Science of the Total Environment 649 (2019) 388–395

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Characterization of polybrominated diphenyl ethers (PBDEs) in various aqueous samples in Taiwan

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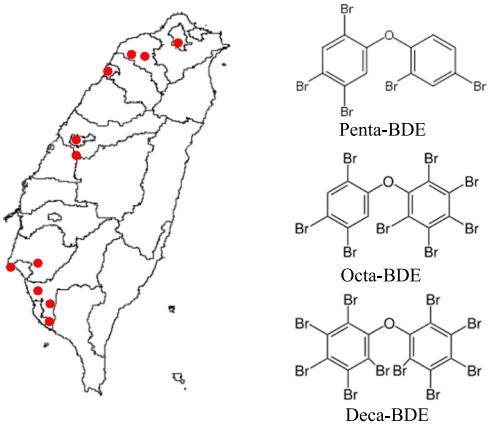
HIGHLIGHTS

- PBDEs levels measured in some groundwater samples reflected significant contamination.
- PBDEs predominated in solid phase in groundwater and surface water.
- Deca-BDE (BDE-209) was predominant congener.
- PBDEs levels in surface water were higher in wintertime compared with summertime.
- Sources and possible debromination of PBDEs in groundwater were identified.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 7 June 2018
Received in revised form 14 August 2018
Accepted 15 August 2018
Available online 17 August 2018

Editor: Yolanda Picó

Keywords:
Positive matrix factorization (PMF)
Groundwater
Water treatment plant
Seasonal variation
Debromination
Persistent organic pollutants (POPs)

ABSTRACT

In this study, 20 groundwater samples and 7 surface water samples were collected and analyzed by HRGC-HRMS to evaluate the levels, congener distributions, and dissolved/solid partitioning of polybrominated diphenyl ethers (PBDEs) in water matrix as well as the removal efficiency of a typical water treatment plant (WTP). The results indicated that the level of PBDEs concentrations ranging from 18.51 to 4212 pg/L and 30.24 to 1021 pg/L were found in groundwater and surface water, respectively. BDE-209 predominated and contributed over 90% of total PBDEs concentrations for all samples analyzed. In addition, the dissolved/solid distribution indicated that 60–80% of PBDEs were measured in solid phase. 97% of total PBDEs was removed in a WTP. Positive matrix factorization (PMF) analysis was conducted for groundwater samples and the results indicated that 3% and 41% of PBDEs were attributed to octa and deca-BDEs commercial mixtures, respectively, while 56% resulted from anaerobic microorganism debromination process. Understanding the PBDEs occurrences, distribution and debromination process as well as their removal efficiency of water treatment plant could provide valuable information on the fate of those compounds in environment.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of chemicals which consist of two benzene rings linked by one oxygen atom with

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https://doi.org/10.1016/j.scitotenv.2018.08.204
0048-9697/

the general formula $C_{12}H_{(10-n)}Br_nO$ ($1 \le n \le 10$). PBDEs are widely used as an additive of brominated flame retardants (BFRs) in numerous combustible materials such as plastics, wood, paper, textiles and electronic devices to reduce the risk of fire and meet fire safety regulations in many countries (Ward et al., 2008). Three typical commercial PBDEs mixtures are produced for industrial application, i.e., penta-BDE, octa-BDE and deca-BDE, and are classified on the basis of their average bromine content (Alaee et al., 2003). Due to high toxicity to human and wildlife, persistence in environment and high tendency to bioaccumulate in food chain (Darnerud, 2003; Legler and Brouwer, 2003; Hamers et al., 2006), penta-, octa- and deca-BDE commercial mixtures have been listed as persistent organic pollutants (POPs) in Annex A (elimination) under the Stockholm Convention (UNEP, 2018).

Data on PBDEs production and consumption in Taiwan are not available, however, intensive development of petrochemical industries and electronic manufacturing process in the island could release tons of these pollutants into the environment. Relevant studies reported levels of PBDEs in ambient air (Tu et al., 2012), indoor and outdoor dust (Chao et al., 2016), stack gas (Tu et al., 2011; Lin et al., 2012), sediment (Jiang et al., 2011), fish (Peng et al., 2007) and human body (Chao et al., 2007), but the level of PBDEs in water matrix are rarely reported in Taiwan. Therefore, understanding the levels and fate of PBDEs in water matrix is important to evaluate their distribution in environment and possibly effect of these pollutants on human health. The levels of PBDEs in coastal, river and lake waters worldwide (as listed in Table 1) have been reported but limited attempts have been made to quantify the levels of these chemicals in groundwater. Due to low solubilities (Palm et al., 2002), PBDEs were more likely to distribute in suspended solid material rather than liquid phase but their partitioning in water were rarely reported. Deng et al. (2015) indicated that the partitioning of PBDEs in suspended solid could affect their removal efficiency by water treatment process. Therefore, study investigating the partitioning of PBDEs between dissolved phase and solid phase in groundwater and surface water is needed. In addition, the removal efficiency of PBDEs of waste water treatment plants (WWTPs) were reported in Hong Kong (Deng et al., 2015) and China (Peng et al., 2009) ranged from 93% to 99% and 52% to 80%, respectively, but those of water treatment plant (WTP) were rarely investigated. Due to the high risk of PBDEs entering human body, the PBDEs removal efficiency should be evaluated to provide relevant information on protecting the public health.

Debromination of PBDEs in the natural environments was not fully investigated. One of the challenges to confirm debromination in the environment was identifying the debromination signal and the relatively small amount of debromination products. Tokarz et al. (2008) indicated that microbial debromination was more likely to take place at meta and para position and PBDEs 17 and 28 were major microbial debromination products of high molecular weight PBDEs in anaerobic sediment which could be the PBDEs debromination indicator in the environment. Positive matrix factorization (PMF) has been used to identify and quantify the sources of pollutants (Paatero and Tapper, 1994) and dehalogenation processes for polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzo-furans (PCDFs), polychlorinated biphenyls (PCBs) and PBDEs (Zou et al., 2013) in the environment in general and water matrix in particular (Rodenburg et al., 2014). Therefore, the application of PMF model not only improve the understanding of PBDEs sources in Taiwan groundwater and their debromination process, but also provides valuable information on the fate of these compounds in the environment.

The purpose of this study was to investigate the levels of PBDEs in 20 groundwater samples collected from various industrial sites and 6 surface water samples collected throughout Taiwan. Characteristics of PBDEs congener distributions as well as dissolved/solid phase partitioning were also determined. In addition, variations in levels and congeners distribution of these contaminants between raw and treated water of a typical WTP are also discussed. Data presented in this study would help us to better understand the background PBDEs contamination in groundwater and surface water and the removal efficiencies of PBDEs achieved with typical water treatment processes.

2. Methodology

2.1. Sample collection

20 groundwater samples (GW01~20) were collected in various locations in Taiwan including the vicinity of institutions sites, industrial sites, plastic manufacture sites, steel industrial sites, incinerator sites, pentachlorophenol contaminated sites, organic solvent and hazardous waste landfills (Fig. 1). For groundwater sampling, the well-purging were conducted to remove the "aged" water until water quality parameters were stabilized (i.e., standard deviation of pH < ±0.2, conductivity < ±3%, dissolved oxygen < ±10% or ± 0.3 mg/L, etc.). After water quality was stabilized, a pump was used to perform a stable and representative water sampling. As for surface water samples, a raw water sample from the inlet (SW02) and outlet (SW07) of a water treatment plant in northern Taiwan were collected simultaneously. In addition, One river surface water sample (SW01) was collected 10 km upstream to the WTP. To evaluate the seasonality variation of PBDEs levels in raw water of the WTP, the summer time (SW03 and SW04) and winter time (SW05 and SW06) raw water samples were taken in July and December, respectively, at the same position as the previous raw water sample (SW02). All surface water sampling locations were demonstrated in Fig. S1, Supplementary material. Because PBDEs were of low concentrations in water phase, a relatively high sampling rate (1 L/min) was applied and the volumes of water sampled in each

Table 1
PBDEs concentrations in surface water reported worldwide.

Location	Concentration	Reference
Seawater		
San Francisco Bay, USA	Σ_{22}PBDE: 3.00 to 513 pg/L	Oros et al. (2005)
Izmir Bay, Turkey	Σ_7PBDE: 52.3 pg/L	Cetin and Odabasi (2007)
Hong Kong's coastal water	Σ_8PBDE: 98.8 pg/L	Wurl et al. (2006)
Bohai Sea, China	Σ_8PBDE: 15400–65,500 pg/L	Wang et al. (2017)
	Σ_{17}PBDE: 344–68,000 pg/L	Guan et al. (2007)
River water		
Zhejiang, China	Near urban area: Σ_7PBDE: 3500–7300 pg/L	Wang et al. (2011)
	Near an e-waste recycling area: Σ_7PBDE: 10–40 × 10^3 pg/L	
Other water samples		
Pond water near an e-waste recycling site of China	Σ_{18}PBDE: 24400 pg/L	Wu et al. (2008)
Waste water treatment plant, China	Σ_8PBDE: 1–254 × 10^3 pg/L (influent), 12–27 × 10^3 pg/L (effluent)	Deng et al. (2015)
Great Lakes, USA	Σ_7PBDE: 5.00–52.0 pg/L	Strandberg et al. (2001)
Groundwater, Canada	Σ_{17}PBDE: 120 to 94,000 pg/L	Levison et al. (2012)
Groundwater	Σ_{24}PBDE: 9.91 to 4212 pg/L (mean: 367.6 pg/L)	This study
Surface water	Σ_{24}PBDE: 30.2 to 1021 pg/L (mean: 365.6 pg/L)	