Quantitative Speciation of Chlorine in Electronic Waste Open Burning Soils:

Focus on Water-insoluble Fractions

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Introduction

Generally, organochlorine compounds (OCs) are water insoluble¹, and some inorganic chlorine (Cl) compounds in ash following combustion are also insoluble in aqueous solutions². Electronic waste (E-waste) open burning soils (soil/ash mixture beneath a combustion residue) have been reported to be contaminated by various kinds of persistent and toxic OCs, including polychlorinated dibenzo-*p*-dioxins/furans (PCDD/DFs), polychlorinated biphenyls (PCBs), polychlorinated benzenes (CBzs), mixed halogenated dibenzo-*p*-dioxins/furans (PXDD/DFs), and chlorinated polycyclic aromatic hydrocarbons (Cl-PAHs)³⁻⁷. In addition, the occurrence of high concentrations of unidentified OCs in E-waste open burning soils has been reported in previous research⁷. Considering that these OCs are generally water insoluble, the concentration of Cl in the water-insoluble fraction (insoluble Cl) can be treated as a potential marker for OCs, including unidentified OCs. However, waterinsoluble inorganic Cl compounds are also expected to remain in E-waste open burning soils, and these inorganic compounds contribute, to some extent, to the concentration of insoluble Cl.

In a previous study⁸, we established a method to determine the concentrations of aromatic organic Cl (aromatic-Cl), aliphatic organic Cl (aliphatic-Cl), and inorganic Cl individually by combining quantification of insoluble Cl by combustion ion chromatography with speciation analysis by Cl K-edge X-ray absorption near edge structure (XANES).

In this study, we applied this technique to E-waste open burning soils from three different countries (Vietnam [VN], the Philippines [PHI], and Ghana [GH]) and determined the concentrations of aromatic-Cl, aliphatic-Cl, and inorganic Cl. Furthermore, we compared these concentrations with those of other individual compounds. We also estimated the chemical forms of insoluble inorganic Cl and considered differences among soils.

Materials and methods

Samples: A reference soil sample (Control) was collected in Duong Quang, Hanoi, VN, where E-waste recycling is not conducted. E-waste open burning soil was collected at an informal open burning site in Bui Dau, Hanoi, VN. Wires and cables were mainly open-air burned at this location. E-waste open burning soil was also collected from one of the temporal E-waste open burning sites along the bank of the Marilao River in Caloocan, Metro Manila, PHI, where informal E-waste recycling activities are conducted⁹. The products of E-waste that are burned there were not identified. Finally, E-waste open burning soil was collected at Agbogbloshie market, GH. This area is the largest informal E-waste recycling site in GH; however, numerous small E-waste recycling workshops also surround the market. Wires, cables, printed circuit boards, and other materials, including plastics, are mixed and burned along the edge of the market¹⁰.

At each site, blackened E-waste open burning soil samples were collected from the area directly beneath combustion residue using a shovel, and then packed in plastic bags and stored in a cooler. In the laboratory, samples were air-dried for 1 week, sieved (≤ 2 mm), and homogenized. They were then stored in a refrigerator until each analysis.

The control, VN, and PHI samples were the same as those studied in our previous work, in which the concentrations of PCBs, CBzs, PCDD/DFs, Cl-PAHs, and 14 metals were reported^{4,7}.

Washing pretreatment for water-insoluble fractions: For each sample, 0.1 g of sample was mixed with 5 mL of KNO₃ (4.1 g/500 mL) and shaken for 1 hour. After the suspension was centrifuged, the residue was placed in another bottle and washed with 10 mL of ultrapure water, shaken for 1 hour, and centrifuged. The same process was then repeated, and the residue was dried in a desiccator.

Determination of total Cl (TCl) and insoluble Cl: TCl is defined as Cl in the original sample, and insoluble Cl is defined as Cl in the residue after washing (insoluble fraction). Concentrations of Cl were measured by combustion ion chromatography. A 5 mg amount of the original sample (for TCl) or residue (for insoluble Cl)

was placed on a ceramic boat with 25 mg of WO₃ and introduced into a combustion unit (AQF-2100H; Mitsubishi Chemical Analytech), where Cl was decomposed into HCl or Cl_2 and absorbed into H₂O₂. Then, the solution was pumped into a suppressor-type ion chromatography system (HIC-20ASP; Shimadzu).

Cl K-edge XANES measurement and analysis: Cl K-edge XANES spectra of samples and standard compounds were measured between 2,810 and 2,860 eV using the total fluorescence yield (TFY) method at beamline BL-11B or BL-9A of the Photon Factory in Tsukuba, Japan. The original sample (for TCl) or residue (for insoluble Cl) was applied to carbon tape and irradiated with soft X-rays. Cl speciation of samples was conducted using linear combination fitting (LCF) of sample spectra with the standard spectra. Athena software (ver. 0.9.25) was used for the analysis.

Analysis of individual compounds: For the GH soil, 2–6 chlorinated CBz congeners, 2–10 chlorinated PCB congeners, and 24 Cl-PAH congeners were analyzed by gas chromatography–mass spectrometry (QP2010; Shimadzu). Detailed information about the pretreatment procedures for individual analyses are described in the previous studies.^{4,7}

Results and discussion

Spectra before and after washing: XANES spectra are shown in Figure 1A. By focusing on the energy position of the maximum peak, we can identify the dominant form of Cl in each sample. The peak within the range of around 2,822–2,826 eV is derived from inorganic Cl, and the peak at 2,819.5–2,821.2 eV is from organic Cl (peak of aliphatic-Cl occurs at 2,820.4 eV and peak of aromatic-Cl occurs at 2,821.1 \pm 0.1 eV)^{11, 12}. In GH and Control, changes in spectra were observed after washing. A peak appeared at 2,821.5 eV after washing (Figure 1A, marked with arrows). This indicates that inorganic Cl was dominant before washing, while organic Cl became dominant after washing because most of the inorganic Cl had been removed. On the other hand, VN and PHI showed almost no change after washing. This suggests that water-insoluble inorganic Cl was still dominant in the insoluble fractions of VN and PHI. Mukai et al. reported that inorganic Cl was still the dominant form of Cl following washing, in the case of municipal solid waste incineration fly ash and bottom ash¹³. VN and PHI showed similar patterns, indicating the formation of insoluble Cl through a similar mechanism related to certain combustion processes.



Figure 1. (A) CI K-edge XANES spectra of each soil sample (indicated by bold solid lines) and fitting spectra by the linear combination of references (indicated by dotted circles). (B) Concentrations of chlorine "before" and "after" washing each soil. (C) Concentrations of three chlorine chemical forms (aromatic, aliphatic and inorganic) in each sample. (D) Concentrations of chlorine derives from PCDD/DFs, PCBs, CBzs, CIPAHs.

	VN			PHI			GH		Control	
	тсі	Insoluble	CI	тсі	Insolut	ole Cl	тсі	Insoluble CI	тсі	Insoluble CI
Fraction of chemical forms of CI (%)										
Inorganic CI	96	59		100	95		91	24	82	54
Aqueous Cl ⁻							46		9	
CaCl ₂	28			27						
KCI				3						
NaCl	17			2						
CaClOH				17						
FeCl ₃	4						8			
AgCI						19				
CuCl									28	
AICl ₃ •6H ₂ O			12			64				
Cu ₂ (OH) ₃ Cl	23		43	20		12	9	24	45	54
Friedel's salt	20		4				28			
11CaO•7Al ₂ O ₃ •CaCl ₂	4			32						
Aliphatic-Cl	4	28		_ ^a	5		9	26	_ ^a	_a
Aromatic-Cl	_ ^a	12		_ ^a	0.4		_ ^a	50	19	46

 Table 1. Fractions of the different chemical forms of CI in each sample. Bold numbers indicate percentages exceeding 10%.

 Aliphatic-CI and Aromatic-CI indicate chlorine associated with aliphatic and aromatic carbon, respectively.

^aNot fitted

Concentrations of TCl and insoluble Cl: Concentrations of insoluble Cl were 5–10% of the concentrations of TCl (Figure 1B). Thus, most of the Cl (mainly in the form of water soluble salts) was removed by the washing.

Speciation of TCl and insoluble Cl: The results of the LCF analysis are shown in Figure 1B and C and Table 1. The contributions of aromatic-Cl and aliphatic-Cl became reliable (larger than 10%) after washing, except for the case of PHI (Table 1). This indicates that the washing was effective for reliably estimating the potential concentrations of aromatic-Cl and aliphatic-Cl. In PHI, the contributions of aromatic-Cl and aliphatic-Cl did not become large enough to be reliable. This may have occurred because some insoluble inorganic Cl compounds (with spectra similar to that of $AlCl_3 \cdot 6H_2O$) were uniquely present or because organic Cl itself had low abundance in PHI. We use the contributions of aromatic-Cl and aliphatic-Cl and aliphatic-Cl and aliphatic-Cl and aliphatic-Cl and aliphatic-Cl in the insoluble fractions in the further discussion below.

The ratio of aromatic-Cl to aliphatic-Cl was different depending on the sample. In VN, the amount of aliphatic-Cl was about two-fold larger than that of aromatic-Cl. On the other hand, the amount of aromatic-Cl was twice that of aliphatic-Cl in GH. As wires and cables were mainly burned in VN, the polyvinyl chloride (PVC) used as a coating for wires and cables may have decomposed into certain aliphatic OCs. In GH, wires and cables, as well as printed circuit boards and other plastics, are burned at the same time. The nonmetal parts of printed circuit boards consist mainly of thermoset resins, which generally contain benzene ring structures¹⁴. It is possible that these benzene ring structures combine with Cl during the thermo-chemical process.

We also estimated the chemical forms of inorganic Cl (Table 1). From the results, $Cu_2(OH)_3Cl$ or similar compounds were produced, or existed, in all samples, including the control soil. This indicates that $Cu_2(OH)_3Cl$ or similar compounds play some role in the formation of OCs, or are produced at the same time as OCs. Fujimori et al. reported that copper chlorides, including $Cu_2(OH)_3Cl$, show a correlation with PCDDs, PCDFs, PCBs, and CBzs¹⁵, which is supported by this study.

Comparison with individual compounds: We compared the concentrations of identified Cl from PCDD/DFs, PCBs, CBzs, and Cl-PAHs among the soil samples from all three countries (Figure 1D). The concentration of identified Cl was highest in VN. Open burning of wires and cables has been reported to be a significant source of dioxin-related compounds (DRCs) due to the coexistence of copper and PVC⁵. Fujimori et al. suggested that PVC interacts thermo-chemically with copper and copper chlorides, thus influencing the formation of DRCs during E-waste open burning⁵. The result of this study, where aliphatic-Cl, aromatic-Cl, $Cu_2(OH)_3Cl$, and identified Cl were all present in the highest concentrations in the soil from VN, agrees with the previous report⁵.

The concentration of identified Cl was highest in the order of VN, GH, and PHI, respectively (Figure 1D). A similar trend was observed for both aromatic-Cl and organic Cl, as shown in Figure 1C. This indicates that other OCs are produced along similar pathways during E-waste open burning.

The composition of identified Cl was similar between the VN and PHI soils, with Cl from PCBs (PCBs-Cl) being present in high amounts in both. Meanwhile, Cl from CBzs (CBzs-Cl) was predominantly seen in the GH soil. This may have occurred because inorganic chloride, which catalyzes the formation of PCDD/DFs or PCBs from CBzs, was present in lower amounts in the GH soil. Lustenhouwer et al. showed that PCDD/DFs and PCBs are produced via CBzs from PVC¹⁶. Another possible explanation for the difference among sites relates to differences in the products burned as E-waste. As mentioned above, we suspect that polymers with a benzene ring structure were present in thermoset resins of the E-waste burned in GH. Differences in the products or materials burned can affect the formation of OCs as mentioned in a previous study¹⁷.

We also calculated the contributions of individual compounds to aromatic-Cl. Identified Cl accounted for 0.8– 7.4% of the aromatic-Cl in the E-waste open burning soil samples. This means that more than 90% of the aromatic-Cl in the E-waste open burning soils consisted of unidentified chlorinated aromatic compounds. Indeed, some of these unidentified chlorinated aromatic compounds exist originally in natural soils, but considering that aromatic Cl was present in amounts more than 10-fold greater in the E-waste open burning soils than in the control soil, at least 80% of the aromatic-Cl in the E-waste open burning soils was produced by the combustion of E-waste, or was derived from the E-waste itself.

The difference in the contribution of identified Cl to aromatic-Cl between the different E-waste open burning soil samples (less than 1% in VN and GH vs. 7.4% in PHI) may be due to the underestimation of aromatic-Cl in PHI. Due to a larger amount of inorganic Cl remaining after washing, the LCF value for aromatic-Cl in insoluble Cl was low in the PHI soil (0.4%).

Conclusion: In this study, we determined the concentrations of aromatic-Cl, aliphatic-Cl, and inorganic Cl in water-insoluble fractions of E-waste open burning soils. We showed that concentrations of aromatic-Cl and organic Cl can serve as potential indicators of the presence of OCs, including unidentified compounds. In aromatic-Cl, 89–99.6% is unidentified OCs. A similar trend were observed for aromatic-Cl, organic-Cl, and identified Cl, indicating that unidentified OCs are also produced via similar mechanisms during E-waste open burning. The composition of inorganic Cl also provides important information. Thus, determining the levels of aromatic and organic Cl, and the concentrations of other individual compounds, is important to achieve a comprehensive understanding of the formation mechanisms and dynamics of, and potential risks posed by, OCs. Further studies are needed regarding the potential values of organic Cl.

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