

QUANTIFICATION OF TOTAL ORGANOHALOGENS (TOX) IN ENVIRONMENTAL SOLID SAMPLES BY USING COMBUSTION-ION CHROMATOGRAPHY

Mukai K¹, Fujimori T^{1,2*}, Shiota K¹, Takaoka M^{1,2}, Funakawa S³, Takeda A⁴, Takahashi S^{5,6}

¹Department of Environmental Engineering, Graduate School of Engineering, Kyoto University, Kyoto, 615-8540, Japan; ²Department of Global Ecology, Graduate School of Global Environmental Studies, Kyoto University, Kyoto, 615-8540, Japan; ³Graduate School of Agriculture, Kyoto University, Kyoto 606-8502, Japan; ⁴Department of Radioecology, Institute for Environmental Sciences, Rokkasho-mura, Aomori, 039-3212, Japan; ⁵Center for Marine Environmental Studies, Ehime University, Matsuyama, Ehime 790-8577, Japan; ⁶Center of Advanced Technology for the Environment, Faculty of Agriculture, Ehime University, Tarumi, Ehime, 790-8566, Japan

Introduction

Large amounts of organohalogen compounds are released into the environment by human activities. Industrially produced organohalogen compounds are used in many products, such as pesticides, solvents, and flame retardants, and unintentionally produced organohalogen compounds, such as dioxin-related compounds (DRCs), are produced as by-products of industrial processes, for example, chlorine bleaching and waste incineration. Several new sources of DRCs have been identified over recent decades, such as house dust and electronic waste (e-waste) open burning activities. Besides anthropogenic release, many studies have shown that organohalogen compounds are also produced naturally in forest soil by microbial activities and abiotic processes [1, 2]. It is nearly impossible to determine all of these compounds individually; therefore, quantification of the total amount of organohalogen compounds is necessary. This information can be used for screening, and also provides information about unknown DRCs and biogeochemical cycling of halogens.

The most important step in the analysis of total organohalogen compounds in solid samples is pretreatment, namely, the removal of inorganic halides, or extraction of organic halogens. However, there are some uncertainties surrounding complete removal of inorganic halides, and different pretreatment methods have been applied depending on the research field and target samples. Total organohalogen (TOX) is a group parameter that gives the concentration of halogens after washing by aqueous solution; TOX has been mainly used for forest soil and few studies have used TOX for anthropogenic samples.

In this study, we investigated the optimal pretreatment method for TOX analysis, using municipal solid waste incineration (MSWI) fly ash and forest soil. Then, the optimal pretreating method was applied to various environmental solid samples (forest soil, paddy soil, e-waste open burning soil, house dust, MSWI bottom ash, and MSWI fly ash) and TOX was measured using combustion-ion chromatography (combustion-IC). In this study, “halogen” denotes chlorine (Cl) and bromine (Br). Cl and Br 1s X-ray adsorption near-edge structure (XANES) analysis was also used to assess the level of removal of inorganic halogens.

Material and methods

Sample: Forest soil (forest) was collected from the A horizon (depth: 5–10 cm) at Mt. Yoshida, Japan, in August 2016. The vegetation in the area is dominated by deciduous trees, and soil from this area has previously been classified according to soil taxonomy [3]. Paddy soil (paddy) was collected from a rice paddy field in Aomori, Japan, in March 2003. This soil was an Andosol, and concentrations of ions were determined by NAA and ICP-MS after combustion [4]. E-waste open burning soil (e-waste) was collected from the Agboghloshie market, Ghana, in 2013. Soil collected from the same point in 2010 was studied in previous research [5]. The house dust (dust) sample came from the NIST standard reference material 2585, and was taken from vacuum cleaner bags collected from homes, cleaning services, motels, and hotels in America in 1993–1994. The MSWI bottom ash (bottom) sample was taken from the standard reference material, JSAC 0512, and the MSWI fly ash (fly) sample was taken from the standard reference material, JSAC 0511. These ash samples were collected from a waste (mainly wood waste) incineration plant in Japan.

Pretreatment: Prior to TOX measurements, three studies (a–c) were conducted to determine the optimal pretreatment method for TOX. Here, the concentrations of TOX reported are those in the residue sample; the result was NOT converted into the concentration in the original sample.

a) Shaking time: A dried and sifted sample (fly ash, 0.1 g) was mixed with 5 mL of KNO₃ (4.1 g/500 mL) and shaken; the suspension was then filtered through a 0.45- μ m filter. The residue was dried and then measured by

combustion-IC. A range of shaking times (5 minutes, 30 minutes, 1 hour, 3 hours, 6 hours, 12 hours, 24 hours, 48 hours, and 75 hours) were used to obtain nine different residues.

b) Number of washes: A dried and sifted sample (forest and fly, 0.1 g) was mixed with 5 mL of KNO₃ (4.1 g/500 mL) and shaken for 1 hour; the suspension was then filtered through a 0.45- μ m filter to produce Residue 1. The residue was washed into another bottle using 5 mL of ultra-pure water and shaken for 1 hour, and then filtered again through a 0.45- μ m filter to produce Residue 2. The same process was repeated (wash into bottle, shake, and filter) twice more (Residues 3, 4), and all of Residues 1–4 were dried and measured with combustion-IC.

c) Solid-liquid separation: Dried and sifted sample (forest and fly, 0.1 g) was mixed with 10 mL of ultra-pure water and shaken for 1 hour; then, the suspension was separated into solid and liquid phases. The same process (wash into bottle, shake, and solid-liquid separation) was repeated twice more. Three different filters (1 μ m, 0.45 μ m, and 0.2 μ m) and centrifugation were used for solid-liquid separation. These four different residues were measured using combustion-IC.

Combustion ion-chromatography (combustion-IC): Five milligrams of dried residue was placed into a ceramic boat with 25 mg of WO₃ and introduced into a combustion unit (AQF-2100H, Mitsubishi Chemical Analytech). After halogens were decomposed and absorbed into H₂O₂, the solution was pumped into a suppressor-type ion chromatograph (HIC-20ASP, Shimadzu).

Cl 1s XANES analysis: XANES spectra were measured between 2810 and 2860 eV using the total-fluorescence-yield (TFY) method and total-electron-yield (TEY) method at beamline BL-11B of the Photon Factory in Tsukuba, Japan. Each sample was applied to carbon tape and irradiated with soft X-rays. Analytical software (REX2000, Ver. 2.5, Rigaku) was used for analysis.

Br 1s XANES analysis: XANES spectra were measured between 13,400 and 13,560 eV at beamline BL01B1 of Spring-8 in Hyogo, Japan. Each sample was measured in transmission mode using ionization chambers and in fluorescent mode using a 19-element Ge solid-state detector. Analytical software (Athena, Ver. 0.9.25) was used for analysis [6].

Results and discussion

Optimal pretreatment method

a) Shaking time

For shaking times from 5 to 30 minutes, both total organochlorine (TOCl, mg/kg) and total organobromine (TOBr, mg/kg) decreased. From 1 to 75 hours, both TOCl and TOBr were stable. This indicates that 1 hour is sufficient shaking time to remove inorganic halogens.

b) Number of washes

For forest soil, TOCl decreased as the number of washes increased from one to three, and TOBr decreased as the number of washes increased from one to two. For fly ash, both TOCl and TOBr decreased as the number of washes increased from one to three. This indicates that three washes are sufficient to remove inorganic halogens.

c) Solid-liquid separation

For forest soil, there were no significant differences with different separation methods for both TOCl and TOBr. For fly ash, there were no significant differences with different separation methods for TOCl; however, TOBr increased as the pore diameter of the filter increased. This is because the total weight loss by washing had a large influence, and led to overestimation of the concentration. Taking these factors into consideration, it can be concluded that there was no significant difference in TOX depending on separation method (filtration using 1- μ m, 0.45- μ m, and 0.2- μ m filters/centrifugation). Hence, centrifugation was chosen as the optimal solid-liquid separation method.

From these three studies (a–c), the optimal pretreatment method was determined as follows: shaking time: 1 hour, number of washes: 3, and solid-liquid separation method: centrifugation (Figure 1).

Quantification of TOX

Dried and sifted samples (0.1 g) were mixed with 5 mL of KNO₃ (4.1 g/500 mL) and shaken for 1 hour. After the suspension was centrifuged, the residue was washed into another bottle by 10 mL of ultra-pure water and

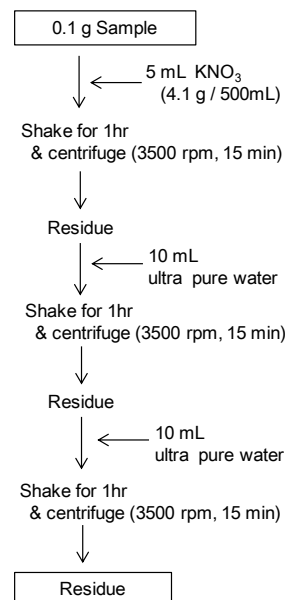


Figure 1 The optimal pretreatment method determined in this study.

shaken for 1 hour. The same process (wash into bottle, shake, and centrifuge) was repeated once and the residue was measured by combustion-IC (Figure 1).

Here, TOX is the result converted into the concentration in the original sample. Figure 2 shows the results for TOCl and TOBr. In all samples, considerable amounts of TOCl were detected and TOCl varied greatly between samples. For TOBr, there were few differences between samples except for the concentrations measured in fly ash.

Previous research on Norway coniferous forest [7] found concentrations of TOCl of 128–631 mg/kg and of TOBr of 24–69 mg/kg in the F and H soil layer (depth: 5–25 cm). Comparison with the results in this study shows similar concentrations of TOCl and TOBr regardless of differences in soil type and vegetation. The results indicate overall that organochlorine and organobromine are ubiquitous in forest soils. This suggests the possibility that some organohalogen compounds are produced naturally and that halogens play important roles in natural forest ecosystems.

The concentrations of both TOCl and TOBr in paddy soil were slightly higher than in forest soil.

High concentrations of TOCl were found in ash samples (fly ash and bottom ash). Most studies on total concentrations of organohalogens in ash samples used extractable organohalogens (EOX), which is the total concentration of halogens in extracts of organic solvent. Previous research on ash samples from waste incinerators in Japan showed an extractable organochlorine (EOCl) concentration of 24 mg/kg, and an extractable organobromine (EOBr) concentration of 2.5 mg/kg in fly ash. EOCl and EOBr concentrations were reported as 18 mg/kg and 0.2 mg/kg, respectively, in bottom ash [8]. Compared with the results in this study, EOX is about 1–5% of TOX. There are two possible reasons for this. The first is that EOX underestimates the real total concentration because not all organohalogen compounds can be extracted by organic solvents. The second is that TOX overestimates the real total concentration because not all inorganic halides can be removed by aqueous solution. This will be discussed further.

The TOCl concentration in house dust was as high as that in ash samples. This indicates that there are significant amounts of organochlorine compounds in our living environment.

In e-waste open burning soil, the TOCl concentration was higher than that of forest soil and lower than that of ash samples. The TOBr concentration was the same as that in forest soil.

Cl XANES spectroscopy

Figure 3(A) shows the Cl XANES spectra. Focusing on the energy position of the maximum peak, we can see the dominant form of Cl in the sample; the peak at 2820.4 eV (line E₁) derives from aliphatic Cl, the peak at 2821.1 ± 0.1 eV (line E₂) derives from aromatic Cl, and the peak within the range around 2822–2826 eV (range E₃) derives from inorganic Cl [9]. For forest soil, the peak at line E₂ existed both before and after pretreatment, indicating that aromatic Cl was dominant in forest soil even before pretreatment and thus the TOCl concentration measured is reasonable for forest soil. For paddy soil, the form of the spectra changed after pretreatment but no clear peak was seen around 2820–2821 eV. This suggests that the TOCl concentration measured for paddy soil overestimated the real total Cl concentration because of insoluble inorganic salts. For e-waste open burning soil, the peak was within the range E₃ before pretreatment. After pretreatment, however, two peaks were observed (at line E₂ and in range E₃), indicating that certain amounts of inorganic Cl were removed by pretreatment. The peak at line E₂ indicates that aromatic Cl is dominant in TOCl; however, another spectrum (not provided in this paper) showed a peak at 2820 eV. Thus, it is not possible to confirm that aromatic Cl is dominant in TOCl concentrations in e-waste open burning soil. For house dust, the peak was within the range E₃ before pretreatment; however, after pretreatment, the peak was at line E₁. This indicates that inorganic Cl was removed effectively by the pretreatment and that the TOCl concentration measured for house dust is reasonable. In addition, we can conclude that aliphatic Cl was dominant in the TOCl of house dust. For fly ash and bottom ash,

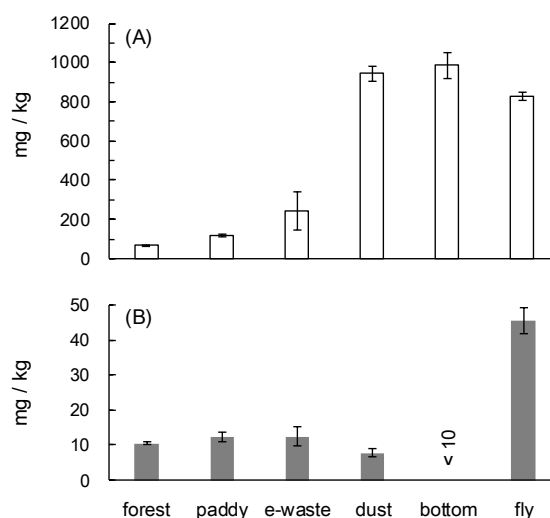


Figure 2 Concentrations of halogens in the residues of each sample. (A) TOCl, (B) TOBr

the peak was in the range E_3 both before and after pretreatment. This indicates the existence of large amounts of insoluble chloride salts, that the TOCl concentration measured for fly ash and bottom ash overestimates the real total organochlorine concentration.

Br XANES spectroscopy

Figure 3(B) shows the Br XANES spectra. Focusing on the energy position of the maximum peak, we can see the dominant form of Br in the sample; the peak at 13,471–13,473 eV (line E_4) is derived from organic Br and the peak within 13,475–13,481 eV (range E_5) is derived from inorganic Br [10]. For forest soil and paddy soil, the peak at line E_4 existed both before and after pretreatment, indicating that organic Br was dominant in forest soil and paddy soil even before pretreatment. Therefore, the TOBr concentration measured is reasonable for forest soil and paddy soil. For e-waste open burning soil, the peak was within the range E_5 before pretreatment, and two peaks were observed (at line E_4 and in range

E_5) after pretreatment. This means that inorganic Br was removed by pretreatment. For fly ash, the peak was in the range E_5 both before and after pretreatment; this indicates the existence of large amounts of insoluble bromide salts and thus TOBr concentration measured for fly ash overestimates the real total organobromine concentration. There are no Br XANES spectra for house dust and bottom ash, and these will be measured in future work to assess whether inorganic Br is removed well by the pretreatment process for these samples.

Conclusion

In this study, an optimal pretreatment method for TOX was presented, and the TOX concentrations of various environmental solid samples were measured. The results showed that large amounts of organohalogens exist in solid samples and the amounts of TOX vary for each sample. XANES spectra showed that the meaning of TOX differed between samples. For forest soil, e-waste open burning soil, and house dust, TOX was a reasonable parameter that accurately represented the total organohalogen concentration. For paddy soil, the TOX value seemed to exceed the real total concentrations. For fly ash and bottom ash, TOX was not a good parameter because large amounts of insoluble inorganic salts remained in the sample after pretreatment. These differences can provide information on the kinds of halogen compounds present in each sample. More research is needed to establish methods for determining real total organohalogen concentrations.

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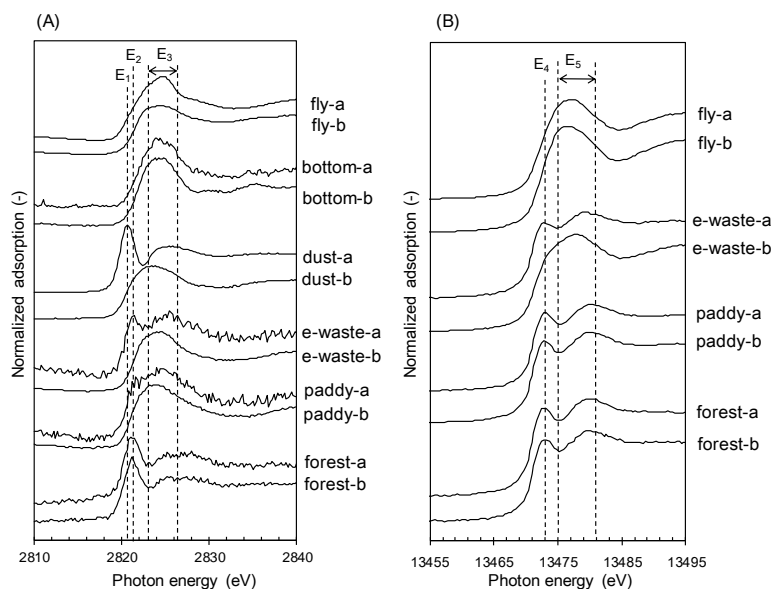


Figure 3 XANES spectra of each sample (a: after pretreatment / b: before pretreatment). (A) Cl-K XANES spectra, (B) Br-K XANES spectra