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Persistent organic pollutant emission via dust deposition throughout Pakistan: Spatial patterns, regional cycling and their implication for human health risks

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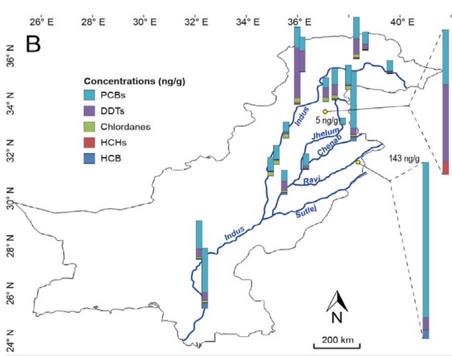
HIGHLIGHTS

- Persistent Organic Pollutants (POPs) in outdoor dust along the Indus river system of Pakistan.
- DDTs and PCBs were the predominant contaminants identified in dust
- Recent emission of DDTs in regions used for crop protection and malarial control.
- PCB homologue into samples identify the use of commercial PCBs mixture including arochlor-1248, -1254, -1260, and-1262
- Human risk assessment analysis of contaminated dust shows that DDTs and PCBs are the major constituent chemicals of concern

GRAPHICAL ABSTRACT



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ABSTRACT

In the current study, Persistent Organic Pollutants (POPs) in outdoor dustfall was monitored for the first time along the Indus river system of Pakistan. Among the studied OCPs (ng/g, dry weight), DDTs (0.16–62) were the predominant contaminants identified in deposited dust followed by HCHs (0.1–10.2), HCB (0.09–7.4) and chlordanes (0.1–2.8). The indicative diagnostic ratio for DDTs and HCHs suggested recent emission of DDTs as well as historical emission of both chemicals in regions where they were used for crop protection and malarial control. The levels of $\sum_{31}$PCBs (ng/g, dry weight) in dust ranged from 0.95–125, and compositional profiles suggested arochlor-1248, -1254 commercial mixtures as source. A few exceptions were samples from urban areas that reflected the use of aroclor-1260, and-1262 and/or unintentional leakage from several industrial processes. The WHO_{05}-TEQ values for dioxin-like PCBs (with major contributions of PCB-126) were found to be 0.07–34.5 (median; 1.87) pg TEQ g^{-1}dw for all the studied samples. Correlation analysis identified that DDTs, HCHs, HCB and PCBs were significantly associated ($r = 90$; $p < 0.01$) with dusts collected in proximity to urban centers with widespread anthropogenic activities in these areas. A few cases where high levels of POPs from remote

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Human risk
Pakistan

mountain highlands were detected, point to the potential for long range transport of these chemicals. Human risk assessment analysis of contaminated dust showed that DDTs and PCBs are major constituent chemicals of concern with regard to the development of cancer in children, with ingestion being the main route of exposure of dust-borne DDTs (0.12–1.03 × 10^{-6}) and PCBs (0.86–12.43 × 10^{-6}).

1. Introduction

Despite being a signatory of the Stockholm Convention (2001) to eliminate/reduce the emission and use of Persistent Organic Pollutants (POPs), widespread occurrence of polychlorinated biphenyles (PCBs) and organochlorine pesticides (OCPs) have been widely reported in various settings of subtropical/tropical regions, including Pakistan (Zhang et al., 2008; Eqani et al., 2012; Nasir et al., 2014). Additionally, in the context of long range atmospheric transport (LRAT) of POPs into pristine areas of the globe, subtropical/tropical countries are thought to be important repositories of these banned chemicals of concern (Wania and Westgate, 2008; Shen et al., 2009; Nasir et al., 2014). POP-related health concerns, including endocrine disruption, cancer and reproductive failure, have been observed in many avian species and other wildlife species (fish, invertebrates etc.) (Meeker et al., 2007; Khan et al., 2016; Eqani et al., 2013a, 2013b).

It has been reported that the majority of OCPs (i.e., cyclodiens, DDTs, HCHs, etc.) and PCBs used in Pakistan were imported from Europe and the USA during the last few decades (Ahad et al., 2010) although prior to 2001, 1000 tonnes of DDTs were also produced locally in several industrial operations around the country (Zehra et al., 2015). In an effort to abide to the Stockholm Convention (2001), government authorities collected these chemicals in strategic locations throughout the country to stop further distribution by provincial departments for plant protection (Ahad et al., 2010; Alamdar et al., 2014). Furthermore, DDT-producing factories were demolished throughout the country in 2001 (Ahad et al., 2010). Pakistan thus holds one of the largest stockpiles of obsolete pesticides in the world. Improper storage and rough handling has led to a preponderance of damaged containers, rotten sacks and corroded metal drums, such that these chemicals have leaked into and/or are continuing to leach and contaminate the surrounding environment (Ahad et al., 2010; Alamdar et al., 2014). Countrywide data on the usage of PCBs is lacking and only a few reports in recent years have documented their levels and sources in urban and industrial settings in Pakistan (Zehra et al., 2015). These recent studies documented that the main sources of PCB contamination in Pakistan are accidental leakage during transportation, the auction of old transformers and other industrial/urban activities (i.e. paints, steel manufacturing, electrical appliances) (Eqani et al., 2012; Zehra et al., 2015). Other studies have documented PCB sources including off gassing of closed systems, electric appliances, paint additives, manufacturing of PVC (polyvinylchloride) and various other industrial processes, such as steel manufacturing and coal burning during iron ore sintering (Wang et al., 2011; Khairy et al., 2015). Although banned, these dangerous chemicals (i.e., OCPs and PCBs) are still expected to be found in the environment due to illegal use and leakage from legacy sites throughout the country, which highlights the need to regularly monitor them to enforce the regulations of the Stockholm Convention (Ali et al., 2014; Nasir et al., 2014).

Pakistan possesses diversified landscapes and climatic conditions throughout the country, with the northern frozen areas of high elevation, the wet mountain areas in the lower Himalayan region, the adjoining floodplain areas along the Indus river, and the southern low lying coastal areas. Different parts of country receive dust burden from both local and regional sources depending upon various climatic factors including local and regional wind circulation patterns. During the monsoon months, air movement passes from and the Arabian sea to the northern Himalayas and vice versa and it is expected to receive the dust particles from nearby countries including India and China into northern areas of Pakistan and also from the south part of Pakistan into lower Himalyian stretch as reported by Eqani et al. (2016). Moreover, forceful wind from central Asian countries and also from Afghanistan are also reported to contribute towards the dust transportation into the north western and western part of the country. Pakistan's fertile Indus plain has an arid to semi-arid climate and is inhabited by >100 million people. Given that deflation (a variety of wind erosion) occur due to rapid industrialization and urbanization as well as high velocity winds, which are largely responsible for transporting silt-sized material to long distance (Eqani et al., 2016). Therefore, environmental monitoring of OCPs and PCBs into the dust particles is very useful to assess the spatial distributional patterns and their sources (Wang et al., 2013; Ali et al., 2014; Nasir et al., 2014) in weathered soils of arid and semi-arid regions (e.g. low and mid-elevation regions of the Indus flood plain) and deforested areas (e.g. lower Himalayan urban mountainous areas). Moreover, data can also be used to investigate recent POP emissions through their indicative diagnostics (Yang et al., 2010). In the current study, we collected outdoor dust samples at different locations throughout the country to assess OCPs and PCBs spatial emission patterns, sources, recent emissions and cycling (long-range and short-distance dustfall) in the region. This study provides important data for evaluating Pakistan's contribution to global POPs emissions as well as the effectiveness of control measures taken by regional and international authorities under the Stockholm Convention.

2. Materials and methods

2.1. Sampling strategy and collection

In this study, we collected 110 dust samples from 19 sampling sites along the Indus River and its tributaries (Fig. 1) covering four elevation zones: remote mountain highlands (RMA), lower Himalayan urban mountains (UMA), Indus plain agricultural areas (IPAA), and Indus plain urban areas (IPIA). Details have been described by Eqani et al. (2016). In brief, composite deposited dustfall samples were collected during May and June 2013. Windstorms and dust storms are a regular feature across Pakistan, particularly during the spring and summer months. A room with windows on all four sides was set up at each site. A wooden table with mirror was placed inside the room for 2 months. The deposited dust that had settled on the mirror surface was periodically brushed off twice a week and collected in sampling bags. The total glass area receiving the dustfall was used to compute the dust per unit area. In order to avoid external contamination of the samples, dust was collected by hand in a plastic pan, using a clean, metal-free plastic brush, and was directly deposited into an airtight bag. Separate brushes were used during sampling in order to minimize cross contamination between sites. Samples were wrapped in aluminum foil, transferred into air-tight plastic bags, sealed, and taken to the laboratory. All samples were kept at 4 °C. The rate of dustfall, major human activities, and demographic data were recorded at the time of sampling and used later for risk estimation.

2.2. Analytical procedures

OCPs and PCBs were extracted from dust samples (<180 μm) using the Soxhlet extraction method (Eqani et al., 2012). Approximately 5 g of dust samples were extracted over 48 h with dichloromethane