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Short Communication

PBDEs as indicator chemicals of urbanization along an urban/rural gradient in South China

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HIGHLIGHTS

- ▸ Sediment PBDEs exhibited a positive association with catchment's urbanization level.
- ▸ Similar to "urban heat island effect", an "urban pollution island effect" was observed.
- ▸ PBDEs can be used as indicator chemicals of urbanization process in this region.

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ABSTRACT

Fourteen polybrominated diphenyl ethers (PBDEs) were measured in surface sediments collected from an urban watershed in a rapidly urbanizing region, Shenzhen, China. BDE209 was the predominant congener of PBDEs detected in surface sediments, which was consistent with the fact that technical deca-BDE mixtures are the dominant PBDE formulation used in China, especially the Pearl River Delta. A positive association between sediment PBDEs and catchment degree of urbanization suggested that the rapid urbanization process may be affecting the PBDEs levels in surface sediments. Similar to the "urban heat island effect", an "urban pollution island effect" was observed in the present study. These results indicated that PBDEs can be used as potential indicator chemicals of catchment's urbanization process in the present region.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are additive flame-retardants and have been widely used in many consumer products, such as plastics, electrical components, textiles, rubber, and other casing materials (Guan et al., 2007; Athanasiadou et al., 2008; Ni et al., 2011a; Qin et al., 2011). The global demand for PBDEs has increased rapidly since the 1970s until being banned recently (Schecter et al., 2011; Ma et al., 2012). In China, the domestic demand and production of PBDEs are enormous and have increased yearly (Mai et al., 2005; Guan et al., 2007). Because of their persistence, long-range atmospheric transport, widespread distribution, potential for bioaccumulation, and possible adverse effects in wildlife and humans, PBDEs have been of concern to many environmental researchers in the world (Li et al., 2012). In 2009, PBDEs were added to the list of banned chemicals in the Stockholm Convention on Persistent Organic Pollutants (Ma et al., 2012). The production and use of penta- and octa-BDE mixtures were banned in Europe, the US, and Canada in 2004. Deca-BDE was also banned by the European Union in 2008 and will be phased out in Canada and the United States by the end of 2013 (Gentes et al., 2012; Salvadó et al., 2012; Venier et al., 2012). However, no such restrictions are currently in place in China (Bao et al., 2012). Clearly, there are large reservoirs of PBDEs in consumer products either still in use or entombed in landfills (Salvadó et al., 2012). In addition, imported electronic waste has become a potential dominant source of PBDEs as China is currently the world's largest importer and recycler of e-waste (Ni and Zeng, 2009). For the coming years, continuing release of PBDEs into the environment is anticipated (Guo et al., 2012). Therefore, the potential environmental hazards posed by these PBDE- containing products in China will not disappear in the near future.

Sediments act as an ultimate sink for organic pollutants in the aquatic environment derived from various human activities, especially for the urban river sediments (Fu et al., 2003). These sedi-

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ments may accumulate large amount of anthropogenic pollutants coming from sewage discharge from industrial and residential areas (Guan et al., 2007). Generally, studies on PBDEs in sediments focus on the spatial and temporal distributions in river, estuary, and adjacent marine environments (Chen et al., 2006; Moon et al., 2007; Wang et al., 2007; Guan et al., 2009; Zhao et al., 2011). However, no studies of the relationship between sediment PBDEs in urban river and the catchment's degree of urbanization is available, except for some reports about PBDEs in peregrine falcon (*Falco peregrinus*) eggs as a function of the human population density surrounding the falcon nest areas (Potter et al., 2009; Newsome et al., 2010).

Accordingly, we examine here this issue in an urban watershed in Shenzhen, China. As the first special economic zone in China, Shenzhen has experienced rapid urbanization in the last 30 years. Intensive anthropogenic activities have released large amounts of organic pollutants, such as PBDEs, polycyclic aromatic hydrocarbons, and organochlorine pesticides (Cao et al., 2010; Ni et al., 2011b, 2011c; Qin et al., 2011). This provides an opportunity to examine the occurrences of PBDEs in urban river surface sediments and its relationship with catchment's degree of urbanization.

2. Materials and methods

2.1. Materials

Fourteen PBDE congeners (BDE28, 47, 49, 85, 99, 100, 138, 153, 154, 183, 196, 206, 208, and 209) were selected for quantitative analysis. Standards were obtained from Cambridge Isotope Laboratories (Andover, MA). The sum of all congeners except BDE209 is provided as Σ_{13}PBDE. ^{13}C–PCB208 was used as an internal standard. ^{13}C-BDE15, ^{13}C-BDE77, and ^{13}C-BDE209 were used as surrogate standards. Silica gel (100–200 mesh) and alumina (100–200 mesh) were Soxhlet extracted with methanol for 24 h and then with dichloromethane for another 24 h. Silica gel and alumina were then activated at 180 °C and 250 °C for 12 h, respectively, and deactivated with distilled water (3%, w/w) prior to use. All organic solvents were redistilled using a glass system.

2.2. Sampling and sample preparation

A total of 114 surface sediment samples (0–10 cm) were collected from the Maozhou River watershed in Shenzhen, China using a pre-cleaned stainless steel sampler from December 2009 to January 2010. The sample sites include 43 urban, 32 rural, and 26 remote sites. In addition, 13 sites were chosen to survey point source emissions (Fig. 1). All the samples were transported to the laboratory immediately and stored at −4 °C until analysed.

Surface sediments were freeze-dried, ground, and homogenized by sieving through a stainless steel sieve (80 mesh) and stored in aluminum foil at −4 °C until extraction. Samples (10 g) were Soxhlet extracted using a mixture of 200 mL dichloromethane and n-hexane (3:1, v:v) for 24 h. A known amount of recovery surrogate standards was added to the samples prior to extraction. The extracts were concentrated to 2 mL using a rotary evaporator and then purified and fractionated using a glass column packed with silica gel/alumina. The silica/alumina column was packed, from the bottom to top, with neutral alumina (6 cm, 3% deactivated, w:w), neutral silica gel (2 cm, 3% deactivated, w:w), 33% sodium hydroxide silica (5 cm), neutral silica gel (2 cm, 3% deactivated, w:w), and 44% sulfuric acid silica (6 cm). The PBDE mixture was eluted with 70 mL of hexane: dichloromethane (1:1, v:v), and this eluent was concentrated by rotary evaporation and further reduced with a gentle N_2 stream to a final volume of 500 μL. A known amount of internal standard was added to the extracts prior to instrumental analysis.

2.3. Instrumental analysis

Concentrations of target analytes were determined using a Shimadzu Model 2010 gas chromatograph coupled with a Model QP2010 plus mass spectrometer (Shimadzu, Japan) using negative chemical ionization in the selected ion monitoring mode. A 15 m DB-5MS capillary column (0.25 mm i.d., 0.10 μm film thickness) was used for the determination of PBDE congeners. The samples were injected in the splitless mode using an AOC-20i auto injector (Shimadzu, Japan). The column temperature was programmed

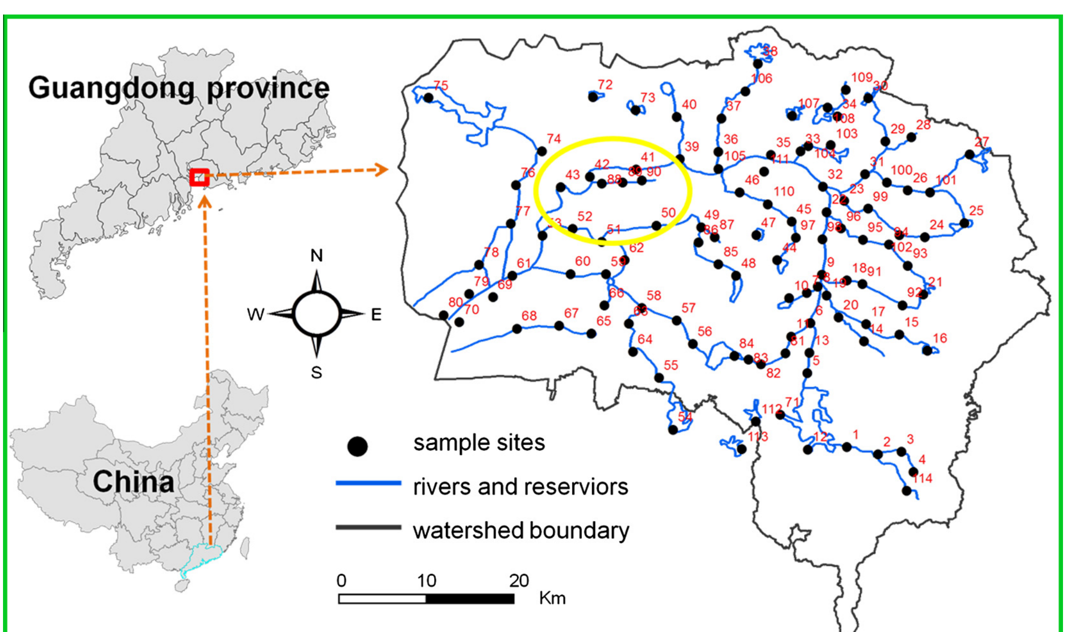

Fig. 1. Map of the sampling sites of surface sediments in the Maozhou River in Shenzhen, China. 1, 2, 3..., 114 represent the sample number. The area within the yellow oval has extremely high levels of PBDEs. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)