Organochlorines in surface soil at electronic-waste wire burning sites and metal contribution evaluated using quantitative X-ray speciation

Takashi Fujimori\textsuperscript{1,2}, Hidetaka Takigami\textsuperscript{1} and Masaki Takaoka\textsuperscript{2}

\textsuperscript{1} Center for Material Cycles and Waste Management Research, National Institute for Environmental Studies (NIES), 16-2 Onogawa, Tsukuba, 305-8506, Ibaraki, Japan  
\textsuperscript{2} Department of Environmental Engineering, Graduate School of Engineering, Kyoto University, Katsura, Nisikyo-ku, 615-8540, Kyoto, Japan  

E-mail: fujimori.takashi.3e@kyoto-u.ac.jp, fujimori.takashi@nies.go.jp

Abstract. Heavy metals and toxic chlorinated aromatic compounds (aromatic-Cls) such as dioxins and polychlorinated biphenyls (PCBs) are found at high concentrations and persist in surface soil at wire burning sites (WBSs) in developing countries in which various wire cables are recycled to yield pure metals. Chlorine K-edge near-edge X-ray absorption fine structure (NEXAFS) is used to detect the specific chemical form of Cl and estimate its amount using a spectrum jump in the solid phase. Quantitative X-ray speciation of Cl was applied to study the mechanisms of aromatic-Cls formation in surface soil at WBSs in Southeast Asia. Relationships between aromatic-Cls and chlorides of heavy metals were evaluated because heavy metals are promoters of the thermochemical solid-phase formation of aromatic-Cls.

1. Introduction

Toxic chlorinated aromatic compounds (aromatic-Cls) such as dioxins, polychlorinated biphenyls (PCBs), and chlorobenzenes are produced by various anthropogenic thermal processes. High concentrations of dioxins and PCBs are found in soil at wire burning sites (WBSs) \cite{1}. Wire burning is performed in developing countries and relatively pure metals (especially copper) have been recovered by direct oil burning of various wires and cables from dismantled electronic-wastes on natural soil surfaces. Figure 1a shows a WBS at Vietnam visited of this study. Because exhausted gas and residual soil at WBSs can increase the health risks of workers and local citizens, knowing the total concentration and thermochemical behavior of aromatic-Cls at WBSs is necessary.

Chlorine K-edge near-edge X-ray absorption fine structure (NEXAFS) can be used to detect a specific chemical form of Cl \cite{2,3} and to estimate Cl concentrations using a spectrum jump \cite{4} in the solid phase. Studies have applied Cl K-edge NEXAFS to natural soils \cite{2} and fly ashes in anthropogenic thermal processes \cite{3}; however, characteristic soils at WBSs have not been studied using this technique. Quantitative X-ray speciation of Cl was applied to evaluate the mechanisms of aromatic-Cls formation in surface soil at WBSs in Southeast Asia. The relationship between aromatic-Cls and chlorides of heavy metals was further evaluated since heavy metals are a well-known promoter of the thermochemical solid-phase formation of aromatic-Cls \cite{5}. Recently, Otsuka et al. analyzed copper chloride as a major chemical form of copper at WBS by using Cu K-edge X-ray absorption spectroscopy \cite{6}. So, Cl K-edge NEXAFS also has the possibility of detection of copper chlorides.
2. Materials and methods

Environmental soil samples were collected around Metro Manila, the Philippines (PHI), during August 2010, as well as Hanoi, Vietnam (VN), in January, 2011. Detailed sampling procedures were based on our previous study [7]. Environmental soil samples were selected as blackened soil at WBSs in VN and PHI after direct open-air wire burning, non-black soil at WBS similar to the ash color in VN, surface soil near the WBS (25 m from WBS) in VN, and control surface soil in VN. After drying the soil samples under air atmosphere for approximately 1 week, soil preparations were made. Fig. 1b shows representative soil colors. Powdered soil samples were mounted on carbon tape. Measurements of the Cl K-edge NEXAFS spectrum were taken for each sample between 2810 and 2860 eV detected by X-ray fluorescence using BL-11B at the Photon Factory in Tsukuba, Japan. We used “difference between intensity at 2850.8 and baseline at pre-edge” (denoted by “Δμt”) of the raw Cl K-edge NEXAFS spectrum to quantify total chlorine concentration (mg/kg) in a soil sample by referring to a calibration curve (1–1,400 mg/kg) by Leri et al. [4], as shown in Fig. 1b. Furthermore, measurements were taken of a sample with high Cl concentrations (>10,000 mg/kg) using field-portable X-ray fluorescence spectroscopy (FP-XRF, Innov-X alpha; Innov-X Systems, Woburn, MA). High Cl concentrations had similar values between Cl K-edge NEXAFS and FP-XRF. Therefore, Δμt was a useful indicator of Cl quantification below nonmeasurable ranges using the XRF method. Ratios of Cl chemical forms in soil samples were analyzed by linear combination fitting (LCF) using inorganic chlorides (KCl, NaCl, CaCl₂, MgCl₂), metal chlorides [Cu₂(OH)₃Cl, CuCl₂, CuCl, FeCl₃, FeCl₂·4H₂O PbCl₂, ZnCl₂], and organic chlorides. Organic chlorides showed similar NEXAFS spectra depending on aliphatic and aromatic structures [2,3]. Representative chemicals were used such as 2,3-chlorophenol (aromatic) and polyvinyl chloride (aliphatic). To explore the variability of LCF results, five types of fitting ranges (2810–2830, ~2835, ~2840, ~2845, ~2850 eV) were examined. Next, the average and standard deviation of five types of fitting results were calculated. Fitting example with representative reference spectra is shown in supplementary Fig. S1. By combining the concentrations of total Cl using the Δμt ratio of chlorinated aromatic compounds by LCF, the concentration of aromatic-Cls was estimated. Detailed analytical procedures were described previously [3].

3. Results and discussion

Total Cl concentrations in blackened soils at WBSs showed the highest values of 21,000 mg/kg in at the WBS in VN and 16,000 mg/kg in the WBS in PHI, respectively, based on Δμt analysis (Fig. 1b), which suggests that the interregional similarity was due to informal wire burning activity between VN and PHI. In contrast, control soil (VN) had the lowest concentration of total Cl (120 mg/kg). Therefore, surface soil at the WBS was heavily polluted by chlorine derived from wire and cable insulation-coating materials. Surrounding surface soil at the WBS (25 m from WBS) in VN contained 720 mg/kg Cl. Therefore, contaminated Cl in blackened soil may not spread to the surrounding environment.
Non-blackened soil at the WBS, such as the ash color in VN, contained high concentrations of total Cl (5,400 mg/kg); however, its concentration was lower than blackened soil at the WBS, partly due to the mixing of blackened soil with natural soil. Blackness of soil at the WBS was thought to be a useful indicator of pollution level of chlorine (and aromatic-Cls described below) as well as heavy metals [6].

Chemical forms of chlorine in soil samples at the WBSs were analyzed using LCF of Cl K-edge NEXAFS spectra. Chlorine was partially connected with aromatic carbon (5.2–18% of total Cl) in all types of surface soils, as shown in Fig. 2. According to the distribution pattern of 11 references, blackened soils at WBSs in PHI and VN showed a relatively similar pattern and were distinguished from other soils, which suggested that wire burning was performed using similar electronic-waste materials in PHI and VN. Control soil contained no MgCl$_2$ or CaCl$_2$, which were detected in blackened soils at the WBS by LCF and showed the highest ratio of Cl connected with aromatic carbon [2]. Non-blackened soil at the WBS in VN was thought to have an average distribution pattern from blackened (VN) and control soil (VN). Therefore, mixing blackened soil with natural soil may contribute to this characteristic distribution pattern. The surrounding surface soil at the WBS (25 m from WBS) in VN showed a high ratio of Cl connected with aromatic carbons (Fig. 2), which reflects natural soil characteristics.

Quantitative speciation of Cl revealed aromatic-Cls concentrations in environmental soil at the WBSs. Figure 3 shows that blackened soil at the WBSs contained high levels of aromatic-Cls. The WBS in VN and the one in PHI were assessed as having 1,000 ± 570 and 1,200 ± 240 mg/kg, respectively, of aromatic-Cls in blackened soils. Non-blackened soil at the WBS in VN showed relatively high aromatic-Cls concentrations (500 ± 47 mg/kg). The lowest and relatively low concentrations of aromatic-Cls were respectively assessed in control soil (18 ± 4.8 mg/kg) and surrounding soil at the WBS in VN (110 ± 13 mg/kg). Compared with global measurements of natural aromatic-Cls concentrations by Asplund and Grimvall [8], blackened and non-blackened soils at the WBSs had concentrations higher than the maximum value (360 mg/kg) measured in natural soils at 26 sampling sites denoted by Natural (World) in Fig. 3. In contrast, aromatic-Cls concentrations in the surrounding soil (25 m from WBS) in VN was at median (75%) levels based on the Natural (World), while control soil (VN) concentrations were under the 25% level. Although some have reported toxic aromatic-Cls concentrated in soil at the WBS, the total concentration of PCDD/Fs and PCBs in WBS soil was only a few mg/kg [1]. Therefore, blackened soil at the WBS contained toxic aromatic-Cls at concentrations of a few hundred mg/kg, which also contained unreported toxins such as chlorobenzenes, chlorinated PAHs, and unknown chlorinated organics, excluding reported toxins (PCDD/Fs and PCBs) [1] and natural background (median: 69 mg/kg, range: 4–360 mg/kg [8]).
Quantitative speciation revealed correlations between inorganic chlorides and aromatic-Cls. High positive correlation coefficients were found between aromatic-Cls and Cu$_2$(OH)$_3$Cl ($R^2 = 0.97$), NaCl (0.98), MgCl$_2$ (0.97), PbCl$_2$ (0.92), and KCl (0.85). Previous reports have identified the thermochemical chlorination mechanism of carbon triggered by metal chlorides [5]. Recent copper study did not have the Cu$_2$(OH)$_3$Cl in their library [6]. The present study was the first to report detection of Cu$_2$(OH)$_3$Cl in soil at the WBSs. Cu$_2$(OH)$_3$Cl played a key role as a strong catalytic promoter to generate aromatic-Cls in the solid phase during thermochemical processes [5,9,10]. This suggests that high concentrations of aromatic-Cls in WBSs were derived from thermochemical interactions of carbon matrix in the soil surface or insulation-coating materials with oxychlorination of metal copper in wires and cables, which produced Cu$_2$(OH)$_3$Cl.

The present studies applied quantitative speciation using Cl K-edge NEXAFS to estimate total Cl content, the chemical form of Cl, aromatic-Cls concentration, and correlations in relation to the formation mechanism of aromatic-Cls in various soils at WBSs. Although the accuracy of this analytical technique compared with other quantitative methods remains unknown, Cl-connected compounds can be quantified at a broad range of concentrations, which can be used to perform quantitative speciation of chlorine in various environmental solid matrices.

**Acknowledgements**

We thank G. Suzuki (NIES) and S. Sakata (IDE-JETRO) for supporting field sampling; K. Shiota (Kyoto Univ.), Y. Kitajima (KEK-PF, BL-11B), and Y. Inada (KEK-PF, BL-9A) for helping with Cl K-edge NEXAFS measurement at Photon Factory (proposal 2007G069).

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