Characterization of polychlorinated polybromodiphenyl ethers (PBDEs) in various aqueous samples in Taiwan

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Introduction

PBDEs are widely used as an additive of brominated flame retardants (BFRs) in numerous combustible materials such as plastics, wood, paper, textiles and electrical devices to reduce the risk of fire and meet fire safety regulations in many countries. Due to strong toxicity to human and wildlife, high persistence in the environment and high tendency to bioaccumulate in the food chain, penta- and deca-BDE commercial mixtures have been identified and listed as persistent organic pollutants (POPs) in Annex A (elimination) under the Stockholm Convention. There is no official report on PBDEs production and consumption in Taiwan, however, the intensive development of heavy industries and electronic manufacturing in the island could release tons of these pollutants into the environment. The levels of PBDEs in coastal, river and lake waters have been reported but no attempt has been made to quantify the levels of these chemicals in groundwater. Therefore, understanding the levels and fate of PBDEs in ground and surface water is important to evaluate the effects of these pollutants on human health. The purpose of this study is to investigate the levels of PBDEs in 20 groundwater samples collected from various industrial sites and 6 surface water samples throughout Taiwan. The characteristics of PBDEs congener distributions as well as dissolved/solid phase partitioning are also determined. In addition, the change in levels and congeners distribution of PBDEs between raw and treated water of a water treatment plant is also discussed. Data presented in this study would help us to better understand the background PBDEs contamination in fresh water and their removal efficiencies achieved with typical water treatment processes.

Methodology

20 groundwater samples are collected in various locations in Taiwan including the vicinity of institutions, recycling factories, plastic manufacturers, steel industrial sites, incinerator sites, pentachlorophenol contaminated sites and organic solvent landfills/hazardous waste landfills. In term of surface water, 6 samples from the inlet and

outlet of a water treatment plant located in northern Taiwan are collected. The solid phase is collected by glass fiber filters (GFF) while dissolved phase is adsorbed by polyurethane foam (PUF). Because PBDEs are of low concentration in water phase, a relatively high sampling rate (1 L/min) is applied. Two layer of GFFs are applied in this campaign (3 μm and 0.5 μm pore sizes) to separate large and small particles in order to reduce the pressure drop with a high sampling rate. After sampling, GFF and PUF are extracted with toluene and then concentrated to 2 mL. The concentrated solutions are first transferred into the acid-silica column and then to the Cape column by n-hexane to remove the impurities before being analyzed by HRGC-HRMS.

Results and discussion

This is the first study to report the levels of PBDEs in groundwater in Taiwan. A wide range of PBDEs concentrations are found in the groundwater samples which range from 18.5~68.2 pg/L, 9.91~32.8 pg/L, 10.2~652 pg/L, 34.3~184 pg/L, 19.5~4212 pg/L, 14.4~ 22.2 pg/L and 121~226 pg/L for institutional, industrial, plastic manufacturer, steel industrial, municipal waste incinerators (MWIs), pentachlorophenol contaminated and organic solvent/ hazardous waste landfills areas, respectively. Redfern et al. [1] indicate that the global PBDEs emission from combustion processes is estimated around 6.75 tons per year, and is considered as the most important PBDE emitters to the environment. Therefore, the highest PBDEs concentration measured in groundwater is found from that sample in MWI plant (4212 pg/L) possibly due to the leaching of PBDEs-containing material.

The dissolved-solid partitioning reveals that PBDEs in ground and surface water samples are dominated by solid phase (around 60~80%) due to low solubility. BDE-209 predominates congener distribution and contributes 65 to 95% of total PBDEs concentration in groundwater while it contributes 82.5 to 97.1% of total PBDEs concentration in surface water. This reflects the high consumption of deca-BDE commercial mixtures in Taiwan. However, if BDE-209 is not taken into account, the PBDEs congeners distribution indicates that the major congeners in all the groundwater samples are BDE-206, BDE-207 and BDE-47, which accounts for 19.9 - 51.4% (mean: 27.4%), 17.6 - 34.1% (mean: 25.6%) and 6.9 - 24.1% (mean: 17.2%), respectively. BDE-99 is a major component (44.8 –48.6%) of the penta-BDE commercial mixtures, followed by BDE-47 (38.2–42.8%) and BDE-100 (7.82–13.1%). Therefore, penta-BDE commercial mixtures could affect groundwater quality significantly in these areas. Relatively high contributions of BDE-183, -196 and -153, the major components of octa-BDE commercial mixture, are found at plastic manufacture area.

Removal efficiency of PBDEs in a conventional water treatment plant (WTP) is also investigated in this study. PBDEs in raw and treated water samples are measured as 1002 pg/L and 30.2 pg/L, respectively. As a result, 97% of PBDEs in raw water is removed during this process, particularly, during the sedimentation process. The PBDEs congeners profiles in water samples before and after treatment also show the dominance of BDE-209 (Figure 2).

Table 1. Concentration of PBDEs in groundwater samples.

	Institution area (n = 5)	Industrial area (n = 2)	Plastic manufacture area (n = 3)	Steel industry area (n = 2)	Incinerators area (n = 4)	PCP contaminated area (n = 2)	Organic solvent /hazardous waste landfills (n = 2)
Average sampling volume (L)	229	151	152	125	133	250	250
PBDEs (pg/L)	47.0	21.3	245	109	1434	18.3	173

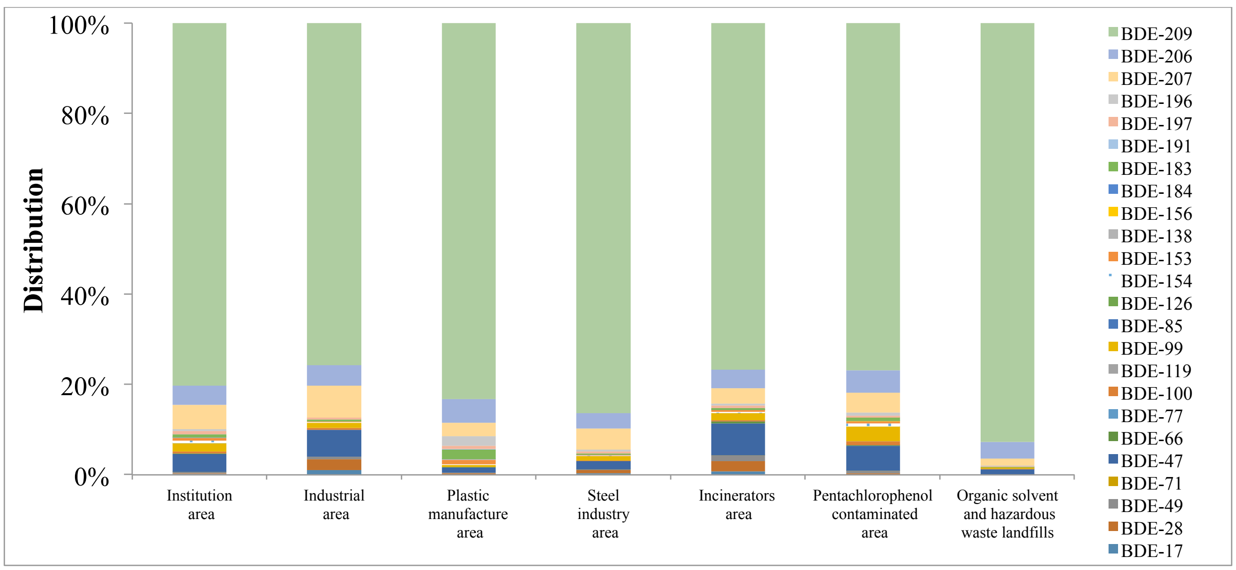

Figure 1. PBDEs congener distribution of groundwater samples.

The influence of seasonality on PBDEs concentration is reported in Figure 3. Although the precipitation in northern Taiwan during winter (<100 mm) is lower if compared with that during summer (200-300 mm), higher PBDEs levels are measured in raw water samples collected in winter if compared with summer samples. Moon et al. (2007) indicated that atmospheric levels and deposition flux of PBDEs measured in urban locations of South Korea in winter is significantly higher than those in summer. The higher PBDEs concentration in winter compared to summer may cause the higher concentration of PBDEs in surface water samples measured in Taiwan.

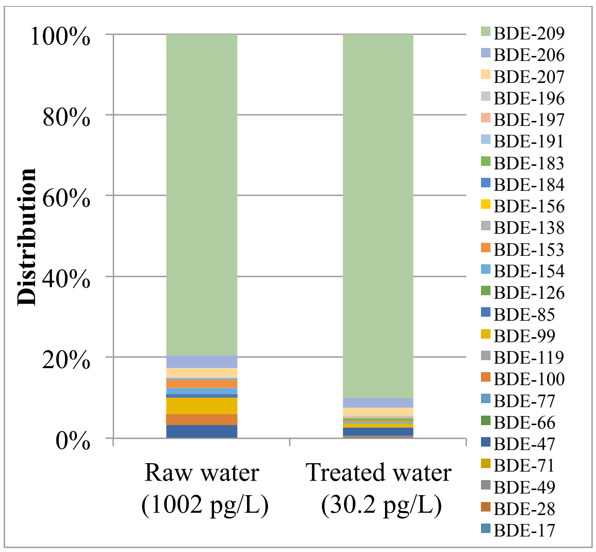

Figure 2. PBDEs concentrations and congeners distributions in raw and treated water samples of a WTP.

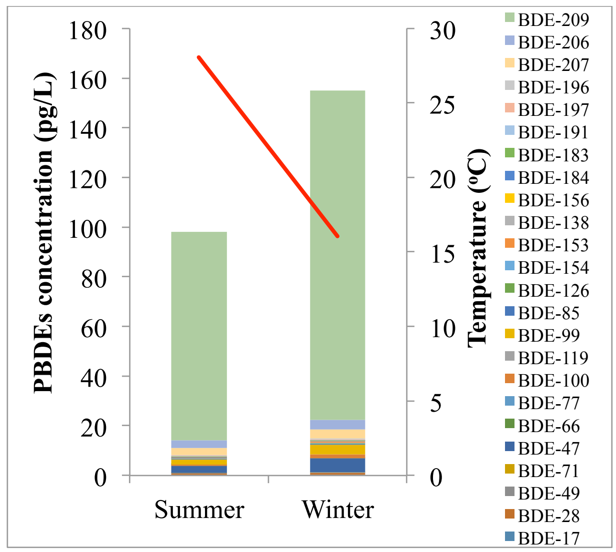

Figure 3. Effect of water temperature on PBDEs levels in raw water samples.

Reference:

[1] Redfern, F. M., Lee, W.J., Yan, P., Mwangi, J. K., Wang, L.C. and Shih, C.H. (2017). "Overview and perspectives on emissions of polybrominated diphenyl ethers on a global basis: evaporative and fugitive releases from commercial PBDE mixtures and emissions from combustion sources." Aerosol Air Qual. Res. 17(5): 1117-1131.

[2] Moon, H. B., Kannan, K., Lee, S. J. and Choi, M. (2007). "Atmospheric deposition of polybrominated diphenyl ethers (PBDEs) in coastal areas in Korea." Chemosphere 66(4): 585-593.