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SURFACE ANALYSIS OF SUSPENDED PARTICLES IN ESTUARINE AND COASTAL WATERS USING X-RAY PHOTOELECTRON SPECTROSCOPY

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Surface compositions of suspended particles in estuarine and coastal waters were examined by X-ray photoelectron spectroscopy (XPS). It has been found that the surface compositions markedly changed, depending on the sampling locations in the estuarine and coastal areas.

Suspended particles in natural waters have been recognized as important components in water, since some dissolved materials in water are removed from water through their particle formation$^{1)}$ and vertical transportation of materials in water column depend mainly on the movement of suspended particles.$^{2)}$ Many studies have been carried out to elucidate the mechanisms of interactions between suspended particles and dissolved materials in seawater.$^{3-5)}$ It has been noticed that some trace metals are adsorbed onto and desorbed from suspended particles in waters.$^{3,4)}$ These facts may indicate that some physico-chemical reactions such as adsorption and desorption near the particle surfaces are important. According to our survey, however, no investigation has been reported to clarify the chemical composition of the surfaces of suspended particles.

We measured the trace metal distributions for estuarine and coastal waters in the Tamagawa River-Tokyo Bay area, and found that each element showed a specific distribution.$^{6)}$ This fact suggests that selective reactions between dissolved metals and suspended particles might take place for each element. In the present study, therefore, the surface compositions of the particles in estuarine and coastal sea waters of the same area have been investigated by using X-ray photoelectron spectroscopy (XPS) which has a great advantage providing important chemical informations of very thin surface (20-60 Å). The molar fractions of elements on the particle surface have been estimated to evaluate the surface compositions of particles.

Sampling points were in the Tamagawa River estuary and Tokyo Bay area, and they were the same as those appeared in the previous paper.$^{6)}$ The location of Station 1 was about 2 km upstream from the river mouth, and that of Station 4 approximately at the center of Tokyo Bay. Between the two stations, seawaters were collected at two other stations. The sampler used was of Van Dorn type.

One liter of seawater was immediately transferred to a polyethylene bottle which had been pre-cleaned with 1:1 HNO_3 solution and water. The seawater was filtered on the same day with Nuclepore filter (pore size 0.4 μm). Suspended particles collected on the filter were dried at room temperature, and served for surface analysis of suspended particles by XPS.

The XPS apparatus used was ESCA Lab. 5 system from Vacuum Generator Co., Ltd. The analytical conditions were 12 kV x 10 mA for X-ray power, 50 V for electron pass energy, and 4 mm for width of the entrance slit.

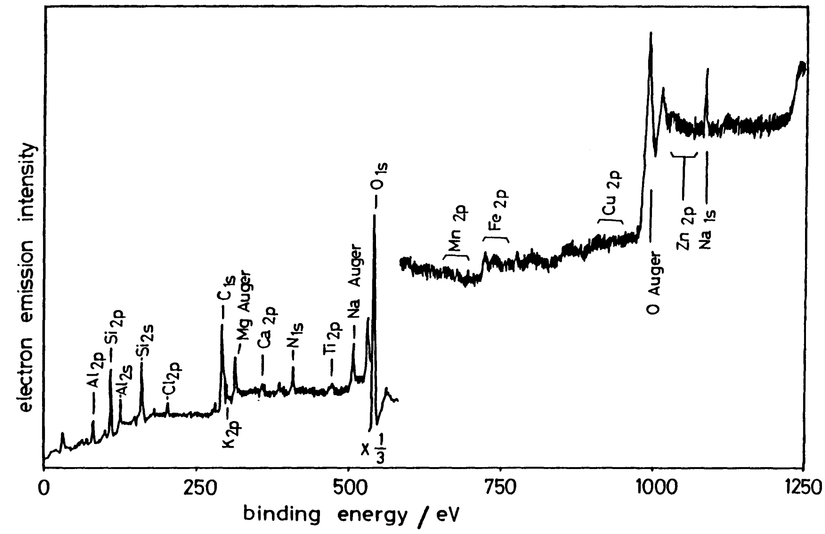

Fig. 1. XPS spectrum of suspended particles collected at the surface of Station 1, excited by Al Kα radiation.

The filter on which suspended particles were collected was cut to a circle of 1 cm diameter, and was placed on to a stainless steel sample holder with both-sided tape. The sample holder was then set in the analyser chamber of XPS. The analytical procedure was the same as that described by Seyama et al.[7)] The coefficients used to convert the peak intensities of elements to their concentration ratios were obtained from the previous paper.[7)] The excitation source was mainly Al Kα, while for Ti 2p and Cu 2p measurements Mg Kα radiation was used in order to avoid line overlapping with some satellites and Auger peaks. Calibration of binding energy was performed by measuring the peak position of Au $4f_{7/2}$ line (83.8 eV) on the sample treated with gold evaporation. For the sample which was not treated with gold, calibrations were done against C 1s.

The wide scan spectrum of the suspended particles excited by Al Kα radiation is shown in Fig. 1. The sample was collected at the surface of Station 1. Assignments for peaks are also indicated in Fig. 1. Relatively strong peaks were observed for Al 2p, Si 2p, Si 2s, C 1s, Mg Auger, N 1s, Na Auger, O 1s, O Auger, and Na 1s. The peaks of Ti 2p, Mn 2p, Fe 2p, Cu 2p, and Zn 2p were weak, but the profiles of these peaks could be measured by accumulating the electron emission intensities. In Fig. 2, the peak profile for Mn 2p is shown. The sample for the spectrum was the same one as that for Fig. 1. One hundred and twenty eight scans over 4 hours were accumulated so as to obtain the spectrum. The peak profile shown in Fig. 2 was clear enough to measure the peak intensity. The peaks of O 1s, C 1s, Si 2s, N 1s, Al 2p, Fe 2p, Zn 2p, Cu 2p, Mn 2p, and Ti 2p were used for the calculation of the molar fractions of particle surface.

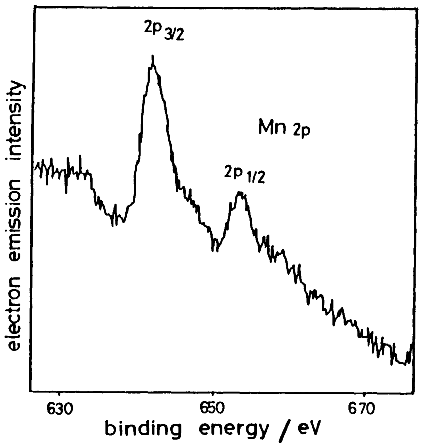

Fig. 2. Spectrum of Mn 2p region of suspended particles collected at the surface of Station 1, excited by Al Kα radiation.

The Nuclepore filter itself provided electron emission. Therefore, the influences of the uncovered part of the filter to the peak intensities of elements were examined. It was found from the measurement of XRF (X-ray fluorescence spectrometry) that a constant amount of bromine also existed in the filter. The relative standard deviation of bromine concentration in 10 sheets of filter was about 5%. Since the naturally occurring particles contained far less amount of bromine than the filter, the analytical error caused by the filter area which suspended particles did not cover was corrected by using the peak intensity of bromine (Br 3d; 69 eV) as an index of uncovered area. The relative intensity of each element in the surface of the filter was measured by XPS. Thus it was found that the corrections were required only for O, C, and N. The relative intensities of these elements to that of Br 3d in the blank filter were 30.6 for O 1s, 59.4 for C 1s, and 2.45 for N 1s. These values were used to correct the peak intensities of O, C, and N. Percentages of the corrected intensities for these elements did not exceed 10% of the original peak intensities.

Table 1. Molar Fractions for Elements on Suspended Particles

Sampling station	1	2	3	4
Distance/km[a)]	-2	0.4	2.2	5.7
Depth/m	0	4	5	25
Salinity/‰	6.7	31.6	30.3	34.09
C	22	37	41	64
O	52	43	42	25
Si	9.9	9.4	8.5	2.8
N	2.2	4.2	4.3	3.2
Al	5.5	1.2	0.70	0.49
Fe	1.4	0.22	0.12	0.19
Mn	0.17	0.22	0.22	0.15
Zn	0.017	0.18	0.14	0.05
Cu	0.04	0.04	-[b)]	0.11
Ti	0.06	-[b)]	-[b)]	-[b)]
Na	1.7	1.7	1.3	0.95
Mg	1.0	1.2	1.3	1.0
Ca	0.3	0.4	0.2	0.3
Cl	0.8	1.8	0.9	1.4

a) Distance from the mouth of the Tama River to the Tokyo Bay. b) Not detected.

The molar fractions of elements in the surface of suspended particles were summarized in Table 1. As can be seen in the table, they varied with the sampling positions and depths. It should be noted that the molar fractions of C and N increased with the distance from the river mouth and depth, while those of O, Si, K, Al, and Fe decreased.

The elemental compositions of naturally occurring materials in seawater are summerized in Table 2. Compared the values in Table 1 with those in Table 2, the surface composition of suspended particles at Station 1 (O : Si : Al = 1 : 0.19 : 0.11) was similar to those of cray minerals such as illite and montmorillonite. On the other hand, that at Station 4 (C : O : N = 2.6 : 1 : 0.13) was more similar to those of humic acid, whose composition was reported as for the sample collected at the Tokyo Bay.[10)] These experimental results suggest that particle surface which showed mineral-rich composition near the river mouth was adsorbed by organic elements when sampling station moved to the center of the Tokyo Bay. Feely et al. obtained the similar results by measuring total compositions of suspended particles collected at the north-east Gulf of Alaska.[8)]

One of the advantage of XPS is its capability of chemical speciation utilizing chemical shifts of elements. The binding energies showed some variations, but they did not have any certain correlations with sampling distance and depth. In other words, the individual components which formed the suspended particles did not change so much in the area. On the basis of chemical shift, nitrogen (N 1s; 399.3-399.7 eV) could be attributed to amino acids, carbon (C 1s; 284.8 eV) mainly to hydrocarbons, silicon (Si 2s; 153.0 eV) to silicate oxide rather than aluminosilicates, aluminum (Al 2p; 73.9-74.2 eV), iron (Fe 2p; 711.0-712.0 eV) and manganese (Mn 2p; 641.3-642.0 eV) to their oxides.

Table 2. Elemental Compositions of Materials Contained in Natural Seawater

Material	C	O[a]	N	Si	Al	Fe	Cu
Kaolinite[b]		1.0		0.29	0.29		
Illite[b]		1.0		0.3	0.1	0.01	
Montmorillonite[b]		1.0		0.3	<0.06	<0.01	
Opal		1.0		0.5			
Calcite	0.33	1.0					
Humic acid[c]	2.03	1.0	0.16		0.3×10^{-3}	0.1×10^{-3}	0.6×10^{-3}
Lipid[d]	10	1.0					
Amino acid[d]	1-2	1.0	0.5				
Plankton[e]	0.96	1.0	0.145				
Urea	1	1.0	2				

a) Compositions of oxygen are defined as 1.0. b) Cited from Ref. 9.
c) Cited from Refs. 10 and 11. d) Cited from Ref. 12. e) Cited from Ref. 13.

It may be concluded from the experimental results mentioned above that mineral-rich suspended particles which are carried by the Tamagawa River waters are covered with organic materials such as humic acid during their flow to the center of the Tokyo Bay. It is of great concern how such particle surfaces change and interact with dissolved components in natural waters. For further discussion on the role of suspended particles in the coastal region, total concentrations of elements as well as surface compositions may be required in terms of suspended particles in various locations. Such investigation is in progress.

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