Chemosphere xxx (2016) 1–9

Contents lists available at ScienceDirect

Chemosphere

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

Passive air sampling of persistent organic pollutants (POPs) and emerging compounds in Kolkata megacity and rural mangrove wetland Sundarban in India: An approach to regional monitoring

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HIGHLIGHTS

- POPs were detected in the air of Kolkata city and Sagar in Sundarban, West-Bengala.
- HCHs and DDTs showed the highest concentrations of POPs in air.
- The results are lower than previous studies in urban areas of India.
- Higher concentration of PCBs and PBDEs were detected at Kolkota urban sites.

ARTICLE INFO

Article history:
Received 2 June 2016
Received in revised form
12 September 2016
Accepted 14 September 2016
Available online xxx

Handling Editor: Myrto Petreas

Keywords:
Kolkata megacity
Sundarban wetland
DDTs
POPs
PAS-PUF

ABSTRACT

Polyurethane foam (PUF) disk passive air samplers were deployed concurrently at five sites across Kolkata megacity and the rural mangrove wetland of Sundarban (UNESCO World Heritage Site) between January–March in 2014. Samples were analyzed for hexachlorocyclohexanes (HCHs), dichlorodiphenyltricholoroethanes (DDTs), polychlorinated biphenyls (PCBs) and, polybrominated diphenyl ethers (PBDEs) using gas chromatography and mass spectrometry (GC-MS). Derived air concentrations (pg/m^3) for Kolkata ranged: for $\sum\alpha$- and γ-HCH between 70 and 207 (114 ± 62), $\sum_6$DDTs: 127–216 (161 ± 36), $\sum_7$PCBs: 53–213 (141 ± 64), and $\sum_{10}$PBDEs: 0.30–23 (11 ± 9). Low values for all the studied POPs were recorded in the remote area of the Sundarban site (with the exception of DDTs: *o,p'*-DDT and *p,p'*-DDT), where $\sum_4$DDTs was 161 ± 36. In particular, the site of Ballygunge, located in the southern part of Kolkata, showed the highest level of all the metabolites/congeners of POPs, suggesting a potential hot spot of usage and emissions. From HCHs, α-/γ-HCH isomers ratio was low (0.67–1.96) indicating a possible sporadic source of lindane. γ-HCH dominated the HCH signal (at 3 sites) reflecting wide spread use of lindane both in Kolkata and the Sundarban region; however, isomeric composition in Kolkata also suggests potential technical HCHs use. Among DDT metabolites, both *o,p'*-DDT and *p,p'*-DDT shared the dominant percentages accounting for ~26–46% of total DDTs followed by *p,p'*-DDE (~12–19%). The PCB congener profile was dominated by tri- and tetra-Cl at the southern and eastern part of Kolkata. These results are one of the few contributions that reports air concentrations of POPs, concurrently, at urban and remote villages in India. These data are useful to assess atmospheric pollution levels and to motivate

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http://dx.doi.org/10.1016/j.chemosphere.2016.09.055

local and regional authorities to better understand the potential human exposure risk associated to urban areas in India.

1. Introduction

Persistent organic pollutants (POPs) are semi-volatile organic compounds and have immense global interest as these transboundary pollutants suffer long-range atmospheric transport (LRAT). These compounds can be found within all environmental segments including remote areas (Daly and Wania, 2005; Shen and Wania, 2005). In order to manage POPs, International efforts included the global treaty of the Stockholm Convention (SC) on POPs that was signed in 2001 and came into force in 2004 with the aim of reducing and eliminating the release of POPs into the environment (UNEP, 2010).

POPs are still used in the tropical lower latitude regions and can be emitted from primary and secondary sources and subsequently transported from atmospheric emission sources via deposition into terrestrial and aquatic ecosystems. Direct quantification of sources is often difficult due to scarce information on past chemical usage and inventories. However, environmental data are essential for all regions of the globe to better understand regional or global sources of POPs and the concerned processes that control their global distribution. At present there is a paucity of environmental data on the levels of most POPs compounds in some Asian regions, and it would be necessary to study them in order to assess the effectiveness of global efforts to minimize the release of these compounds into the environment. This is quite relevant for tropical countries particularly in India, which might be considered a key country for chemical production and usage.

Kolkata (former Calcutta) is the second largest metropolis in South Asia and is one of the most polluted cities in the world. Kolkata has a tropical wet–and–dry climate with an annual mean temperature of 26.8 °C. The city experiences 3 distinct seasons, namely, summer, monsoon and winter. May is the hottest month with daily temperatures ranging from 27 to 38 °C. South–West Monsoons pick up moisture from the Bay of Bengal and bring rain from mid–June to the end of September. Winter lasts for about two–and–a–half months, January being the coldest with temperatures ranging from 9 to 23 °C (Spiroska et al., 2011).

As a result of heavy air pollution, 41.3% and 47.8% of the Kolkata population suffers from upper and lower respiratory tract symptoms respectively, compared to 13.5% and 35% of the rural Bengal population (WBPCB, 2001). Suspended particulate matter alone was responsible for more than 10,000 premature deaths in Kolkata in 1995 (Kazimuddin and Banerjee, 2000). Recent studies have also documented the association of air pollution with adverse health effects in Kolkata (Lahiri et al., 2000) and Delhi, the capital city of India (Maji et al., 2015). But, there is still a lack of information regarding atmospheric organic pollutants such POPs and emergent compounds in the Indian atmosphere.

Polyurethane foam disk passive air samplers (PUF-PAS) are a potentially useful and cost effective tool for monitoring POPs simultaneously at numerous sites such as local (Harner et al., 2004), continental (Jaward et al., 2004) as well as on a wide scale (Pozo et al., 2009; Bogdal et al., 2013). Previously, high levels of POPs were reported in the Indian atmosphere by several authors namely Baburajendran et al., 1999; Iwata et al., 1994; Ramesh et al., 1989. Recently, high levels of selected organochlorine pesticides (OCPs) have been reported in the atmosphere of agricultural areas (Pozo et al., 2011), in seven major coastal and inland Indian cities by using PUF-PAS and high volume air sampling concurrently (Chakraborty et al., 2010), and along the coastal sites of India during a PUF-PAS campaign (Zhang et al., 2008). However, no concrete and continuous data are available on an atmospheric level for organochlorine pesticides (OCPs) from Sagar Island, the extreme western part of the Indian Sundarban wetland, which is part of the UNESCO World Heritage Site. Therefore, the present study aims to elucidate firstly the spatial trends and the degree of contamination of POPs in the atmosphere of Kolkata as well as in Sundarban as a background belt and secondly, to provide further information regarding POPs in the Indian atmosphere. In order to elucidate potential source contribution, principal component analysis (PCA) was also conducted.

2. Materials and methods

2.1. Study area

Kolkata is the capital of the West Bengal state and is under the jurisdiction of the Kolkata Municipal Corporation (KMC) with an area of 187.33 km^2 and a population density of around 24.252 km^2 (62.810 sq/mi^1) (Government of India, 2013). This is the second largest metropolis in South Asia and is one of the most polluted cities in the world. Greater Kolkata, covering an area of 1480 km^2, is home of numerous large and small–scale industries of different categories, thermal power plants, ports and is notorious for heavy traffic. A more detailed description is given in the Supporting Material (SM), Text S1.

The major sources of air pollution in Kolkata city are industries, vehicular emissions and re-suspension of road dust. The other main sources of air pollution at the residential site are solid waste dumping, coal combustion, and cooking and at the industrial site. These sources are coal combustion, electroplating industries, tire wear and secondary aerosols (Karar and Gupta, 2007). A study conducted at major traffic junctions of Kolkata showed that the key pollutants like lead, NO_X, PM_{10}, SO_2, CO are in excess of permitted levels (Ghose et al., 2004). In addition, a rural background location was also considered, namely Sagar (N 22° 39.171'; E 88° 4.572′), the extreme southern part of Sagar Island in Indian Sundarban, a low lying, tide-dominated mangrove wetland belt. The Sundarban (Bengali: Sundar means beautiful) is a natural region comprising southern Bangladesh and a part in the Indian state of West Bengal. It is the largest single block of tidal halophytic mangrove forest in the world. The Sundarbans covers approximately 10.000 km^2, mainly in Bangladesh with the remainder in India. The Sundarbans is a UNESCO World Heritage Site (Sundarban Wildlife Sanctuaries, 2014).

2.2. Sample collection and deployment

A total of six PUF disks were deployed concurrently in West-Bengal, five of the sampling sites in residential areas in Kolkata city and one in the Island of Sagar. This was done in order to obtain a representation of the average air quality of the city during the winter season (December 28 to March 27, 2014) when the inversion layer remains close to the ground and pollutant levels are highest during

Please cite this article in press as: Pozo, K., et al., Passive air sampling of persistent organic pollutants (POPs) and emerging compounds in Kolkata megacity and rural mangrove wetland Sundarban in India: An approach to regional monitoring, Chemosphere (2016), http://dx.doi.org/10.1016/j.chemosphere.2016.09.055