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Are unintentionally produced polychlorinated biphenyls the main source of polychlorinated biphenyl occurrence in soils?

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ABSTRACT

The production of polychlorinated biphenyls (PCBs) has been banned globally for decades, but PCB concentrations in environmental media remain relatively high, especially in urban areas. Emissions estimates, studies of soil gradients between urban and rural areas, and quantitative identification of regional sources of PCBs in soils are necessary for understanding the environmental behavior of PCBs. In this study, regional PCB emissions were estimated at a resolution of 10 km × 10 km, and the spatial distribution of soil PCBs from urban to rural areas was studied along the Bohai and Yellow Sea regions. Compared with rural areas, mean PCB concentrations in urban soils (20.7 ng/g) were found to be higher, and concentrations decreased with distance from the city. Across both latitude and longitude directions, high PCB emissions in urban areas matched the distribution of total PCB concentrations in soils. The concentrations of the pollutants PCB28, PCB52, PCB101, PCB118, PCB138, PCB153, and PCB180 in soils originated from 5-year emissions, and accounted for 97%, 95%, 84%, 81%, 58%, 57%, and 27% of the total emissions, respectively. Unintentionally produced PCB (UP-PCB) emissions, which are mainly derived from cement (42%), pig iron (37%), crude steel (18%), and rolled steel (3%) industries, are the major contributors to PCBs in soils. Further identification of the sources and fates of PCBs requires a combination of field, laboratory, and modeling efforts.

1. Introduction

Polychlorinated biphenyls (PCBs) are among the 26 persistent organic pollutants (POPs) listed in the Stockholm Convention as global priorities for emissions reduction. Although production of PCBs ceased across most of the world beginning in the 1970s, PCB residues in environmental media are still increasing in some regions (Hogarh et al., 2012; Jaward et al., 2005; Zhang et al., 2008). Unintentionally produced PCBs (UP-PCBs) have been found to be as important as intentionally produced PCBs (IP-PCBs) (Cui et al., 2015) as environmental pollutants. Continuous increases in UP-PCBs may be a causal mechanism for the high PCB accumulation observed in soils (Cui et al., 2017). However, little is known about how much of the PCB concentration in soil comes from UP-PCB emissions at a regional scale. In addition, due to the impacts of industrial agglomeration and urbanization, new problems arise due to the significant differences in PCB levels between urban and rural soils. Quantitative identification of regional sources of PCBs in soils and of emissions from urban to rural areas is therefore scientifically valuable, not only for understanding the environmental behavior of pollutants, but also for assessing their ecological impacts and for establishing pollutant emission control measures.

Estimates of PCB emissions are important for compiling emission inventories for different sectors, and for identifying pollutant sources and chemical fates across multiple media. Global emission inventories of IP-PCBs first began when Breivik et al. (2002a) determined a global cumulative production of commercial PCBs

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of 1.3×10^6 t, of which approximately 440–92 000 t were distributed across various environmental media. Emissions of IP-PCBs and UP-PCB in China were estimated at 130.1 t and 146 t, respectively (Cui et al., 2015; Cui et al., 2013). Yang et al. (2010) also compiled a similar estimate of total UP-PCB emissions in China, with major emissions from the cement industry (91.3%), followed by steel (7.1%). In addition, some reports indicated that international trade in waste electrical and electronic equipment (WEEE) led to high concentrations of PCBs at both e-waste handling sites and at main shipping ports (Breivik et al., 2016; Breivik et al., 2011). However, e-waste cycling cannot be entirely accountable for the apparent increase in atmospheric PCBs across China (Cui et al., 2013). Furthermore, atmospheric PCB concentrations in China have increased in recent years, particularly along eastern coastal areas (Hogarh et al., 2012; Jaward et al., 2005; Zhang et al., 2008), due to rapid industrialization and corresponding high PCB use within specific zones (Gluge et al., 2016; Yang et al., 2010). However, there are few studies that provide an inventory of regional-scale emissions of PCBs in China, though this is considered to be an essential prerequisite for studying their regional spatial distribution and environmental fate.

The volatility of PCBs allows them to enter the atmosphere, and their susceptibility to long-distance transport causes them to be redistributed into other media (Wania and Mackay, 1996), including soils, due to both their strong sorption and high resistance to degradation (Batterman et al., 2009; Wenzel et al., 2002). Differences in chemical properties, environmental media and regional emissions have led to differences in soil concentrations of PCBs from urban to rural areas. For example, an investigation by Zhang et al. (2008) across 20 provinces in China revealed PCB concentrations of 3352 pg/g and 1354 pg/g for urban and rural soils, respectively. Csiszar et al. (2013) regarded urban areas as major sources of PCBs to their surrounding regions, because emissions of PCBs in urban areas may be several to even thousands of times higher than in rural areas (Song et al., 2016). However, other studies have shown that concentrations of total PCBs in urban soils are higher, while surface soils in rural areas contain higher concentrations of low-chlorine PCBs (Harner et al., 2004). Furthermore, IP-PCB emissions are responsible for higher atmospheric PCB concentrations at urban sites. Conversely, UP-PCB emissions are responsible for increasing atmospheric PCB concentrations at rural sites (Cui et al., 2015). Another important question that remains is how many PCBs in soils come from intentional vs. unintentional emissions. Therefore, a comprehensive consideration of regional emissions and quantitative identification of soil PCB sources is vital to understanding the emissions, sources, and fate of PCBs, and to controlling the risks posed by PCBs in soils.

The objectives of this study were: (1) to reveal the spatial distribution of urban-to-rural PCBs in soils through large-scale sampling, and to refine the PCB gradient between urban and rural areas, (2) to compile a regional (10 km × 10 km) emission inventory for IP-PCBs and UP-PCBs, and to study the associations between the inventory and soil concentrations, and (3) to conduct a quantitative source identification of PCBs in soils, and to identify whether UP-PCBs or IP-PCBs are the main source of PCBs in soils.

2. Material and methods

2.1. Study area and samples

The study area is one of the regions in China that is experiencing rapid economic development, and included the provinces of Liaoning, Hebei, Shandong, and Jiangsu, as well as the municipality of Tianjin along the Bohai and Yellow Seas. A total of 153 surface (0–10 cm) soil samples were collected from 21 coastal cities (Fig. 1). Samples were collected using a stainless steel trowel that had been rinsed with methanol. Two to three sampling sites were included in each $50 \times 50\ \mathrm{km}^2$ grid by considering representative land covers and distances from urban areas. Samples were each comprised of five sub-samples, collected from the center and four corners of an area of $100 \times 100\ \mathrm{m}^2$. All samples were stored in clean polypropylene zip lock bags in the field, and were then freeze-dried in the lab, homogenized with a porcelain mortar and pestle, sieved with a 100 mesh for PCBs, and stored in polypropylene bottles until extraction. The analytes studied included seven known pollutants: PCB-28, PCB-52, PCB-101, PCB-118, PCB-153, PCB-138, and PCB-180. The analytical and quality control methods are given in the Supplemental Information (SI.1).

2.2. Gridded emissions calculations of intentionally produced polychlorinated biphenyls (IP-PCBs)

A mass-balance model is typically used to estimate IP-PCB emissions (Breivik et al., 2002b). In this study, a modified model (Eq. (1)) (Cui et al., 2015) was used to consider three usage subcategories (open usage, small capacitors, and closed systems), four disposal processes (landfills, open burning, storage, and destruction), and two accidental-release pathways (land spills and fires), in order to calculate regional emissions. Details of the calculations were described by Cui et al. (2015).

$$E_{total}(t) = \sum_{u=1-3} [E_u(t)] + \sum_{d=l,o,s,d} [E_d(t)] + E_{af} + E_{as} + E_{Dins} \quad (1)$$

where u is the usage category, d is the disposal process, E_u is the emission of each usage category, E_{af} and E_{as} are the accidental emissions from fires and spills on to soils, respectively, of the usage categories, E_d is the disposal emission for usage categories corresponding to the end of a product's life, and E_{Dins} is the emission after input to the soils by disposal (i.e., storage and destruction).

From 1965 to 1974, China produced nearly 10,000 t of PCBs that were mainly used in the manufacture of transformers and power capacitors. Given China's economic development and rising gross domestic product (GDP) over the past several decades, open usage, small capacitors, and closed systems have accounted for 10%, 5%, and 85% of total PCB output (Cui et al., 2015). In this study, emissions were divided into three groups: (1) usage emission, (2) emission by accidental release, and (3) disposal emission at the end of a product's life. Lifetimes of 25 years for open systems, 20 years for small capacitors, and 50 years for closed systems were assigned. The provincial distribution of PCB usage was based on the work of Harner et al. (2004). On the basis of previous work (Breivik et al., 2002a; b; Cui et al., 2015), there appears to be a strong correlation between population densities and usage volumes of PCBs. We therefore allocated the emission dataset estimated by surrogate parameters (i.e., population densities) on the grid system with a 10 km × 10 km resolution. The gridded population data set were provided by the Data Center for Resources and Environmental Sciences, Chinese Academy of Sciences (RESDC; http://www.resdc.cn). The spatial distribution of total PCB usage is shown in Fig. S1.

2.3. Gridded emissions calculations of unintentionally produced polychlorinated biphenyls (UP-PCBs)

The production capacity data for 2013 of potential UP-PCB source industries (including cement kilns, electric furnace steelmaking (EFS), iron and steel sintering (ISS), cast and forged steel manufacturing (CFS), copper, lead, zinc, aluminum, and coke production, thermal power generation, and waste incineration) of each city were provided by the National Bureau of Statistics of the