

D-2.1.2 Preliminary Study on Accumulation to Ocean Sediment and Behavior concerning Toxic Metals and Chemical Substances

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Abstract

To investigate the accumulation and behavior of toxic metals in the sediments, more than two hundred marine bottom surface and core sediments collected from the southeastern coastal margin of the Sea of Japan were analyzed for heavy metals and some other elements. Mercury is concentrated clearly in the uppermost layer of the core sediments, suggesting recent anthropogenic inputs. The vertical profiles of Pb and Zn in the core sediments are also thought to be a result of recent environmental pollutions, and that of Mn is due to upward migration during early diagenesis. A supercritical fluid extraction (SFE) method using modified supercritical CO₂ was developed for the simultaneous extraction of PCBs in sediments. The use of SFE is rapid, accurate and specific for the analysis of PCBs in environmental samples. The concentrations of organic halogens in the sediments and marine mammals were measured by neutron activation analysis. Organic halogen concentrations in the sediment samples from the Sea of Japan were lower than those in the sediment samples from the estuary of River Tama and the Bay of Osaka. It suggests that the sediments located at the Bay of Tokyo and Osaka were so much effected by human activities. Organic halogens in most of the mammal samples were greater than 50 µg/g and especially high in the samples from the mid-latitude of the North Pacific, suggesting the influence of industrial activities. It was also found that an unidentified low molecular organic bromine compound showed a higher bioaccumulation potential than known compounds such as PCB and DDT. Characterization by GPC was conducted with organic halogens in sediment samples.

Key Words Marine Pollution, Sediment, Toxic Heavy Metals, Hazardous Chemical Substances, Unknown Pollutants

1. Introduction

The huge amounts of toxic heavy metals and hazardous chemical substances have been transported from land to sea by the recent global industrialization. It has been so far believed that the wastes disposed into ocean would not be accumulated to ocean sediment because of the decomposition and diffusion during sedimentation. However, sediments highly contaminated with heavy metals and organohalogenes have been found recently. These pollutants may be harmful to human beings through the food chain. Thus it is an urgent problem to study the distribution in ocean sediment and the behavior of these pollutants. The objective of this research is to investigate the accumulation and behavior of such pollutants in the sediments and to clarify the unidentified organohalogenes.

2. Results and Discussion

(1) Accumulation and behavior of toxic metals in marine sediments

In order to investigate the accumulation and geochemical behavior of toxic metals in the sediments, more than two hundred marine bottom surface and core sediments collected from the southeastern coastal margin of the Japan Sea were analyzed for heavy metals and some other elements. The details of the results have been reported¹⁻⁶). A brief summary is given as follows.

It has been generally accepted that most heavy metals are enriched more in fine fractions than coarse fractions of sediments. The clay fraction content of the sediments studied is positively correlated with Cu, Pb, Ni, V or Li content. However, there is no such a trend in the case of Fe, Zn, Co or Be. The enrichment of Fe and Be in the sandy sediments is caused by glauconite and/or iron sand. Ultramafic rocks occurred in the catchment area of the Hime River, Niigata Prefecture are the major sources of Ni and Cr to the sediments of southeastern coastal margin of the Japan Sea. Three elements, Pb, Zn and Mn are generally enriched in the uppermost layers of the core sediments, while Fe, Ni, Cr and S behave in different manner. The vertical profiles of Pb and Zn in the core sediments are through to be a result of recent

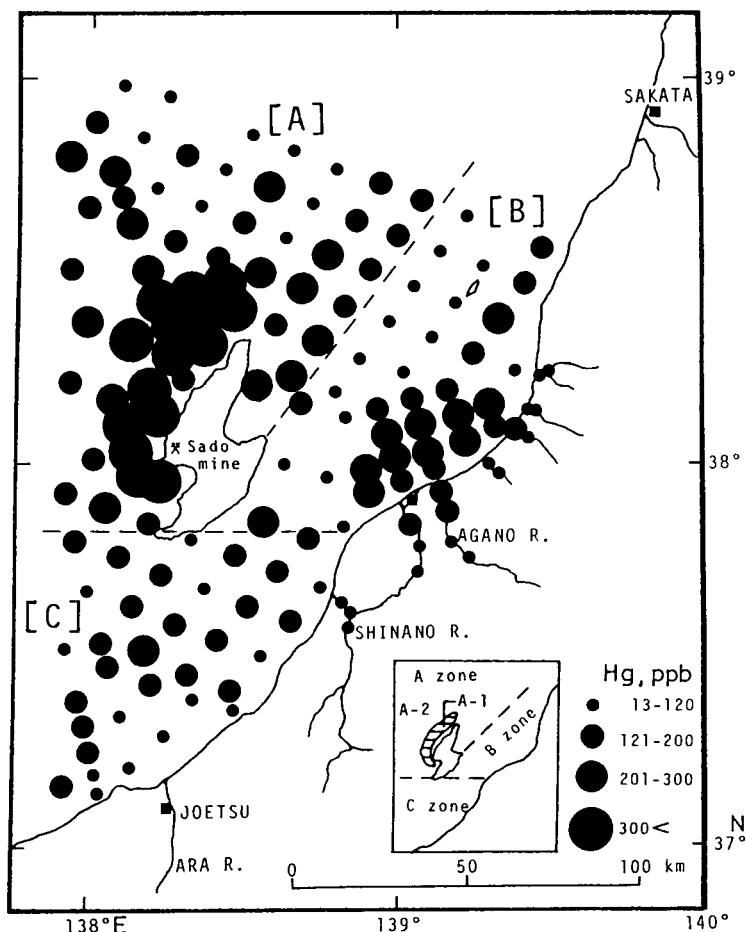


Fig. 1 Regional variation of Hg Content

Table 1 Average metal contents in studied marine sediments.

Sea area	Hg (ppb)	Au (ppb)	Cu (ppm)	Pb (ppm)	Mn (ppm)	Fe (%)
Off Niigata						
A-1 zone	612	22.5	19	33	630	3.45
A-2 zone	174	4.8	24	37	3170	3.98
B-zone	143	1.8	19	32	490	4.23
C-zone	131	1.7	18	34	1540	4.40
avg.	191	4.7	21	34	1790	4.11
Suruga Bay	157	1.6	49	-	513	-
South of Kii Strait	117	1.6	28	15	416	3.05
Off NE Japan	111	3.1	61	11	679	2.96
Ryukyu-Mariana	41	4.6	120	27	2724	5.02
Central Pacific	56	1.8	345	40	7487	4.15

environmental pollutions, and that of Mn is due to upward migration during early diagenesis.

Total and acid (0.6 M HCl) soluble As was analyzed by automated hydride generation and electrothermal atomic absorption spectrometry. The content of total As varies greatly with locality from 4.0 to 59.2 ppm (avg. 18.2), and the value is more or less similar to those of the river sediments collected from the catchment areas. The total or acid soluble As is generally enriched in fine sediment fraction, and positively correlated with water depth. In rare cases, however, anomalously high total As content of more than 50 ppm was found in sandy sediments, reflecting a close association with iron sand. The acid soluble As in the most muddy sediments amounts to about half of the total As concentrations,

being formed mainly by the adsorption and co-precipitation with hydrous Fe/Mn oxides.

Mercury was analyzed by cold vapor atomic absorption spectrometry (Table 1). Anomalously high Hg content of more than 300 ppb is found in the sediments around Sado Island (Fig. 1). This anomalous Hg is likely to have originated from Au-Ag mining activity in the island. In this case, Hg is probably presented in the form of Au-Ag-Hg amalgam. As for the other samples, the Hg is generally enriched in the fine sediment fraction and positively correlated with Au, Cu, Pb, S and organic carbon. The inverse correlation between the Hg content and redox potential of the sediment suggests that Hg is enriched in reducing environments. In general, mercury is concentrated clearly in the uppermost layer of the core sediments (Fig. 2). This may be caused by recent anthropogenic inputs because the mercury enrichment during early diagenesis is assumed to be negligible.

(2) Supercritical Fluid Extraction for Polychlorinated Biphenyls From Sediments

In recent years, there have been a large number of reports on supercritical fluid extraction (SFE) as a potential replacement for conventional liquid solvents for the extraction of organic pollutants from environmental samples. Extractions of polychlorinated biphenyls (PCBs) from solid materials such as river sediments, sludges and fly ash are typically performed with liquid solvents either in a Soxhlet extraction or sonication sample preparation techniques. These traditional liquid solvent extraction techniques are time consuming, labor-intensive, require relatively large volumes of organic solvents, and often fail to yield incomplete recovery and/or quantitative extraction.

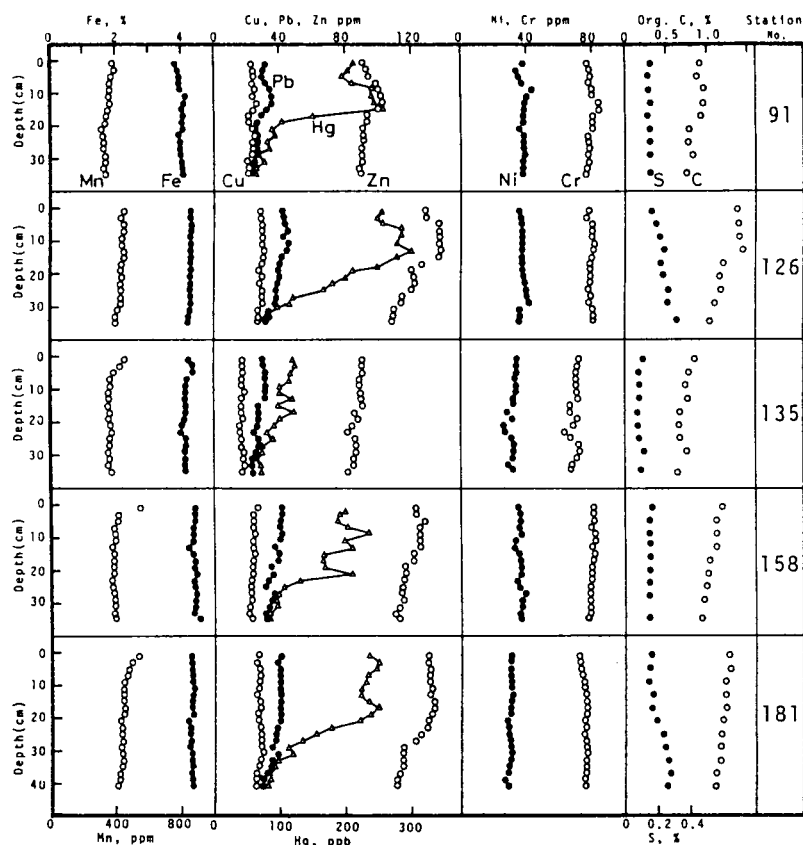


Fig. 2 Vertical variation of the concentrations of ten elements

positively correlated with Au, Cu, Pb, S and organic carbon. The inverse correlation between the Hg content and redox potential of the sediment suggests that Hg is enriched in reducing environments. In general, mercury is concentrated clearly in the uppermost layer of the core sediments (Fig. 2). This may be caused by recent anthropogenic inputs because the mercury enrichment during early diagenesis is assumed to be negligible.

(i) Materials and Methods

Samples: All samples used in this work contained native (not spiked) analytes and were used without any pretreatment. The PCB-contaminated sediment was collected from Dokai Bay, Kyushu, Japan. The sample was air dried at room temperature for one week. Before extraction, the sample was cryogenic-ground and sieved through a screen having 0.297 mm holes (mesh no. 48) to remove debris before use. The river sediment standard reference material (SRM 1939) was obtained commercially from the NIST and used without further purification.

Supercritical Fluid Extraction Procedure: All the supercritical fluid extractions were performed in the dynamic mode using a JASCO Super 200 SFE/SFC system (Tokyo, Japan) which consisted of two syringe pumps (Model 880-PU). An ethylene glycol-filled cooler was used to maintain the head of carbon dioxide delivery pump at -5 °C and the other pump delivered solvent modifier, both pumps operated at a flow rate of 1.0 ml/min. Extraction was performed by placing the sample (0.5 g) into an extraction cell (Model EV-1, JASCO) having an internal volume of 1.0 ml, and extracting for 60 min with dichloromethane-modified carbon dioxide (15% by volume). An isotope labelled 2,4,4'-trichlorobiphenyl was used as an internal standard and 20 µl was spiked onto each sample before extraction.

A column oven (Model CO-866, JASCO) was used for elevating the temperature of carbon dioxide and the extraction cell above its critical temperature. The SFE extract of the Dokai Bay sediment was cleaned up on two stainless-steel (4.6 mm by 50 mm) columns connecting in series, packed with 20-40 mesh carbotrap graphitized carbon black (Supelco, Inc., USA) and Florisil (Wako Pure Chemical Industries Ltd.). The extract was then finally subjected to a sulfur cleanup with 3 g activated copper granules (Wako Pure Chemical Industries Ltd.) which was placed in the collection vial.

(ii) Results and Discussion

Optimization of Operating Conditions: The optimum pressure, temperature, time factors and cosolvent composition that enable maximum extraction of all PCBs were determined by using SRM 1939. The uses of supercritical CO₂ with 15% dichloromethane modifier at 200 kg/cm² and 80 °C, with 60 min dynamic extraction were found to be the optimum conditions.

Comparison with Soxhlet Extraction: A major problem in sediment analysis is the presence of organic matters and elementary sulfur. If not removed, these inevitably will cause significant interference with the GC analysis when electron capture detection or mass spectrometric detection was used⁷). In this work, the sulfur cleanup step was performed after SFE by placing the activated copper granules directly into the collection vessel. Carbotrap graphitized carbon black and Florisil were employed as a trapping material for removing contaminants from the extract during SFE.

To determine the recoveries of PCBs in a real environmental sample, the sediment was sieved and extracted by SFE and Soxhlet extraction. Both extracts were analyzed by GC-MS. The levels of PCBs from trichloro-biphenyls to hexachlorobiphenyls in the Dokai Bay sample obtained by Soxhlet as well as SFE procedures were summarized in Table 2. It is clear that SFE on this sample produces recoveries that are very similar to those obtained from Soxhlet extraction.

Compared to conventional liquid extraction methods, the main advantages of SFE are that the chances of sample contamination are greatly reduced as sample handling is minimized and reduces the usage of organic solvents. A much less solvent evaporation, and a simplified cleanup step are also the other advantages of SFE.

Table 2 Comparison of Soxhlet Extraction with SFE using dichloromethane modified CO₂ for the recovery of PCBs from Dokai Bay sediment.

PCB	Soxhlet (ng/g)	SFE (ng/g)
trichlorobiphenyls	27	27
tetrachlorobiphenyls	54	57
pentachlorobiphenyls	37	39
hexachlorobiphenyls	11	14

(3) Investigation on Unidentified Organohalogens

The huge amounts of industrial chemicals and pesticides are produced by human⁸). It is well known that synthetic organochlorine compounds such as PCBs, DDTs, HCHs and chlordane compounds have widely spread in the environment^{9,10}). These compounds are stable in the environment and bioaccumulative in the food web of terrestrial and marine ecosystems¹⁰).

The evidence for the presence of other unidentified organohalogens in the environmental samples have also been revealed in some papers published previously^{11,12}). On the other hand, it is known that some kinds of marine and terrestrial organisms produce compounds having halogen elements in their chemical structures¹³). Accordingly, sediment and mammal samples were analysed to determine organic bound halogens. Analysis of organic bound halogens will be of help to understand the levels of unidentified organic halogens when organic bound halogens and identified organic halogen concentrations are compared.

(i) Materials and Methods

Sediment samples were collected at off Sadolsland in the Sea of Japan and the estuary of River Tama in the Tokyo Bay, and marine mammal samples were taken at the North Pacific Ocean. The organic halogens in these samples were extracted with organic solvents, and the extracts were washed with deionized and distilled water. The extracts were then fractionated with SX-3 (Bio-Rad Laboratories) gel permeation column chromatography (GPC).

Concentration of extractable organic halogen (EOX) in each fraction was determined by instrumental neutron activation analysis. The samples were irradiated at a neutron flux of 3.7×10^{13} n/cm²s for 2 min using JRR-4 nuclear reactor of the Japan Atomic Energy Research Institute, Ibaraki. Individual organohalogen compounds such as PCBs, DDTs, HCHs and CHLs were analysed by GC-ECD and GC-MS¹⁰).

(ii) Results and Discussion

Organic halogen concentrations in sediment and organism samples were in the order of Cl > Br > I. Concentrations of EOX in the sediment samples from the Sea of Japan were 160 to 420 ng/g (dry weight basis) for chlorine, 44 to 130 ng/g for bromine and 40 to 220 ng/g for iodine. These figures are lower than those in the sediment samples from the estuary of River Tama and the Bay of Osaka¹²). It suggests that the sediments located the Bay of Tokyo and Osaka were so much effected by human activities.

In the case of marine mammals, organic halogens in most of the samples were greater than 50 ug/g. More than a half of organic halogen in each samples was organic chlorine. Concentrations of organic chlorine and bromine in samples from the mid-latitude of North Pacific were relatively higher than those in samples of other locations (more than 150 ug/g), suggesting the effects caused by industrial activities.

In order to estimate bioaccumulation potential of organic halogens through trophic levels in marine ecosystem, concentration ratio is determined between the concentration in marine mammal and its diet, fish. The results showed that the ratios of low molecular weight fraction were higher than those of the high molecular weight fraction for all halogens investigated. The ratios of low molecular weight fraction for EOBr in marine mammals is especially high among halogens, suggesting the presence of persistent bromine-containing compounds as well as known organochlorines such as DDTs.

Characterization by GPC was conducted with EOX in sediment samples. The results were obtained that EOX in the sediment sample from the estuary of River Tama were eluted into the fractions in the wide range. It means that there are many organic compounds having halogens in this sample. On the other hand, the fractionation of EOX in extracts of marine mammal samples was performed with GPC. EOCl and EOBr in low molecular fraction, which contained synthetic organohalogenes, were slightly higher than those in high molecular weight fraction. For most of the samples, more than 90% out of EOX content in high molecular weight fraction, which contained lipids, was found to be EOI. It was observed that, before lipolysis, more than 60% of EOCl, EOBr and EOI were present in triacylglycerol fraction and were negligible in fatty acid fraction. After lipolysis, more than 50% of EOCl, EOBr and EOI were found in fatty acid fraction. This suggests that these halogens are present in fatty acid molecules^{14,15}) and/or bind the chemical structure similar to fatty acids.

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