Heavy Metal Pollution in Sediment from the Seto Inland Sea, Japan

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To discuss the geochemical and environmental behaviors of heavy metals in the Seto Inland Sea which is the largest semi-closed coastal sea in Japan, (1) distributions of heavy metals concerning pollution were examined and (2) mass balances of Zn and Cu were studied by applying a simple box model. Increase in heavy metal contents of core sediments already started in the late 1800s and is considered to be due to human activities. Recently, the pollution of sediment in Osaka Bay which is most contaminated sea area in the Sea, seems to have tended to decrease. In 1980, total sedimentary loads of Cu and Zn over the whole area of the Sea were estimated to be 630 and 3,500 tons/yr, respectively. Further, the sedimentary loads without and with human activities were estimated separately to be, respectively, 320 and 310 tons/yr for Cu and 1,800 and 1,700 tons/yr for Zn. Total inputs of Cu and Zn into the Sea were estimated to be 870 and 4,250 tons/yr and about one half of this being the results of human activities. 70% of the Cu input and 80% of the Zn input are accumulated into the sediments.

The Seto Inland Sea (Fig. 1) is the largest semi-closed inland sea in Japan. The Sea consists of several basins called "Nada" and bays which are connected to each other through narrow waterways. The great scenic beauties of nature characterized by highly irregular and delicated coastline, have been enjoyed by many people since *Manyo* era, ten centuries ago.

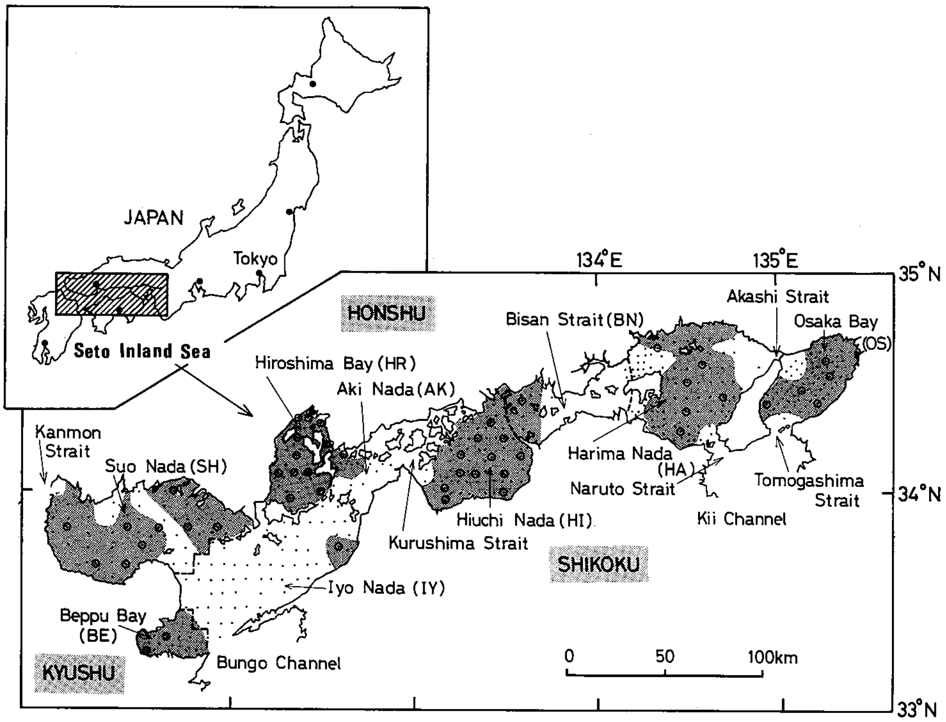

Fig. 1. Map of the Seto Inland Sea and sampling stations. ◎, core sampling; •, surface sediment sampling. Shaded area shows bottom covered with mud of Mdϕ >4.

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Because of the large amounts of organic and heavy metal pollutants and nutrients discharged through human activities along with a recent rapid economic growth in Japan, the pollutions in marine environment of the Seto Inland Sea, particularly in Osaka Bay, Hiuchi-Nada and Hiroshima Bay, have become a serious social problem. The purposes of this paper are to discuss the distributions and the pollution histories of heavy metals in sediments, and to determine the mass balances of Cu and Zn in the Seto Inland Sea, based on a simple box model for the Sea.

EXPERIMENTAL

The Seto Inland Sea has an area of ~17,100 km^2. The water volume is 520 km^3, and the average water depth is ~30 m. Water mass exchange between the Seto Inland Sea and open ocean occurs through Kii and Bungo Channels and Kanmon Strait (Fig. 1). The investigation was carried out during from 1979 to 1982. As seen from Fig. 1, the surface sediments were collected with a Smith-Mclntyre grab sampler and also core samples were collected with a 1-m gravity corer to determine ages of the sediment (sedimentation rate) and to analyze their heavy metal contents. To monitor the recent sediment pollutions, surface sediments were sampled at seriously polluted Osaka Bay area, in 1988.

The age of the core sediment were determined by the ^{210}Pb dating method after HNO_3 digestion of sediment sample. Total heavy metals contents of the sediments were analyzed by atomic absorption spectrophotometry after decomposition of sediment sample with a mixed solution of concentrated acid (HF, HNO_3 and $HClO_4$) under heating at 130°C. Organic carbon was determined by combustion at 880°C with a CN analyzer.

RESULTS AND DISCUSSION

Sedimental environments and heavy metal loads into sediments of the Seto Inland Sea

As may be seen from Fig. 1, the bottom covered with mud (median grain size: Mdϕ >4) in the Seto Inland Sea occupies ~55% of the whole area of the Sea. The sediments of bottoms in which M_2 tidal current velocity is lower than ~30 cm/s, 40~100 cm/s and higher than ~100 cm/s, correspond to mud, sand (4 >Mdϕ >1) and coarse sand (Mdϕ <1) in grain size, respectively. The distribution of organic carbon content (TOC) more than 2% of the surface sediments is similar to those of mud and weak tidal current velocity (<~30 cm/s). On the other hand, the bottoms around channels are characterized by sand and/or coarse sand, and low organic carbon below 1%. These observation indicate that the stagnant area of sea water seems to be an accumulation area of fine particles; clay minerals, organic materials and metal pollutants etc.. In these coastal areas the oxygen deficient and the eutrophication in the bottom water has been appeared seriously during a summer season. Since heavy metals are hardly accumulated to sandy bottom (Hoshika and Shiozawa, 1985), the bottom covered with mud is considered to be a major accumulation area in the Seto Inland Sea for heavy metals.

The sedimentary load of heavy metal was calculated as the product of sedimentation rate, which ranges from 0.1 to 0.4 g/cm^2 yr in the Sea, and the metal content of a sediment. Figure 2 shows historical changes in total Cu and Zn loads into sediments of the whole sea with those of the individual area in the Seto Inland Sea. The significant loads of Cu and Zn already started in the late 1800s in Hiuchi-Nada and Osaka Bay. Because the change in Cu load into the sediments of Hiuchi-Nada corresponds to the history of Cu smelting in the area of Bessi around the Nada, the early beginning of the increase in Cu contents is considered to be the start of pollution due to human activities. Total Cu and Zn

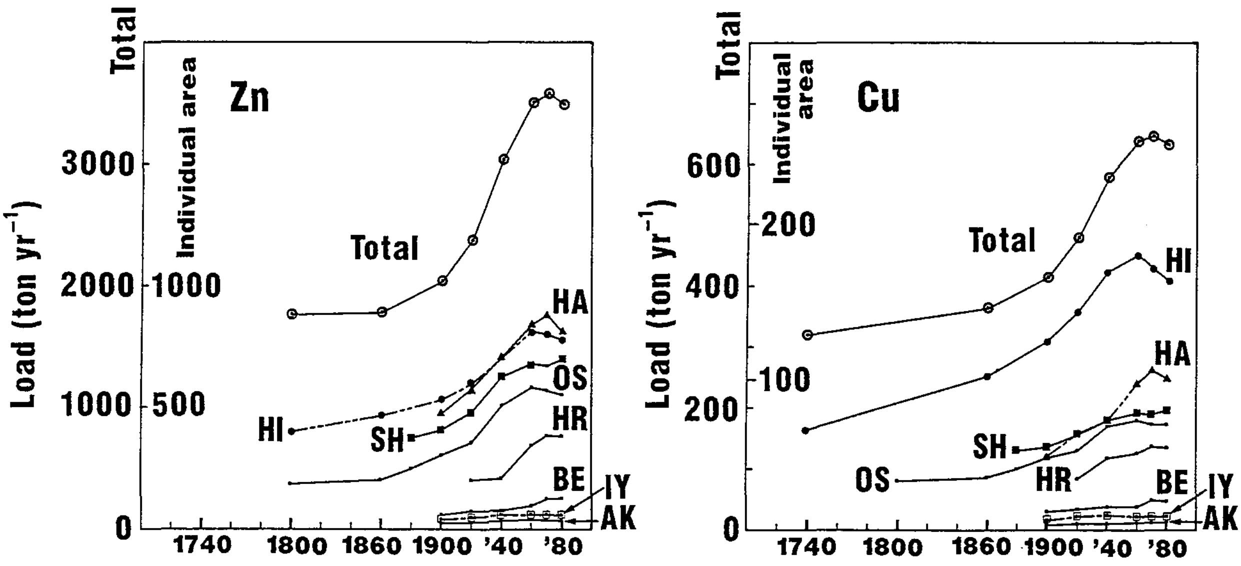

Fig. 2. History of Cu and Zn loads into sediments of the various regions of the Seto Inland Sea.

loads then gradually increased reaching maximum values in the 1960s. Cu and Zn loads (320 and 1,800 tons/yr, respectively), prior to the late 1800s when pollution started, are considered as natural loads. The total sedimentary loads are 630 tons/yr for Cu and 3,500 tons/yr for Zn in 1980. Thus Cu and Zn loads in 1980 due to human activities are considered to be 310 and 1,700 tons/yr, respectively. Natural and human loads of Cu and also Zn into sediments in the Seto Inland Sea are, therefore, considered to be nearly equal with each other in 1980.

Osaka Bay is located at the east end of the Seto Inland Sea (Fig. 1) and is most polluted sea area in the Sea. Various industrial and domestic waste waters have been entered the innerpart of the bay, and such s discharge of pollutants could have a significant effect on the formation of an anoxic environment in the bottom water in the innerpart of the Bay during summer season. As seen from Fig. 3, at

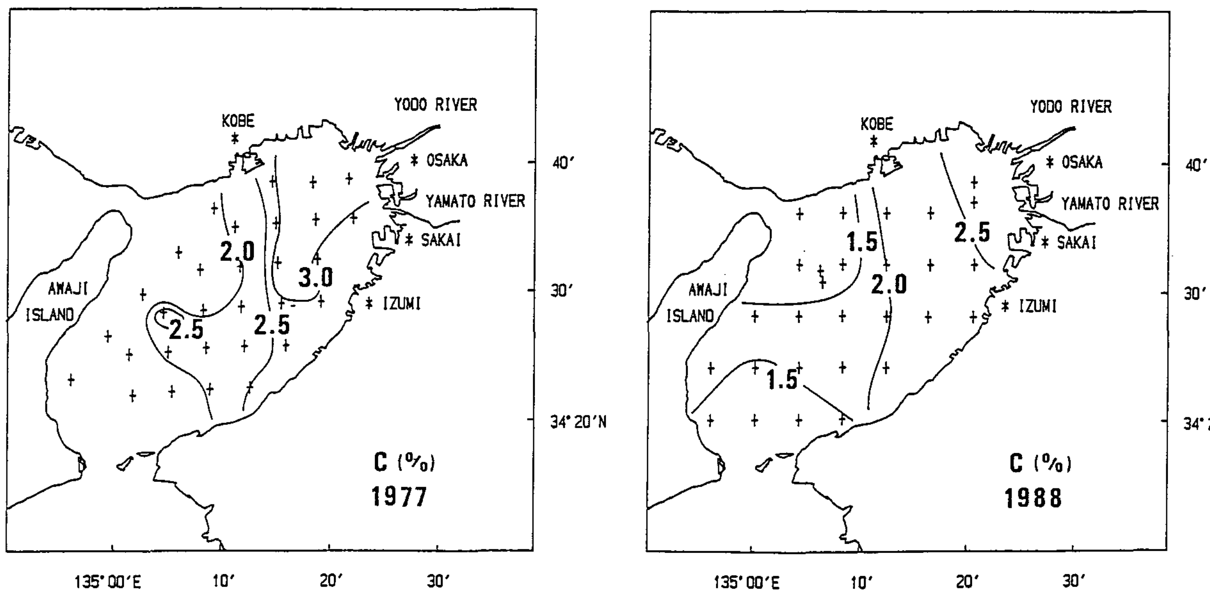

Fig. 3. Distributions of TOC of surface sediments collected from Osaka Bay in 1977 and 1988.

the present time, the TOC contents of surface sediments show decrease over the whole area of the Bay in contrast to those in 1977. At present, TOC loads into the sediments (43,900 tons/yr) could be reduced by 85% of those (52,500 tons/yr) in 1977. The changes in the distributions and the sedimentary loads of Zn and Cu in the last ten years is similar to those of TOC. In contrast to the distributions of TOC, Zn and Cu, the Mn content is lower in the innerpart of the bay and increase gradually toward the central part of the bay. This may be explained as the result of characteristic behavior of Mn; reduction of Mn under anoxic conditions of the innermost part of the bay and subsequent reprecipitation as oxides in oxidezed sediment of the central part of the bay. It is noted that Mn content seems to increase even in the innerpart of the bay, now. We think that the increase in the Mn content is not caused by increase in anthropogenic input but rather by reduction of the appearance of anoxic condition in the innerpart of the bay with the reduction of organic pollutants into the sediment. At present (2,400 tons/yr), Mn loads into the sediments increases at 20% of those in 1977 (2,000 tons/yr).

Mass balance of heavy metal in the Seto Inland Sea

The behavior of heavy metals in polluted coastal environments may be understood by showing their mass balances of heavy metals in the environments. The processes for supply and removal of heavy metals in the Seto Inland Sea water are; (1) supply and removal through an exchange of water between the Seto Inland Sea and open area; (2) supply via rainfall and river discharge under natural condition without human activities and also supply due to human activities, and (3) removal through accumulation into sediment. In these processes, the supplies due to human activities and river discharge are important but uncertain. The accumulation of metals into sediment was estimated earlier in this paper. The amounts of individual heavy metals removed and supplied through seawater exchange can be estimated using a box model for salinity. Since the values in the two processes (1) and (3) can be estimated, the value in the process (2) is calculated. The mass balance of salinity is shown as follows;

$$S_i*(X+Q)=S_o*X \qquad (1)$$

where S_i is the mean salinity value of the Seto Inland Sea water. S_i is calculated to be 32.7 ‰. S_o is the mean salinity value (34.4 ‰) of the open sea far from Bungo Strait (Fujiwara,1985). Q is annual mean discharge of fresh water (30 km^3/yr), into the Sea, this value being the sum of rain fall, river discharge and evaporation. The X value is annual input of sea water from the open sea through straits. From equation (1), X is calculated to be 560 km^3/yr. V is the water volume of the Seto Inland Sea (520 km^3). A mean residence time of sea water, therefore, is calculated as 0.9 years.

It is noted that a fairly large amount of heavy metals from industries (one of the most important human activities) may be dumped into the Sea almost directly, not via river and rainfall. The mass balance of heavy metal in the Seto Inland Sea is shown as follows:

$$L_1 + C_o*X = L_2 + C_i*(X+Q) \qquad (2)$$

where C_o and C_i are average concentrations of heavy metal in the open sea and the Seto Inland Sea waters, respectively. The average concentrations of Cu and Zn (C_i) were calculated to be 0.5μg/l and 1.3μg/l, respectively, using the values reported by Tubota et al. (1984). And Cu and Zn concentrations in the open sea water (C_o) far from Bungo Straight are 0.09 and 0.08μg/l, respectively. Thus the net amounts of Cu and Zn carried away from the Seto Inland Sea to the open ocean are calculated to be 240 and 750 tons/yr, respectively. The total Cu and Zn loads into sediment (L_2) were already given in this paper. Thus from equation

(2), the total supplies (L_1) of Cu and Zn into the Seto Inland Sea are calculated to be 870 and 4,250 tons/yr respectively, at the present time, 70 and 80% of the total amounts of Cu and Zn supplied to the Seto Inland Sea are accumulated into sediments, respectively.

Since human and natural metal loads into sediments were estimated separately, as described earlier, the supply of heavy metals due to human activities ($L_{1,human}$) in the Seto Inland Sea can be estimated as follows:

The ratio of natural origin to human origin for total heavy metal content of sediment is considered to be similar to that of seawater. Thus, it seems reasonable to assume that about one half of Cu and Zn concentrations in the Seto Inland Sea water is caused by human activities. The increase in the heavy metal concentrations in the open sea water due to human activities is considered to be negligibly small. The amounts of heavy metals supplied through human activities into the Seto inland Sea ($L_{1,human}$) can, therefore, be calculated.

Since L_{2human} is 310 and 1,700 tons/yr, C_o is 0 and 0 $\mu g/l$ and C_I 0.25 and 0.65 $\mu g/l$ for Cu and Zn, concerning only human activities, respectively, from equation (2). $L_{1,human}$ is calculated to be 460 tons/yr for Cu and 2,100 tons/yr for Zn. The heavy metal supply to the Seto Inland Sea via non-polluted rainfall ($L_{1,rain}$) is estimated to be 10 for Cu and 20 tons/yr for Zn, as the products of rain fall and heavy metal concentrations in non-polluted rain water estimated by Kitano (1984), which are 0.5 $\mu g/l$ for Cu and 1 $\mu g/l$ for Zn. The amounts of Cu and Zn supplied via non-polluted river can, therefore, be calculated to be 400 and 2,130 tons/yr, respectively as seen from Fig. 4, although the analytical results of the heavy metal concentrations in non-polluted river water are very uncertain.

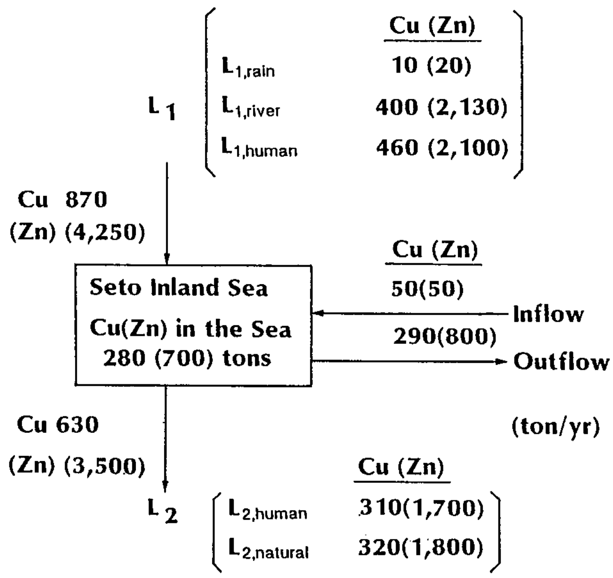

Fig. 4. Mass balances of Cu and Zn in the Seto Inland Sea (tons/yr). L1, load into the Sea, L2, load into sediment, ( ), Zn.

Mean residence times of Cu and Zn are calculated to be ~0.3 and ~0.2 years, respectively. These small values, compared to the mean residence time of the sea water (0.9 years), suggest that Cu and Zn supplied to the Seto Inland Sea are accumulated rapidly into sediments.

References

Fujiwara, T., 1985. Flux and balance of mass in the Seto Inland Sea. Ph. D. thesis, Tokyo University 253pp.

Hoshika, A. and Shiozawa, T., 1985. Sedimentation rates and heavy metal pollution of sediments in the Seto Inland Sea, Part 4. Suo-Nada. J. Oceanogr. Soc. Jpn., 41: 283-290.

Kitano, Y., 1984. Environmental Chemistry of the Earth. Shokabo, Tokyo, 237pp.

Tubota, H., Hayase, K., Kodama, T. and Koshimizu, T., 1984. Heavy metal concentrations in seawater of the Seto Inland Sea. In: Review for General Assessment in the Environment of the Inland Sea of Seto. Rep. Sci. Res. Minist. Educ. Cult. Sci., Jpn., 3: 17-28.