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Organochlorines in Surface Soil at Wire Burning and Metal Contribution by means of Quantitative X-ray Speciation

Takashi Fujimori[1,2,*], Hidetaka Takigami[1] and Masaki Takaoka[2]

[1]National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba, 305-8506, Ibaraki, Japan

[2]Kyoto University, Katsura, Nisikyo-ku, 615-8540, Kyoto, Japan

1 Introduction

Toxic chlorinated aromatic compounds (aromatic-Cls) were known to be produced by various anthropogenic thermal processes. Recent studies found high concentration of aromatic-Cls in soil at wire burning sites (WBS) [1]. Workers recovered relative pure metals (especially copper) through the wire burning which was conducted by direct oil burning of various wires and cables from dismantled electronic-wastes on natural soil surface. Chlorine K-edge near-edge X-ray absorption fine structure (NEXAFS) enables us to detect the specific chemical form of Cl [2,3] and to estimate the amount of Cl present by using a spectrum jump [4] in the solid phase. In this study, we applied quantitative X-ray speciation of Cl to study the mechanisms of aromatic-Cl formation in surface soil at WBS in Southeast Asia.

2 Experiment

We collected environmental soil samples around Metro Manila, the Philippines (PHI), at August, 2010, and around Hanoi, Vietnam (VN), at January, 2011.

Powdered soil samples were mounted on carbon tape. We measured Cl K-edge NEXAFS spectrum of each sample between 2810 and 2860 eV detected by X-ray fluorescence using BL-11B in Photon Factory (Tsukuba, Japan). We used "difference between intensity at 2850.8 and baseline at pre edge" (denoted by "$\Delta\mu t$") of raw Cl K-edge NEXAFS spectrum to quantify total chlorine concentration (ppm) in a soil sample referred a calibration curve (1~1,400 ppm) by Leri et al. [4]. $\Delta\mu t$ was thought to be useful indicator as Cl quantification below non-measurable range by ordinary XRF method. In this study, ratios of Cl chemical forms in soil sample were analyzed by linear combination fitting (LCF) by using inorganic chlorides, metal chlorides, and organic chlorides. Organic chlorides showed quite similar NEXAFS spectra depending on aliphatic and aromatic structures [2, 3]. So, we used representative chemicals such as 2,3-chlorophenol (aromatic) and polyvinyl chloride (aliphatic). To understand variability of LCF result, we examined 5 types of fitting range (2810~2830, ~2835, ~2840, ~2845, ~2850 eV). We calculated average and standard deviation of 5-types fitting results. Through combination concentration of total Cl by $\Delta\mu t$ with ratio of chlorinated aromatic compound by LCF, concentration of aromatic-Cls was estimated.

3 Results and Discussion

We attempted to apply quantitative speciation by using Cl K-edge NEXAFS to estimate total Cl content, chemical form of Cl, aromatic-Cls concentration, and correlationship in relation to formation mechanism of aromatic-Cls in various soils at WBS. Quantitative speciation of Cl revealed aromatic-Cls concentration in environmental soil at WBS. Fig. 1 shows that blacken soil at WBS concentrated the highest aromatic-Cls. Compared with previous global measurements of natural aromatic-Cls concentrations [6], blacken and non-black soils at WBS had higher concentrations than a maximum value (360 mg/kg) among natural soils in 26 sampling sites denoted by Natural (World). We also explored the relationship between aromatic-Cls and chlorides of heavy metals. Heavy metals are well-known promoters of the thermochemical solid-phase formation of aromatic-Cls [5]. Although we need to study measurement accuracy of this analytical technique, Cl-connected compounds are able to be quantified with wide concentration range and we are possible to apply the quantitative speciation of chlorine to various environmental solid matrices.
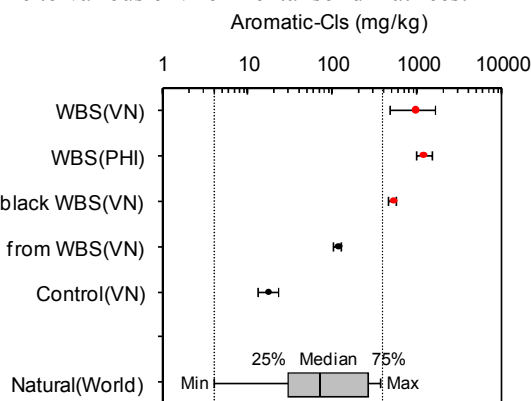

Fig. 1: Amount of aromatic-Cls by quantitative speciation of Cl K-edge NEXAFS.

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* fujimori.takashi.3e@kyoto-u.ac.jp