

MASS BALANCE TRENDS OF ORGANOBROMINE COMPOUNDS IN A SEDIMENT CORE FROM BEPPU BAY, JAPAN

Ito K¹, Fujimori T^{1,2}, Mukai K¹, Anh H Q³, Fukutani S¹, Takaoka M¹, Takahashi S³

¹Department of Environmental Engineering, Graduate School of Engineering, Kyoto University, Kyoto, Japan, 615-8540, itou.kento.32c@st.kyoto-u.ac.jp; ²Faculty of Advanced Science and Technology, Ryukoku University, Otsu, Japan, 520-2194; ³Center of Advanced Technology for the Environment (CATE), Graduate School of Agriculture, Ehime University, Matsuyama, Japan, 790-8566

Introduction

Some organobromine compounds are classed as persistent organic pollutants (POPs), which are highly accumulative and toxic, and are therefore subject to international restrictions on their production and use under the Stockholm Convention. The number of compounds registered as POPs is increasing, and some substitutes, analogues, and unintentional generators have been reported to have similar properties¹. A comprehensive evaluation of this vast array of substances is therefore necessary. After POPs are released into the environment, they migrate based on their physicochemical properties and are known to be distributed in sediment². Dated sediment core samples are therefore suitable for exploring the trends in these contaminants³.

In this study, we determined the potential environmental contamination by organobromine compounds in sediment core samples collected in Beppu Bay, Japan. Fractionation of bromine in sediment samples was conducted by focusing on the poor water solubility, extractability, and molecular weight (less than 1000 g/mol) of organobromine compounds, and the bromine concentrations in each fraction were measured (Figure 1). Time trends of different organobromine compounds were compared, and the trend of extractable organobromine in low-molecular-weight fractions (EOBr-L) was compared with those of polybrominated diphenyl ethers (PBDEs) and decabromodiphenyl ethane (DBDPE) in the same samples reported in previous studies⁴.

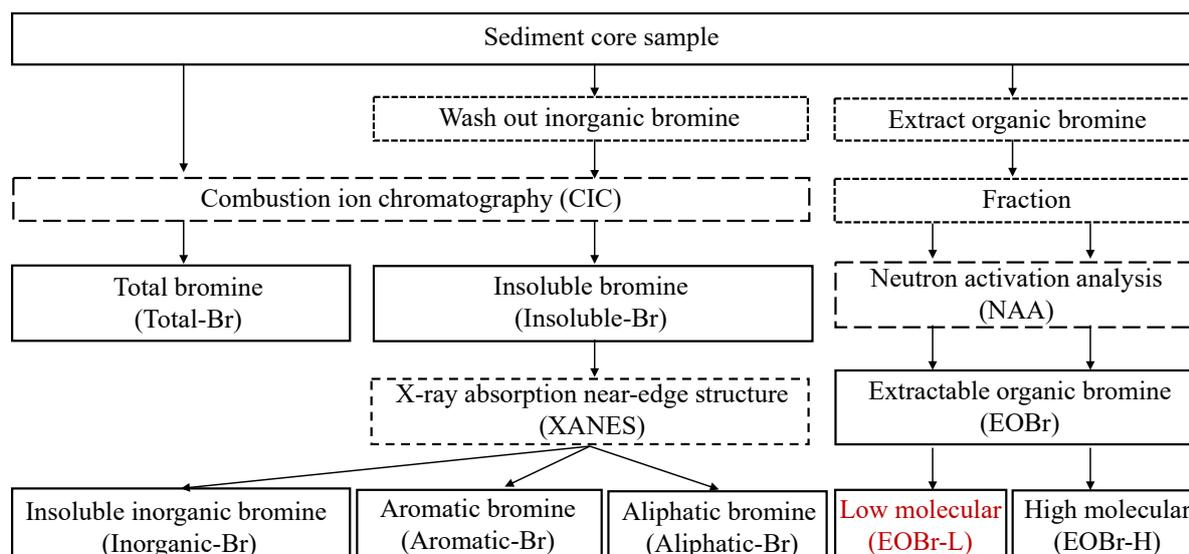


Figure 1. Sediment fractions measured in this study and their pretreatment and measurement methods.

Materials and methods

Materials: The samples were collected in May 2018 from Beppu Bay, Japan, where well-preserved sediment cores were available. Core chronology was determined by the constant rate of supply model of lead-210 dating⁵.

Pretreatment for insoluble bromine (Insoluble-Br): To remove inorganic bromine (Inorganic-Br), a washing pretreatment was performed the following published method⁶. First, 0.1 g of the sample was added to 5 mL of potassium nitrate (special grade reagent; Wako Pure Chemicals, Osaka, Japan) aqueous solution (0.41 g/50 mL). The sample was shaken gently by hand, placed in a horizontal shaker (SA300; Yamato Kagaku, Osaka, Japan) in a lying position and shaken horizontally (250 rpm, 1 h), and then centrifuged (H-36; Kokusan, Tokyo, Japan) for 15 min at 3,500 rpm. After removing the supernatant liquid, 10 mL of ultrapure water was added, horizontal shaking (250 rpm, 1 h) and centrifugation (3500 rpm, 15 min) were performed again, and then the supernatant liquid was removed again. The residue was dried thoroughly in a desiccator.

Combustion ion chromatography: The amount of bromine in non-pretreated samples and washed samples were measured by combustion ion chromatography. The total bromine (Total-Br) in the sediment was the bromine

concentration in non-pretreated samples. Combustion ion chromatography uses a combination of a combustion unit (AQF-2100H; Mitsubishi Chemical, Tokyo, Japan) and ion chromatography (HIC-20A-SP; Shimadzu, Kyoto, Japan). The sample and WO_3 powder were placed on a blanked magnetic boat, mixed with a spoon, and introduced into the combustion section. The sample was then burned at 900–1000°C according to the pre-optimized combustion program. The bromine in the sample was decomposed into HBr by combustion. This gas was absorbed by H_2O_2 and HBr was converted into bromide ions through a reduction reaction, and the concentration was determined by ion chromatography.

Type quantification of Total-Br and Insoluble-Br: To identify the chemical forms of bromine in the sediment before and after washing, the samples were irradiated with hard X-rays and the Br-K-edge X-ray absorption near edge structure (XANES) was measured. The measurements were performed at the Photon Factory beamline BL-12C in Tsukuba, Ibaraki Prefecture, Japan, using the fluorescence yield method. The Athna (ver. 0.9.26) software was used for the analysis. By performing a linear combination fitting (LCF) analysis, in which the XANES spectra of a sample with an unknown chemical form of bromine was superimposed on multiple spectra of a known standard sample, the fraction of bromine present in each chemical form in the sample was estimated⁷. Quantitative speciation was performed to determine the concentration of each chemical form using the Total-Br and Insoluble-Br concentrations.

Pretreatment for extractable bromine: The extraction followed a previously published method⁴. First, 2 g of freeze-dried sample was Soxhlet extracted with toluene and the extract was replaced with hexane. Inorganic chlorine and bromine were washed out. Then, 150 mL of 5% sodium sulfate/ultrapure water solution was placed in a separatory funnel together with 5 mL of the extract and 30 mL of a methyl tert-butyl ether (MTBE)/hexane mixture [1:1, v:v]. The mixture was shaken gently by hand three times to remove gas, and then shaken vertically at 250 rpm for 15 min. After 30 min of standing, the aqueous and organic layers were separated. The aqueous layer was returned to the separatory funnel and 20 mL of the MTBE/hexane mixture was added. The mixture was degassed, shaken (250 rpm, 15 min), and then allowed to stand. About three tablespoons of anhydrous sodium sulfate was added to the organic layer, which was allowed to stand, filtered, and then replaced with a cyclohexane/ethyl acetate mixture [1:1, v:v] to make 10 mL. Fractionation was then carried out using gel permeation column chromatography based on a molecular weight of 1000 g/mol. Each extract was concentrated to 1–2 mL and then diluted to 5 mL with hexane. A 2 mL volume of diluted extract was nitrogen-concentrated to 1 mL and placed in a polyethylene (PE) bag along with a filter paper. The extract was dried under normal temperature and pressure until the liquid components were completely volatilized, and the bag was sealed. The samples were folded into 1.5 cm squares, placed in PE bags, double sealed with another PE bag, and finally sealed in a further thin PE bag.

Neutron activation analysis: Samples were irradiated for 15 min with a thermal neutron flux of $2.0\text{--}2.4 \times 10^{13} \text{ cm}^{-2}\cdot\text{s}^{-1}$ at the Kyoto University Institute for Integrated Radiation and Nuclear Science. The ^{80}Br ($t_{1/2} = 17.6 \text{ min}$, $E_\gamma = 616 \text{ keV}$) isotope was measured using a germanium semiconductor detector for 60 s. In the same way, samples of a PE bag only, and filter paper and PE bag were also prepared and measured. The halogen concentration in the sediment samples was determined by subtracting the halogen concentration in the PE bags and filter papers.

Results and Discussion

Figure 2 shows the bromine concentration measured in each sediment fraction in this study, and the changes in PBDEs, DBDPE, total organic carbon (TOC), and water content reported in previous studies.

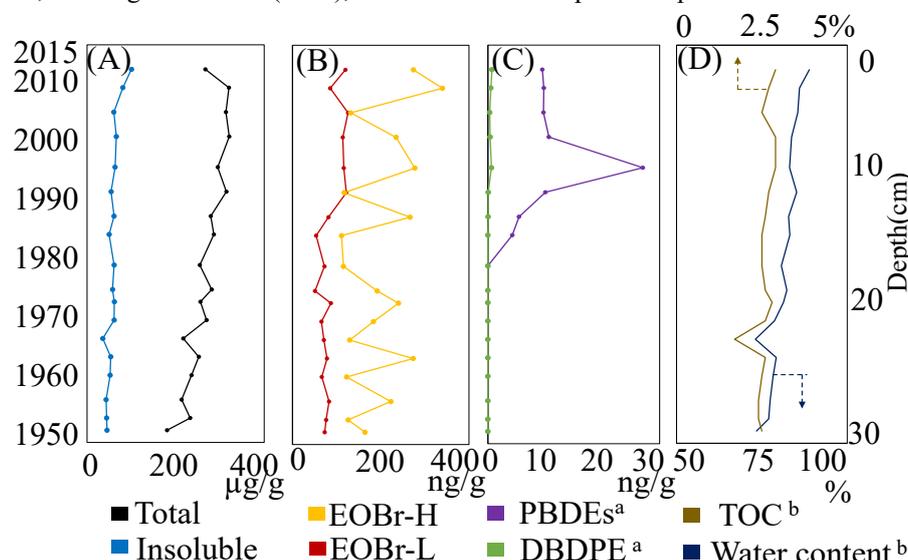


Figure 2. Bromine fraction concentrations, including values reported in previous research (denoted by “a” and “b”). A, Total-Br and Insoluble-Br. B, EOBBr-L (low molecular weight) and EOBBr-H (high-molecular weight). C, PBDEs and DBDPE, reported as the bromine concentration⁴. D, TOC and water content⁵.

The Total-Br and water contents decreased with depth in the sediment core. The decrease in the amount of pore water with depth in the sediment may have decreased the amount of inorganic bromine in the pore water and affected the Total-Br concentration. The Insoluble-Br fraction contained both inorganic and organic bromine. There was a strong correlation between TOC and Insoluble-Br ($p = 0.0007$, correlation coefficient = 0.702). Similarly, a previous study⁸ showed a correlation between TOC and organobromine. Thus, it is likely that the percentage content of organobromine is high in Insoluble-Br. Figure 3A shows the results of a XANES measurement. In Figure 3A, the shoulder of an organobromine peak can be seen in the spectrum of a sediment sample after washing (Insoluble-Br). This shoulder was not apparent before washing, which indicated that the washing process removed the water-soluble inorganic bromine. Figure 3B shows the results of the LCF analysis, and notes that there is an error of up to 10% in the LCF analysis. The findings indicated that aliphatic bromine was almost non-existent. Although water-soluble inorganic bromine could be removed by washing, poorly water-soluble inorganic bromine was still present in the sediment. Aromatic bromine (Aromatic-Br) was also slightly reduced by cleaning. Inorganic-Br did not vary little by depth; however, the Aromatic-Br concentration was lower at greater depths. The percentage content of organic bromine in the Insoluble-Br fraction was about 57%. Figure 3C shows the change in the ratio of Insoluble-Br to Total-Br. The ratio decreased in the surface layer (0–5 cm), suggesting that poorly water-soluble organic bromine may have been converted into water-soluble inorganic bromine via microbial debromination⁹.

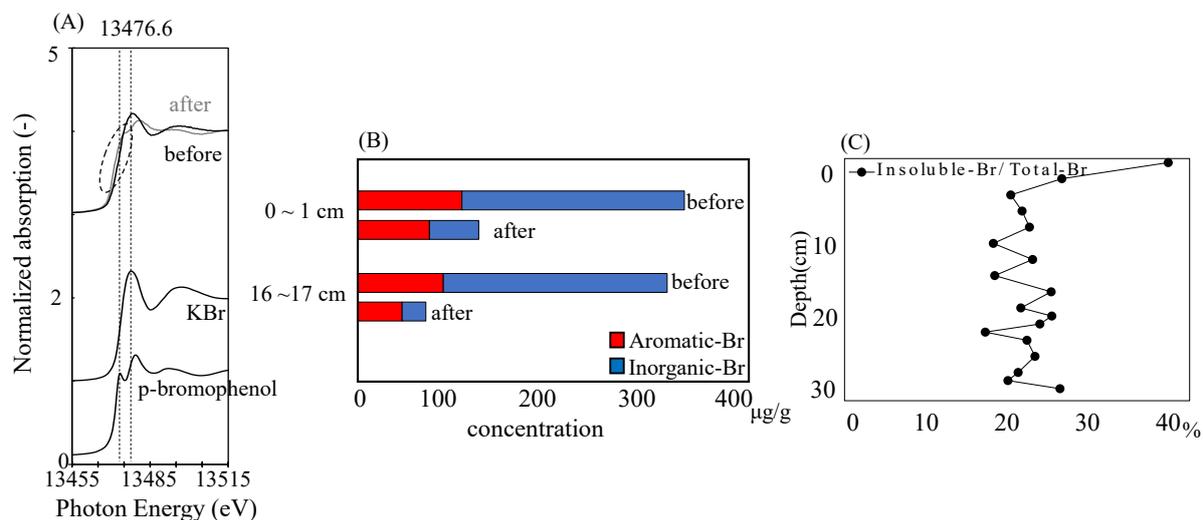


Figure 3. A, the Br K-edge XANES spectra of sediment samples (core depth: 0–1 cm) and standard compounds used for linear combination fitting. The lines are the peaks of aromatic bromine (13473.5 eV) and inorganic bromine (13476.6 eV). The shoulder of an organobromine peak is shown in the circle. “Before” refers to samples before washing (Total-Br) and “after” refers to after washing (Insoluble-Br). The KBr spectrum was used as it is representative of inorganic bromine compounds, and the spectrum of p-bromophenol was used to represent aromatic bromine compounds. B, estimated Aromatic-Br and Inorganic-Br concentrations in samples before (Total-Br) and after (Insoluble-Br) washing (core depth: 0–1 cm, 16–17 cm). C, vertical profile of the proportion of Insoluble-Br in Total-Br in sediment core samples from Beppu Bay, Japan.

In this study, we compared the temporal changes in the bromine concentrations of low-molecular-weight fractions, which are used as indicators of POPs and other substances (Figure 4A, 4B). Until around 1980, the effects of PBDE and DBDPE pollution were almost unnoticeable, and the EOBBr-L concentration did not change much. However, in the 1990s, the PBDE and DBDPE concentrations increased, and at the same time the EOBBr-L concentration also increased (pink area, Figures 4A and 4B). A decreasing trend for PBDEs was apparent after 2000, whereas there was an increasing trend for EOBBr-L and DBDPE. Some organobromines and unknown bromines were detected that could not be ascribed to known compounds.

Naturally occurring organobromine is constantly taken up by the sediment and does not have a strong effect on changes in the bromine concentration. In this study, the average EOBBr-L concentration before contamination by individual substances had an effect was defined as the natural bromine concentration (Background-Br, Figure 4C). We also investigated the trend in unidentified bromine in EOBBr-L (Unknown-Br) by subtracting the concentrations of Background-Br and individual substances from the concentration of EOBBr-L (Figure 4C). Unknown-Br

decreased in 2008, but increased again in 2011. When the Background-Br was excluded, Unknown-Br accounted for 36–83% of the total content. Candidate compounds for the unknown bromine may include 4-bromophenol¹⁰, brominated dibenzo-p-dioxins and dibenzofurans¹¹, and hexabromocyclododecane. Thus, despite the presumed occurrence of microbial debromination, the concentration of unknown POPs has been increasing in recent years.

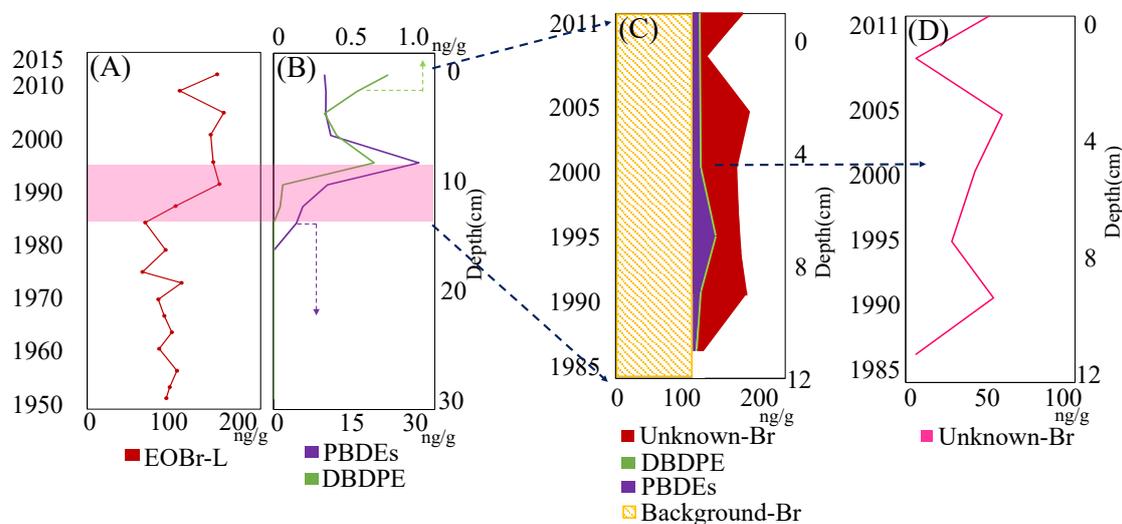


Figure 4. Temporal trends in bromine concentrations. A, EOBBr-L. B, PBDEs and DBDPE. C, Unknown-Br, DBDPE, PBDEs, and Background-Br in EOBBr-L. D, Unknown-Br.

Conclusion

Various factors, such as physical processes and microbial activity, are intricately related to the bromine concentration in the sediment collected from Beppu Bay, Japan. The decrease in the EOBBr-L concentration in the surface layer could be related to microbial bromination.

Over time, the concentrations of known POPs and EOBBr-L concurrently increased. The percentage content of PBDEs and DBDPEs in EOBBr-L was 5.3–19%, which could not completely explain the change in the EOBBr-L concentration.

Comparing the temporal changes in the EOBBr-L concentration with those of known POPs enabled an estimation of the concentration due to naturally occurring bromine compounds, and revealed the temporal trend of the concentrations of unknown anthropogenic organobromine compounds. Unknown-Br increased from 1995 onward, decreased around 2008, and then decreased again in recent years. This suggests the possibility that unknown organobromine compounds may be increasing. Therefore, EOBBr-L could be one of the indicators used to reveal the trend of unknown bromine compounds.

Acknowledgements

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