Comparison of the Mass Balance Trends of Organobromine in Sediments from Osaka Bay, Beppu Bay, and Lake Biwa

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1 Introduction

Organobromine compounds have many uses, especially as flame retardants. However, some are persistent, highly accumulative, and toxic and can be transported long distances; furthermore, and subject to international regulation under the Stockholm Convention as persistent organic pollutants (POPs). Since the number of registered POPs is increasing, and substitutes and analogues with similar properties have been found, a comprehensive assessment of POP-like substances is attracting attention. By comparing comprehensive assessments with individual substances, it is possible to quantify how many unknown POP-like compounds exist and the potential environmental contamination. POPs released into the environment can accumulate in sediments, and sediment core samples can be used to determine contamination trends[1]. Total and extractable organobromine (EOBr) have been evaluated in comprehensive assessments of sediment samples, but natural organobromine in sediments comprises a large proportion, hindering comprehensive assessments of EOBr in sediment[2]. Although the low-molecular-weight fraction of extractable organobromine (EOBr-L) has been measured in various biological and environmental samples[3], few studies have measured it in sediment samples, and no study has measured the temporal trend in the EOBr-L concentration. Therefore, this study assessed the potential environmental pollution of organobromine using sediment samples. The vertical changes in the EOBr-L concentration in sediment core samples collected from multiple sites were measured and compared by region to estimate trends in natural organobromine in sediment. By comparing the changes in polybrominated diphenyl ether (PBDE) and decabromodiphenyl ethane (DBDPE) concentrations in the same samples with those reported previously[4,5,6], the possibility of unknown POPs is discussed considering mass balance trends (Figure 1).

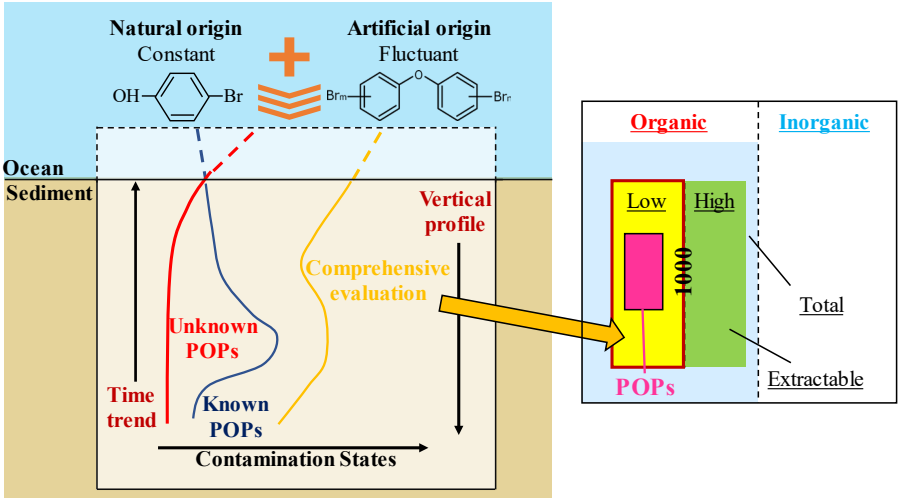


Figure 1: An outline of this study and comprehensive assessment.

2 Materials and Methods

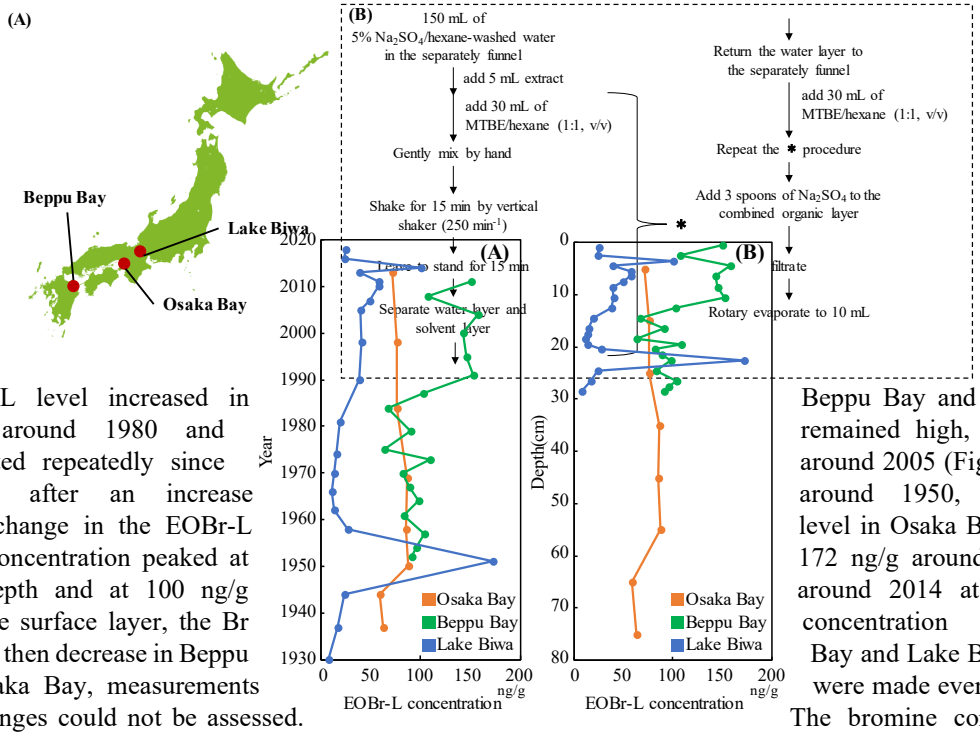
Materials: Sediment samples were collected from three different areas in Japan: Beppu Bay, Osaka Bay, and Lake Biwa. Beppu Bay provides cores with good sedimentary conditions due to its topographical features. Osaka Bay is located next to an industrial city and has been the focus of much research on POPs. Lake Biwa is a freshwater area, allowing comparison with seawater areas (Figure 2A). Each of the core samples collected was dated[4,5,6].

Methods: Sediment core samples were collected, freeze-dried, and then cut into 1-, 2-, and 10-cm layers. Extraction methods followed those of previous studies[37]. First, the samples were subjected to Soxhlet extraction with toluene, and then inorganic bromine was removed by washing with sodium sulfate solution (Figure 2B). The resulting extract was inverted into a cyclohexane/ethyl acetate mixture [1:1, v:v] and then fractionated using gel permeation column chromatography at a molecular weight of 1000 g/mol. After fractionation, the liquid was concentrated using nitrogen gas and placed in a polyethylene (PE) bag to volatilize the liquid component under normal temperature and pressure. The liquid was then placed in a double PE bag and sealed. As a standard sample, ammonium bromide solution was

dropped onto filter paper in a PE bag, and the bag was sealed, as with the sediment samples. Neutron activation analysis was performed at the Kyoto University Institute for Integrated Radiation and Nuclear Science. Samples were irradiated with thermal neutron fluxes of 2.0–2.4 × 10^{13} $cm^{-2} \cdot S^{-1}$, and the generated ^{80}Br (t1/2 = 17.6 min, Eγ = 616 keV) isotope was measured; samples of a PE bag only and of a PE bag and filter paper only were measured in the same manner. The concentrations in the sediment samples were calculated by comparison with a standard sample after removing the bromine in the PE bag itself from the measurement results for the unknown sample.

Figure 2: (A) The locations where the cores were collected. (B) The extract washing procedure.

3 Results



The EOBr-L level increased in Beppu Bay and Lake Biwa beginning around 1980 and remained high, although it has fluctuated repeatedly since around 2005 (Figure 3A). In comparison, after an increase around 1950, there was almost no change in the EOBr-L level in Osaka Bay. In Lake Biwa, the concentration peaked at 172 ng/g around 1951 at a 22.5 cm depth and at 100 ng/g around 2014 at a 3.5 cm depth. In the surface layer, the Br concentration tended to increase and then decrease in Beppu Bay and Lake Biwa (Figure 3B). In Osaka Bay, measurements were made every 10 cm, so detailed changes could not be assessed. The bromine concentrations in Osaka Bay and Beppu Bay were similar from 1950 to 1980s (or 15 to 30 cm), while the concentration in Lake Biwa was lower than that in the marine cores.

Figure 3: Changes in the EOBr-L concentration in the sediment cores from Osaka Bay, Beppu Bay, and Lake Biwa according to time (A) and depth (B).

4 Discussion

Comparison of EOBr-L: Natural disasters are thought to have caused the peak in the organobromine concentration in Lake Biwa (Figure 3). A layer reflecting the effects of a natural disaster is called an event layer, and an event layer is related to the bromine and total organic carbon (TOC) concentrations[8,9]. The Ado River, which flows through Takashima near where the core was obtain, was flooded during typhoons occurring in 1953 and 2013[10], which is similar to the timing of the peak concentrations seen in Figure 3A. It is possible that the river flooding caused anthropogenic bromine compounds and natural organic compounds of terrestrial origin to flow into Lake Biwa.

However, since there was no significant change in the TOC concentration[4], and the peak concentrations were very high, further investigation is needed to determine if the peak concentrations were affected by natural disasters. The concentration changes in Beppu Bay and Lake Biwa were similar (Figure 3B). Factors contributing to naturally occurring bromine concentration changes in sediments include debromination reactions and formation of bromine compounds. The sediment environments may be similar.

Mass balance trends:

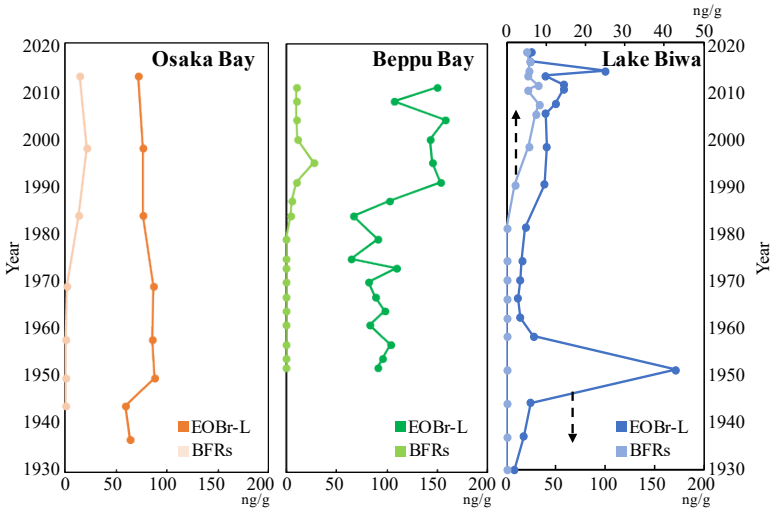


Figure 4: The changes in the EOBr-L concentrations measured in this study and the BFR concentrations reported in the sediment cores from Osaka Bay, Beppu Bay, and Lake Biwa.

In Beppu Bay, the concentrations of brominated flame retardants (BFRs), specifically PBDEs and DBDPE, began increasing in the 1980s, in parallel with the EOBr-L concentration (Figure 4); since the late 1990s, the BFR concentrations have been decreasing, whereas the EOBr-L concentration have not decreased much. In Lake Biwa, the BFR and EOBr-L concentrations both increased during the same period. In Osaka Bay, the concentrations of individual substances also increased during the same period, but there was no obvious increase in the EOBr-L concentration. The increase in the EOBr-L concentration observed in Beppu Bay and Lake Biwa cannot be explained by BFRs, but the fact that they occurred at the same time suggests some relationship. Because the bromine concentration in a layer before the effects of anthropogenic POPs appear is derived from naturally produced organobromine compounds, the difference in concentration between marine and freshwater areas is thought to reflect the difference in natural bromine production systems (Figure 3A). The presence of organisms, such as acorn worms, that produce natural phenol bromine compounds on the seafloor in marine areas and the bromide ion concentration are thought to influence this difference.

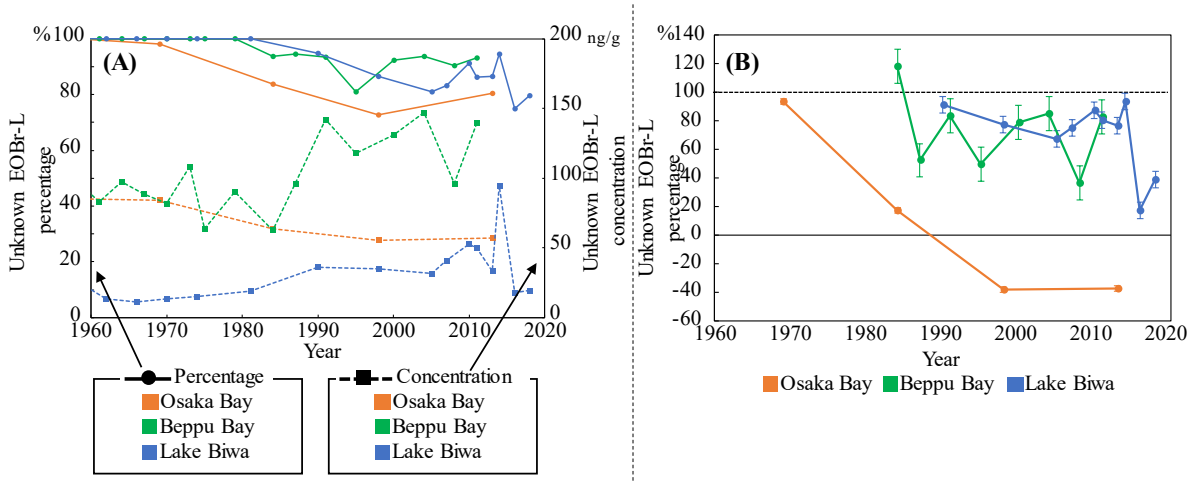
Trends in Unknown POP-like substances: The concentrations and percentages of EOBr-L compounds other than BFRs are referred to as “unknown” (Figure 5A). Note that the unknown percentage was 100% up to approximately 1970 because there was no BFR contamination. In all cores, the unknown percentage decreased from 1980 to 2000, indicating that PBDEs account for a larger proportion of EOBr-L. However, the unknown percentage increased in each core after 2000. This could have two contrasting explanations: the proportion of POP-like substances other than PBDEs is increasing, or the effect of PBDE contamination is decreasing such that the proportion of naturally occurring organobromine compounds is increasing. The unknown concentrations had been decreasing in Osaka Bay since the 1980s but have remained constant since 2000. As they might increase in the future, caution is required. In Beppu Bay and Lake Biwa, the concentrations were higher in 2010 than in 2000, but it is difficult to determine the overall trend because of the effects of the debromination reaction in the surface layer and the concentration peak caused by the natural disasters mentioned above. However, this trend is still important because the EOBr-L concentration is slightly higher than that before the effects of anthropogenic pollution appeared.

The bromine concentrations in the sediment depend on the production regime in the region[2]. Therefore, for each core, the average concentration of naturally occurring bromine was taken as the average concentration of bromine in the sediment before the effects of PBDE contamination were apparent in the sediment (the high concentration layer thought to be derived from natural disasters was excluded). The average bromine concentrations were 61 ± 1.9, 90 ± 11.9, and 16 ± 5.7 ng/g in Osaka Bay, Beppu Bay, and Lake Biwa, respectively. Figure 5B shows the changes in bromine concentrations other than PBDEs in EOBr-L, excluding naturally occurring concentrations. In Osaka Bay, the concentrations have been decreasing since 1970 and have been below 0% since 1990, indicating that the effects of unknown POP-like substances are not significant. By contrast, in Beppu Bay, the percentage continues to fluctuate between 40% and 80%, although the percentage is lower than that in the 1980s. In Lake Biwa, the percentage has been decreasing since 1990; although there was an increase in around 2010, the unknown percentage has been low

since 2010. While the concentrations in Lake Biwa and Beppu Bay were similar, the percentag in Osaka Bay decreased earlier and at a slower rate. If the percentages in Osaka Bay are similar to those in Lake Biwa and Beppu Bay, this suggests that the "naturally occurring" concentrations in Osaka Bay are also affected by anthropogenic influences. This means that the sediment in Osaka Bay would have been affected by other anthropogenic bromine compounds before 1980. Since those compounds would have been decreasing at the same time that PBDEs were increasing, EOBr-L was not significantly affected. This hypothesis is supported by the increase in the EOBr-L concentration in Osaka Bay since approximately 1950 (Figure 3A). In this case, it is too early to decide whether unknown contaminants in Osaka Bay have an impact today, and further studies are needed.

Figure 5: The temporal trends (A) in the unknown EOBr-L percentage and concentration in each core and (B) in the unknown EOBr-L percentage above "natural origin bromine".

5 Conclusions



The EOBr-L concentration in the sediment allowed us to quantify temporal trends in the presence of POP-like substances. However, not all EOBr-L pose risks on the environment. EOBr-L is affected not only by anthropogenic factors but also naturally occurring bromine compounds, the concentrations of which are affected by natural disasters and microorganism activities in the sediment. The change in the mass balance between EOBr-L and BFRs showed that the increase in BFR concentration coincided with the increase in EOBr-L concentration, indicating that the increased EOBr-L concentration was not due to natural disasters, which suggests a relationship between EOBr-L and individual substances. No obvious effects of unknown compounds were observed in any core, and there was no obvious environmental contamination, such as that caused by PBDEs in the past. However, a definitive determination requires further comparisons to investigate the changes in the EOBr-L concentration in environmental samples and organisms other than sediments.

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