Atmospheric Polychlorinated biphenyls in Indian cities: Levels, Emission Sources and Toxicity Equivalents

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24 **Abstract**

25

26 Atmospheric concentration of Polychlorinated biphenyls (PCBs) were measured on diurnal basis by

27 active air sampling during Dec 2006 to Feb 2007 in seven major cities from the northern (New Delhi

28 and Agra), eastern (Kolkata), western (Mumbai and Goa) and southern (Chennai and Bangalore) parts

29 of India. Average concentration of Σ_{25}PCBs in the Indian atmosphere was 4460 ($\pm$2200) pg/m^{-3} with a

30 dominance of congeners with 4-7 chlorine atoms. Model results (HYSPLIT, FLEXPART) indicate that

31 the source areas are likely confined to local or regional proximity. Results from the FLEXPART model

32 show that existing emission inventories cannot explain the high concentrations observed for PCB-28.

33 Electronic waste, ship breaking activities and dumped solid waste are attributed as the possible sources

34 of PCBs in India. Σ_{25}PCB concentrations for each city showed significant linear correlation with

35 Toxicity equivalence (TEQ) and Neurotoxic equivalence (NEQ) values.

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37 **Key words: Polychlorinated biphenyles, Air, India, FLEXPART, HYSPLIT, toxicity equivalents**

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39 Capsule: Measurement of atmospheric Polychlorinated biphenyls in seven major Indian cities

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Contents

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 et al., 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-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 hour 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 Figure 1.

Air volumes of 72 m^3 in 12h was drawn through quartz microfiber filter (QFF) (Grade GF/A, 8.9cm 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

140 original transport containers, and returned to the laboratory where they were stored at -20°C until

141 extraction.

2.2.   PCB Analysis

144 Prior to extraction a mixture of surrogate standards (2,4,5,6-tetrachloro-m-xylene (TCmX),

145 decachlorobiphenyl (PCB209), $^{13}C_{12}$-PCB138 and $^{13}C_{12}$-PCB180 was added to each of the samples. The

146 samples were Soxhlet extracted for 18 h with DCM. Activated copper granules were added to the

147 collection flask to remove potential elemental sulfur. The extract was rotary evaporated and transferred

148 with hexane to a 15mL amber vial. This was blown down under a gentle stream of nitrogen to about 0.5

149 mL and cleaned on a 8 mm i.d. column with 6 cm alumina (BDH neutral Alumina 3% deactivated),

150 10cm of silica gel (Merck Silica 60 3% deactivated), 10 cm of 50% sulfuric acid silica and 1 cm of

151 baked sodium sulfate (all baked at 450°C overnight) and the column was eluted with 30 ml mixture of

152 50:50 hexane: DCM (v/v). The samples were reduced to a final volume of 25μl after adding 25 μl of

153 dodecane as solvent keeper and a known quantity of pentachloronitrobenzene (PCNB) and PCB-54 was

154 added as an internal standard prior to GC-MSD analysis. PCB analysis was carried out on a Finigan-

155 TRACE GC-MS system with a CP-Sil 8 CB capillary column (50 m, 0.25 mm, 0.25 μm), operating

156 under single-ion monitoring (SIM) mode. Helium was used as the carrier gas at 1.2 mL/min under

157 constant-flow mode. The oven temperature began at 60 °C for 1 min and increased to 290 °C (10 min

158 hold time) at a rate of 4 °C /min. Splitless injection of a 1 μL sample was performed with a 5 min solvent

159 delay time. Injector temperature was at 250 °C. A total of 25 PCB congeners (PCB -28, -37, -44, -49, -

160 52, -60, -66, -70, -74, -77, -82, -87, -99, -101,-105, -114, -118, -126, -128, -138, -158, -166, -179, -180,-

161 187) were detected and quantified.

2.3.   QA/QC

164 Chemical standards were purchased from Accustandard Co. US. Field and lab blanks were collected

165 and analyzed to provide an indication of the overall precision of both the sampling and laboratory

166 methods. Laboratory and field (i.e., samplers sent to/from field sites unopened) blanks consisting of

167 pre-extracted PUF disks were extracted and analyzed in the same way as the samples. 14 AAS PUF

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168   (two from each city) and 7 filter field blanks (one from each city) and14 and 12 laboratory blanks were

169   used for AAS PUF and AAS filter respectively.

170   During each set of extractions, a filter field blank and a PUF plug field blank were included. Detection

171   limits were derived from the blanks and quantified as the mean plus three times the standard deviation

172   of the concentration in the blanks, based on 12 h sampling. The limit of detection (LOD) for every PCB

173   congener was determined by adding three standard deviations (average$\pm$3xSD) to the average of the

174   blanks. Values smaller than the LOD were not included in the calculation. Each PCB congener in the

175   samples was blank corrected. LOD values varied from 0.05-0.42 ng/sample for PUF samples and from

176   0.00023-0.00146 ng/sample and for QFF with the highest LODs observed for trichlorinated congeners.

177   There was no difference (t-test significance, <95%) between concentrations of analytes in the laboratory

178   and field blanks, indicating contamination was minimal during sample collection, transport, storage,

179   and analysis. Field blanks and procedural blanks were below the instrument quantification limit.

180   Surrogate recoveries were 85-125% (mean 94%) for PCB209 and 69-74% (mean 72%) for TC*m*X.

181   Concentrations of the samples were corrected based on those results. The recoveries are comparable to

182   a previous study in the same lab (Zhang et al., 2008).

183   *2.4.   Toxicity Equivalents (TEQs) and Neurotoxic Equivalents (NEQs)*
184

185   TEQs were estimated using the Toxicity equivalent factor (TEFs) for mono-ortho PCBs (PCB-

186   105,114,118), di-ortho (PCB-180) and non-ortho substituted PCBs (PCB-77, 126) using a tiered

187   approach by World Health Organization (Van den Berg et al., 2006). Neurotoxic Equivalency Factors

188   (NEFs) were evaluated for the observed PCB congeners as developed by (Simon et al., 2007) in the

189   same fashion that the dioxin TEQ scheme represents the Ah-receptor related toxicity.

190

191   **3.   Results and discussion**

192   *3.1. Atmospheric levels of PCBs*
193

194   Atmospheric Σ_{25}PCB in pg/m^3 in India varied between 1000-9560 (avg, 4460) in the gaseous phase and

195   0.03-660 (avg, 101) in the particulate phase. Highest range of Σ_{25}PCB in the gaseous phase has been

196   observed in the urban site of Mumbai and is consistent with the observation of 1989 (Iwata et al., 1994)

197   followed by New Delhi. Cities located in the west (Mumbai and Goa) and northern (New Delhi and

198   Agra) India have very high levels followed by Kolkata in the east. Southern India (Chennai and

199   Bangalore) has comparatively lower levels of Σ_{25}PCB (Table 1). Details of each PCB congener for each

200   site for both gaseous and particulate phases have been given in supplementary data, Table S-1 and 2.

201   Typically, less than 10% of the total atmospheric Σ_{25}PCB burden was found in the particle phase (Figure

202   2). Higher average percentage in particulate phase is observed for New Delhi and Agra where during

203   the entire sampling period the average atmospheric temperature was ~15 degrees colder than at the other

204   cities (12ºC and 9ºC respectively) (Chakraborty et al., 2010). Hence lowering the vapor pressure of

205   PCB congeners at lower temperature increases the sorption onto airborne particles. The percentage is

206   also higher for higher molecular weight (MW) PCBs. For other sites, where temperature mostly varied

207   between 23-25ºC, much lower levels of PCBs (<5%) were observed in the particulate phase. Such a

208   variation occurred since higher temperatures for the sites under tropical climate triggers revolatilisation

209   of the semivolatile PCBs and results in higher gaseous air concentrations (Pozo et al., 2006). Gas-phase

210   PCBs are dominated by tetrachlorinated congeners with heavier homologue groups comprising

211   decreasing percentages with increasing MW. 4-Cl homologues contributed about 44-65 % of the total

212   PCB level followed by 5-Cl (18-28%) except in New Delhi where the 6-Cl (20%) has been found higher

213   than 5-Cl (18%). The pattern of PCB congeners showed an abundance of 4-Cl-to 7-Cl PCBs (Figure 3)

214   and was consistent among the cities.

215   PCB levels in the present study do not seem to have declined since 1989 and are fairly consistent with

216   elevated levels of PCBs previously measured in India (Iwata et al., 1994). The average Σ_{25}PCB levels

217   are broadly comparable to historical active air sample data from different cities of USA, Europe (mainly

218   1990-1992) and some urban sites of Turkey and Asian developing nations like Taiwan and China (Table

219   1). However, it is important to note that a direct comparison of data listed in Table 1 is difficult as the

220   data reflect different sum of congeners and time periods. For example, the PCB levels in Europe

221 (Schuster et al., 2010) and USA (Sun et al., 2006) has reduced drastically in the recent years. Still, the

222 concentrations from this study are much higher when compared to the levels reported in Italy, Germany,

223 Singapore and Korea. PCBs levels in New Delhi have increased drastically since 1989 and is consistent

224 with the recent observation under GAPS study where elevated levels have been observed at New

225 Delhi (Pozo et al., 2008). The levels in New Delhi in this study is again comparable or even occasionally

226 lower than the observed levels in more remote regions of northern India reported by a seasonal passive

227 air sampling study (Pozo et al., 2011).

228 PCB congener profiles were compared using correlation coefficients to assess whether the sources for

229 PCBs are similar or different across sites (Supplementary data, Table S-3). The result suggests that

230 excluding Bangalore and rural site of Mumbai, all other major cities of India may be affected by similar

231 sources of PCB emissions.

232 *3.2. Potential PCB sources in India*

233

234 In order to assess the possible source areas for PCBs in the active air samples, the HYSPLIT model, a

235 comprehensive modeling system developed by the National Oceanic and Atmospheric Administration

236 (NOAA) Air Resource Laboratory (Draxler et al., 2003), was used.

237 Simulations of atmospheric transport were additionally made using the Lagrangian particle dispersion

238 model FLEXPART (Stohl, 1998; Stohl et al., 2005). FLEXPART releases so-called tracer particles at

239 emission sources and calculates their trajectories using the mean winds interpolated from the

240 meteorological input fields plus random motions representing turbulence, a deep convection scheme

241 (Emanuel et al., 1999) and atmospheric reactions by OH radicals (Eckhardt, 2009).

242 HYSPLIT back trajectory plots gave a qualitative impression of the variability of the trajectories within

243 each site. Although considerable variability within each individual cluster is evident,

244 there is ample evidence that the clustering procedure grouped the trajectories into three clearly distinct

245 cluster types. The three mean cluster types. Supplementary data, Figure S1 shows the three general air

246 mass pathways to each site in terms of direction of flow, wind speed and the preferential transport

247 height. FLEXPART has given the source regions (Figure 4). FLEXPART results do not consider

248 potential diurnal variability in atmospheric emissions (Figure 5).

249 Daily maximum PCB concentrations in all cities exceeded the minimum by a factor of 1-2 and for few

250 samples by a factor of 3. This phenomenon may be due to temperature-controlled air-terrestrial surface

251 exchange of PCBs which in turn influences the diurnal variability in air concentrations (Figure 5). The

252 elevated temperature encountered in tropical climate of India is very different from those in former use

253 regions at mid-latitudes. The trends of variation for PCBs in the major metropolitan cities viz., New

254 Delhi, Kolkata, Mumbai and Chennai could be due to the re-emission of PCBs from the primary source

255 areas in these cities due to higher ambient temperature. Temperature ranges between day time high

256 temperatures and night time low temperatures at each city (Chakraborty et al., 2010). Hence unlike the

257 modeled PCB-28 levels, the measured PCB-28 showed higher concentration during day time and lower

258 concentrations during night time (Figure 5).

259 *3.2.1   Electronic waste recycling*
260

261 E-waste recycling in the subtropical and tropical regions has reported several environmental and health

262 impacts due to atmospheric emission of PCBs associated with the end of life cycle of electrical and

263 electronic equipment in China (Wong et al., 2007) and Africa (Asante et al.). Strict domestic laws and

264 higher recycling and/or disposal costs has resulted in transportation of the e-waste from the developed

265 nations to the developing countries including India. The highest percentage of 6-Cl and 7-Cl (34-35%)

266 has been observed in northern India at New Delhi and Agra. During the sampling period in New Delhi

267 and Agra the air mass traversed through Uttar Pradesh before ending at these sites (Supplementary data,

268 Figure S1) where most of the e-waste recycling takes place (Jain et al., 2006). Elevated level of PCBs

269 in New Delhi could be associated with their emission during e-waste recycling units in the informal e-

270 waste recycling sites at the eastern part of New Delhi. There are four main e-waste recycling units

271 around New Delhi. While Northern India is not a leading generator, it happens to be the leading

272 processing centre of e-waste in India. Even though Bangalore is the silicon valley of India, the PCB

273 concentration especially for dl-PCBs is comparatively low since Bangalore supports the safe and

274 controlled recycling of corporate e-waste. In addition Indian power sector and steel industries owns

275 71% and 18% respectively of PCB containing equipment like transformers and capacitors. The

276 electricity companies auction the decommissioned transformers which ultimately end up in the e-waste

277 recycling units for further processing. PCB containing oil contained in these transformers are removed

278 and sold out to transformer oil reprocessors. The recycling units lack appropriate infrastructure and

279 procedures for e-waste recycling and disposal. In this study a statistically significant (R^2=0.9842,

280 p<0.001) linear correlation has been observed between the average atmospheric concentration of PCBs

281 sum of the amount of e-waste generated in each city and PCB containing oil available from the old

282 capacitor and transformer from the states where each of these cities are located or/and the adjoining

283 state.

3.2.2   *Ship breaking activities*

286 Ship breaking activities have been found to be another potential source for the release of PCBs in the

287 developing regions (Hossain et al., 2008; Gioia et al., 2011). India has emerged as leading nation

288 involved in ship breaking activities because of demand of re-rollable and melting scrap steel and other

289 items within the country. Largest volume of ship dismantling activity in the world takes place in the

290 western part of India and has contributed to the release of PCBs in the atmosphere of Arabian Sea (Wurl

291 et al., 2006). A typical merchant ship to be dismantled for scrap contains between 250-800 kg of PCBs,

292 principally in the paint and left on the scrap metal in the vessel machinery that is rerolled or

293 remelted (Hess et al., 2001). And, given that ship breaking activities are prevalent within the city of

294 Mumbai at Darukhana and the adjoining west coast in the state of Gujarat, it can be suggested to be

295 another potential important source contributing to the maximum loads of PCBs in Mumbai. Similarity

296 in the elevated levels of 5-Cl (24-28%) (Figure 3) from urban Mumbai and Goa possibly attributed to

297 the same reason which is again consistent with our recent passive air sampling study where high levels

298 of atmospheric PCBs have been observed in the west coast of India (Zhang et al., 2008). But the rural

299 site of Mumbai showed deviation from the urban site and Goa which can also be explained with the air

300 mass ending at this site. HYSPLIT model shows that 50% of the air mass originated from Arabian Sea

301 (Supplementary data Figure S1) before ending to the rural site of Mumbai. Remaining 50% is affected

302 by the surrounding region of which 21% originated more than 400km away from the central part of

303　India where less possibility of PCB source exists. Hence the 28% air mass mostly traversing through

304　the city limit of Mumbai (Supplementary data Material Figure S1 and Figure 4) possibly accounts for

305　nearly 3 folds lower PCB levels in the rural site of Mumbai.

3.2.3.   *Open dumping and burning of municipal solid waste*
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308　As the quantity of discarded computer equipment and other consumer electronics increases, the

309　possibility of increased open burning becomes more likely. PCBs have been used in hydraulic and heat

310　transfer fluids, paints, sealants, plasticizers and carbonless copy paper (Breivik et al., 2002). PCBs were

311　also extensively used in small capacitors in cars in the past (Cummins, 1988; Harrad et al., 1994). The

312　landfill areas in India where municipal solid waste is dumped are mostly open and being ubiquitous

313　there are chances for chemical accumulation. Most of the dumped municipal solid wastes are combusted

314　by the rag pickers thereby releasing dioxins or furans and related compounds (Minh et al., 2003). In

315　addition, the soil in the dumping grounds may be contaminated by PCBs leaked out from the electrical

316　appliances containing technical PCB mixtures. Each of these cities has open dumping grounds for solid

317　waste including e-wastes components like plastic chips, wire insulations, PVC materials and metal

318　scraps (Wong et al., 2007). Mumbai houses large number of computer parks and the e-waste inevitably

319　finds its way to the dumping grounds located within the city limit. New Delhi is the biggest recycler

320　and scrap market of e-waste in India. The e-waste recycling units around Delhi has a poor collection

321　system, hence e-waste finds its way to landfill lacking proper disposal methods. FLEXPART model

322　shows that the samples with the highest concentration of PCBs from urban Mumbai, Chennai, New

323　Delhi and Kolkata are affected by the air mass with the highest emission concentration encircling around

324　the city limits. All these cities have open dumps and most of these are poorly managed. Municipal solid

325　wastes are mostly disposed into such open landfills that are often ignited, resulting in uncontrolled field

326　burning (Jha, 2008). Very high levels of dl-PCBs were previously observed in the human milk of the

327　women residing within the solid waste dumping ground of Kolkata (Someya et al., 2009). Elevated

328　levels of dl-PCBs, especially PCB-126,were observed only in New Delhi, Mumbai and Kolkata which

329　could be associated with the piling and burning of the solid waste in these cities since concentrations of

330   PCB-126 is generated specifically through combustion reactions (Oliver et al., 1988; Lohmann et al.,

331   2000), and this may account for the elevated concentration of this congener.

332   *3.2.4.   Biomass burning*

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334   Biomass burning has been found to be an important source of PCBs (Eckhardt et al., 2007). Biomass

335   burning was explored by investigating potential similarities between observed concentrations of PCBs

336   and predicted concentrations of CO using FLEXPART. The biomass burning tracer was used together

337   with MODIS hot spot data which indicate biomass burning regions. Supplemental data, Figure S2 shows

338   the predicted CO concentrations and the expected influence from fires. The sample collected from

339   Kolkata on 8th Feb'2007 (between 08:00-20:00 hrs) not only had the highest predicted concentration of

340   CO, but also the highest observed concentration of Σ_{25}PCBs. The fire source region for this sample

341   (Supplementary data Figure S2 and Figure 4) covers areas of Myanmar where highest level of biomass

342   burning has been spotted.

343   The observed atmospheric levels obtained from this study cannot be rationalized on the basis of data

344   from an existing global emission inventory (Breivik et al., 2007). Firstly, because we observed for PCB-

345   28, the predicted concentrations were typically about a factor of ∼100 lower than observed air

346   concentrations of PCB-28 found in this study (Figure 5). Secondly, global emissions of PCBs have been

347   predicted to decline over the last decades (Breivik et al., 2007), which does not correspond well with

348   observations from India (Table 1).

349   **4.   Toxic equivalency for measured PCBs**

350

351   Atmospheric sources of PCBs are of interest not only because they play a role as a source of PCB

352   deposition, but also is a source of inhalation exposure. The predominant source of human exposure to

353   PCBs is the diet, but occupational exposure has received increasing attention in recent years (Harrad et

354   al., 2006; Hu et al., 2010). Though the toxic effects on humans through direct inhalation are not yet

355   clear but lower chlorinated congeners, predominating in air, may expose humans to reactive, possibly

356   genotoxic/carcinogenic intermediates because they are relatively easier metabolized (Ludewig et al.,

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357   2008). Corresponding to 12 dl-PCBs, the remaining congeners are referred to as the non-dioxin-like

358   congeners (ndl-PCB). Although these congeners exert weak or no effect on Ah-receptors but they

359   interfere with intracellular signaling pathways that are regulated and modulated by Ca^{2+}, such as those

360   involving ryanodine receptors, protein kinase C, inositol triphosphate or arachidonic acid, and, thus,

361   cause neurotoxicity (Kodavanti 2004; Simon 2007).

362   Concentrations of some of the non-*ortho* PCBs (PCB-77, 126), mono-*ortho* PCBs (viz., PCB- 105, 114

363   and 118) and di-*ortho* PCB (PCB-180) in the present study showed significant higher concentration in

364   majority of the samples in all the cities. Among the dl-PCBs, the contribution of CB-77 TEQ was the

365   highest for all the cities except for New Delhi, Urban site of Mumbai and Kolkata where for some

366   samples PCB-126 showed the maximum contribution to the TEQ levels concentrations. The

367   contributions of PCB-77 to the total TEQ for all cities excluding New Delhi, Urban site of Mumbai and

368   Kolkata were significant ($p < 0.01$) supporting again the impact from a particular contamination source.

369   This difference might have resulted due to the practice of open burning of dumped waste in these cities

370   supporting again the impact of open burning in the dumping grounds (Watanabe et al., 2005).

371   As for dl-PCBs, non-ortho congener CB-126 predominantly contributed to total TEQs (>95% of the

372   total TEQs) for 3 samples each from Mumbai and New Delhi and 9 samples from Kolkata. TEQ input

373   of coplanar PCBs was mainly contributed by PCB congeners CB-77, -105, -118, -156, and to a lesser

374   extent CB-126 (Alcock et al., 1998). PCB-126 in the above samples from these three cities could be a

375   summated influence of the domestic burning of coal and wood (Lohmann et al., 2000) for residential

376   cooking and heating and combustion of the solid waste (Oliver et al., 1988; Lohmann et al., 2000). The

377   trend in total daily intake (TDI) levels (assuming respiration rates of 22 $m^3 day^{-1}$ for an adult) is identical

378   (Supporting Information Table 4). TDI levels were slightly higher than WHO's limit of exposure to dl-

379   PCBs for, few samples of Mumbai and Goa. Significant correlation (R^2=0.438; p<0.01) has been

380   observed between the dl-PCBs from Kolkata and the human milk data from dumpsites of Kolkata

381   (Someya et al., 2009).

382   Significant correlation between the sum of TEQ values and Σ_{25}PCBs in Indian cities is associated with

383   the measured total PCB concentrations (R^2=0.1071-0.8414). In addition NEQ values are strongly

384   significant with Σ_{25}PCBs thereby indicating that neurotoxic toxicity is also predictable (R^2=0.3833-

385　0.9526). The neurotoxic equivalence (NEQ) concentrations are linearly correlated with $\Sigma_{25}PCBs$

386　($p<0.01$) for all the seven cities in India. The findings of this study suggest that airborne PCBs in the

387　urban centers of India are widely present and the atmospheric emission includes congeners associated

388　with dioxin-like as well as neurotoxic effects.

389

390　**Conclusion**
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392　PCB levels are decreasing in developed regions like USA and Europe, but like many developing nations

393　like China and countries in South Africa, the level of PCBs in India is showing an increasing trend

394　particularly for New Delhi, where the level has drastically increased in more than one and a half decade.

395　Existing PCB emission inventories cannot explain the elevated PCB-28 levels in India. Local or

396　regional sources for PCB emission in India include electronic waste recycling units, ship breaking

397　activities and open solid waste dumping grounds. Exposure to atmospheric PCBs especially the dioxin

398　like PCBs explain the immediate need to control PCB releasing sources in India and protect human

399　health and the ambient environment. Dioxin-like PCB emissions are currently not controlled by

400　legislation and are not routinely monitored. Direct inhalation exposures constitute only a small

401　proportion of the total exposure, in the order of 1–2% of the daily intake from food. For people living

402　or working in the source areas are exposed to PCBs primarily via air which could contribute

403　significantly to the overall PCB exposure.

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Appendix A. Supplementary data

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574 Table 1. Comparison of average total PCBs with other studies and previous study in Indian
575 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., 96)
Tainan city	106	2610 (1740-3370)	Rural	Oct 1992-Apr 1993 (Lee et al., 96)
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)

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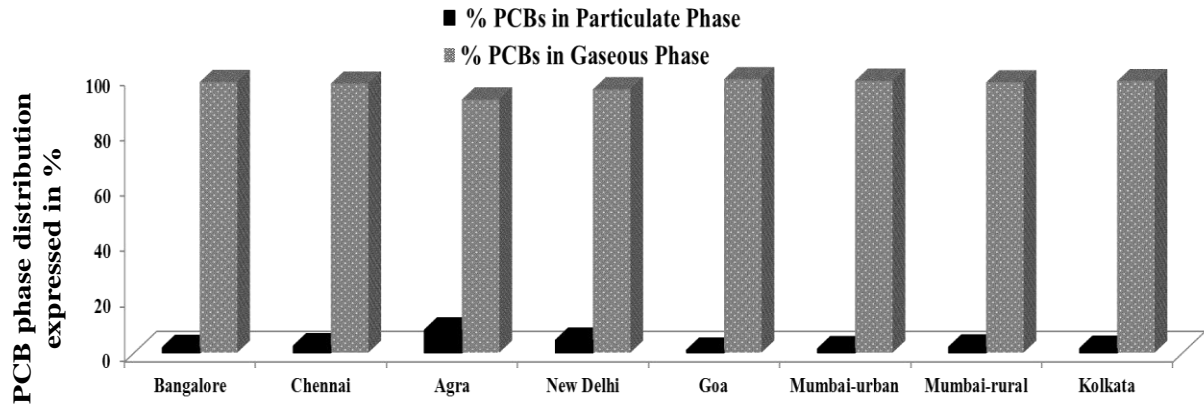
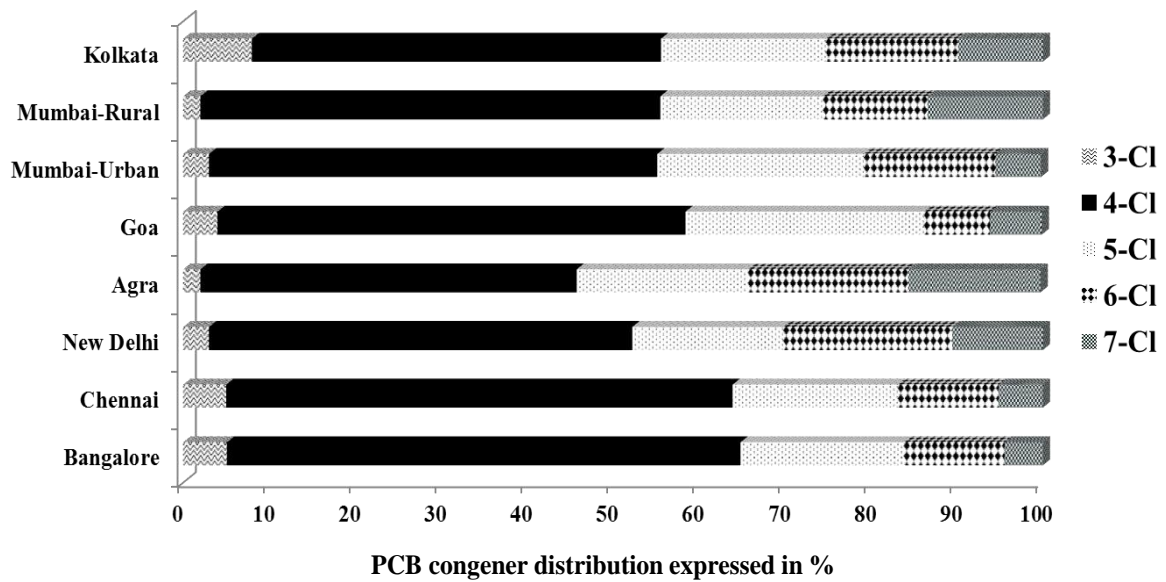580   Fig 1. Sampling sites in India

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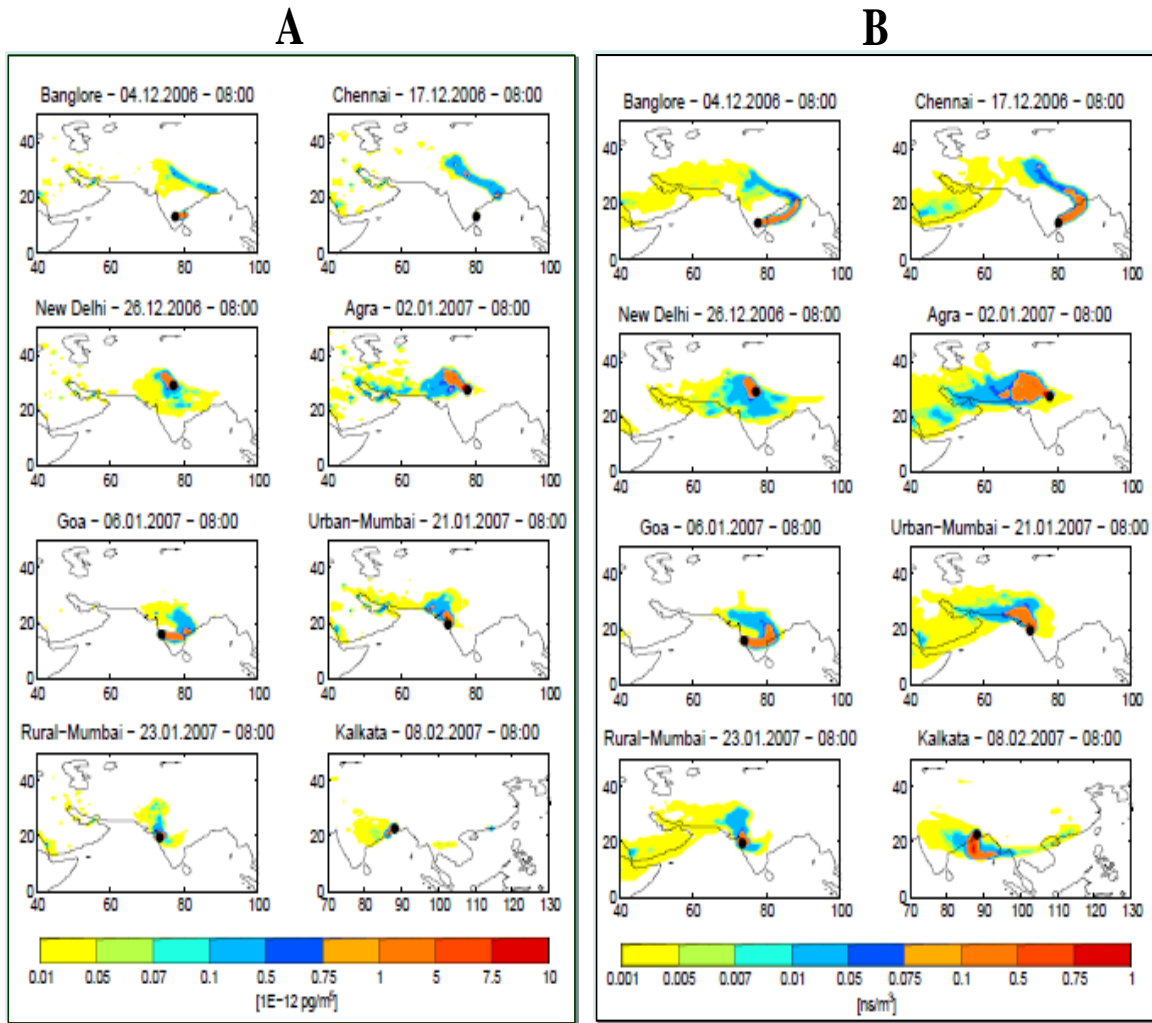

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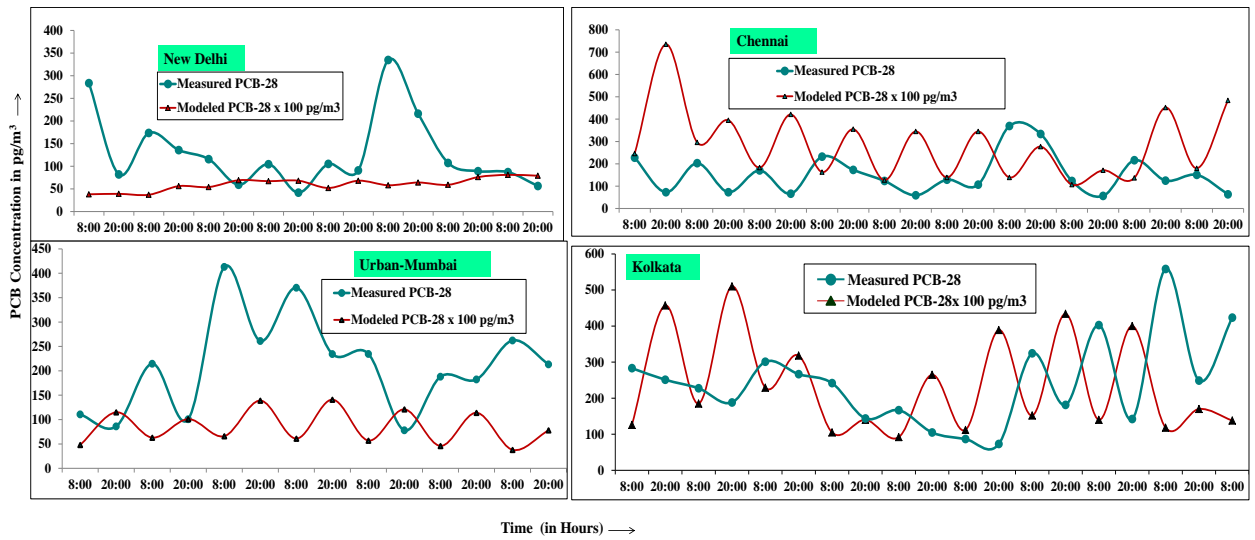Figure 3. Atmospheric distribution of PCB congeners in seven major Indian cities

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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

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Figure 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.