



## The major components of particles emitted during recycling of waste printed circuit boards in a typical e-waste workshop of South China

Xinhui Bi<sup>a,\*</sup>, Bernd R.T. Simoneit<sup>b,c</sup>, ZhenZhen Wang<sup>a</sup>, Xinming Wang<sup>a</sup>, Guoying Sheng<sup>a</sup>, Jiamo Fu<sup>a</sup>

<sup>a</sup>State Key Laboratory of Organic Geochemistry, Guangdong Key Laboratory of Environment and Resources, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, PR China

<sup>b</sup>COGER, King Saud University, 11451 Riyadh, Saudi Arabia

<sup>c</sup>Department of Chemistry, Oregon State University, Corvallis, OR 97331, USA

### ARTICLE INFO

#### Article history:

Received 25 March 2010

Received in revised form

21 July 2010

Accepted 21 July 2010

#### Keywords:

Printed circuit board

Triphenyl phosphite

Flame retardants

Molecular marker

Bisphenol A

Electronic waste

Particulate matter

Indoor air

China

### ABSTRACT

Electronic waste from across the world is dismantled and disposed of in China. The low-tech recycling methods have caused severe air pollution. Air particle samples from a typical workshop of South China engaged in recycling waste printed circuit boards have been analyzed with respect to chemical constituents. This is the first report on the chemical composition of particulate matter (PM) emitted in an e-waste recycling workshop of South China. The results show that the composition of PM from this recycling process was totally different from other emission sources. Organic matter comprised 46.7–51.6% of the PM. The major organic constituents were organophosphates consisting mainly of triphenyl phosphite (TPP) and its methyl substituted compounds, methyl esters of hexadecanoic and octadecanoic acids, levoglucosan and bisphenol A. TPP and bisphenol A were present at 1–5 orders of magnitude higher than in other indoor and outdoor environments throughout the world, which implies that they might be used as potential markers for e-waste recycling. The elemental carbon, inorganic elements and ions had a minor contribution to the PM (<5% each). The inorganic elements were dominated by phosphorus and followed by crustal elements and metal elements Pb, Zn, Sn, and lesser Cu, Sb, Mn, Ni, Ba and Cd. The recycling of printed circuit boards was demonstrated as an important contributor of heavy metal contamination, particularly Cd, Pb and Ni, to the local environment. These findings suggest that this recycling method represents a strong source of PM associated with pollutants to the ambient atmosphere of an e-waste recycling locale.

© 2010 Elsevier Ltd. All rights reserved.

### 1. Introduction

The electronics industry is the world's largest and fastest growing manufacturing sector, and as a consequence of this growth, electrical and electronic waste (e-waste), such as computers, printers, mobile phones, television sets, stereos, radios, etc., is generated in large quantities around the world. E-waste is becoming a major environmental concern, particularly in China, where most e-waste produced worldwide is imported illegally for "recycling". A cottage industry sector (i.e., family-run workshops) plays an important role in recycling of e-wastes. The current recycling system in China has caused significant harm to the environment and public health (Bi et al., 2007; Leung et al., 2007; Wong et al., 2007a,b; Li et al., 2008), partly because many electronic products contain hazardous materials or parts and they are

recycled using primitive methods without facilities to control or decrease pollutant emissions. In the previous studies, researchers paid much attention to several potential carcinogenic and hazardous substances such as toxic metals (e.g. mercury (Hg), lead (Pb), copper (Cu), chromium (Cr) and cadmium (Cd)), persistent organic pollutants (POPs, e.g. polychlorinated biphenyls, polychlorinated dibenzo-*p*-dioxins and dibenzofurans, polycyclic aromatic hydrocarbons and polybrominated diphenyl ethers) and estrogenic compounds (Deng et al., 2006; Leung et al., 2007, 2008; Chen et al., 2009; Li et al., 2009). However, it is important to characterize the particulate matter (PM) emitted from e-waste recycling in order to distinguish its contribution to atmospheric pollution and to determine the influence on nearby regions.

Printed circuit boards are the essential part of almost all electrical and electronic equipment systems. They usually contain various metals such as Cu, iron (Fe), Pb, zinc (Zn), gold (Au), silver (Ag), platinum (Pt), etc. (Gullett et al., 2007). The organic part in printed circuit boards is mainly thermoplastic with contents of flame retardants. It is not easy to recycle printed circuit boards.

\* Corresponding author. Tel.: +86 20 85290195; fax: +86 20 85290192.  
E-mail address: [bixh@gig.ac.cn](mailto:bixh@gig.ac.cn) (X. Bi).

Currently in South China, some primitive recycling methods are used because of low cost and easy operation. Printed circuit boards are disassembled manually from waste equipment, and then sent to small workshops, where reusable electronic components are removed from the boards by heating over a grill on a stove burning honeycombed coal briquettes or by an electrothermal machine, and sold as second-hand goods. During this 'roasting' process, plenty of organic chemicals as well as heavy metals, POPs and flame retardants can be released into the smoke. Particle inhalation would thus seem to be an important route of exposure for the workers. It is therefore necessary to identify the components in smoke emissions in order to provide data for determining human exposure levels to airborne pollutants and for modeling regional air quality.

Chemical signatures of emission sources have been utilized to distinguish specific input from point sources. The emissions for various sources have been characterized, as for example for coal smoke (Oros and Simoneit, 2000; Simoneit et al., 2007), biomass burning (Oros and Simoneit, 2001a,b; Oros et al., 2006; Medeiros and Simoneit, 2008), petroleum-based fuels (Rogge et al., 1993a,b), burning of municipal refuse (Simoneit et al., 2005), and soil resuspension (Simoneit et al., 2004a). We could find no previously published study that reported the chemical composition of PM from the recycling of printed circuit boards in China. However, reports by Owens et al. (2007) and Stewart and Lemieux (2003) described the behavior of estrogenic compounds and metals during the controlled incineration of circuit boards. The aim of the present study is to characterize the chemical composition of air PM from a workshop that recycles printed circuit boards. The results include total suspended particles, organic and elemental carbon, ionic species, elemental species, and specific organic compounds. The composition data of PM are important for understanding the chemical component contribution from recycling of printed circuit boards to atmospheric chemistry, and complement the existing data in atmospheric source apportionment studies. This information is also important for understanding the public health risk of such recycling. The purpose is: (1) to characterize the chemical composition of PM from recycling of printed circuit boards; and (2) to find key tracer compounds for emissions from such recycling. In addition, the PM samples were also analyzed to determine if they contain toxic halogenated organic pollutants but that characterization will be presented in a separate publication.

## 2. Experimental section

### 2.1. Sampling site

The total suspended particle (TSP) samples were collected in a typical workshop (23.324 N, 116.367E) for recycling of printed circuit boards in Guiyu town, Shantou City, Guangdong Province, with a total area of 52 km<sup>2</sup> and a population of 150,000. Particle samples were collected during the course of four working days while the workers were removing electronic components from circuit boards by heating over grills on stoves burning honeycombed coal briquettes. In this workshop, there were 24 stoves along the sides of three walls and about five tons of waste printed circuit boards near the other wall. The sampler was placed close to the middle stove, about 1.5 m away from the side of one worker so not to hinder him in his work. Eight employees were working in the area. Sampling was carried out in September, 2007, with an average ambient temperature and relative humidity of 27.0 ± 1.2 °C and 83.5 ± 7.4%, respectively, during the sampling interval.

All PM samples were collected on quartz fiber filters (annealed at 600 °C for 4 h to remove residual carbon levels associated with new filters, exposed filter area = 18 × 22 cm<sup>2</sup>) using a high volume air sampler. Prior to use, the sampler was rinsed with dichloromethane

(DCM). The flow rate was 250–278 L min<sup>-1</sup> and sampling periods lasted for 8–10 h.

### 2.2. Organic analysis

The analytical procedure is given elsewhere (Simoneit et al., 2004b) but a brief summary follows. The samples of filter aliquots (1/10) were sonicated twice for 15 min each with DCM/methanol (2:1, v:v). The solvent extract was filtered and concentrated by use of a rotary evaporator and then under blow-down with dry nitrogen gas. Aliquots of the total extracts were reacted with N,O-bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane and pyridine for 3 h at 70 °C to convert polar compounds to the trimethylsilyl (TMS) derivatives. This procedure derivatizes COOH and OH groups to the corresponding TMS esters and ethers, respectively. The silylated extracts were dried under N<sub>2</sub> blow-down to remove the remaining BSTFA and pyridine, and then dissolved with *n*-hexane prior to injection. Deuterated tetracosane was added to all samples before extraction. Prior to instrumental analysis, known quantities of internal standard hexamethylbenzene were added to the samples.

All samples were analyzed using a Hewlett-Packard (HP) 6890 gas chromatograph, equipped with a DB-5 capillary column (30 m × 0.25 mm × 0.25 μm film thickness), and coupled to a quadrupole mass spectrometer (Micromass VG Platform II) operated in the electron impact mode (70 eV). The temperature program began at 80 °C, after a hold for 5 min, then increased to 290 °C at 4 °C min<sup>-1</sup>, with another isothermal hold for 30 min. The carrier gas was helium (He) at a constant flow rate of 1.2 mL min<sup>-1</sup>. A 1 μL sample was injected in the splitless mode. The mass range of 50–700 da was used for quantitative determinations. Data acquisition and processing were controlled by a Masslynx data system.

The chromatographic peaks of the samples were identified by comparison of mass spectra with literature and library data, comparison with authentic standards, and interpretation of mass spectrometric fragmentation patterns. GC-MS response factors were determined using authentic external standards.

### 2.3. Organic carbon (OC)/elemental carbon (EC) analysis

A Thermal/Optical Carbon Aerosol Analyzer (Sunset Laboratory) operating with a modified NIOSH (National Institute of Occupational Safety and Health) thermal-optical transmission (TOT) protocol was used for the carbon analysis. The punch aliquot of filter was heated stepwise at temperatures of 310, 475, 615, and 840 °C in a pure He atmosphere for detecting the OC fraction, and at temperatures of 550, 625, 700, 775 and 850 °C in an oxidizing atmosphere of 2% oxygen in a balance of He for detecting the EC fraction. The carbon evolved at each temperature is oxidized to carbon dioxide and then reduced to methane for quantification with a flame ionization detector. Some of the OC pyrolyzes to EC as the temperature increases in inert He and is subtracted from the EC area according to the initial laser absorbance. At the end of every analysis, a fixed volume loop of methane is injected automatically as an internal standard to calculate the carbon results. Replicate analyses were performed to eliminate the nonuniformity of filter samples. The difference determined from replicate analyses was smaller than 15% for OC and EC. The detection limits for OC and EC were below 0.1 μg cm<sup>-2</sup>.

### 2.4. Water-soluble inorganic ions

The details for the ion chromatography procedure are described elsewhere (Tan et al., 2009). Briefly, ultrasonic agitation was used to extract inorganic ions from samples, where the filter aliquot

(9 cm<sup>2</sup>) was submerged in a vial with 15 ml ultra pure water, sealed and subjected to ultrasound for 20 min for extraction. The extract was then analyzed by ion chromatography (Dionex 1400) to determine the concentrations of the inorganic ions.

### 2.5. Elemental analysis

Aliquots of filters (6 cm<sup>2</sup>) were digested with 5 ml concentrated nitric acid (ultra-pure) in closed Teflon bombs at 150 °C for five days. The acid solution with filter was agitated using an ultrasonic system every 24 h. After the PM on the filter was completely dissolved in the acid solution, the digestate was filtered and then diluted to less than 2% acidity with ultra-pure Milli-Q water. Calibration of the ICP-MS instrument was performed with standard multi-element solutions (Misa04-06) from 5 to 500 ng ml<sup>-1</sup> for trace elements. For major elements, an additional standard from 1000 to 5000 ng ml<sup>-1</sup> was used. 50 ng ml<sup>-1</sup> Re was used as internal standard. The diluted solution was analyzed with a Perkin–Elmer Elan 6000/ICP-MS.

### 3. Results and discussion

This is the first report on the chemical composition of PM in an e-waste recycling workshop of South China. The concentrations of PM as well as OC and EC, organic matter (OM), key ionic species and inorganic elements from recycling of printed circuit boards are listed in Table 1. The PM concentrations ranged from 1129 to 1688, average 1430 μg m<sup>-3</sup>, which was considerably less than the maximum allowed occupational levels in Sweden (10 mg m<sup>-3</sup> for TSP) (Sjödin et al., 2001) and the maximum level of eight-hour average exposure to TSP in a working environment (4 mg m<sup>-3</sup>) recommended by the NIOSH (Zhao et al., 2007). The chemical

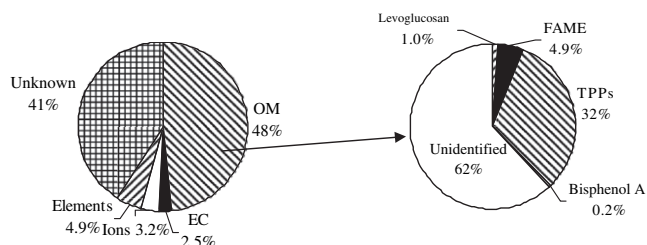
**Table 1**  
The concentrations of particulate matter (PM), organic and elemental carbon (OC and EC), organic matter (OM), key ionic species and inorganic elements from recycling of printed circuit boards (units: μg m<sup>3</sup>).

	NO.1	NO.2	NO.3	NO.4	Average
PM	1494	1688	1409	1129	1430
OC	510.1	562.6	519.6	381.9	493.6
EC	42.4	35.6	40.7	26.3	36.2
OC/EC	12.0	15.8	12.8	14.5	13.8
OM	714.1	787.7	727.5	534.7	691.0
<i>Key ionic species</i>					
SO <sub>4</sub> <sup>2-</sup>	14.01	18.66	14.36	11.02	14.51
Cl <sup>-</sup>	3.52	4.19	2.93	1.99	3.16
NO <sub>3</sub> <sup>-</sup>	3.35	4.00	2.64	2.55	3.13
NH <sub>4</sub> <sup>+</sup>	12.06	16.86	10.15	8.70	11.94
K <sup>+</sup>	4.47	6.92	3.16	3.28	4.46
Na <sup>+</sup>	3.21	5.13	2.79	1.61	3.18
Ca <sup>2+</sup>	4.81	1.03	1.98	4.10	2.98
<i>Elements</i>					
P	22.25	27.36	26.68	15.92	23.05
Ca	16.50	13.31	9.16	8.13	11.78
Fe	16.33	13.45	8.33	7.86	11.49
Na	8.81	5.70	6.80	4.03	6.34
Al	6.97	6.19	4.17	3.63	5.24
Pb	5.53	5.80	3.79	2.54	4.42
Zn	4.64	3.92	2.61	2.10	3.32
Sn	3.84	1.10	1.32	2.10	2.09
Mg	1.69	1.46	1.13	0.82	1.28
Cu	0.65	0.65	0.69	0.29	0.57
Ti	0.23	0.16	0.13	0.12	0.16
Mn	0.21	0.19	0.13	0.11	0.16
Sb	0.21	0.20	0.12	0.08	0.15
Ba	0.14	0.13	0.07	0.06	0.10
Ni	0.12	0.09	0.06	0.05	0.08
Cd	0.13	0.05	0.05	0.07	0.08

species associated with PM can be classified into five major components: OM, EC, water-soluble ions, elements and unknown components. OC was converted to OM by a factor of 1.4 to account for associated oxygen and hydrogen mass (Andreae et al., 1984). The relative abundances of the chemical components are presented in Fig. 1. It can be seen that the identified components accounted for 59% of the PM and 41% was still undetermined. The major constituents of the emitted PM were carbonaceous particles. The total carbonaceous content ranged between 48.8 and 54.5%, of which OM contributed 46.7–51.6% of the PM. The average ratio of OC/EC was 13.8. Although EC only consisted of 2.5% of the PM, it should be significant regarding its effects on the environment and public health. The inorganic elements and ions had a minor contribution to the PM.

### 4. Organic composition

The organic compounds quantified in the solvent soluble fraction of the PM are given in Table 2 and a representative chromatogram is depicted in Fig. 2. The total amounts of quantified organic compounds accounted for 29.2–53.1%, average 38.0% of the OM (Fig. 1). The strongest peaks in the chromatograms of the total organic extract were organophosphates (OPs), followed by fatty acid methyl esters (FAME) consisting mainly of hexadecanoic and octadecanoic acids, levoglucosan and 2,2-bis(4'-hydroxyphenyl) propane (bisphenol A). Other compounds had a relatively minor contribution to the total extracts and consisted of mainly butyl and diethylhexyl phthalates, 4-hydroxybenzoic acid, terephthalic acid, bis(hydroxyphenyl)methanes, anhydrofructofuranose and *n*-alkanes. These compounds are not considered further. The high OPs were not identified in other emission sources such as coal combustion smoke (Oros and Simoneit, 2000; Simoneit et al., 2007), biomass burning (Oros and Simoneit, 2001a,b), vehicle emissions (Rogge et al., 1993b), cooking smoke (Rogge et al., 1991; He et al., 2004) and so on. The major OPs in this study were several structures of aryl-phosphates: triphenyl phosphate (TPP), *m/z* 326; mono-alkylphenyldiphenyl phosphates (C<sub>1</sub>-TPPs), *m/z* 340 (i.e. cresyldiphenyl phosphates); di-alkylphenyl-phenyl phosphates (C<sub>2</sub>-TPPs), *m/z* 354; and tri-alkylphenyl phosphates (C<sub>3</sub>-TPPs), *m/z* 368. The total amounts of aryl-phosphates ranged from 158 to 330 μg m<sup>-3</sup>, comprising on average 83.9% of the sum of the quantified organic compounds and 32% of the PM. Aryl-phosphate esters are used mainly as fire retardant additives for electrical appliances, so they may leak out, in part react and vaporize during this recycling process. Halogenated fire retardants, which were extensively used in the past, have been phased out since the 1980s due to the environmental issues of halogen compounds and replaced with non-halogenated fire retardants. Among the non-halogenated fire retardants, aryl-phosphates are representative and include mono-phosphates, such as TPP, tricresyl phosphate, dicresylphenyl phosphate, cresyldiphenyl phosphate, trixylyl phosphate, etc., and bis-phosphates including resorcinol bis(diphenyl



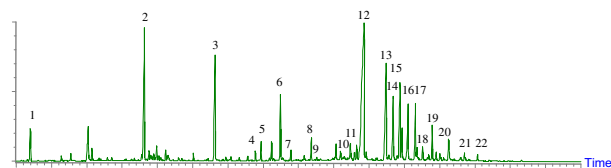
**Fig. 1.** Pie diagrams showing the relative abundances of the chemical components in PM (left) and organic matter (right) from printed circuit boards recycling workshop.

**Table 2**  
Concentrations of organic compounds quantified in extracts of PM emitted during recycling of waste printed circuit boards. (unit:  $\mu\text{g m}^{-3}$ ).

Compound name	Composition	MW	NO.1	NO.2	NO.3	NO.4	Average
Levoglucosan	$\text{C}_6\text{H}_{10}\text{O}_5$	162	9.63	5.58	7.31	4.65	6.79
Methyl hexadecanoate	$\text{C}_{17}\text{H}_{34}\text{O}_2$	270	17.0	20.3	30.4	15.9	20.9
Hexadecanoic (palmitic) acid	$\text{C}_{16}\text{H}_{32}\text{O}_2$	256	0.68	1.67	1.17	1.83	1.34
Methyl octadecanoate	$\text{C}_{19}\text{H}_{38}\text{O}_2$	298	7.59	7.91	14.15	7.33	9.24
Bisphenol A	$\text{C}_{15}\text{H}_{16}\text{O}_2$	228	1.01	1.06	1.02	1.35	1.11
Octadecanoic (stearic) acid	$\text{C}_{18}\text{H}_{36}\text{O}_2$	284	0.28	0.68	0.62	1.19	0.69
Methyl eicosanoate	$\text{C}_{21}\text{H}_{42}\text{O}_2$	326	0.57	1.13	1.76	2.23	1.42
Triphenyl phosphate (TPP)	$\text{C}_{18}\text{H}_{15}\text{O}_4\text{P}$	326	46.6	38.4	72.6	28.6	46.5
Sum ( $\text{C}_1$ -TPP)	$\text{C}_{19}\text{H}_{17}\text{O}_4\text{P}$	340	62.3	59.7	98.7	45.2	66.5
Sum ( $\text{C}_2$ -TPP)	$\text{C}_{20}\text{H}_{19}\text{O}_4\text{P}$	354	42.3	41.2	67.7	39.7	47.7
Sum ( $\text{C}_3$ -TPP)	$\text{C}_{21}\text{H}_{21}\text{O}_4\text{P}$	368	50.8	52.7	91.4	44.8	59.9

phosphate (RDP), bisphenol A bis(diphenyl) phosphate, etc. The OPs detected in the PM from the recycling workshop for printed circuit boards were also reported in the thermal degradation products from polycarbonate (PC)/TPP or PC/RDP mixtures (Jang and Wilkie, 2005a). The presence of pseudohomologous phosphates such as  $m/z$  326, 340, 354 and 368 implies an occurrence of an alcoholysis reaction between phosphate and one, two or all three P-O bonds of a TPP and phenolic products evolved during PC degradation (Jang and Wilkie, 2005a,b). In this workshop, the printed circuit boards were heated over coal-stoves and moved away within 5 sec. Therefore, flash pyrolysis likely occurred, although the temperature was probably not as high as in the study performed by Jang and Wilkie (2005a).

OP flame retardants have been widely detected in air, but usually at low levels (Marklund et al., 2005; Staaf and Ostman, 2005; Reemtsma et al., 2008; Takigami et al., 2009). Of the OPs studied so far, the chlorinated organophosphate triesters tris(chloropropyl) phosphate and tris(2-chloroethyl) phosphate appear to be the most abundant in atmosphere (Ingerowski et al., 2001; Hartmann et al., 2004), which was totally different from this study. Only TPP and its methyl substituted compounds, especially a high amount of cresyldiphenyl phosphate (30.1% of the total OPs), were detected in this recycling workshop. This is probably due to the fact that the e-waste in this workshop consisted of printed circuit boards from computers. In a previous study it was shown that computers can act as sources of TPP even though there is a decline in the emissions over time (Carlsson et al., 2000). A high concentration of TPP ( $10.3 \mu\text{g m}^{-3}$ ) has been reported for electronics dismantling facilities (Makinen et al., 2009), which was lower than the values presented in this study ( $28.6\text{--}72.6 \mu\text{g m}^{-3}$ ).



**Fig. 2.** GC-MS data for a total organic extract of an aerosol sample from printed circuit boards recycling workshop (TMS derivatized). Peak number 1: Hexamethylbenzene (i.s.), 2: Levoglucosan, 3: Hexadecanoic acid methyl ester, 4: Hexadecanoic acid, 5: Bis(4-hydroxyphenyl)methane, 6: Octadecanoic acid methyl ester, 7: Bis(4-hydroxyphenyl)methane, 8: 2,2'-Bis(4-OH)phenyl propane (Bisphenol A), 9: Octadecanoic acid, 10: Eicosanoic acid methyl ester, 11: D50-tetracosane, 12: Triphenyl phosphate (TPP), 13–14: Diphenyltolyl phosphates ( $\text{C}_1$ -TPPs), 15: Tritolyl phosphate ( $\text{C}_3$ -TPP), 16–18: Ditolylphenyl phosphates ( $\text{C}_2$ -TPPs), 19: Tritolyl phosphate ( $\text{C}_3$ -TPP), 20–21:  $\text{C}_6$ -Triphenyl phosphates, 22:  $\text{C}_9$ -Triphenyl phosphate.

This result suggests that triphenyl phosphates and their alkyl pseudohomologues may be good candidates as molecular tracers for recycling of waste printed circuit boards.

Normal alkanolic acids, consisting mainly of the methyl esters of palmitic ( $\text{C}_{16}$ ) and stearic ( $\text{C}_{18}$ ) acids and minor  $\text{C}_{16}$ ,  $\text{C}_{18}$  and  $\text{C}_{20}$  fatty acids, were the second most abundant group of compounds in the solvent-extractable organic matter with concentrations ranging from 26.1 to  $48.1 \mu\text{g m}^{-3}$ . Levoglucosan, which has been used as a specific marker for wood combustion in ambient aerosol particles (Simoneit, 1999), was found in notable concentrations in this study (range  $4.7\text{--}9.6 \mu\text{g m}^{-3}$ , 1.9–4.0% of the quantified organic compounds). However, FAME and levoglucosan are not specific organic markers for tracing printed circuit board recycling. They also could be emitted from coal combustion and biomass burning (Bi et al., 2008; Wang et al., 2009). In this study, printed circuit boards were processed by heating over a grill on coal stoves. Wood debris was probably used as kindling fuel to start the honeycombed coal briquettes. Therefore, we cannot exclude the contribution of coal combustion and biomass burning to the indoor air. Compared to smoke from wood and leaf combustion (Schmidl et al., 2008a,b), the levoglucosan concentration relative to PM in this study tended to be lower. Additionally, hydroxy-polycyclic aromatic hydrocarbons (OH-PAHs), the abundant organic components emitted directly in coal smoke particles (Bi et al., 2008), were not detected in this study. Consequently, the results suggest that biomass and coal burning were not the dominant contributors of PM loading in this workshop.

It is noteworthy that bisphenol A was present at the level of  $1.11 \pm 0.16 \mu\text{g m}^{-3}$  and bisphenol B [2,2-bis(4'-hydroxyphenyl)butane] was 2% of the bisphenol A, probably an impurity. The bisphenol A concentration was several orders of magnitude higher than that observed in other work and indoor environments. It is used mainly as a cross link material in the production of epoxy resins and PC plastics, which are widely used in electrical appliances. It was reported that bisphenol A was emitted mainly via hydrolysis/alcoholysis and chain scission along the weak bonds of carbonate links during thermal degradation of these plastics (Jang and Wilkie, 2004, 2005b). Research has shown that pyrolysis or thermal decomposition of bisphenol A-polycarbonate polymer contained in e-waste plastics resulted in the formation of free bisphenol A (Carroccio et al., 2002) and probably also degradation products such as the minor 4-hydroxybenzoic acid and bis(4-hydroxyphenyl)methanes. Rudel et al. (2003) found significant bisphenol A concentrations in air of a workplace for plastics ( $208 \text{ ng m}^{-3}$ ), which was much lower than those values in this study. Therefore, bisphenol A can also be used as an organic tracer for recycling of waste printed circuit boards.

## 5. Inorganic composition

Water-soluble inorganic ions constituted a mean of 3.2% of the particle mass (Table 1). Among the inorganic ions, sulfate ( $\text{SO}_4^{2-}$ ), ammonium ( $\text{NH}_4^+$ ) and potassium ( $\text{K}^+$ ) were the most abundant species, constituting 31.9%, 26.3% and 9.8%, respectively, of the total inorganic ionic species mass, followed by sodium ( $\text{Na}^+$ ), chloride ( $\text{Cl}^-$ ) and nitrate ( $\text{NO}_3^-$ ) (about 7% each). The average concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ , and  $\text{NO}_3^-$  were  $14.51$ ,  $11.94$  and  $3.13 \mu\text{g m}^{-3}$ , respectively. The ratio of the micro-equivalents of  $\text{NH}_4^+$  ( $0.66 \mu\text{N m}^{-3}$ ) to the sum of  $\text{SO}_4^{2-}$  ( $0.30 \mu\text{N m}^{-3}$ ) and  $\text{NO}_3^-$  ( $0.06 \mu\text{N m}^{-3}$ ) averaged 1.9, indicating full neutralization of acidic particles and the PM in the workshop was ammonium-rich. Similar ammonium-rich ambient environments have also been observed in urban (Guangzhou) (Pathak et al., 2009) and rural (Xinken) areas of South China (Hu et al., 2008). Moreover, the concentrations of water-soluble ions were close to those in these same areas of South China.



Therefore, the water-soluble ions in the PM of the workshop might be from outdoor air pervasion. Non-mineral  $K^+$  has been suggested as a tracer for wood smoke (Echalar et al., 1995). The relatively high levels of  $K^+$  in this study may be associated with emissions from biomass burning, which is consistent with the presence of the organic tracer levoglucosan.

Just as in the case of the water-soluble inorganic ions, the inorganic elements were also not major components, representing a mean of 5.0% of the PM. The mineral elemental compositions of unburned and burned circuit boards were determined by Gullett et al. (2007). Large quantities of Cu as well as significant quantities of tin (Sn), Zn, bromine (Br) and Pb were found in the unburned circuit boards, while in residual ash from charring had high levels of Pb, Cu, and Sn. Phosphorus (P) was not measured in that study. ICP-MS analysis of the particles in this study indicated very high levels of P (average  $23.05 \mu\text{g m}^{-3}$  and 31.9% of the total inorganic elements). This can be compared with the average amount of aryl-phosphates ( $221 \mu\text{g m}^{-3}$ ), which would be equivalent to approximately  $20 \mu\text{g m}^{-3}$  P. That is, the elemental P associated with the PM is mainly due to organic phosphates. Crustal elements, such as Ca, Fe, Na and Al were also abundant in this study, which may be attributed to the frequent activities at this workshop. Compared with the data from IC measurements, the elevated concentrations of elements Ca and Na indicate the existence of insoluble compounds.

In addition, significant concentrations of Pb (6.1% of the total inorganic elements), Zn (4.6%), Sn (2.9%), and lesser (<1%) Cu, antimony (Sb), manganese (Mn), nickel (Ni), barium (Ba) and cadmium (Cd) were also found in the PM of the workshop. Compared with floor dust, which was collected in several recycling workshops for printed circuit boards in Guiyu (Leung et al., 2008), the heavy metal concentrations in this PM study (Pb  $3019 \text{ mg kg}^{-1}$ , Cu  $392 \text{ mg kg}^{-1}$ , Zn  $2285 \text{ mg kg}^{-1}$ ) were much lower, despite the slightly different composition. In floor dust, Pb ( $110\,000 \text{ mg kg}^{-1}$ ) was the major component of the seven heavy metals investigated, followed by Cu ( $6170 \text{ mg kg}^{-1}$ ) and Zn ( $2370 \text{ mg kg}^{-1}$ ). The different composition was likely due to the relatively nonvolatile nature of these metals in the atmosphere. Additionally, Cd, Pb and Ni concentrations in the PM from the recycling workshop were an order greater than in the ambient air PM samples of Guiyu ( $23^\circ 32' \text{N}$ ,  $116^\circ 34' \text{E}$ ) (Fig. 3). This location was not far away from the workshop in this study and is characterized by residential and commercial buildings involved in e-waste recycling, where chromium (Cr) and Zn were the most enriched metals, followed by Cu, Pb, Mn and arsenic (As) (Deng et al., 2006). The ratios of Cu/Zn, which could be used to distinguish gasoline- ( $0.21 \pm 0.15$ ) and diesel-powered ( $0.01 \pm 0.003$ ) vehicles (Cadle et al., 1999), were 0.46 for the ambient air samples of Guiyu (Deng et al., 2006) and in the range of 0.14–0.26 in this study. Apparently, this ratio cannot be used to distinguish recycling of printed circuit boards from vehicle

emissions. Nevertheless, such recycling is an important contributor of heavy metal contamination, particularly Cd, Pb and Ni, to the local environment.

## 6. Conclusion

Waste printed circuit boards are disposed by some primitive recycling methods in South China, thus contributing high PM to the indoor and ambient atmospheric environment. During the recycling process, biomass burning and coal combustion as well as heating of printed circuit boards emit a lot of pollutants. This primitive recycling method was found here as a significant contributor of heavy metals, organophosphates (OPs), levoglucosan, FAME and bisphenol A to the emitted PM. OPs and bisphenol A are proposed as potential tracers for emissions from e-waste recycling. These results warrant further studies to evaluate potential health effects from inhalation and dermal exposure.

## Acknowledgements

We thank Dr. Xiangying Zeng for assistance in sample collection. This work was supported by the Knowledge Innovation Key Projects of the Chinese Academy of Sciences (kzcx2-yw-139), the National Natural Science Foundation of China (40873073) and the State Key Laboratory of Organic Geochemistry (sklog2009A03). We thank Mr. T.S. Xiang for assistance in GC-MS analysis. This is contribution No. is 1225 from GIGCAS.

## References

- Andreae, M.O., Andreae, T.W., Ferek, R.J., Raemdonck, H., 1984. Long-range transport of soot carbon in the marine atmosphere. *The Science of the Total Environment* 36, 73–80.
- Bi, X.H., Simoneit, B.R.T., Sheng, G.Y., Fu, J.M., 2008. Characterization of molecular markers in smoke from residential coal combustion in China. *Fuel* 87, 112–119.
- Bi, X.H., Thomas, G.O., Jones, K.C., Qu, W.Y., Sheng, G.Y., Martin, F.L., Fu, J.M., 2007. Exposure of electronics dismantling workers to polybrominated diphenyl ethers, polychlorinated biphenyls, and organochlorine pesticides in South China. *Environmental Science & Technology* 41, 5647–5653.
- Cadle, S.H., Mulawa, P.A., Hunsanger, E.C., 1999. Composition of light-duty motor vehicle exhaust particulate matter in the Denver, Colorado area. *Environmental Science & Technology* 33, 2328–2339.
- Carlsson, H., Nilsson, U., Ostman, C., 2000. Video display units: An emission source of the contact allergenic flame retardant triphenyl phosphate indoor environment. *Environmental Science & Technology* 34, 3885–3889.
- Carroccio, S., Puglisi, C., Montaudo, G., 2002. Mechanisms of thermal oxidation of poly(bisphenol A carbonate). *Macromolecules* 35, 4297–4305.
- Chen, D.H., Bi, X.H., Zhao, J.P., Chen, L.G., Tan, J.H., Mai, B.X., Sheng, G.Y., Fu, J.M., Wong, M.H., 2009. Pollution characterization and diurnal variation of PBDEs in the atmosphere of an E-waste dismantling region. *Environmental Pollution* 157, 1051–1057.
- Deng, W.J., Louie, P.K.K., Liu, W.K., Bi, X.H., Fu, J.M., Wong, M.H., 2006. Atmospheric levels and cytotoxicity of PAHs and heavy metals in TSP and PM<sub>2.5</sub> at an electronic waste recycling site in southeast China. *Atmospheric Environment* 40, 6945–6955.
- Echalar, F., Gaudichet, A., Cachier, H., Artaxo, P., 1995. Aerosol emissions by tropical forest and savanna biomass burning: characteristic trace elements and fluxes. *Geophysical Research Letters* 22, 3034–3042.
- Gullett, B.K., Linak, W.P., Touati, A., Wasson, S.J., Gatica, S., King, C.J., 2007. Characterization of air emissions and residual ash from open burning of electronic wastes during simulated rudimentary recycling operations. *Journal of Material Cycles and Waste Management* 9, 69–79.
- Hartmann, P.C., Burgi, D., Giger, W., 2004. Organophosphate flame retardants and plasticizers in indoor air. *Chemosphere* 57, 781–787.
- He, L.Y., Hu, M., Huang, X.F., Yu, B.D., Zhang, Y.H., Liu, D.Q., 2004. Measurement of emissions of fine particulate organic matter from Chinese cooking. *Atmospheric Environment* 38, 6557–6564.
- Hu, M., Wu, Z.J., Slanina, J., Lin, P., Liu, S., Zeng, L.M., 2008. Acidic gases, ammonia and water-soluble ions in PM<sub>2.5</sub> at a coastal site in the Pearl River Delta, China. *Atmospheric Environment* 42, 6310–6320.
- Ingerowski, G., Friedle, A., Thumulla, J., 2001. Chlorinated ethyl and isopropyl phosphoric acid triesters in the indoor environment - An inter-laboratory exposure study. *Indoor Air-International Journal of Indoor Air Quality and Climate* 11, 145–149.

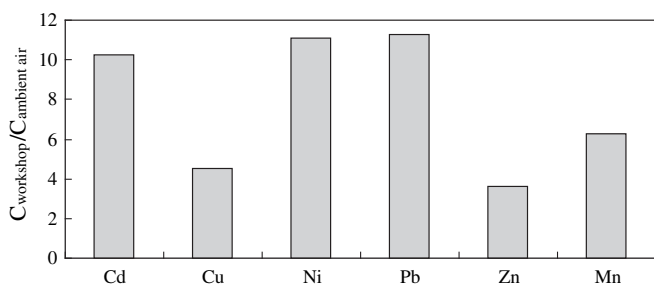


Fig. 3. Comparison of the heavy metal concentrations between in indoor air of the PCBs recycling workshop and the ambient air of the e-waste recycling site.

- Jang, B.N., Wilkie, C.A., 2004. A TGA/FTIR and mass spectral study on the thermal degradation of bisphenol A polycarbonate. *Polymer Degradation and Stability* 86, 419–430.
- Jang, B.N., Wilkie, C.A., 2005a. The effects of triphenylphosphate and recorcinolbis (diphenylphosphate) on the thermal degradation of polycarbonate in air. *Thermochimica Acta* 433, 1–12.
- Jang, B.N., Wilkie, C.A., 2005b. The thermal degradation of bisphenol A polycarbonate in air. *Thermochimica Acta* 426, 73–84.
- Leung, A.O.W., Duzgoren-Aydin, N.S., Cheung, K.C., Wong, M.H., 2008. Heavy metals concentrations of surface dust from e-waste recycling and its human health implications in southeast China. *Environmental Science & Technology* 42, 2674–2680.
- Leung, A.O.W., Luksemburg, W.J., Wong, A.S., Wong, M.H., 2007. Spatial distribution of polybrominated diphenyl ethers and polychlorinated dibenzo-p-dioxins and dibenzofurans in soil and combusted residue at Guiyu, an electronic waste recycling site in southeast China. *Environmental Science & Technology* 41, 2730–2737.
- Li, Y.D., Richardson, J.B., Bricka, R.M., Niu, X.J., Yang, H.B., Li, L., Jimenez, A., 2009. Leaching of heavy metals from E-waste in simulated landfill columns. *Waste Management* 29, 2147–2150.
- Li, Y.M., Jiang, G.B., Wang, Y.W., Wang, P., Zhang, Q.H., 2008. Concentrations, profiles and gas-particle partitioning of PCDD/Fs, PCBs and PBDEs in the ambient air of an E-waste dismantling area, southeast China. *Chinese Science Bulletin* 53, 521–528.
- Makinen, M.S.E., Makinen, M.R.A., Koistinen, J.T.B., Pasanen, A.L., Pasanen, P.O., Kalliokoski, P.I., Korpi, A.M., 2009. Respiratory and dermal exposure to organophosphorus flame retardants and tetrabromobisphenol A at five work environments. *Environmental Science & Technology* 43, 941–947.
- Marklund, A., Andersson, B., Haglund, P., 2005. Organophosphorus flame retardants and plasticizers in air from various indoor environments. *Journal of Environmental Monitoring* 7, 814–819.
- Medeiros, P.M., Simoneit, B.R.T., 2008. Source profiles of organic compounds emitted upon combustion of green vegetation from temperate climate forests. *Environmental Science & Technology* 42, 8310–8316.
- Oros, D.R., bin Abas, M.R., Omar, N., Rahman, N.A., Simoneit, B.R.T., 2006. Identification and emission factors of molecular tracers in organic aerosols from biomass burning: Part 3. Grasses. *Applied Geochemistry* 21, 919–940.
- Oros, D.R., Simoneit, B.R.T., 2000. Identification and emission rates of molecular tracers in coal smoke particulate matter. *Fuel* 79, 515–536.
- Oros, D.R., Simoneit, B.R.T., 2001a. Identification and emission factors of molecular tracers in organic aerosols from biomass burning Part 1. Temperate climate conifers. *Applied Geochemistry* 16, 1513–1544.
- Oros, D.R., Simoneit, B.R.T., 2001b. Identification and emission factors of molecular tracers in organic aerosols from biomass burning Part 2. Deciduous trees. *Applied Geochemistry* 16, 1545–1565.
- Owens Jr., C.V., Lambright, C., Bobseine, K., Ryan, B., Gray Jr., L.E., Gullett, B.K., Wilson, V.S., 2007. Identification of estrogenic compounds emitted from the combustion of computer printed circuit boards in electronic waste. *Environmental Science & Technology* 41, 8506–8511.
- Pathak, P.K., Wu, W.S., Wang, T., 2009. Summertime PM<sub>2.5</sub> ionic species in four major cities of China: nitrate formation in an ammonia-deficient atmosphere. *Atmospheric Chemistry and Physics* 9, 1711–1722.
- Reemtsma, T., Quintana, J.B., Rodil, R., Garcia-Lopez, M., Rodriguez, I., 2008. Organophosphorus flame retardants and plasticizers in water and air I. Occurrence and fate. *Trac-Trends in Analytical Chemistry* 27, 727–737.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1993a. Sources of fine organic aerosol. 5. Natural-gas home appliances. *Environmental Science & Technology* 27, 2736–2744.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1993b. Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. *Environmental Science & Technology* 27, 636–651.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1991. Sources of fine organic aerosol. 1. Charbroilers and meat cooking operations. *Environmental Science & Technology* 25, 1112–1125.
- Rudel, R.A., Camann, D.E., Spengler, J.D., Korn, L.R., Brody, J.G., 2003. Phthalates, alkylphenols, pesticides, polybrominated diphenyl ethers, and other endocrine-disrupting compounds in indoor air and dust. *Environmental Science & Technology* 37, 4543–4555.
- Schmidl, C., Bauer, H., Dattler, A., Hitzenberger, R., Weissenboeck, G., Marr, I.L., Puxbaum, H., 2008a. Chemical characterization of particle emissions from burning leaves. *Atmospheric Environment* 42, 9070–9079.
- Schmidl, C., Marr, I.L., Caseiro, A., Kotianova, P., Berner, A., Bauer, H., Kasper-Giebl, A., Puxbaum, H., 2008b. Chemical characterization of fine particle emissions from wood stove combustion of common woods growing in mid-European Alpine regions. *Atmospheric Environment* 42, 126–141.
- Simoneit, B.R.T., 1999. A review of biomarker compounds as source indicators and tracers for air pollution. *Environmental Science and Pollution Research* 6, 159–169.
- Simoneit, B.R.T., Bi, X.H., Oros, D.R., Medeiros, P.M., Sheng, G.Y., Fu, J.M., 2007. Phenols and hydroxy-PAHs (arylphenols) as tracers for coal smoke particulate matter: Source tests and ambient aerosol assessments. *Environmental Science & Technology* 41, 7294–7302.
- Simoneit, B.R.T., Elias, V.O., Kobayashi, M., Kawamura, K., Rushdi, A.I., Medeiros, P.M., Rogge, W.F., Didyk, B.M., 2004a. Sugars – dominant water-soluble organic compounds in soils and characterization as tracers in atmospheric particulate matter. *Environmental Science & Technology* 38, 5939–5949.
- Simoneit, B.R.T., Kobayashi, M., Mochida, M., Kawamura, K., Huebert, B.J., 2004b. Aerosol particles collected on aircraft flights over the northwestern Pacific region during the ACE-Asia campaign: composition and major sources of the organic compounds. *Journal of Geophysical Research-Atmospheres* 109. doi:10.1029/2004JD004565 D19S09/1–13.
- Simoneit, B.R.T., Medeiros, P.M., Didyk, B.M., 2005. Combustion products of plastics as indicators for refuse burning in the atmosphere. *Environmental Science & Technology* 39, 6961–6970.
- Sjödin, A., Carlsson, H., Thuresson, K., Sjödin, S., Bergman, Å., Östman, C., 2001. Flame retardants in indoor air at an electronics recycling plant and at other work environments. *Environmental Science and Technology* 35, 448–454.
- Staaft, T., Ostman, C., 2005. Organophosphate triesters in indoor environments. *Journal of Environmental Monitoring* 7, 883–887.
- Stewart, E.S., Lemieux, P.M., 2003. Emissions from the incineration of electronics industry waste. In: 2003 IEEE International Symposium on Electronics and the Environment, Boston, MA, May 19–22.
- Takigami, H., Suzuki, G., Hirai, Y., Ishikawa, Y., Sunami, M., Sakai, S., 2009. Flame retardants in indoor dust and air of a hotel in Japan. *Environment International* 35, 688–693.
- Tan, J.H., Duan, J.C., Chen, D.H., Wang, X.H., Guo, S.J., Bi, X.H., Sheng, G.Y., He, K.B., Fu, J.M., 2009. Chemical characteristics of haze during summer and winter in Guangzhou. *Atmospheric Research* 94, 238–245.
- Wang, Z.Z., Bi, X.H., Sheng, G.Y., Fu, J.M., 2009. Characterization of organic compounds and molecular tracers from biomass burning smoke in South China I: broad-leaf trees and shrubs. *Atmospheric Environment* 43, 3096–3102.
- Wong, C.S.C., Wu, S.C., Duzgoren-Aydin, N.S., Aydin, A., Wong, M.H., 2007a. Trace metal contamination of sediments in an e-waste processing village in China. *Environmental Pollution* 145, 434–442.
- Wong, M.H., Wu, S.C., Deng, W.J., Yu, X.Z., Luo, Q., Leung, A.O.W., Wong, C.S.C., Luksemburg, W.J., Wong, A.S., 2007b. Export of toxic chemicals – a review of the case of uncontrolled electronic-waste recycling. *Environmental Pollution* 149, 131–140.
- Zhao, L.Y., Brugger, M.F., Manuzon, R.B., Arnold, G., Imerman, E., 2007. Variations in air quality of new Ohio dairy facilities with natural ventilation systems. *Applied Engineering in Agriculture* 23, 339–346.