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Levels and Ages of Selenium and Metals in Sedimentary Cores of Ise Bay as Determined by 210-Pb Dating Technique

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Ise Bay is connected with estuaries of Nagoya harbor which is one of the most active industrial areas in Japan. Nagoya harbor estuaries are recipient of a large quanitity of municipal and industrial discharge with total fresh water input estimated to be approximately 4.5 million m^3 per day (Itoh 1975). The land boundaries of estuaries are sites of the manufacturing industries and they are utilized by oil tankers and cargo vessels. Accumulation of various kinds of metal such as selenium, mercury, zinc, copper, lead, and chromium have occured in sediments for many years. We have carried out an extensive investigation on the selenium pollution of sea water and sediments of Nagoya harbor estuaries (Itoh et al. 1985, 1986). Sugimura et al. (1977) showed that selenite and selenate are present in sea water, and thermodynamically stable sexivalent state is more predominant. Cutter et al. (1984) showed the existence of three states of dissolved selenium, namely selenite, selenate and organic selenide in sea water. Furthermore, they reported that in surface water, the ratio of organic selenide to the total dissolved selenium was estimated to be about 80 % and that of selenite was lower than that of selenate in any depths of vertical profile. On the other hand, chemical and phase state of the selenium in sediments is more complex than those in sea water. Howard (1977) reported that elementary state, ferroselite and insoluble metal selenide are the chemical state of sedimentary selenium, and selenite and hydrogen selenite are present by the adsorption to the hydrated surface of ferric oxides.

The input of selenium to Ise Bay has occurred ever since the industrial activity was established in Nagoya city. Matsumoto (1978, 1979) and Hoshika (1984)

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reported the sedimentary record of metals of Tokyo Bay, Osaka Bay and Seto Inland Sea. Sato et al. (1983) reported the pollution caused by polynuclear aromatic hydrocarbon in sediments of Ise Bay, but did not mention metals. In an attempt to investigate the ages of the pollution, we determined metals including selenium in the sedimentary core samples given by Sato et al. The ages of those samples were already estimated by Sato et al. by 210-Pb dating technique.

MATERIALS AND METHODS

The sampling locations for the sediments in Nagoya harbor estuaries and cores in Ise Bay are shown in Figure 1. Sedimentary samples (No.1-14) were taken by using an Ekman grab sampling device on a boat in estuaries (September 1985). Core samples (No.15-17) were taken from three points located near the central part of Ise Bay (September 1982). The sedimentary cores given by Sato were about 50 cm long and 10 cm in diameter. Immediately after collection, they were cut vertically at 1 and 2 cm intervals from the surface to 10 cm and from 20 cm to 50 cm, respectively, and stored in polyethylene bottles.

Total mercury was analyzed by cold vapor generation atomic absorption spectrometry. Wet sample (1 g) was digested with 50 % (v/v) nitric acid (50 ml) in a 200 ml conical beaker with a watch glass cover on the hot plate for 2 hours. After cooling, 3 % (w/v) potassium permanganate solution (10 ml) was added, and some additional volume of this solution, when necessary. Then 10 % (w/v) urea solution (10 ml) and 20 % (w/v) hydroxylamine hydrochloride solution were added to the sample solution until red color of potassium permanganate disappears at room temperature. The mixture was filtered through a filter paper (Toyo No.5A) and diluted to 100 ml. The solution (1-20 ng) was transferred into a 100 ml reaction vessel and diluted to 20 ml with water and 50 % (v/v) sulfuric acid (1 ml). The reaction vessel was connected with an atomic absorption spectrophotometer (Nippon Instruments Mercury Detector R-2) and 10 % (w/v) stannous chloride (1 ml) was added to the sample solution. An air flow (1.0 l/min) was started through the reaction vessel and the resulting mercury vapor was swept from it to the mercury detector. Concentration of mercury was calculated from the calibration graphs of mercury chloride standard solution (100 ng/ml) with 0.1 M sodium chloride prepared freshly each day. The precision was within 9 % in relative error for 3.9 g of mercury per 1 g of sediments.

Selenium was analyzed by fluorimetry with 2,3-diaminonaphthalene (DAN) after the coprecipitation with tellurium for the separation of selenium (Itoh et al. 1986). Wet sample (1 g) was digested with hydrofluoric acid, nitric acid and perchloric acid. Nitric acid was removed completely from the final digested solution and selenium was reduced to quadrivalent state by heating the solution with hydrochloric acid. Tellurium carrier solution and ascorbic acid were added to the solution. Precipitates of tellurium then appeared and coagulated. Selenium was collected with the precipitates on the filter and that was dissolved with nitric acid. Fluorescence intensity of selenium-DAN complex extracted with cyclohexane was measured at a fluorescent wavelength of 520 nm and an exciting wavelength of 378 nm (Nippon Bunko model EP-4 fluorospectrophotometer with a xenon lamp). The optimum range of the determination is 0.1-1.0 μg of selenium per 10 ml of cyclohexane. The precision was within 4 % in relative error for 10 g of selenium per 1 g of sediments.

Zinc, copper, lead and chromium were determined by atomic absorption spectrometry after the decomposition with hydrofluoric acid, nitric acid and sulfuric acid. A 100 ml teflon beaker was used for the decomposition of silicate. Organic matters were completely digested by heating for a further 30 minutes after white fumes of perchloric acid had appeared. The digested solution was diluted to 100 ml of 0.1 N hydrochloric acid solution. Zinc and copper were determined by spraying hydrochloric acid solution into an air-acetylene flame and lead was determined by using a deuterium lamp background correction (Hitachi 308 AAS). Chromium was determined by spraying hydrochloric acid solution with 1 % sodium sulfate into a nitrous oxide acetylene flame. The National Bureau of Standards, river sediment NBS-1645 and the National Research Council Canada, marine sediment MESS-1 were used as standard samples to examine the precision of our analysis. The results obtained on the standard substances were in the range of the certified values, and our procedure was confirmed to be satisfactory.

RESULTS AND DISCUSSION

Table 1 shows the results obtained on the samples taken from the different sites in Ise Bay and Nagoya harbor estuaries. The distribution does not differ so much among metals examined. The site No. 3 had the highest total content of all metals as shown in Table 1 in Nagoya harbor estuaries. High values were obtained in the sediments of the mouth of the river which accepted the input of a large quantity of municipal and industrial discharge. The contents of metals decreased with the distance from the site No. 1, which is a mouth of the river running through the center of Nagoya city. The values increased again a little in the center of Ise Bay. Selenium content ranged from 0.14 to 11 g/g dry weight. The selenium contents of No. 3 and 6 were very high and the chemical industrial discharges were found near these sites. They are considered to be main source of the input of selenium to Ise Bay. Many kinds of heavy metals have been discharged as shown in Table 1. Particularly, mercury pollution of Nagoya harbor estuaries is attributed to these industries which produced caustic soda by mercury electrolysis in the past. They commenced the operation of mercury electrolysis in 1936 and 1951, and both operations were abolished in 1973. At present they do not discharge mercury any more but mercury had already accumulated in the sediments in these areas.

Figures 2 and 3 show vertical profiles of the various metals in several core samples taken from Ise Bay. The estimated ages of sedimentary cores measured by Sato et al. were also shown in the figures. In the site of 5 km north from No. 15, the site No. 16 and No.17, the sedimentation rates were 0.36, 0.19, and 0.30 g $cm^{-2}y^{-1}$, respectively (Sato et al. 1983). Figures 2 and 3 show the results obtained in the sediments from 1930 to 1980. The sedimentation rate of No. 15 has not been measured by Sato et al. and the ages of No. 15 in the figures are those of the site of 5 km north from No.15, which were measured by Sato et al. As shown in Figure 2, since one of the industries of the mercury electrolysis began to operate, in 1930's, the mercury pollution had increased. In 1950's both of two factories were in opration actively and it became highest at about 1955. At that time, Minamata Disease caused by mercury was announced officially in Japan. Since 1960's, it has decreased. Similar status is observed in the cases of copper and zinc evidently and the copper pollution became highest at about 1955. The zinc pollution became highest at 1960's. In the cases of lead and chromium, however, the date that their pollution became highest is not observed clearly in Figure 3, but their concentrations seem to be high in 1955-1965.

In the case of selenium, the dates of the peaks of the selenium contents were different in the different sites, as shown in Figure 2. This observation may be attributed to volatilizability of selenium during the storage of the sample and/or the presence in the sediments for many years. Whereas, mercury, zinc and copper may be converted into their sulfides in reducing environments. Selenium is largely controlled by the behavior of iron in both oxidizing and reducing environments, and selenium in sediments exists mostly

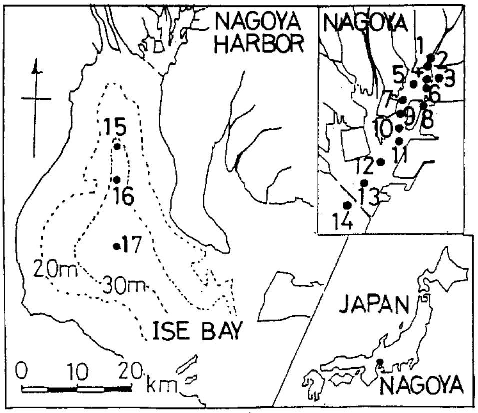

Figure 1. Sampling location for sediments in Ise Bay and Nagoya harbor estuaries.

Table 1. Heavy metal contents in surface layer of bottom sediments.

Location of Sampling	Hg (μg)	Se (μg)	Zn (mg)	Cu (mg)	Pb (mg)	Cr (mg)
No.1	4.0	2.2	2.8	0.59	0.26	0.77
No.2	1.5	1.8	1.3	0.26	0.16	0.42
No.3	38	11.2	4.7	0.59	0.90	1.4
No.4	3.8	4.7	1.4	0.26	0.18	0.49
No.5	1.1	1.9	0.75	0.19	0.090	0.23
No.6	5.3	9.7	1.9	0.28	0.41	0.19
No.7	0.44	0.14	0.31	0.082	0.15	0.093
No.8	0.75	0.58	0.31	0.073	0.070	0.11
No.9	0.82	1.0	0.65	0.12	0.070	0.19
No.10	0.19	0.58	0.14	0.046	0.051	0.070
No.11	0.20	0.67	0.21	0.050	0.060	0.073
No.12	0.20	0.53	0.14	0.041	0.048	0.058
No.13	0.11	0.34	0.12	0.034	0.043	0.057
No.14	0.16	0.28	0.079	0.021	0.028	0.036
No.15	0.32	0.58	0.18	0.043	0.065	0.067
No.16	0.19	0.61	0.20	0.037	0.062	0.074
No.17	0.17	0.70	0.18	0.037	0.058	0.063

Samples of No.1-14 and No.15-17 were collected in September 1985 and in September 1982, respectively.

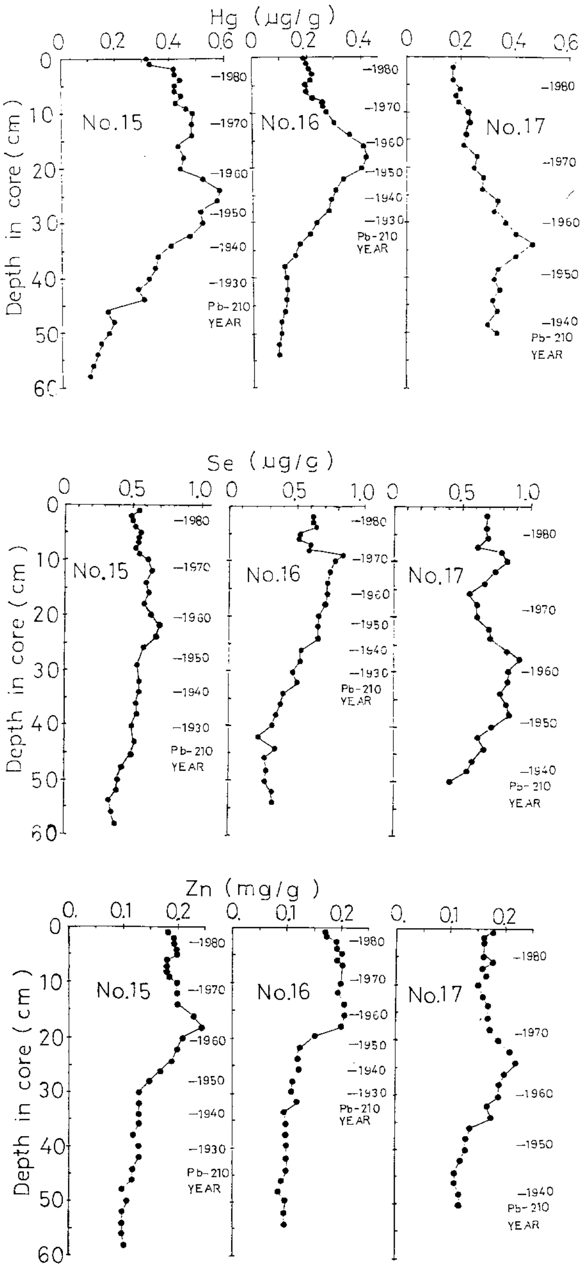

Figure 2. Concentration-depth profiles of the various chemical elements in cores.

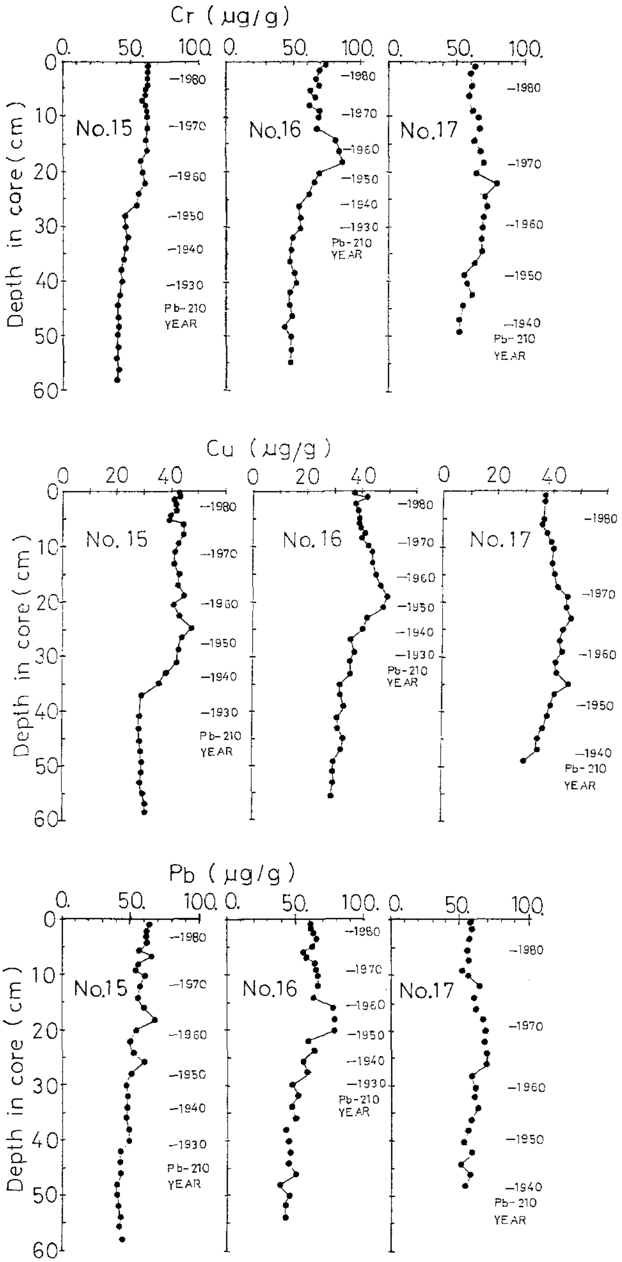

Figure 3. Concentration-depth profiles of the various chemical elements in cores.

in the elemental state and ferroselite (Howard 1977). Cutter reported that selenium is present mostly as elemental selenium or insoluble selenide in sediments (Cutter 1985). When excess sulfur is present, ferroselite is less stable than pyrite, and under the conditions, elemental selenium is present in the equilibrium with pyrite, and elemental selenium can be oxidised to selenite by aerated water. However, the history of the pollution caused by selenium is also considered to be in rough analogy to that of mercury. The selenium pollution was highest from 1955 to 1965. Before 1930, selenium contents in sediments were found to be similar to back-ground values (0.3-0.5 μg/g dry weight). Since 1970 up to present, they have varied in the range from 0.5 to 0.8 μg/g dry weight, which are higher than the back-ground value. As shown in Table 1, the chemical industrial discharges near the sites No. 3 and 6 are still being continued even at present and they will be observed also in future.

Matsumoto studied on the sedimentary cores of Tokyo Bay (1979), and reported that the pollution caused by many kinds of metal reached the maximum at the depth of 15-20 cm, the ages of about 1970, which were estimated by 210-Pb dating technique. In Tokyo Bay, the history of the polltion is considered to correspond to that in Ise Bay as for mercury, copper, zinc, lead and chromium, although the contents of these metals in the sediments are different from those in Ise Bay. Matsumoto (1978) reported that in Osaka Bay the pollution of heavy metals reached its highest at about 1970 which is the same as that of Tokyo Bay. Hoshika and Shiozawa (1984) reported that in Seto Inland Sea, the pollution of copper and zinc reached its maximum at the depth of 15-20 cm, which is the ages of 1960's estimated by 210-Pb dating technique. The ages of the highest metal pollution in Seto Inland Sea are different from those of Tokyo Bay and Osaka Bay.

Based on studies on the sedimental cores in Ise Bay, which are the same samples as those of our study, Sato et al. (1984) reported that the pollution caused by polynuclear aromatic hydrocarbons reached its maximum at the depth of 10 cm, the age of about 1973, and that corresponds to the time of the highest consumption of petroleum, and a slight decrease was observed in year of oil shock. The ages of the maximum of polynuclear aromatic hydrocarbons are later than those of any metal shown in Figures 2 and 3. However, the air pollution of sulfur oxide caused by burning fuel came to its maximum from 1966 to 1969 in this area. It has decreased since 1970, because discharge of sulfur oxide from industrial facilities has been strictly controlled by the Ambient Air Quality Standards. On the other hand, in water, the level of the biological oxygen demand (BOD) came to its maximum at about 1965. It has also decreased in this area since 1966, because discharge of waste water from industrial facilities has been strictly controlled by Environmental Water Quality Standards. In conclusion, the maximum ages of the pollution caused by metals vary appreciably depending upon the strictness in official control. Mercury which has been very strictly controlled came to its maximum at about 1955, when Minamata Disease was reported officially to be caused by the discharge of mercury from industrial facilities. The pollution caused by mercury has decreased since 1960's. The pollution caused by other metals corresponds to the water pollution estimated by the level of BOD, and it came to its highest later than that of mercury or in almost the same ages. The pollution caused by zinc came to its highest at 1960's. The pollution caused by selenium also corresponds roughly to that of zinc. Decrease of the discharge of metals except mercury was not observed evidently, and pollution caused by these metals to Ise Bay seems to be still continuing.

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