



Polycyclic aromatic hydrocarbons (PAHs) in soils and vegetation near an e-waste recycling site in South China: Concentration, distribution, source, and risk assessment[☆]

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HIGHLIGHTS

- ▶ PAH levels of vegetables from e-waste recycling site were quantified.
- ▶ High molecular weight PAHs were enriched in plants relative to soils.
- ▶ Soil and plant profiles indicated that uptake of PAHs by plants were selectable.
- ▶ High level of PAHs in vegetable may pose a potential risk to the consumers.

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ABSTRACT

This study determined the concentrations of PAHs generated from e-waste recycling activities and their potential impacts on soil, vegetation, and human health. The total PAH concentrations in soils and plants ranged from 127 to 10,600 and 199 to 2420 ng/g, respectively. Samples from an e-waste burning site had higher PAH concentrations than samples from adjacent locations. The PAHs in plants varied with plant species and tissue, and *Lactuca sativa* L. contained the highest PAHs of all the vegetable species. Various land use types showed different PAH concentrations in soils, with vegetable fields showing higher concentrations than paddy fields. Low molecular weight PAHs, such as phenanthrene, were the predominant congeners in soils, whereas high molecular weight PAHs, such as fluoranthene, pyrene, and benzo[a]anthracene, were enriched in plants relative to soils. Dissimilar PAH profiles in soil and the corresponding vegetation indicated that the uptake of PAHs by plants was selective. A source analysis showed that the contamination by PAHs originated primarily from the open burning of e-waste. The total daily intakes of PAHs and carcinogenic PAHs through vegetables at the e-waste dismantling site were estimated to be 279 and 108 ng/kg/d, respectively, indicating that the consumption of vegetables grown near e-waste recycling sites is risky and should be completely avoided.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), a class of ubiquitous organic contaminants composed of two or more fused aromatic rings of carbon and hydrogen atoms, derive mainly from the incomplete combustion or pyrolysis of organic material. Great environmental concerns have been focused on PAHs due to their genotoxic and carcinogenic potential and ubiquitous presence in the environment (Tang et al., 2005;

Tao et al., 2006; Zohair et al., 2006; Peng et al., 2011). Sixteen PAHs have been identified as priority pollutants by both China and the United States Environmental Protection Agency (US EPA), and seven of them are considered probable carcinogens (Cai et al., 2007).

As the most rapidly growing waste problem in the world, electronic-waste (e-waste) has drawn substantial attention from scientists as a new source of environmental contamination (Halluite et al., 2005; Wong et al., 2007; Ma et al., 2009a, 2009b; Zhao et al., 2009; Luo et al., 2011). Not only harmful materials contained and released by the e-waste itself, such as polychlorinated biphenyls (PCBs), brominated flame retardants (BFRs), and heavy metals (HMs), but also the toxic chemicals created during the recycling and disposal processes, such as PAHs and dioxins (PCDDs/PCDFs), can pose risks to the surrounding environment and human beings. China is one of the largest dumping sites

[☆] Capsule: PAHs created during e-waste recycling activities may pose a potential health risk to the local ecosystem and inhabitants through the food chain.

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of e-waste in the world due to lower labor costs and less stringent environmental regulations. Driven by the profits potentially available from e-waste dumping, the techniques used in the recycling of e-waste are very primitive (e.g. open heating and burning), with no appropriate facilities to safeguard the environment. In the process of burning polyvinyl chloride (PVC), PBDE protected cables, computer casings, and circuit boards to recover metals, toxic fumes and ash containing PAHs and other toxicants (e.g., PCDDs/PCDFs) can be produced and released. Those toxic chemicals can accumulate in soils and organisms and can cause serious environmental and health problems, either directly or indirectly.

Numerous studies have demonstrated that vegetables can take up and accumulate PAHs from the contaminated environment (Wennrich et al., 2002; Zohair et al., 2006; Khan and Cao, 2012). The mechanisms responsible for the PAH transfer to plant tissues primarily include sorption from soil particles, uptake by the roots through transpiration, and absorption through the waxy leaf cuticle or through stomata (Wild et al., 2004; Meudec et al., 2006). Thus, heavy pollution at an e-waste recycling area may result in an elevated uptake of PAHs into vegetables. Because diet is considered the major source of human exposure to PAHs (Phillips, 1999) and vegetables are the basic food in the Chinese diet, potential health risks might be involved in consuming these contaminated vegetables (Tao et al., 2004; Zhao et al., 2009; Khan and Cao, 2012). However, most previous studies have focused on contamination by PCBs and BFRs (Ma et al., 2009a; Zhao et al., 2009; Wang et al., 2011a), and few studies were performed on the accumulation, distribution, and potential health risk of PAHs, especially in vegetables grown near e-waste recycling areas.

The area selected for this study is located in Longtang Town, Guangdong Province, South China. This area contains one of the China's largest e-waste recycling places with millions of tons of e-waste processed annually for decades. Uncontrolled e-waste processing sites were located primarily on or near fields where vegetables and rice

consumed by the local residents were planted. The purpose of this research was to assess the effect of uncontrolled e-waste recycling activities on the PAH contamination of soils and vegetation. This assessment was particularly important in the case of the vegetables that played an important role in the daily dietary exposure of the local people to PAHs. The results of the study may be very helpful in protecting the residents from the potential health hazards caused by e-waste recycling activities.

2. Materials and methods

2.1. Sampling area

As shown in Fig. 1, the sampling area is located in northern Guangdong Province [23° 34' N, 113° 0' E], South China. Intensive uncontrolled e-waste processing operations left many e-waste open burning sites on or close to (< 500 m) agricultural fields, where rice and vegetable cultivation still occurs. The sampling sites can be classified into five different groups according to their land use types: e-waste open burning site (BS), vegetable field (VF), paddy field (PF), deserted soil (DS), and pond sediment (SD).

2.2. Soil and vegetation sampling

All samples were collected in September 2007. The surface layers of the soil (0–15 cm) from the e-waste burning site and the surrounding vegetable fields, paddy fields, and deserted places and the top sediments (0–5 cm) from pond areas were collected. Wild plants, vegetables, rice stalks, and the soils where they were grown were also sampled. Each sample was composed of 5 subsamples. All the samples were wrapped with aluminum foil, put in polythene zip-bags, and transported to the laboratory. Each individual plant sample was separated into shoot and root subsamples. The fresh plant samples were first washed with tap water, and then rinsed 3 times with deionized

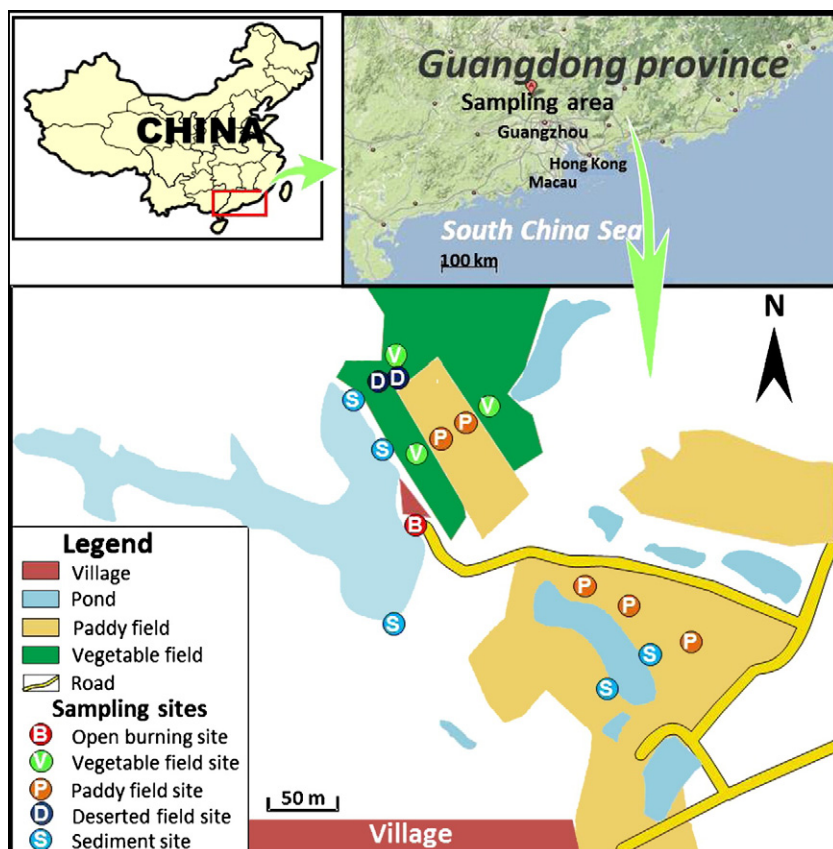


Fig. 1. Map of the sampling locations. (BS, burning site; PF, paddy field; VF, vegetable field; DS, deserted soil; SD, pond sediment).

water. The soil and plant samples were freeze-dried, ground in an agate mortar, and stored at -20°C until further chemical analysis.

2.3. Sample extraction and analysis

Briefly, soil samples weighing approximately 20 g and spiked with deuterium-labeled surrogate standards (naphthalene- D_8 , acenaphthene- D_{10} , phenanthrene- D_{10} , chrysene- D_{12} , and perylene- D_{12}) were Soxhlet extracted with dichloromethane (DCM) for 48 h, with activated copper added to remove the sulfur. Plant samples weighing approximately 5 g and homogenized with 5 g anhydrous sodium sulfate (baked at 450°C for 4 h) were spiked with surrogate standards, and extracted with DCM/acetone (3:1, v/v) and activated copper for 72 h. The extracts of soil or plant were concentrated to approximately 0.5 mL after solvent exchange with hexane (Wang et al., 2011b). The extracts were cleaned by passing through a multi-layer silica gel/alumina column containing anhydrous Na_2SO_4 , neutral silica gel (3% deactivated), and neutral alumina (3% deactivated) from the top to the bottom with an eluent of 20 mL hexane/DCM (1:1, v/v). The plant extracts were purified again on a gel permeation chromatography column (GPC, 2.0 cm i.d., packed with 12 g of S-X3 Biobeads, Accustandard Co., USA) to eliminate lipids. After extract loading, the GPC column was eluted with 80 mL hexane/DCM (1:1, v/v). The first 35 mL of eluent was discarded, and the following 45 mL was collected. After being concentrated to approximately 0.2 mL under a gentle stream of nitrogen, 1000 ng of hexamethyl benzene was added as an internal standard prior to analysis.

GC-EI-MS (Agilent 7890GC coupled with 5975MSD) applied with a DB5-MS capillary column (30 m \times 0.25 mm i.d. \times 0.25 μm) was used for the determination of 16 PAH congeners characterized by the US EPA as priority pollutants, including naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenz[a,h]anthracene (DahA), benzo[g,h,i]perylene (BghiP), and indeno[1,2,3-cd]pyrene (IcdP). Each extract (1 μL) was injected in splitless mode. High-purity helium was used as the carrier gas, with a flow rate of 1.83 mL/min. The temperatures of the injector and transfer lines were 290°C and 300°C , respectively. The initial oven temperature was set at 60°C for 1 min, increased to 290°C at a rate of $4^{\circ}\text{C}/\text{min}$ and then maintained for 20 min.

2.4. QA/QC

A procedural blank, a spiked blank, and a duplicate sample were run with each batch of 10 samples to assess potential sample contamination and the repeatability of the analysis. The results showed that no target compounds except NAP were detected in the laboratory blanks. The average surrogate recoveries for naphthalene- D_8 , acenaphthene- D_{10} , phenanthrene- D_{10} , chrysene- D_{12} , and perylene- D_{12} in all samples were $69 \pm 16\%$, $74 \pm 14\%$, $81 \pm 15\%$, $89 \pm 14\%$, and $95 \pm 11\%$, respectively. All the results reported in the study were corrected for the blanks but not corrected for the surrogate recoveries. All data were expressed on a dry-weight basis (ng/g dry wt.).

2.5. Statistical analysis

Principal component analysis (PCA) has been widely applied to discriminate the different origins of environmental pollutants. The 16 PAH congeners were treated as variables, and all the samples were treated as cases. Individual PAH congeners that were below the estimated analytical detection limit were set at one-half of the detection limit. The eigenvectors were normal-varimax rotated to facilitate the interpretation of the results. Statistical analysis was performed with SPSS 13.0 for Windows.

3. Results and discussion

3.1. Concentration and distribution of PAHs in soil and plant samples

The PAH concentrations found in the soils are listed in Table 1. The total concentrations of the 16 PAHs (ΣPAHs) ranged from 127 (deserted site) to 10,600 ng/g (burning site) with an average of 1230 ng/g. The total concentrations of the 7 carcinogenic PAHs ($\Sigma\text{PAHs}_{\text{carc}}$: BaA, CHR, BbF, BkF, BaP, IcdP, and DahA) in soils were in the range of 30.4–1800 ng/g. In general, PAHs in soils showed a general decreasing trend of $\text{BS} > \text{VF} > \text{SD} > \text{PF} > \text{DS}$ (Table 1). The highest concentration in the soil of burning site was more than 1 order of magnitude higher than those in the soils from the other sites. The PAH levels in the soils varied widely with different land use types, even for those soils at the same distance from the e-waste recycling site. The PAHs in the vegetable soils were approximately 3 times higher than those in the paddy soils, as deep plowing in the paddy field may enhance the loss of low molecular weight PAHs, dilute the PAH concentrations in the top soil, and cause them to transfer to the subsoil (Bierl et al., 1984; Wang et al., 2011a). The deserted field without any vegetation coverage had the lowest PAH concentrations. Because the total organic carbon (TOC) values in the soil samples were comparable (BS (0.68–0.91%), VF (1.43–1.78%), PF (1.38–1.60%), DS (0.83–1.14%)), the TOC-normalized concentrations showed the same decreasing trend. The soil levels of PAHs also showed a decreasing trend with the distance from the e-waste recycling site, suggesting that the surrounding areas were contaminated due to the deposition of fly ash and emissions from the principal point source – e-waste open burning.

The ΣPAHs in the vegetation samples were 199–2420 ng/g, with an average of 665 ng/g, whereas the $\Sigma\text{PAHs}_{\text{carc}}$ was in the range of 35.5–1090 ng/g (Table 2). As expected, high concentrations were found in wild plants from the open burning site, followed by vegetables and paddy stalks. For vegetables, only the edible parts were included in this study. The ΣPAHs in all of the vegetables ranged widely from 199 to 957 ng/g, whereas the $\Sigma\text{PAHs}_{\text{carc}}$ ranged from 35.5 to 448 ng/g (Table 3). The highest PAH level was found in the shoots of *Lactuca sativa* L var. *longifolia* Lam., and the lowest level was found in the tubers of *Colocasia esculenta* L. Difference among species and tissues can also influence the uptake of PAHs and produce variation in PAH levels (Tao et al., 2004; Zohair et al., 2006). Table 3 also shows that the PAH concentrations in leafy vegetables were much higher than those in root vegetables (including tubers). Gaseous deposition has been reported as the principal pathway for the accumulation of PAHs in vegetables (Kipopoulou et al., 1999). In certain cases, uptake by roots from the soil may also be a possible pathway by which PAHs can enter plants (Wild et al., 1992; Tao et al., 2004). Therefore, the edible part of the leafy vegetables can accumulate more PAHs than the root vegetables.

The PAH concentrations in the soils from the study area were comparable with those from other e-waste recycling sites, such as Guiyu (44.8–3206 ng/g, Yu et al., 2006; 93.7–593 ng/g, Leung et al., 2006) in Guangdong Province and Taizhou (262.6–3420.2 ng/g, Tang et al., 2010) in Zhejiang Province, but much higher than those in soils from other cities in South China, such as Guangzhou (376 ng/g, Chen et al., 2005), Hong Kong (550 ng/g, Zhang et al., 2006), and Shenzhen (546 ng/g, Cao et al., 2010). According to the criteria established by Maliszewska-Kordybach (1996), most of the soils near the e-waste recycling site in the studied area were contaminated by PAHs. The PAH concentrations in vegetables in the present study were also higher than those in vegetables cultivated in industrialized regions in Greece (Voutsas and Samara, 1998), Brazil (Camargo and Toledo, 2003), and northern China (Tao et al., 2004).

3.2. Congener profile of PAHs in soil and plant samples

As shown in Table 1, the PAH congener profiles in the soils from the five sampling sites were quite similar. The compositions found for the

Table 1
Concentrations of PAHs in soil samples. (BS, burning site; PF, paddy field; VF, vegetable field; DS, deserted soil; SD, pond sediment).

Congener (ng/g)	BS (n = 5 ^d)		VF (n = 10)		PF (n = 14)		DS (n = 4)		SD (n = 6)	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
NAP	875	432–1440	72.1	30.1–163	40.9	25.1–69.1	35.5	23.2–45.9	95.8	23.4–283
ACY	36.2	24.1–44.2	12.7	9.2–19.4	7.7	3.7–15.8	3.9	3.3–4.7	6.6	4.2–11.0
ACE	42.6	13.6–84.7	8.8	6.1–13.1	4.9	n.d.–6.7	3.2	2.7–4.2	8.0	4.3–15.9
FLU	242	33.8–654	17.4	12.8–25.1	15.3	7.5–23.7	7.1	5.8–8.2	26.4	8.9–64.9
PHE	1210	174–3370	48.7	35.4–67.8	42.7	31.6–78.6	18.8	16.9–22.0	88.5	25.0–256
ANT	148	20.0–391	14.3	7.2–23.3	5.8	3.8–8.2	3.7	3.2–4.8	15.5	4.7–39.3
FLA	582	94.6–1910	80.0	33.5–154	39.7	26.2–61.8	10.2	9.2–11.3	73.5	11.9–203
PYR	537	80.5–1650	65.3	19.6–127	23.6	8.5–36.5	10.3	8.7–13.6	70.5	8.5–212
BaA ^a	257	49.3–492	44.8	2.9–96.5	9.9	5.0–14.5	7.2	5.7–10.0	42.6	4.9–130
CHR ^a	274	50.1–578	49.1	10.5–98.4	19.7	10.5–30.5	13.0	12.0–15.2	61.5	7.1–189
BbF ^a	289	78.3–419	92.9	11.7–183	23.6	10.7–30.9	12.3	10.4–15.8	62.3	7.3–182
BkF ^a	60.5	14.2–95.2	29.7	3.3–61.8	7.6	3.5–10.5	6.3	4.9–8.9	21.0	4.3–55.7
BaP ^a	119	33.0–190	53.0	2.0–109	9.2	4.7–11.8	6.6	5.2–9.1	34.7	4.8–102
IcdP ^a	99.8	30.3–179	61.5	n.d. ^e –121	10.6	n.d.–16.6	8.4	6.1–12.1	31.3	5.9–88.1
DahA ^a	59.8	8.7–119	9.7	n.d.–29.1	1.3	n.d.–7.2	n.d.	n.d.	14.1	n.d.–36.2
BghiP	108	29.2–211	44.8	n.d.–94.2	8.3	1.4–14.9	5.7	3.9–8.8	33.3	3.2–98.8
ΣPAHs ^b	4940	1170–10,600	705	237–1280	271	189–412	152	127–177	686	129–1970
ΣPAHs _{carc} ^c	1160	264–1800	341	30.4–699	81.9	42.2–111	53.8	44.6–68.2	268	34.4–783

^a Carcinogenic PAH compounds.

^b Sum concentration of 16 PAH compounds.

^c Sum concentration of 7 carcinogenic PAH compounds.

^d Number of samples.

^e Not detectable.

first 4 dominant PAH congeners (PHE, NAP, FLA, and PYR) according to the average concentrations of all soil samples were 20%, 16%, 12%, and 10%, respectively. Most of the PAH contamination in the soils was due to atmospheric transport from point sources of pollution (Aamot et al., 1996). The various PAH compositions may be attributed to difference in transfer ability, which decreases with increases in molecular weight (Meharg et al., 1998). Thus, low molecular weight (LMW) PAHs that usually remain in the gaseous phase, such as NAP and PHE, can be distributed over longer distance than high molecular weight (HMW) PAHs (Yu et al., 2006).

The PAH profiles in the vegetation from different sites also resembled each other (Tables 2 and 3) but differed from those in the soils,

even the soil from which the vegetation was sampled. The most strongly predominant PAH congeners in the plant samples were NAP (13%), FLA (11%), BaA (10%), PYR (10%), CHR (9%), and PHE (7%). Because emissions from e-waste burning activity may be the principal source of PAHs for soils and plants, the differences between the profiles in vegetation and those in the corresponding soils may be due to the different bioavailability (Wild and Jones, 1994) and absorption pathways for individual PAH congeners. The dissimilar profiles in soil and the corresponding vegetation also suggested that the uptake of PAHs by plants was selective. This suggestion was consistent with the dissimilar congener profiles in different plant and vegetable species (Tables 2 and 3). The PAHs in the vegetables may result from absorption by leaves from the atmosphere due to the deposition of fly ash and/or gaseous emissions from e-waste open burning. LMW PAHs have often been found to be highly abundant in vegetables due to their greater water solubility, volatility, and bioavailability (Wild and Jones, 1994; Voutsas and Samara, 1998). In contrast, HMW PAHs are primarily associated with soil particles and airborne particulates, and their uptake through roots or foliage has been considered difficult. However, our study showed that HMW PAHs (e.g., BaA, FLA, and PYR) dominated in vegetables near the e-waste burning site. This finding suggests that in addition to gaseous deposition, the deposition of particles was also important for the foliar uptake of HMW PAHs in the source area. A similar observation was also discovered by Welsch-Pausch et al. (1995), which showed that the deposition of large particles was important for the more chlorinated PCDDs. Nevertheless, further studies need to be performed to determine the reason that the abundance of PHE was lower than that of BaA and PYR in the plant samples.

3.3. Source identification of PAHs

The loading plot and score plot (PC1 vs. PC2) showing the PCA results for the PAHs in the soil and plant samples are presented in Fig. 2. The first two principal components (PCs) explained approximately 48% and 36% of the total variance, respectively. The PCA loading plot (Fig. 2a) for the individual components of the PAHs shows that all the congeners were located in the first quadrant of the Cartesian coordinate system. The result indicates that PAHs in the study area may originate from the same sources. Moreover, the congeners can be divided into two groups based on their different physicochemical properties. One

Table 2
Concentrations of PAHs in plant samples.

Congener (ng/g)	Wild plant n = 10 ^d		Vegetable n = 10		Paddy stalk n = 2	
	Mean	Range	Mean	Range	Mean	Range
NAP	132	56.3–359	61.0	37.7–86.5	80.3	73.8–86.7
ACY	45.0	18.4–113	21.7	14.4–30.7	24.3	23.1–25.5
ACE	4.8	n.d. ^e –20.5	0.9	n.d.–14.2	11.0	8.0–14.0
FLU	57.3	27.4–143	28.5	18.7–40.5	34.6	33.9–35.2
PHE	46.2	11.4–94.6	50.4	9.3–93.3	53.1	49.1–57.1
ANT	59.6	24.4–159	29.1	19.0–41.7	31.0	30.3–31.7
FLA	77.1	29.9–162	76.1	24.4–163	49.8	49.6–50.0
PYR	71.4	23.3–152	64.1	26.0–111	44.9	40.9–48.9
BaA ^a	91.9	32.4–227	53.3	n.d.–84.8	59.6	54.0–65.2
CHR ^a	78.6	26.0–201	56.2	25.5–98.8	45.2	40.2–50.1
BbF ^a	73.0	n.d.–221	44.0	n.d.–76.9	44.8	40.1–49.6
BkF ^a	69.2	n.d.–213	34.7	n.d.–66.1	40.4	35.7–45.1
BaP ^a	47.0	n.d.–230	14.0	n.d.–60.4	43.0	38.0–48.1
IcdP ^a	7.2	n.d.–57.6	13.4	n.d.–71.3	n.d.	n.d.
DahA ^a	n.d.	n.d.	0.0	n.d.	n.d.	n.d.
BghiP	36.5	n.d.–175	10.9	n.d.–43.8	32.1	28.5–35.7
ΣPAHs ^b	896	334–2420	558	199–957	594	583–605
ΣPAHs _{carc} ^c	367	115–1090	216	35.5–448	233	208–258

^a Carcinogenic PAH compounds.

^b Sum concentration of 16 PAH compounds.

^c Sum concentration of 7 carcinogenic PAH compounds.

^d Number of samples.

^e Not detectable.

Table 3
Concentrations of PAHs in different vegetables ^a.

Congener (ng/g)	<i>Lactuca sativa</i> L. var. <i>longifolia</i> Lam. ^e	<i>Chrysanthemum coronarium</i> L. ^e	<i>L. sativa</i> L. var. <i>romana</i> Gars ^e	<i>Brassica rapa</i> L. ^e	<i>Brassica oleracea</i> L. ^e	<i>Pisum sativum</i> L. ^e	<i>Allium ascalonicum</i> L. ^e	<i>Daucus carota</i> L. ^f	<i>Raphanus sativus</i> L. ^f	<i>Colocasia esculenta</i> L. ^f
NAP	86.5	74.2	64.7	51.1	41.9	75.8	78.5	45.8	44.3	37.7
ACY	27.7	30.7	21.6	17.4	16.4	24.0	29.8	18.2	17.8	14.4
ACE	n.d. ^g	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FLU	33.9	35.6	29.2	19.7	23.6	32.9	32.4	24.8	20.6	18.7
PHE	59.5	93.3	65.2	62.4	55.9	55.4	47.6	38.6	9.3	23.3
ANT	35.3	39.3	29.7	21.5	23.6	33.3	34.6	24.5	23.5	19.0
FLA	112	163	87.6	62.0	72.8	79.5	63.5	57.0	30.6	24.4
PYR	111	104	90.2	44.8	55.6	58.0	58.1	45.4	27.3	26.0
BaA ^b	84.8	66.3	67.5	38.6	49.0	58.4	61.6	45.0	34.0	10.0
CHR ^b	98.8	78.6	72.9	36.4	39.4	67.4	62.9	39.6	28.9	25.5
BbF ^b	73.9	61.2	60.5	32.8	37.9	54.4	55.1	36.5	n.d.	n.d.
BkF ^b	58.9	49.3	49.2	28.6	33.9	18.2	52.8	36.3	n.d.	n.d.
BaP ^b	60.4	49.4	50.7	n.d.	n.d.	18.1	n.d.	n.d.	n.d.	n.d.
IcdP ^b	71.3	62.1	n.d.	36.2	n.d.	22.0	n.d.	n.d.	n.d.	n.d.
DahA ^b	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BghiP	43.8	38.0	37.8	n.d.	n.d.	13.3	n.d.	n.d.	27.6	n.d.
ΣPAHs ^c	957	945	727	451	450	611	577	412	264	199
ΣPAHs _{carc} ^d	448	367	301	173	160	238	232	157	63.0	35.5

^a Composite samples of 5 sub-samples.

^b Carcinogenic PAH compounds.

^c Sum concentration of 16 PAH compounds.

^d Sum concentration of 7 carcinogenic PAH compounds.

^e Shoot.

^f Root (include tuber).

^g Not detectable.

group contained most of the LMW PAHs, whereas the other group contained most of the HMW PAHs. Almost all of the samples were close to each other in the score plot, with the exception of one soil sample from the e-waste dumping site (Fig. 2b), indicating that the PAHs at these sites may derive from the same source – dispersion in the ash or gaseous emissions from the open burning activity. This hypothesis was also supported by the significant correlations among the 16 PAH congeners ($r > 0.266$, $p < 0.04$; except for ACE vs. ACY). The score plot also suggested that although the PAH levels varied widely among different land use types (e.g., vegetable field, paddy field, deserted field), they were still originated from the same source – e-waste recycling activities. This result also confirmed that the different tillage patterns of various agricultural soils were the principal reason for the differences in PAH concentrations. The concentrations of PCBs, PBDEs, and HMs in the same samples were also analyzed and reported (Luo et al., 2011; Wang et al., 2011a, 2011b). A correlation analysis found significant correlations between PAHs, PAHs_{carc}, PCBs, PBDEs, BDE 209, and HMs (Table 4), which also implied that the contamination by PAHs originated primarily from e-waste recycling processes, since the other materials cited had been found to be derived from this source. Previous research also suggested that the gas, fly ash, and suspended particles containing

PAHs generated from open burning activity may produce the high PAH levels in the surrounding soils through long-range atmospheric transport and deposition (Yu et al., 2006).

3.4. Estimation of daily dietary intake of PAHs by vegetables

Because PAHs can be biotransferable and bioaccumulated in human bodies through dietary intake, we calculated the total daily dietary intakes (TDIs) of PAHs to evaluate the potential risk to the residents living around the e-waste disposal sites through the intake of vegetables. The TDIs of PAHs and PAHs_{carc} for the residents were estimated according to the following equation:

$$TDI = \frac{1}{BW} \sum_{i=1} c_i \times (1-w_i) \times DDI_i, \quad (1)$$

where BW is the body weight for an adult (assumed to be 60 kg); c_i (ng/g dry wt.) is the concentration of PAHs or PAHs_{carc} in vegetables; w_i (g/g) is the ratio of water content for vegetables (90%); and DDI_i (g/d) is the daily dietary intake of vegetables by the adult residents (300 g/d, according to the China Statistical Yearbook – 2010).

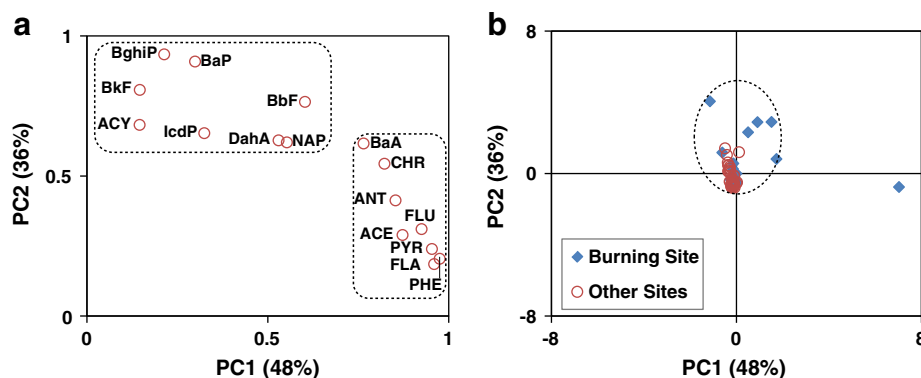


Fig. 2. Two-dimensional principal component loading plot (a) and score plot (b).

Table 4
Correlation coefficient matrix for PAHs, PCBs, PBDEs, and heavy metals (n = 61).

	PAHs ^a	PAHs _{carc} ^b	PCBs ^c	PBDEs ^d	BDE 209	HMs ^e
PAHs	1.000					
PAHs _{carc}	0.917**	1.000				
PCBs	0.865**	0.772**	1.000			
PBDEs	0.668**	0.752**	0.629**	1.000		
BDE 209	0.601**	0.686**	0.614**	0.984**	1.000	
HMs	0.788**	0.824**	0.732**	0.924**	0.873**	1.000

** Significant at 0.01 level.

^a Sum of 16 PAHs.

^b Sum of 7 carcinogenic PAHs.

^c Sum of 32 PCBs (PCB 8, 28, 37, 52, 49, 44, 74, 70, 66, 60, 77, 101, 99, 87, 82, 118, 114, 105, 126, 153, 138, 158, 166, 128, 156, 169, 179, 187, 183, 180, 170, and 189).

^d Sum of 8 PBDEs (BDE 28, 47, 99, 100, 153, 154, 183, and 209).

^e Sum of 6 heavy metals (Cd, Cr, Cu, Ni, Pb, Zn).

The TDI of individual PAH congeners via vegetables based on the average concentrations found by the present study ranged from n.d. (DahA) to 38.0 (FLA) ng/kg/d. The TDIs of Σ PAHs and Σ PAHs_{carc} through vegetables were 279 and 108 ng/kg/d, respectively. In order to estimate the carcinogenicity, the toxic equivalency factors (TEFs) adopted by the US EPA (2002) were employed to calculate all of the PAHs as “BaP equivalents” (TEFs for BaA 0.1, CHR 0.001, BbF 0.1, BkF 0.01, BaP 1, DahA 1, and IcdP 0.1). The TDI of total “BaP equivalents” via vegetables was 12.8 ng/kg/d. Although the daily dietary intake of PAHs in this e-waste recycling area was only based on vegetable consumption, it was still much higher than the total daily dietary intake of PAHs in Spain (Yoon et al., 2007; Martorell et al., 2010) and the UK (Phillips, 1999; Ramesh et al., 2004). Moreover, the TDIs of Σ PCBs and Σ PBDEs, according to the results of our previous research (Wang et al., 2011a, 2011b), also reached 16.4 and 6.4 ng/kg/d. The PAHs in the vegetables can produce a potential health risk, although the level of contamination was relatively less serious than those found for PCBs and HMs. Given that many other sources of daily intake (e.g., through other forms of ingestion or inhalation) of PAHs and other toxic chemicals occur, the vegetables grown in the soils of the e-waste recycling sites are not suitable to eat and should be closely monitored.

4. Conclusions

The former uncontrolled recycling and disposal of e-waste have resulted in severe contamination and in the migration of PAHs into the surrounding environment. The levels of PAHs in the soil and vegetation samples collected near the e-waste dumps were significantly enriched relative to those from other locations. The concentrations of PAHs in soils varied widely for the different sampling sites, with burning site > vegetable field > paddy field > deserted field. The concentrations of PAHs in vegetation were dependent on both sampling locations and plant species. Different profiles of PAHs in the soil and the corresponding vegetation implied that the uptake of PAHs by plants was selective. Gaseous emission and particle deposition from the e-waste open burning activities were the main sources of PAHs in the recycling area. PAHs have entered the food chain through vegetables and result in high daily dietary intakes via vegetables in the e-waste recycling area. Vegetable cultivation near the e-waste recycling sites should be strictly avoided.

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