

## PERCENTAGE CONTRIBUTIONS OF CHLORINATED AROMATIC COMPOUNDS IN ELECTRONIC WASTE OPEN BURNING SOILS

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### Introduction

With the rapid growth in the use of electrical and electronic products, the lifespan of each product is becoming increasingly short. Consequently, older electronic products are rapidly becoming obsolete and are being discarded in considerable amounts, and the improper disposal of those electronic-waste (e-waste) is a serious problem worldwide. One of the greatest concerns is that large quantities of e-waste are being illegally transported to developing countries and are being recycled inadequately<sup>1</sup>. In 2005, the the United Nations Environment Programme reported that 50-80% of e-waste collected for recycling in industrialized countries end up in developing countries, taking advantage of their lower labor costs and less stringent environmental regulations. The e-waste recycling techniques used in these countries are also inferior, such as dismantling, acid leaching, and open burning, and cause serious environmental pollution in the ecosystems near the recycling areas<sup>2</sup>. Recently, studies in China have demonstrated that e-waste recycling activities, especially open burning, produces toxic chlorinated aromatic compounds such as dioxin-like polychlorinated biphenyls (DL-PCBs), polychlorinated dibenzo-p-dioxins (PCDDs), and dibenzofuran (PCDFs)<sup>3</sup>. However, little information is available on the concentration of total PCBs in soils where open burning occurred, and there have been no studies of the concentration of chlorobenzenes (CBzs) in these soils. CBzs are especially toxic, and their homologues have been included in the list of 12 prior-controlled persistent organic pollutants by the Stockholm Convention. Furthermore, while several studies have examined specific concentrations, none have examined the percentage contributions of chlorinated aromatic compounds to total organic chloride (TOCl). In this study, we measured the concentrations of TOCl and four toxic chlorinated aromatic compounds (CBzs, PCBs, PCDDs, and PCDFs) in open burning soils to identify the pollution status of these sites. We also measured the concentrations of 11 metals and examined the correlations between these concentrations and the concentrations of the 4 chlorinated aromatic compounds. Furthermore, we calculated the percentage contributions to TOCl of the four chlorinated aromatic compounds to reveal the possibility that other more serious chlorinated compounds were generated by open burning. This is the first study to examine not only the concentrations, but also the percentage contributions, of chlorine from CBzs, PCBs, PCDDs, and PCDFs to TOCl in open burning soils.

### Materials and methods

**Sample collection and sample preparation.** Three soil samples were collected in Dong Quang and Bui Dau in January 2011, and in Caloocan in August 2010. The first soil sample was collected from a controlled site in Dong Quang, where e-waste recycling is not conducted (Control). The second sample was collected at an informal site for open burning wires and cables in Bui Dau, a town known for its e-waste recycling activities, in Hung Yung Province in northern Vietnam (VN). The third sample was collected from an e-waste open burning site on the Marilao river bank in Caloocan, Philippines (PHI). Open burning soil samples were collected from directly beneath combusted residue at each site. All samples were collected using a shovel, packed in plastic bags, and stored in a cooler. They were then air-dried for 1 week, sieved (< 2 mm), and homogenized in the laboratory prior to analyses.

**Sample preparation and analysis for CBzs, PCBs, PCDDs and PCDFs.** Each soil sample (1 g) was digested with HCl (2 mol/L) for 4 h and filtered through Whatman filter paper. Filtered residues were spiked with 10- $\mu$ L <sup>13</sup>C-labeled internal standards and were Soxhlet-extracted with toluene at around 170°C for 1 day. Following

this, the extract liquid was concentrated in a rotary evaporator, filtered through a multilayered silica gel column, and concentrated in a rotary evaporator again. The concentrated liquid was further concentrated in a nitrogen concentrator to a final volume of <100  $\mu$ L. The extracts were analyzed using gas chromatography-mass spectrometry (Shimadzu QP2010), and concentrations of PCDDs and PCDFs were analyzed according to Ministry of the Environment, Japan (2009) using gas chromatography (Hewlett Packard HP-6890)/high-resolution mass spectrometer (JEOL JMS-700).

**Sample preparation and analysis for metals.** Each soil sample (0.2 g) was digested in a microwave oven after adding 10-mL mixed acids (HF:HNO<sub>3</sub>:H<sub>2</sub>O<sub>2</sub> = 6:3:1). After cooling, the solutions were transferred to a beaker and 0.5-mL H<sub>2</sub>SO<sub>4</sub> was added. The solutions were then evaporated on a hotplate at 180°C until white smoke was generated, followed by the addition of 10-mL Aqua regia solution (HNO<sub>3</sub>: HCl =1:3, v/v), and returned to the hotplate at 180°C until one drop remained. The solutions were filtered through KIRIYAMA no. 5B filter paper and diluted to 100 mL with Milli-Q water. Concentrations of 14 metals (Al, As, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Zn) were analyzed using inductively coupled plasma atomic emission spectroscopy (Thermo Electrom IRIS Intrepid).

**Sample preparation and analysis for TOCl.** Soil samples were digested in KNO<sub>3</sub> solution (NO<sub>3</sub> = 5 g/L) overnight and filtered through Whatman filter paper to remove inorganic chlorine. WO<sub>3</sub> was then added to the dried filtration residue to prevent the combustion tube from being damaged by Na<sup>+</sup> and K<sup>+</sup>, and the concentration of TOCl in soils was analyzed by Combustion Ion Chromatography (Mitsubishi Chemical Analytech AQF-2100).

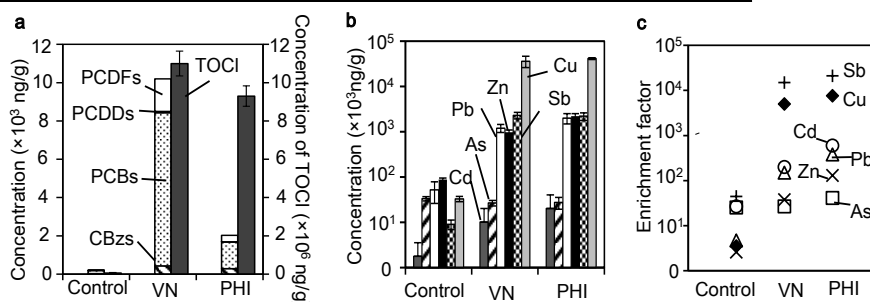
## Results and discussion

**Concentrations and trends of chlorinated aromatic compounds.** The respective concentrations of CBzs, PCBs, PCDDs, and PCDFs in soils are presented in Table 1 and Fig. 1a. The total of the 4 chlorinated aromatic compounds decreased in each soil as follows: VN (10,000 ng/g) > PHI (2,000 ng/g) > Control (200 ng/g). Of the 4 chlorinated aromatic compounds, PCBs existed in the highest abundance in all the three soils. This distributions of the four chlorinated aromatic compounds in soils was different from the one in fly ashes from Japanese municipal solid waste facilities, in which concentration of CBzs was the highest of the 4 compounds<sup>4</sup>.

**Table 1.** Respective concentrations of CBzs (ng/g), PCBs (ng/g), PCDDs (ng/g), PCDFs (ng/g), TOCl ( $\times 10^3$  ng-Cl/g), and metals ( $\times 10^3$  ng/g) in soils. Toxic equivalent concentrations (pg WHO-TEQ/g) of PCBs, PCDDs, and PCDFs were calculated.

analyte				analyte					
	Control	VN	PHI		Control	VN	PHI		
CBzs (ng/g) (n = 2)	D2	17	170	180	PCDFs	T4	2.0	730	150
	T3	2.1	110	56	(ng/g)	P5	0.17	520	100
	T4	1.5	67	25	(n = 1)	H6	0.025	280	57
	P5	3.0	53	23	H7	0.034	96	19	
	H6	0.53	30	7.6	O8	0.075	24	4.2	
	Total CBzs	24	430	290		Total PCDFs	2.3	1,700	330
PCBs (ng/g) (n = 2)	D2	44	490	170	(pg WHO-TEQ/g)		5.2	20,000	4,300
	T3	74	1,700	310	TOCl ( $\times 10^3$ ng/g) (n = 3)		60	11,000	9,300
	T4	31	410	90	metals	Al	51,000	39,000	28,000
	P5	20	1,600	430	( $\times 10^3$ ng/g)	As	33	27	28
	H6	0.29	2,000	290	(n = 3)	Cd	1.8	10	20
	H7	N.D.	1,600	130	Cr	70	110	85	
	O8	N.D.	180	9.2	Cu	33	36,000	41,000	
	N9	N.D.	57	3.8	K	14,000	7,600	1,700	
	D10	N.D.	N.D.	N.D.	Fe	30,000	14,000	25,000	
		total PCBs	170	8,000	1,400	Mg	4,000	3,400	5,200
	Dioxin-like PCBs	1.2	170	44	Mn	550	170	660	
	(pg WHO-TEQ/g)	3.4	2,300	150	Na	3,200	1,400	2,400	
PCDDs (ng/g) (n = 1)	T4	0.016	15	0.31	Ni	17	43	39	
	P5	0.0073	14	0.31	Pb	53	1,200	2,000	
	H6	0.025	17	N.D.	Sb	9.1	2,300	2,200	
	H7	0.049	11	1.3	Zn	88	970	2,200	
	O8	0.29	7.8	0.75					
	Total PCDDs	0.39	65	2.7					
	(pg WHO-TEQ/g)	0.31	1,100	4.8					

The CBzs concentrations in soils decreased as follows: VN > PHI > Control; PCBs, PCDDs, and PCDFs followed the same trend of decreasing concentration. In the CBzs, we found that more Penta-CBzs and Hexa-CBz, two well-known POPs, were generated in VN and PHI than in the controlled site. The concentrations of PCBs



**Figure 1.** a, Concentrations of CBzs, PCBs, PCDDs, PCDFs and TOCl in soils. b, Concentrations of metals (As, Cd, Cu, Pb, Sb, Zn) in soils. c, Enrichment factors of metals (As, Cd, Cu, Pb, Sb, Zn) in soils.

and DL-PCBs were also considerably higher than those at other open burning sites<sup>5</sup>. The total toxicity equivalency (TEQ) values in soils decreased as follows: VN (23,000 pg WHO-TEQ/g) > PHI (4,500 pg WHO-TEQ/g) > Control (8.8 pg WHO-TEQ/g). The TEQs of VN and PHI were higher than the controlled site, and exceeded the Environmental Quality Standard of Japan (1,000 pg WHO-TEQ/g; MOE, 2003). The total TEQ in VN were much higher than values of other open burning sites<sup>5</sup>. In VN, exceeded Environmental Quality Standard of Japan alone. 2,3,7,8-Cl-substituted congener pattern for PCDDs in VN was similar to the results of emission factor of simulated insulated wire open burning<sup>6</sup>. The homologue distribution for PCDFs in VN and PHI were similar to that of emission factor of simulated insulated wire open burning<sup>6</sup>. That suggested these distributions are intrinsic to the wire open burning soil.

**Concentrations and enrichment factors of metals.** The concentrations of metals are presented in Table 1 and Fig. 1b, and the enrichment factors ( $E_f$ ) of metals are presented in Fig. 1c.  $E_f$  was defined as:  $E_f = (E_C/Al)_{\text{sample}} / (E_C/Al)_{\text{crust}}$ , where  $E_C$  is the concentration of an element  $E$  in soil and Al is the concentration of aluminum in soil; Al was used as a base material.  $(E_C/Al)_{\text{sample}}$  signifies the measured concentrations of  $E_C$  and Al in a soil sample, and  $(E_C/Al)_{\text{crust}}$  signifies the concentrations of  $E_C$  and Al in the average crust<sup>6</sup>.  $E_f$  represents the level of enrichment compared to the average crust, a high value denotes that the element is enriched in the soil. Fig. 1c demonstrated that  $E_f$  in VN and PHI had the following trend: Sb > Cu > Cd > Pb > Zn > As > 25; this indicates that all six elements were enriched in these locations. The concentrations of Cu and Pb in VN and PHI exceeded the values for considerably exceeded the concentrations of Japanese soil standard (Cu: 125 mg/kg,

Pb: 150 mg/kg). Furthermore, we calculated correlations among the four aromatic chlorinated compounds and metals in five soils. CBzs had strong positive correlations with Cu ( $r = 0.92, p < 0.05$ ) and Sb ( $r = 0.96, p < 0.01$ ), and had a strong negative correlation with Na ( $r = -0.91, p < 0.05$ ). PCBs, PCDDs, and PCDFs had strong negative correlations with Fe and Na ( $r = -0.91, p < 0.05$ ). Here, two soil samples were added for calculation of correlations.

**TOCl.** The average TOCl concentration in soils decreased as follows: VN (11,000,000 ng-Cl/g) > PHI (9,300,000 ng-Cl/g) > Control (60,000 ng-Cl/g). The TOCl concentration in the controlled site was consistent with the average adsorbed organic chlorine (AOCl) concentration in natural soil samples obtained worldwide<sup>7</sup>. We also calculated the ratio of TOCl to total organic carbon (TOCl/TOC mg-Cl/g-C) for each site, and while the value in the control was within the range of the ratio of AOCl to TOC (AOCl/TOC mg-Cl/g-C)<sup>7</sup>, the values in VN and PHI were 10- and 3-fold higher than maximum value of AOCl/TOC, respectively. This suggests that open burning activities produced more TOCl than TOC.

### Percentage contributions to TOCl of total chlorine from CBzs, PCBs, PCDDs, and PCDFs.

Percentage contributions of total chlorine from CBzs, PCBs, PCDDs, and PCDFs to TOCl in soils are presented in Table 2, with only 0.14% in the controlled site, 0.049% in VN, and 0.011% in PHI. This suggests that the remaining TOCl (99.86 %) in the control was composed of unidentified naturally produced

organic chlorinated compounds, and is consistent with recent reports that the number of naturally produced chlorinated compounds is approximately 1,500 (e.g., alkenes, steroids, and fatty acids)<sup>8,9</sup>. Soils and decayed plant litter contained significant quantities of chlorinated aromatic polymers; for example, 5-chlorovanillin and 2-chlorosyringaldehyde were found at  $\approx 10,000$  ng/g, respectively<sup>10</sup>. The percentage contributions in VH and PHI suggest that more than 99.9% of TOCl were unidentified organic chlorinated compounds. Furthermore, except for naturally produced unidentified organic chlorinated compounds, more than 99.3% of TOCl was unidentified and anthropogenic organic chlorinated compounds, generated by open burning.

### Conclusion

In conclusion, there are high concentrations of CBzs, PCBs, PCDDs, PCDFs, and metals such as Cu, Pb, and Sb in open burning soils. While the concentrations of the four chlorinated aromatic compounds were very high, the percentage contribution of each to TOCl in open burning sites was small; it suggests that several unidentified chlorinated compounds may also have been generated by open burning.

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**Table 2.** Concentrations (ng-Cl/g) of chlorine from CBzs, PCBs, PCDDs, and PCDFs and their percentage contributions (%) to TOCl in soils.

	Control		VN		PHI	
	(ng-Cl/g)	(%) <sup>d</sup>	(ng-Cl/g)	(%) <sup>d</sup>	(ng-Cl/g)	(%) <sup>d</sup>
CBzs-Cl <sup>a</sup>	13	0.022	250	0.0023	160	0.0017
PCBs-Cl <sup>a</sup>	71	0.12	4,300	0.039	720	0.0077
PCDDs-Cl <sup>a</sup>	0.23	0.00039	34	0.00031	1.5	0.0000163
PCDFs-Cl <sup>a</sup>	1.1	0.00183	840	0.0076	170	0.00183
other-Cl <sup>b</sup>	59,915	99.86	10,994,576	99.95	9,298,948	99.99
TOCl <sup>c</sup>	60,000	100	11,000,000	100	9,300,000	100

<sup>a</sup>The values (ng-Cl/g) were calculated by converting each compound concentration into chlorine concentration

<sup>b</sup>Other-Cl (ng-Cl/g) was calculated by TOCl (ng-Cl/g) minus total chlorine from the 4 compounds (ng-Cl/g)

<sup>c</sup>TOCl (ng-Cl/g) was analyzed by AQF-2100H

<sup>d</sup>Percentage contribution (%) to TOCl in soils.

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