

Investigation of levels in ambient air near sources of Polychlorinated Biphenyls (PCBs) in Kanpur, India, and risk assessment due to inhalation

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Abstract Polychlorinated biphenyls (PCBs) are a class of organic compounds listed as persistent organic pollutant and have been banned for use under Stockholm Convention (1972). They were used primarily in transformers and capacitors, paint, flame retardants, plasticizers, and lubricants. PCBs can be emitted through the primary and secondary sources into the atmosphere, undergo long-range atmospheric transport, and hence have been detected worldwide. Reported levels in ambient air are generally higher in urban areas. Active sampling of ambient air was conducted in Kanpur, a densely populated and industrialized city in the Indo-Gangetic Plain, for detection of 32 priority PCBs, with the aim to determine the concentration in gas/particle phase and assess exposure risk. More than 50 % of PCBs were detected in air. Occurrence in particles was dominated by heavier congeners, and levels in gas phase were below detection. Levels determined in this study are lower than the levels in Coastal areas of India but are at par with other Asian countries where majority of sites chosen for sampling were urban industrial areas. Human health risk estimates through air inhalation pathway were made in terms of lifetime average daily dose (LADD) and incremental lifetime cancer risks (ILCR).

The study found lower concentrations of PCBs than guideline values and low health risk estimates through inhalation within acceptable levels, indicating a minimum risk to the adults due to exposure to PCBs present in ambient air in Kanpur.

Keywords PCBs · Homologue distribution · Aroclor · Phase distribution · Cancer risk · POP · Dioxin

Introduction

Polychlorinated biphenyls (PCBs), a class of chlorinated hydrocarbons (Fig. 1), are artificial or man-made organic compounds. Although they were formulated for the first time in 1881, their commercial production started almost 50 years later in 1929. Owing to their high thermal stability and low electrical conductivity, PCBs have been used in heat exchange fluids in transformers and capacitors, plasticizers, retarders, softeners, and lubricator. High applicability led to high usage and production; more than 10^6 (one million) tons since 1930 with a peak production of 33,000 tons in the USA alone in 1970 (Cajal 2007).

There are 209 possible congeners of PCBs containing varying number of chlorine atoms substituted at one biphenyl molecule. There are 130 PCB congeners found in the commercial mixtures which can be released to the environment. Atmospheric air serves as the primary medium of global transport for persistent organic pollutants. Soil and sediment act as important reservoirs for them globally, and vegetation acts as scavenging

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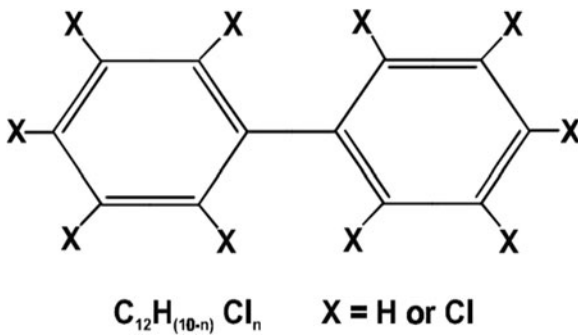


Fig. 1 Chemical structure of PCBs

medium and as a major vector of organic pollutants into terrestrial food chain (Kumar et al. 2012).

PCBs are extremely hydrophobic and lipophilic compounds, and they have a tendency to bio-accumulate in organisms among all trophic levels (Oliver and Niimi 1988; Harding et al. 1997; Kucklick and Baker 1998). PCBs bio-accumulate in the fatty tissues of exposed animals and humans, causing a wide variety of acute health effects such as skin rashes, eye irritation, disturbances in liver and immune system, and chronic effects like liver damage, cancer, and problems in human reproductive system (Ponnambalam 1998; Neumeier 1998; Fiedler 1997). As early as the 1960s, PCBs were found to pose a threat to human and ecosystem health (Shifrin and Toole 1998). Knowledge of their environmental persistence and toxicity led to PCBs being classified as a persistent organic pollutant (POP) at the Stockholm Convention in 1972 (United Nations Conference on the Human Environment, Stockholm Sweden) resulting in prohibition of use during the 1980s and 1990s worldwide.

PCB usage in commercial products has been classified as closed systems, nominally closed systems, and open-ended systems (WHO survey report). The main percentage of production (about 56 %) was used in completely closed systems (capacitors and transformers) as dielectric fluids. Therefore, the majority of PCB in atmosphere comes from the volatilization from oil used in transformers and capacitors containing PCB (Robertson and Hansen 2001).

PCBs were never produced in India, and import was banned in 1998 (UNIDO FSP India PCBs, 2009). Surprisingly, global distribution of PCB emissions shows India emitting more PCBs than other surrounding countries, which appears to affect levels of PCBs in the Himalayas (Kang et al. 2009). Collection of passive air samples in urban, rural, and wetland sites along the

coastal length of India (Zhang et al. 2008) reported higher concentrations (216–1077 pg/m^3) than obtained in other Asian countries (5–340 pg/m^3) but are comparable to urban locations in Europe (20–1700 pg/m^3). A similar study examining occurrence and PCB levels in air in industrial and agricultural regions of Punjab Province in Pakistan (Syed et al. 2013) reports that total PCB levels ranged from 34 to 389 pg/m^3 in air, which is much lower than that reported for India. It is interesting to note that the highest PCB concentrations were observed at urban locations or sites at close proximity to urban centers in both studies conducted in India and Pakistan (Zhang et al. 2008; Syed et al. 2013). The most likely reason for this observation is PCB additives in oil used in transformers and capacitors to increase dielectric strength. Syed et al. (2013) also suggest that soils are a potential secondary source of PCBs in agricultural areas, whereas they are in equilibrium or atmospheric deposition in industrial and urban areas of Punjab Province, Pakistan.

Studies on PCBs in environment under Indian conditions are few. Based on observations from these studies which have detected PCBs in air in urban areas, a need for an air quality study in the most densely populated region of the country which is also highly industrialized is warranted.

This study was conducted in Kanpur, one of the major industrial cities in Uttar Pradesh, India. Active ambient air sampling near possible sources, for detection of 32 priority PCBs, with the aim to determine levels and phase distribution in ambient air and map potential contamination hotspots, was planned and conducted at three different locations in Kanpur. Samples were collected in winters and summers (2012–2013) to determine variation in PCB congener concentration. Air samples from three locations at Panki and Kalyanpur were analyzed to compare PCB congener pattern, occurrence, and levels. Efforts have been made to assess health risk posed through inhalation.

Materials and methods

Sampling locations

Ambient air sampling was conducted in proximity of electric transformers of varying sizes (400, 220, and 33 kV) at three sub-stations (Fig. 2) and included Panki

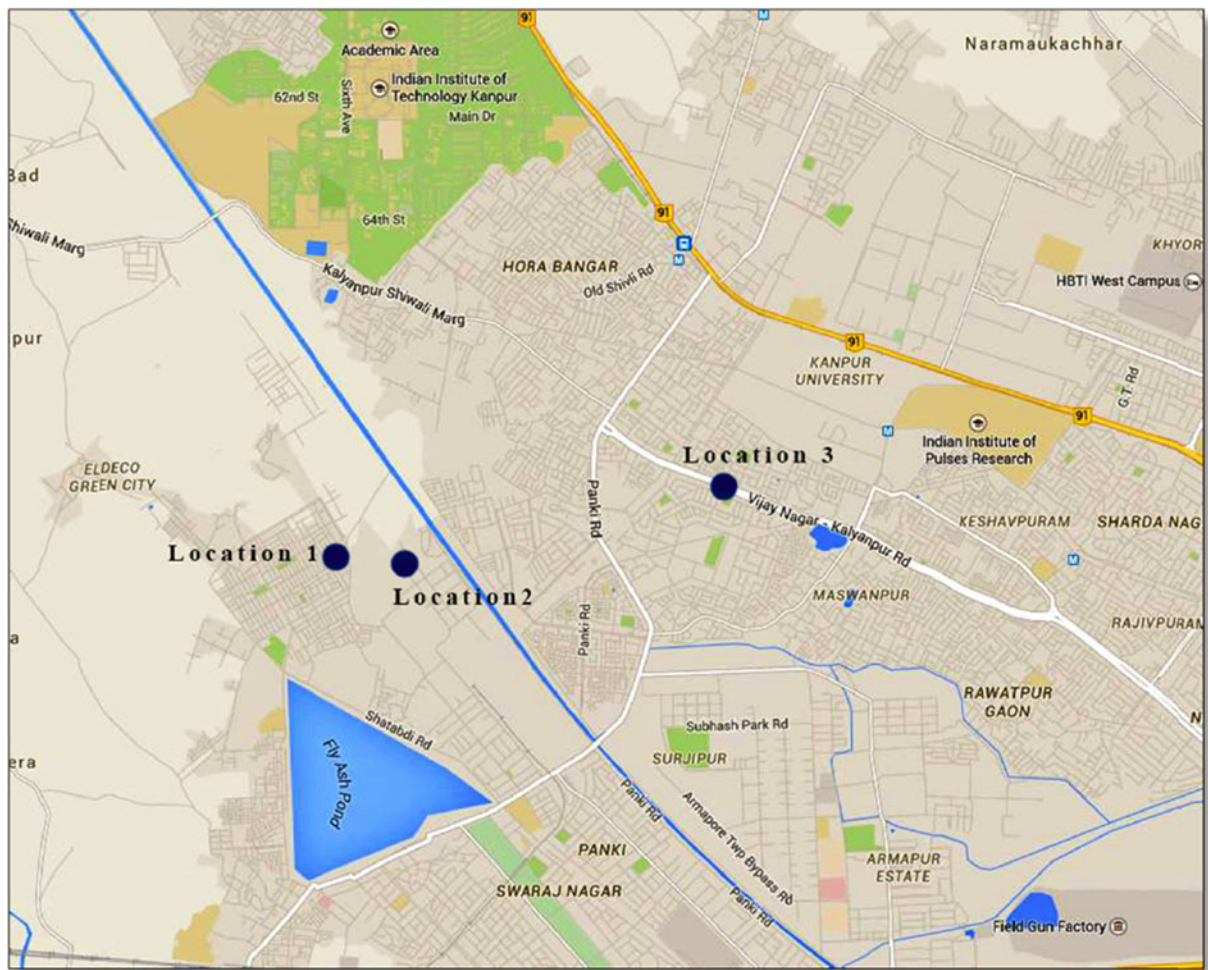


Fig. 2 Map of Kanpur showing the sampling locations. Location1: Panki 400 kV sub-station (P1); location 2: Panki 220 kV sub-station (P2); location 3: Kalyanpur 33 kV sub-station (K1)

(400 kV; P1), Panki (220 kV; P2), and Kalyanpur (33 kV; K1). Both the large sub-stations, P1&P2, have double transformers and capacitors as compared to the smaller sub-station, K1. The sites were chosen based on the fact that preponderance of PCBs was used in transformer oil owing to their chemical stability, low inflammability, and electric insulating property. To permit assessment of risk posed through inhalation, proximity of sampling location to local population was also considered. It is interesting to note that at P1 power station some transformers were installed roughly 20 years earlier, i.e., early 1990s when PCBs were used in transformer oil.

Sites at Panki are in proximity of fly ash pond of Panki Thermal Power Station. Wind direction during sample collection, discussed in next section, was from North West resulting in pond being downstream of

sampling locations. The fact that all three sites lie upstream of the fly ash pond (Fig. 2) confirms that the likelihood of air samples at the three locations being influenced by fly ash is negligible.

Sample collection

A total of 18 ambient air samples in proximity to sources, were collected during summer (April and May, 2013). Samples were collected at each location for at least three consecutive days using optical particle counter (OPC) with flow rate of 1.2 LPM and organic vapor sampler (OVS; APM 856). OPC provides information on particle size distribution (PSD) in respirable range, while OVS collects gas phase samples by adsorption on an activated charcoal column. The organics

collected on charcoal column are desorbed and analyzed via a gas chromatograph to estimate the actual concentration in ambient air. Mass of particles collected was determined through gravimetric analysis of OPC filters. To ensure collection of quantifiable levels in particle phase, the same filter was used for all 3 days in OPC.

Meteorological data Onsite air temperature measured on an hourly basis reveals similar average temperatures in both months (~30.3 °C in April and 31.1 °C in May). Other meteorological parameters like relative humidity and wind speed were recorded as ~34.6 % and 8.3 km/h in April and 29.2 % and 9.2 km/h in May, respectively. Wind direction was from North West.

Sample preparation

Levels of PCBs in gas phase were determined from OVS charcoal tubes and in particle phase from filters collected from OPC. Details for sample extraction are provided in Upadhyay (2013). Briefly, all samples were extracted using hexane:DCM (1:1). PCB 138 was used as surrogate standard and added to the filter/charcoal tube before extraction. The filters were spiked with the surrogate standards and kept in the desiccator for 1 h. Multilayered silica gel column chromatography was used for extract clean-up. The sample extract obtained was further concentrated under gentle stream of purified nitrogen gas to 1 ml with PCB 30 added as internal standard. Quantification with gas chromatography-mass spectroscopy (GC-MS). GC-MS (Perkin Elmer, Model Clarus 600) was conducted in electron impacted (EI) mode using a fused silica capillary column. Helium (zero grade) was used as a carrier gas.

QA/QC

All analytical procedures were monitored using strict quality assurance and control measures. Analysis of procedural blanks was performed along with real samples. Certified chemical standards were purchased from Accu-Standard Inc. with 99.9 % purity. Teflon filters, used as laboratory blanks, were extracted and analyzed in the same way as samples. Five-point calibration curve method was used for analysis of the standards on GC-MS. Surrogate recoveries were between 68 and 116 %. Reported values were not recovery corrected.

Estimation of levels in gas phase using Junge-Pankow Model

Junge-Pankow model, the most widely used model for estimating adsorption onto aerosols, has been used to predict levels in gas phase based on measured values in particles. Briefly, Junge-Pankow equation (Eq. 1) relates the fraction of particulate POPs to the saturation liquid-phase vapor pressure of the compound and the surface area of particles per unit volume of air.

$$\phi = \frac{C_p \text{TSP}}{C_g + C_p \text{TSP}}, \quad (1)$$

where

ϕ	fraction of particulate POPs
C_p (ng/ μg particle)	concentration of POPs associated with aerosol
C_g (ng/ m^3)	gas phase concentration
TSP	total suspended particles

Calculations have been performed for K1 and P2. Particle mass measured on OPC filters was used as TSP in calculations (TSP value for K1 = 5.92 $\mu\text{g}/\text{m}^3$ and for P2 = 8.45 $\mu\text{g}/\text{m}^3$).

Results and discussion

PCBs could be detected and quantified only in the particles and showed an abundance of the heavier congeners. While only the homologues with four to seven chlorine atoms in the molecule (tri, tetra, and hepta) could be quantified, various other heavier congeners were also detected.

Levels in gas phase were below detection limits and hence are not referred to in the following discussion.

Occurrence and levels of PCBs in ambient air in Kanpur, India

Data for occurrence in particle phase combined for all the sites reveals detection of more than 50 % (18) of the 32 PCB congeners analyzed. Among these, detection and levels of six major components at the three locations are presented in Table 3. The highest reported concentrations among the three sites are listed in Table 2.

Levels of PCBs in air reported for Asia, Europe, India and GAPS study

Levels of PCBs in air reported for Asia, Europe, India and GAPS study are presented in Table 1. The GAPS study, with 40 sites over seven continents, reports the highest range of PCBs. A potentially important source of PCBs is known to be dielectric fluid used in transformers and capacitors. The study observes that PCBs were elevated at urban/suburban sites consistent with their historical use pattern. It must be noted that GAPS 2006 did not have any site in India or Pakistan. However, passive air monitoring in agricultural regions of India in 2006–2007 (Pozo et al. 2011) reports high values (972 pg/m³) comparable with those reported for coastal India (Zhang et al. 2008). Three out of total six agricultural locations in the study are in Southern India, near the coast, three near Delhi. The only location that is urban and part of Indo-Gangetic Plain is Patna, Bihar.

As expected, levels determined at an industrial city in Northern India in this study are at par with other Asian countries where majority of sites chosen for sampling were urban industrial areas (Table 1). It is interesting to note that levels in

this study are lower than the levels in coastal and agricultural areas of India.

Levels of PCBs in ambient air in Kanpur, India

Short range transport from local sources

Highest measured levels at the three sites of six congeners of PCB detected in particle phase, in increasing order of mass, are listed in Table 2. Detection of high molecular weight PCB congeners such as: 187, 189, and that too at highest levels among the 6 congeners (>125 pg/m³), strongly suggest a local source. This observation is in contrast to that reported in Pakistan (Syed et al. 2013) where levels reported for industrial and agricultural locations steadily decrease with increase in PCB mass, with the lowest reported for PCB189 (which occurs at the highest level in this study). This results in authors’ (Syed et al. 2013) interpretation of impact of long-range transport from distant sources on levels observed in ambient air in Punjab Province, Pakistan. However, it must be mentioned here that sampling was conducted in proximity to sources in this study,

Table 1 Levels of PCBs detected (pg/m³) in Asia, Europe, and GAP study

Study locations	Concentration range (ΣPCB) (pg/m ³)	Source
Asia, India (Kanpur, 3 sites)	254–432	This study
Asia, Pakistan (Karachi, Lahore)	48–61	Nasir et al. 2014
Asia, Pakistan (Punjab Province)	34–389	Syed et al. 2013
Asia, India (7 cities; Kolkata, New Delhi, Agra, Mumbai, Goa, Chennai and Bangalore)	1000–9650 (December 2006 to Feb 2007)	Chakraborty et al. 2013
Asia, India (Agricultural region), (Passive air sampling)	972	Pozo et al. 2011
Asia, India (Coastal Areas, 18 sites)	216–1077	Zhang et al. 2008
Global Atmospheric Passive Sampling (GAPS) study (40 sites on 7 continents)	0.1–2830 (December 2004 to March 2005)	Pozo et al. 2006
Asia (China, Singapore, Japan, South Korea)	5–340	Jaward et al. 2005
Europe, UK (London & Manchester)	1000–2000	Jaward et al. 2004
Europe (22 countries)	20–1700	Jaward et al. 2004

Table 2 Maximum observed concentrations in ambient air (pg/m^3) at three sub-stations, Kanpur

PCB Congener	Maximum observed concentration (pg/m^3)	
	This study: near 3 sub-stations in industrial city Kanpur P1 (400 kV), P2 (220 kV), K1 (33 kV)	Pakistan (Syed et al. 2013) Industrial cities and agricultural areas Punjab, Faisalabad, Sheikhpura and Lahore
PCB 28	102.4	130
PCB 60	94.8	28
PCB 70	121.6	8.7
PCB 77	105.8	11
PCB 187	133.9	1.5
PCB 189	129.1	0.41

and sample collection at distant locations for further interpretation is required.

Variation in PCB levels between the three sites at Kanpur

The results for PCB levels obtained at the three locations were contrary to expectations. As mentioned earlier, at the biggest power station in this study, P1 (Panki 400 kV), some transformers were installed roughly 20 years earlier, when PCBs were used in transformer oil. This suggests greater chances of PCB detection at P1, followed by the second largest station P2. However, at the bigger size power stations in Panki (P1 400 kV; P2

Table 3 Comparison of PCB levels (pg/m^3) at three sites (in increasing order of capacity) in Kanpur

PCB congener	K1 Kalyanpur (33 kV)	P2 Panki (220 kV)	P1 Panki (400 kV)
PCB 28	102.4	ND	BDL
PCB 60	94.8	ND	ND
PCB 70	BDL	121.6	ND
PCB 77	105.8	ND	ND
PCB 187	ND	133.9	ND
PCB 189	129.1	ND	ND
\sum PCB	432.0	254.5	BDL

ND not detected, BDL below detection limit

220 kV), most PCBs were either not detected (ND) or could not be quantified (BDL) (Table 3) while they showed higher concentrations at the smallest power station (K1 33 kV).

This contrary observation, lower levels at bigger sub-station and highest levels at smallest sub-station, can be attributed to poor management of the transformer yard and improper disposal of oil leaks at K1. Soil near the transformer at K1 was noted to be saturated with oil during sampling. However, soil sample collection was not permitted at this site, and hence, the possibility of soil acting as secondary source of PCBs in air, as suggested in a recent study from Pakistan (Syed et al. 2013), cannot be verified. Owing to proper maintenance and disposal of leaked oil from transformers, lower concentrations were detected at P2 and P1. Need for implementation of proper maintenance rules is highlighted by these observations.

Statistical analysis of levels observed at the three stations

Even though only few PCB congeners were detected in this study, an attempt has been made to compare levels between the three sites through a hypothesis test on the acquired data set (Table 2). For simplicity of calculations, ND and BDL are assumed to be zero. One sample t test has been performed, and details are given in Table 4. P1 does not have sufficient data and comparison is presented only between K1 and P2.

In this test, the difference between the observed average values of the two sites, with difference ~ 30 units, has been taken into account. The null hypothesis was assumed as “mean of levels at K1 $>$ mean of levels at P1,” and the hypothesized mean difference is taken as 30. The result shows that with a confidence interval of 95 % (corresponding α value is 0.05), the null hypothesis is accepted with a calculated p value of 0.494

Table 4 Results of t test

Parameter	t test results
Mean at K1 (33 kV)	72.017
Mean at P2 (220 kV)	42.583
α value	0.05
Hypothesized mean difference	30
P (one tail)	0.493809

Table 5 Contribution to RSPM to PM10 load at all three sites

Location	Day 1	Day 2	Day 3
K1: Kalyanpur, 33 kV	0.41	0.31	0.27
P1: Panki 220 kV, P	0.25	0.26	0.32
P2: Panki 400 kV	0.34	0.28	0.22

(> $\alpha=0.05$). In short, the levels at the smallest of the three sub-stations K1 (Kalyanpur 33 kV) are significantly higher than at P2 (Panki 220 kV).

Contribution of RSPM to particle load

Respirable particles (RSPM=PM2.5) for all three sites over 3 days of sampling contributed <~40 % of particle load (=PM10) (ranged from 22 to 41 %) with the highest PM2.5/PM10 ratios at K1 (Table 5). Occurrence of respirable particles (PM2.5) in higher fraction at K1, along with highest levels of PCBs measured, would suggest greater health risk at the location.

PCB homologue distribution

As mentioned earlier, about 56 % of PCB production worldwide was used in completely closed systems

Table 6 Uses of aroclors (source: USEPA)

Operation	Possible PCB aroclor used
Manufacture/synthesis of aroclor PCBs	All aroclors
Filling of transformers	Aroclor 1260 and some 1254
Filling of capacitors	Aroclor 1016, 1242, and 1254
Recycling of used fluids	All aroclors
Rework of transformers	Aroclor 1260 and 1254
Heat transfer operations	Aroclors 1248, 1254, and 1260
Hydraulic fluids	Aroclors 1242, 1248, and 1254
Paints and caulks	Aroclors 1242 and 1254
Polymers and rubbers	Aroclors 1242 and 1248
Printing and copying	Aroclor 1242
Lost wax casting	Aroclor 1254

(capacitors and transformers) as dielectric fluids. The most common commercial mixture of PCBs was the aroclor series. Table 6 lists the various uses of aroclor mixtures. PCBs were manufactured as a mixture of various PCB congeners through progressive chlorination of batches of biphenyl until a certain target percentage of chlorine by weight was achieved.

Table 7 lists *aroclor mixtures used in transformers and capacitors*. These aroclor mixtures are present in homologues having high number of chlorine atoms

Table 7 Homologue groups represented by aroclor mixture (source: USEPA)

Homologue groups (Groups of congeners with same <u>number</u> of chlorines)	Chlorine (weight percent)	Aroclor mixture % by weight						
		1221	1232	1016	1242	1248	1254	1260
Biphenyl-no chlorines (0)	0	10	–	–	–	–	–	–
Mono-chlorinated biphenyls (1)	18.8	50	26	2	3	–	–	–
Di-chlorinated biphenyls (2)	31.81	35	29	19	13	2	–	–
Tri-chlorinated biphenyls (3)	41.3	4	24	57	28	18	–	–
Tetra-chlorinated biphenyls (4)	48.61	1	15	22	30	40	11	–
Penta-chlorinated biphenyls (5)	54.4	–	–	–	22	36	49	12
Hexa-chlorinated biphenyls (6)	59	–	–	–	4	4	34	38
Hepta-chlorinated biphenyls (7)	62.8	–	–	–	–	–	6	41
Octa-chlorinated biphenyls (8)	66	–	–	–	–	–	–	8
Non-chlorinated biphenyls (9)	68.8	–	–	–	–	–	–	1
Deca-chlorinated biphenyls (10)	–	–	–	–	–	–	–	–

typically tetra-, penta-, hexa-, hepta-chlorobiphenyl. As listed, aroclor mixtures used in filling and rework of transformers are mainly aroclor 1260 and 1254. For heat transfer operations, aroclor mixture 1248 is also used.

This section examines the co-relation between aroclor homologues used in closed systems and those detected in air in this study.

PCB congener profile in the present study showed an abundance of the heavier congeners. While only the homologues with four to seven chlorine atoms in the molecule (tri, tetra, and hepta) could be quantified, various other heavier congeners were also detected. Figure 3 presents contribution of PCB homologues to total PCB concentration (combined data for three sites). Hepta-chlorobiphenyls contributed almost half of total PCB concentration (47 %), followed by tetra- and trichlorobiphenyl. Contribution of tri-chlorobiphenyls to total PCB load measured in this study (15 %) compares very well with 18 % mass contribution to aroclor 1248 mixture by tri-chlorinated biphenyls (Table 7). Similarly, contribution of 47 % by hepta-chlorinated biphenyls noted here compare well with 41 % by mass of hepta-chlorinated biphenyls in aroclor 1260. Considering that the samples were collected in close proximity to transformers at all sub-stations, it is evident that emissions from local sources has an impact on the levels detected in ambient air. This observation is strengthened by recalling that higher mass PCBs were detected in higher concentrations on particles (Table 2).

Occurrence of dioxin-like PCBs in this study

PCBs can be dioxin-like or non-dioxin-like in nature. Dioxin-like PCB are POPs covered by the Stockholm Convention. They are highly toxic compounds with a range of health effects,

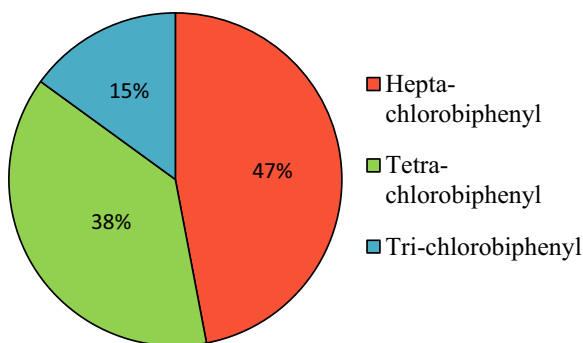


Fig. 3 PCB homologue distribution at the three sites in this study

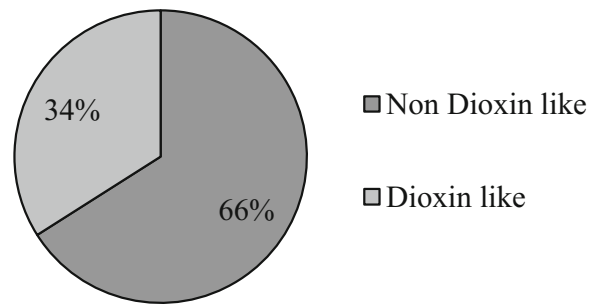


Fig. 4 Total PCB concentration for dioxin and non-dioxin-like PCB

including immunotoxicity, developmental and neuro developmental effects, and changes in thyroid and steroid hormones and reproductive function. They can travel long distances from the source of emission and bio-accumulate in food chains.

Dioxin-like PCBs occurred in quantifiable range in this study. Concentration of total dioxin-like PCBs for all the three sites combined was determined to be 234.9 $\mu\text{g}/\text{m}^3$ contributing one third (34 %) of total PCB load (Fig. 4). The high level of dioxin-like PCBs raises concern about health of people exposed near these locations, and cancer risk calculations have been performed separately for dioxin-like and non-dioxin-like PCBs in [Health risk estimation section](#).

Predicting gas phase concentrations using Junge-Pankow model

As mentioned earlier, PCBs could not be quantified in gas phase samples. Using levels of PCBs mea-

Table 8 Measuring of gas particle distribution using Junge-Pankow Model

PCB congener	Measured particle phase concentration C_p ($\mu\text{g}/\text{m}^3$)	Predicted gas phase concentration C_g ($\mu\text{g}/\text{m}^3$)
PCB 28	102.39	0.018
PCB 60	94.76	0.014
PCB 70	121.62	0.097
PCB 77	105.83	0.085
PCB 187	133.90	0.050
PCB 189	129.06	0.0018

Table 9 Parameters used for ILCR calculation

Parameter	Description	Unit	Value
Cs	Total PCBs concentration in air	$\mu\text{g}/\text{m}^3$	Variable
IR	Inhalation rate	m^3/day	For adults: 20 (adult, average, EPA1989d)
F	Unit conversion factor	–	10^{-6}
ET	Exposure time	h/day	8 h/day
ED	Exposure duration	Year	70 (adults)
BW	Body weight	kg	70 (adults)
LT	Lifetime = exposure duration \times 365 days	Days	–
CSF	Cancer slope factor	$\text{mg kg}^{-1} \text{day}^{-1}$	For dioxin TEQ:150,000 For non-dl-PCBs:2 (upper bound)

sured in particle phase, through OPC filters, levels in gas phase were predicted using Junge-Pankow model and results are presented in Table 8.

The fact that predicted levels are lower than detection limits for most analytical instruments explains why gas samples collected by OVS, a low volume sampler, could not be quantified. These observations strongly suggest that measurement of concentrations in gas phase will require collection of large sample volume to permit detection.

Influence of mass and size on occurrence in gas phase

The effect of large molecular size and mass resulting in increased hydrophobicity and lower volatility is reflected by decrease in amount present in gas phase with increasing PCB size (Table 8). This is demonstrated by observing that even though maximum particle phase levels of PCB 187 and PCB 189 are not very different (134 and 129 pg/m^3 , respectively), level in gas phase for lighter congener, PCB 187, is an order

of magnitude higher than that for heavier congener, PCB 189.

Health risk estimation

Cancer risk to people working at sampling locations

Based on the levels detected on particles, daily dose of PCBs through inhalation leading to incremental lifetime cancer risk (ILCR) to a male adult was calculated.

Detection of dioxin-like compounds in the environment results in use of special risk estimation approach and hence ILCR calculation has been performed separately for dioxin-like and non-dioxin-like PCBs. The basic equations used to calculate ILCR are given below. Details of parameters used are presented in Table 9 and results in Table 10.

Equations for calculation of ILCR: lifetime cancer risk determined for dioxin-like and non-dioxin-like PCB is given in Table 10.

Table 10 Lifetime cancer risk

	Concentration	LAAD (mg/kg day) adults	Regulations/acceptable limits	Risk ILCR
Dioxin TEQ	234.9 pg/m^3	0.54×10^{-12}	a. TDI for dioxins: 1.0 $\text{pg TEQ kg}^{-1} \text{day}^{-1}$	8.05×10^{-5}
Non-dioxin PCB	452.7 pg/m^3	1.04×10^{-12}	b. Acceptable weekly intake: dioxins: 14 $\text{pg TEQ}/\text{kg body weight}$ and dioxin-like PCBs: 12 pg	2.06×10^{-12}

a. FAO/WHO Expert Committee on Food Additives for acute, subchronic and chronic exposures to dioxins. b. European Commission

Incremental lifetime cancer risk:

1. LADD = $(C_s \times IR \times ET \times F \times EF \times ED) / (BW \times LT)$
2. ILCR = LADD \times cancer slope factor (CSF) ,

where

LADD lifetime average daily dose ($\text{mg kg}^{-1} \text{ day}^{-1}$)

Tolerable daily intake (TDI) is the amount of intake per kilogram of body weight per day of a chemical substance suspected of having adverse health effects when absorbed into the body over a long period of time. TDI has been set by international agencies to ensure public health safety.

As per USEPA, acceptable risk distribution is equal to 10^{-5} for carcinogens. The observed lifetime average daily dose (LADD) for adults ($0.537 \times 10^{-12} \text{ mg TEQ kg}^{-1} \text{ day}^{-1}$) is much lower than recommended acceptable daily intake. ILCR for dioxin-like PCBs, which form <35 % of the total PCB load, is at the boundary of this limit. Results suggest minimum risk to adults working in those sub-stations due to exposure to PCBs in ambient air through inhalation.

Conclusion

PCBs were detected in ambient air of three sub-stations of varying capacity in Kanpur city sampled in summer 2012. As confirmed through use of Junge-Pankow partition model, levels were below detection limits in gas phase and greater than half of 32 congeners were detected on particles. Detections were dominated by heavier congeners, suggesting local sources. Analysis of homologue distribution revealed that heavier congeners belong to the homologue group of aroclor mixtures that are used for filling transformers and capacitors. This leads to an obvious conclusion that occurrence of PCBs in ambient air can be attributed to proximity of sampling location to transformers. Highest PCB levels in ambient air were recorded at the location with the smallest transformer size (33 kV). Although the dioxin-like PCBs contribute <35 % of total PCB load, the lifetime cancer risk to a male adult is significant and warrants further examination.

The results from this study highlight the need for stricter implementation of transformer maintenance procedures, and minimizing leakage of oils from the unit. This facility showing highest levels had the worst

maintenance record among all three centers sampled and oil leakage from this transformer into soil below was observed. Examination of contaminated soil as a possible source, and assessment of PCB levels and occurrence of any transformation products, at locations distant from source, is warranted.

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References

- Cajal, M.P. (2007). *Fenton treatment of PCB contaminated surfaces*, Tampere University of Technology.
- Chakraborty, P., Zhang, G., Eckhardt, S., Li, J., Breivik, K., Lam, P. K. S., Tanabe, S., & Jones, K. C. (2013). Atmospheric polychlorinated biphenyls in Indian cities: levels, emission sources and toxicity equivalents. *Environmental Pollution*, 182, 283–290.
- Environmentally sound management and final disposal of PCBs in India, CEO Endorsement form UNIDO FSP.(Accessed: 25 Nov 2009).
- Fiedler, H. (1997). *Polychlorinated biphenyls: uses and releases. July 1–4, 1997. Proceedings of the subregional awareness raising workshop on persistent organic pollutants (POPs)*. St. Petersburg: United Nations Environmental Program (UNEP) Chemicals webpage.
- Harding, G. C., Leblanc, R. J., Vass, W. P., Addison, R. F., Hargrave, B. T., Pearre, S., Dupuis, A., & Brodie, P. F. (1997). Bioaccumulation of polychlorinated biphenyls (PCBs) in the marine pelagic food web, based on a seasonal study in the southern gulf of st. Lawrence, 1976–1977. *Marine Chemistry*, 56(3–4), 145–179.
- Jaward, F. M., Farrar, N. J., Hamer, T., Sweetman, A. J., & Jones, K. C. (2004). Passive air sampling of PCBs, PBDEs, and organochlorine pesticides across Europe. *Environmental Science & Technology*, 38(1), 34–41.
- Jaward, F. M., Zhang, G., Nam, J. J., Sweetman, A. J., Obbard, J. P., Kobara, Y., & Jones, K. C. (2005). Passive air sampling of polychlorinated biphenyls, organochlorine compounds, and polybrominated diphenyl ethers across Asia. *Environmental Science & Technology*, 39(22), 8638–8645.
- Kang, J. H., Choi, S. D., Park, H., Baek, S. Y., Hong, S., & Chang, Y. (2009). Atmospheric deposition of persistent organic pollutants to the east Rongbuk glacier in the Himalayas. *Science of the Total Environment*, 408, 57–63.
- Kucklick, J., & Baker, J. (1998). Organochlorines in Lake Superior's food web. *Environmental Science & Technology*, 32, 1192–1198.
- Kumar, B., Verma, V. K., Singh, S. K., Kumar, S., & Sharma, C. S. (2012). Occurrence of congener specific polychlorinated biphenyls in soils from roadside agricultural fields. *Asian Journal of Plant Science and Research*, 2(3), 299.

- Nasir, J., Wang, X., Xu, B., Wang, C., Joswiak, D. R., Rehman, S., Lodhi, A., Shafiq, S., & Jilani, R. (2014). Selected organochlorine pesticides and polychlorinated biphenyls in urban atmosphere of Pakistan: concentration, spatial variation and sources. *Environmental Science & Technology*, 48(5), 2610–2618.
- Neumeier, G. (1998). The technical life-cycle of PCBs. Presented at the sub-regional awareness raising workshop on persistent organic pollutants (POPs), Kranjska Gora, Slovenia, May 1998.
- Oliver, B. G., & Niimi, A. J. (1988). Trophodynamic analysis of polychlorinated biphenyl congeners and other chlorinated hydrocarbons in the lake Ontario ecosystem. *Environmental Science & Technology*, 22(4), 388–397.
- Ponnambalam, M. (1998). Control and management of PCBs in oil and gas industry. Presented at the sub-regional awareness raising workshop on Persistent Organic Pollutants (POPs), Abu-Dhabi, UAE, June 1998.
- Pozo, K., Harner, T., Wania, F., Muir, D., Jones, K. C., & Barrie, L. A. (2006). Towards a global network for persistent organic pollutants in air: results from the GAPS study. *Environmental Science & Technology*, 40(16), 4867–73.
- Pozo, K., Harner, T., Lee, S. C., Sinha, R. K., Sengupta, B., Loewen, M., Geethalakshmi, V., & Volpi, V. (2011). Assessing seasonal and spatial trends of persistent organic pollutants (POPs) in Indian agricultural regions using PUF disk passive air samplers. *Environmental Pollution*, 159(2), 646–653.
- Robertson, L.W., & Hansen, L.G. (2001). PCBs: Recent advances in environmental toxicology and health effects, The University Press of Kentucky.
- Shifrin, N. S., & Toole, A. P. (1998). Historical perspective on PCBs. *Environmental Engineering Science*, 15(3), 247–257.
- Syed, J. H., Malik, R. N., Li, J., Zhang, G., & Jones, K. C. (2013). Levels, distribution and air–soil exchange fluxes of polychlorinated biphenyls (PCBs) in the environment of Punjab Province, Pakistan. Elsevier. *Ecotoxicology and Environment Safety*, 97, 189–195.
- Upadhayay, K., (2013). Occurrence and risk assessment of polychlorinated biphenyls in ambient air near power stations in Kanpur. M.Tech thesis, IIT Kanpur.
- WHO (Section 2.1.3, Page: 103). (n.d.) Europe Heart Survey EURO_EHS_22, Retrieved from http://whqlibdoc.who.int/euro/ehs/EURO_EHS_23_part2.pdf
- Zhang, G., Chakraborty, P., Junli, Kumar, P. S., Balasubramanian, T., Ykathiresan, K., Shintakahashi, Subramanian, A., Shinsuketanabe, & 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. *Environmental Science & Technology*, 42, 8218–8223.