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# Geochemical Characterization of Suspended Particles in Estuarine and Coastal Seawater by X-Ray Fluorescence Spectrometry

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The elemental compositions of suspended particles collected in Tokyo Bay and Tamagawa River Estuary were determined by X-ray fluorescence spectrometry. It has been found that the concentrations of Al, Ti, and Fe in SP were decreased more rapidly than those of Si, Ca, K, Cu, and Zn from the estuarine to the bay areas.

The estuarine area, where river water mixes with seawater, has been receiving increasing attention in order to discuss the input flux of materials to oceans$^{1)}$ and the trapping effects of river-borne materials.$^{2)}$ It has been reported that some materials which are carried to the ocean through river are deposited in the estuarine area.$^{3)}$ In these processes observed in the estuarine area, suspended particles (SPs) are considered to play an important role.

We have measured the distributions of dissolved trace elements in the Tamagawa River and Tokyo Bay area$^{4)}$ and also the surface chemical compositions of SPs in the area.$^{5)}$ Each dissolved trace element showed a characteristic distribution and the surface compositions of SPs changed markedly depending on the sampling locations and water depths in the area. It has been also known that the distributions of the dissolved elements were regulated by their interactions with SPs.$^{6)}$ In order to elucidate the chemical and/or physical interactions between dissolved trace elements and SPs through the particulate surface, thus, it is required that the chemical substances which compose the SPs should be characterized for further understandings from the view point of geochemistry, oceanography and environmental science.

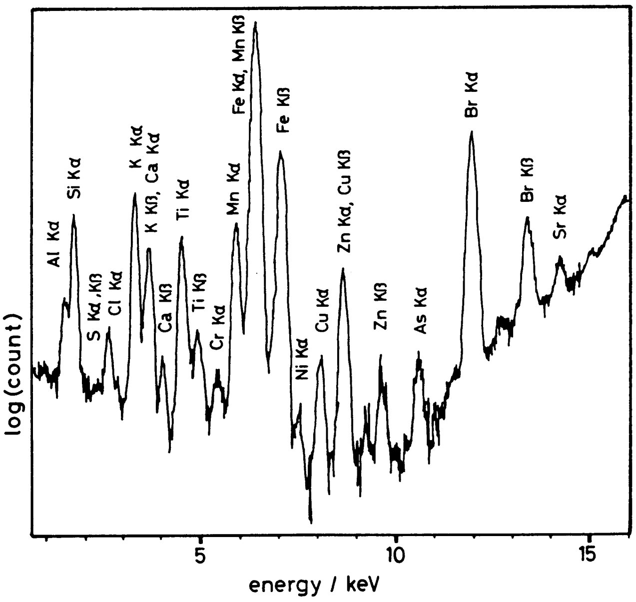

Fig. 1. XRF spectrum of suspended particle collected at about 2 km upstream from the river mouth of Tamagawa River. (Sampling: November, 1982)

In the present study, the total compositional analysis of the SPs using X-ray fluorescence spectrometry (XRF) was carried out in order to obtain the chemical information of the SPs in Tamagawa River estuary and Tokyo Bay area. Samples were collected two times with the cruises in the middle of November, 1982 and the end of June, 1984. Sampling stations of the first cruise were the same as those appeared in the previous papers.[4,5] The sampling stations in the second cruise were almost similar to those of the first one, but three other stations were added. The location of Station 1 in the second cruise was approximately at the center of Tokyo Bay, and Stations 6 and 7 were located about 2 and 8 km upstream from the river mouth, respectively. Between Stations 1 and 6, seawater samples were collected at 4 other stations. The sampler used was Van Dorn and Niskin type.

About 50-500 ml of seawater was immediately transferred to a polyethylene bottle which had been precleaned with 1:1 $HNO_3$ solution and water. The seawater was filtered on the same day with a Nuclepore filter (pore size 0.4 μm). SPs collected on the filter were dried at room temperature before setting on the XRF sample holder. Another one liter of seawater was filtered through the pre-weighed filter in the same manner to measure weight of SP.

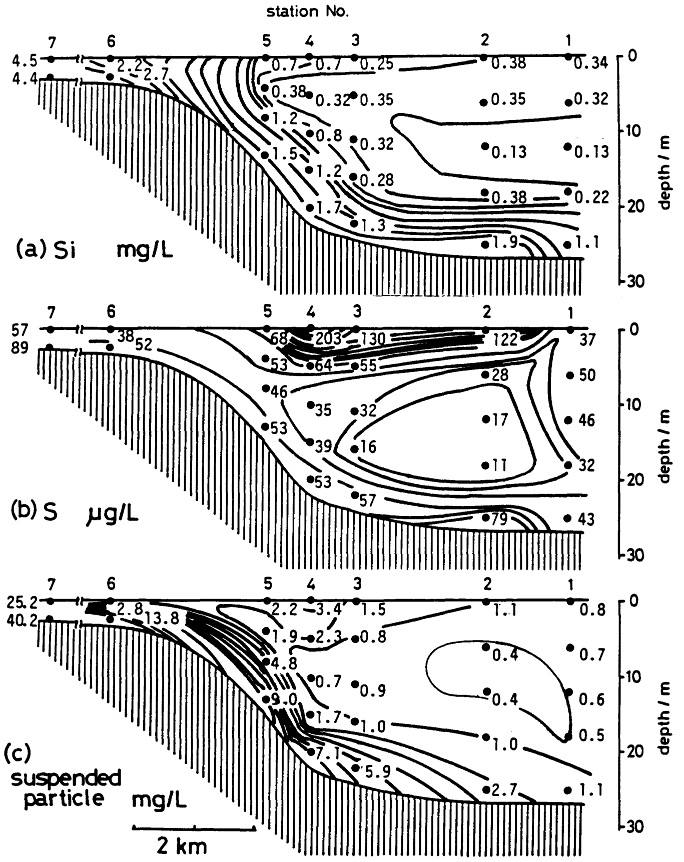

Fig. 2. Sectional views of Si (a) and S (b) contents of suspended particles and its weight (c) in 1 l water. (Sampling: July, 1984)

In XRF analysis, a non-dispersive X-ray fluorescence spectrometer of TEFA 6110 system (Ortec Inc., U.S.A.) with a Mo anode and Mo filter was used. The X-ray tube was operated at 35 kV with the anode current of 200 μA. The measurement was done under vacuum for 1000 s. Several samples were also measured by inductively coupled plasma atomic emission spectrometry after proper digestion in order to make the calibration curve of each element for XRF analysis.

In Fig. 1 an XRF spectrum of SP collected at 2 km upstream from the river mouth in the first cruise is shown. The intensity of each peak is indicated in logarithm of peak count. The intense peaks of characteristic X-rays from Si, Cl, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, As, Br, and Sr could be observed explicitly. The peak of S, which is not clear in Fig. 1, was strong enough to measure the peak intensities at other stations. The peaks of Br were caused by the Nuclepore filter itself. Hereafter discussion will be made mainly by using the data for the samples obtained in the second cruise.

Sectional views of the contents of some typical elements (Si and S) of SP from 1 l water are shown in Fig. 2 along with the weight distributions of SP. The

Si content was largest at the river and gradually decreased with the distance from the river mouth. In the bay area the vertical distribution of Si showed a minimum at the middle layer and was rather larger at the bottom. The distributions of Al, Ti, Fe, K, and Ca in SP were similar to that of Si.

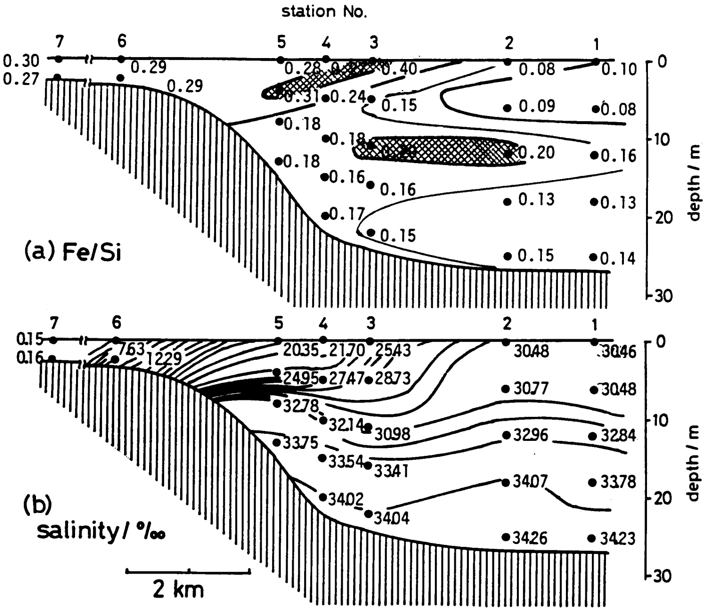

Fig. 3. Sectional views of concentration ratio of Fe to Si in suspended particles (a) and salinity (b) in estuarine and sea water. (Sampling: July, 1984)

The sectional view of S was much different from that of Si. The distribution of S was maximum at the surface of Station 4, about 2 km downstream from the river mouth, and generally showed the larger contents at the surface. On the contrary, the weight of SP was larger near the surface and bottom layers rather than in the middle layer, and also the distribution of SP was not largest at the maximum distribution of S. These facts suggest that the S content of SP near the surface of Station 4 was quite large, compared to those in other locations. Kamatani et al. reported that the content of organic SP was larger in the surface water near estuarine area.[7] Furthermore, it was found that biological activity was often high in estuarine water of salinity of about 20 ‰.[8,9] Thus the large content of S near Station 4 may be due to organic sulfur assimilated from inorganic sulfur by biological activity.

Vertical views of the concentration ratio of Fe to Si (Fe/Si ratio) in SP and salinity are shown in Fig. 3. The Fe/Si ratio generally decreased with the distance from the river mouth, although there were two layers (hatched zones in Fig. 3.) where the Fe/Si ratios were larger than those ambient waters. As can be seen in Fig. 3, the Fe/Si ratios of the hatched zones were more than 0.3 and about 0.2, corresponding to the salinity values of about 24-25 ‰ and 31-32 ‰, respectively. The decrease of the Fe/Si ratio in the estuarine area may be explained by rapid removal of Fe-rich SP rather than Si-rich SP. In fact Sakamoto reported that quartz could be carried much far away than clay minerals.[10] It was also suggested that clay minerals were coagulated through flocculation and easily deposited on sea floor in the estuarine area.[11] In the two layers where the Fe/Si ratios were large, salinity changed quite suddenly and thus the water density markedly changed. It can be speculated that the Fe-rich SP may be retained for longer time during sedimentation in these layers.

As for the concentration ratios of Ti and Al to Si, the results similar to the Fe/Si ratio were obtained. The ratios of Cu, Zn, and Ni to Si increased with distance from the river mouth, while the ratios of Ca and K were rather constant. The elements such as Cu, Zn, and Ni are known to be bio-elements and easily accumulated in microorganisms and planktons. Thus the ratios of Cu, Zn, and Ni to

Si may also reflect the biological activities in the estuarine area.

From all the experimental results, the following conclusive remarks can be noted. Tamagawa River water carries silicate and clay minerals which are rich in Si, K, and Ca, and in Si, Al, Ti, and Fe, respectively. During the flow into the Tokyo Bay area, such minerals are deposited on sea floor. The clay minerals may be more rapidly deposited than silicate minerals, but in some water front, where salinity changes markedly, clay mineral stays for longer time. Organic SPs including microorganisms become rich in the area where the river and sea waters are mixed. According to surface analysis of SPs, reported previously,[5] mineral-rich SP carried by the river water are covered with organic materials such as humic acid during the flow near the estuarine area. These facts suggest that the biological activities should be taken into consideration to discuss the elemental distributions of SPs as well as dissolved forms in the estuarine area. For further discussion on the role of SPs in the estuarine and coastal areas, identification of composite minerals of SPs will be helpful. Such studies are in progress.

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