Polybrominated biphenyl ethers (PBDEs) in the atmosphere of the Pearl River Delta, South China: atmospheric deposition and transboundary transport

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Introduction

Located in southern China, the Pearl River Delta (PRD) has a land area of c.a. 41,700 km^2. It is one of the largest 3 regional economic zones in China, and has subjected to fast industrialization and urbanization during approximately the last 25 years. Previous studies reported high PBDE concentrations in the atmosphere of Guangzhou (Chen et al., 2006), and very high BDE-209 concentrations in sediments from the Pearl River estuary (Mai et al., 2003). Although widespread and large scale electronic, plastic and furniture manufacturers in the PRD may be responsible for the high PBDE concentrations observed in the environment, recently, the amounts of PBDEs released to the environment from the processes of uncontrolled electronic-waste recycling were highlighted to be of great concern.

Geographically, Hong Kong is part of the PRD. However, the historical application/usage and management of chemicals in Hong Kong has been distinctively different from the mainland China, owing to the unique colony history and 'one country, two systems' policy. Largely the chemical management policy in Hong Kong has been along with the developed countries, while mainland China followed its own way. In the context of PBDEs, contrary to the mainland part of the PRD, no e-waste recycling activities were permitted/spotted in Hong Kong, and open burning of any waste is strictly prohibited in Hong Kong.

POPs in the atmosphere may be introduced to land surface via wet and dry atmospheric deposition, and may subject to transboundary transport, at different scale, both in gaseous or particulate-associated phases. There may be considerable seasonal variations of atmospheric wet and dry deposition of POPs due to the distinct seasonality of rainfall and temperature in a tropical/subtropical region like the PRD, which features a typical monsoon climate. And, on the other hand, the unique difference in the application and management policy of POPs between Hong Kong and the PRD would provide a field venue to look at the potential intra-regional transboundary air transport of POPs from the mainland PRD to Hong Kong.

Materials and Methods

A total of 90 bulk deposition samples were collected at the 15 monitoring stations. Year-round bulk deposition samples were collected at 13 sites in the Pearl River Delta (PRD) on a bimonthly basis from Dec 2003 to Dec 2004. While deposition sampling at 2 stations in Zhongshan University (GZ3) in Guangzhou and at The Hong Kong Polytechnic University (PU), respectively, were on a biweekly basis.

Bulk particle deposition (wet and dry) collection was achieved using a stainless steel funnel with a receiving area of 0.049 m^2, attached to a filter holder in a blinded screen housing. The bulk deposition samples were filtered on situ through pre-combusted (4 h at 450 ^oC) 90 mm diameter glass microfiber

(GF) (Whatman Type GF/F, nominal pore size 0.7 μm). After sampling, the inner surfaces of the stainless steel funnels were wiped with pre-cleaned cotton too. The cotton and GF/F filter paper were combined together as particle bound deposition samples.

To match the deposition samples, active Hi-Vol samplers (Anderson type) were also deployed to collect aerosol samples at GZ3 and PU sites on a biweekly basis in the same sampling period. The airborne particulates were collected on a pre-heated (4 hr at 450°C) quartz microfibre filter (QFF, Whatman QM-A, 20.3×25.4 cm) at a flow rate of 0.217 - 0.228 m^3 min^{-1}. A total of 43 samples were collected at the two sites.

A mixture of surrogate standards of decachlorobiphenyl (PCB209), 13C12-PCB138 and 13C12-PCB180 was added to each of the samples prior to extraction. The GF/F filter paper was soxhlet-extracted with dichloromethane (DCM) for 24 hours. The extract was concentrated and solvent-exchanged to hexane and purified on an 8 mm i.d. alumina/silica gel column. After adding 25 μl of dodecane keeper containing 5 ng of pentachloronitrobenzene (PCNB) and 2 ng of BDE-71 as the internal standards, the solution was reduced to a final volume of 25 μl under a gentle nitrogen stream. PBDE analysis was performed with a Shimadzu model 2010 gas chromatograph (GC) coupled with a model QP2010 mass spectrometer (MS) (Shimadzu, Japan) using negative chemical ionization (NCI) under SIM mode. A CP-Sil 13 CB (12.5 m×0.25 mm i.d, 0.2 μm film thickness) capillary column was used to measure BDE-209, while a DB-5MS (30 m × 0.25 mm i.d., 0.25 μm film thickness) capillary column was used for the determination of other PBDE congeners. A total of 10 congeners, including BDE-28, -47, -66, -99, -100, -138, -153, -154, -183, and -209, was quantified using an internal calibration method.

Results and Discussion

Annual particle bound BDE-209 deposition in the PRD and Hong Kong. Owing to the long exposure time (2 months) of the deposition samplers, only BDE-209 which is considered to be firmly associated with particulate and less modified by potential after-deposition rinse by rainwater. The annual deposition fluxes of BDE-209 varied from 32.6 to 1970 $\mu g \cdot m^{-2} \cdot yr^{-1}$. Spatial variations were higher in the mainland PRD and much lower at all of the sites in Hong Kong. Taking the values at PU as the urban deposition fluxes and the mean values at other four sites in Hong Kong representing the other landscape, the particle deposition flux of BDE-209 loading to Hong Kong was estimated at 93 $kg \cdot yr^{-1}$, while that for the mainland PRD was 13,400 $kg \cdot yr^{-1}$. Clearly, the regional source of BDE209 is located in the mainland PRD.

Implication for fate of BDE-209 in the regional soil. The atmospheric deposition of particle phase BDE-209 is the major sources of BDE-209 in regional soil. The inventory of BDE 209 in the PRD soils was estimated at 44.4 t in 2002 (Zou et al. 2007). In addition, a recent study analyzing 30 year depositional sediment cores found that BDE-209 increased exponentially after 1990 and higher concentrations appeared from about 1995 in the PRD (Chen et al. 2007). Based on our bulk deposition data, we assumed the BDE-209 in soils accumulated from 1995 with average deposition fluxes of 13400 $kg \cdot yr^{-1}$. By comparing the estimated total deposition between 1990 and 2002 (107 t) with the estimated burden in the soils (44.4 t) in 2002, the apparent half time of BDE-209 in soil in PRD was estimated, roughly, to be ~3 years.

Congener profiles of the PBDE deposition in Guangzhou and Hong Kong. The dominance of BDE-209 in the total PBDEs is apparent. The contribution of BDE-209 ranged from 83.2% to 99.9%

of the total PBDEs. Other than BDE-209, BDE-47, -99 and -183 were the predominant compounds among the nine tri- to hepta-BDE congeners (Σ_9PBDEs) with the mean contribution of 21%, 35% and 24% in Guangzhou and 37%, 33% and 25% in Hong Kong, respectively. There is no significant correlation between BDE-209 with other major congeners such as BDE-47, -99, and -183, implying that debromination of BDE-209 was not responsible for these PBDE congeners. In general, the congener profiles of PBDE deposition reflects the usage of deca- (predominant), octa-, and penta-BDE commercial products in the PRD.

Seasonal variations of PBDE deposition in Guangzhou and Hong Kong. Different seasonal trends for PBDE deposition fluxes between two cities were displayed. In Guangzhou (ZU), the deposition fluxes of BDE-209 exhibited less temporal variability with several lower concentrations during one year sampling campaign; the concentrations of the other PBDEs during the wet season from April to September were found significantly higher than those during the dry season. However, distinguished seasonal patterns were found in the PBDE depositional fluxes in Hong Kong (PU). The concentrations of all PBDE compounds during the sampling time from late August to November 2004 were significantly higher than at other time. In particular, the high levels of particle-phase PBDEs deposition fluxes in Hong Kong were found during the winter monsoon seasons with the prevailing northeastern or northern wind direction, suggesting that industrial and other emissions in the PRD region could contribute to the enrichment of BDE-209 deposition fluxes in the downwind areas, *i. e.* Hong Kong.

Deposition velocities and washout ratios. Dry deposition velocities and washout ratios of particulate PBDEs can be attained by calculation from the particulate PBDE deposition fluxes combined with aerosol concentration data. At PU site in Hong Kong, the calculated average dry particulate deposition velocities of BDE-47, -99, and -209 were 0.32 ± 0.12 cm/s, 0.24 ± 0.16 cm/s, and 0.28 ± 0.01 cm/s, respectively. There were no significant differences of the particle-phase dry deposition velocity of PBDEs among the different molecular weighted compounds. The particle washout ratios estimated from the bulk deposition fluxes vary seasonally, with higher particle scavenging efficiencies occurring during dry seasons relative to the wet seasons. From wet seasons to dry seasons, the washout ratios of BDE-47, -99 and -209 increased from 7.7×10^3 to 2.8×10^7, from 7.8×10^3 to 2.6×10^7, and from 4.2×10^4 to 3.5×10^8, respectively. And the median washout ratios of BDE-47, -99 and -209 were 1.1×10^5, 3.1×10^5, and 5.1×10^5, respectively.

PBDEs in aerosols over Guangzhou and Hong Kong (Li et al., 2009). The concentrations of BDE-209 and Σ_9PBDEs in Guangzhou ranged from 758 to 21,900 pg/m3 and from 31.8 to 3,320 pg/m3, respectively, and in Hong Kong ranged from 8.5 to 895 pg/m3 and from 1.0 to 386 pg/m3, respectively. Elevated concentrations of PBDEs were observed in Guangzhou, showing significant atmospheric PBDE pollution. BDE-209, -47, and -99 were the dominant congeners in all the samples, suggesting that the widely used commercial penta- and deca-BDE products were the original sources. Distinct seasonal patterns were observed in the PBDE concentrations of aerosols in Hong Kong, higher during the winter monsoon period, and lower during summertime. The less distinct seasonal variations of PBDE concentrations in the aerosols of Guangzhou suggested the dominance of local pollution sources around the city. Significant correlations were found between BDE-209 and Organic Carbon (OC) or Element Carbon (EC) in the two cities, suggesting that combustion may be an important pathway introducing BDE-209 to the atmosphere. The lower BDE-209 concentrations along with higher OC/EC ratios implied that a quick loss of BDE-209 may occur during aerosol aging processes.

Implication for trans-boundary transport of PBDEs to Hong Kong. Hong Kong is a transition zone of East Asian monsoon system, where different air masses meet under the control of large-scale monsoon winds. Topography and monsoon flows put Hong Kong as a receptor of the large amounts of pollutant emissions in the East Asian Pacific Rim. Back trajectory analysis showed that, during the measurement period, generally three categories of air masses can be identified, 1) CI – air masses coming from the north or northeast that originated from the continental inland areas of northern China, Mongolia, Central Asia and Siberia and reaching the South China region through the inland areas of China; 2) CT – air masses from the north or northeast that originated from continental inland areas of the northern China, reaching the South China region through the Southeast China coast; 3) SS – air masses coming from the south, southwest, or east that originated mostly from the sea, including the South China Sea, the Indian Ocean and the Pacific Ocean. The elevated PBDEs concentrations in aerosol over Hong Kong were related with the air masses CI, suggesting a potential atmospheric movement of PBDEs from inland areas to Hong Kong. For examples, at PU site, elevated BDE-209 concentrations were observed on 31st Dec 2003, 24th Aug 2004, 19th Oct 2004, and 15th Dec 2004, at 534, 398, 752 and 895 pg/m3, respectively, when the northerly winds prevailed during the winter monsoon period. Back trajectory shows that the air mass passed through the PRD areas before reaching Hong Kong via northerly winds. Industrial and other emissions in northern inland areas of China and the PRD region could contribute to the enrichment of BDE-209 in the downwind areas of Hong Kong. This is in consistent with the observed higher deposition fluxes of PBDEs in Hong Kong were found during the winter monsoon seasons with the prevailing northeastern or northern wind direction. It is noteworthy to remark here that PBDEs may be an excellent indicator to the continental/inland outflow of atmospheric pollution to Hong Kong and, further, the northern South China Sea.

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