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Publisher: Taylor & Francis

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International Journal of Environmental Health Research

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/cije20>

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Version of record first published: 21 Nov 2011.

To cite this article: Chunyang Liao, Jungang Lv, Jianjie Fu, Zongshan Zhao, Fang Liu, Qinzhaoh Xue & Guibin Jiang (2012): Occurrence and profiles of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in soils from a typical e-waste recycling area in Southeast China, International Journal of Environmental Health Research, 22:4, 317-330

To link to this article: <http://dx.doi.org/10.1080/09603123.2011.634392>

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Occurrence and profiles of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in soils from a typical e-waste recycling area in Southeast China

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(Received 5 July 2011; final version received 29 August 2011)

Surface soils collected from Taizhou, a typical e-waste recycling area in Southeast China, were analyzed for the residues of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and organochlorine pesticides (OCPs) by using microwave-assisted extraction and gas chromatography-mass spectrometry (GC-MS). The total concentrations of 16 PAHs in US EPA's priority list (Σ PAHs), six indicator PCBs (Σ PCBs), 15 OCPs widely used in China (Σ OCPs) in soils ranged from 125 to 4737 ng/g (average: 854 ng/g), from not detected to 55.4 ng/g (3.16 ng/g), and from 47.9 to 820 ng/g (276 ng/g), respectively. Individual PAHs were ubiquitously found in soil samples with detected ratio of 96% and their residual levels were comparable with those of serious polluted sites. Principal component analysis in combination with diagnostic ratios suggested that the combustion of coal, wood, and plastic wastes that are closely associated with illegal and unsafe recycling operations of e-wastes was the main source of PAHs in this area. Compared with other polluted sites, the PCBs residues in soils were generally low except for those in the major recycling site. The residual levels of OCPs in this region were also relatively higher and hexachlorocyclohexane (HCH), dichlorodiphenyltrichloroethane (DDT) and its metabolite forms including dichlorodiphenyldichloroethane (DDD) and dichlorodiphenyldichloroethylene (DDE), hexachlorobenzene (HCB), and dicofol were dominant species. The composition analysis indicated that the HCHs residues in soils might originate from the application of lindane (pure γ -HCH) and parts of DDTs possibly from the wide use of dicofol with high impurity of DDT compounds in this region.

Keywords: e-waste; soil; PAHs; PCBs; OCPs; residue

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in the environment are of great concern due to their global occurrence, toxicity and long-range transport issue (Hoh and Hites 2004; Chen et al. 2005; Carpenter 2006; Liu et al. 2008a). PAHs are a group of ubiquitous

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environmental contaminants originating from wide usage of fossil fuels and from the various combustion processes. These compounds have multiple toxicities such as mutagenic, carcinogenic and endocrine disrupting effects (WHO 1997), thus the knowledge of the fate of PAHs is of interest (Douben 2003). PCBs are a class of chlorinated compounds that include up to 209 congeners, which are mainly used in transformers, capacitors and paints (Cai et al. 2008). The chemical stability of these synthetic compounds accounts for their persistence in the environment, and PCBs can also be found almost anywhere on the Earth (Tanabe and Kunisue 2007; Cai et al. 2008). OCPs have been extensively studied in recent decades due to their large production and usage, their impact on non-target organisms, bioaccumulation, and persistence in the environment (Li and Macdonald 2005b). Although production of PCBs and many OCPs has been banned widely for many years, their residues still remain as contaminants in various environmental matrices, such as food, air, water, soil, sediments, and biological tissues (Rea 1996; Tanabe and Kunisue 2007).

Illegal and unsafe recycling operations of electronic and electric wastes (e-wastes) have caused severe environmental pollution around the recycling sites (Osibanjo and Nnorom 2007; Huo et al. 2007). About 80% of the world's e-wastes, including computers, electronic appliances and transformer carcasses, are exported to Asia, 90% of which flows into China (BAN 2002). Taizhou, located in Zhejiang province, has really become a well-known e-waste recycling centre in Southeast China, where millions of e-wastes are recycled in the illegal workshops mainly based on some simple techniques such as sorting, firing, incineration, and acidic wash (Zhao et al. 2007; Fu et al. 2008). Various contaminants including PAHs and PCBs are thus released into the ambient environment, which poses great threat to ecosystem and human health (Ma et al. 2009a; Liu et al. 2008b).

Zhejiang province is also a famous place for agricultural production in China (Van den Berg et al. 2007). Lots of OCPs such as hexachlorocyclohexane (HCH), dichlorodiphenyltrichloroethane (DDT), and hexachlorobenzene (HCB) have been widely used in this field for many years (Gao et al. 2006). Considering their adverse effects, many efforts have been made to reduce or withdraw the registered usage of OCPs, including aldrin, dieldrin, endrin, mirex, and so on. However, some OCPs such as HCH, DDT and lindane (pure γ -HCH) are still used in some countries for agricultural purposes and control of mosquitoes. For example, dicofol with high impurity of DDT compounds is widely used in cotton cultivation and has become an important source of DDT pollution in China (Qiu et al. 2005; Yang et al. 2008). Although the levels of OCPs in the environment have been considerably declined in the past 20 years, recent evidences indicate that the residues in various environmental matrices are still high (Wu et al. 1999; Nakata et al. 2002; Tao et al. 2008). This paper aims to investigate the residue levels of PAHs, PCBs and OCPs in soil samples collected from Taizhou and their contamination profiles and possible sources are also discussed.

2. Material and methods

2.1. Study area and sample collection

Twenty-nine surface soil (red soil, depth 0–20 cm, pH 6.20, organic matter contents 37.5 g/kg) samples were collected from the recycling sites and vicinity in Taizhou area (E121.2°, N28.3°) during June 2008. As shown in Figure 1, sampling site 1 is the most important recycling site in Taizhou and there is little recycling activity in site 2.



Figure 1. Map showing the study area and sampling sites.

Other sites are adjacent to sites 1 and 2. Each surface soil sample was obtained by mixing at least five adjacent sub-samples from 1 site. The samples were immediately transferred to the laboratory and frozen at -20°C until processed for analysis.

2.2. Chemicals

All solvents used were of pesticide grade (Fisher, Germany). The standard with 16 individual PAHs (EPA M-610, 0.1 mg/mL in methanol:dichloromethane (1:1, v/v)) containing naphthalene (Nap), acenaphthylene (Acpy), fluorene (Flu), acenaphthene (Acp), phenanthrene (Pa), anthracene (Ant), fluoranthene (Fl), pyrene (Pyr), benz(a)anthracene (Baa), chrysene (Chr), benzo(b)fluoranthene (Bbf), benzo(k)fluoranthene (Bkf), benzo(a)pyrene (Bap), indeno(1,2,3-cd)pyrene (Ind), dibenz(a,h)anthracene (Dba), and benzo(g,h,i)perylene (Bghip) and the deuterated surrogate standards (EPA M-525-IS, 2.0 mg/mL in acetone) containing d10-acenaphthylene, d12-chrysene, d12-perylene and d10-phenanthrene were purchased from Accustandard Inc. (CT, USA). The standard with six indicator PCB individuals (10 $\mu\text{g}/\text{mL}$ in cyclohexane) containing PCB-28, PCB-52, PCB-101, PCB-138, PCB-153, and PCB-180 was from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The single standards of OCPs (1000 mg/L, in acetone or methanol), kind gifts from Institute of

Environmental Protection and Monitoring, Minister of Agriculture, China, were mixed into one mixture standard at 10 $\mu\text{g}/\text{mL}$ before use. Working solutions were prepared by diluting the standard solutions with dichloromethane.

2.3. Sample pretreatment and analysis

Soil samples were homogenized, freeze-dried, and sieved by a 63- μm sieve before extraction. About 2 g of soil was weighed and spiked with 5 ng of surrogates. Soils were extracted with 10 mL acetone: *n*-hexane (1:1, v/v) in a Mars Xpress laboratory microwave extraction system (CEM, Matthews, NC, USA) at 50% of the microwave power (600 W) for 30 min. The extraction procedure was subsequently repeated twice. Extracts were then reduced to around 1–2 mL under gentle nitrogen gas stream. The concentrated extracts were cleaned by passing through a SPE cartridge (*Oasis* HLB 200 mg/6 cc, Waters, Millford, MA, USA) pre-conditioned with about 10 mL acetone: *n*-hexane (1:1, v/v). The analytes were eluted by approximate 12 mL acetone: *n*-hexane (1:1, v/v). The combined effluents were concentrated to near dryness again under gentle nitrogen gas stream, and then made up to 0.5 mL with hexane before being injected into GC–MS.

GC–MS analysis was performed by using an Agilent 6890N gas chromatography coupled with an Agilent 5973N mass spectrometer with electron impact (EI) ion source (Agilent Technologies, Wilmington, DE, USA). On-line data collection and processing were accomplished in a HP Chemstation interface (Agilent) with relative response factors following previously published method with minor modification (Song et al. 2007). A DB-5MS fused silica capillary column (30 m \times 0.25 mm i.d., 0.25 μm film thickness; J&W Scientific, Folsom, CA, USA) was used for separation with high-purity helium (99.999%) as the carrier gas at flow rate of 1.0 mL/min. Injections of 2 μL were performed in splitless mode by using a 7673 auto sampler (Agilent). The electron emission energy was set at 70 eV. The source temperature and quadrupole were set at 230 and 150°C, respectively. The oven temperature program was 60°C held for 2 min, ramped to 200°C at 19°C/min, held for 2 min, then to 240°C at 4.5°C/min, held for 2 min and finally to 290°C at 2.5°C/min, held for 2 min.

2.4. Quality control and assurance (QC/QA)

All the equipments used for sample collection, transportation, and preparation were rinsed with acetone and hexane before use. For every batch of 10 samples, a procedural blank was run to check for interference and cross-contamination, and a spiked sample with standards was run to check for the recovery of method. Three PAHs containing Nap, Pa, and Fl were the most prevalent contaminants in the blanks for the analysis of PAHs. The three PAHs contributed much less (<5%) to the corresponding concentrations detected in the soil samples and were thus subtracted. All of the samples were spiked with the deuterated PAHs as surrogates to monitor the recoveries of the method. The inlet degradation of DDT was <15% as daily checked. The method detection limits (MDLs), defined as three times the signal to noise ratio (S/N), ranged from 0.17 ng/g (Pa) to 4.68 ng/g (Dba) for PAHs, from 0.15 ng/g (PCB-101) to 0.20 ng/g (PCB-153) for PCBs, and from 0.01 ng/g (Atrazine) to 0.06 ng/g (δ -HCH) for OCPs. The spiked recoveries were in the range of 72–124% for PAHs, 92–127% for PCBs, and 70–139% for OCPs and the relative standard derivation (RSD, $n = 5$) values were all less than 10%. The recoveries of

surrogates were in the range of 61–106% (average: 80%), 66–108% (84%), 62–103% (71%), and 61–118% (84%) for d10-acenaphthylene, d12-chrysene, d12-perylene, and d10-phenanthrene, respectively. Quantification was done by the isotope-dilution method based on the responses of surrogates spiked into each soil sample. Instrumental calibration was verified by injecting 2 μ L of 0.01, 0.02, 0.05, 0.1, 0.5, 1, 5, and 10 ng/mL standards at the beginning of analysis of every batch of 10 samples. The regression coefficient (r) of the calibration curve was >0.99 .

3. Results and discussion

All the concentrations were expressed as ng/g based on a dry weight basis.

3.1. Concentration profiles and potential sources of PAHs

Sixteen PAHs listed by US Environmental Protection Agency (US EPA) as priority pollutants were examined in this study. The concentrations of PAHs in surface soils were summarized in Table 1 and the percentages of different individual PAHs were shown in Figure 2a. Individual PAHs were widely found in 29 soil samples (collected from 25 sites) with the detected ratio of 96% and the dominant species among the 16 PAHs were Pa, Fl, Ind, DbA, and BghiP with the concentrations ranging 33.0–273 (average: 120), 14.3–326 (82.5), 1.50–791 (102), 1.08–689 (89.0), and 1.19–734 (92.7) ng/g, which made up in average 20%, 11%, 9.5%, 8.0%, and 8.7% of the total concentrations of PAHs (Σ PAHs), respectively. There appeared no obvious differences in the composition patterns of PAHs in different sampling sites (Figure 2a), which might suggest the similar contamination sources. The soil Σ PAHs concentrations ranged from 125 ng/g (site 6) to 4737 ng/g (site 17) with an average of 854 ng/g (Figure 3a). This average value of Σ PAHs was comparable with those of serious polluted sites, e.g. 814 ng/g in Tianjing (a city with abundant industries and agricultures in Northern China; Jiao et al. 2009), and largely higher than those of adjacent area, e.g. 350 ng/g in the sites along Qiantang River basin in Zhejiang province (Zhu et al. 2008) and 33.2 ng/g in a valley in the Yangtze Delta region (Xing et al. 2006). Maliszewska-Kordybach (1996) proposed a classification of soil contamination as non-contaminated soil (<200 ng/g), weakly contaminated soil (200–600 ng/g), contaminated soil (600–1000 ng/g), and heavily contaminated soil (>1000 ng/g). According to this classification, 19 out of 29 sites can be classified as contaminated, five sites as heavily contaminated, and only three sites as non-contaminated. This indicates that the soils collected from the e-waste recycling sites and vicinity in Taizhou area were heavily polluted by PAHs.

PAHs originate from both the natural sources such as volcanic eruptions, plant emissions and forest fires, and anthropogenic sources that are mostly from the combustion of carbonaceous materials such as coals, gasoline, diesel and other fuels (Kavouras et al. 2001). Principal component analysis (PCA), a multivariate analytical tool, has been effectively used for source apportionment of PAHs in various environmental matrices (Larsen and Baker, 2003). In this study, PCA extracted two principal components (PCs) with Eigenvalues greater than one, which accounted for 86% of the total variability in the original data (Table 2). Explaining 70% of the total variance, PC1 is positively characterized by high molecular weight (greater than four fused rings, HMW) PAHs such as Fl, Pyr, Baa, Bbf, Bap, Ind, DbA, BghiP, etc. HMW PAHs were reported as representative of pyrogenic sources,

Table 1. PAHs, PCBs and OCPs residues in surface soils (ng/g).

No.	Compounds	Sites																														
		1	2	3	4-1	4-2	5	6	7	8	9	10	11-1	11-2	12	13	14-1	14-2	15	16	17	18	19	20	21	22	23-1	23-2	24	25		
1	Nap	35.5	56.6	37.4	59.0	64.6	5.07	17.9	22.0	28.5	26.3	54.6	17.7	32.4	69.8	55.1	38.7	24.9	20.2	7.49	30.8	27.8	57.3	30.2	40.5	36.8	56.8	49.0	49.0			
2	Acpy	6.99			7.97				9.98		31.5	31.7	38.9	7.25			7.06	7.41	5.06	13.6							7.99	7.56	7.56			
3	Flu	1.79	41.6	40.2	46.8	41.1	23.5						2.19	11.0	9.49	37.0	33.4	23.1	0.45	39.0	45.4	4.23	14.8	30.3	30.4	32.0	35.4	1.63	41.1			
4	Acp	9.63	6.70		5.62	2.40	1.17		3.77					3.13	3.13	3.78	3.46	2.81		4.48				2.01	3.60	4.39	4.41	1.27	5.30			
5	Pa	116	158	149	208	164	94.4	33.0	125	17.0	113	146	33.1	83.8	114	92.5	152	105	80.0	78.7	273	151	64.6	61.1	132	125	129	139	37.2	142		
6	Ant	4.61	10.6	7.28	9.41	12.6	9.31	0.40	8.29	8.30	6.66	18.0	3.76	5.90	6.15	6.33	13.1	6.14	3.65	13.6	57.9	8.30	4.08	2.94	12.6	6.31	10.0	9.16	1.57	9.37		
7	Fl	142	84.7	71.8	124	83.2	17.9	14.3	125	137	47.6	142	37.7	62.5	98.3	49.8	102	25.7	17.3	166	326	28.0	31.6	20.0	99.8	93.2	85.9	74.5	30.0	53.4		
8	Pyr	63.0	51.6	36.7	57.3	44.9	11.6	6.73	60.2	57.8	34.7	111	28.3	39.1	50.4	35.2	84.9	16.4	11.1	139	259	17.9	20.7	71.3	78.2	37.7	47.0	40.5	13.1	40.0		
9	Baa	28.9	26.4	21.4	24.4	21.0	2.02	1.94	22.4	24.5	16.7	120	14.1	18.8	22.9	30.5	57.3	5.84	3.65	108	273	4.46	15.3	0.86	68.0	23.6	31.4	26.2	5.85	30.5		
10	Chr	76.2	46.1	37.9	48.6	46.0	2.83	4.46	40.7	51.3	22.7	108	13.6	34.8	50.5	26.8	60.3	10.3	8.13	127	210	7.24	17.1	4.97	69.1	60.1	46.3	45.1	15.4	45.2		
11	Bbf	103	67.5	51.9	57.9	64.0	6.54	12.8	61.3	62.0	46.4	199	27.7	55.5	79.8	58.5	102	20.2	18.8	129	370	18.2	34.5	5.89	109	76.2	84.6	71.1	12.4	71.3		
12	Bkf	56.8	41.2	29.1	30.5	32.7	4.02	6.07	35.8	30.5	31.9	151	18.0	30.1	41.5	39.1	68.7	10.4	7.41	124	295	10.6	23.0	2.83	85.0	37.5	47.6	37.2	8.41	45.1		
13	Bap	24.6	32.4	30.3	14.9	22.9		3.37	21.2	17.5	26.5	169	19.5	22.9	19.9	40.2	78.5	8.44		8.32	111	399	8.21	24.1	1.22	85.9	27.7	45.7	33.3	3.89	38.2	
14	Ind	107	78.8	72.3	37.8	68.3	10.1	7.01	53.9	37.1	67.9	396	34.5	66.6	69.0	73.0	158	23.0	21.9	88.8	791	24.7	52.7	1.50	195	82.1	116	90.8	4.94	125		
15	Dba	98.1	71.9	70.2	33.0	61.8	8.89	9.29	49.4	39.9	53.3	326	30.4	57.8	67.5	72.3	116	19.1	23.6	15.9	689	14.8	38.4		213	66.1	94.0	68.9	1.08	82.6		
16	Bghi-p	81.0	70.9	71.3	32.2	63.7	14.8	6.32	43.0	30.1	61.1	359	40.4	63.8	55.5	56.6	150	23.0	23.0	91.4	734	20.5	45.3	1.19	185	70.3	96.0	77.8	3.92	116		
17	PCB-28	15.0					0.72	4.29									0.62	0.92	0.93	3.25				2.99						0.47		
18	PCB-52	6.46					0.48	0.31	1.54	0.78	0.73						0.49	0.62	0.43	0.74												
19	PCB-101	11.1																		0.86												
20	PCB-138	7.84	0.63	0.28	0.29	0.49			0.98	0.53			0.21	0.23	0.51				0.50						0.32	0.60	0.35	0.20	0.29			
21	PCB-153	12.1	0.66	0.29	0.38	0.65			1.60	0.69			0.29	0.29	0.45	0.49			0.26						0.40	0.84	0.51	0.36	0.32			
22	PCB-180	2.96							0.51	0.39						0.56									0.32							
23	α -HCH			1.84					1.02	1.94				1.59			1.05															
24	γ -HCH	49.1	44.8	33.9	40.9	46.3	38.9	15.8	27.2	39.4	41.7	37.8	17.8	41.1	24.0	69.4	42.1	39.7	46.0	21.0	31.6	742	19.2	38.0	43.1	53.1	51.4	44.9	35.2	48.4		
25	δ -HCH															13.0																
26	α , p' -DDE	0.68	0.76	0.74	1.67	0.61			0.88	4.63		5.39		0.58	4.01	1.70	1.42	1.00		0.28	0.80			10.9	0.72						0.53	
27	p , p' -DDE	14.3	12.3	14.9	24.5	21.6	0.83	2.78	17.7	69.8	71.6	35.4	2.96	6.40	24.9	25.4	49.4	13.2	9.74	8.99	13.5	16.4	2.30	7.39	8.86	12.7	7.36	14.3	9.07	5.58		
28	α , p' -DDD	5.56	4.45	4.14	12.5	5.74			0.53	10.8	37.4	1.15	5.25	1.20	2.03	9.33	3.35	10.1	6.45	0.83	2.48	6.53	1.50	1.11	1.99	4.31	4.20	2.57	3.81	1.19		
29	p , p' -DDD								4.05																							
30	α , p' -DDT	11.2	13.1	14.8	42.9	22.1	1.05	1.42	24.1	129	7.46	9.65	2.20	4.20	38.3	3.19	48.5	14.7	2.62	5.72	17.1	6.89	1.69	29.2	2.92	16.0	11.1	6.66	118	4.43		
31	p , p' -DDT				11.2							23.8					16.1							3.87	26.8	25.9	15.0	15.1	89.3	89.3		
32	Hexachlorobenzene	2.35	3.13	5.55	4.07	2.41	0.95	1.43	3.02	3.13	3.39	3.11	4.66	6.63	2.54	4.83	11.9	2.25	2.33	2.15	1.89	3.15	1.89	0.77	3.37	8.28	2.08	4.16	0.83	9.47		
33	Atrazine	7.56			7.67	47.0			2.57	2.83	2.43	61.4		6.04	36.8					2.83	5.98			73.3	4.07	55.2	11.5	88.6		25.4		
34	Heptachlor				1.50	1.55	2.10	1.15	1.18	3.82		1.15	1.22	1.97	0.82	1.37	1.34	1.46		1.10			1.73	0.95			2.01	2.74	1.70	7.38	1.60	
35	Dicofol	78.1	67.4	125	259	162			12.0	184	497	33.9	276	10.4	95.0	259	102	230	145	30.2	27.7	143	29.0	10.6	136	90.5	66.2	54.1	44.9	36.6		
36	Endosulfan	30.8	23.1	43.4	12.7		30.0	10.2	47.6	20.0	23.8		20.3	32.5	18.1		21.9	137	15.0			22.7	18.8	65.1	0.63	50.9	106	15.2	61.6			
37	Chlorobenzilate	3.42	3.10		3.86				4.20			6.08		5.28	3.77							5.10		7.86	6.41	6.08					1.58	

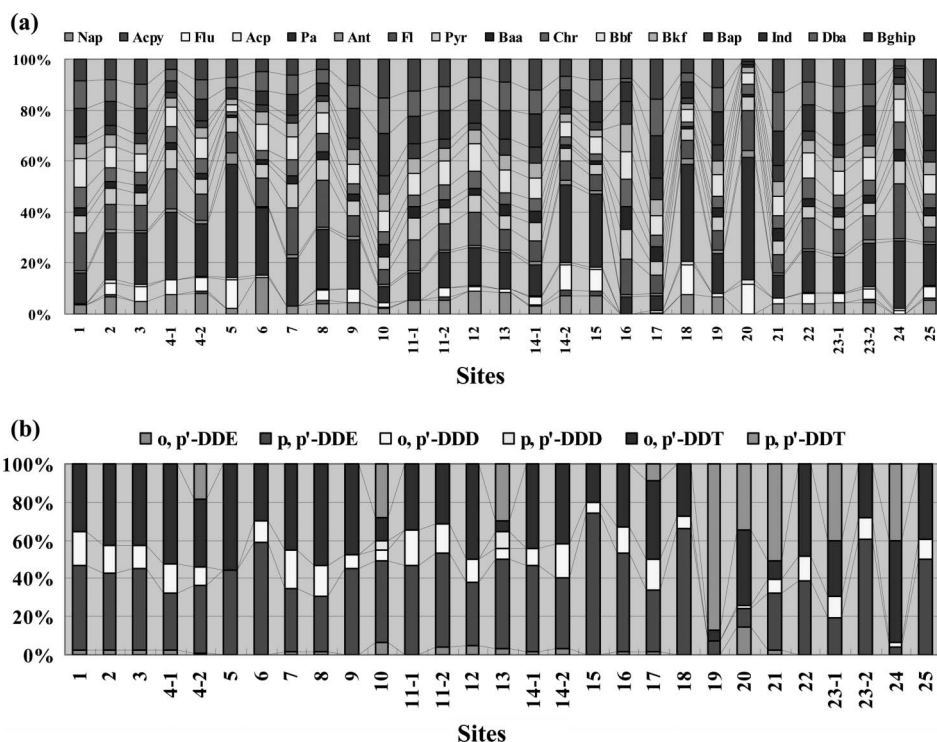


Figure 2. Composition patterns of PAHs (a) and DDTs (b) in the surface soils.

which derived from combustion of wood, grass, coal, gasoline, diesel, and other fuel (Khalili et al. 1995). The study area has been known as an important e-waste recycling site in China and coal combustion was usually used to recycle various metals and the chips of circuit boards. The incomplete combustion of plastic wastes in the vicinity of recycling workshops also accounts for the PAHs emissions (Yu et al. 2006). Furthermore, wood and grass were burned in this suburban area for daily cooking and charcoal for heating during winters. Among these individual PAHs, Pyr, Chr, Bkf, and Dbu are generally associated with vehicular emissions that may derive from the popular motorcycles in this area (Khalili et al. 1995). Explaining 15% of the total variance, PC2 is positively characterized by low molecular weight (2–3 fused rings, LMW) PAHs such as Nap, Flu, Acp. LMW PAHs are commonly associated with unburned and residual fossil fuels (namely petrogenic sources; de Abrantes et al. 2004). There are many factories in this area and diesel truck is common as well. Therefore the diesel truck may be a contributor to the PAH levels in the soil samples. Taken together, the PCA results suggested that the combustion of coal, wood, and plastic wastes that are closely associated with illegal and unsafe recycling operations of e-wastes is the main sources of PAHs in this area. In addition, the vehicular emissions, including motorcycle and diesel truck emissions, also contributed to the PAHs contamination in some extent.

The diagnostic ratios of $Fl/(Fl + Pyr)$, $Baa/(Baa + Chr)$, and HMW to LMW PAHs (Yunker et al. 1999, 2002; Soclo et al. 2000), were further used to identify the possible sources of PAHs in soils (Table 3). The ratios of $Fl/(Fl + Pyr)$ ranged from 0.55 to 0.74 with an average of 0.63. These values are all within the typical range for

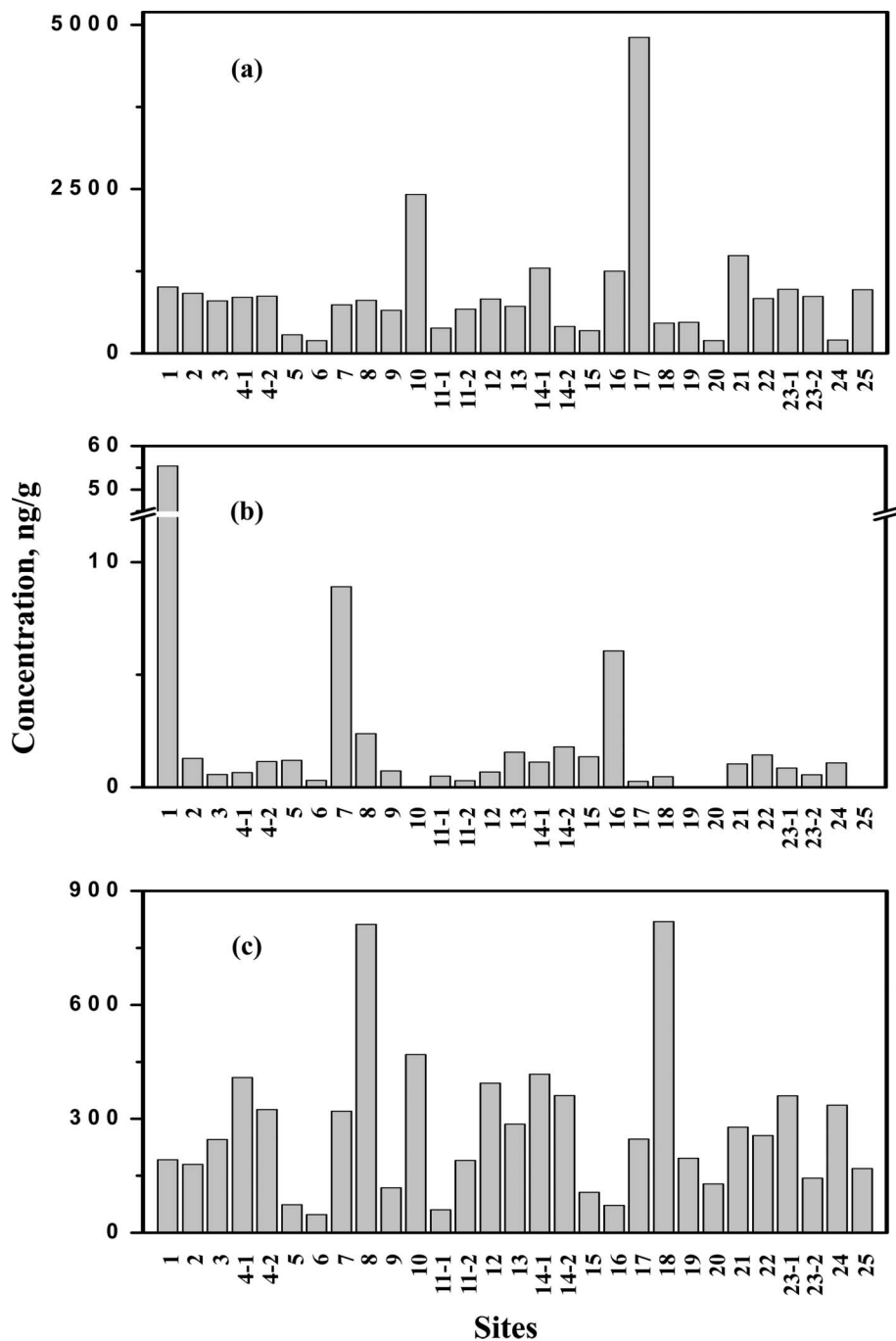


Figure 3. The distribution of Σ PAHs (a), Σ PCBs (b), and Σ OCs (c) in different sites.

combustion-derived products. Nineteen out of 29 ratio (66%) of Baa/(Baa + Chr) and 25 out of 29 ratio (86%) of HMW to LMW PAHs fell into the ranges which are characteristic of combustion, suggesting that pyrogenic sources especially coal

Table 2. Component loadings of PAHs in soil samples.

PAHs	PC1	PC2
Nap	0.047	0.680
Acpy	0.606	0.443
Flu	0.336	0.843
Acp	-0.021	0.832
Pa	0.723	0.530
Ant	0.963	-0.003
Fl	0.908	-0.088
Pyr	0.963	-0.153
Baa	0.977	-0.169
Chr	0.943	-0.110
Bbf	0.987	-0.061
Bkf	0.980	-0.146
Bap	0.975	-0.145
Ind	0.973	-0.040
DbA	0.956	-0.024
Bghip	0.973	-0.045
Eigenvalue	11.224	2.464
% Variance explained	70.149	15.399

Table 3. Diagnostic ratios of PAHs.

Ratio	Characteristic ratio of coal combustion	Average	Range	Percentage (%)
Fl/(Fl + Pyr)	> 0.5	0.628	0.545-0.737	100
Baa/(Baa + Chr)	> 0.35	0.383	0.147-0.565	65.5
HMW/LMW	> 1	3.255	0.564-11.866	86.2

combustion are the major sources of PAHs in soils. The source apportionment of PAHs contamination by diagnostic ratios further confirmed the result of PCA as mentioned above.

3.2. Concentration profiles of PCBs

Six indicator PCBs including PCB-28, PCB-52, PCB-101, PCB-138, PCB-153, and PCB-180 were analyzed for evaluating the contamination status of PCBs in Taizhou area. Soil concentrations of individual PCBs were in the range from 0.20 to 15.0 ng/g with an average of 1.48 ng/g (Table 1). Unlike PAHs, few PCBs were found in the soil samples and the detected ratio was just 36%. The concentrations with two orders of magnitude variation (average: 1.48 ng/g) found in this work were far lower than those found in heavily contaminated sites, e.g. 100 ng/g in industrial area in France (Motelay-Massei et al. 2004), comparable with those found in lightly contaminated sites, e.g. 4.0 ng/g in UK (Lead et al. 1997) and 1.63 ng/g in Harbin (one of major industrial cities in Northeast China, Ma et al. 2009b), and a little higher than those found in background sites, e.g. 0.42 ng/g in Huairou, Beijing (the capital of China where most of industries have been transferred to other cities, Chu et al. 1999). The total concentrations of six indicator PCBs (Σ PCBs) varied from site to site and the

highest value (55.4 ng/g) was found in the major disposal site (Site 1 in this study, Figure 3b). Release from the waste transformers might account for the relatively serious pollution in this site where we observed that many transformer carcasses were randomly deposited in open fields when we sampled in this area. In general, the soils in Taizhou area were slightly polluted by PCBs.

3.3. Concentration profiles and potential sources of OCPs

Fifteen OCPs that have been widely used in China were investigated and the individual concentrations were summarized in Table 1. The dominant OCPs were γ -HCH (detected ratio: 100%), *p*, *p'*-DDE (100%), *o*, *p'*-DDD (93.1%), *o*, *p'*-DDT (100%), HCB (100%), and dicofol (93%), with the concentrations ranging 15.8–742 (average: 62.9), 0.83–69.8 (15.9), 0.53–37.4 (5.57), 1.05–129 (21.0), 0.77–11.9 (3.65), 10.4–497 (119) ng/g, respectively. Other OCPs, including atrazine, heptachlor, endosulfan, and chlorobenzilate, were also frequently detected with relatively high residual levels in soil samples in this area (Table 1). According to Figure 3c, we could find that the total concentrations of 15 OCPs (Σ OCPs) in the surface soils varied with approximately an order of magnitude among sampling locations and the highest Σ OCPs concentration (820 ng/g) was detected at site 18. The total concentrations of HCHs (Σ HCHs) including α -HCH, γ -HCH and δ -HCH, and DDTs (Σ DDTs) including DDT, its metabolites DDD and DDE were in the range of 15.8–742 ng/g with an average 63.7 ng/g and 1.88–240 ng/g with an average 51.5 ng/g, respectively. The residual levels of Σ HCHs and Σ DDTs found here were lower than those found in heavily polluted area, e.g. 387–4689 ng/g (Σ HCHs) and 628–2841 ng/g (Σ DDTs) in outskirts sewage-irrigated soils in Tianjin of China (Gong et al. 2002), were comparable with those (122–638 and 13–238 ng/g) in paddy soils in Dehradun of India (Babu et al. 2003), and were much higher than those found in adjacent area, e.g. 0–3.4 and 0–5.3 ng/g in paddy soils in Taihu Lake region of Jiangsu province of China (Feng et al. 2003). The frequent detection and relatively high concentrations of these toxic OCPs in surface soils indicate that the usage of OCPs still poses threat to the local ecosystem and human health and close attention should be paid to OCPs residues in Taizhou soils.

China is the second largest pesticides producer in the world and HCHs and DDTs were the most extensively used OCPs in China for several decades (Zhou et al. 2001). Although the government has banned their production since 1983, lindane (pure γ -HCH) and DDTs have still been used in lower amounts to control certain insects in China (UNEP Regional Report, 2002), which would impact the ecosystems for years to come. Composition profiles of HCH isomers and DDT congeners in the environment samples have been widely used to appoint the latent contamination sources (Doong et al. 2002). Technical HCHs are usually composed of 55–80% α -, 5–14% β -, 8–15% γ -, and 2–16% δ -isomers, respectively (Yang et al. 2005). Frequent detection in environmental samples generally suggests recent applications of technical HCHs (Doong et al. 2002). In the present study, HCH isomer compositions varied with the sites (Table 1): γ -isomer was the dominant species (detected ratio: 100%), few α - and δ -isomers were detected and no β -isomer was detected in soil samples from this area. These results indicated that there is no recent application of technical HCHs while lindane (pure γ -HCH) may still be used in Taizhou region.

Technical DDTs are usually composed of 75% *p*, *p'*-DDT, 15% *o*, *p'*-DDT, 5% *p*, *p'*-DDE, and < 5% others (Yang et al. 2007). DDT can be biodegraded to DDE

by soil microorganisms under aerobic conditions and to DDD under anaerobic conditions, and thus it is expected that the concentration of DDE is generally higher than that of DDD in surface soils (Doong et al. 2002). In this study, DDE, including *o*, *p'*-DDE and *p*, *p'*-DDE, was more frequently found in surface soil samples (detected ratio: 81%) than DDD including *o*, *p'*-DDD and *p*, *p'*-DDD (50%), and the average value (10.6 ng/g) of DDE was also higher than that (5.49 ng/g) of DDD, which was consistent of the above speculation. As shown in Figure 2b, the most abundant congeners were *p*, *p'*-DDE and *o*, *p'*-DDD (detected ratios were both 100%) accounting for around 40% and 36% of the Σ DDTs, followed by *p*, *p'*-DDT and *o*, *p'*-DDD accounting for around 13% and 11% of the Σ DDTs, respectively. The ratio of (DDE + DDD)/ Σ DDT > 0.5 can be thought to be subjected to a long-term weathering (Hites and Day 1992) and here the ratio ranged from 0.06 to 0.80 with an average 0.53 in the surface soils, which suggested that the degradation occurred significantly in this area. The ratio of DDT/(DDE + DDD) was in the range 0.25–15.5 with an average of 1.80. Since the production and usage of DDT and HCH in China were officially banned in 1983, the high residual levels of Σ DDT and the high percentage of DDT indicated the possible fresh input of DDT into the soils in Taizhou area (Li et al. 2005a). Dicofol, an acaricide widespread in use, with high impurity of DDT compounds (approximately 15%) is widely used for the control of mites in cottons, fruit trees and flowers and is suspected to become a new source of DDT pollution in China (Qiu et al. 2005; Yang et al. 2008). In the present study, the dicofol was widely found in soil samples with detected ratio of 93% (Table 1) and accordingly, parts of DDTs in soils possibly originated from the use of dicofol.

Conclusion

This study investigated the contamination status of PAHs, PCBs and OCPs in surface soil from an e-waste recycling area in southeast of China. The results show that PAHs exist widely in this area and the irregular recycling activity of e-waste may be the main contamination source. PCBs residues in soils are at low levels as compared with other polluted sites. Widespread occurrence of OCPs in this area is mainly due to the usage in agricultural production and HCH, DDT and its metabolites including DDD and DDE, and HCB are the dominant species. The composition analysis indicates that lindane (pure γ -HCH) may still be used and parts of DDTs in soils possibly originated from the use of dicofol in this area.

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