82, -87, -99, -101, -105, -114, -118, -126, -128, -138, -158, -166, -179, -180,-187) were detected and quantified.

2.3. QA/QC

Chemical standards were purchased from Accustandard Co. US. Field and lab blanks were collected and analyzed to provide an indication of the overall precision of both the sampling and laboratory methods. Laboratory and field (i.e., samplers sent to/from field sites unopened) blanks consisting of pre-extracted PUF disks were extracted and analyzed in the same way as the samples. 14 AAS PUF (two from each city) and 7 filter field blanks (one from each city) and 14 and 12 laboratory blanks were used for AAS PUF and AAS filter respectively.

During each set of extractions, a filter field blank and a PUF plug field blank were included. Detection limits were derived from the blanks and quantified as the mean plus three times the standard deviation of the concentration in the blanks, based on 12 h sampling. The limit of detection (LOD) for every PCB congener was determined by adding three standard deviations (average $\pm$ 3 $\times$ SD) to the average of the blanks. Values smaller than the LOD were not included in the calculation. Each PCB congener in the samples was blank corrected. LOD values varied from 0.05 to 0.42 ng/sample for PUF samples and from 0.00023 to 0.00146 ng/sample and for QFF with the highest LODs observed for trichlorinated congeners. There was no difference (*t*-test significance, <95%) between concentrations of analytes in the laboratory and field blanks, indicating contamination was minimal during sample collection, transport, storage, and analysis. Field blanks and procedural blanks were below the instrument quantification limit. Surrogate recoveries were 85–125% (mean 94%) for PCB209 and 69–74% (mean 72%) for TC*m*X. Concentrations of the samples were corrected based on those results. The recoveries are comparable to a previous study in the same lab (Zhang et al., 2008).

2.4. Toxicity equivalents (TEQs) and neurotoxic equivalents (NEQs)

TEQs were estimated using the Toxicity equivalent factor (TEFs) for mono-ortho PCBs (PCB-105, 114, 118), di-ortho (PCB-180) and non-ortho substituted PCBs (PCB-77, 126) using a tiered approach by World Health Organization (Van den Berg et al., 2006). Neurotoxic Equivalency Factors (NEFs) were evaluated for the observed PCB congeners as developed by Simon et al. (2007) in the same fashion that the dioxin TEQ scheme represents the Ah-receptor related toxicity.

3. Results and discussion

3.1. Atmospheric levels of PCBs

Atmospheric Σ_{25}PCB in pg/m^3 in India varied between 1000 and 9560 (avg, 4460) in the gaseous phase and 0.03–660 (avg, 101) in the particulate phase. Highest range of Σ_{25}PCB in the gaseous phase has been observed in the urban site of Mumbai and is consistent with the observation of 1989 (Iwata et al., 1994) followed by New Delhi. Cities located in the west (Mumbai and Goa) and northern (New Delhi and Agra) India have very high levels followed by

Kolkata in the east. Southern India (Chennai and Bangalore) has comparatively lower levels of Σ_{25}PCB (Table 1). Details of each PCB congener for each site for both gaseous and particulate phases have been given in supplementary data, Tables S1 and S2.

Typically, less than 10% of the total atmospheric Σ_{25}PCB burden was found in the particle phase (Fig. 2). Higher average percentage in particulate phase is observed for New Delhi and Agra where during the entire sampling period the average atmospheric temperature was ~15° colder than at the other cities (12 °C and 9 °C respectively) (Chakraborty et al., 2010). Hence lowering the vapor pressure of PCB congeners at lower temperature increases the sorption onto airborne particles. The percentage is also higher for higher molecular weight (MW) PCBs. For other sites, where temperature mostly varied between 23 and 25 °C, much lower levels of PCBs (<5%) were observed in the particulate phase. Such a variation occurred since higher temperatures for the sites under tropical climate triggers revolatilisation of the semivolatile PCBs and results in higher gaseous air concentrations (Pozo et al., 2006). Gas-phase PCBs are dominated by tetrachlorinated congeners with heavier homologue groups comprising decreasing percentages with increasing MW. 4-Cl homologues contributed about 44–65% of the total PCB level followed by 5-Cl (18–28%) except in New Delhi where the 6-Cl (20%) has been found higher than 5-Cl (18%). The pattern of PCB congeners showed an abundance of 4-Cl-to 7-Cl PCBs (Fig. 3) and was consistent among the cities.

PCB levels in the present study do not seem to have declined since 1989 and are fairly consistent with elevated levels of PCBs previously measured in India (Iwata et al., 1994). The average Σ_{25}PCB levels are broadly comparable to historical active air sample data from different cities of USA, Europe (mainly 1990–1992) and some urban sites of Turkey and Asian developing nations like Taiwan and China (Table 1). However, it is important to note that a direct comparison of data listed in Table 1 is difficult as the data reflect different sum of congeners and time periods. For example, the PCB levels in Europe (Schuster et al., 2010) and USA (Sun et al., 2006) has reduced drastically in the recent years. Still, the concentrations from this study are much higher when compared to the levels reported in Italy, Germany, Singapore and Korea. PCBs levels in New Delhi have increased drastically since 1989 and is consistent with the recent observation under GAPS study where elevated levels have been observed at New Delhi (Pozo et al., 2008). The levels in New Delhi in this study is again comparable or even occasionally lower than the observed levels in more remote regions of northern India reported by a seasonal passive air sampling study (Pozo et al., 2011).

PCB congener profiles were compared using correlation coefficients to assess whether the sources for PCBs are similar or different across sites (Supplementary data, Table 3). The result suggests that excluding Bangalore and rural site of Mumbai, all other major cities of India may be affected by similar sources of PCB emissions.

3.2. Potential PCB sources in India

In order to assess the possible source areas for PCBs in the active air samples, the HYSPLIT model, a comprehensive modeling system developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resource Laboratory (Draxler and Rolph, 2003), was used.

Simulations of atmospheric transport were additionally made using the Lagrangian particle dispersion model FLEXPART (Stohl, 1998; Stohl et al., 2005). FLEXPART releases so-called tracer particles at emission sources and calculates their trajectories using the mean winds interpolated from the meteorological input fields plus random motions representing turbulence, a deep convection scheme (Emanuel and Zivkovic, 1999) and atmospheric reactions by OH radicals (Eckhardt et al., 2009).

HYSPLIT back trajectory plots gave a qualitative impression of the variability of the trajectories within each cluster for all the sites. Although considerable variability within each individual cluster is evident, there is ample evidence that the clustering procedure grouped the trajectories into three clearly distinct cluster types. The

Table 1
Comparison of average total PCBs with other studies and previous study in Indian cities with the present study (NA = Not Available).

Location	No of PCBs	Mean (range)	Sampling site type	Year
Asia-India – Bangalore	25	2640 (1830–3560)	Urban	This study
Chennai	25	2660 (990–6190)	Urban	This study
New Delhi	25	4980 (2400–7850)	Urban	This study
Agra	25	3760 (3050–4440)	Urban	This study
Goa	25	4680(3660–5810)	Urban	This study
Mumbai	25	6080 (3450–8460)	Urban	This study
Mumbai	25	1940 (1250–2550)	Rural	This study
Kolkata	25	2620 (960–5850)	Urban	This study
Bangalore	NA	1700	Urban	Dec-89 (Iwata et al., 1994)
Chennai	NA	2200	Urban	Dec-89 (Iwata et al., 1994)
New Delhi	NA	74	Urban	Dec-89 (Iwata et al., 1994)
Goa	NA	2300	Urban	Dec-89 (Iwata et al., 1994)
Mumbai	NA	4600	Urban	Dec-89 (Iwata et al., 1994)
Kolkata	NA		Urban	Dec-89 (Iwata et al., 1994)
China Guangzhou	64	935 (172–2720)	Urban, suburban	Jun-2004 (Chen et al., 2009)
Taiwan – Tainan city	106	5020 (2620–7120)	Urban	Oct 1992–Apr 1993 (Lee et al., 1996)
Tainan city	106	2610 (1740–3370)	Rural	Oct 1992–Apr 1993 (Lee et al., 1996)
Japan – Kobe	NA	160–1500	Urban	(Nakano et al., 1990)
Europe – London	7	8.04–2774	Urban	1991–2008(Schuster et al., 2010)
Manchester	7	31.43–703	Urban	1991–2008(Schuster et al., 2010)
High Muffles	7	0.60–90	Rural	1991–2008(Schuster et al., 2010)
Middlesbrough	7	14.6–482.3	Rural	1991–2008(Schuster et al., 2010)
Hazelrigg	7	0.78–198.3	Semi-rural	1991–2008(Schuster et al., 2010)
Turkey-Izmir–summer	36	3137	Industrial	April–June 2005(Cetin et al., 2007)
Izmir-winter	36	1371	Industrial	April–June 2005(Cetin et al., 2007)
Izmir-summer	29	2119	Coastal	April–June 2005(Cetin et al., 2007)
Izmir-winter	29	1712	Coastal	April–June 2005(Cetin et al., 2007)
USA Chicago, IL	84	1400 (100–9500)	Urban	1996–2003(Sun et al., 2006)

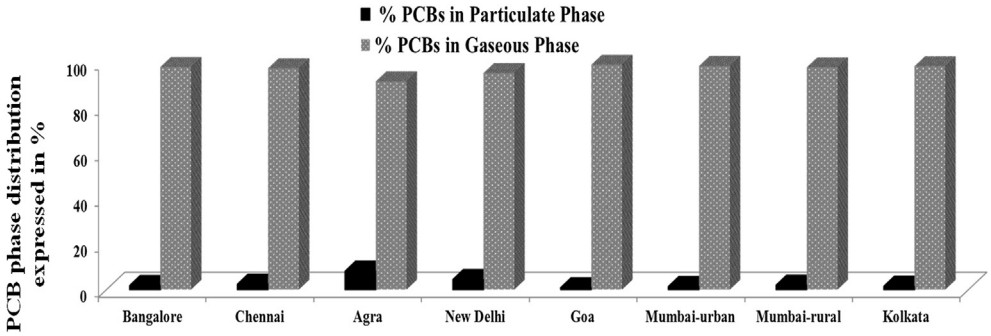

Fig. 2. Distribution of PCBs in gaseous and particulate phases in Indian atmosphere.

three mean cluster types. Supplementary data, Fig. S1 shows the three general air mass pathways to each site in terms of direction of flow, wind speed and the preferential transport height. FLEXPART has given the source regions (Fig. 4). FLEXPART results do not consider potential diurnal variability in atmospheric emissions (Fig. 5).

Daily maximum PCB concentrations in all cities exceeded the minimum by a factor of 1–2 and for few samples by a factor of 3. This phenomenon may be due to temperature-controlled air-terrestrial surface exchange of PCBs which in turn influences the diurnal variability in air concentrations (Fig. 5). The elevated temperature encountered in tropical climate of India is very different from those in former use regions at mid-latitudes. The trends of variation for PCBs in the major metropolitan cities viz., New Delhi, Kolkata, Mumbai and Chennai could be due to the re-emission of PCBs from the primary source areas in these cities due to higher ambient temperature. Temperature ranges between day time high temperatures and night time low temperatures at each city (Chakraborty et al., 2010). Hence unlike the modeled PCB-28 levels, the measured PCB-28 showed higher concentration during day time and lower concentrations during night time (Fig. 5).

3.2.1. Electronic waste recycling

E-waste recycling in the subtropical and tropical regions has reported several environmental and health impacts due to atmospheric emission of PCBs associated with the end of life cycle of electrical and electronic equipment in China (Wong et al., 2007) and Africa (Asante et al., 2011). Strict domestic laws and higher recycling and/or disposal costs has resulted in transportation of the e-waste from the developed nations to the developing countries including India. The highest percentage of 6-Cl and 7-Cl (34–35%) has been observed in northern India at New Delhi and Agra. During the sampling period in New Delhi and Agra the air mass traversed through Uttar Pradesh before ending at these sites (Supplementary data, Fig. S1) where most of the e-waste recycling takes place (Jain and Sareen, 2006). Elevated level of PCBs in New Delhi could be associated with their emission during e-waste recycling units in the informal e-waste recycling sites at the eastern part of New Delhi. There are four main e-waste recycling units around New Delhi. While Northern India is not a leading generator, it happens to be the leading processing centre of e-waste in India. Even though Bangalore is the silicon valley of India, the PCB concentration especially for dl-PCBs is comparatively low since Bangalore supports the safe and controlled recycling of corporate e-waste. In addition Indian power sector and steel industries owns 71% and 18% respectively of PCB containing equipment like transformers and capacitors. The electricity companies auction the decommissioned transformers which ultimately end up in the e-waste recycling units for further processing. PCB containing oil contained in these transformers are removed and sold out to transformer oil reprocessors. The recycling units lack appropriate infrastructure and procedures for e-waste recycling and disposal. In this study a statistically significant ($R^2 = 0.9842$, $p < 0.001$) linear correlation has been observed between the average atmospheric concentration of PCBs sum of the amount of e-waste generated in each city and PCB containing oil available from the old capacitor and transformer from the states where each of these cities are located or/and the adjoining state.

3.2.2. Ship breaking activities

Ship breaking activities have been found to be another potential source for the release of PCBs in the developing regions (Hossain

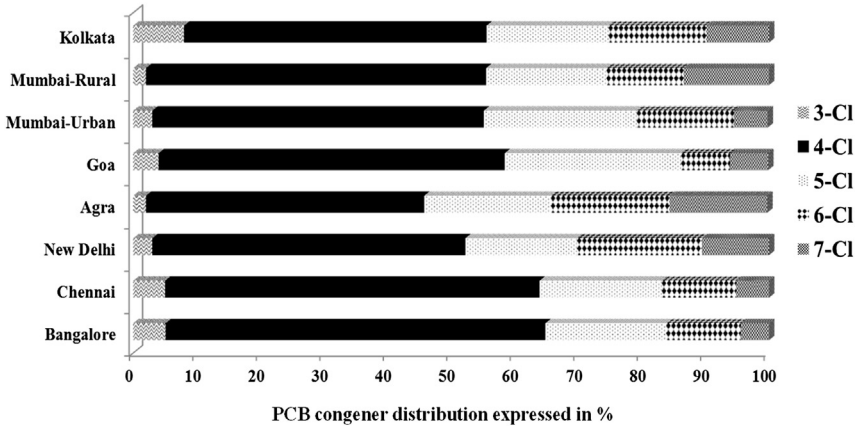

Fig. 3. Distribution of PCB congeners in seven major Indian cities.

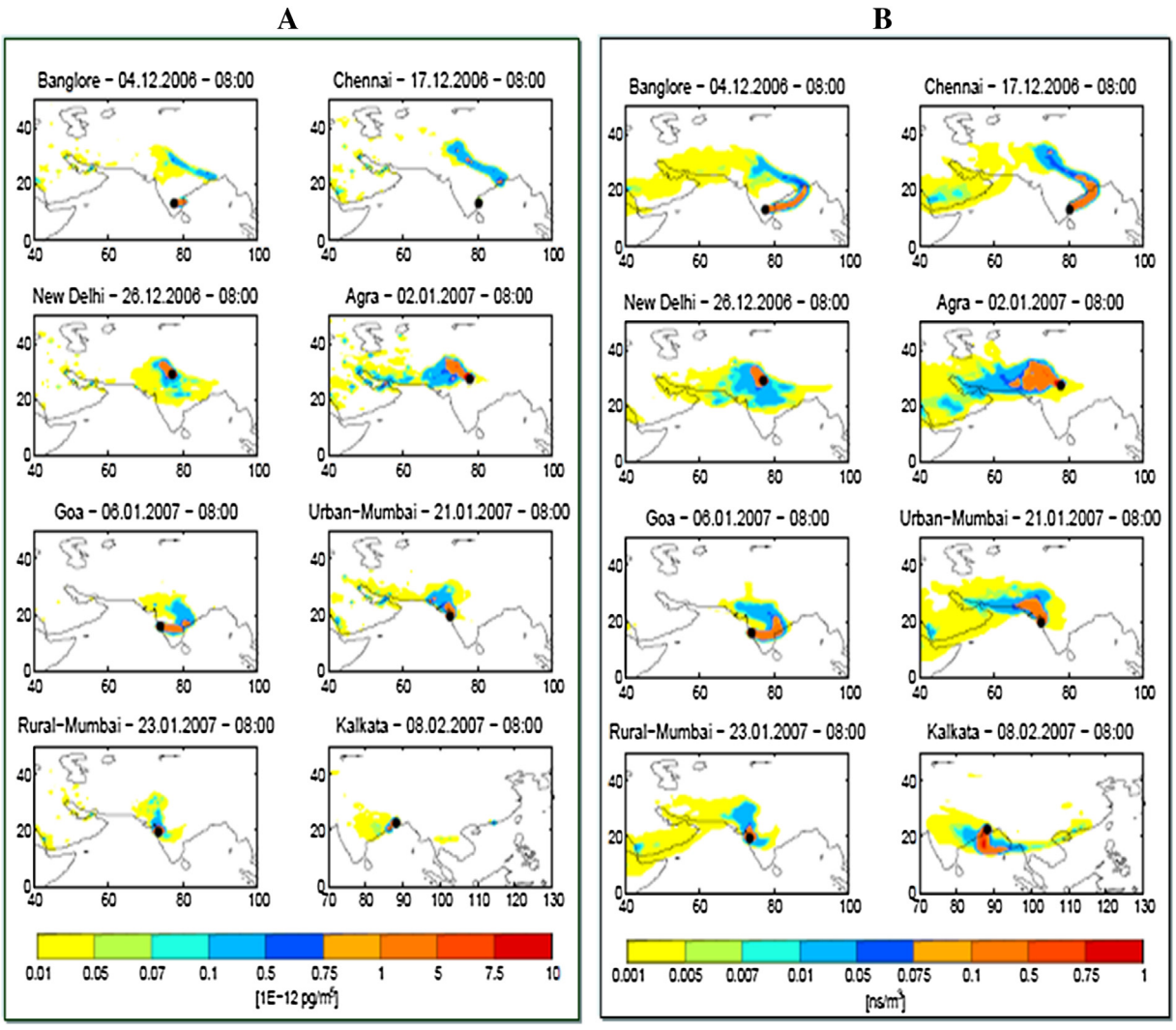

Fig. 4. Footprint EC maps (A) and ES (B) maps for the dates with the highest level of PCB-28 in the gaseous phase for the seven major Indian cities.

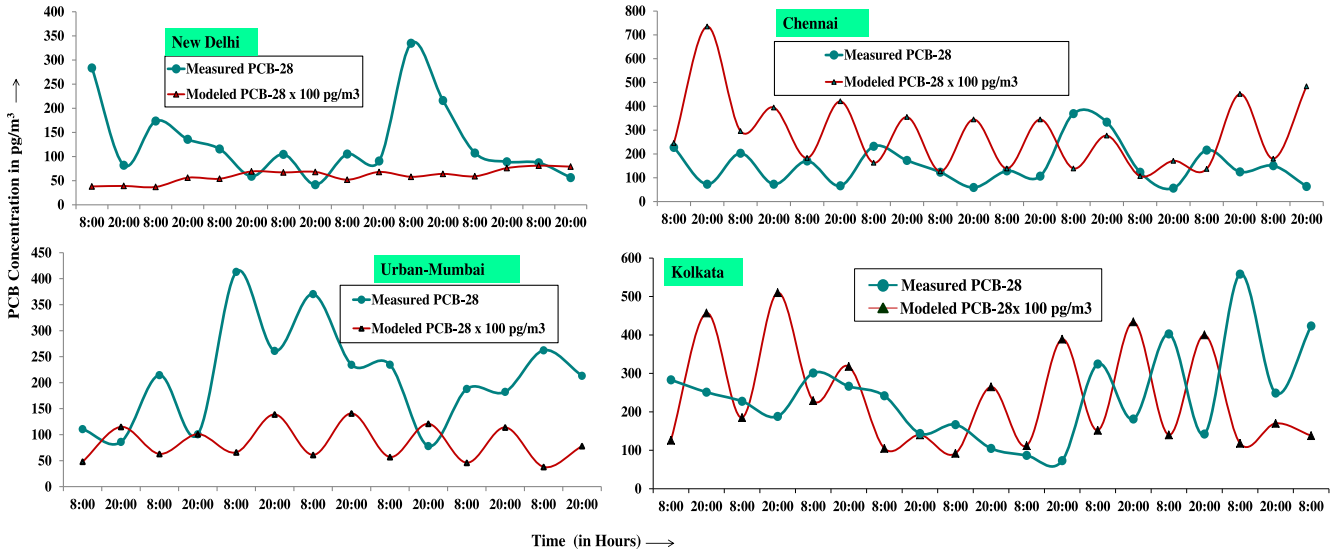

Fig. 5. Measured levels of PCB-28 and FLEXPART modeled values of PCB-28 using emission inventory multiplied by 100 to fit with the scale of the observed concentrations for all the samples of the four major Indian cities.

et al., 2008; Gioia et al., 2011). India has emerged as leading nation involved in ship breaking activities because of demand of re-rollable and melting scrap steel and other items within the country. Largest volume of ship dismantling activity in the world takes place in the western part of India and has contributed to the release of PCBs in the atmosphere of Arabian Sea (Wurl et al., 2006). A typical merchant ship to be dismantled for scrap contains between 250 and 800 kg of PCBs, principally in the paint and left on the scrap metal in the vessel machinery that is rerolled or remelted (Hess et al., 2001). And, given that ship breaking activities are prevalent within the city of Mumbai at Darukhana and the adjoining west coast in the state of Gujarat, it can be suggested to be another potential important source contributing to the maximum loads of PCBs in Mumbai. Similarity in the elevated levels of 5-Cl (24–28%) (Fig. 3) from urban Mumbai and Goa possibly attributed to the same reason which is again consistent with our recent passive air sampling study where high levels of atmospheric PCBs have been observed in the west coast of India (Zhang et al., 2008). But the rural site of Mumbai showed deviation from the urban site and Goa which can also be explained with the air mass ending at this site. HYSPLIT model shows that 50% of the air mass originated from Arabian Sea (Supplementary data Fig. S1) before ending to the rural site of Mumbai. Remaining 50% is affected by the surrounding region of which 21% originated more than 400 km away from the central part of India where less possibility of PCB source exists. Hence the 28% air mass mostly traversing through the city limit of Mumbai (Fig 4 and Supplementary data Material Fig. S1) possibly accounts for nearly 3 folds lower PCB levels in the rural site of Mumbai.

3.2.3. Open dumping and burning of municipal solid waste

As the quantity of discarded computer equipment and other consumer electronics increases, the possibility of increased open burning becomes more likely. PCBs have been used in hydraulic and heat transfer fluids, paints, sealants, plasticizers and carbonless copy paper (Breivik et al., 2002). PCBs were also extensively used in small capacitors in cars in the past (Cummins, 1988; Harrad et al., 1994). The landfill areas in India where municipal solid waste is dumped are mostly open and being ubiquitous there are chances for chemical accumulation. Most of the dumped municipal solid wastes are combusted by the rag pickers thereby releasing dioxins or furans and related compounds (Minh et al., 2003). In addition, the soil in the dumping grounds may be contaminated by PCBs leaked out from the electrical appliances containing technical PCB mixtures. Each of these cities has open dumping grounds for solid waste including e-wastes components like plastic chips, wire insulations, PVC materials and metal scraps (Wong et al., 2007). Mumbai houses large number of computer parks and the e-waste inevitably finds its way to the dumping grounds located within the city limit. New Delhi is the biggest recycler and scrap market of e-waste in India. The e-waste recycling units around Delhi has a poor collection system, hence e-waste finds its way to landfill lacking proper disposal methods. FLEXPART model shows that the samples with the highest concentration of PCBs from urban Mumbai, Chennai, New Delhi and Kolkata are affected by the air mass with the highest emission concentration encircling around the city limits. All these cities have open dumps and most of these are poorly managed. Municipal solid wastes are mostly disposed into such open landfills that are often ignited, resulting in uncontrolled field burning (Jha et al., 2008). Very high levels of dl-PCBs were previously observed in the human milk of the women residing within the solid waste dumping ground of Kolkata (Someya et al., 2009). Elevated levels of dl-PCBs, especially PCB-126,were observed only in New Delhi, Mumbai and Kolkata which could be associated with the piling and burning of the solid waste in these cities since concentrations of PCB-126 is generated specifically through combustion reactions (Oliver and Niimi, 1988; Lohmann et al., 2000), and this may account for the elevated concentration of this congener.

3.2.4. Biomass burning

Biomass burning has been found to be an important source of PCBs (Eckhardt et al., 2007). Biomass burning was explored by investigating potential similarities between observed concentrations of PCBs and predicted concentrations of CO using FLEXPART. The biomass burning tracer was used together with MODIS hot spot data which indicate biomass burning regions. Supplemental data, Fig. S2 shows the predicted CO concentrations and the expected influence from fires. The sample collected from Kolkata on 8th Feb'2007 (between 08:00–20:00 h) not only had the highest predicted concentration of CO, but also the highest observed concentration of Σ_{25}PCBs. The fire source region for this sample (Supplementary data Fig. S2 and Fig. 4) covers areas of Myanmar where highest level of biomass burning has been spotted.

The observed atmospheric levels obtained from this study cannot be rationalized on the basis of data from an existing global emission inventory (Breivik et al., 2007). Firstly, because we observed for PCB-28, the predicted concentrations were typically about a factor of ~100 lower than observed air concentrations of PCB-28 found in this study (Fig. 5). Secondly, global emissions of PCBs have been predicted to decline over the last decades (Breivik et al., 2007), which does not correspond well with observations from India (Table 1).

4. Toxic equivalency for measured PCBs

Atmospheric sources of PCBs are of interest not only because they play a role as a source of PCB deposition, but also is a source of inhalation exposure. The predominant source of human exposure to PCBs is the diet, but occupational exposure has received increasing attention in recent years (Harrad et al., 2006; Hu et al., 2010). Though the toxic effects on humans through direct inhalation are not yet clear but lower chlorinated congeners, predominating in air, may expose humans to reactive, possibly genotoxic/carcinogenic intermediates because they are relatively easier metabolized (Ludewig et al., 2008). Corresponding to 12 dl-PCBs, the remaining congeners are referred to as the non-dioxin-like congeners (ndl-PCB). Although these congeners exert weak or no effect on Ah-receptors but they interfere with intracellular signaling pathways that are regulated and modulated by Ca^{2+}, such as those involving ryanodine receptors, protein kinase C, inositol triphosphate or arachidonic acid, and, thus, cause neurotoxicity (Kodavanti, 2004; Simon et al., 2007).

Concentrations of some of the non-*ortho* PCBs (PCB-77, 126), mono-*ortho* PCBs (viz., PCB-105, 114 and 118) and di-*ortho* PCB (PCB-180) in the present study showed significant higher concentration in majority of the samples in all the cities. Among the dl-PCBs, the contribution of CB-77 TEQ was the highest for all the cities except for New Delhi, Urban site of Mumbai and Kolkata where for some samples PCB-126 showed the maximum contribution to the TEQ levels. The contributions of PCB-77 to the total TEQ for all cities excluding New Delhi, Urban site of Mumbai and Kolkata were significant ($p < 0.01$) supporting again the impact from a particular contamination source. This difference might have resulted due to the practice of open burning of dumped waste in these cities supporting again the impact of open burning in the dumping grounds (Watanabe et al., 2005).

As for dl-PCBs, non-ortho congener CB-126 predominantly contributed to total TEQs (>95% of the total TEQs) for 3 samples each from Mumbai and New Delhi and 9 samples from Kolkata. TEQ

input of coplanar PCBs was mainly contributed by PCB congeners CB-77, -105, -118, -156, and to a lesser extent CB-126 (Alcock et al., 1998). PCB-126 in the above samples from these three cities could be a summated influence of the domestic burning of coal and wood (Lohmann et al., 2000) for residential cooking and heating and combustion of the solid waste (Oliver and Niimi, 1988; Lohmann et al., 2000). The trend in total daily intake (TDI) levels (assuming respiration rates of 22 m^3 day^{-1} for an adult) is identical (Supporting Information Table 4). TDI levels were slightly higher than WHO's limit of exposure to dl-PCBs for few samples of Mumbai and Goa. Significant correlation ($R^2 = 0.438$; $p < 0.01$) has been observed between the dl-PCBs from Kolkata and the human milk data from dumpsites of Kolkata (Someya et al., 2009).

Significant correlation between the sum of TEQ values and Σ_{25}PCBs in Indian cities is associated with the measured total PCB concentrations (R^2 = 0.1071–0.8414). In addition NEQ values are strongly significant with Σ_{25}PCBs thereby indicating that neurotoxic toxicity is also predictable (R^2 = 0.3833–0.9526). The neurotoxic equivalence (NEQ) concentrations are linearly correlated with Σ_{25}PCBs ($p < 0.01$) for all the seven cities in India. The findings of this study suggest that airborne PCBs in the urban centers of India are widely present and the atmospheric emission includes congeners associated with neurotoxic effects and toxic effects due to dioxin-like PCBs.

5. Conclusion

PCB levels are decreasing in developed regions like USA and Europe, but like many developing nations like China and countries in South Africa, the level of PCBs in India is showing an increasing trend particularly for New Delhi, where the level has drastically increased in more than one and a half decade. Existing PCB emission inventories cannot explain the elevated PCB-28 levels in India. Local or regional sources for PCB emission in India include electronic waste recycling units, ship breaking activities and open solid waste dumping grounds. Exposure to atmospheric PCBs especially the dioxin like PCBs explain the immediate need to control PCB releasing sources in India and protect human health and the ambient environment. Dioxin-like PCB emissions are currently not controlled by legislation and are not routinely monitored. Direct inhalation exposures constitute only a small proportion of the total exposure, in the order of 1–2% of the daily intake from food. For people living or working in the source areas are exposed to PCBs primarily via air which could contribute significantly to the overall PCB exposure.

Acknowledgment

This work was supported by the Chinese Academy of Sciences (No. KZCX2-YW-GJ02) and Natural Scientific Foundation of China (NSFC) (Project No. 41025020), the Area of Excellence Scheme under the University Grants Committee of the Hong Kong Special Administrative Region, China (Project No. AoE/P-04/2004) and manuscript and model preparation was completed with the support of the Fast Track Grant under Young Scientist Scheme by the Depart of Science and Technology, Government of India (SR/FTP/EE-44/2012). SE and KB was supported by the Research Council of Norway (213577/F10). The authors would like to thank Mumbai resident Mr. Elvis Dsouza for his extensive support during sampling.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2013.07.032.

References

Alcock, R.E., Behnisch, P.A., Jones, K.C., Hagenmaier, H., 1998. Dioxin-like PCBs in the environment – human exposure and the significance of sources. Chemosphere 37, 1457–1472.
Asante, K.A., Adu-Kumi, S., Nakahiro, K., Takahashi, S., Isobe, T., Sudaryanto, A., Devanathan, G., Clarke, E., Ansa-Asare, O.D., Dapaah-Siakwan, S., Tanabe, S., 2011. Human exposure to PCBs, PBDEs and HBCDs in Ghana: temporal variation, sources of exposure and estimation of daily intakes by infants. Environ. Int. 37, 921–928.
Biterna, M., Voutsa, D., 2005. Polychlorinated biphenyls in ambient air of NW Greece and in particulate emissions. Environ. Int. 31, 671–677.
Breivik, K., Gioia, R., Chakraborty, P., Zhang, G., Jones, K.C., 2011. Are reductions in industrial organic contaminants emissions in rich countries achieved partly by export of toxic wastes? Environ. Sci. Technol. 45, 9154–9160.
Breivik, K., Sweetman, A., Pacyna, J.M., Jones, K.C., 2002. Towards a global historical emission inventory for selected PCB congeners – a mass balance approach 2. Emissions. Sci. Total Environ. 290, 199–224.
Breivik, K., Sweetman, A., Pacyna, J.M., Jones, K.C., 2007. Towards a global historical emission inventory for selected PCB congeners–a mass balance approach 3. An update. Sci. Total Environ. 377, 296–307.
Cetin, B., Yatkin, S., Bayram, A., Odabasi, M., 2007. Ambient concentrations and source apportionment of PCBs and trace elements around an industrial area in Izmir, Turkey. Chemosphere 69, 1267–1277.
Chakraborty, P., Zhang, G., Li, J., Xu, Y., Liu, X., Tanabe, S., Jones, K.C., 2010. Selected organochlorine pesticides in the atmosphere of major Indian cities: levels, regional versus local variations, and sources. Environ. Sci. Technol. 44, 8038–8043.
Chen, L., Peng, X., Huang, Y., Xu, Z., Mai, B., Sheng, G., Fu, J., Wang, X., 2009. Polychlorinated biphenyls in the atmosphere of an urban city: levels, distribution, and emissions. Arch. Environ. Contam. Toxicol. 57, 437–446.
Cummins, J.E., 1988. Extinction: the PCB threat to marine mammals. The Ecologist 18, 193–195.
Draxler, R.R., Rolph, G.D., 2003. NOAA. Air Resources Laboratory, Silver Spring, MD. Available at: http://www.arl.noaa.gov/ready/hysplit4.html.
Eckhardt, S., Breivik, K., Mano, S., Stohl, A., 2007. Record high peaks in PCB concentrations in the Arctic due to long-range transport after biomass burning. Atmos. Chem. Phys. 7, 4527–4536.
Eckhardt, S., Breivik, K., Li, Y.F., Mano, S., Stohl, A., 2009. Source regions of some persistent organic pollutants measured in the atmosphere at Birkenes, Norway. Atmos. Chem. Phys. 9, 6597–6610.
Emanuel, K., Zivkovic, R., 1999. Development and evaluation of a convection scheme for use in climate models. J. Atmos. Sci. 56, 1766–1782.
Gioia, R., Eckhardt, S., Breivik, K., Jaward, F.M., Prieto, A., Nizzetto, L., Jones, K.C., 2011. Evidence for major emissions of PCBs in the West African region. Environ. Sci. Technol. 45, 1349–1355.
Harrad, S., Hazrati, S., Ibarra, C., 2006. Concentrations of polychlorinated biphenyls in indoor air and polybrominated diphenyl ethers in indoor air and dust in Birmingham, United Kingdom: implications for human exposure. Environ. Sci. Technol. 40, 4633–4638.
Harrad, S.J., Sewart, A.P., Alcock, R., Boumphrey, R., Burnett, V., Duartedavidson, R., Halsall, C., Sanders, G., Waterhouse, K., Wild, S.R., Jones, K.C., 1994. Polychlorianted biphenyls (PCBs) in the British environment – sinks, sources and temporal trends. Environ. Pollut. 85, 131–146.
Hess, R., Rushworth, D., Hynes, M.V., Peters, J.E., 2001. Disposal Options for Ships. Rand, Santa Monica, CA.
Hossain, M.S., Chowdhury, S.R., Jabbar, S.M.A., Saifullah, S.M., Rahman, M.A., 2008. Occupational health hazards of ship scrapping workers at Chittagong coastal zone, Bangladesh. Chiang Mai J. Sci. 35, 370–381.
Hu, X., Adamcakova-Dodd, A., Lehmler, H.-J., Hu, D., Kania-Korwel, I., Hornbuckle, K.C., Thorne, P.S., 2010. Time course of congener uptake and elimination in rats after short-term inhalation exposure to an airborne polychlorinated biphenyl (PCB) mixture. Environ. Sci. Technol. 44, 6893–6900.
Iwata, H., Tanabe, S., Sakai, N., Nishimura, A., Tatsukawa, R., 1994. Geographical distribution of persistent organochlorines in air, water and sediments from Asia and Oceania, and their implications for global redistribution from lower latitudes. Environ. Pollut. 85, 15–33.
Jain, A., Sareen, R., 2006. E-waste assessment methodology and validation in India. J. Material Cycles Waste Manage. 8, 40–45.
Jha, A.K., Sharma, C., Singh, N., Ramesh, R., Purvaja, R., Gupta, P.K., 2008. Greenhouse gas emissions from municipal solid waste management in Indian megacities: a case study of Chennai landfill sites. Chemosphere 71, 750–758.
Kodavanti, P.R.S., 2004. Intracellular signaling and developmental neurotoxicity. In: Zawia, N.H. (Ed.), Molecular Neurotoxicology: Environmental Agents and Transcription–Transduction Coupling. CRC Press, Boca Raton, FL, pp. 151–182.
Lee, W.-J., Lin Lewis, S.J., Chen, Y.-Y., Wang, Y.-F., Sheu, H.-L., Su, C.-C., Fan, Y.-C., 1996. Polychlorinated biphenyls in the ambient air of petroleum refinery, urban and rural areas. Atmos. Environ. 30, 2371–2378.
Lohmann, R., Northcott, G.L., Jones, K.C., 2000. Assessing the contribution of diffuse domestic burning as a source of PCDD/Fs, PCBs, and PAHs to the U.K. Atmosphere. Environ. Sci.Technol. 34, 2892–2899.
Ludewig, G., Lehmann, L., Esch, H., Robertson, L.W., 2008. Metabolic activation of PCBs to carcinogens in vivo-A review. Environ. Toxicol. Pharmacol. 25, 241–246.
Mandal, P.K., 2005. Dioxin: a review of its environmental effects and aryl hydrocarbon receptor biology. J. Comp. Physiol. B 175, 221–230.

Minh, N.H., Minh, T.B., Watanabe, M., Kunisue, T., Monirith, I., Tanabe, S., Sakai, S., Subramanian, A., Sasikumar, K., Viet, P.H., Tuyen, B.C., Tana, T.S., Prudente, M.S., 2003. Open dumping site in Asian developing countries: a potential source of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans. Environ. Sci. Technol. 37, 1493–1502.

Nakano, T., Tsuji, M., Okuno, T., 1990. Distribution of PCDDs, PCDFs and PCBs in the atmosphere. Atmos. Environment. Part A. Gen. Top. 24, 1361–1368.

Oliver, B.G., Niimi, A.J., 1988. Trophodynamic analysis of polychlorinated biphenyl congeners and other chlorinated hydrocarbons in the Lake Ontario ecosystem. Environ. Sci. Technol. 22, 388–397.

Pozo, K., Harner, T., Lee, S.C., Sinha, R.K., Sengupta, B., Loewen, M., Geethalakshmi, V., Kannan, K., Volpi, V., 2011. Assessing seasonal and spatial trends of persistent organic pollutants (POPs) in Indian agricultural regions using PUF disk passive air samplers. Environ. Pollut. 159, 8.

Pozo, K., Harner, T., Lee, S.C., Wania, F., Muir, D.C.G., Jones, K.C., 2008. Seasonally resolved concentrations of persistent organic pollutants in the global atmosphere from the first year of the GAPS study. Environ. Sci. 43, 796–803.

Pozo, K., Harner, T., Wania, F., Muir, D.C.G., Jones, K.C., Barrie, L.A., 2006. Toward a global network for persistent organic pollutants in air: results from the GAPS study. Environ. Sci. Technol. 40, 4867–4873.

Ruiz, P., Faroon, O., Moudgal, C.J., Hansen, H., De Rosa, C.T., Mumtaz, M., 2008. Prediction of the health effects of polychlorinated biphenyls (PCBs) and their metabolites using quantitative structure–activity relationship (QSAR). Toxicol. Lett. 181, 53–65.

Schuster, J.K., Gioia, R., Breivik, K., Steinnes, E., Scheringer, M., Jones, K.C., 2010. Trends in European background air reflect reductions in primary emissions of PCBs and PBDEs. Environ. Sci. Technol. 44, 6760–6766.

Simon, T., Britt, J.K., James, R.C., 2007. Development of a neurotoxic equivalence scheme of relative potency for assessing the risk of PCB mixtures. Regul. Toxicol. Pharmacol. 48, 148–170.

Someya, M., Ohtake, M., Kunisue, T., Subramanian, A., Takahashi, S., Chakraborty, P., Ramachandran, R., Tanabe, S., 2009. 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. Environ. Int. 36, 27–35.

Stohl, A., 1998. Computation, accuracy and applications of trajectories-A review and bibliography. Atmos. Environ. 32, 947–966.

Stohl, A., Forster, C., Frank, A., Seibert, P., Wotawa, G., 2005. Technical note: the Lagrangian particle dispersion model FLEXPART version 6.2. Atmos. Chem. Phys. 5, 2461–2474.

Sun, P., Basu, I., Hites, R.A., 2006. Temporal trends of polychlorinated biphenyls in precipitation and air at Chicago. Environ. Sci.Technol. 40, 1178–1183.

Totten, L.A., Gigliotti, C.L., VanRy, D.A., Offenberg, J.H., Nelson, E.D., Dachs, J., Reinfelder, J.R., Eisenreich, S.J., 2004. Atmospheric concentrations and deposition of polychlorinated biphenyls to the Hudson River Estuary. Environ. Sci.. 38, 2568–2573.

UNEP, 2001. Regionally Based Assessment of Persistent Toxic Substances: Central and North–East Asia Region: No.10; United Nations Environment Programme: Nairobi, Kenya, 2001.

Van den Berg, M., 2006. The 2005 WHO re-evaluation of toxic equivalency factors for dioxin like compounds–Implications for risk assessment and limitations of the concept. Toxicol. Lett. 164, S55–S56.

Van den Berg, M., Birnbaum, L.S., Denison, M., De Vito, M., Farland, W., Feeley, M., Fiedler, H., Hakansson, H., Hanberg, A., Haws, L., Rose, M., Safe, S., Schrenk, D., Tohyama, C., Tritscher, A., Tuomisto, J., Tysklind, M., Walker, N., Peterson, R.E., 2006. The 2005 World Health Organization reevaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. Toxicol. Sci. 93, 223–241.

Watanabe, M.X., Iwata, H., Watanabe, M., Tanabe, S., Subramanian, A., Yoneda, K., Hashimoto, T., 2005. Bioaccumulation of organochlorines in crows from an Indian open waste dumping site: evidence for direct transfer of dioxin-like congeners from the contaminated soil. Environ. Sci. Technol. 39, 4421–4430.

Watanabe, S., Laovakul, W., Boonyathumanondh, R., Tabucanon, M.S., Ohgaki, S., 1996. Concentrations and composition of PCB congeners in the air around stored used capacitors containing PCB insulator oil in a suburb of Bangkok, Thailand. Environ. Pollut. 92, 289–297.

Wong, M.H., Wu, S.C., Deng, W.J., Yu, X.Z., Luo, Q., Leung, A.O.W., Wong, C.S.C., Luksemburg, W.J., Wong, A.S., 2007. Export of toxic chemicals – a review of the case of uncontrolled electronic-waste recycling. Environ. Pollut. 149, 131–140.

Wurl, O., Potter, J.R., Obbard, J.P., Durville, C., 2006. Persistent organic pollutants in the equatorial atmosphere over the open Indian ocean. Environ. Sci. Technol. 40, 1454–1461.

Zhang, G., Chakraborty, P., Li, J., Sampathkumar, P., Balasubramanian, T., Kathiresan, K., Takahashi, S., Subramanian, A., Tanabe, S., Jones, K.C., 2008. Passive atmospheric sampling of organochlorine pesticides, polychlorinated biphenyls, and polybrominated diphenyl ethers in urban, rural, and wetland sites along the coastal length of India. Environ. Sci. Technol. 42, 8218–8223.