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Physicochemical Speciation of Trace Elements in River Water by Means of Ultrafiltration

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Ultrafiltration and Millipore filtration techniques have been used in the speciation of trace elements in Tama River water. The size distribution was clarified for 32 elements by means of neutron-activation analysis in order to discuss their chemical or physical forms. Alkali and alkaline-earth elements were primarily found in the dissolved-size fraction ($<0.45\ \mu m$). Their dissolved species were mostly distributed in the smallest-molecular-weight fraction (<MW 500), although the alkaline-earth elements were also recognized to a significant extent (20—30%) in the middle-molecular-weight fraction (MW 10^4—500). Transition elements were principally associated with the suspended-size fraction ($>0.45\ \mu m$) in the upper reaches of the river, but in the lower reaches they were chiefly fractionated as the dissolved species, with the exception of Sc and Fe. The dissolved V and Mn were distributed in the smallest-molecular-weight fraction, while the Co, Ni, and Zn were divided between two smaller-molecular-weight fractions (MW 10^4—500 and <MW 500). Light rare-earth elements were mostly associated with suspended materials. Heavier rare-earth elements were, on the contrary, mainly found in the dissolved-size fraction, while their dissolved species were concentrated in the middle-molecular-weight fraction. The dissolved species for As, Se, Sb, and W were divided into two smaller-molecular-weight fractions, although As, Se, and W were predominantly found in the middle-molecular-weight fraction and Sb was mainly detected in the smallest-molecular-weight fraction. Aluminium and Ag were mainly associated with suspended materials. Furthermore, the dissolved Al was mostly distributed in the smallest-molecular-weight fraction, while the Ag was concentrated in the largest-molecular-weight fraction (>MW 10^4).

Trace elements in natural water are found in various physical or chemical forms, such as simple ions, ion pairs, organic or inorganic complexes, and metal ions sorbed onto particulates or colloids. The determination of thier chemical species is of great importance not only in order to substantiate their geochemical behavior in natural water, but also in order to estimate their utilities and toxicities towards aquatic organisms. A variety of physicochemical separation techniques have been used in the study of trace-element characterizations in natural water.[1–3] The size-separation methods, such as filtration,[4–7] ultrafiltration,[8–11] gel filtration, and dialysis[12,13] are used the most commonly because of their simplicities. However, no one has yet applied the size-separation techniques to a systematic analysis of multi-elements. In a previous paper,[14] we ourselves reported on the physicochemical speciation of 31 elements in Tama River water, using a combination of the Millipore filtration (MF) technique and neutron-activation analysis (NAA). However, it was not possible to separate perfectly trace elements between "colloidals" and "true solutions," for the smallest pore size of commercially available Millipore filter is 0.025 μm, even though the boundary in size between the above two states probably lies in the range of 0.01—0.001 μm.[1,2,15] The ultrafiltration (UF) technique is extensively used to separate dissolved compounds into various molecular-weight ranges using a variety of membrane filters. In this paper, we tried to separate 32 elements and 6 major components dissolved in Tama River water into several molecular-weight fractions by utilizing the UF technique in order to estimate their chemical species.

Experimental

Water Samples. The river water samples were collected from three stations of the Tama River, Hamura (Station A), Kinuta (B), and Denenchofu (C). The sampling stations are shown in Fig. 1. The Hamura site lies near prime agricultural land, while the Kinuta and Denenchofu sites lie near industrial/urban stretches. Thirty liters of each water sample was placed in a clean Pyrex glass bottle and then immediately pre-filtrated using a Millipore filter with pore size of 8 μm in order to remove large particles. Another five liters of the water sample was taken as the original material in a polyethylene bottle without any filtration, it was then acidified immediately with 30 ml of nitric acid (Super Special Grade). The water qualities at the time of sampling are listed in Table 1 for the three stations.

Filtration. The pre-filtrated water samples were divided into six 5-liter portions. Two portions of the filtrate were used for the MF experiment, and the other four portions were used for the UF experiment. The sample from the Hamura site was not, however, submitted to the UF experiment.

(A) Millipore filtration. An all-glass Millipore apparatus and two kinds of Type HA Millipore filters, with a diameter of 142 mm and with average pore sizes of 0.45 and 0.05 μm, were used for the MF experiment. The procedures have been described in detail in the previous paper.[14]

(B) Ultrafiltration. A Model UHP-150 ultrafiltration cell (Toyo Roshi Corp.) and four kinds of ultrafilters, UK-200 (molecular-weight cut-off 2×10^5), UK-10 (10^4), UH-1 (1000), and UH-05 (500), with diameter of 150 mm, were employed for the UF experiment. The decontamination and washing of each filter were done by soaking them successively in a sodium hydroxide solution (1 mol dm^{-3}) for 1 d and a sodium hydrogencarbonate solution, followed by passing 5 liters of redistilled water through the filter under the pure-

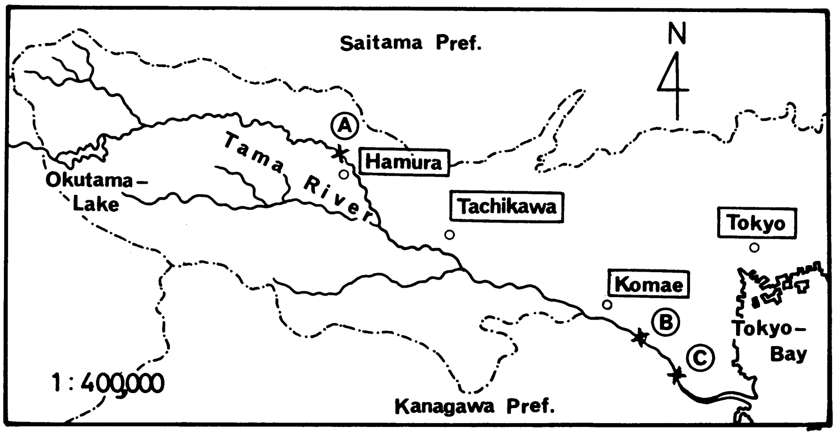

Fig. 1. Sampling locality.

Table 1. Water quality of the Tama river at the time of sampling

Parameter	River-water sample		
	A	B	C
Sampling station	Hamura	Kinuta	Denenchofu
Date	1/11/82	31/10/83	12/12/83
Water temp/°C	14.7	13.9	9.3
pH	8.2	7.0	6.9
Conductivity/μS cm^{-1}	80	246	275
ER$^{a)}$/mg l^{-1}	101	273	348
SiO_2/mg l^{-1}	25	21	20
4.3 Bx./mequiv l^{-1}	0.71	1.16	1.64
SO_4^{2-}/mg l^{-1}	13.2	30.7	52.8
Cl^-/mg l^{-1}	1.6	26.9	41.6
TOC$^{b)}$/mg l^{-1}	0.55	1.79	4.06

a) Amount of evaporated residue. b) Total organic carbon.

nitrogen gas pressure. Four portions of pre-filtrated samples were filtered using the four kinds of ultrafilters, one by one. The filtration was carried out under stirring and under nitrogengas pressures of 2—4.5 atm according to the molecularweight cut-off of the filters. The resulting four filtrates were transferred to a clean 5-liter polyethylene bottle and then acidified with 30 ml of the nitric acid in order to prevent any adsorption of trace elements on the walls of the bottles.

Neutron-activation Analysis. The procedures for the NAA experiment, the preparation of the neutron-irradiation samples, the neutron irradiation, and the gamma-ray counting were reported in detail in our previous papers.[14,16,17]

Analysis of Major Components. The concentration of silica (SiO_2) in the river water was determined by colorimetry using ammonium molybdate, while the sulfate (SO_4^{2-}) concentration was measured by turbidimetry using a barium chloride-gelatin solution. The alkalinity (4.3 Bx) was titrated with sulfuric acid (0.01 mol dm^{-3}) in the presence of a Bromocresol Green (BCG) indicator. The concentration of chloride ions (Cl^-) was measured by Mohl's method. The determination of the total organic carbon (TOC) concentration was performed by utilizing a TOC analyzer (Shimazu Model 10A).

Results and Discussion

The concentrations of the 32 elements were determined for the six filtrates resulting from the MF and UF experiments and for the original (non-filtrated) water sample by means of NAA. The statistical errors based on the gamma-ray counting were 5—30% for Ag, Ba, Ce, Cr, Eu, Ho, K, Fe, La, Mg, Se, Tb, Tm, and U, and less than 5% for the other 18 elements.

The trace-element concentrations in the pre-filtrated water sample and the residual water in the ultrafiltration cell were also determined in order to calculate the mass balance of the trace elements during the UF experiment. The results show that the loss due to adsorption was 20—50% for Fe, Ag, U, La, Ce, Sm, Eu, and Tb. For the other elements, the loss or contamination was less than 10%.

The size distributions in diameter (μm) and in the molecular-weight ranges were calculated for the 32 elements and 6 major components by means of the scheme shown in Fig. 2. The results were classified by size into two fractions, F (>0.45 μm) and F (<0.45 μm); furthermore, in the later fraction, they were classified into three molecular-weight fractions, F (>MW 10^4), F (MW 10^4—500), and F (<MW 500). The results are shown in Tables 2—8.

As a general rule, chemical constituents with a size smaller than 0.45 μm are defined as "dissolved," while those with a size larger than 0.45 μm are clas-

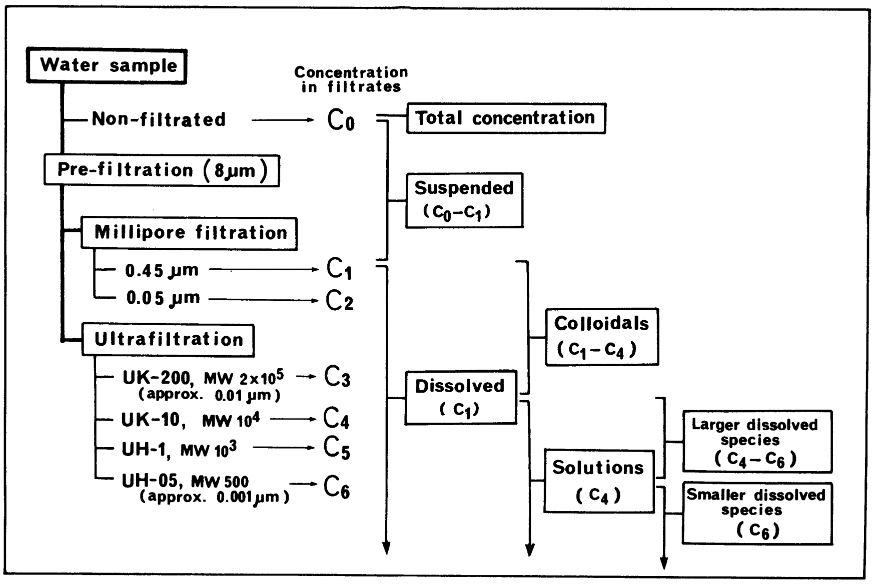

Fig. 2. Scheme for speciation of trace elements in river water by size fractionation techniques.

Table 2. Fractionation results of major components in the river water

Component	Sampling station	Total content	Millipore filtration		Ultrafiltration of dissolved species		
			>0.45μm (suspended)	<0.45μm (dissolved)	>MW 10^4 (colloidals)	MW 10^4—500 (larger dissolved species)	<MW 500 (smaller dissolved species)
ER (mg/l)	A	101	2(2.0)	99(98.0)	—	—	—
	B	273	12(4.4)	261(95.6)	0(0)	44(16.9)	217(83.1)
	C	348	16(4.6)	332(95.4)	4(1.2)	60(18.1)	268(80.7)
SiO_2 (mg/l)	A	25.3	—	—	—	—	—
	B	20.6	0(0)	20.6(100)	0(0)	1.8(8.7)	18.8(91.3)
	C	20.4	0(0)	20.4(100)	0(0)	2.1(10.3)	18.3(89.7)
4.3Bx (meq/l)	A	0.71	0(0)	0.71(100)	—	—	—
	B	1.16	0(0)	1.16(100)	0(0)	0.21(18.1)	0.95(81.9)
	C	1.64	0.03(1.8)	1.61(98.2)	0(0)	0.25(15.5)	1.36(84.5)
SO_4^{2-} (mg/l)	A	13.2	0(0)	13.2(100)	—	—	—
	B	30.7	2.4(7.8)	28.3(92.2)	0.9(3.2)	16.4(57.9)	11.0(38.9)
	C	52.8	0(0)	52.8(100)	0(0)	28.8(54.5)	24.0(45.5)
Cl^- (mg/l)	A	1.6	0(0)	1.6(100)	—	—	—
	B	26.9	0(0)	26.9(100)	0(0)	0.4(1.5)	26.5(98.5)
	C	41.6	0(0)	41.6(100)	0(0)	0.6(1.4)	41.0(98.6)
TOC (mg/l)	A	0.55	0.23(41.8)	0.32(58.2)	—	—	—
	B	1.79	0.25(14.0)	1.54(86.0)	0.35(22.7)	1.01(65.6)	0.18(11.7)
	C	4.06	0.39(9.6)	3.67(90.4)	1.18(32.1)	1.97(53.7)	0.52(14.2)

The values in parenthesis are the percentages of each fraction.

sified as "particulate" or "suspended." The "dissolved" constituents need not be in a true solution, but can include "colloidals."[3] In this paper, it is assumed that the constituents with a size larger than molecular weight 10^4 (>MW 10^4) are "colloidals," while those with a size smaller than molecular weight 10^4 are "true solution," according to the method reported by Steinnes.[2] Furthermore, the constituents with molecular weights ranging from 10^4 to 500 (MW 10^4—500) are defined as larger dissolved species, while those passing through the ultrafilter with a molecular-weight cut-off of 500 (<MW 500) are classified as smaller dissolved species. The larger dissolved species included organic complexes, polyhydroxo complexes, *etc.*, while the smaller dissolved species are made up of free ions, ion pairs, *etc.*[2]

Major Components (ER, SiO_2, 4.3 Bx, SO_4^{2-}, Cl^-, and TOC). The total contents of all the major components except for SiO_2 were higher in the lower reaches (Stations B and C) of the Tama River than those in the upper reaches (Station A), as can be seen in Table 2. Especially, the high enrichments in Cl^- and TOC concentrations for Stations B and C indicate that the lower reaches of the river are greatly influenced by anthropogeneous pollution. This is proved too by the enrichments of the other com-

TABLE 3. FRACTIONATION RESULTS OF ALKALI ELEMENTS IN THE RIVER WATER

Element	Sampling station	Total content	Millipore filtration		Ultrafiltration of dissolved species		
			>0.45μm	<0.45μm	>MW 10^4	MW 10^4—500	<MW 500
Na (mg/l)	A	3.4	0(0)	3.4(100)	—	—	—
	B	23.3	0(0)	23.3(100)	0.5(2.1)	1.3(5.6)	21.5(92.3)
	C	37.1	0(0)	37.1(100)	1.0(2.7)	3.3(8.9)	32.8(88.4)
K (mg/l)	A	1.0	0(0)	1.0(100)	—	—	—
	B	4.0	0(0)	4.0(100)	0(0)	0.3(7.5)	3.7(92.5)
	C	6.3	0(0)	6.3(100)	0(0)	0.8(12.7)	5.5(87.3)
Rb (μg/l)	A	1.62	0.75(46.3)	0.87(53.7)	—	—	—
	B	2.19	0.12(5.5)	2.07(94.5)	0.12(5.8)	0.14(6.8)	1.81(87.4)
	C	4.29	0(0)	4.29(100)	0.09(2.1)	0.26(6.1)	3.94(91.8)
Cs (μg/l)	A	0.097	0.081(83.5)	0.016(16.5)	—	—	—
	B	0.033	0.017(51.5)	0.016(48.5)	0.002(12.5)	0(0)	0.014(87.5)
	C	0.053	0.008(15.1)	0.045(84.9)	0.003(6.7)	0.002(4.4)	0.040(88.9)

TABLE 4. FRACTIONATION RESULTS OF ALKALINE-EARTH ELEMENTS IN THE RIVER WATER

Element	Sampling station	Total content	Millipore filtration		Ultrafiltration of dissolved species		
			>0.45μm	<0.45μm	>MW 10^4	MW 10^4—500	<MW 500
Mg (mg/l)	A	1.0	0(0)	1.0(100)	—	—	—
	B	5.1	0(0)	5.1(100)	0.8(15.7)	1.1(21.6)	3.2(62.7)
	C	6.1	0(0)	6.1(100)	0.4(6.6)	1.4(22.9)	4.3(70.5)
Ca (mg/l)	A	14.9	0(0)	14.9(100)	—	—	—
	B	21.2	0(0)	21.2(100)	4.2(19.8)	3.6(17.0)	13.4(63.2)
	C	25.8	0(0)	25.8(100)	2.2(8.5)	7.2(27.9)	16.4(63.6)
Sr (μg/l)	A	58	0(0)	58(100)	—	—	—
	B	124	0(0)	124(100)	2(1.6)	35(28.2)	87(70.2)
	C	159	0(0)	159(100)	5(3.2)	53(33.3)	101(63.5)
Ba (μg/l)	A	8.1	3.8(46.9)	4.3(53.1)	—	—	—
	B	11.6	1.3(11.2)	10.3(88.8)	0.6(5.8)	2.4(23.3)	7.3(70.9)
	C	16.1	2.3(14.3)	13.8(85.7)	1.0(7.3)	3.8(27.5)	9.0(65.2)

ponents, such as Na, Mg, and heavy metals, which will be discussed later.

The major components were mostly fractionated as dissolved species (<0.45 μm), although 42, 14, and 10% of TOC for Stations A, B, and C respectively were associated with suspended materials (>0.45 μm). Most (81—99%) of the dissolved species for evaporated residue (ER), SiO_2, 4.3 Bx, and Cl^- was found in the smallest-molecular-weight fraction (<MW 500). Consequently, these four components are mainly present in the water as smaller dissolved species. The dissolved $SO_4{}^{2-}$, on the other hand, was chiefly divided between two smaller-molecular-weight fractions (MW 10^4—500 and <MW 500). This indicates that $SO_4{}^{2-}$ is present in the water not only as simple ions, but also as larger molecules. The dissolved TOC was mainly distributed in the middle-molecular-weight fraction (MW 10^4—500), although 23—32% of the TOC was also found in the largest-molecular-weight fraction (>MW 10^4). Organic materials occurring in natural water have a very heterogeneous composition. The bulk of these natural organics is made up of fulvic and humic acids which have molecular-weight ranges of roughly 10^2—10^4 and 10^4—10^6 respectively, although their structures are generally poorly known and the above values are not to be regarded as definitive in any way.[2] These fulvic and humic acids contribute greatly to the dissolution of trace elements.[9,13,18,19]

Alkali and Alkaline-earth Elements (Na, K, Rb, Cs, Mg, Ca, Sr, and Ba). The total concentrations of Na, K, and Mg in the lower reaches of the river were higher than those in the upper reaches by a factor of 4—12, as can be seen in Tables 3 and 4. No significant differences in the total concentrations for Rb, Ca, Sr, and Ba could be found among the three sampling stations, even though they were also given in the higher values to some extent (about 2 times) for the lower reaches. On the other hand, higher Cs concentration was observed in the upper reaches.

Almost all the Na, K, and Rb was fractionated as dissolved species (<0.45 μm), although 46% of the Rb at Station A was distributed in the suspended-size fraction (>0.45 μm). Cesium was mainly associated with suspended materials at Station A. At Station C, on the contrary, it was predominantly found in the dissolved-size fraction. The Cs at Station B was divided between two fractions. Most (87—92%) of the dissolved alkali-metal elements were distributed in the smallest-molecular-weight fraction (<MW 500). It is well known that alkali-metal elements are dissolved in natural water as univalent cations. The

TABLE 5. FRACTIONATION RESULTS OF TRANSITION ELEMENTS IN THE RIVER WATER

Element	Sampling station	Total content	Millipore filtration		Ultrafiltration of dissolved species		
			>0.45μm	<0.45μm	>MW 10^4	MW 10^4—500	<MW 500
Sc (μg/l)	A	0.095	0.092(96.8)	0.003(3.2)	—	—	—
	B	0.068	0.055(80.9)	0.013(19.1)	0.001(7.7)	0.011(84.6)	0.001(7.7)
	C	0.044	0.028(63.6)	0.016(36.4)	0.002(12.5)	0.012(75.0)	0.002(12.5)
V (μg/l)	A	1.22	0.55(45.1)	0.67(54.9)	—	—	—
	B	1.51	0.20(13.2)	1.31(86.8)	0.08(6.1)	0.16(12.2)	1.07(81.7)
	C	3.35	0.42(12.5)	2.93(87.5)	0.28(9.6)	0.42(14.3)	2.23(76.1)
Cr (μg/l)	A	0.370	0.240(64.9)	0.130(35.1)	—	—	—
	B	0.331	0.200(60.4)	0.131(39.6)	0.026(19.9)	0.056(42.7)	0.049(37.4)
	C	0.416	0.145(34.9)	0.271(65.1)	0.096(35.4)	0.101(37.3)	0.074(27.3)
Mn (μg/l)	A	9.6	8.5(88.5)	1.1(11.5)	—	—	—
	B	37.6	14.0(37.2)	23.6(62.8)	1.4(5.9)	8.0(33.9)	14.2(60.2)
	C	76.5	3.9(5.1)	72.6(94.9)	7.8(10.7)	15.1(20.8)	49.7(68.5)
Fe (μg/l)	A	349	344(98.6)	5(1.4)	—	—	—
	B	177	164(92.7)	13(7.3)	9(69.2)	3(23.1)	1(7.7)
	C	289	234(81.0)	55(19.0)	46(83.6)	6(10.9)	3(5.5)
Co (μg/l)	A	0.127	0.106(83.5)	0.021(16.5)	—	—	—
	B	0.236	0.068(28.8)	0.168(71.2)	0.006(3.6)	0.091(54.2)	0.071(42.2)
	C	0.433	0.029(6.7)	0.404(93.3)	0.033(8.2)	0.241(59.6)	0.130(32.2)
Ni (μg/l)	A	0.85	0(0)	0.85(100)	—	—	—
	B	3.39	0(0)	3.39(100)	0.17(5.0)	1.85(54.6)	1.37(40.4)
	C	7.19	0(0)	7.19(100)	0(0)	4.85(67.5)	2.34(32.5)
Zn (μg/l)	A	2.52	1.81(71.8)	0.71(28.2)	—	—	—
	B	6.88	3.00(43.6)	3.88(56.4)	0.24(6.2)	1.72(44.3)	1.92(49.5)
	C	10.2	1.61(15.8)	8.59(84.2)	2.11(24.6)	2.44(28.4)	4.04(47.0)

fractionation results are in fair agreement with this knowledge.

The Mg, Ca, and Sr were completely fractionated as dissolved species. For Ba, 47% in the upper reaches and 11—14% in the lower reaches were associated with suspended materials. Although the dissolved alkaline-earth elements were chiefly classified in the smallest-molecular-weight fraction, like the alkali-metal elements, considerable amounts (30—37%) of them were also found in two larger-molecular-weight fractions (>MW 10^4 and MW 10^4—500). This shows that a large portion (63—70%) of the alkaline-earth elements are dissolved in the river water as simple bivalent cations, while the remainder are present as complexes or colloids with a larger molecular weight.

Transition Elements (Sc, V, Cr, Mn, Fe, Co, Ni, and Zn). The total concentrations of Sc and Fe in the upper reaches (Station A) were higher than those in the lower reaches (Stations B and C). On the other hand, higher concentrations of V, Mn, Co, Ni, and Zn were observed for the lower reaches, as is shown in Table 5. This indicates that the Sc and Fe in the river water are mainly derived from rocks or their efflorescences in the drainage basin, while the other five heavy metals are chiefly supplied by anthropogeneous sources.[14]

The transition elements in the upper reaches were generally associated with the suspended-size fraction (>0.45 μm), except for Ni. In the lower reaches, however, they were mainly fractionated as dissolved species (<0.45 μm), although 64% of the Sc and 81% of the Fe were still recognized in the suspended-size fraction even at Station C. Exceptionally, Ni was found in the dissolved-size fraction from all the sampling stations. Large portions of the dissolved V and Mn (76—82% and 60—68% respectively) were distributed in the smallest-molecular-weight fraction (<MW 500). Therefore, V and Mn are mainly dissolved in the river water as inorganic ions, such as $VO_2(OH)_3^{2-}$, Mn^{2+} or their simple compounds.[20] A considerable part (21—34%) of the Mn was also found in the middle-molecular-weight fraction (MW 10^4—500), so that the possibility of the occurrence of a Mn-organic complex cannot be neglected. Although the majority of the Sc and Fe was associated with suspended materials, as has been stated above, the remaining, dissolved portions of these elements were mostly distributed in the middle- and the largest-molecular-weight fractions respectively. Only 5—12% of these could be detected in the smallest-molecular-weight fraction. This shows that the chief dissolved species of Sc is a larger complex such as polyhydroxide, while Fe is present in the colloidal state.[21] The dissolved Co, Ni, and Zn were mainly divided into two smaller-molecular-weight fractions (MW 10^4—500 and <MW 500), though a considerable part (25%) of the Zn from Station C was found in the largest-molecular-weight fraction (>MW 10^4). Therefore, these three elements may be expected to be present in the river water not only as bivalent cations (M^{2+}), but also as complexes with naturally occurring organic ligands. On the other hand, Cr was divided into three molecular-weight fractions. Consequently, the dissolved Cr in the river water is composed of a sexivalent ion (CrO_4^{2-}), an inorganic

TABLE 6. FRACTIONATION RESULTS OF RARE-EARTH ELEMENTS IN THE RIVER WATER

Element	Sampling station	Total content	Millipore filtration		Ultrafiltration of dissolved species		
			$>0.45\mu m$	$<0.45\mu m$	$>$MW 10^4	MW 10^4—500	$<$MW 500
La (ng/l)	A	193	179(92.7)	14(7.3)	—	—	—
	B	140	128(91.4)	12(8.6)	4(33.3)	6(50.0)	2(16.7)
	C	97	70(72.2)	27(27.8)	21(77.8)	4(14.8)	2(7.4)
Ce (ng/l)	A	575	541(94.1)	34(5.9)	—	—	—
	B	174	150(86.2)	24(13.8)	2(8.3)	13(54.2)	9(37.5)
	C	122	83(68.0)	39(32.0)	20(51.3)	11(28.2)	8(20.5)
Sm (ng/l)	A	36.2	33.9(93.6)	2.3(6.4)	—	—	—
	B	21.7	19.8(91.2)	1.9(8.8)	0.6(31.6)	1.0(52.6)	0.3(15.8)
	C	16.0	12.0(75.0)	4.0(25.0)	1.2(30.0)	2.2(55.0)	0.6(15.0)
Eu (ng/l)	A	9.55	9.15(95.8)	0.40(4.2)	—	—	—
	B	5.71	5.09(89.1)	0.62(10.9)	0.25(40.3)	0.28(45.2)	0.09(14.5)
	C	3.50	2.79(79.7)	0.71(20.3)	0.45(63.4)	0.21(29.6)	0.05(7.0)
Tb (ng/l)	A	ND	—	—	—	—	—
	B	1.86	1.41(75.8)	0.45(24.2)	0.04(8.9)	0.33(73.3)	0.08(17.8)
	C	7.16	2.00(27.9)	5.16(72.1)	1.50(29.1)	3.38(65.5)	0.28(5.4)
Ho (ng/l)	A	ND	—	—	—	—	—
	B	—	—	—	—	—	—
	C	9.40	1.89(20.1)	7.51(79.9)	1.51(20.1)	5.42(72.2)	0.58(7.7)
Tm (ng/l)	A	ND	—	—	—	—	—
	B	7.57	3.07(40.6)	4.50(59.4)	—	—	—
	C	30.2	4.9(16.2)	25.3(83.8)	2.8(11.1)	19.8(78.3)	2.7(10.6)
Yb (ng/l)	A	ND	—	—	—	—	—
	B	34.5	8.2(23.8)	26.3(76.2)	4.6(17.5)	19.0(72.2)	2.7(10.3)
	C	68.9	6.5(9.4)	62.4(90.6)	7.7(12.3)	50.3(80.6)	4.4(7.1)
Lu (ng/l)	A	ND	—	—	—	—	—
	B	7.05	0.83(11.8)	6.22(88.2)	0.68(10.9)	5.11(82.2)	0.43(6.9)
	C	27.5	2.8(10.2)	24.7(89.8)	3.0(12.1)	20.2(81.8)	1.5(6.1)

or organic complex, and inorganic Cr(III), which is quantitative co-precipitated on colloidal iron(III) hydroxide.[22]

Rare-earth Elements (REEs; La, Ce, Sm, Eu, Tb, Ho, Tm, Yb, and Lu). The total concentrations of such light REEs as La, Ce, Sm, and Eu in the upper reaches (Station A) were higher than those in the lower reaches (Stations B and C). For such heavier REEs as Tb, Ho, Tm, Yb, and Lu, on the contrary, higher concentrations were observed in the lower reaches, as is shown in Table 6.

The light REEs were mostly found in the suspended-size fraction ($>0.45\ \mu m$), even though a considerable part (20—32%) of these elements at Station C was fractionated as dissolved species ($<0.45\ \mu m$). On the other hand, heavier REEs in the lower reaches were mainly distributed in the dissolved-size fraction, although, at Station B, 76% of the Tb and 41% of the Tm were still associated with suspended materials. In the upper reaches, these elements could not be detected. The dissolved light REEs were mainly divided between two larger-molecular-weight fractions ($>$MW 10^4 and MW 10^4—500). On the other hand, the heavier REEs were chiefly (65—82%) distributed in the middle-molecular-weight fraction (MW 10^4—500). These findings suggest that the REEs in the river water are primarily derived from rocks or their efflorescences, and then that heavier REEs are dissolved by forming complexes in the lower reaches of the river, where the water has an abundance of complexing ligands, such as natural organics and anions. In the upper reaches, with a poor TOC concentration, they cannot be detected. Light REEs tend to co-precipitate with iron(III) hydroxide,[14] so that they are still associated with suspended materials or colloids.

Others (As, Se, Sb, W, Al, Ag, and U). The total concentrations of Al and U in the upper reaches were considerably higher than those in the lower reaches, as is shown in Table 8. This indicates that these elements are derived from rocks in the drainage basin in a manner similar to Fe, Sc, Cs, and light REEs. On the contrary, a higher Ag concentration was observed in the lower reaches, where the river water was greatly polluted by artificial sources. In the upper reaches, Ag was not detected. There were no large differences in the total concentrations of As, Se, Sb, and W among the three sampling stations, as can be seen in Table 7.

Almost all the As, Se, Sb, and W was distributed in the dissolved-size fraction ($<0.45\ \mu m$). The dissolved species of these elements were mainly divided into two smaller-molecular-weight fractions (MW 10^4—500 and $<$MW 500), although As, Se, and W were predominantly found in the middle-molecular-weight fraction, while Sb was more concentrated in the smallest-molecular-weight fraction. It is well known that these four elements tend to form oxoanions, such as $HAsO_4^{2-}$, SeO_3^{2-}, $Sb(OH)_6^-$, and WO_4^{2-}, in natural water, as do V or Cr. However, the fractionation

TABLE 7. FRACTIONATION RESULTS OF ARSENIC, SELENIUM, ANTIMONY, AND TUNGSTEN IN THE RIVER WATER

Element	Sampling station	Total content	Millipore filtration		Ultrafiltration of dissolved species		
			>0.45µm	<0.45µm	>MW 10^4	MW 10^4—500	<MW 500
As (µg/l)	A	0.610	0(0)	0.610(100)	—	—	—
	B	0.754	0.035(4.6)	0.719(95.4)	0.036(5.0)	0.426(59.3)	0.257(35.7)
	C	0.535	0(0)	0.535(100)	0.088(16.4)	0.256(47.9)	0.191(35.7)
Se (µg/l)	A	0.086	0(0)	0.086(100)	—	—	—
	B	0.091	0.005(5.5)	0.086(94.5)	0.008(9.3)	0.063(73.3)	0.015(17.4)
	C	0.128	0.016(12.5)	0.112(87.5)	0.023(20.5)	0.061(54.5)	0.028(25.0)
Sb (µg/l)	A	0.176	0(0)	0.176(100)	—	—	—
	B	0.264	0(0)	0.264(100)	0.021(8.0)	0.059(22.3)	0.184(69.7)
	C	0.258	0(0)	0.258(100)	0.019(7.4)	0.089(34.5)	0.150(58.1)
W (µg/l)	A	0.072	0(0)	0.072(100)	—	—	—
	B	0.098	0(0)	0.098(100)	0.006(6.1)	0.058(59.2)	0.034(34.7)
	C	0.067	0(0)	0.067(100)	0.008(11.9)	0.042(62.7)	0.017(25.4)

TABLE 8. FRACTIONATION RESULTS OF ALUMINIUM, SILVER, AND URANIUM IN THE RIVER WATER

Element	Sampling station	Total content	Millipore filtration		Ultrafiltration of dissolved species		
			>0.45µm	<0.45µm	>MW 10^4	MW 10^4—500	<MW 500
Al (µg/l)	A	603	524(86.9)	79(13.1)	—	—	—
	B	263	196(74.5)	67(25.5)	0(0)	1(1.5)	66(98.5)
	C	229	127(55.5)	102(44.5)	9(8.8)	1(1.0)	92(90.2)
Ag (µg/l)	A	ND	—	—	—	—	—
	B	0.069	0.053(76.8)	0.016(23.2)	0.012(75.0)	0.002(12.5)	0.002(12.5)
	C	0.126	0.069(54.8)	0.057(45.2)	0.049(85.9)	0.003(5.3)	0.005(8.8)
U (µg/l)	A	0.058	0.012(20.7)	0.046(79.3)	—	—	—
	B	0.022	0.005(22.7)	0.017(77.3)	0.004(23.5)	0.011(64.7)	0.002(11.8)
	C	0.025	0.003(12.0)	0.022(88.0)	0.005(22.7)	0.014(63.7)	0.003(13.6)

results show that As, Se, and W are present in the river water as such larger dissolved compounds as organic complexes,23) in preference to those simple oxoanions.

Aluminium was, in the upper reaches, mainly distributed in the suspended-size fraction, while in the lower reaches it was fractionated as dissolved species to a considerable extent (25—44%). For Ag, 77% in Station B and 55% in Station C were associated with suspended materials. Most (77—88%) of the U was found in the dissolved-size fraction at all the sampling stations. The dissolved Al, Ag, and U were predominantly found in the smallest-, the largest-, and the middle-molecular-weight fractions respectively. This indicates that the dissolved Al exists as simple inorganic ions, and that the Ag is chiefly associated with colloidal materials, while the U can be expected to be present in the form of an uranil complex.

Conclusions

Using the UF technique and the NAA method, it was possible to obtain some knowledge about the dissolved species of trace elements existing in Tama River water. Alkali and alkaline-earth elements, Al, V, Mn, and Sb, dissolved in the river water were predominantly present as simple ions or their small molecule compounds, although a considerable part (20—30%) of the alkaline-earth elements, Mn, and Sb were also dissolved as complexes with larger-molecular-weight sizes. The dissolved Co, Ni, Zn, and As were mainly divided into the smallest- and middle-molecular-weight fractions, so that their chief dissolved species were probably both simple ions and complexes. The dissolved Sc, heavier REEs, Se, W, and U were mainly present by forming complexes. On the other hand, Fe, Ag, and some light REEs dissolved in the river water were primarily associated with colloidal materials.

Several tedious problems, however, still remain to be examined concerning the UF technique, much as with the MF technique.14) For example, the pore diameter of the filter may show considerable variation, so that a precise separation of trace elements is difficult. Furthermore, a clogging of the filter pores, contamination from the filtering apparatus and the filter themselves, and losses due to adsorption on the filter are more insidious problems in the UF experiment. Further consideration in greater detail will be necessary to minimize analytical errors.

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