

A Study on Mineral Compositions of Suspended Particles  
in Coastal and Estuarine Water Using X-Ray Diffractiometry

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Mineral compositions of suspended particles (SPs) collected at coastal and estuarine areas in Tokyo Bay were investigated by X-ray diffraction spectrometry, where quartz, feldspar, illite, montmorillonite, kaolinite, and gibbsite were identified. The behaviors of such minerals in the estuarine area will be discussed.

Manifold reactions among dissolved matters and suspended particles (SPs) are supposed to occur in estuarine area.<sup>1-3)</sup> Adsorption onto SPs,<sup>1)</sup> desorption from SPs,<sup>2)</sup> and flocculation<sup>3)</sup> have been proposed as such reactions. It is, therefore, desirable to determine the individual components in estuarine and coastal water for elucidation of such reactions. From such standpoints, we have investigated the distributions of dissolved metals,<sup>4)</sup> elemental compositions of total SPs,<sup>5)</sup> and surface composition of SPs<sup>6)</sup> by using the advanced spectroscopic methods.

Minerals, which are supplied from the rivers, are considered to act as cores to scavenge dissolved matters in waters, and thus the behaviors of minerals in the estuary region are very interesting. Hence, in this study, mineral compositions of SPs collected in Tamagawa River and Tokyo Bay areas have been further examined by X-ray diffractiometry (XRD) after treatment of mineral extraction.

Water samples of 300 l were collected from Tamagawa River estuary and Tokyo Bay areas in June, 1984, at the same time when seawater sampling for investigation of elemental composition of SPs was performed as reported previously.<sup>5)</sup> The sampling sites were at the center of Tokyo Bay (Stn. 1), and at 1 km downstream (Stn. 5) and 8 km upstream (Stn. 7) from Tamagawa River mouth. Two surface water samples from Stns. 5 and 7 and one water sample from 18 m deep below surface at Stn. 1 were taken with a Niskin type sampler. Salinity of these three samples were 33.775‰ at Stn. 1, 20.348‰ at Stn. 5, and 0.150‰ at Stn. 7. One hundred l of each water sample was filtered within two days after sampling with a large volume filtration device, purchased from Toyo Filter Co., Ltd. The filters used were Nuclepore filter of pore size 0.4  $\mu$ m and diameter 270 mm. The filters, on which SPs were collected, were stored in a freezer until sequent treatment for mineral extraction was made.

Mineral extraction was carried out with ammonium acetate, hydroxylamine

hydrochloride, acetic acid, hydrogen peroxide, and nitric acid.<sup>7)</sup> The final mineral residue was dried at 90 °C in an oven, and set on a sample holding plate for the XRD measurement. After the measurement of the XRD patterns, the same SP samples were treated with hydraulic elutriation in order to collect clay minerals which had the diameters smaller than 2  $\mu\text{m}$ , and then the treated samples were provided again for the XRD measurement. A XRD system utilized was a spectrometer of model Geigerflex RAD-1A from Rigaku Denki Co. Ltd. The X ray tube (Cu K $\alpha$ ) was operated at 35 kV with a current of 15 mA.

The X-ray diffraction patterns of the SPs after mineral extraction are shown in Fig. 1. The upper, middle, and lower patterns in Fig. 1 correspond to the SPs collected at Stn. 7, Stn. 5, and Stn. 1, respectively. In all the patterns, the peaks for quartz ( $d=3.31$ ,  $4.23$ ), feldspar ( $d=3.19$ ), illite ( $d=9.94$ ), and kaolinite ( $d=7.08$ - $7.37$ ) were found as the clear diffraction peaks. These mineral species are similar to those observed for sediment in Tokyo Bay.<sup>8)</sup> From the figure, it can be noted that peak intensities for illite and kaolinite decreased when the sampling station moved from Stn. 7 to Stn. 1, i.e., from the estuary to the center of the bay while those for quartz and feldspar remained almost constant.

In Table 1, the contents of elements composing the SPs, measured by X-ray fluorescence spectrometry (XRF), are summarized, where the same samples utilized in the previous page<sup>5)</sup> were used. Although the data in Table 1 have large deviations due to analytical uncertainty and sample inhomogeneity, the comparison with XRD patterns and XRF data is helpful to interpret the general changes and behaviors of SPs in the estuary and coastal areas. According to

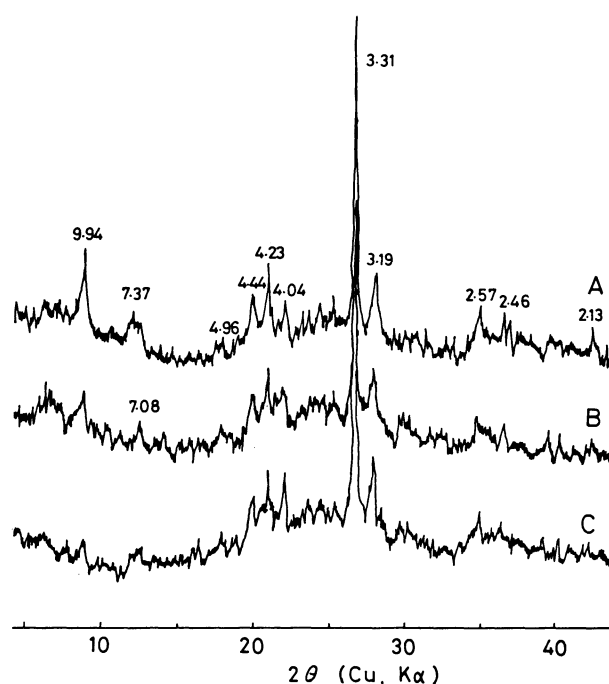


Fig. 1. X-Ray diffraction patterns of the suspended particles after treatment of mineral extraction, A: surface water 2 km towards upper stream from the river mouth, B: surface water at the river mouth, C: 18 m deep water at center of the bay, collected in the Tamagawa River estuary and Tokyo Bay areas.

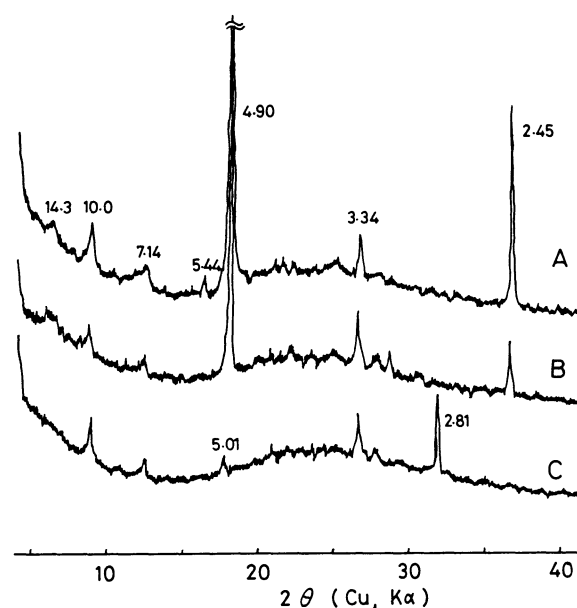


Fig. 2. X-Ray diffraction patterns of the suspended particles after treatment of mineral extraction and hydraulic elutriation. The samples for A, B, and C are the same ones used in Fig. 1.

Table 1. Analytical results of suspended particles by X-ray fluorescence spectrometry

Sta. No.	Location /km <sup>a</sup> )	Depth/m	Concentration, $\mu\text{g/l}$									
			Si	K	Ca	S	Al	Ti	Fe	Mn	Ni	Zn
1	5.7	0	340	82	14	37	-	1.3	33	17	4.4	1.0
		6	320	68	14	50	-	0.6	26	14	0.72	0.73
		12	130	19	11	46	10	0.7	21	9.2	0.56	0.20
		18	220	33	14	32	-	1.5	29	8.5	0.50	0.45
		25	1100	120	43	43	240	8.9	150	20	7.0	1.3
2	4.3	0	380	92	30	120	130	1.3	32	17	1.0	2.1
		6	350	65	21	28	40	1.2	30	15	0.87	0.70
		12	120	18	10	17	30	0.7	22	9.1	0.45	0.28
		18	380	48	14	11	80	3.0	48	9.6	0.52	0.36
		25	1900	250	66	79	440	20	290	23	1.2	2.2
3	2.1	0	250	110	40	130	120	2.9	100	36	5.5	2.7
		5	350	94	32	55	60	1.2	54	24	0.98	1.4
		11	320	56	19	32	70	2.9	63	15	0.77	0.67
		16	280	37	17	16	90	2.3	45	11	0.51	0.41
		22	1340	180	50	57	380	13	200	18	0.81	1.3
4	1.4	0	710	210	74	200	180	5.9	200	38	4.9	3.5
		5	330	81	27	64	40	2.3	78	20	1.1	0.81
		10	780	110	46	35	300	8.2	140	14	1.0	1.3
		15	1200	160	42	39	260	12	180	15	0.48	1.1
		20	1700	250	65	53	540	17	280	21	0.77	1.6
5	0.6	0	700	140	66	68	330	3.9	190	38	2.4	3.1
		4	380	90	29	53	160	1.6	120	32	1.3	1.4
		8	1200	170	49	46	330	9.7	210	17	1.4	1.4
		13	1500	210	58	53	390	17	270	18	0.92	1.7
6	-2	0	2200	280	80	38	1000	34	640	9.6	2.1	5.4
		3	2700	400	110	52	1200	43	770	9.9	2.1	5.7
7	-8	0	4600	570	230	57	1900	93	1300	28	2.8	15
		3	4400	540	210	89	1700	79	1200	27	2.6	15

a) Distance from the river mouth towards the center of the bay.

the calculation from the data in Table 1, generally the ratios of Al, Ti, and Fe contents in SPs to Si, K, or Ca decreased during the water flow from the estuary to the bay center.<sup>5)</sup> The results by XRD analysis may agree with those by XRF analysis, if Si, K, and Ca in SPs are main constituents of quartz and feldspar, and Si, Fe, Al, and Ti are those of clay minerals. On the other hand, it was found in the previous study<sup>5)</sup> that the content ratios of heavy metals such as Mn and Ni to Si in SPs at the bay became larger than those at the estuarine areas. When the present results for mineral compositions of SPs are taken into consideration, the increase in the content ratios of such heavy metals in SPs can not be attributed directly to mineral compositions such as clays, quartz, and feldspar. It is quite reasonable to assume the existence of other components such as organic matters on SP surface. This may be supported by the findings that organic matters were more abundant on the surface of SPs taken in coastal areas than in estuarine areas, as discussed previously.<sup>6)</sup>

Further, clay minerals which had particle size smaller than 2  $\mu\text{m}$  were separated from the mineral samples by hydraulic elutriation, and their X-ray diffraction patterns are shown in Fig. 2. The peaks for illite ( $d=10.00$ , 5.01, 3.34) and kaolinite ( $d=7.14$ ), which are also observed in Fig. 1, can be seen clearly in the treated clay minerals. Besides these peaks, the strong peaks of gibbsite ( $d=4.90$ , 2.45) were observed in Fig. 2. The peak intensities of gibbsite changed markedly at the different sampling locations. At the Stn. 1, the center

of the Tokyo Bay, the peak of gibbsite disappeared as shown in Fig. 2-C. Gibbsite is one form of aluminum hydroxide and the final weathered mineral from aluminosilicates.<sup>9)</sup> Two reasons may be considered as for the significant change of gibbsite concentration. That is, gibbsite may deposit directly onto sea floor or it may be dissolved in seawater during the water flow. According to our previous observation,<sup>4)</sup> the concentration of dissolved Al decreased with the distance from the river mouth towards the bay center. Further Boyle et al. reported that iron hydroxide coagulates with organic matters in estuary.<sup>3)</sup> Thus it is more possible to consider that gibbsite deposits onto sea floor after coagulation with precipitates such as iron hydroxide. Under these circumstances, adsorption of other dissolved metals onto the coagulated matters easily takes place, which results in removal of such trace metals from seawater.

The distribution of each mineral perhaps depends on its physicochemical properties. It is worthwhile to note that these minerals will deposit onto sea floor sooner or later and be exposed to diagenesis, which is of great importance for coastal environment.<sup>8)</sup> According to the experimental results in Figs. 1 and 2, the peaks for clay minerals and gibbsite with smaller particle size disappeared more rapidly than those for quartz. These facts suggest that the coagulation and/or flocculation processes may be the main deposition mechanism of these clay minerals. At the same time, heavy metals are possibly accumulated in the coagulated and/or flocculated matters. The previous ESCA<sup>5)</sup> and XRF<sup>6)</sup> studies on SPs in the estuary area also suggested important roles of organic matters in removal of dissolved heavy metals. Further investigation on organic matters on SPs, however, is necessary to discuss the kinetic removal mechanisms of heavy metals in the estuary and coastal areas.

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