

SPECIATION OF CHLORINE AND BROMINE IN SOLID ENVIRONMENTAL SAMPLES: FOCUS ON THE INSOLUBLE AND EXTRACTABLE FRACTIONS

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Introduction

The quantification of organically bound halogen (X = chlorine [Cl] and bromine [Br]) and the analysis of individual organohalogen compounds (OHCs) is an effective way to clarify the mass balance of the identified and unidentified organohalogen compounds in the environment. Previous studies have indicated the abundance of unidentified organohalogen compounds¹⁻³. To quantify organically bound X (organo-X), the “insoluble” and “extractable” fractions are examined. Insoluble fraction was studied based on the principle that most inorganic chlorine compounds are water-soluble and most OCs are hydrophobic. Mukai *et al.* applied X-ray absorption near edge structure (XANES) analysis and combustion ion chromatography (CIC) to the insoluble fraction and determined the concentrations of aromatic-Cl, aliphatic-Cl, and organo-Cl¹. Solid environmental samples have also been treated with organic solvents to make the extractable fraction². Gel permeation chromatography (GPC) has been used to fractionate extracts into high- and low-molecular-weight fractions, with neutron activation analysis (NAA) used for the halogens determination². Here, we investigated the speciation of halogens focusing on the insoluble and extractable fractions in solid environmental samples, including house dust, urban particulate matter (PM), and forest soil. We also calculated the identified X from individual analyses and certified values for standard reference materials (SRMs) and evaluated the mass balance of identified and unidentified OHCs. This study integrated the mass balance of halogens from two different viewpoints (insoluble and extractable) and characterized halogens in different solid environmental samples.

Materials and Methods

Samples: House dust was acquired from the National Institute for Standards and Technology (NIST) SRM 2585. The concentrations of the 42 polychlorinated biphenyl (PCB) congeners and 14 chlorinated pesticides are provided as certified or reference values. Urban PM was taken from the NIST SRM 1648a. Certified or reference values for the 58 PCB congeners and 34 chlorinated pesticides are provided. Forest soil was obtained from the Japan Society for Analytical Chemistry (JSAC) SRM 0422. The concentrations of polychlorinated dibenzo-*p*-dioxins and dibenzofurans and 12 dioxin-like PCB congeners were certified.

Halogen analysis: The concentration of X in the original sample (total X) was measured using CIC¹. The concentration of X in the residue after three washes with aqueous solution (insoluble X) was also measured by CIC¹. Briefly, the sample was washed once with KNO₃ solution and twice with ultrapure water. The chemical speciation of X in the original sample and residue after washing was determined using XANES at the Photon Factory (Cl XANES) and SPring-8 (Br XANES)^{1,4}. From the linear combination fitting analysis of XANES using the analytical software Athena, we determined the proportions of X bonded with aromatic carbon (aromatic-X), X bonded with aliphatic carbon (aliphatic-X), and inorganic X. By multiplying the concentrations of Cl and proportions of chemical species, the concentrations of each chemical species were estimated. The concentrations of X in the low- (< 1,000) and high-molecular-weight (> 1,000) fractions of the extract (EOX-L and EOX-H, respectively) were measured by NAA at the Kyoto University Reactor (KUR)². Briefly, the sample was extracted with acetone, acetone/hexane (1:1, v/v), and toluene, then washed with a mixture of 5% Na₂SO₄ solution and methyl *tert*-butyl ether/hexane (1:1, v/v). Then, the washed extract was fractionated by GPC. The fractionation point was determined using a standard solution containing corn oil and a mixture of di- to decabrominated diphenyl ethers. For NAA, 2 mL of the fractionated extract was used. The sample was placed in a polyethylene (PE) bag and dried under normal temperature and pressure. Then, the PE bag was sealed and placed in another PE bag, which was also sealed. Samples in the PE bags were placed in a capsule and irradiated for 10 or 15 min with a thermal neutron flux of 2.0–2.4 × 10¹³ cm⁻²·s⁻¹ at KUR. The radioactivity of ³⁸Cl and ⁸⁰Br was measured for 5 min using a Ge semiconductor detector. Quantification was based on γ -peak areas from ³⁸Cl ($t_{1/2}$ = 37.18 min, E_{γ} = 1,642 keV) and ⁸⁰Br ($t_{1/2}$ = 17.6 min, E_{γ} = 616 keV).

Analysis of PBDEs: Crude extracts of urban PM and forest soil were purified by treating them with concentrated sulfuric acid and passing them through an activated silica gel column. Then, the PBDEs were quantified using a gas chromatograph connected to a quadrupole mass spectrometer (GCMS-QP2010 Ultra, Shimadzu). The detailed procedures have been described elsewhere⁵.

Analysis of PCDD/Fs: Crude extracts of house dust and urban PM were cleaned-up with concentrated sulfuric acid, multi-layer silica gel and activated carbon-impregnated silica gel. Then, tetra- to octa-substituted PCDD/Fs

were analyzed using gas chromatography–high-resolution mass spectrometry (GC–HRMS). The analytical instruments consisted of a 6890N gas chromatograph (Agilent Technologies) connected to a JMS-800D mass spectrometer (JEOL). The detailed procedures have been described elsewhere⁶.

Calculation of identified X: The identified X is the sum of the X concentrations accounted for by identified individual organohalogen compounds and calculated from the certified concentrations for SRMs and measured concentration of PBDEs.

Results and Discussion

Speciation of halogens: Figure 1 shows the Cl and Br K-edge XANES spectra of samples (original and residue). The XANES spectra differed markedly between the original and residual samples of house dust and urban PM. The peak at 2,821.2 eV (the line in Figure 1A) is due to aromatic-Cl, that at 2,820.5 eV is due to aliphatic-Cl, and that at 2,822–2,825 eV is due to inorganic Cl. The peak at 13,473.5 eV (the line in Figure 1B) is due to aromatic-Br, that at 13,472.8 eV is due to aliphatic-Br, and that at 13,476–13,480 eV is due to inorganic Br. Inorganic X was dominant in the original samples of house dust and urban PM, while organo-X was dominant after washing. From the linear combination fitting of sample spectra (Figure 1) with those of standard chemicals, the proportions of aromatic-X, aliphatic-X, and inorganic X in the total X

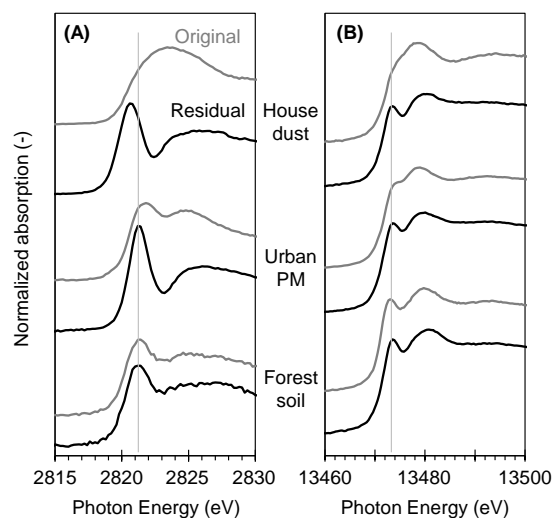


Figure 1 (A) The Cl and (B) Br K-edge X-ray absorption near-edge structure (XANES) spectra of the samples. The vertical line at 2,821.1 eV is the peak due to aromatic organochlorine and the one at 13,473.5 eV is the peak due to aromatic organobromine.

Table 1 Concentrations ($\mu\text{g/g}$) of Cl and Br in each fraction of the three solid environmental samples.

Sample	House dust	Urban PM	Forest soil	Sample	House dust	Urban PM	Forest soil
Concentrations of Cl ($\mu\text{g/g}$)				Concentrations of Br ($\mu\text{g/g}$)			
Total Cl	10,000	4,300	810	Total Br	30	430	84
Organo-Cl ^a	<1,000	930	440	Organo-Br ^a	11	330	84
Aromatic-Cl	<1,000	930	280	Aromatic-Br	11	91	44
Aliphatic-Cl	<1,000	<430	160	Aliphatic-Br	<3	110	40
Inorganic Cl	10,000	3,400	370	Inorganic Br	19	94	<8.4
Insoluble Cl	1,200	800	630	Insoluble Br	7.8	120	52
Organo-Cl ^a	870	670	310	Organo-Br ^a	5.8	120	52
Aromatic-Cl	220	560	200	Aromatic-Br	5.8	91	52
Aliphatic-Cl	640	110	110	Aliphatic-Br	<0.78	31	<5.2
Inorganic Cl	340	130	310	Inorganic Br	1.9	<12	<5.2
EOCl ^b	43	170	9.3	EOBr ^b	5.6	19	0.15
EOCl-H	30	74	4.6	EOBr-H	0.95	5.2	0.048
EOCl-L	13	98	4.7	EOBr-L	4.6	14	0.11
Identified Cl ^c	1.1	0.61	0.0058	Identified Br ^c	3.7	0.11	0.057
PCBs	0.28	0.40	0.0016 ^d	PBDEs	3.7	0.088	0.057
PCDD/Fs	0.0094	0.12	0.0042	HBCD	0.016	na	na
Pesticides	0.81 ^e	0.21 ^f	na	PBB	na	0.018	nd
CBzs	0.015 ^g	0.0039 ^h	na	other-BFRs ⁱ	na	nd	0.00056

Na, not analyzed; nd, not detected. ^a Sum of aromatic-Cl(Br) and aliphatic-Cl(Br). ^b Sum of EOCl(Br)-H and EOCl(Br)-L.

^c Calculated from the measured concentrations or certified values.

^d Only dioxin-like PCBs are included.

^e Dichlorodiphenyltrichloroethane (DDT), chlordane-related compounds (CHLs), hexachlorocyclohexane isomers (HCHs), drins, and heptachlors are included.

^f DDTs, CHLs, HCHs, and toxaphene are included. ^g Only pentachlorobenzene is included. ^h Only hexachlorobenzene is included.

ⁱ Decabromodiphenyl ethane (DBDPE) and 1,2-bis-(2,4,6-tribromophenoxy)ethane (BTBPE) are included.

and insoluble X were estimated (Table 1, Figure 2)¹.

Concentrations of halogens in each fraction: Table 1 and Figure 2 summarize the concentrations of halogens in each fraction. The concentrations and chemical forms of the halogens differed markedly depending on the samples and elements (Cl or Br). In all samples, the concentrations decreased in the following order: total X > insoluble X > EOX > identified X (Table 1, Figure 2). Focusing on the organo-X fraction, the concentration of insoluble organo-X (ISOX) exceeded that of EOX in all samples (Table 1, Figure 2). This indicates that the ISOX fraction consists of greater variety of organohalogens with a greater range of polarity, while the EOX fraction consists only of non-polar or less polar organohalogens.

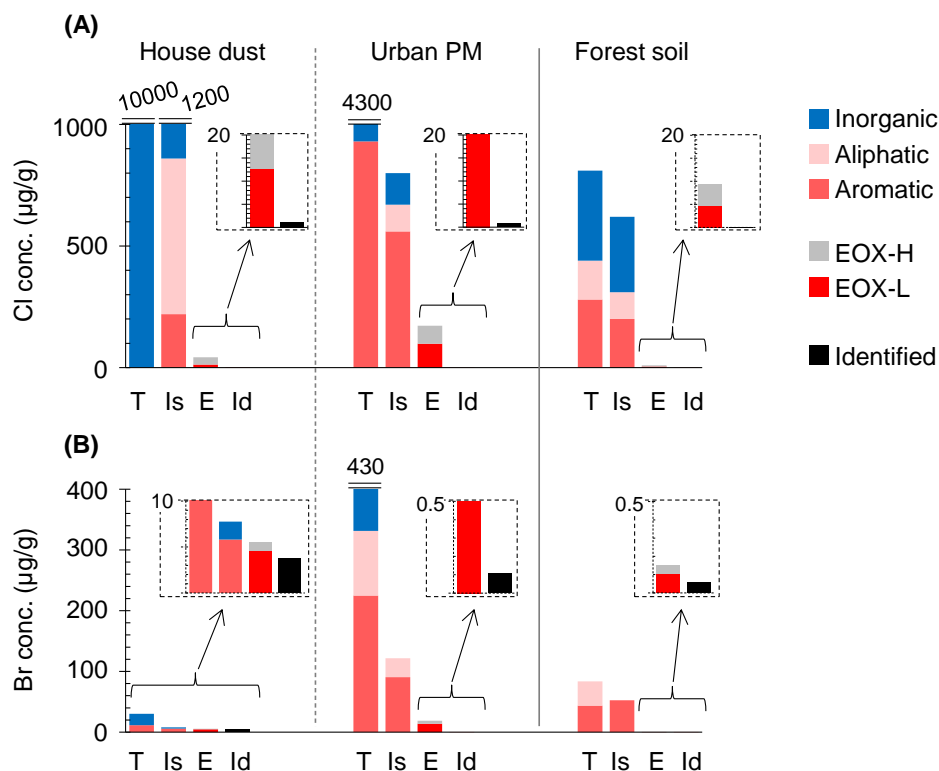


Figure 2 Concentrations ($\mu\text{g/g}$) of (A) Cl and (B) Br in four different fractions T (total), Is (insoluble), E (extractable), and Id (identified) environmental solid samples.

Chlorine: The respective percentages of insoluble organo-Cl (ISOC1) and extractable organo-Cl (EOC1) to total Cl were 8.6% and 0.43% (ISOC1 : EOC1 = 20 : 1) in house dust, 16% and 4.0% (ISOC1 : EOC1 = 4 : 1) in urban PM, and 38% and 1.2% (ISOC1 : EOC1 = 32 : 1) in forest soil (Table 1, Figure 2). These results suggest that non-extractable organochlorine compounds (with higher polarity) contribute largely to organo-Cl in house dust and forest soil. In house dust, 74% of the ISOC1 was aliphatic-Cl and 70% of the EOC1 was in high-molecular-weight compounds, suggesting that high-molecular-weight aliphatic compounds such as polymers⁷, flame retardants⁸, chlorinated paraffin⁹, and animal-related compounds⁷ are the dominant forms of organo-Cl. In forest soil, 63% of the ISOC1 was aromatic-Cl and 49% of the EOC1 was EOC1-H, suggesting that humic and fulvic substances¹⁰ with a wide range of molecular weights are the dominant forms of organo-Cl. In comparison, ISOC1 and EOC1 did not differ much in urban PM, indicating that non-polar or less polar compounds contribute more to organo-Cl. In addition, 84% of the ISOC1 was aromatic-Cl and 44% of the EOX was EOX-H. Identified Cl (including chlorinated pesticides, PCBs, and PCDD/Fs) accounted for only 0.36% of EOC1. Xu *et al.*³ reported a similar order of magnitude of EOC1 in PM_{2.5}, identifying < 0.5% of EOC1 as chlorinated pesticides and PCBs. These results imply that unidentified organochlorine compounds (non-polar or less polar, aromatic) are abundant in the atmosphere from both anthropogenic and natural sources. Reactive chlorine species occur in the atmosphere and organic matter can be chlorinated in the presence of a strong oxidant (*e.g.*, ozone) and chloride^{11,12}.

Bromine: The respective percentages of insoluble organo-Br (ISOBr) and extractable organo-Br (EOBr) to the total Br were 19% and 18% (ISOBr : EOBr = 1 : 1) in house dust, 29% and 4.4% (ISOBr : EOBr = 6.5 : 1) in urban PM, and 63% and 0.18% (ISOBr : EOBr = 340 : 1) in forest soil. In house dust, there were similar amounts of ISOBr and EOBr, indicating that most of the insoluble organobromine compounds were extractable (non-polar or less polar). The finding that 82% of the EOBr was EOBr-L indicates that most of the organobromine compounds were low-molecular-weight compounds. This is consistent with the finding that

considerable portions of ISOBr and EOBr are Br associated with PBDEs (Table 1, Figure 2). In forest soil, the concentration of ISOBr was two orders of magnitude higher than that of EOBr. Therefore, non-extractable polar compounds are the predominant species of organo-Br. Humic or fulvic substances (with low molecular weights) are likely the predominant compounds because more than 90% of ISOBr was aromatic-Br and 73% of EOBr was EOBr-L. In urban PM, contributions of both less polar and polar compounds are expected. Considering that 75% of ISOBr was aromatic-Br and 74% of EOBr was EOBr-L, aromatic organobromine compounds (with low molecular weights) likely predominate. Only 0.46% of EOBr was identified as PBDEs, suggesting the presence of unidentified organobromine compounds. A similar order of magnitude of EOBr has been reported for PM_{2.5}³, although the contributions of individual compounds have not been investigated. Our study provides further information on the chemical characteristics and mass balance in urban PM. Both anthropogenic (*e.g.*, hexabromocyclododecane and tetrabromobisphenol A) and natural compounds are expected to be unidentified organobromine compounds. Reactive bromine species are released from various sources (*e.g.*, photo-activated sea-salt aerosol) and react with secondary organic aerosols¹².

Conclusion

This study investigated the chemical characteristics of X (Cl and Br). Comparing the insoluble and extractable fractions, we discussed the polarity of organohalogen compounds in each sample. The ratio of EOX to ISOX differed in the samples, indicating that the proportions of non-polar and less polar compounds to organo-X were different. In house dust, high-molecular-weight aliphatic organochlorine compounds were the dominant organo-Cl and PBDEs were the dominant organo-Br. In urban PM, non-polar or less polar aromatic compounds with a wide range of molecular weights dominated the organo-Cl and low-molecular-weight aromatic organobromine compounds dominated the organo-Br. In forest soil, humic and fulvic substances⁹ with a wide range of molecular weights are likely the dominant forms of organo-Cl and humic or fulvic substances with low molecular weights are likely the predominant organo-Br compounds. Combining the determination of halogens with fractionation based on different chemical characteristics provided information on the chemical properties of organohalogen compounds in each sample. Further fractionation is expected to identify unidentified organohalogen compounds in solid environmental samples.

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