



# Heavy metal and persistent organic compound contamination in soil from Wenling: An emerging e-waste recycling city in Taizhou area, China

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## ABSTRACT

The present study was conducted to investigate the levels and sources of heavy metals (Cu, Cr, Cd, Pb, Zn, Hg and As) and persistent organic compounds including polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in soils taken from Wenling, an emerging e-waste recycling city in Taizhou, China. The results suggested that most heavy metals exceeded the respective Grade II value of soil quality standards from State Environmental Protection Administration of China and also exceeded the Dutch optimum values. Total PAHs in soil ranged from 371.8 to 1231.2  $\mu\text{g}/\text{kg}$ , and relatively higher PAHs concentrations were found in soils taken from simple household workshops. PCBs were detectable in all samples with total concentrations ranging from 52.0 to 5789.5  $\mu\text{g}/\text{kg}$ , which were 2.1–232.5 times higher than that from the reference site (24.9  $\mu\text{g}/\text{kg}$ ). Results of this study suggested soil in the Wenling e-waste recycling area were heavily contaminated by heavy metals, PAHs and PCBs. Furthermore, compared with large-scale plants, simple household workshops contributed more heavy metals, PAHs and PCBs pollution to the soil environment, indicating that soil contamination from e-waste recycling in simple household workshops should be given more attention.

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## 1. Introduction

Electronic and electric waste (e-waste) refers to end-of-life electronic products including computers, printers, photocopy machines, television sets, mobile phones, and toys [1,2]. It has been estimated that over 500 million computers became obsolete between 1997 and 2007 in the United States alone and more than 50 million tonnes of e-waste are produced annually in the world [3,4]. Large quantities of e-waste represent an emerging environmental problem, as electrical and electronic waste equipment already constitutes more than 5% of municipal waste and is still growing fast in developed countries [5]. Taking advantage of lower labor costs, and less stringent environmental regulations, developing countries, especially China, face a rapidly increasing amount of e-waste that is imported illegally from developed countries for recycling. A report by Toxics Link found that 70% of the e-waste collected at recycling units in New Delhi, India, was actually exported or dumped by developed countries and about 50–80% of the e-waste collected for recycling in the western U.S. is being exported to Asia, about 90% of which is sent to China for recycling [6,7]. However, the recycling techniques in these countries are often crude

and do not have the appropriate facilities; the processes include toner sweeping, dismantling of electronic equipment, selling computer monitors to copper recovery operations, plastic chipping and melting, burning wires to recover copper, heating circuit boards over honeycombed coal blocks, and using acid chemical strippers to recover gold and other metals [8,9]. In addition, open burning of unwanted e-waste and their open dumping has been found universally. Such unregulated salvaging operations and optional dumping of the e-waste have resulted in severe and complex contamination of the surrounding environment by toxic chemicals such as heavy metals (Cd, Pb, Cu and Hg), as well as persistent organic compounds such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) [1,10–12]. These compounds could expose the workers and local residents through inhalation, dermal exposure, and even oral intake (of contaminated food), with the health risk being highest for the workers. Once taken into the body, these compounds are stored in certain tissues, leading to intoxication episodes that can be described as acute or long-term intoxications and producing illness when the levels reach critical values [13].

Taizhou area, located in Zhejiang province, East China, has been involved in e-waste recycling for nearly 25 years. It is one of the best known e-waste processing centres of China [10]. The e-waste in Taizhou includes many varieties, such as electric power capacitors, transformers and electromotors and their components, which could contain and release more persistent toxic substances like

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PCBs during the crude recycling operation [8,9]. Since Chu et al. [14] first reported that the soil in the vicinity of a PCB-containing equipment trading and dismantling site was heavily contaminated with PCBs in Luqiao district, the centre city of Taizhou, numerous research studies have been focused on Luqiao [8–11,15]. Therefore, the local government in Luqiao had to take action to regulate the e-waste recycling industry to protect the local environment, which led to the formation of strict environmental policy in this district.

Wenling city is one of the major cities involved in e-waste recycling close to the city centre in Taizhou area, where the economy is not so developed and has less strict environmental policies. Due to this weaker environmental policy in Wenling, a large fraction of e-waste shifted to Wenling for recycling. Furthermore, most of the crude simple household workshops which were previously banned in Luqiao also shifted to Wenling. Therefore, environmental problems arising from e-waste recycling have become serious in Wenling city. Fu et al. [16] investigated 10 heavy metals (As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Ni and Pb) contents in paddy soil from one village in Wenling and found the paddy soil was primarily contaminated by Cd (1.19 mg/kg), followed by Cu (9.98 mg/kg) and Hg (0.32 mg/kg). Recent studies by Zhao et al. [17,18] reported that soil samples ( $n=6$ ) collected from four e-waste disassembly sites in Wenling had higher PCBs levels (ranging from 27.8 to 738.9  $\mu\text{g}/\text{kg}$ , with a mean of 152.8  $\mu\text{g}/\text{kg}$ ) compared with those observed in soils from the control site. These limited studies investigated only a few soil samples and focused on several e-waste recycling sites, but there has been no systematic study of soil pollution effected by primitive e-waste recycling in this area. Leung et al. [12] had identified the sources and quantified the levels of various heavy metals and persistent organic compounds resulting from e-waste recycling in Guiyu, another e-waste recycling centre in Guangdong Province, China. This did much to elucidate the extent of contamination by e-waste recycling activities and assess the human health risk for local residents in Guiyu. With the above background in mind, the main objective of this study is to identify the levels and sources of heavy metals (Cu, Cr, Cd, Pb, Zn, Hg and As) and persistent organic compounds (PAHs and PCBs) generated from the emerging e-waste recycling activities in Wenling, located in Taizhou area, Zhejiang Province, China.

## 2. Materials and methods

### 2.1. Research area and sampling

A preliminary survey of contaminant levels in Wenling was conducted in August 2008, with the aid of a global positioning system. The location of the sampling sites in addition to e-waste activity sites is shown in Fig. 1. Sites A–G were relatively large-scale recycling plants, sites H and I were large-scale gold recovering plants, while sites J–L were small simple household recycling workshops. Site M was chosen as the reference site and was located in the JQ town in Taizhou city, about 15 km north of Wenling city (not shown in Fig. 1), where there was no e-waste recycling industry. Three sub-samples (0–30 cm) adjacent to the sampling location were mixed to obtain about 1000 g representative composite samples. All of the surface soils ( $n=39$ ) were collected using acid-washed stainless steel scoops and were immediately transferred to prewashed aluminum boxes. Description of the sampling sites and characteristics of samples are shown in Table 1.

### 2.2. Sample treatment and analysis

The soil samples were air-dried and sieved to  $<0.25$  mm, then stored in desiccators prior to analysis of heavy metals, PAHs and PCBs.

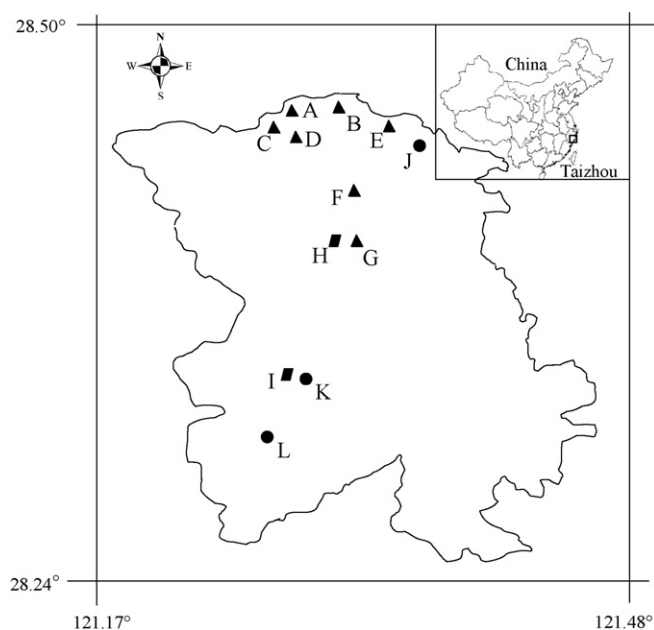


Fig. 1. Map of study area in Wenling city and sampling locations: (▲) large-scale e-waste recycling plants; (■) Large-scale gold recovering plants; (●) Simple household e-waste recycling workshops. Also see Table 1 for a description of sample sites A–L.

#### 2.2.1. Heavy metals analysis

The samples were digested using the method described by Hseu et al. [19]. 0.5 g of dry sample was weighed and digested with a mixture of nitric acid ( $\text{HNO}_3$ ) and perchloric acid ( $\text{HClO}_4$ ). Concentrations of Cu, Cr, Cd, Pb and Zn were determined by flame atomic absorption spectrometry (AAS, Solaar-MK II-M6). Hg and As concentrations in the digestion liquid were determined by atomic fluorescence spectrometry (AFS-2202a) [20].

#### 2.2.2. PAHs analysis

Samples (5 g) were extracted for 24 h with 200 ml hexane and acetone (v:v, 1:1) in a Soxhlet apparatus. Soxhlet extracts were passed through a silica gel/aluminum oxide column to obtain PAHs fractions by eluting with 70 ml of dichloromethane/hexane (3:7, v/v). The eluate was evaporated to less than 2 ml prior to analysis [9,21]. GC–MS analysis was performed on a Agilent 6890 GC system coupled to a mass selective detector and a  $30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$  DB-5 capillary column (J & W Scientific Co. Ltd., USA). The EPA Standard Method 8270C [22] was used to determine the following 16 PAHs: naphthalene (Nap), acenaphthylene (Any), acenaphthene (Ane), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benz(a)anthracene (BaA), chrysene (Chr), benzo(a)pyrene (BaP), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), indeno(1,2,3-cd)pyrene (IcdP), dibenz(a,h)anthracene (DahA) and benzo(g,h,i)perylene (BghiP).

#### 2.2.3. PCBs analysis

Following the soxhlet procedure as described above, the concentrated extract was cleaned up by a Florisil/anhydrous sodium sulphate column and eluted with 100 ml hexane. The concentrations of 58 PCB congeners, including six indicator PCBs (PCB-28, -52, -101, -118, -153, -138), were measured by a gas chromatograph equipped with a  $^{63}\text{Ni}$  electron capture detector (Agilent 6890) [9].

### 2.3. Quality control

All procedures were performed under strict quality control to meet USEPA requirements for field studies. Phenanthrene- $\text{d}_{10}$ ,

**Table 1**  
Description of sampling sites and characteristics of samples.

Sample named	Sample numbers	pH <sup>a</sup>	SOM <sup>b</sup>	Sampling sites	
				Location	Description
A	n = 4	6.3	5.23%	XH plant	Large-scale e-waste recycling plants, huge amounts of e-waste such as metal computer hardware, cellphones and plastic printer casings are being disposed and recycled among these plants, some workers have little or no consideration of self-protection during recycling activities
B	n = 1	5.2	4.73%	FS plant	
C	n = 1	5.3	4.30%	SH plant	
D	n = 4	6.2	5.35%	HY plant	
E	n = 1	5.6	1.53%	YT plant	
F	n = 2	6.0	5.33%	XX plant	
G	n = 2	6.6	4.93%	HX plant	
H	n = 3	4.2	5.43%	SX plant	Large-scale gold recovering plants, using acid chemical strippers to recover gold and other noble metals, wastewater discharged from these plants without effective treatments
I	n = 2	5.7	2.57%	JS plant	
J	n = 8	6.2	5.30%	XZ village	Simple household e-waste recycling workshops, the small workshops are downstream of the industrial chain of e-waste recycling sites and deal with residual components of e-waste supplied by the large-scale plants
K	n = 5	6.0	4.92%	TS Village	
L	n = 5	5.9	6.91%	MK village	
M	n = 1	6.8	4.54%	JQ town	

<sup>a</sup> Average results.<sup>b</sup> SOM, soil organic matter, average results.

2,4,5,6-tetrachloro-m-xylene (TMX) and PCB209 were spiked to detect the recoveries. The recoveries of surrogate standards for PAHs and PCBs determinations were in ranges of 84.0–114.3%, and 81.0–109.5%, respectively. In this study, the final concentrations of compounds of interest in soils were not corrected with recoveries. The detection limits were in the range of 0.37–3.1 µg/kg for PAHs and 0.014–0.091 µg/kg for PCBs, respectively. For heavy metals, all samples were digested and analyzed in replicate.

#### 2.4. Statistical analysis

All the statistical analysis was performed using SPSS software version 13.0 (SPSS Inc., Chicago, USA). One-way analysis of variance (ANOVA) was used for statistical comparisons and Pearson coefficient was used for correlation analysis. A value of  $P < 0.05$  was considered to be statistically significant.

### 3. Results and discussion

#### 3.1. Heavy metals

The heavy metal concentrations measured in soil samples are shown in Table 2 together with soil quality standards. Hg, Cu, Cd, Pb, and Zn were the most abundant metals found in the environmental samples. Hg was the most serious metal pollutant in Wenling area, with the Hg contents exceeding the Grade II value (0.3 mg/kg) by 1.0–31.0 times, except for sites B and C, which were lower than 0.3 mg/kg. Site K was very seriously polluted by Hg with an average of 654.1 mg/kg in the soil. In the reference soil, Hg concentrations were below or close to the limits for the natural background as defined by the Chinese Environmental Quality Standards. Cu concentrations ranged from 77.9 to 1641.3 mg/kg, with an average of 361.6 mg/kg, which exceeded the Grade II value of soil quality standards from State Environmental Protection Administration of

**Table 2**  
Average concentrations of heavy metals in soil collected from Wenling, Taizhou.

Sampling site		Heavy metals (mg/kg dw)						
		Cu	Cr	Cd	Pb	Zn	Ni	Hg
Large-scale e-waste recycling plants	A	296.3	269.1	2.6	501.9	432.7	48.0	1.0
	B	77.9	21.0	1.7	170.3	210.4	14.3	0.2
	C	155.7	16.4	1.9	173.7	177.7	11.7	0.2
	D	205.2	95.6	2.4	177.2	399.9	52.6	0.9
	E	140.8	112.7	7.4	81.3	660.8	66.3	0.3
	F	227.3	91.3	1.7	91.5	283.5	83.8	0.4
	G	161.4	102.9	3.3	115.2	237.2	66.1	0.3
Large-scale gold recovering plants	H	576.7	91.3	9.6	184.4	263.0	120.4	3.2
	I	272.3	88.6	0.6	102.8	143.8	107.4	0.4
Simple household e-waste recycling workshops	J	222.5	125.9	2.8	200.1	221.2	71.0	1.7
	K	361.7	65.9	7.9	295.2	437.3	53.3	654.1
	L	1641.3	40.5	12.5	2374.1	518.7	68.6	9.3
Reference site	M	32.3	56.5	0.04	33.0	157.8	N.D. <sup>a</sup>	N.D.
Dutch standards <sup>b</sup>	Optimum	36	100	0.8	85	140	35	N.D.
	Action	190	380	12	530	720	210	N.D.
	Grade I	35	90	0.2	35	100	40	0.15
China standards <sup>c</sup>	Grade II (pH < 6.5)	50	250	0.3	250	200	40	0.30
	Grade III	400	500	1.0	500	500	200	1.50

<sup>a</sup> N.D.: not detected.<sup>b</sup> From VROM [24].<sup>c</sup> From SEPA [23].

**Table 3**  
Average concentrations of PAHs in soil collected from Wenling, Taizhou ( $\mu\text{g}/\text{kg dw}$ ).

Compound	Large-scale e-waste recycling plants							Large gold recovering plants		Simple household e-waste recycling workshops			Reference site
	A	B	C	D	E	F	G	H	I	J	K	L	
Nap	23.7	23.8	27.8	4.0	95.3	23.9	7.7	7.0	24.5	7.4	17.1	60.0	9.5
Any	N.D. <sup>a</sup>	7.3	7.3	3.4	19.9	7.4	3.6	1.7	1.6	3.1	9.4	6.5	N.D.
Ane	N.D.	N.D.	N.D.	2.5	15.9	3.3	N.D.	0.4	N.D.	1.6	5.3	1.7	N.D.
Fla	6.6	6.6	6.6	29.6	27.8	10.7	12.5	22.2	7.4	15.9	14.6	15.7	2.6
Phe	218.7	231.2	199.2	243.5	270.0	244.9	260.4	203.4	64.4	145.5	169.9	128.3	19.6
Ant	221.4	230.0	197.9	119.7	47.7	0.0	144.2	203.0	64.7	144.3	160.5	128.1	16.0
Fla	39.0	43.1	35.1	92.3	47.7	55.5	74.4	166.8	62.7	129.4	166.3	105.9	14.8
Pyr	32.4	28.5	20.5	62.9	63.5	20.6	32.2	113.0	48.2	96.6	135.7	85.8	13.0
BaA <sup>b</sup>	N.D.	10.9	6.9	25.8	43.7	23.1	3.4	18.0	9.6	17.9	64.1	22.8	3.6
Chr <sup>b</sup>	24.7	28.8	20.8	28.5	39.7	20.9	30.5	14.5	17.7	32.3	136.6	54.8	5.2
BaP <sup>b</sup>	79.9	80.1	72.1	88.3	N.D.	68.5	67.3	77.7	62.9	80.6	139.3	98.5	8.1
BkF <sup>b</sup>	20.0	20.0	12.0	29.7	N.D.	8.1	45.3	19.1	4.7	21.9	76.5	38.1	2.5
BaP <sup>b</sup>	5.1	5.1	1.1	7.1	1.1	1.2	3.1	3.9	3.3	7.0	25.6	6.7	5.1
IcdP <sup>b</sup>	N.D.	N.D.	N.D.	14.8	N.D.	N.D.	N.D.	N.D.	N.D.	14.1	54.6	18.7	1.4
DahA	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	3.2
BghiP <sup>b</sup>	47.9	N.D.	N.D.	11.9	N.D.	N.D.	N.D.	N.D.	N.D.	12.8	43.2	15.8	0.4
Total PAHs	719.4	715.5	607.2	764.0	672.2	488.0	684.6	850.7	371.8	730.5	1231.2	787.3	105.0
Carcinogenic PAHs	129.7	145.0	112.9	194.3	84.5	121.8	149.7	133.2	98.2	173.8	509.3	239.6	29.1
LMW PAHs	470.4	498.9	438.7	402.6	476.5	290.2	428.4	437.7	162.6	317.8	376.8	340.3	47.7
HMW PAHs	249.0	216.6	168.5	361.4	195.7	197.8	256.2	413.0	209.2	412.7	854.4	447.0	57.3
Ant/(Ant + Phe)	0.50	0.50	0.50	0.33	0.15	N.D.	0.36	0.50	0.50	0.50	0.49	0.50	0.4
Flt/(Flt + Pyr)	0.55	0.60	0.63	0.59	0.43	0.73	0.70	0.60	0.57	0.57	0.55	0.55	0.5

<sup>a</sup> Not detected.

<sup>b</sup> Carcinogenic PAHs.

China (SEPA) (50 mg/kg) [23], and the new Dutch list action value of 190 mg/kg [24]. Moreover, Cd, Pb, and Zn concentrations for most of the sites surpassed the Grade II value of soil quality standards from SEPA and Dutch optimum values. There were no values for Cr and Ni that exceeded the Dutch action level, while most sites (except sites B and C) had higher levels compared with the Grade II value of soil quality standards from SEPA.

The pollution features of heavy metals in Wenling were not similar to those in Luqiao district, the city centre in Taizhou. Zhang and Ming [25] found that paddy soils were heavily contaminated with Cd ( $6.4 \text{ mg kg}^{-1}$ ), and weakly contaminated with Cu ( $256.4 \text{ mg kg}^{-1}$ ) and Zn ( $209.9 \text{ mg kg}^{-1}$ ), indicating that soils from Luqiao were less strongly contaminated with heavy metals. However, the heavy metal concentrations in soils from Wenling were consistent with those observed in soil close to an open-burning site in Guiyu [1,2,26], where the soil was markedly contaminated by heavy metals, except for Cr. These results confirmed that the heavy metal pollution in Wenling e-waste recycling area was relatively serious.

When comparing metal concentrations to the soil quality standards of SEPA, pH value is necessary. Relative pH values are listed in Table 1, with the average of 5.7. Generally, the pH of the soil in the e-waste recycling area was much lower than that of the reference site, suggesting that the soil pH was also affected by the crude e-waste recycling activities.

### 3.2. PAHs

The total concentrations of the 16 USEPA priority PAHs, including 7 carcinogenic PAHs in soils from Wenling, are listed in Table 3. Results showed that total concentrations in all soil samples varied from 371.8 to 1231.2  $\mu\text{g}/\text{kg}$ , while the concentrations of the 7 carcinogenic PAHs ranged from 98.2 to 509.3  $\mu\text{g}/\text{kg}$ , accounting for 15.7–36.6% of the total PAHs. Site K had the highest concentration of PAHs, i.e. 1231.2  $\mu\text{g}/\text{kg}$  for total PAHs and 509.3  $\mu\text{g}/\text{kg}$  for 7 carcinogenic PAHs (41.6% of total PAHs). Compared with the reference site M, sites from A to L were all highly contaminated by PAHs.

Since China has no available soil standards for PAHs, criteria constituted in other countries were used to evaluate the extent of pollution. According to the new Dutch list, the total concentrations of ten VROM PAHs (Nap, Ant, Phe, Fla, BaA, Chr, BaP, BghiP, BkF and IcdP) in soil should not exceed the maximum value of 1000  $\mu\text{g}/\text{kg}$  [24]. In the present study, the concentrations of the VROM PAHs in all soil samples did not exceed this value. Additionally, except for site K, the concentrations of 7 carcinogenic PAHs also did not exceed the Swedish soil limit of 300  $\mu\text{g}/\text{kg dw}$  for sensitive land use [27]. However, the total PAHs concentrations of all the samples exceeded the typical concentration of arable topsoil (around 200  $\mu\text{g}/\text{kg}$ ) in Sweden [28]. The target established by the Dutch government for PAHs in uncontaminated soil is 20–50  $\mu\text{g}/\text{kg dw}$  [29]. Since the PAHs concentrations in all of the soils were above 50  $\mu\text{g}/\text{kg}$ , the soils in Wenling were considered to be heavily polluted by PAHs.

Soil taken from the city centre of Luqiao, contained 7 carcinogenic PAHs at concentrations varying from 128.8 to 687.2  $\mu\text{g}/\text{kg dw}$  with a mean value of 299.3  $\mu\text{g}/\text{kg dw}$  at recycling sites [8]. It seemed that PAHs in soils from Wenling were in the same range. Further, the average level of total PAHs (718.5  $\mu\text{g}/\text{kg}$ ) was similar to that observed in the areas near burning sites (851  $\mu\text{g}/\text{kg}$ ) and a printer roller dump site (590  $\mu\text{g}/\text{kg}$ ) in Guiyu [2,26]. However, the PAHs concentrations in Wenling were higher than those obtained in other cities in southeast China, such as Nanjing (178.4  $\mu\text{g}/\text{kg}$ ), Hangzhou (300  $\mu\text{g}/\text{kg}$ ), Guangzhou (380  $\mu\text{g}/\text{kg}$ ), and Hong Kong (55  $\mu\text{g}/\text{kg}$ ) [30–33].

The PAHs profile has been commonly used as a preferable fingerprint to identify the emission source [34]. As shown in Table 3 and Fig. 2, soils near the large-scale e-waste recycling plants were dominated by low molecular weight (LMW, 2–3 rings) PAHs, accounting for 59.4–72.3% of the total concentration, which originate mainly from a petrogenic source. Higher molecular weight (HMW, 4–6 rings) PAHs could be found in soils near simple household workshops, and these accounted for more than 56% of total PAHs, implying pyrolytic sources of soil PAHs. In general, there was no significant difference between LMW PAHs and HMW PAHs in the three kinds of sampling areas ( $P > 0.05$ ) and the PAHs profile in the Wenling soil suggested both petrogenic and pyrolytic sources of

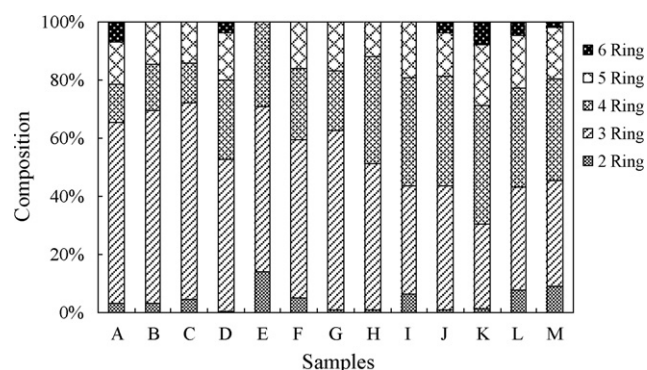
**Table 4**  
Average concentrations of PCBs in soil collected from Wenling, Taizhou ( $\mu\text{g}/\text{kg dw}$ ).

Compound	Large-scale e-waste recycling plants							Large-scale gold recovering plants		Simple household e-waste recycling workshops		
	A	B	C	D	E	F	G	H	I	J	K	L
PCB-28	34.8	0.4	3.8	48.9	8.1	1.2	1.2	1.4	19.2	113.9	667.2	105.4
PCB-52	10.4	N.D. <sup>a</sup>	0.1	9.1	N.D.	N.D.	N.D.	N.D.	3.4	38.4	225.6	37.0
PCB-101	14.6	0.3	4.1	5.4	1.9	0.5	1.1	N.D.	N.D.	14.4	215.2	24.8
PCB-118	24.5	5.9	11.6	11.9	8.0	2.0	5.9	0.6	N.D.	27.9	335.0	20.9
PCB-153	25.4	4.9	12.5	11.8	8.4	2.2	7.1	0.8	N.D.	26.2	369.8	18.3
PCB-138	17.0	3.8	9.7	7.6	6.8	2.0	6.0	0.8	N.D.	17.6	248.3	8.6
Total indicator PCBs	126.7	15.3	41.9	94.7	33.2	7.8	21.3	3.6	22.6	238.4	2061.0	215.1
Tri-PCBs	77.8	2.4	8.9	94.0	10.2	2.7	4.3	3.0	54.5	174.1	1699.1	269.0
Tetra-PCBs	80.3	12.3	19.4	68.2	11.9	12.6	15.4	15.4	44.8	158.2	1395.0	284.2
Penta-PCBs	101.2	24.8	39.3	49.2	19.8	15.9	32.5	35.1	1.6	114.0	1228.5	190.5
Hexa-PCBs	76.9	24.8	41.0	40.7	24.8	14.2	33.2	27.1	N.D.	78.5	990.9	54.5
Hepta-PCBs	28.2	13.1	14.4	13.6	7.1	6.7	11.2	4.2	1.2	27.6	476.0	27.9
Total 58 PCBs	364.3	77.4	123.0	265.7	73.8	52.0	96.5	84.7	102.2	552.3	5789.5	826.0

<sup>a</sup> Not detected.

soil PAHs. The ratios of Ant/(Ant + Phe) and Flt/(Flt + Pyr) were also calculated as a method of inferring PAHs sources [32,35]. It is suggested that the ratio of Ant/(Ant + Phe) <0.1 implies a petroleum source, and the ratio >0.1 signifies extensive combustion [30,36]. In our investigation, the ratios varied from 0.15 to 0.50 with an average value of 0.41 for Ant/(Ant + Phe), showing an extensive combustion source. Yunker et al. [37] reported that a ratio of Flt/(Flt + Pyr) <0.4 means a petroleum source, while a ratio >0.5 suggests straw and coal combustion, with an intermediate ratio (0.4–0.5) indicating liquid fossil fuel combustion. The Flt/(Flt + Pyr) ratios in our study were between 0.43 and 0.70, with an average of 0.58, suggesting that PAHs contamination of soils in Wenling was generally derived from straw and coal combustion. Therefore, it is suspected that the open burning of plastic e-waste and combustion of straw and coal used to melt circuit boards for releasing valuable chips in simple household workshops might be the main source of PAHs in Wenling city.

Soil organic matter (SOM) was determined because organic carbon is known as one of the primary factors controlling the distribution of the PAHs [38]. Average SOM for each sampling site ranged from 1.53% to 6.91% (shown in Table 1). The correlation coefficients between SOM and the total PAHs concentrations in soils were also calculated. As a whole, no correlation was found ( $R = 0.154$ ,  $P > 0.05$ ), suggesting that PAHs concentrations in Wenling soil were not significantly influenced by SOM. Other factors such as dry or wet deposition, distance to the contamination sources, land use, crop type, or soil properties might also have impacts on the PAHs level and distribution [30].



**Fig. 2.** Composition of PAH homologues in soils from e-waste recycling area in Wenling.

### 3.3. PCBs

As listed in Tables 4 and 5, the samples were analyzed for a total of 58 PCB congeners, including 6 indicator PCBs (PCB-28, -52, -101, -118, -153, -138). PCBs were detectable in all the samples with total concentrations ranging from 52.0 to 5789.5  $\mu\text{g}/\text{kg}$ , whereas the total concentrations of 6 indicator PCBs ranged from 3.6 to 2061.0  $\mu\text{g}/\text{kg}$ . With the exception of site K, the average concentration of total PCBs from e-waste recycling plants and workshops was 238.0  $\mu\text{g}/\text{kg}$ , which was much higher than that from the reference site (24.9  $\mu\text{g}/\text{kg}$ ). It is clear from Table 5 that location K was highly contaminated by PCBs. The concentrations of 6 indicator and total PCBs in five soil samples taken from this village were in the range of 397.6–347,613.0  $\mu\text{g}/\text{kg}$  and 1664.4–484,500.0  $\mu\text{g}/\text{kg}$ , respectively. Moreover, the concentrations of 6 indicator PCBs correlated very well with the total concentrations of 58 PCBs at all locations except for site K ( $R = 0.89$ ,  $P < 0.05$ ).

In China, there is no environmental standard for the concentration of PCBs in soil. Nevertheless, the concentrations of PCBs in soils from sites A, C, D were almost twice as high as the allowable level of 60  $\mu\text{g}/\text{kg}$  for PCBs in ambient soil stipulated by the former USSR Ministry of Health in 1991 [39]. However, the PCBs concentrations of the soils from some sites in Wenling did exceed the less stringent Dutch action value of 1000  $\mu\text{g}/\text{kg}$  for PCBs [24], the Australian and New Zealand ecological investigation level of 1000  $\mu\text{g}/\text{kg}$  [40], and the Canadian soil guideline for residential areas (1300  $\mu\text{g}/\text{kg}$ ) [41].

The concentrations of PCBs in the Wenling soil indicated a similar level of contamination as those of heavily polluted sites in Luqiao and Guiyu [1,2,8–11]. It seemed that PCBs pollution was also similar to that of polluted sites in other countries [42–44]. Although information from China on soil PCBs concentration has been very limited up to now, the PCBs concentrations in Wenling soil were higher than those obtained from some other areas in China, such as Beijing, Shenyang, Hong Kong, and Tibet [45,46]. Moreover, soils at the large-scale plants (sites A–I) also exhibited a notable presence of PCBs (52.0–364.3  $\mu\text{g}/\text{kg}$ ), however, this was below the highest concentration (788  $\mu\text{g}/\text{kg}$ ) detected by Chu et al. [14] in soil in the vicinity of a site of illegal trading and dismantling of PCB-containing equipment from Luqiao.

Compositions of PCBs homologues in soils from Wenling e-waste recycling area are shown in Fig. 3. In general, similar profiles of PCB congeners were observed at all plants and workshops, suggesting that PCBs must have come from similar sources. Among PCB congeners, lesser chlorinated congeners such tri-, tetra- and penta-PCBs were the most prevalent homologues, accounting for more than 50% of the total PCBs concentrations at all the locations. Fig. 3 also

**Table 5**  
Concentrations of PCBs in soil collected from TS village and reference site ( $\mu\text{g}/\text{kg dw}$ ).

Compound	Simple household e-waste recycling workshops					Reference site M
	K1	K2	K3	K4	K5	
PCB-28	1533.1	288.0	185.4	662.1	318,578.5	0.2
PCB-52	418.3	79.8	135.6	268.6	8,252.5	0.5
PCB-101	64.0	10.9	444.0	342.1	12,498.5	0.6
PCB-118	48.4	9.0	681.4	601.1	951.0	0.2
PCB-153	43.4	8.2	672.4	755.2	7,322.2	0.8
PCB-138	4.5	1.7	478.4	508.4	10.3	0.2
Total indicator PCBs	2111.7	397.6	2597.3	3137.4	347,613.0	2.6
Tri-PCBs	4282.6	952.2	472.1	1089.4	318,578.5	5.5
Tetra-PCBs	3025.9	597.8	857.1	1099.2	46,804.9	7.9
Penta-PCBs	518.1	93.4	2270.2	2032.2	109,286.8	5.7
Hexa-PCBs	79.2	14.8	1825.2	2044.5	8,977.8	4.7
Hepta-PCBs	8.4	6.2	617.7	1271.8	851.9	1.1
Total 58 PCBs	7914.1	1664.4	6042.3	7537.1	484,500.0	24.9

shows that lesser chlorinated congeners were the most prevalent homologues, accounting for 69–87% of the total PCBs concentrations in the soils from the simple household e-waste recycling workshops. There were some simple household e-waste recycling workshops dealing with the disposal of electric power capacitors or transformers which contained PCBs. Previous studies also reported the presence of lower chlorinated PCB congeners in soils collected from the vicinity of an illegal trading and dismantling site for PCB-containing equipment in this area [8–10]. It is well known that Aroclor 1242 was widely used as the dielectric medium in transformers and capacitors in the past. Therefore, it seems that the PCBs might originate from Aroclor 1242 during the recycling of electric power capacitors or transformers. However, PCBs were also suspected of being discharged from the incineration of electric wires and printed circuit boards. A study carried out in Wanli, China, a former e-waste disposal centre, also found that combustion of waste electric wires and magnetic cards could result in soil PCB contamination [47].

#### 3.4. Comparison of pollution in three e-waste recycling sites

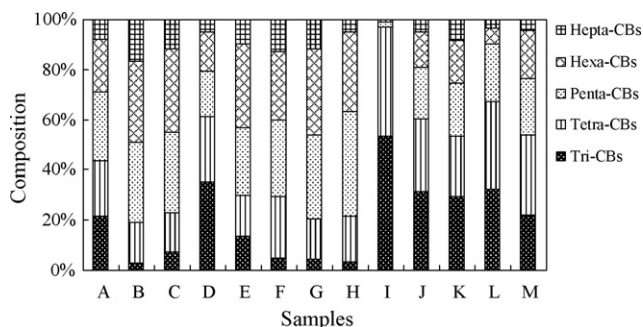
Among all the studied sites, sites K and L were most heavily polluted by heavy metals, while site J also had a higher Hg concentration as well as the same pollution levels of other heavy metals compared with sites A–I. Regarding PAHs, in comparison with sites A–I (with an average PAHs concentration of 652.6  $\mu\text{g}/\text{kg}$ ), higher PAHs concentrations were found in soils from sites J, K and L, with an average of 916.3  $\mu\text{g}/\text{kg}$ . However, there were no statistical differences in the PAHs levels ( $P > 0.05$ ). Furthermore, for the PCBs, significantly higher PCBs concentrations were found in soils from sites J, K and L compared with sites A–I ( $P < 0.05$ ). The differences in heavy metals, PAHs and PCBs between simple household workshops (sites J, K and L) and large-scale plants (sites A–I)

confirmed that simple household workshops contributed more pollution to the soil environment. The simple household workshops were downstream of the industrial chain of e-waste recycling sites and dealt with residual components of e-waste supplied by the large-scale plants [8]. However, the residue was difficult to dismantled, and more manual or crude operations were utilized, which might cause severe damage to the environment and expose the workers and local residents to more toxic chemicals [12]. Especially, in sites J, K and L, it was found that women were also involved in e-waste recycling activities and children were playing around these simple household workshops with little or no consideration to protection of health, suggesting the human health risk for these populations would be of particularly concern. However, relevant data about human exposure are still limited and further studies need to be conducted.

When comparing with the pollution levels among e-waste recycling plants (sites A–G) and gold recovering plants (sites H and I), it was found that there was no significant difference for the PAHs and PCBs ( $P > 0.05$ ). However, higher Cu, Cd, and Hg were found at site H compared with sites A–G. At this gold recovering plant, wastewater and emissions were discharged without adequate treatment. These contained high levels of heavy metals due to the gold washing techniques using water and acid, presumably contributing to the higher heavy metals in the soil around this plant. In contrast, site I had less heavy metal contamination due to better wastewater and emission treatments and management.

Moreover, according to Pearson correlation analysis, a moderately strong correlation between PAHs and PCBs ( $R = 0.682$ ,  $P < 0.05$ ) was found, with similar correlations found between PAHs and Cd ( $R = 0.626$ ,  $P < 0.05$ ), PAHs and Hg ( $R = 0.646$ ,  $P < 0.05$ ), and PCBs and Hg ( $R = 0.991$ ,  $P < 0.01$ ). The correlation analysis results suggested that these contaminants might have come from similar sources. The good correlations were also found between heavy metals (Pb, Ni, and Mn) and PAHs, and between PCBs and PAHs in soil from an industrialized urban area in Linz, Upper Austria, subsequently, a common source of soil pollution was suggested [48]. Furthermore, the high correlation also indicated that e-waste recycling activities always produced soil contamination with various compounds, which might increase the human health risk.

In summary, the comparison results of the three e-waste recycling sites indicated that simple household workshops contributed more heavy metal, PAHs and PCBs pollution to the soil environment. It has been suggested that working at the simple household workshops without any self-protection might involve more contaminants exposure and induce more adverse impacts on human health. Therefore, it is hoped that more efficient and effective actions will be taken to deal with the current e-waste recycling issues, especially for the simple household workshops. For example, the simple household workshops should be banned completely



**Fig. 3.** Composition of PCB homologues in soils from e-waste recycling area in Wenling.

and large-scale plants should be built to assure more safety and protection.

#### 4. Conclusion

Taking advantage of relatively lax environmental policies, the crude e-waste recycling activities shifted from Luqiao to Wenling, subsequently, environmental problems generated from recycling activities became more complex and serious in Wenling city. The results of the present study suggested that the soil in the Wenling area was heavily polluted by heavy metals, PAHs and PCBs caused by e-waste recycling activities. Compared with large-scale plants, simple household workshops contributed relatively more heavy metal, PAHs and PCBs pollution to the soil environment. The results might contribute to a greater awareness of the hazardous implications of current e-waste recycling, especially for e-waste recycling in simple household workshops. It is desirable to propose more efficient and effective policies, such as the abandonment of simple household workshops and the construction of large-scale plants designed for better safety and protection assurance. To further elucidate the effects of these particular e-waste activities on environmental and human health risk, detailed information about the e-waste recycling industry and assessments of human health impacts from oral intake, inhalation, and dermal contact would hopefully be investigated in future research.

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