

Heavy metals and polycyclic aromatic hydrocarbons in soils and vegetables in an electronic waste processing site, south China

Chunling Luo¹, Yan Wang², Chuanping Liu³, Gan Zhang², Fangbai Li³, Xiangdong Li^{1,*}

¹*Department of Civil and Structural Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong*

²*Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China*

³*Guangdong Public Laboratory of Environmental Science and Technology, Guangdong Institute of Eco-Environmental and Soil Sciences, Guangzhou 510650, China*

Abstract

In the present study, a primitive e-waste processing facility was investigated. Soils of e-waste open burning sites, surrounding paddy fields and vegetable gardens, as well as common vegetable samples were collected and analysed for heavy metals and polycyclic aromatic hydrocarbons (PAHs). Results showed that the soils of former burning sites had the highest concentrations of Cd, Cu, Pb and Zn with the mean values of 17.1, 11140, 4500, 3690 mg kg⁻¹, respectively. The soils of nearby paddy fields and vegetable gardens also had relatively high concentrations of Cd and Cu. In the edible tissues of vegetable, the concentrations of Cd and Pb in most samples exceeded the maximum level of metals for food in China. Sequential leaching tests revealed that Cu, Pb and Zn were dominantly associated with the residual fraction followed by the carbonate/specifically adsorbed phases except for Cd, which was mainly in the extractable form in paddy fields and vegetable soils. The PAHs analysis showed the concentration of 17 PAHs in soils varied between 0.1 and 10.6 mg kg⁻¹, with the descending order of burning sites (4.87 mg kg⁻¹) > vegetable gardens (0.71 mg kg⁻¹) > paddy fields (0.27 mg kg⁻¹). In the edible tissues of vegetable, the mean concentration of the total PAHs reached 0.54 mg kg⁻¹. The data showed that past primitive e-waste processing operations caused severe pollution to local soils and vegetable. The clean-up of former burning sites should be the priority task in the future remediation work.

Key words: Heavy metals, PAHs, E-waste, Soil, Vegetable

Introduction

Uncontrolled E-waste recycling process has been reported in a number of locations of China, and it is becoming a new important source for the environmental pollution in these regions, such as Guiyu¹ and Taizhou² in south China. The operations used in the precious metal extraction, such as open burning of the dismantled components, can lead to the release of large amounts of toxic metals and organic substances into the environment.

* Corresponding author (X. D. Li). *E-mail address:* cexdli@polyu.edu.hk; Fax: +852-2334-6389; Tel.: +852-2766-6041.

Operators may be seriously affected through direct inhalation and dermal contact. High concentrations of toxic substance (e.g., Pb, PBDE etc) has been reported in the blood of workers conducting this kind e-waste recycling job^{3,4}. On the other hand, these contaminants discharged into the environment can further precipitate into the soil where vegetable and crop are grown, and may be uptaken by the plant roots, transported upwards to the shoots, and finally accumulated inside the plant tissues. Direct foliar uptake of heavy metals and PAHs from the atmosphere can also occur during plant growth. Consumption of contaminated food has been proved to be an important pathway of transferring heavy metals from the environment to human bodies.

The current study was carried out in a small town in northern Guangdong province. Intensive e-waste recycling was active in the past several years. In this study, soil samples from former burning sites and surrounding vegetable gardens, paddy fields, a deserted soil site, and a reservoir area, together with the vegetable samples were collected. The project aims to investigate the effect of e-waste recycling activities on the surrounding environment and the food products. Useful information can be expected for appropriate protective measures for the local community, and possible clean-up measures for the deteriorated environment in the affected area.

Materials and methods

Soil and vegetable sampling

Top soils (0-20 cm) from e-waste burning sites and surrounding vegetable gardens, paddy fields, and a reservoir were collected using stainless spade. Vegetables from garden fields with the corresponding soils were also collected. All the samples were put in polythene zip-bags and transported to the laboratory immediately after collection. Each individual plant sample was separated into shoot and root. The fresh plant samples were washed with tap water, rinsed with DIW and subjected to freezing-dry process. Then the sub-samples of the plant and soil collected were ground with agate mortar for chemical analysis.

Metal and PAHs analysis

The total concentrations of metals were determined by ICP-AES (Perkin-Elmer Optima 3300 DV) after strong acid digestion (1:4 concentrated HNO₃ and HClO₄ (v/v)) on about 200 mg plant and soil samples⁵.

For the analysis of PAHs, freezing-dried soil samples (20 g) were extracted for 48 h with dichloromethane (80 ml) in a Soxhlet apparatus according to the EPA Standard Method 3540C⁶. Five grams of vegetable powder were mixed with 5 g of anhydrous sodium sulfate (baked for 6 h at 450°C in oven before use), packed in a stainless extracting cell. The samples were spiked with a known aliquot of naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂ and perylene-d₁₂ as analyte surrogates. Dichloromethane (DCM) and acetone (3:1, V:V) was used as solvent, and the samples were extracted for 72 h in a Soxhlet apparatus followed by the addition of five grams of activated copper slices to the extracts to remove elemental sulfur. Florisil column clean-up was used for purification of the concentrated extract (EPA Standard Method 3620B).

PAHs compounds were separated on a 30 m×0.25 mm DB-5MS capillary column (film thickness 0.25 mm) and analyzed using a Agilent 7890A gas chromatography and 5972 mass selective (GC-MSD) detector operated in the electron impact mode (70 eV). The standard curve was obtained by using 0.2, 0.5, 1, 2, 5, and 10 mg kg⁻¹ PAH standards. The response curves for the 16 PAHs were linear, and the correlation coefficients were higher than 0.99.

Quality control and statistical analysis

In the analysis of metals, certified standard reference materials NIST (SRM 1515 and SRM 2709) of the National Institute of Standards and Technology, U.S.A., were used in the digestion and analysis as part of the QA/QC protocol. Reagent blank and analytical duplicates were also used where appropriate to test the accuracy and precision of the analysis. The recovery rates were around 90±6% for reported metals in the soil and plant reference materials (NIST SRM 1515 and 2709). The data reported in this paper were the mean values based on the three replicates.

QA/QC procedures for PAHs analysis included regular injection of solvent-prepared standard solutions, procedural blanks, spiked blanks (PAHs acenaphthene-d10, phenanthrene-d10, chrysene-d12 and perylene-d12) and duplicate extractions for each bath of 10 field samples to monitor for quantitative reproducibility and instrument sensitivity. The recovery of all PAHs was in the range of 74-128 % for all the reference materials.

Results and discussion

The concentrations of heavy metals in different soil samples is presented in Table 1.

Table 1 Metal concentration (mg kg⁻¹ DW) in different sampling sites

	Cd	Cr	Cu	Ni	Pb	Zn
Vegetable garden	0.26-1.17 (0.9±0.3) ^a	9.66-19 (12.3±3.1)	210-450 (324±72)	7.04-10.3 (8.83±0.9)	73.3-134 (95.6±19.5)	92.4-142 (122±15.7)
Paddy field	0.04-1.43 (1.0±0.4)	10.5-24.1 (17.3±4.1)	40.1-260 (155±64)	10.8-66 (34.5±16.6)	48.1-97 (61.8±14)	62.1-252 (166±56.7)
Burning site	3.05-46.8 (17.1±12.5)	23.6-122 (68.9±33)	1500-21400 (11140±7000)	12.2-132 (60.1±39)	629-7720 (4500±2370)	682-8970 (3690±2680)
Deserted soil	0.08-0.39 (0.25±0.16)	3.84-11.1 (6.41±4.04)	49.9-95.4 (72.4±22.8)	4.58-19.7 (10±8.4)	47.2-60.2 (52.2±7)	44.5-72.3 (62.6±15.7)
Reservoir area	0.57-18.3 (5.45±7.43)	14-105 (38.9±38.4)	142-12900 (3550±5480)	18.9-44.9 (32.2±10.7)	37.9-7760 (1880±3340)	123-3800 (1160±1580)
Background value ^b	0.06	50.5	17	14.4	36	47.3
Chinese standard for agricultural soil ^c	≤0.3	≤250	≤50	≤40	≤250	≤200

^a The value in brackets indicates mean value ± S.D.

^b Metal background value in the soil of Guangdong province

^c GB15618-1995

Table 2 Metal concentration (mg kg⁻¹ FW) in the edible part of different vegetables

	Cd	Cr	Cu	Ni	Pb	Zn
<i>Pisum sativum</i> L.	0.04±0.01	n.d. ^a	1.04±0.2	0.10±0.01	0.24±0.02	9.79±0.1
<i>Chrysanthemum coronarium</i> L.	0.29±0.1	0.01±0.01	2.57±0.4	0.18±0.05	0.46±0.05	20.4±3.2
<i>Brassica rapa</i> L. (Pekinensis group)	0.24±0.03	n.d.	3.99±0.05	0.42±0.05	0.32±0.04	21.9±2
<i>Lactuca sativa</i> L. var. romana Gars	0.28±0.04	n.d.	1.71±0.2	0.16±0.1	0.39±0.06	15.7±2.5
<i>Raphanus sativus</i> L.	0.05±0.01	n.d.	0.59±0.6	0.05±0.01	0.11±0.02	7.20±1
<i>Colocasia esculenta</i> (L.)Schott	0.32±0.04	0.08±0.03	2.87±0.5	0.92±0.2	1.30±0.4	10.1±1.5
<i>Allium ascalonicum</i> L.	0.33±0.05	n.d.	1.10±0.3	0.06±0.05	0.35±0.5	8.85±0.9
<i>Brassica oleracea</i> L. var. capitata L	0.25±0.03	0.03±0.01	1.42±0.4	0.05±0.03	0.79±0.1	8.06±0.5
<i>Lactuca sativa</i> L.	0.38±0.08	n.d.	2.09±0.3	0.10±0.08	0.77±0.2	15.5±4.5
<i>Daucus carota</i> L.	0.18±0.04	0.12±0.01	0.99±0.2	0.08±0.05	0.48±0.3	3.69±0.65
Maximum allowable level in food ^b	0.05	0.5	10	0.6 ^c	0.2	20

^a n.d.: not detectable

^b Tolerance limit of contaminants in food: Cd, GB 15201-94; Cr, GB14961-94; Cu, GB 15199-94; Pb, GB 14935-94; Zn, GB 13106-91

^c National Bureau of standards of China (1995)

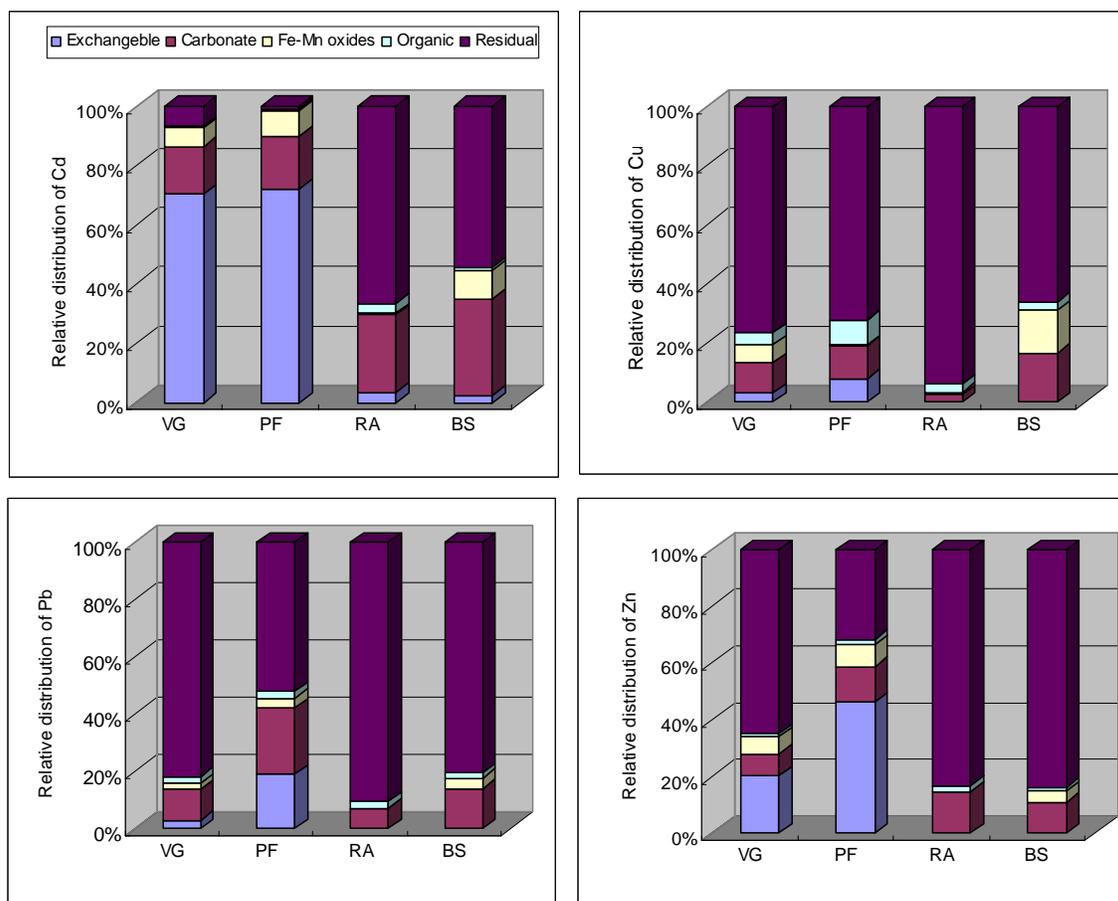


Fig. 1. Sequential chemical fractions of Cd, Cu, Pb and Zn in selected soil samples. VG, vegetable garden; PF, paddy field; RA, reservoir area; BS, burning site.

It can be seen that the former burning site had the highest concentrations of metals, which highlighted the impact of e-waste processing at these spots. High concentrations of metals were also found in the reservoir area, which is close to burning sites. In comparison with the maximum allowable concentrations of metals in agricultural soil in China, the soils in the study area were primarily contaminated by Cd and Cu, followed by Pb and Zn. No significant contamination of Cr was observed in all the samples. As for the metal contamination in the vegetable samples, the concentration of Cd and Pb in most vegetables exceeded the food safety limit in China (see Table 3). However, there was no contamination of Cu in these samples. Chemical speciation of heavy metals in the soil samples were analyzed using a modified Tessier sequential chemical extraction method. The results indicated that Cu, Pb and Zn were dominantly associated with the residual fraction followed by the carbonate/specifically adsorbed phases except for Cd, which was mainly in the extractable form in paddy fields and vegetable soils (see Fig 1.). The high extractable Cd in the vegetable garden soil was probably responsible for the direct uptake of Cd by the plant roots from the soil solution and accumulation in the edible parts of vegetable.

The concentrations of PAHs in the vegetable and soil samples are listed in Table 3. The mean concentration of \sum PAHs in all the vegetables reached 536 ng g^{-1} , with HMW being higher than the LMW. Regarding the soils, the open burning sites had the highest levels of PAHs (4870 ng g^{-1}), followed by the reservoir area and vegetable gardens. The average concentration of PAHs in the soils was much higher than the background level (100 ng g^{-1} dry weight) at remote or rural sites without anthropogenic activities⁷ and the endogenous concentration ($1\text{--}10 \text{ ng g}^{-1}$ for individual PAHs) resulting from biosynthesis and forest fires.

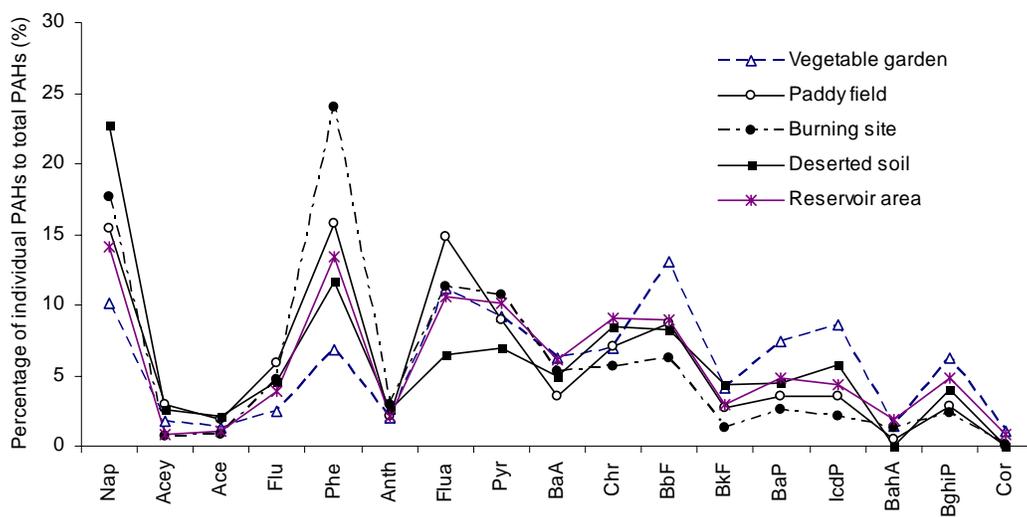


Fig. 2. Profiles of PAHs in soils at different sampling sites.

PAH profiles (distribution patterns of 17 PAHs) in five sampling areas showed was similar in different sites, with Nap and Phe being the most abundant, while Acey, Ace,

coronene and Anth being the least components. Phe was dominant in the open burning area, accounting for 24% of the total PAHs, while Nap accounted for 17.6%. Nap and Phe were dominant in the reservoir area, each accounting for 14.4% and 13.4% of the total PAHs, respectively. In other three areas, Nap, Phe and Flua were the most abundant. The very similar PAH profiles in the five sampling areas indicated the similar sources of PAHs. The primitive e-waste recycling process, especially open burning and coal combustion, were the main sources of PAHs in this region.

Table 3 The concentration of PAHs (ng g⁻¹) in vegetables and different soil samples

PAHs	Vegetables	Vegetable garden	Paddy field	Burning site	Deserted soil	Reservoir area
Naphthalene (Nap)	59.2±16	72.1±35.2	41.6 ±15.7	858±338	35.9±9.4	120±142
Acenaphthylene (Acey)	20.9±6.07	12.7±3.7	7.9 ±3.5	35.8±6.7	4.1±0.7	7.3±3.4
Acenaphthene (Ace)	1.57±4.6	8.8±2.5	5.0 ±1.8	41.1±22.6	3.4±0.7	9.1±6.1
Fluorene (Flu)	27.7±6.76	17.4±3.5	15.8 ±5.4	227±210	7.2±1.0	33.0±28.8
Phenanthrene (Phe)	50.4±21.6	48.7±10.4	42.7 ±11.8	1170±1020	18.4±2.5	114±124
Anthracene (Anth)	28.2±7.4	14.3±4.3	5.7 ±1.6	145±117	4.0±0.9	18.3±18.5
Fluoranthene (Flua)	72.4±33.5	80.0±37.9	40.0 ±9.5	553±610	10.2±0.9	89.8±100
Pyrene (Pyr)	61.6±26.3	65.3±34.9	24.1 ±7.2	519±511	10.9±2.3	86.2±110
Benzo(a)anthracene (BaA)	50.1±22.4	44.8±29.3	9.7±2.8	259±131	7.8±2.1	51.7±68.6
Chrysene (Chr)	55.3±23.1	49.1±27.1	19.2±6.4	278±161	13.4±1.6	76.9±98.2
Benzo(b)fluoranthene (BbF)	41.2±22.9	92.9±55.3	23.6±5.0	306±127	13.1±2.6	76.1±92.7
Benzo(k)fluoranthene (BkF)	32.5±20.6	29.7±18.0	7.3±2.8	65.1±31.7	6.9±1.9	24.7±27.3
Benzo(a)pyrene (BaP)	14±21.7	53.0±34.1	9.4±1.8	124±51.3	7.1±1.8	41.3±52.8
Indeno(1,2,3-cd)pyrene (IcdP)	11.9±23.8	61.5±37.8	9.7±6.0	106±51.8	9.2±2.9	36.9±44.6
Bibenz(a,h)anthracene (BahA)	0	9.7±8.5	1.3 ±2.6	65.0±34.6	n.d.	16.3±18.4
Benzo(g,h,i)perylene (BghiP)	9.65±16.4	44.8±28.7	7.8 ±4.1	116±68.6	6.4±2.4	40.7±51.0
Coronene (Cor)	0	7.4±5.9	n.d.	4.2±3.9	n.d.	6.8±11.8
Total PAHs	536±219	712±319	271±52.2	4870±2880	158±23	850±997
LMW PAHs	187±63	174±39.2	119±29.6	2480±1400	73.0±12.9	302±322
HMW PAHs	349±211	538±313	152±32.3	2390±1510	85.0±17.4	547±674

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