Environmental Pollution 214 (2016) 705–712

Contents lists available at ScienceDirect

Environmental Pollution

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

Plant selective uptake of halogenated flame retardants at an e-waste recycling site in southern China[☆]

Shaorui Wang [a, d], Yan Wang [b], Chunling Luo [a, *], Jun Li [a], Hua Yin [c], Gan Zhang [a]

[a] *Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China*
[b] *Key Laboratory of Industrial Ecology and Environmental Engineering (MOE), School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, China*
[c] *College of Environment and Energy, South China University of Technology, Guangzhou, China*
[d] *Graduate University of Chinese Academy of Sciences, Beijing 100039, China*

ARTICLE INFO

Article history:
Received 4 January 2016
Received in revised form
11 April 2016
Accepted 19 April 2016

Keywords:
Vegetable
E-waste
Plant uptake
PBDEs
NBFRs
DPs

ABSTRACT

The concentrations and homolog patterns of halogenated flame retardants (HFRs) in vegetables grown at an e-waste contaminated site were investigated. Polybrominated diphenyl ethers (PBDEs) were the dominant HFRs in vegetable tissues, with concentrations ranging from 10.3 to 164 ng g^{-1} and 1.16–107 ng g^{-1} in shoots and roots, respectively, followed by novel brominated flame retardants (NBFRs) and dechlorane plus (DPs). This is an indication that PBDE contamination in vegetables grown around e-waste recycling sites may pose a risk to the local terrestrial ecosystem and residents. In addition, this is the first report on the concentrations and compositions of NBFRs in vegetables around e-waste recycling sites. The HFRs concentrations in vegetables varied greatly with the vegetable species, with the highest concentrations observed in *Brassica oleracea* var. *capitata*. Root concentration factors (RCF) decreased with increasing log K_{ow} of HFRs, which indicated that the uptake of HFRs was controlled mainly by log K_{ow}. Dissimilar HFRs profiles in shoots and roots suggested that the uptake and translocation of HFRs by plants were selective, with lower halogenated congeners prone to accumulation in vegetable tissues. Positive relationships between PBDEs and their substitutes were observed in vegetable tissues, suggesting that the replacement of PBDEs by NBFRs has not resulted in an obvious transition in plants within the study area.

1. Introduction

Driven by profit, the recycling of electronic waste (e-waste) using primitive processes is being carried out extensively in developing countries (Leung et al., 2011; Zhang et al., 2012). Approximately 70% of e-waste generated worldwide is processed in China every year (Fujimori and Takigami, 2014; Robinson, 2009). Although China has already drafted and implemented laws and regulations to control illegal handling of e-waste, ineffective enforcement has facilitated serious environmental pollution to occur (Tong, 2004).

Polybrominated diphenyl ethers (PBDEs) and Dechlorane Plus (DPs) are a group of chemicals historically used widely as flame retardants in a variety of electronic products (Morf et al., 2005). Primitive e-waste processing, such as open air incineration, acid washing, and manual disassembling, undertaken has resulted in extensive release of these compounds into the surrounding environment (Wong et al., 2007). For instance, high concentrations of PBDEs have been observed in soil (2720–4250 ng/g) (Leung et al., 2007), air (21.5 ng/m^3) (Deng et al., 2007), sediment (6000–30 000 ng/g), and biota samples (3100 ng/g lipid, processing workers) (Bi et al., 2007) around e-waste dismantling sites. Due to the growing recognition of their adverse environmental and ecological effects, many PBDE formulations have come under increasing regulatory control. Following the phase-out of PBDEs, novel brominated flame retardants (NBFRs) which commonly consist of 1,2-bis(2,4,6-tribromophenoxy) ethane (TBE), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB), bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (TBPH), hexabromobenzene (HBB), pentabromoethylbenzene (PBEB) and decabromodiphenylethane (DBDPE) have been marketed (Tian et al., 2012). Recently, more

---

[☆] This paper has been recommended for acceptance by Baoshan Xing.
[*] Corresponding author.
E-mail address: clluo@gig.ac.cn (C. Luo).

http://dx.doi.org/10.1016/j.envpol.2016.04.071
0269-7491/© 2016 Published by Elsevier Ltd.

information related to the environmental occurrence of NBFRs, particularly regarding their fate, toxicological profile, and transport characteristics, has been obtained (de Wit et al., 2010; Ismail et al., 2009; Shi et al., 2009). However, limited publications are available on the distribution pattern of old and emerging flame retardants in vegetation from e-waste recycling sites, in particular for vegetables consumed by local residents.

The uptake of persistent organic pollutants (POPs) from environmental matrices into plants has attracted considerable research interest, because it plays an important role in trapping and transferring POPs to terrestrial ecosystems, with a corresponding ecological risk (Luo et al., 2015). Soil-air-leaf and soil-root pathways are the two widely accepted routes for organic chemical uptake by plants, which have generally been described by the transpiration stream concentration factor and octanol-air or octanol-water partitioning (log K_{oa} or log K_{ow}) (Limmer and Burken, 2014; Tian et al., 2012). However, the translocation of some hydrophilic compounds in plants reveals the limited ability of chemical physicochemical properties, such as K_{ow}, in accurate descriptions of the translocation of organic contaminants, because their log K_{ow} values do not fall within an intermediate hydrophobicity range (Dettenmaier et al., 2008; Limmer and Burken, 2014). In addition, environmental conditions, the plant species, and plant physiology have been reported as factors controlling plant uptake of POPs (Wang et al., 2014b). Assessing accumulation of POPs in plants solely by gathering exhaustive experimental data such as using pot experiments, while reliable, is overly resource intensive and unsustainable, particularly when considering the diversity of plant varieties and the number of chemicals being generated in abundance. In contrast, plant uptake of POPs from contaminated sites in the presence of multiple contaminants, is a pressing area for further investigation.

The present study was conducted in an intensive e-waste recycling region, Guiyu, which is one of the most notorious e-waste recycling areas in China. Active aqua- and agricultural operations can still be observed amid recycling activities, in rivers and farmlands surrounding the area. The distribution and composition of HFRs in rhizosphere and non-rhizosphere soils of farmland in this region were investigated in our previous study. However, limited investigations have been undertaken on the accumulation of POPs in vegetation affected by e-waste recycling activities. Thus, this study was designed to (a) determine the *in-situ* distribution and composition of HFRs in vegetables grown at the e-waste recycling site, (b) elucidate the potential relationship between the physicochemical properties of HFRs and accumulation in vegetation, and provide greater insight into the potential effects of e-waste recycling on terrestrial ecosystems.

2. Materials and methods

2.1. Sampling site

As shown in Fig. 1, all of the sampling sites were adjacent to an e-waste dismantling site in Guiyu town [23° 3′ N, 116° 03′ E], eastern Guangdong Province, South China. The agrotype in this area is red earth, the average annual rainfall and average annual temperature are approximately 1721 mm and 21.5 °C, respectively (Yu et al., 2006). The samples were collected in December 2012. In total, 14 types of vegetables, including cabbage lettuce (*Lactuca sativa* L. var. capitata L, P1), Chinese cabbage (*Brassica pekinensis*, P2), celery (*Apium graveolens*, P3), Chinese kale (*Brassica alboglabra* L. H. Bailey, P4), broccoli (*Brassica oleracea* L. var. botrytis L, P5), shallot (*Allium fistulosum*, P6), cabbage (*Brassica oleracea* var. *capitata*, P7), radish (*Raphanus sativus* L, P8), taro (*Colocasia esculenta* (L.) Schoot, P9), crown daisy (*Chrysanthemum coronarium* L., P10), pakchoi (*Brassica campestris* L. ssp., P11), snow peas (*Pisum sativum*, P12), sweet potato (*Ipomoea batatas* (L.) Lam., P13), and lettuce (*Lactuca sativa*, P14) were sampled. In addition, the corresponding rhizosphere soils were also collected, and the detail descriptions can be found in our previous study (Wang et al., 2016). Each sample was composed of at least three subsamples collected from the same type of vegetable around the sampling site. All samples were wrapped in aluminium foil, placed in polythene zip-lock bags, and transported to the lab immediately.

Fig. 1. Sampling sites.

2.2. Chemical analysis

All plant samples were washed with tap water and rinsed with deionized water. Each individual plant sample was divided into shoot (aboveground parts) and root subsamples. The samples were freeze-dried and ground into fine powder. Subsequently, approximately 5 g plant samples homogenized with 3 g anhydrous sodium sulfate, spiked with relevant recovery standards (PCB 30, PCB 198, and PCB 209), were soxhlet extracted using hexane/acetone (3:1, V/V) for 72 h. The fractionated plants were concentrated to ~0.5 mL after solvent-exchange to hexane. The plant extracts were washed with sulfuric acid and then cleaned up using a multi-layer column containing neutral alumina (3% deactivated), neutral silica gel (3% deactivated), 50% (w/w) sulfuric acid-silica gel, and anhydrous Na_2SO_4, from bottom to top, using an eluent of 20 ml hexane/DCM (1:1, V/V). After evaporating to approx. 50 μl, ^{13}C-PCB 141 was added as the internal standard before instrumental analysis.

2.3. Instrumental analysis

GC-ENCI-MS (Agilent GC7890 coupled with 5975C MSD) applied with a CP-Sil 13 CB column (15 m × 25 mm i.d. × 0.25 μm film thickness) was used to analyse BDE 209. Eight PBDEs (BDE 28, 47, 99, 100, 154, 153, 183, and 209), two DPs (syn-DP and anti-DP), and six NBFRs (TBE, TBB, TBPH, HBB, PBEB, and DBDPE) were analysed separately using a DB5-MS capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness). Analytical details have been described previously (Wang et al., 2011).

2.4. QA/QC

A procedural blank, a spiked blank containing all chemicals, and