

CURRENT SCENARIO OF POLYCHLORINATED BIPHENYLES (PCBS) IN THE INDIAN ATMOSPHERE

Paromita Chakraborty¹, Ningombam Linthoingambi Devi², Gan Zhang³, Kenneth Sajwan¹ and Kevin C Jones⁴

¹Dept of Natural Science, Savannah State University, Georgia, USA; ² State Key Laboratory of Biogeology and Environmental Geology, School of Environmental Studies, China University of Geosciences, Wuhan 430074, China. ³State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China. ⁴Department of Environmental Sciences, Institute of Environmental and Natural Sciences, Lancaster University, Lancaster, LA1 4YQ, UK

Abstract

Presently atmospheric levels of polychlorinated biphenyles (PCBs) in India seems to have largely increased since what was reported by Iwata *et al.*, in 1994⁹. A predominant gradient in the maximum concentration of \sum_{25} PCB has been observed between urban-rural-wetland/background with an exceptionally higher level in the wetland region of Sunderban (544 pg.m⁻³). PCBs in the Indian atmosphere showed a dominance of congeners with 5-7 chlorine atoms (heavy PCBs), and dioxin-like PCBs were significant in the descending order of Mumbai, New Delhi, Agra, Kolkata, and Chennai. The metro-cities are of prime interest in this case because of the electronic waste generated with the rapid growth of improper electronic waste recycling units. Elevated levels have been also observed in Manipur when air mass originated from the northern and eastern regions thereby indicating regional atmospheric transport of PCBs from major cities to remote/pristine sites in India.

Introduction

In the recent years various studies highlighted that Asia mainly China and India has been the hotspots of PCBs although Asia was not identified as an important source in global emission inventories for PCBs. There are growing concerns that most of the electronic waste (e-waste) generated in developed countries is ending up in developing countries that are economically challenged and lack the infrastructure. India is of prime concern because tropical climate of India would facilitate the rapid entry of PCBs to the atmosphere from some sources such as incineration of PCB containing materials, vaporization from landfill, air-water/soil exchange, vaporization from contaminated surfaces, sludge dewatering beds, and electronic devices containing PCBs^{1,2}. Total waste generated by obsolete or broken down electronic and electrical equipment in India has been estimated to be 1,46,000 tons per year³. Incomplete combustion of e-waste in open air and dumping of processed materials are the major sources of various toxic chemicals including PCBs⁴. Co-disposal of e-waste with domestic waste in open dumps is generally practiced in many Asian countries including India. Another important source for PCBs in India may include dumping of PCB-containing wastes with release via volatilization and uncontrolled burning, and the storage and breakup of old ships. India is world's largest ship breaking nation in terms of volume. Most of the ships dismantled today were built in the 1970s. That is to say prior to the banning of many hazardous materials. Hence present work aims to show the PCB levels in the Indian atmosphere from the results obtained from 3 sampling campaigns:

1. Passive air sampling (PAS) along the coastal length of India
2. Active air sampling (AAS) in seven major Indian cities
3. Monthly PAS at Manipur, a land locked state in the hilly region of north-eastern part of India, for a period of one year.

Materials and methods

Air sampling

PUF-PAS were deployed along the coastal length of India concurrently at 18 locations and exposed for 6 weeks from 30th July to 26th September 2006 along the coastal length of India, as the first trial to screen for PCBs in the atmosphere. AAS was conducted on diurnal basis for two days each at Bangalore, Agra, Goa and for 8-10 days

in Chennai, New Delhi, Mumbai and Kolkata. Air volumes of 72 m³ in 12h was drawn through quartz microfibre filter (QFF) using a high-volume sampler (of the Anderson type) at a flow rate of 0.1m³ min⁻¹. All together 86 QFFs and 86 PUF samples were obtained from the seven major cities of India on diurnal basis by running an active air sampler for two days each at Bangalore, Agra and Goa and for 8-10 days in Chennai, New Delhi, Mumbai and Kolkata (Figure 1) between Dec 3rd2006 to Mar 24th2007. Manipur is an inland region located in the north-eastern part of India at latitude of 23°83'N--25°68'N and longitude of 93°03'E--94°78'E covering an area of 22,327 km² along the Burma border. PUF-PAS were deployed in Manipur at urban, rural and mountain sites over a period of 12 months during January to December, 2009. PUF disks were changed regularly every month for this all the sites of Manipur.



Fig 1. Sampling sites

Extraction

Prior to extraction a mixture of surrogate standards (2,4,5,6-tetrachloro-m-xylene (TCmX), decachlorobiphenyl (PCB209), ¹³C₁₂-PCB138 and ¹³C₁₂-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 15mL amber vial. This was blown down under a gentle stream of nitrogen to about 0.5mL and cleaned on a 8 mm i.d. chromatography column with 6 cm alumina (BDH neutral Alumina 3% deactivated), 10cm of silica gel (Merck Silica 60 3% deactivated), 10 cm of 50% sulfuric acid silica and 1 cm of baked sodium sulfate (all baked at 450°C overnight) and the column was eluted with 10 ml mixture of 50:50 hexane: DCM (v/v). The samples were reduced to a final volume of 25µl 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. PCBs analysis was carried out on a Finigan-TRACE GC-MS system with a CP-Sil 8 CB capillary column (50 m, 0.25 mm, 0.25 µm), operating under single-ion monitoring (SIM) mode. Helium was used as the carrier gas at 1.2 mL min⁻¹ under constant-flow mode. The oven temperature began at 60 °C for 1 min and increased to 290 °C (10 min hold time) at a rate of 4 °C min⁻¹. Splitless/split injection of a 1 µL sample was performed with a 5 min solvent delay time. Injector temperature was at 250 °C. Details of the instruments, GC temperature programs, and monitored ions have been reported elsewhere⁴. 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.

QA/QC

One field blank for each PAS site and 14 AAS PUF and QFFs (two from each city) and 7 filter field blanks (one from each city) and 10, 14 and 12 laboratory blanks respectively were used. Field and lab blanks were collected and analyzed to provide an indication of the overall precision of both the sampling and laboratory methods. Field and lab blanks were <3% of sample values for PCBs. There was no difference (t-test significance, <95%) between concentrations of analytes in the laboratory and field blanks, indicating contamination was minimal during transport, storage, and analysis. Field blanks and method blanks were below the instrument quantification limit.

Results and discussion

1. Back trajectory analysis

Level of PCBs has drastically increased since early 1990s¹. Hence to assess the possible sources areas of PCBs the HYSPLIT model (HYbrid Single-Particle Lagrangian Integrated Trajectory, Version 4.7), a comprehensive modelling system developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resource Laboratory⁵ was used. 5 Days mean back trajectories ending at each sampling site at 0600 UTC, i.e. 11:30 local time for all sampling dates, were calculated for each of the sampling dates. In order to classify the air masses, the trajectories ended at the height of 500m AGL (above ground level), a level of about half the height of the mean day time planet boundary layer (PBL), to represent general transport conditions in the PBL.

2.1.PCBs along coastal length of India

The spatial distribution of PAS derived Σ_{25} PCB air concentrations along the coastal length of India ranged from 120 to 1100 pg.m^{-3} . This indicates a much higher concentration than the levels obtained in other Asian countries⁶, but are comparable to the urban locations of European PAS survey⁷ and GAPS study⁸. The highest PCB levels were detected at urban sites or sites at close proximity to urban centres with a predominant gradient in the maximum concentration of Σ_{25} PCBs and a significant elevated level at the Sunderban wetland (544 pg.m^{-3}). The PCB congener profile along the coastal length of India showed a higher abundance of the heavier congeners (those with 5-7 chlorine atoms in the molecules) in the urban locations, compared to more remote locations.

2.2. PCBs in the seven major cities of India

Average Σ_{25} PCBs in the Indian atmosphere is 4460 (± 2210) pg.m^{-3} and showed a dominance of congeners with 4-7 chlorine atoms. This level is comparable to the levels observed in developed nations and data reported by GAPs study. Highest level was observed at Mumbai and is consistent with the observation of 1994⁹. Typically, less than 10% of the total atmospheric Σ_{25} PCB burden is found in the particle phase. Higher average percentage in particulate phase is for New Delhi and Agra where the average atmospheric temperature during the entire sampling period was 12°C and 9°C respectively. Hence lowering the vapor pressure of PCB congeners at lower temperatures and increasing sorption onto airborne particles. The percentage is also higher, for the higher molecular weight PCBs.

2.3.PCBs in Manipur, India

In urban air of Manipur twenty five Σ_{25} PCBs concentration ranges from 1800–3200 pg.m^{-3} , with the levels in the decreasing order of: urban>rural>background site in the mountains.

3. Possible sources for PCBs in India

The order of magnitude for Σ_{25} PCBs between the highest and lowest levels varied by ~ 3 orders showing an urban-rural gradient with the highest values at the core urban sites amidst the metro cities and the lowest range in the remote wetland sites. Mumbai produces 11,017 tonnes of e-waste annually. Delhi comes next with 9,730 tonnes of e-waste. Surprisingly, India's Silicon Valley, Bangalore, comes third, producing 4,648 tonnes. Next is Chennai with 4,132 tonnes and Kolkata with 4,025 tonnes³. A statistically significant ($p < 0.05$) positive linear correlation has been observed between the amount of e-waste generated in 2005 and the atmospheric concentration of PCBs in Bangalore, Chennai, New Delhi, Mumbai and Kolkata. And, given that ship breaking activities are prevalent in the city of Mumbai at Darukhana and the adjoining west coast in the state of Gujrat, it can be suggested to be another potential important source contributing to the loads of PCBs in those areas. In many occasion e-waste is burnt in the open air along with garbage. Another potentially important source is the improper management of ship breaking activities in India and Bangladesh. A typical merchant ship to be dismantled for scrap contains between 250 kg – 800 kg of PCBs, which is found principally in the paint as well as left on the scrap metal in the vessel machinery that is re-rolled or re-melted could be another source of PCBs pollution¹⁰. Urban PCBs sources also include off gassing from closed systems such as older equipments (e.g., transformers that contain large quantities of PCB fluids)¹¹. Back trajectory analysis (Fig 2A) shows regional air mass movement during the overall AAS period in the metro cities and air was encircling within India during PAS along the coastal length (Fig 2B). It is noteworthy that, PCB congener showed a higher abundance of the heavier congeners at the urban sites thereby reflecting the potential

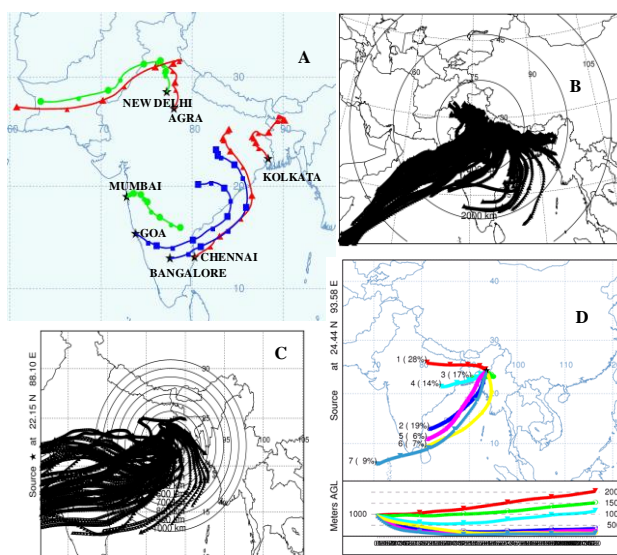


Fig 2. 5 Days mean back trajectory analysis for A: during AAS in major Indian cities; B: during PAS along the coastal length of India; C: during PAS at the Sunderban; D: during PAS at Manipur.

primary sources and a lower molecular weight composition, enriched in more volatile PCB congeners at the more remote locations. 5-Cl contributing about 43% of the total PCBs in the present study has been found to be present almost 38% in the urban sites, 16% in the rural sites and 9% in the remote locations except at Sunderban showing about 37% almost close to the urban level of contamination along the coastal length of India. Sunderban is sandwiched between the metro city Kolkata in eastern part of India and Bangladesh and the air mass reaching to this site encircled Kolkata and Bangladesh (Fig 2C) possibly leading to regional atmospheric transport of PCBs to the Sunderban wetlands. Back trajectory analysis (Fig 2D) further shows highest levels for Manipur were observed in the months when the air masses originated from north or north-eastern parts of India possibly via long range atmospheric transport from cities like New Delhi or Kolkata where high levels have been observed.

Conclusion

PCB related to dumped waste in India is becoming more complicated by the invasion of e-waste, particularly computer waste. This projects the upcoming emission sources of this group of pollutants mostly from the urban locations with cumulative growth of electronic waste recycling among the informal scrap dealers and ship breaking activities. There exists an urgent need for a detailed assessment of the current and future scenario including quantification, characteristics, existing disposal practices, environmental impacts etc so as to prevent long range atmospheric transport of PCBs to the pristine/background environments, e.g., in this case the wetland regions of Sunderban or in the landlocked state of Manipur.

Acknowledgement

This study is a joint contribution from the Savannah State University, Georgia, USA, the National Natural Scientific Foundation of China (NSFC 40590391, 40673076). The preparation of this manuscript is supported by US-DOE and EPA contract No. DE-FG09-96SR18558.

References

1. Biterna, M.; Voutsas, D. *Environment International*. (2005), 31 (5), 671-677.
2. Totten, L. A.; Gigliotti, C. L.; VanRy, D. A.; Offenber, J. H.; Nelson, E. D.; *et al.*, *Environmental Science & Technology*. (2004), 38 (9), 2568-2573.
3. Green Business Opportunities, Confederation of Indian Industry, Delhi. **2006**, 12 (1).
4. Wong, M. H.; Wu, S. C.; Deng, W. J.; Yu, X. Z.; Luo, *et al.*, *Environmental Pollution*. (2007), 149 (2), 131-140.
5. Draxler, R. R.; Rolph, G. D. *NOAA Air Resources Laboratory, Silver Spring, MD*. (2003). Available at: <http://www.arl.noaa.gov/ready/hysplit4.html>.
6. Jaward F M, Zhang G, Nam J J, Sweetman A J, Obbard J P, Kobara Y et al., (2005). Asia. *Environmental Science and Technology*, 39: 8638--8645.
7. Jaward F M, Farrar N J, Harner T, Sweetman A J, Jones K C, (2004). Europe. *Environmental Science and Technology*, 38: 34-41.
8. Pozo K, Harner T, Wania F, Muir D C G, Jones K C, Barrie L A, (2006). *Environmental Science and Technology*, 40: 4867--4873.
9. Iwata H, Tanabe S, Sakai N, Nishimura A, Tatukawa R, (1994). *Environmental Pollution*, 85: 15--33.
10. Wurl, O.; Potter, J. R.; Obbard, J. P.; Durville, C. *Environ. Sci. Technol.* (2006), 40 (5), 1454-1461.
11. Breivik K.; Sweetman A.; Pacyna J.M.; Jones K. C. *Sci. Tot. Environ.*, (2007), 377, 296-307.