

INVESTIGATION OF UNIDENTIFIED ORGANOCHLORINE COMPOUNDS IN SOIL AFTER OPEN BURNING OF E-WASTE USING TD/PY-GC/MS

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Introduction

In some countries, open burning of electronic waste (e-waste) are conducted as informal e-waste recycling to recover valuable metal from the e-waste. These activities can release toxic chlorinated aromatic compounds and cause health problems for people living near the open burning sites.^{1,2} Previous, we measured higher concentrations of chlorinated aromatic compounds, such as polychlorinated dibenzo-*p*-dioxins and dibenzofurans, polychlorinated biphenyls, chlorobenzenes, and chlorinated polycyclic aromatic hydrocarbons in soil from e-waste open burning sites compared with reference soil and soil from other e-waste recycling sites.^{3,4} The concentrations of chlorinated dioxins in some soil samples collected from the e-waste open burning sites exceeded the environmental quality standards. We also reported that the percentage contributions of chlorine from the measured chlorinated aromatic compounds to the total organic chlorine (TOCl) were negligible and that more than 99.9% of the TOCl comprised unidentified organochlorine compounds, even in the soil from e-waste open burning sites where the highest concentrations of chlorinated aromatic compounds were detected.³ Even after excluding naturally produced unidentified organochlorine compounds, more than 99% of the TOCl was unidentified organochlorine compounds generated anthropogenically by open burning of e-waste. No study has investigated unidentified organochlorine compounds in soil contaminated by open burning of e-waste, although many studies have quantified specific identified chlorinated compounds. To identify unidentified organochlorine compounds in soil from e-waste open burning sites, we performed thermal desorption/pyrolysis-gas chromatography-mass spectrometry (TD/PY-GC/MS) analysis, which has been used to assess soil organic matter including high-molecular-weight compounds.^{5,6} We selected this analytical method because we postulated that the unidentified chlorinated compounds were high-molecular-weight compounds, such as fragments of polyvinyl chloride (PVC), because wires and cables coated with PVC were one of the main materials burnt at open burning sites, and because the highest concentration of chlorinated aromatic compounds was detected in soil from e-waste open burning sites collected in Vietnam, where wires and cables were mainly burnt.^{3,4} We investigated on unidentified organochlorine compounds in soil after open burning of e-waste using TD/PY-GC/MS.

Materials and Methods

Sample collection and sample preparation: This study examined reference soil and soil from an e-waste open burning site. The reference soil sample (RS) was collected in Duong Quang, Vietnam, where no e-waste recycling activities were observed. The e-waste open burning soil sample (EOBS) was collected at an open burning site of wires and cables in Bui Dau, Vietnam, a town known for e-waste recycling activities. EOBS was collected from directly beneath combusted residue after removing as much of the residue as possible. The sampling locations are described in detail elsewhere.⁴ All samples were collected using a shovel, packed in plastic bags, and stored in a cooler. Then, they were air-dried for 1 week, sieved (< 2 mm), and homogenized in the laboratory before analysis.

Measurement conditions and procedure: The soil samples were analyzed using an apparatus consisting of a

Table 1. Measurement condition

condition		EGA analysis	TD analysis	PY analysis
Pyrolyzer condition	apparatus	Py-2020D (Frontier Lab)		
	temperature program	50 °C (0.5 min) - (20 °C/min) → 800 °C (2.0 min)	50 °C - (30 °C/min) → 400 °C (1.3 min)	800 °C for 0.5 min
	flow gas	He		
GC condition	apparatus	7890A GC (Agilent Technology)		
	column	EGA tube	GC capillary column 15 m x 0.25 mm x 0.1 μm (SGE Analytical Science)	
	split rate, split flow	-	1/10, 1 mL/min	
	temperature program	-	70 °C (1 min) - (10 °C/min) → 320 °C (1 min)	
MS condition	apparatus	JMS-1050GC (JEOL)		
	ionization method	Electron Ionization		
	m/z	10 - 600 m/z		

double-shot pyrolyzer (Py-2020iD; Frontier Lab) and a GC (7890A GC; Agilent Technology)/MS (JMS-1050GC; JEOL). We conducted three analyses: (1) evolved gas analysis (EGA)-MS to clarify the thermal properties of the soil samples; (2) TD-GC/MS to analyze volatile constituents in the soil samples; and (3) PY-GC/MS to analyze the polymer content of the soil samples as pyrolyzates. **Table 1** shows the measurement conditions for each analysis. Each soil sample (3 mg for EGA and 5 mg for TD/PY-GC/MS) was put into a sample holder. The pyrolyzer used a double-shot sampler. After being heated in the pyrolyzer, the sample was decomposed thermally or pyrolyzed at the temperature programmed for each analysis (**Table 1**). The analytes were transferred from the reaction zone in the pyrolyzer to the GC/MS via a continuous flow of helium gas. **Table 1** also describes the GC/MS conditions. The National Institute of Standards and Technology MS database was used for identification.

Result and Discussion

EGA-MS: First, we conducted EGA to clarify the thermal properties of the soil samples. This was used to select the temperature program for the TD/PY-GC/MS analysis. **Fig. 1** shows EGA thermograms of RS and EOBS. According to a previous study, volatile constituents in soil are released at around 350°C.⁷ **Fig. 1** shows that the thermal decomposition was generally finished by 400°C and that all of the gas had evolved by 800°C in this study. Consequently, we decided to set the temperature range for TD-GC/MS from 50 to 400°C, and the temperature for PY-GC/MS to 800°C.

TD-GC/MS: TD-GC/MS provides a total ion chromatogram (TIC) containing volatile constituents of a sample thermally desorbed in the pyrolyzer. **Fig. 2(a)** shows the TICs of the volatile constituents of the soil samples that evolved at between 50 and 400°C. Some volatile constituents are naturally contained in soil. To identify the organochlorine compounds generated anthropogenically by open burning of e-waste, we compared the TIC of EOBS with that of RS. The hexagons and triangles in **Fig. 2** are the peaks of aromatic and aliphatic compounds, respectively. Solid symbols indicate that the compounds were

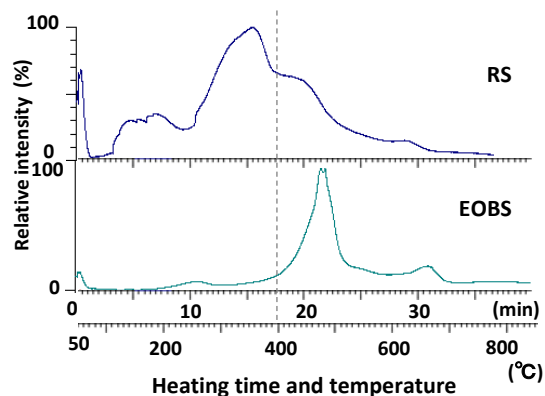


Figure 1. EGA thermograms of a reference soil (RS) and an e-waste open burning soil (EOBS).

detected in both TICs. Open symbols indicate that the compounds were detected only in the TIC of EOBS. We expected there to be more peaks of chlorinated volatile constituents in the TIC of EOBS than in the TIC of RS. As we expected, many peaks were detected only in the TIC of EOBS, while some compounds were detected in both TICs, including cetene [retention time (RT) = 10.5], heptadecene (RT = 13.0), and other higher-molecular-weight aliphatic compounds ($18 < RT$). Sauz-Jimenez and de Leeuw reported that some phthalates, alkanes, and aliphatic compounds trapped in humic acid in soil were released at around 358°C .⁷ Dibutyl phthalate (RT = 14.5) was also detected in both TICs. Though dibutyl phthalate is an artificially synthesized plasticizer, this result can be explained by a report that dibutyl phthalate can be biosynthesized as a microbial metabolite.⁸ Some compounds were detected only in the TIC of EOBS, including the largest peak at RT= 19.48, which was identified as bis(2-ethylhexyl) phthalate. The compound is used as a plasticizer in PVC. This result was consistent with the burnt wire and cables observed at the EOBS sampling site. We analyzed two other e-waste open burning soil samples in a supplementary study (data not shown because of limited space): e-waste open burning soil collected within the same sampling area in Vietnam, where cables were mainly burnt, and e-waste open burning soil from Ghana, where the plastic bodies of electronic products and various kinds of e-waste were mixed and burnt. We also detected the largest bis(2-ethylhexyl) phthalate peak in the cable-burning soil from Vietnam, but did not detect it in the mixed-materials-burning soil in Ghana. Although PVC powder was also analyzed in a supplementary study, bis(2-ethylhexyl) phthalate was not detected in it. This result is consistent with the fact that PVC powder does not

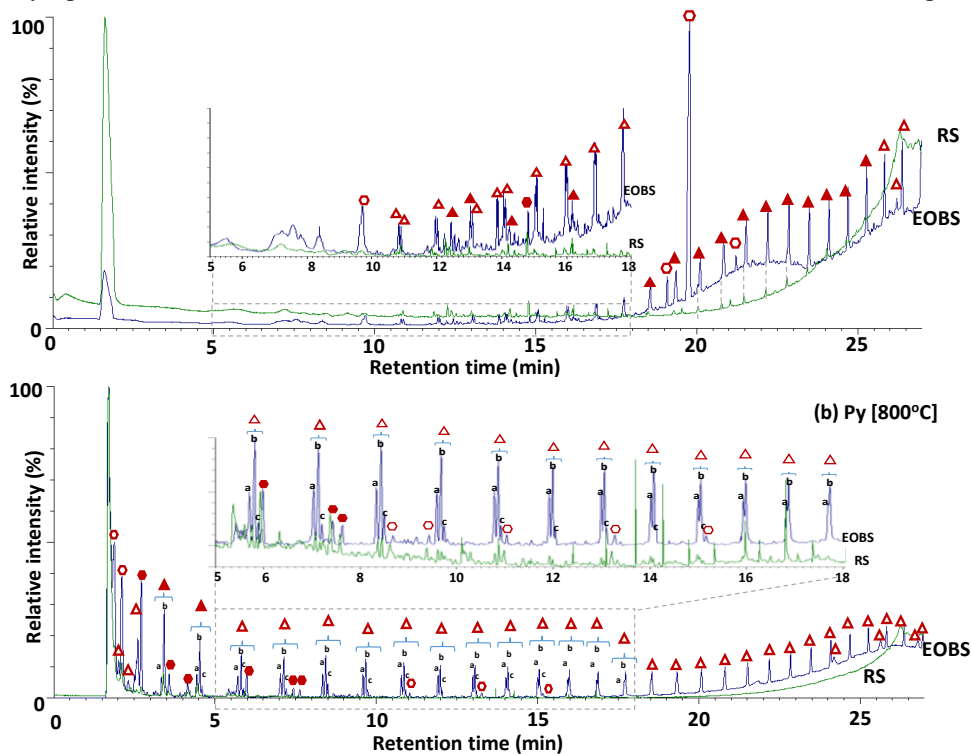


Figure 2. total ion chromatogram of TD-GC/MS and PY-GC/MS

originally contain plasticizer, while the PVC-coated cables, which need flexibility, contain plasticizer. This suggests that bis(2-ethylhexyl) phthalate was not a byproduct of the residual PVC that reacted in the pyrolyzer. This also suggests that bis(2-ethylhexyl) phthalate can be used to trace burnt materials in open burning sites.

PY-GC/MS: Polymeric contents in a sample were pyrolyzed instantly at the pyrolysis temperature of 800°C used in this study and analyzed by PY-GC/MS. To exclude pyrolyzates derived from soil organic matter, and to identify the chlorinated compounds generated by open burning of e-waste, we compared the TIC of EOBS with that of RS from PY-GC/MS. **Fig. 2(b)** shows the pyrolyzates derived from polymer residues in the soil samples. In **Fig. 2(b)**, there are some peaks resulting from aromatic compounds and many peaks of aliphatic compounds in the TIC of EOBS. We expected that there would be more peaks of chlorinated pyrolyzates derived from unidentified organochlorine compounds in the TIC of EOBS than in the TIC of RS. Some aromatic compounds were detected in both TICs, including styrene (RT = 2.4), indene (RT = 4.1), naphthalene (RT = 5.5), 2-methylnaphthalene (RT = 7.2), and 1-methylnaphthalene (RT = 7.3). A previous study reported various pyrolyzates derived from natural soil.⁹ As we expected, there more peaks detected only in the TIC of EOBS and most of them were higher-molecular-weight aliphatic compounds [a, alkadiene; b, alkene; c, alkane in **Fig. 2 (b)**]. Contrary to our expectations, no chlorinated compounds were detected in either TD/PY-GC/MS TIC. We checked the *m/z* 36 mass chromatogram and found a large peak for hydrochlorine with an early RT. These TD/PY-GC/MS results indicate that potentially dechlorinated long-chain compounds exist in soil after open burning of e-waste.

Conclusion: Using TD/PY-GC/MS, we detected potentially dechlorinated long-chain compounds in e-waste open burning soil. We found that the TD-GC/MS chromatogram can be used to trace burnt materials in open burning sites. Previously, we reported that different countries had different customs for open burning of e-waste, including burnt materials and fire methods, and that the differences might affect the combustion products.⁴ In the future, we plan to apply TD/PY-GC/MS to examine differences among combustion products in e-waste open burning soil collected in different countries.

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