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Export of toxic chemicals – A review of the case of uncontrolled electronic-waste recycling

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Abstract

This paper reviews the concentrations of persistent organic pollutants such as flame retardants (PBDEs), dioxins/furans (PCDD/Fs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and heavy metals/metalloid concentrations of different environmental media at Guiyu, a traditional rice-growing village located in southeastern Guangdong Province (PR China), which has turned into an intensive electronic-waste (e-waste) recycling site. Incomplete combustion of e-waste in open air and dumping of processed materials are the major sources of various toxic chemicals. By comparing with existing data available in other areas and also guidelines adopted in different countries, it is obvious that the environment is highly contaminated by these toxic chemicals derived from the recycling processes. For example, the monthly concentration of the sum of 22 PBDE congeners contained in PM_{2.5} (16.8 ng m⁻³) of air samples at Guiyu was 100 times higher than published data. In order to safeguard the environment and human health, detailed investigations are urgently needed, especially on tracking the exposure pathways of different toxic chemicals which may affect the workers and local residents especially mothers, infants and children.

Keywords: Electronic waste; Environmental media; Heavy metals; PAHs; PBDEs; PCBs; PCDD/Fs

1. Introduction

1.1. Definition of electronic-waste

Electronic-waste (e-waste) refers to end-of-life electronic products including computers, printers, photocopy machines, television sets, mobile phones, and toys, which are made of sophisticated blends of plastics, metals, among other materials. Due to the demand for newer, more efficient and effective technology, the life span of electronic products is becoming shorter and shorter. As a consequence, older and outdated electronic items are becoming obsolete and are being discarded in significant amounts worldwide. E-waste is growing at about 4% per year, and has become the fastest growing waste stream in the industrialized world (UNEP, 2005). It was estimated that over 315 million computers became obsolete between 1997 and 2004 in the United States alone (National Safety Council, 1999). About 50–80% of the e-waste collected for recycling in industrialized countries end up in recycling centers in China, India, Pakistan, Vietnam and the Philippines (UNEP, 2005), taking advantage of the lower labor costs, and less stringent environmental regulations in these countries. The Chinese Government has tightened up its regulations regarding e-waste, and as a consequence, a substantial number of e-waste has been stored in the New Territories of Hong Kong (HKEPD, 2005). It is expected that most of these waste materials will end up in other countries in the region, repeating the same mistakes, in terms of the adverse impacts on environment and human health.

1.2. Recycling techniques

The techniques used in recycling of e-waste are often primitive, without the appropriate facilities to safeguard environmental and human health. These include (1) stripping of metals in open-pit acid baths to recover gold and other metals, (2) removing electronic components from printed circuit boards by heating over a grill using honeycombed coal blocks (coal mixed with river sediment which is contaminated) as fuel, (3) chipping and melting plastics without proper ventilation, (4) burning cables for recovering metals, and also burning unwanted materials in open air, (5) disposing unsalvageable materials in the fields and riverbanks, (6) toner sweeping, (7) dismantling electronic equipment, and (8) selling computer monitor yokes to copper recovery operations. These contribute to the release of toxic metals (such as lead [Pb]) as well as persistent organic pollutants (POPs, such as dioxins/furans [PCDD/Fs], and flame retardants [PBDEs]) into the environment, which may affect human health either directly or indirectly. For example, the recovery of copper wires through the burning of polyvinyl chloride (PVC) and PBDE protected cables can release toxic chlorinated and brominated dioxins (PCDD/PBDD) and furans (PCDF/PBDF), and the open burning of computer casings and circuit boards stripped of metal parts can produce toxic fumes and ashes containing polycyclic aromatic hydrocarbons (PAHs). Due to its wide historical use as coolants and lubricants in transformers and capacitors, and as hydraulic and heat exchange fluids, polychlorinated biphenyls (PCBs) are also expected to be present in the e-waste stream.

1.3. Guiyu e the e-waste site

Guiyu town is located in Chaoyang District, Shantou City, Guangdong Province, southeast China, with a total area of 52 km² and a population of 150,000. Guiyu soils are ferric acrisols in accordance with the Soil Map of the People's Republic of China (Revised Version, 1990, based on the FAO/ UNESCO Soil Map of the World). The area belongs to a sub-tropical climate, with an annual average temperature of 21.5 °C, relative humidity of 80% and mean annual rainfall of 1721 mm. The prevailing wind is from the northeast except in the summer, which is in the southwesterly direction. In the northern part of Guiyu, there is a reservoir and a large area of hilly woodlands.

The traditionally rice-growing community at Guiyu has turned into an intensive e-waste recycling center since 1995. Over 75% of the 300 individual workshops have been involved in the business of dismantling or processing e-waste with nearly 100,000 migrant laborers (from countryside of poorer provinces north of Guangdong Province) employed in Guiyu, with minimal or no consideration to health and environment protection. There are at least three large scale e-waste open-burning sites distributed in the rice fields and along riversides, which are still in daily operation. These e-waste recycling activities cause severe damage to the environment and to the workers as well. Local residents are constantly exposed to toxic chemicals through inhalation, dermal exposure and oral intake (of contaminated food and drinking water). Once taken into the body, the toxic organic chemicals are stored in fatty tissues, bioaccumulating and biomagnifying through the food chains, and consequently increasing the body burden of these toxic chemicals.

1.4. Objective of this paper

This short review paper is an attempt to review the extent of contamination of these toxic chemicals released into the surrounding environment of a typical e-waste recycling site, namely Guiyu, which have received most of the e-waste entering China.

2. Sampling and chemical analyses

Listed below are brief descriptions of the sampling and chemical analyses. Detailed descriptions (including QA/QC) could be found in our previous published articles (Deng et al., 2006; Leung et al., 2006; Yu et al., 2006).

2.1. Air

Thirty sets of air samples including total suspended particulates (TSP, particles less than 30–60 µm), and particles with aerodynamic diameter smaller than 2.5 µm (PM_{2.5}) were collected at Guiyu from 16 August 2004 to 17 September 2004 at the roof of a 3-story high building near open-burning sites, using two compatible high-volume air samplers (Graseby Anderson, and Tianhong Intelligent Instrument Plant, Wuhan, China) (Deng et al., 2006). The particulate-associated contaminants were isolated from the atmosphere by drawing air through a Whatman quartz fibre filter (both at the flow rate 1–1.2 m³ min⁻¹). The concentrations of 22 PBDE congeners and 17 PCDD/F congeners were determined

according to USEPA Draft Method 1614 and USEPA Method 1613. Sixteen USEPA priority PAHs and heavy metals/metalloid were analyzed using GC-MS and ICP-OES after Soxhlet extraction or acid digestion, respectively, according to USEPA Standard Method 3540C, 3620B, C and 8270C.

2.2. Soil

A total of 49 soil samples (0–10 cm soil layer) were collected from different locations throughout Guiyu area between June and December 2004 (Yu et al., 2006). According to the locations, the samples were divided into four groups: reservoir (RS) area, rice field (RF), areas near an open-burning site (NOBS, within 500 m away from the e-waste open-burning site) and at the open-burning site (OBS). All samples were analyzed for 16 USEPA priority PAHs and 36 PCB congeners using GC-MS after Soxhlet extraction according to USEPA Standard Method 3540C, 3620B, C and 8270C. Heavy metal concentrations of all samples were determined using ICP- OES after acid digestion (nitric and perchloric acids). Ten samples were analyzed by Vista Analytical Laboratory, Inc. (formerly Alta Analytical Laboratory, Inc.) for 43 PBDE congeners (mono- to deca-brominated substitutions) and 17 PCDD/F congeners (2,3,7,8-substituted) and total tetra- through octa-homologue concentrations in compliance with USEPA Method 1614 (draft) and 1613 (Revision B).

2.3. Sediment

Twenty-one sediment samples were collected during 2004–2005 from several diverse land uses, specifically, acid leaching of printed circuit boards site, duck pond and rice fields, in addition to river tributaries and water gullies (shown in Fig. 1) (Leung et al., 2006). Samples taken from a reservoir located in the northern part of Guiyu approximately 6 km from the central e-waste processing area and another reservoir located at Shantou University campus, served as controls. All the samples were collected from each of the sites using a stainless steel shovel at a uniform depth of 0–10 cm. The samples were freeze-dried, sieved (<2 mm) and analyzed for 16 USEPA priority PAHs using GC-MS after Soxhlet extraction in accordance with USEPA Standard Method 3540C, 3620C and 8270C. Heavy metal concentrations were determined using ICP-OES after acid digestion (nitric and perchloric acid). Twenty-three PBDE congeners concentration were determined according to USEPA Draft Method 1614 using a Trace GC/PolarisQ ion trap mass spectrometer (Thermo Quest, Austin, TX, USA).

3. Toxic chemicals in different environmental media

3.1. Air

3.1.1. Air PBDEs

Twenty-two PBDE congeners (BDE-3, 7, 15, 17, 28, 49, 71, 47, 66, 77, 100, 119, 99, 85, 126, 154, 153, 138, 156, 184, 183, and 191) in PM_{2.5} were measured. The results showed that monthly concentration of the sum of these 22 congeners contained in PM_{2.5} was 16.8 ng m⁻³, 73.5–87.3% of which were BDE-47, 66, 100, 99, 154, 153, and 183. It also showed that low bromine PBDEs which are more toxic accounted for 94.6% of PPBDE. All congeners tested in the present study were more than 100 times higher than other published data. The

high concentration in the air was due to e-waste open burning since PBDEs are released when plastics containing brominated flame retardants are heated (e.g., melting of polymers) (de Wit, 2002).

3.1.2. Air PCDD/Fs

Ambient air concentrations of the 17 PCDD/Fs which were sampled simultaneously on 4 September 2004 in Guiyu Guangzhou and Hong Kong were measured. The concentration of PCDD/Fs in Guiyu was 6521 fg m^{-3} , which was 1.5 times that of Guangzhou and 3.1 times greater than that of Hong Kong (Table 1). Compared with standards, 24 h total TEQ PCDD/Fs in Guiyu was 0.65 pg WHO-TEQ , which was above the Japan annual standard ($0.6 \text{ pg WHO-TEQ m}^{-3}$) (Government of Japan, 2003). Concentration of 2,3,7,8-TCDD was up to 54 fg m^{-3} , while the USA (Indiana, Kansas and Washington) annual average standard is 30 fg m^{-3} (ATSDR, 1998).

3.1.3. Air PAHs

The total sum of 16 USEPA priority PAHs associated with TSP and $\text{PM}_{2.5}$ ranged from 40.0 to 347 and 22.7 to 263 ng m^{-3} , respectively. Five-ring and six-ring PAHs accounted for 73% of total PAHs. In Guiyu atmosphere, about 70.6% of the total PAHs were found in $\text{PM}_{2.5}$. This suggested that most of the particle-associated PAHs were found in the fine particulate matters, which can reach the deep and sensitive parts of human lungs (Vardar and Noll, 2003). The average concentration of BaP, which is regarded as an indicator of carcinogenic risk was 2×10^6 times higher than in other Asian cities reported by the World Health Organization (WHO, 2000). This possibly reflects the higher emission of PAHs from e-waste recycling, especially due to open burning of insulative plastic to extract the valuable metal inside.

3.1.4. Air heavy metals/metalloid

The results showed that Cr (1161 ng m^{-3}) and Zn (1038 ng m^{-3}) were the most enriched metals in TSP followed by Cu (483 ng m^{-3}), Pb (444 ng m^{-3}), Mn (60.6 ng m^{-3}), and As (10.2 ng m^{-3}), and the same trend was revealed for $\text{PM}_{2.5}$. All metals and As exhibited a predominant occurrence in the fine particulate fraction (78–108%), except for Mn (44%) and Cu (25%). Concentrations of Cr, Cu and Zn (especially Cr and Zn) in $\text{PM}_{2.5}$ of Guiyu were 4–33 times higher than those in other Asian metropolitan cities, such as Tokyo (Japan), Shanghai (PR China), Ho Chi Minh (Vietnam), Taichung (Taiwan) and Seoul (South Korea) (Table 2). The high concentrations of all Cu and Zn toxic elements were not due to vehicle emissions, but due to emissions from the heating and burning of e-waste (Samara et al., 1994; Cadle et al., 1999).

3.2. Soil

3.2.1. Soil PBDEs

Total PBDE concentrations increased sharply in the order of $\text{RS} < \text{RF} < \text{NOBS} < \text{OBS}$. Total PBDE concentration in OBS was more than 7200 times greater than that at RS. Of the PBDE homologues, deca-BDE (BDE-209) had the highest abundance (63–81%) at all

the sites. This was expected as deca-BDE is the most common PBDE flame retardant in commercial use (Söderström et al., 2004). BDE-209 at the rice field was 79-3973 times greater than the background soil value of southern Sweden (Sellström et al., 2005). The concentrations of the sum of BDE-47, 99, 100, 153 and 154 in NOBS and OBS were much higher than the background soils in both UK and Norway (Hassanin et al., 2004) and the polluted soils caused by sewage sludge application (Sellström et al., 2005). In all sampling sites, the predominant congeners (BDE-209, 207, 183, 99, and 47) were similar, which indicated a similar source such as open burning of e-waste. The highest PBDE level in OBS should be derived from the combusted residue and ash of plastic cables and plastic chips, in which PBDEs are often used as fire retardants.

3.2.2. Soil PCDD/Fs

The total PCDD/F concentrations ranged from 466 to 599,156 pg g⁻¹, in the descending order of: OBS > NOBS > RF > RS. In terms of toxicity equivalency, the order of decreasing toxicity was also the same and ranged from 1.15 to 9265 pg I-TEQ g⁻¹. The total PCDD/F concentration in OBS was the highest when compared with other heavy polluted soils, such as soils near an open-burning industrial waste incinerator in Korea (121,400 pg g⁻¹, Im et al., 2002) and soils near a former copper smelter in Germany (266,700 pg g⁻¹, Hagenmaier et al., 1992). The PCDD/F TEQ concentration at the OBS was also extremely high, which exceeded the remediation value (1000 pg TEQ g⁻¹) adopted in the United States. All sampling sites except RS exceeded the Canadian soil guideline value (4 pg TEQ g⁻¹) of PCDD/Fs for agricultural, residential, commercial and industrial land uses. Therefore, Guiyu soils were severely contaminated by PCDD/Fs, due to the open burning of PVC coated copper cables and plastic wastes in OBS and deposition by atmospheric movement.

3.2.3. Soil PAHs

The concentrations of the sum of 16 PAHs ranged from 44.8 to 3206 µg kg⁻¹, in the descending order of OBS > NOBS > RF > RS. The average concentration of total PAH for 49 samples was 582 µg kg⁻¹, which was the highest when compared with other cities in southeast China, such as Shantou (317 µg kg⁻¹, Hao et al., 2004), Guangzhou (376 µg kg⁻¹, Chen et al., 2005), Hong Kong (55 µg kg⁻¹, Zhang et al., 2006) and Hangzhou (298 µg kg⁻¹, Chen et al., 2004). At OBS, piles of plastic waste were combusted daily and the remaining ash gave rise to the high concentration of PAHs in OBS soil. The surrounding areas of the burning site were also contaminated due to deposition of fly ash and emissions emitted from e-waste open burning. Although far away from the open-burning site, RF soil still contained a high level of PAH (354 µg kg⁻¹), which exceeded the typical concentration (around 200 µg kg⁻¹) of arable topsoil (Berset and Holzer, 1995). The PAH profiles of the four sampling areas were similar and dominated by relatively volatile and most easily degradable LMW PAHs (naphthalene and phenanthrene), which suggested that the loss of PAHs in soil were smaller than deposition from the atmosphere (Wilcke, 2000) due to the continuous emission of PAHs derived from open burning of e-waste.

3.2.4. Soil PCBs

The total concentrations of 36 PCB congeners ranged from $3.34 \mu\text{g kg}^{-1}$ in RS to 458mg kg^{-1} in OBS. The total PCB concentrations in RS and RF were higher than the background value ($0.42 \mu\text{g kg}^{-1}$) found in Huairou of North China (Chu et al., 1999), but comparable to the concentration ($4 \mu\text{g kg}^{-1}$) reported in UK soil (Lead et al., 1997). However, the total concentration in OBS was much higher, and comparable to the concentration of polluted soil caused by the illegal dismantling of PCB-containing equipment in southeast China (Chu et al., 1995). The TEQ concentrations of the sum of 12 dioxin-like PCBs varied widely between 0.00784 (RS) and 314 (OBS) pg WHO-TEQ g^{-1} . Compared to the concentration ($0.32\text{--}28 \text{pg WHO-TEQ g}^{-1}$) of polluted soils along river Elbe in Germany (Stachel et al., 2006), the TEQ concentration in OBS was extremely higher, which may be due to the open burning of plastic waste and PVC materials.

3.2.5. Soil heavy metals

Six heavy metals including Cd, Cr, Cu, Ni, Pb and Zn were measured. The heavy metal concentrations in OBS were extremely high when compared with other sites. At OBS, all heavy metal concentrations, except for Cr, exceeded the action values of the New Dutch List (VROM, 2001). Therefore, the soil at the open-burning site was heavily contaminated by heavy metals, which may be due to the dumping and burning of circuit boards or other metal chips (Table 3).

3.3. Sediment

3.3.1. Sediment PAHs

The highest concentration was found at the acid leaching site and the lowest was found at the Guiyu reservoir. The concentration at the acid leaching site was significantly higher ($p < 0.05$) than sediment collected from the duck pond, river tributary and the reservoirs at Guiyu and Shantou University. The total PAHs at the two reservoirs were the same order of magnitude. The concentrations at the duck pond and the river tributary, and the water gully and run-off gully (the latter two both situated adjacent to a rice field) were comparable and ranged from 143 ± 33.2 to $347 \pm 49.1 \text{ng g}^{-1}$. There were no statistical differences ($p < 0.05$) in total PAH concentrations between these sites. Phenanthrene and fluoranthene were significantly higher ($p < 0.05$) at the acid leaching site, duck pond, and the water gully than the Guiyu reservoir and the Shantou University reservoir. The general trend for decreasing PAH concentration in sediment at Guiyu was as follows: acid leaching > water gully > duck pond > run-off gully > river tributary > reservoir.

In general, the sediments in Guiyu contained lower PAH concentrations than sediments from Meiliang Bay, Taihu Lake, China ($1207\text{--}4754 \text{ng g}^{-1}$, average: 2563) (Qiao et al., 2006), and from the coastal region off Macao, China ($294\text{--}12,741 \text{ng g}^{-1}$) (Mai et al., 2003). However, the average sediment PAH concentration from the acid leaching site was higher than that from the Yalujiang River (290ng g^{-1}) (Wu et al., 2003). These values were within the New Dutch List guidelines and also the maximum possible concentration (MPCs) (Kalf et al., 1997), as the concentrations of the sum of 10 New Dutch List PAHs compounds were approximately 500ng g^{-1} or less. However, the values slightly exceeded the Canadian Council (CCME, 2003) interim sediment quality guidelines for naphthalene, phenanthrene, pyrene and benzo (a)pyrene at the acid leaching site.

3.3.2. Sediment heavy metals

In general, all metal concentrations were highest at the acid leaching site ($p < 0.05$). Some values exceeded the New Dutch List Optimum Value (VROM, 2001), for example, Cd, Ni, Pb and Zn by approximately 5.8, 1.6, 2.5 and 2.5 times, respectively, and Cu exceeded the New Dutch List Action Value by three times. When metals enter a river system, it is generally known that metals have a tendency to bind rather cohesively to sediment particles, however, at this acid leaching site, metals bounded to sediment particles may be remobilized under an acidic environment (i.e., the disposal of acid leaching processing solution along the riverbank or into the river). Moreover, due to the low flow rate of the river, the metals may concentrate in the area.

The concentrations of metals in the sediment of the duck pond were below the New Dutch List Optimum Values except for Cd which was slightly higher. Co, Cr, Ni, Pb, and Zn concentrations in the sediments of the river tributary were similar to that of the duck pond, however, average Cu concentrations were almost twice as high. Metal concentrations of the sediments of the water gully located on the perimeter of the rice field exceeded the New Dutch List Optimum Value for Cd, Cu, Ni and Pb. The sediment of the run-off gully (located at a rice field) which may give an indication of the types of metals present in rice field soil, contained higher amounts of Co than the water gully. The metal concentrations were below China's standard for agricultural soil (SEPA, 1995).

3.3.3. Sediment PBDEs

All together 23 PBDEs (from mono- to hepta-BDEs and deca-BDE) were found in the sediment samples. In general, the total PBDE concentrations in sediments ranged from 4 to $407 \mu\text{g kg}^{-1}$ dw ($123.6 \pm 125.2 \mu\text{g kg}^{-1}$) which were much higher than those reported in the Pearl River Delta ($0.15\text{e} 13.03 \mu\text{g kg}^{-1}$ (Zheng et al., 2004)). The figures were also higher than some polluted sites reported in other countries, for example, Japan (at highest concentration $70 \mu\text{g kg}^{-1}$) (Darnerud et al., 2001), Belgium (up to $200 \mu\text{g kg}^{-1}$, but most samples were below $20 \mu\text{g kg}^{-1}$) (de Wit, 2002), and Portugal ($21 \mu\text{g kg}^{-1}$ was observed in sediments collected close to urban and industrial areas, but lowest concentration $0.5 \mu\text{g kg}^{-1}$ was reported in coastal sediments) (Lacorte et al., 2003). In addition, two particular sites with a large amount of burnt residues resulted in extremely high concentrations of total PBDEs (excluding BDE-209) with 7261 (Sed-3), and $6075 \mu\text{g kg}^{-1}$ (Sed-4), which were almost 30 times higher than a sewage sludge sample from Bjergmarken, the sewage treatment plant in Roskilde, Denmark (Christensen et al., 2003). Fig. 2 shows percentage contributions of the predominant PBDE congeners of different sediments. In general, low brominated PBDEs (BDE-47 and 28) and BDE-209 were abundant in the sediment samples. BDE-99, 100, 153, 154, and 183 were dominant congeners commonly reported in sediments (Covaci et al., 2002; Sawal et al., 2004). The diverse and complex PBDE congener distribution patterns in sediments from Guiyu indicate the contaminated sources being diffuse and largely influenced by e-waste recycling materials, for example, the sites which received a large amount of burnt residues (Sed-3 and -4) contained distinctive congener patterns (Table 4).

4. Emission source identification via profile comparison of PAHs

POPs derived from different sources usually have distinct compositions. Among them, the characteristic profile of PAHs has been commonly used as a preferable fingerprint to identify the emission source than using other pollutants (Khalili et al., 1995).

In general, very similar profiles in the soil samples were found among the four sampling areas, dominated by relatively volatile representatives, such as Nap and Phe (Fig. 3). In addition, Fla, Chr, Pyr and BbkF were the most abundant compounds and the sum of these in RS, RF, NOBS and OBS accounted for 14, 48, 30 and 25% of the total concentrations, respectively. The highly significant correlations ($p < 0.01$) among individual PAHs, LMW, HMW and total PAHs confirmed that the profile was fairly constant at different sampling sites and PAHs must have come from similar sources (Amagai et al., 1999; Wilcke et al., 1997; Ma et al., 2005) – in the present study: the OBS. The relatively high abundance of volatile and most easily degradable LMW PAHs (Nap and Phe) in Guiyu soils suggested that the loss of PAH in soils was smaller than that from atmospheric deposition (Wilcke, 2000), due to the continuous emission of PAHs from open burning of e-waste (Wilcke et al., 1999). Fla, Chr, Pyr and BbkF (HMW PAHs) are typical pyrogenic products derived from high temperature condensation of LMW aromatic compounds (Khalili et al., 1995; Soclo et al., 2000). Their large contributions (14–48%) to the total PAHs in Guiyu soils suggested a pyrogenic source (from combustion of fossil fuels). Therefore, the PAH profile in Guiyu soils reflected both petrogenic and pyrogenic sources of soil PAHs. Nap was not found to be correlated with HMW PAHs. Near RS, the percentage of Nap in soil of RS was abnormally high (approximately 70%) due to the possible input of additional biological source from woody plants nearby while the low percentage in RF soil might be attributed to the loss by agricultural practice such as plowing, leading to evaporation of PAHs. However, results of the principal component analyses (PCA) and profile comparisons of the studied POPs among different media (air, soil and sediment) did not match well (data not shown). It is not surprising that even if open burning is the major point source of POPs, the components of the POPs may have altered during deposition to soil and water bodies, or subsequent run-off from soil to water bodies.

In general, the incomplete combustion of plastic wastes (petroleum product) in the OBS seemed to be the main source of PAHs and other POPs detected in Guiyu area. The decrease in concentrations of POPs in soils with increasing distance from the OBS also testifies that the open burning of e-waste was the point source of these pollutants in the area. Besides this, coal combustion and automobile exhausts may be potential sources of POPs (Tang et al., 2005). In e-waste recycling workshops, coal is used to heat circuit boards for releasing valuable chips, while mopeds are the major means of transportation in the area.

5. Conclusion

The present study demonstrated the export of toxic chemicals from developed to developing countries, through uncontrolled recycling of e-waste in the receiving countries. Concentrations of POPs and heavy metals/metalloid detected in the Guiyu air were high

when compared with those from other cities, which were primarily due to incomplete combustion of e-wastes (e.g., plastic chips, wire insulations, PVC materials and metal scraps). This led to the severe pollution of soils by POPs (PCDD/Fs, PBDEs, PAHs, and PCBs) and heavy metals, which may also affect the surrounding environment such as rice fields and rivers by atmospheric movement and deposition. Dumping of waste materials at riverbanks further led to the rather high concentrations of all these toxic chemicals in river sediments which received the dumped materials. The concentrations of some of the POPs and heavy metals in different environmental media are alarming, when compared with data available in other regions/countries. It is envisaged that under such high concentrations of toxic chemicals, the workers and local residents will be adversely affected through inhalation, dermal exposure and oral ingestion of contaminated drinking water and food. As the Chinese Government has tightened up the import regulations, it is expected that a substantial quantity of e-waste will find their way to other countries in the region, and we have to ensure that the same mistakes should not be made in these countries.

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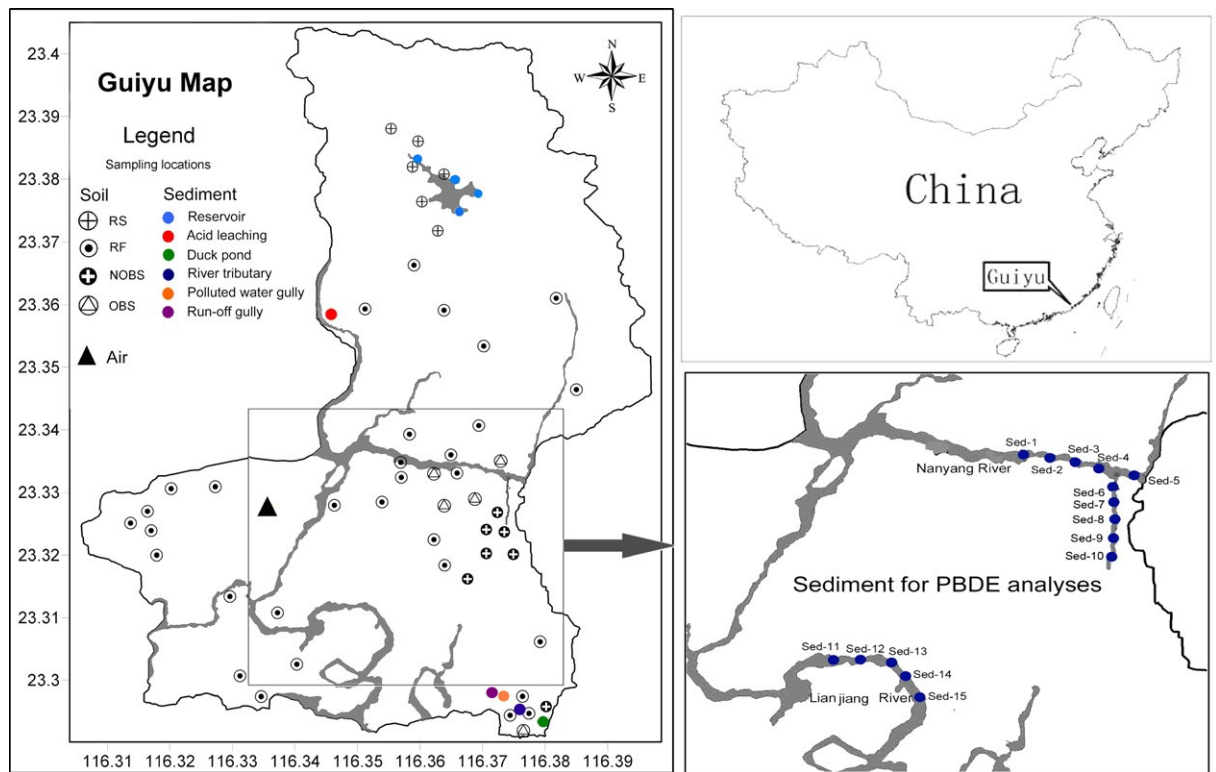


Fig. 1. Maps of sampling locations (air, soil and sediment - left; and sediment for PBDE - right). RS, reservoir area; RF, rice field; NOBS, area near the open-burning site; OBS, at the open-burning site.

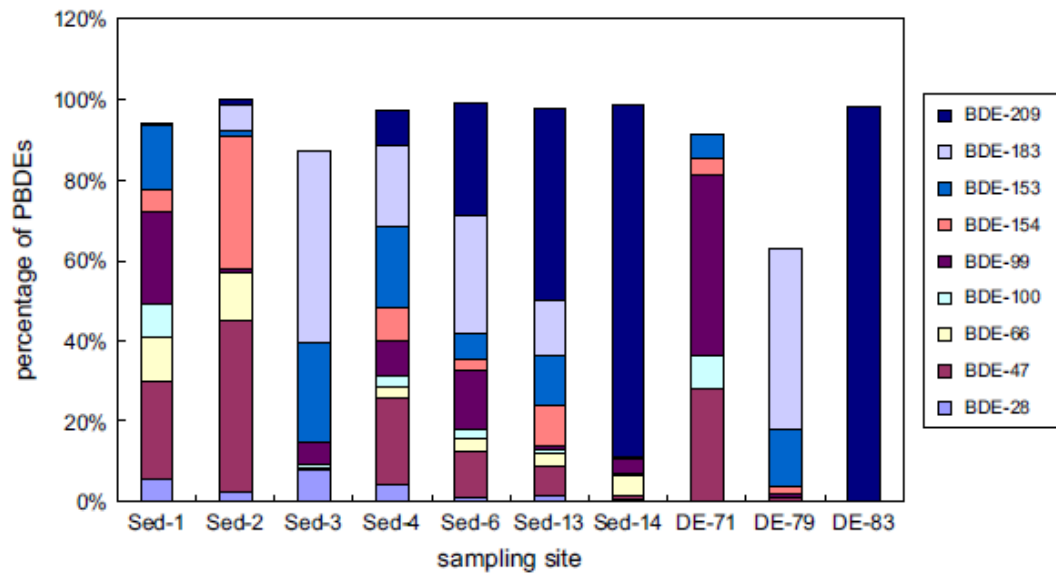


Fig. 2. Percentage contributions of the predominant PBDE congeners were detected in representative sediments from Guiyu, comparing with commercial products (DE-71: penta-BDEs; DE-79: hepta-BDEs; DE-83: deca-BDEs). Both Sed-3, and -4 contained a large amount of burnt residue, but they contained different congener patterns (source: Luo et al., 2005).

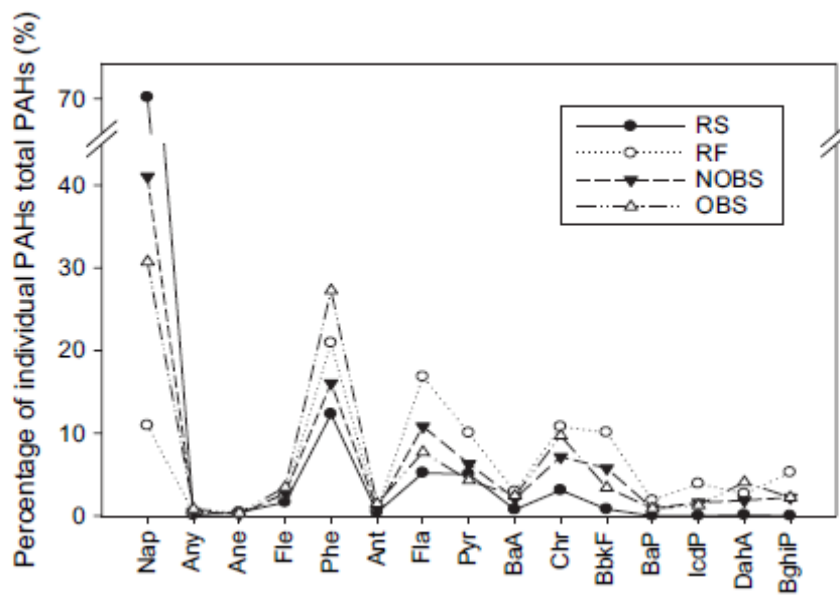


Fig. 3. Profiles of PAHs of the four sampling areas in Guiyu soil. RS, reservoir area; RF, rice field; NOBS, area near the open-burning site; OBS, at the openburning site (source: Yu et al., 2006).

Table 1

An overview of the concentrations of POPs in air samples at Guiyu (source: Deng et al., 2006)

Compounds	Concentration (our study)	Other studies	Guidelines
PBDE (in PM _{2.5}) (pg m ⁻³)			
∑PBDE ^a	16,822 (5397–47,187)	77 in urban US (de Wit, 2002)	—
BDE-47	5226 (1517–16,442)	48 in urban US (de Wit, 2002)	—
BDE-99	5889 (1957–14,859)	25 in urban US (de Wit, 2002)	—
BDE-100	4111 (1480–9245)	3.0 in urban US (de Wit, 2002)	—
Dioxins (particulate and gas phase) (fg m ⁻³)			
PCDD/Fs	6523	500–4000 in rural area (Lohmann and Jones, 1998)	—
pg WHO-TEQ of PCDD/Fs	6500	20–50 rural (Lohmann and Jones, 1998)	6000 (Japan)
2,3,7,8-TCDD	54	14.4 in Taiwan (Chen et al., 2004)	30 (US)
PAHs (particulate phase) (ng m ⁻³)			
∑PAHs	148 (40.0–347)	12.2 in Hong Kong (Sin et al., 2003)	—
BaP	15.4 (2.3–29.9)	0.21 in LA US (Panther et al., 1999)	1.0 (WHO-AQG)

^a Sum of 22 PBDE congeners.

Table 2
Comparison of atmospheric concentrations of heavy metals (ng m^{-3}) between Guiyu and other sites in Asia (source: Deng et al., 2006)

Location	City	Character	Size	Mass ($\mu\text{g m}^{-3}$)	Cd (ng m^{-3})	Cr (ng m^{-3})	Cu (ng m^{-3})	Ni (ng m^{-3})	Pb (ng m^{-3})	Zn (ng m^{-3})	Mn (ng m^{-3})	As (ng m^{-3})
Japan	Sapporo ^a	Urban city	TSP	—	—	2.61	20.9	3.81	43.9	149	16.8	—
	Tokyo ^a		TSP	—	—	6.09	30.2	5.63	125	299	40.1	—
China	Hong Kong ^a	Airbone	TSP	79	—	—	79	—	1421	88	140	—
	Shanghai ^b	University	PM _{2.5}	62.4	—	—	—	—	270	—	—	—
		Urban	PM _{2.5}	67.6	—	—	—	—	280	—	—	—
Vietnam	Ho Chi Minh	Urban	TSP	73.6	—	—	—	—	146	203	—	—
Indonesia	Bukit Tinggi	Rural	PM _{2.5}	9.4	—	—	0.22	—	8.7	22	0.34	—
			PM _{2.5}	23.6	—	—	—	11	26	61	—	—
Taiwan	Pontianak ^a	Rural	TSP	84.1	—	—	—	18	39	105	—	—
	Taichung ^c	Urban	TSP	114	8.5	29.3	199	15.8	574	395	83.7	—
Korea	Taejon ^a	Industrial	PM _{2.5}	42.8	4.3	33.5	11.5	11.8	37.9	283	19.1	—
			TSP	115	—	31.8	54.9	33.6	260	220	66.1	—
	Seoul ^a	Urban	PM _{2.5}	—	—	13.7	27.8	19.6	96.4	163	39	—
(The present study)	Guiyu	E-waste	TSP	124	7.3	1161	483	10.0	444	1038	60.6	10.2
				(33.8–201)	(2.1–21.1)	(181–2155)	(292–1064)	(5.1–17.3)	(106–1063)	(163–1881)	(15.4–109)	(3.6–22.7)
			PM _{2.5}	62.1	7.3	1152	126	7.2	392	924	25.4	6.0
			(28.1–107)	(2.5–15.7)	(155–1968)	(30.3–369)	(2.79–15.6)	(87.2–1208)	(130–1629)	(11.6–46.9)	(1.1–15.0)	

Note: —, not available.

^a Fang et al. (2005).

^b Ye et al. (2003).

^c Fang et al. (2003).

Table 3
Concentrations of toxic chemicals in Guiyu soil samples (dry weight basis) (source: Yu et al., 2006)

Chemicals	RS	RF	NOBS	OBS
PBDEs (ng g ⁻¹)	2.00–6.22	45.1–102	85.0–201	2906–44,473
PCDD/Fs				
Total PCDD/Fs (pg g ⁻¹)	228–834	2748–3103	13317–37418	30,948–967,500
I-TEQ (pg TEQ g ⁻¹)	0.565–1.69	13.2–28.4	129–213	627–13,900
PCBs				
Total 36 PCBs (ng g ⁻¹)	ND–7.84	0.65–19.5	2.51–60.7	73.8–1443
Dioxin-like PCBs (ng g ⁻¹)	ND–0.47	ND–4.79	ND–7.66	22.3–450
WHO-TEQ (pg TEQ g ⁻¹)	ND–0.047	ND–9.21	ND–64.4	6.99–878
PAHs (μg kg ⁻¹)	44.8–233	120–818	480–1899	820–3206
Heavy metals (mg kg ⁻¹)				
Cd	ND	ND	ND	5.51–42.9
Cr	84.1–150	81.9–509	70.2–155	137–477
Cu	29.5–42.7	29.9–240	59.4–114	1374–14,253
Ni	5.47–20.3	3.37–434	4.04–68.7	85.2–722
Pb	79.4–93.1	56.9–155	97.8–123	856–7038
Zn	44.2–106	7.9–114	6.01–42.4	546–5298
Sample no. for PCBs, PAHs and heavy metals analyses	6	30	8	5
Sample no. for PBDE and PCDD/F analyses	3	2	2	3

RS, reservoir area; RF, rice field; NOBS, area near the open-burning site; OBS, at the open-burning site.

Table 4
Concentrations of toxic chemicals in Guiyu sediment samples (dry wt basis) (source: Leung et al., 2006)

Chemical	Acid leaching	Duck pond	River tributary	Water gully	Run-off gully	Reservoir (Guiyu)	Reservoir (Shantou U)
PAHs ($\mu\text{g kg}^{-1}$)	534 (174–831)	307 (214–334)	143 (106–170)	347 (313–382)	296 (237–355)	37.2 (33.2–46.1)	52.1 (37.4–74.5)
Heavy metals (mg kg^{-1})							
Cd	4.67 (1.38–8.66)	1.33 (ND–2.96)	0.18 (ND–0.525)	1.03 (0.98–1.07)	2.59 (1.75–3.43)	0.79 (ND–3.27)	0.7 (0.57–0.83)
Co	14.8 (13.3–16.3)	7.86 (7.03–8.69)	7.1 (5.54–8.71)	7.9 (6.83–8.97)	13.8 (11.8–15.7)	8.05 (1.71–13.7)	6.48 (5.0–7.97)
Cr	22.1 (11.9–38.8)	21.7 (15.5–51.1)	24.4 (15.5–39.6)	23.0 (18.3–27.7)	26.8 (16.0–37.7)	8.67 (0.745–28.2)	5.84 (3.34–8.34)
Cu	601 (186–1745)	22.3 (21.9–46.5)	54.4 (34.3–94.5)	50.3 (48.7–51.9)	38.7 (32.0–45.2)	6.57 (3.2–10.3)	6.35 (6.15–6.55)
Ni	54.5 (45–70)	35.5 (34.7–42.1)	23.0 (13.0–32.4)	44.5 (44.4–44.5)	39.3 (29.0–49.5)	17.1 (7.2–30.1)	19.1 (17.1–21.1)
Pb	217 (67.4–655)	44.5 (34.5–54.5)	53.9 (40.8–65.3)	106 (67.4–145)	73.2 (69.0–77.4)	25.0 (6.1–50.5)	31.4 (29.1–33.8)
Zn	356 (232–671)	96.0 (92.5–116)	91.0 (75.0–109)	103 (98.6–108)	115 (108–121)	52.8 (15.2–82.3)	47.2 (42.4–52.0)