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Brominated and organophosphate flame retardants along a sediment transect encompassing the Guiyu, China e-waste recycling zone

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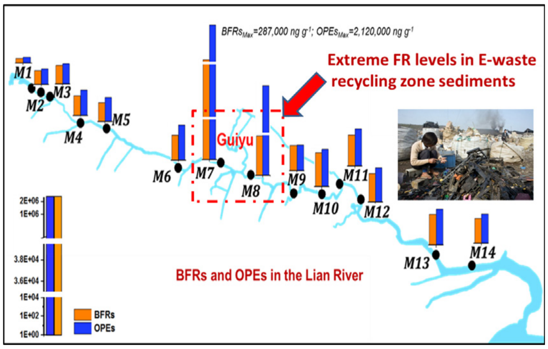
HIGHLIGHTS

- Lian River sediments contained BFR and OPE levels among the highest ever reported.
- e-Waste from Guiyu appeared to be the dominant FR source to the Lian River.
- While seldom associated with e-waste, Penta-BDE, TBBPA, BTBPE and TPP dominated.
- The Guiyu FR profile was mirrored in downstream sediments, suggesting migration.
- Some sediment-associated FRs appeared to pose unacceptable ecological risks.

GRAPHICAL ABSTRACT



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ABSTRACT

e-Waste recycling using crude techniques releases a complex, yet incompletely characterized mixture of hazardous materials, including flame retardants (FRs), to the environment. Their migration downstream and the associated risks also remain undocumented. We examined 26 FRs (18 brominated (BFRs: 12 polybrominated diphenyl ether (PBDE) congeners, plus 6 alternatives) and 8 organophosphate esters (OPEs)) in surficial sediments of the Lian River. Sampling encompassed the river's origin, through the Guiyu e-waste recycling zone, to its mouth, as well as associated tributaries. OPE exceeded BFR concentrations in most sediments, despite their far greater water solubilities. Among OPEs, tris(1-chloro-2-propyl) phosphate dominated upstream, but shifted to triphenyl phosphate in Guiyu and downstream sediments. For PBDEs, Deca-BDE dominated upstream, but Penta-BDE prevailed in Guiyu and at many downstream sites. Among emerging alternative BFRs, decabromodiphenyl ethane dominated upstream, transitioning to 1,2-bis(2,4,6,-tribromophenoxy)ethane in Guiyu sediments. Penta-BDE (BDE-47 + -99, 668–204,000 ng g^{-1}, $\sum$PBDEs 2280–287,000 ng g^{-1}), tetrabromobisphenol A (2,720–41,200 ng g^{-1}), 1,2-bis(2,4,6,-tribromophenoxy)ethane (222–9870 ng g^{-1}) and triphenyl phosphate (4260–1,710,000 ng g^{-1}, OPEs 6010–2,120,000 ng g^{-1}) concentrations in Guiyu sediments were among the highest reported in the world to date. The continuing dominance of these e-waste indicative FRs in sediments downstream of Guiyu suggested that FR migration from Guiyu occurred. Hazard quotients >1.0 indicated that the extreme sediment concentrations of individual FRs posed ecological risks in most Guiyu reach and downstream areas. Simultaneous exposure to multiple FRs likely increased risks. However, risks

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may be mediated if FRs were associated with strong sorbents, e.g. carbon black from burned debris, hydrophobic polymer fragments, or resided as additives within polymer fragments.

1. Introduction

Polymer-based products are increasingly important in modern society. However, the flammability of many polymers has led to the expanding use of flame retardants (FRs), especially in the growing electronics market (Covaci et al., 2011; de Wit et al., 2010; Eljarrat and Barceló, 2011; Wei et al., 2015; Yu et al., 2016). A number of factors determine what FRs are used; these include: country of origin and applicable regulations, date of manufacture, the specific application, a compatibility with the polymer matrix, and cost. Two widely-used classes are brominated FRs (BFRs) and organophosphate esters (OPEs). FR additives may migrate out during the polymer products' life cycle (Eljarrat and Barceló, 2011). Polymer fragmentation by wear, weathering or destruction (e.g. burning) also facilitates environmental dispersal (Rauert and Harrad, 2015; Rauert et al., 2014). The environmental occurrence, behavior and potential adverse effects on human and wildlife of FRs have attracted increasing concern (Covaci et al., 2006, 2011; de Wit et al., 2010; Eljarrat and Barceló, 2011; Law et al., 2014; Liu et al., 2016; Papachlimitzou et al., 2012; van der Veen and de Boer, 2012; Wei et al., 2015; Yu et al., 2016). Among BFRs, the three commercial polybrominated diphenyl ether (PBDE) mixtures and hexabromocyclododecane (HBCD) have been listed as Annex A (slated for elimination) persistent organic pollutants (POPs) by the Stockholm Convention (www.pops.int). Tetrabromobisphenol A (TBBPA), the BFR used in greatest amounts, is not currently regulated. But the European Union is currently assessing it for inclusion in the RoHS directive. It has seldom been reported in substantial concentrations in water, sediments or biota samples; as it has predominantly been employed as a reactive polymer additive. Restrictions on the use of PBDEs and HBCD have resulted in an increasing reliance on alternative BFRs (alt-BFRs) (Covaci et al., 2011; Papachlimitzou et al., 2012). Some alt-BFRs, e.g. decabromodiphenyl ethane (DBDPE, a substitute for Deca-BDE), 1,2-bis(2,4,6,-tribromophenoxy)ethane (BTBPE, an Octa-BDE replacement), bis(2-ethylhexyl) 3,4,5,6-tetrabromophthalate (TBPH, a substitute for Penta-BDE), have begun to be detected in the environment, including remote sites, indicative of long-range dispersal (Covaci et al., 2011; de Wit et al., 2010; Papachlimitzou et al., 2012; Yu et al., 2016). Similarly, global output of the long-used but inadequately investigated OPEs, another important BFR substitutes, increased from 186,000 tons in 2001 to 620,000 tons in 2013 (van der Veen and de Boer, 2012; Wei et al., 2015).

As technology advances, the volume of electronics deemed obsolete increases. The amount to be discarded worldwide in 2017 was estimated to be 65.4 million tons (Breivik et al., 2014). e-Wastes contain both valuable and hazardous substances, representing both a resource and a growing global problem (Breivik et al., 2014; Sthiannopkao and Wong, 2013). Most developed countries have established comprehensive e-waste management programs (Sthiannopkao and Wong, 2013). However, the expense of proper disposal led to the diversion of large amounts of e-waste to developing countries, e.g. China, India, Pakistan and Nigeria (Sthiannopkao and Wong, 2013). There, the majority of e-waste has been handled with inadequate safety and environmental concerns, with residues carelessly discarded. Such practices release substantial amounts of toxic metals and organic contaminants, including FR additives, halogenated dioxins/furans, and polycyclic aromatic hydrocarbon (PAHs) (Li et al., 2007; Ma et al., 2009; Sthiannopkao and Wong, 2013). These hazardous materials may pose risks to the local environment and residents (Awasthi et al., 2016a; Awasthi et al., 2016b; Heacock et al., 2016; Iqbal et al., 2015; Xu et al., 2015).

Guiyu, China, located adjacent to the Lian River, was among the largest e-waste recycling centers in the world (Sthiannopkao and Wong, 2013). Prior to 1995, it was a poor, rural rice-growing area. The Lian River begins at Baikeng Lake, passes through the Guiyu e-waste recycling zone, and eventually flows into the South China Sea at Haimen Bay (famous for its fishery and aquaculture, Fig. 1). Between 1996 and 2015 numerous workshops appeared in local villages and handled up to 1.6 million tons yr^{-1} of predominantly imported e-waste (Bloomberg, 2015). Upon arrival e-wastes were first dismantled into components, generally in Nanyang. The constituents were then sorted and redistributed to other villages where they were subjected to roasting, burning and acid dissolution to extract valuable elements. The residues were burned or much discarded into the Lian watershed (Fig. 2) (The Greenpeace Campaign Report, 2002). In 2015, the small workshops were closed and a central government-run industrial park with stricter environmental controls was created (Bloomberg, 2015). Substantial burdens of PBDEs in air (Chen et al., 2009; Deng et al., 2007), dust (Labunska et al., 2013; Leung et al., 2011), soil (Gao et al., 2011a; Labunska et al., 2013; Leung et al., 2007), sediment (Labunska et al., 2013; Luo et al., 2007; Wang et al., 2005), fish (Luo et al., 2007) and human tissues (Bi et al., 2007; Wu et al., 2010; Xu et al., 2015) near Guiyu have been documented, but data are lacking regarding pollution by coincident emerging alternative BFRs and OPEs. Considering their substantial use in electronics, we hypothesized that they may pose risks on the same order of magnitude as PBDEs.

Shi et al. (2016) investigated PAHs in fish from Haimen Bay and suggested that PAH pollution from Guiyu transported via the Lian River might pose health risks to the large human population living downstream. Labunska et al. (2013) reported sediment PBDEs within Guiyu town as high as 17,000–280,000 ng g^{-1} dw, with site-specific congener profiles. However, migration of PBDEs, as well as other FRs, downstream of Guiyu remains undocumented. FR market structures in China and western countries differ. As e-wastes handled in Guiyu are predominantly foreign in origin, FR pollution profiles might be useful to track migration from Guiyu. To evaluate these hypotheses, we collected surficial sediment samples along a transect of the Lian River (encompassing both mainstem and associated tributaries of the Guiyu reach, both upriver and downriver) to investigate the profiles, spatial distribution and sources of BFRs and OPEs. The goal was to clarify their potential migration and associated risks. In addition, triclosan (TCS), an antimicrobial common in domestic products, was also determined as a possible indicator of non-industrial wastewater input.

2. Experimental

2.1. Sample collection

The Lian River (23°13′N–23°22′N, 116°9′E–116°37′E), located in South China, experiences a subtropical maritime climate. It is 71 km long, has an overall drainage basin area of 1347 km^2, average annual runoff of 5.87×10^8 m^3, whole slope of 0.89%, and connects with 17 tributaries. Thousands of chemical, metal, plastic, clothing and toy factories are located along the river, and the total industrial return in this area was ~$21 billion in 2014 (Guangdong Statistical Yearbook, 2015).

Surface sediment samples (0–15 cm) were collected from the Lian River between January 25 and 28, 2013 with a pre-cleaned stainless steel grab sampler. Samples collected were transferred to zip lock polyethylene bags and placed on ice until received at the lab, where they were freeze-dried and stored at <-20 °C until analyzed. A total of 14