Chemosphere 199 (2018) 603–611

Contents lists available at ScienceDirect

Chemosphere

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

PBDEs and Dechlorane Plus in the environment of Guiyu, Southeast China: A historical location for E-waste recycling (2004, 2014)

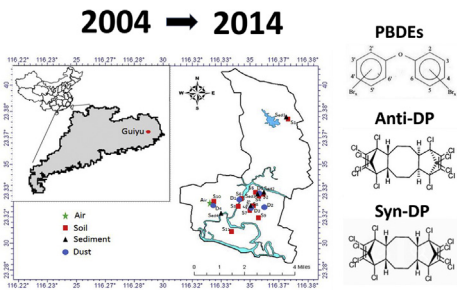
Na Li [a, 1], Xun-Wen Chen [b, 1], Wen-Jing Deng [a, *], John P. Giesy [c, d, e], Hai-Long Zheng [f]

[a] Department of Science and Environmental Studies, The Education University of Hong Kong, 10 Lo Ping Road, Tai Po, Hong Kong
[b] Department of Civil and Environmental Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong
[c] Dept. Veterinary Biomedical Sciences & Toxicology Program Faculty, Toxicology Centre, University of Saskatchewan, Canada
[d] School of Biological Sciences, University of Hong Kong, Hong Kong
[e] State Key Laboratory of Pollution Reference and Resource Reuse, School of the Environment, Nanjing University, Nanjing, People's Republic of China
[f] Department of Soil and Groundwater Remediation, Newgroup Environmental Co.,Ltd, Nanshan, Shenzhen, 518053, People's Republic of China

HIGHLIGHTS

- $\Sigma_{3\text{-}7}$PBDEs in soil, road dust, and sediment in 2014 were a little less than or close to those measured in 2004.
- $\Sigma_{3\text{-}7}$PBDEs in road dust were greater than those in soil, sediment and air particles.
- Greater proportions of lesser-brominated BDE, such as BDE-71, were predominant in air particulates.
- Most of the fractions of anti-DP were consistent among samples, ranging from 70% to 80%.
- The health risk assessment showed that HIs of PBDEs or DPs for child and adult were all lower than 0.16.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 July 2017
Received in revised form
12 December 2017
Accepted 7 February 2018
Available online 13 February 2018

Keywords:
Electronic waste recycling
Polybrominated diphenyl ethers
Dechlorane plus
Health risk assessment

ABSTRACT

Polybrominated diphenyl ethers (PBDEs, tri-to hepta-BDEs) and Dechlorane Plus (DP) in multiple samples (soil, sediment, road dust, and $PM_{2.5}$ particles) in historical locations of our previous work in Guiyu (electronic-waste recycling town) in southeastern China were investigated in 2014. Ten years later, PBDEs and DP were detected in 100% of the samples. $\Sigma_{3\text{-}7}$PBDEs were still relatively great, ranging from 1.2×10^1 to 2.1×10^3 ng/g dry weight (dw) in soil, 2.1 to 3.2×10^3 ng/g dw in sediment, 1.0×10^1 to 1.1×10^4 ng/g dw in road dust, which were a little less than or close to those measured in 2004. However, $\Sigma_{3\text{-}7}$PBDEs in $PM_{2.5}$ (5.0×10^2 to 8.4×10^2 pg/m^3) were significantly lower in 2014. BDE-47, -99, −153, and −183 were predominant congeners, which were also predominant PBDEs reported in Guiyu (2006–2008). Greater proportions of lesser-brominated BDEs were predominant in $PM_{2.5}$ than other samples. DP was detected in 100% of the samples collected with high levels. Total syn-DP and anti-DP concentrations were 3.8 to 2.1×10^3 ng/g dw in soil, 1.1×10^3 to 7.2×10^3 ng/g dw in sediment, 1.4×10^1 to 1.1×10^3 ng/g dw in road dust, and 1.8×10^2 and 1.7×10^2 pg/m^3 in $PM_{2.5}$. Most of the fractions of anti-DP (f_{anti}) (70%–80%) were

* Corresponding author. Department of Science and Environmental Studies, The Education University of Hong Kong, Tai Po, N.T., Hong Kong, China.
E-mail address: wdeng@eduhk.hk (W.-J. Deng).
[1] Na Li and Xun-Wen Chen contributed equally to this paper.

https://doi.org/10.1016/j.chemosphere.2018.02.041

consistent among samples. The health risk assessment showed that hazard indexes (HIs) of PBDEs or DPs for child or adult were all lower than 0.16.

1. Introduction

Electronic waste (e-waste) has been recycled at Guiyu, a small town located in the east of Guangdong Province in southeastern China, since the 1990s. More than 75% of the 300 individual workshops have been involved in the dismantling or processing of e-waste. Due to the crude recycling activities of e-waste, contamination with polybrominated diphenyl ethers (PBDEs), as well as polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and some heavy metals, were detected in many matrices in Guiyu. For example, these contaminants were found to be widely distributed in air (Deng et al., 2007), dust (Leung et al., 2011), soil (Wong et al., 2007), and sediment (Luo et al., 2007). The adverse health effect on humans caused by these organic and inorganic contaminants in e-waste recycling area is a growing issue globally (Heacock et al., 2015). A large number of studies have focused on the contaminants with the premature recycling works in Guiyu, and discovered that humans and wildlife have been severely affected in this area (Leung et al., 2007, 2008a, b; Wong et al., 2007, ; Li et al., 2008).

Of the heavy contaminants in Guiyu, PBDEs have received considerable attention in recent years due to their high production and potential toxic effects, such as interfering with endocrine and nervous systems (Herbstman et al., 2010; Kuriyama et al., 2005). PBDEs belongs to the brominated flame retardants (BFRs), which were widely used as additive FRs in paints, textiles, and electronics and have been massively released into the environment (Covaci et al., 2011; Kierkegaard et al., 2004), especially in some countries in Asia such as China and India, where the recycling of discarded concentrations of congeners associated with these electronic devices (e-wastes) is flourishing. Consequently, PBDEs are ubiquitous in water, sediments, atmosphere, plants, and the tissues of animals in e-waste recycling areas (Hites, 2004; Hu et al., 2014; Rodenburg et al., 2014; She et al., 2013). The contamination status of PBDEs in Guiyu is even more serious (Leung et al., 2011), and the health issues related to PBDEs by our previous work have been reported for concentrations observed in soil, dust, water, and sediment in Guiyu (Leung et al., 2006, 2007, 2011). Since the early 2000s, e-waste has been treated in a government-organized recycling center at Guiyu, instead of in traditional family-based private workshops. The implementation of regulations and the establishment of a central facility with modern controls on the release of pollutants by the government to better manage recycling of e-waste have contained releases of PBDEs to the environment. However, the effect was not confirmed.

Because of high toxicity and persistence, PBDEs were phased out by the European Union beginning in 2004 (Schenker et al., 2008). Alternative additive FRs in commercial products are being developed and used (Chen et al., 2009; Hites, 2004). One of the emerging non-PBDE FRs is Dechlorane Plus (DP), which was first identified in the environment in 2006, are widely used in clothing, furniture, as well as electronic device, such as computer and televisions (Hoh et al., 2006). It was reported that concentrations of PBDEs decreased, whereas alternative FRs, especially DP increased in surface soils and river sediments from the e-waste processing sites in northern Vietnam during 2012–2014 (Matsukami et al., 2017). DP has been reported to be persistent, bioavailable, bioaccumulative, long-range transport and might cause subsequent toxicity to wildlife (Tomy et al., 2007; Sverko et al., 2011). Möller et al. analyzed the air water distribution of DP and suggested that DP was susceptible to long-range atmospheric transport (Möller et al., 2010). Sühring et al. reported the distribution and uptake of DP between sediments and benthic fish (Sühring et al., 2016). Although relatively high concentrations of PBDEs and DP have been found in water, sediments, and some wild animals from e-waste recycling locations (Covaci et al., 2011; Luo et al., 2009), few studies have investigated the DP concentrations in many environmental matrices, especially in e-waste recycling areas. In addition to that, most studies have focused on a single matrix, such as the air or sediment in and around the Great Lakes (Hoh et al., 2006; Shoeib et al., 2012; Zhu et al., 2007), serum (Ren et al., 2009), air (Ren et al., 2008), or soils in China (Wang et al., 2010a, b). Data on DP from various compartments of locations where e-waste is being recycled are more limited (Zhu et al., 2007 (Xu et al., 2017);). More research is required to better quantify the contamination of DP in multiple environmental matrices, especially in e-waste recycling areas.

The primary objective of this study was to determine the effects of the regulations instituted in 2004 on the concentrations of PBDEs and DP in soil, road dust, sediment, and particles from the vicinity of Guiyu. Considering that octa-BDE and penta-BDE were banned in China in 2004 and 2007, respectively, the absolute concentrations and the patterns of the relative concentrations of tri-to hepta-BDEs and DP were examined and compared with data from our previous studies conducted in 2004. Presented here are the results of the first study to investigate and compare the occurrence of PBDEs and DPs in various environmental samples at Guiyu over a decade.

2. Materials and methods

Collection of Samples. Soils were collected from 11 locations, including one reference location near Nanyang reservoir (Fig. 1, shown as S_1 to S_{11}) and sediments were collected from 5 locations. Dust was collected from five areas. The mass of each sub-sample was 10–20 g. $PM_{2.5}$ was collected on the roof of a four-story family building during 23–25 September 2014. According to USEPA acceptance criteria (USEPA, 1998). The details of location and collection was in S1 and S6 in supporting information (SI).

Extraction, cleanup, and quantification. The samples and filters were weighed and spiked with internal standard (^{13}C-OctaCDE), and then vortexed. Ultrasonic extraction method was used with hexane/DCM (1:1) for four times. The extracts were combined and concentrated on a rotary evaporator before cleanup on an aluminum oxide open column (9 g Aluminum oxide and 80 mL solvent). The analytes was eluted by Hexane (with 7% DCM) and concentrated to 500 μL before instrument analyses. All of the solvents, standards of BDE-17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190 and two DP isomers, anti- and syn-DP, of pesticide grade purity were purchased (J.T. Baker, USA). For the analysis of DP, chemical reagents and materials, including dichloromethane, hexane, N-octane, ^{13}C-OctaCDE, and sodium sulfate, were used. Deionized water was generated in house using a Super-Q water generation system. The details was in S6 in SI.