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Physicochemical Speciation of Trace Elements in River Water by Size Fractionation

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Eight kinds of Millipore filters with different pore sizes (8—0.025 μm) were used for the filtration of two water samples taken from the Tama River. The filtrates were analyzed for 31 elements using a neutron activation analysis. Most alkali and alkaline earth elements were distributed in the smallest size fraction (<0.025 μm). The same fractionation pattern was also recognized for As, Se, Mo, Sb, and W, which tend to form oxoanions. But the major transition elements were concentrated in the larger size fractions (>0.45 μm). For the river water sample with higher concentration of total organic carbon, however, most of such elements were found in the smallest size fraction. The solubilities of rare earth elements bacame higher with increasing their ionic potentials.

The analysis of chemical species for various elements in natural water is of great importance not only to substantiate their geochemical behavior such as dissolution, fluidity, adsorption, and precipitation, but also to estimate the toxicity of the elements towards aquatic organisms.[1,2] For trace elements, however, it is very difficult to determine directly their chemical species because of their low concentrations and the complexity of their physical or chemical forms in natural water. Consequently, a physicochemical fractionation technique has been developed for an indirect speciation of the trace elements. Stumm and Bilinski first proposed that trace metal species could usefully be classified according to their size distribution.[3] Subsequently, a few workers studied the effect of filter pore size exerted on the analytical concentrations of some trace elements in filtrates of natural water.[4,5] Laxen and Harrison applied the fractionation technique to speciation of several trace elements in lake water,[6] and to effluents from sewage treatment plants and industrial processes and the river water which receives these effluents.[7,8] This fractionation technique was summarized together with other physicochemical speciation techniques such as centrifugation, ultrafiltration, dialysis and gel filtration chromatography, by Mora and Harrison.[9] But no one has applied the size fractionation technique to a systematic analysis of multielements. In this paper, therefore, we tried to clarify the size distribution of 31 elements found in river water, and to discuss their chemical species, by utilizing this technique and neutron activation analysis (NAA).

Experimental

Water Samples. The river water samples were taken from two points of the Tama River, which runs through the Metropolis of Tokyo, in November 1982 and February 1983. The two sampling points are shown in Fig. 1. They are located up-stream of the Hamura intake dam (A point) and near the Tamagawara bridge (B point). The water qualities are listed in Table 1 for the two points. The river water of B point (sample B) is more enriched in chlorine and total organic carbon (TOC) than those of the river water of A point (sample A) by a factor of 10 or above. This indicates that sample B is largely influenced by anthropogeneous pollutions. Chemical constituents in sample A, on the other hand, are mainly derived from rocks and their efflorescences in the drainage basin or by rainfall, as reported in a previous paper.[10]

Filtration. All-glass Millipore apparatus and eight kinds of Type HA millipore filters (mixed esters of cellulose) with diameter 142 mm, of average pore sizes 8, 3, 1.2, 0.45, 0.22, 0.1, 0.05, and 0.025 μm, were used for all filtrations. Decontamination of each filter was achieved by passing through 30 ml of dilute nitric acid (1:3), followed by 2-l of redistilled water under reduced pressure. The filtration of each water sample was performed in the following way. Forty liters of the water sample was pre-filtrated using the filter with pore size 8 μm, in order to remove large size particles. The filtrate was divided into eight 5-l portions. The seven portions of filtrate were filtrated once again using the other seven kinds of filters, one by one. The eight filtrates were transferred to clean 5-l polyethylene bottles, and then acidified immediately with 30 ml of nitric acid (Super Special Grade) in order to avoid any adsorption of trace elements on

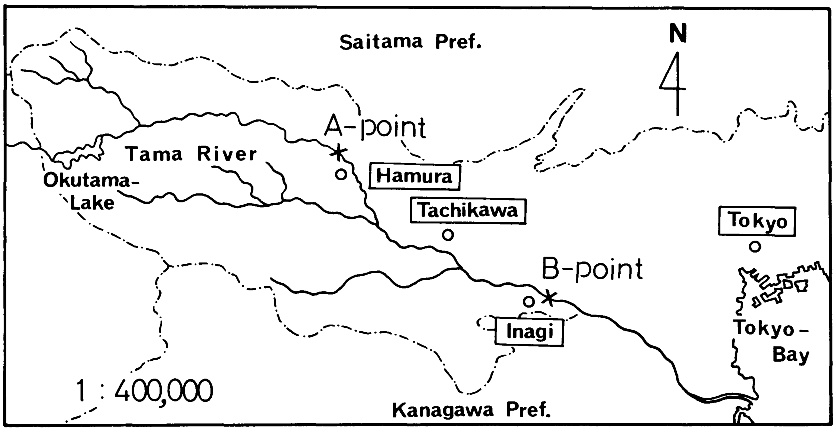

Fig. 1. Sampling locality.

TABLE 1. WATER QUALITY OF THE TAMA RIVER AT THE TIME OF SAMPLING

Parameter	River water sample	
	A	B
Sampling point	Hamura	Inagi
Date	1/11/82	16/2/83
Water temp/°C	14.7	9.8
pH	8.2	6.9
Conductivity/$\mu S\ cm^{-1}$	80	310
4.3 Bx/mequiv l^{-1}	0.71	1.77
ER[a)]/ppm	101	402
TOC[b)]/ppm	0.5	6.9
SO_4^{2-}/ppm	13	49
SiO_2/ppm	18	31
Cl^-/ppm	1.6	51.5

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

the wall of the bottle.

Five-liter of the water sample was taken as the original material in another polyethylene bottle without filtration and was then acidified with 30 ml of the nitric scid.

Preparation of Irradiation Samples. For the NAA in this work, two kinds of irradiation samples, an evaporated residue sample and iron(III) hydroxide coprecipitated one, were prepared from each filtrate and the original (unfiltrated) water sample. The procedures were reported in detail in our previous papers.[10–12)]

Irradiation and Gamma-ray Counting. The irradiation was performed by the TRIGA-Mark II Reactor of Rikkyo University, with a thermal neutron flux of 1.5×10^{12} n/cm^{2}s. The gamma ray spectrometer consists of a high pure germanium detector with 15% efficiency and 2.0 keV resolution, and a 2048 and 4096 channel pulse height analyzer.

The evaporated residue sample was first irradiated for 1 min to determine the elements that result the short life nuclides such as Al (^{28}Al), Ca (^{49}Ca), K (^{42}K), Mg (^{27}Mg), Mn (^{56}Mn), Na (^{24}Na), and V (^{52}V); these radioactivities were measured for 100 s by the spectrometer. One month later, the same sample was irradiated once more for 12 h to determine the elements that result the long life nuclides such as Ag (^{110m}Ag), Ba (^{131}Ba), Ce (^{141}Ce), Co (^{60}Co), Cr (^{51}Cr), Cs (^{134}Cs), Fe (^{59}Fe), Ni (^{58}Co), Rb (^{86}Rb), Sb (^{124}Sb), Sc (^{46}Sc), Se (^{75}Se), Sr (^{85}Sr), Tb (^{160}Tb), and Th (^{233}Pa). The measurement of these long life activities were carried out for 50000 s after a cooling time of 2—4 weeks to reduce the short or medium life nuclides.

The iron(III) hydroxide coprecipitated sample, on the other hand, was also irradiated for 12 h to determine the elements that result the medium life nuclides such as As (^{76}As), Eu (^{152m}Eu), La (^{140}La), Lu (^{177}Lu), Mo (^{99}Mo), Sm (^{153}Sm), U (^{239}Np), W (^{187}W), and Yb (^{175}Yb), and after the cooling time of 1 d, these activities were measured for 2000 s.

Results and Discussion

The concentrations of 31 elements were determined for the eight filtrates and the original water sample by NAA. The statistical errors based on the gamma ray counting were 5—30% for Ag, Ba, Ce, Cr, Eu, Fe, La, Mg, Mn, Mo, Ni, Se, Tb, Th, and U, and less than 5% for the other 16 elements.

The, size distribution of each element is calculated in the following way. When the analytical concentration of an element in the original water sample and the filtrates resulted from the filters with pore size of 8, 3,⋯, 0.05, and 0.025 μm are represented by C_T and C_8, C_3, ⋯, $C_{0.05}$, and $C_{0.025}$, the size distribution (S) of the elements is given by

$$
\begin{array}{lll}
S(>8\,\mu m) & = C_T - C_8 & F(>8\,\mu m) \\
S(8-3\,\mu m) & = C_8 - C_3 & \\
S(3-1.2\,\mu m) & = C_3 - C_{1.2} & F(8-0.45\,\mu m) \\
S(1.2-0.45\,\mu m) & = C_{1.2} - C_{0.45} & \\
S(0.45-0.22\,\mu m) & = C_{0.45} - C_{0.22} & \\
S(0.22-0.1\,\mu m) & = C_{0.22} - C_{0.1} & F(0.45-0.025\,\mu m) \\
S(0.1-0.05\,\mu m) & = C_{0.1} - C_{0.05} & \\
S(0.05-0.025\,\mu m) & = C_{0.05} - C_{0.025} & \\
S(<0.025\,\mu m) & = C_{0.025} & F(<0.025\,\mu m)
\end{array}
$$

The results are classified into four size fractions: F (>8 μm), F (8—0.45 μm), F (0.45—0.025 μm), and F (<0.025 μm); these results are shown in Tables 2—6.

In general, chemical constituents passing through the filter with pore size 0.45 μm are defined as "dissolved", and those retained on the filter are classified as "particulate".[13)] However, the "dissolved" constituents need not be in true solution but can include "colloidals".[3,9)] The boundary in size between "colloidals" and "true solution" probably lies in the range of 0.01—0.001 μm.[9,14)] Consequently, it is difficult to fractionate perfectly chemical constituents in the river water samples between "colloidals" and "true solution" because the smallest pore size of the Millipore filter is 0.025 μm. For convenience, it is assumed in this paper that the constituents passing through the 0.025 μm filter (F (<0.025 μm)) are mostly "true solution", and the materials with size ranging from 0.45 μm to 0.025 μm (F (0.45—0.025 μm)) are "colloidals". The materials with size larger than 0.45 μm (F (>8 μm) and F (8—0.45 μm)) are classified as "particulate".

In order to discuss systematically the fractionation results, the 31 elements are divided into 5 groups in the following manner, as shown in Tables 2—6.

Alkali and Alkaline Earth Elements (Na, K, Rb, Cs, Mg, Ca, Sr, and Ba). The total concentrations are given in the concentrations for the original (unfiltrated) water sample. For alkali and alkaline earth elements in sample A, these concentrations were considerably lower than those in sample B, although the concentration of Cs in sample A was exceptionally high, as can be seen in Table 2. The very high enrichments in Na, K and Mg concentrations for sample B indicate that the B point of the Tama River is largely influenced by anthropogeneous pollutions.

Na, K, Mg, Ca, and Sr were found only in the smallest size fraction (< 0.025 μm) for both samples A and B. It is well known that these elements are dissolved in natural water as uni- or bivalent cations. Rb and Cs in sample A were divided mainly between the particulate (>8 μm and 8—0.45μm) and the smallest size fractions, with few colloidals (0.45—0.025 μm), although in sample B all those elements were also found in the smallest size fraction. 47% of Ba were associated with the particulate, and the remaining 53% were distributed in the smallest size fraction for sample A. For sample B, on the other hand, 15 and 85% of Ba were found in the particulate and the smallest size fractions, respectively. It is supposed that considerable parts of Rb, Cs, and Ba

Table 2. Fractionation results of alkali and alkaline earth elements in the river water

Element	Sampling point	Size fraction(μm)				Sum total
		>8	8—0.45	0.45—0.025	<0.025	
Na	A	0(0)[a]	0(0)	0(0)	3.39(100)	3.39 ppm
	B	0(0)	0(0)	0(0)	45.3(100)	45.3 ppm
K	A	0(0)	0(0)	0(0)	0.98(100)	0.98 ppm
	B	0(0)	0(0)	0(0)	5.9(100)	5.9 ppm
Rb	A	0.63(38.9)	0.12(7.3)	0.14(8.6)	0.73(45.1)	1.62 ppb
	B	0(0)	0(0)	0(0)	5.0(100)	5.0 ppb
Cs	A	0.071(73.2)	0.010(10.3)	0.004(4.1)	0.012(12.4)	0.097 ppb
	B	0(0)	0(0)	0(0)	0.083(100)	0.083 ppb
Mg	A	0(0)	0(0)	0(0)	1.04(100)	1.04 ppm
	B	0(0)	0(0)	0(0)	6.99(100)	6.99 ppm
Ca	A	0(0)	0(0)	0(0)	14.9(100)	14.9 ppm
	B	0(0)	0(0)	0(0)	29.0(100)	29.0 ppm
Sr	A	0(0)	0(0)	0(0)	58.2(100)	58.2 ppb
	B	0(0)	0(0)	0(0)	169(100)	169 ppb
Ba	A	2.7(33.3)	1.1(13.6)	0(0)	4.3(53.1)	8.1 ppb
	B	0.9(7.1)	1.0(7.9)	0(0)	10.8(85.0)	12.7 ppb

a) The parenthesized values are percentages of each fraction.

Table 3. Fractionation results of transition elements in the river water

Element	Sampling point	Size fraction(μm)				Sum total (ppb)
		>8	8—0.45	0.45—0.025	<0.025	
Sc	A	0.0855(90.5)	0.0064(6.7)	0.0011(1.2)	0.0015(1.6)	0.0945
	B	0.0414(75.4)	0.0016(2.9)	0.0010(1.8)	0.0109(19.9)	0.0549
V	A	0.46(37.7)	0.09(7.4)	0(0)	0.67(54.9)	1.22
	B	0.76(27.9)	0(0)	0(0)	1.96(72.1)	2.72
Cr	A	0.21(56.8)	0.03(8.1)	0(0)	0.13(35.1)	0.37
	B	0.28(29.0)	0.18(18.6)	0.05(5.1)	0.46(47.4)	0.97
Mn	A	8.5(88.5)	0(0)	0(0)	1.1(11.5)	9.6
	B	6.5(9.4)	2.4(3.5)	0(0)	60.3(87.1)	69.2
Fe	A	308(88.5)	35.8(10.3)	1.4(0.4)	3.0(0.9)	349
	B	151(72.2)	18.3(8.8)	24.8(11.9)	14.9(7.1)	209
Co	A	0.087(68.5)	0.019(15.0)	0(0)	0.021(16.4)	0.127
	B	0.047(12.6)	0(0)	0.012(3.2)	0.313(84.1)	0.372
Ni	A	0(0)	0(0)	0(0)	0.85(100)	0.85
	B	0.1(1.3)	0(0)	0.5(6.3)	7.3(92.4)	7.9

in sample A are held on ion exchange sites of inorganic suspended materials[15] such as clay minerals or iron(III) hydroxide, which will be explained in later discussion, by the fact that the contents of particulate Al and Fe for sample A are high.

Transition Elements (Sc, V, Cr, Mn, Fe, Co, and Ni). Sample A was more enriched in the total concentrations of Sc and Fe, and deficient in V, Cr, Mn, Co, and Ni in comparison with the concentrations in sample B, as can be seen in Table 3. This indicates that Sc and Fe in the Tama River water are mainly derived from rocks or their efflorescences, while the other five heavy metals are chiefly supplied by anthropogeneous sources.

The major parts (80% or more) of Sc, Mn, Fe, and Co in sample A were distributed in the particulate size fraction. In particular, Sc and Fe were mostly particulate (>97%), and only a few percent of those elements could be fractionated as dissolved species (<0.45 μm). It is known that Fe is the main component of suspended materials in most river water along with Al and SiO_2,[16,17] and it usually forms iron(III) hydroxide.[4,18] The concentration of Sc is very low for ordinary natural water.[10,12] It is supposed that the behavior of Sc in river water with poor TOC concentration is governed by coprecipitation with iron(III) hydroxide. For sample B, on the other hand, although approx. 80% of Sc and Fe were also associated in the particulate size fraction, the remaining 20% were fractionated as the dissolved species. For Mn and Co, 80—90% of them in sample A were found in the particulate size fraction. On the contrary, 80—90% of these elements in sample B were distributed in the smallest size fraction. In general, transition elements are known to have a strong complexing ability for organic substances such as humus.[19–21] Sample B has a

Table 4. Fractionation results of arsenic, selenium, molybdenum, antimony, and tungsten in the river water

Element	Sampling point	Size fraction(μm)				Sum total (ppb)
		>8	8-0.45	0.45-0.025	<0.025	
As	A	0(0)	0(0)	0(0)	0.61(100)	0.61
	B	0(0)	0(0)	0(0)	0.79(100)	0.79
Se	A	0(0)	0(0)	0(0)	0.086(100)	0.086
	B	0(0)	0(0)	0(0)	0.13(100)	0.13
Mo	A	0(0)	0(0)	0(0)	0.24(100)	0.24
	B	0(0)	0(0)	0(0)	0.48(100)	0.48
Sb	A	0(0)	0(0)	0(0)	0.176(100)	0.176
	B	0(0)	0(0)	0(0)	0.376(100)	0.376
W	A	0(0)	0(0)	0(0)	0.072(100)	0.072
	B	0(0)	0(0)	0(0)	0.123(100)	0.123

Table 5. Fractionation results of rare earth elements in the river water

Element	Sampling point	Size fraction(μm)				Sum total (ppt)
		>8	8—0.45	0.45—0.025	<0.025	
La	A	163(84.6)	16(8.3)	1.8(0.9)	11.9(6.2)	193
	B	245(88.1)	13(4.6)	8(3.0)	12(4.4)	278
Ce	A	493(85.7)	48(8.3)	5(0.9)	29(5.0)	575
	B	347(79.7)	51(11.6)	8(1.8)	29(6.8)	435
Sm	A	30.5(84.1)	3.4(9.4)	1.3(3.6)	1.0(2.9)	36.2
	B	15.6(77.8)	1.7(8.6)	1.4(6.9)	1.3(6.7)	20.0
Eu	A	7.97(83.5)	1.18(12.4)	0(0)	0.40(4.1)	9.55
	B	5.04(69.1)	0.52(7.1)	0.73(10.0)	1.00(13.7)	7.29
Tb	A	—	—	—	—	ND
	B	1.81(58.0)	0.26(8.3)	0.26(8.3)	0.76(24.4)	3.12
Yb	A	>9.0(85.7)		<1.3(12.5)	< 0.2(1.8)	10.5
	B	6.5(15.2)	2.2(5.1)	5.7(13.3)	28.5(66.4)	42.9
Lu	A	—	—	—	—	ND
	B	1.54(18.8)	0(0)	1.74(21.3)	4.89(59.9)	8.17

much higher TOC concentration than that of sample A, by a factor of about 14, as listed in Table 1. In sample B, therefore, the transition elements should be mostly present as soluble organic complexes, so that they are distributed in the smallest size fraction. However, it is very difficult to draw any quantitative conclusion about the extent of complexing of the transition elements by organic substances because we have no information on their chemical forms. This remains to be studied.

Even in sample A with poor TOC concentration, V and Cr were found in the smallest size fraction in substantial quantity (55 and 35%, respectively). This can be explained by assuming the existences of their soluble quinque- or sexivalent species such as $V_{10}O_{28}^{6-}$,[22,23] CrO_4^{2-}.[24]

Almost all Ni, which is distinct from the other six transition elements, was found in the smallest size fraction for both samples A and B. This indicates that Ni easily dissolves in natural water as a bivalent species, Ni^{2+}.[25]

The Elements Forming Oxoanions (As, Se, Mo, Sb, and W). The total concentrations of As, Se, Mo, Sb, and W in sample B were higher than those in sample A by a factor of about 2. However, the same fractionation result was observed for all of them, that they were detectable only in the smallest size fraction (<0.025 μm), as can be seen in Table 4. This result is consistent with the view that these elements tend to form soluble oxoanions such as AsO_4^{3-}, SeO_3^{2-}, MoO_4^{2-}, SbO_4^{3-}, WO_4^{2-}[12,26—31] in ordinary natural water.

Rare Earth Elements (REEs: La, Ce, Sm, Eu, Tb, Yb, and Lu). Major parts (86—94%) of La, Ce, and Sm were associated with the particulate size fraction (>8 μm and 8—0.45 μm) for both samples A and B, and those elements distributed in the colloidal (0.45—0.025 μm) and the smallest size fractions (<0.025 μm) were only several percent, as can be seen in Table 5. Europium in sample A was also found mainly in the particulate size fraction, whereas in sample B 10 and 14% of Eu were distributed in the colloidal and the smallest size fractions,respectively. Although Yb in sample A was also mostly the particulate, 33% of Tb and approx. 80% of Yb and Lu in sample B were fractionated as the dissolved species (0.45—0.025 μm and <0.025 μm). These findings suggest that the higher TOC concentration in sample B is largely contributed to the dissolution of the heavier REEs such as Tb, Yb, Lu. This conclusion is substantiated by the analytical data that the total concentrations of the heavier REEs for sample B are higher than those for sample A, even though for the light REEs, except La,

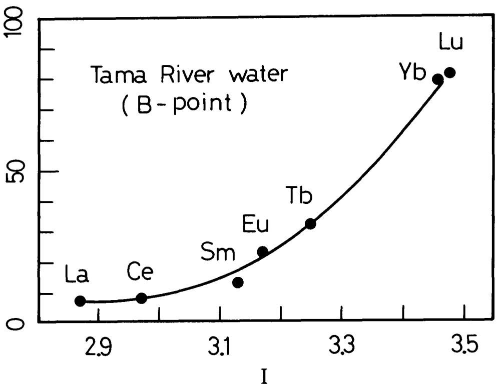

Fig. 2. Plot showing the relation between the solubilities (%) of REEs and their ionic potentials (*I*).

the higher total concentrations were found in sample A, as shown in Table 5.

The relation between the solubilities of the REEs in sample B and their ionic potentials is demonstrated by Fig.2, which is a plot of the proportions(%) of REEs fractionated as the dissolved species to their total concentrations *versus* ratios of the chemical valency to their ionic radii.[32] The diagram shows that the solubilities of the REEs increase with increasing ionic potentials. In other words, the heavier REEs with high ionic potentials tend to form the organic complexes in the river water with high TOC concentration. The monotonous increasing fashion of the solubilities for the heavier REEs illustrated in the diagram agrees with that reported by Goldberg *et al.*,[33] who have studied the behavior of REEs in marine environment.

For the light REEs, on the other hand, it is supposed that most of those elements may be coprecipitated with iron(III) hydroxide. This is explained by the following considerations. The total concentration ratios of La, Ce, and Sm to Fe in samples A and B are (0.55—1.3)$\times10^{-3}$, (1.7—2.1)$\times10^{-3}$, and (0.96—1.0)$\times10^{-4}$, and those in particulate matters in the Thames River water reported by Habib *et al.*[17] are 0.46$\times10^{-3}$,1.9$\times10^{-3}$, and 0.86$\times10^{-4}$, respectively. These values are close to the same ratios for the earth's crust presented by Taylor[34] and Wedepohl[35] (0.53—1.2)$\times10^{-3}$, (1.2—2.1)$\times10^{-3}$, and (1.1—1.9)$\times10^{-4}$. Therefore, it could be said that the behavior of light REEs in the river water is similer to that of Fe, on the process of dissolution or precipitation. Iron tends to form insoluble iron(III) hydroxide in ordinary natural water, as mentioned above, so that the light REEs also precipitate as the hydroxides.

Others (Al, Ag, Th, and U). Sample A was more enriched in the total concentrations of Al and U by a factor of about 2 in the comparison with those in sample B, as can be seen in Table 6. Silver in sample A and Th in sample B were less than the detection limits. Thorium in sample A could not be determined since no standard reference sample was prepared, so that the gamma ray counting ratio was utilized for the discussion. The higher total concentrations of Al, Th, and U in sample A indicate that those elements are mainly derived from the rocks or their efflorescences in the drainage basin, while the higher total concentration of Ag in sample B means that Ag is largely influenced by artificial pollution.

Table 6 notes that 87% of Al in sample A was associated with the particulate, and 11% was found in the smallest size fraction. For sample B, on the other hand, Al amounts distributed in the particulate and the smallest size fractions were 65 and 34%, respectively. The colloidal Al was only a few percent for both samples. Aluminium is one of the main components of suspended materials in most river water as well as Fe and SiO_2, as stated above. However, the proportion of Al fractionated as the dissolved species (0.45—0.025 μm and<0.025 μm) to the total concentration are 13 and 35% for samples A and B, and these values are much higher than those of Fe, 1.3 and 19% respectively. This can be explained in the following way. It is well known that Al in natural water not only precipitates as the hydroxide, but also forms clay minerals in the process of the rock weathering.[36] In general, clay minerals have a small size distribution (<5 μm), and a certain type of them has been found with size smaller than 0.45 μm.[37] Such materials pass through the filter with the corresponding pore size. In addition, Hem and Roberson showed that some finegrained Al compounds suspended in water may be passed through a 0.45 μm membrane filter.[38] Thus, a considerable part of Al can be fractionated as the dissolved species.

Eighty five percent of Ag was found in the particulate size fraction with 14% of the colloidal for sample B. Silver seems to be easily halogenated in the polluted river water, and is predominantly held on clay minerals or iron(III) hydroxide.

Thorium in sample A was also chiefly associated with the particulate size fraction; on the contrary, almost all U was distributed in the smallest size fraction, although approx. 20% of the particulate U was

TABLE 6. FRACTIONATION RESULTS OF ALUMINIUM, SILVER, THORIUM, AND URANIUM IN THE RIVER WATER

Element	Sampling point	Size fraction(μm)				Sum total (ppb)
		>8	8—0.45	0.45—0.025	<0.025	
Al	A	487(80.8)	37(6.1)	13(2.2)	66(10.9)	603
	B	191(58.6)	20(6.1)	5(1.5)	110(33.7)	326
Ag	A	—	—	—	—	ND
	B	1.14(74.3)	0.17(11.0)	0.21(13.7)	0.015(1.0)	1.53
Th	A	—(89.2)	—(7.6)	—(1.3)	—(1.9)	—
	B	—	—	—	—	ND
U	A	0.012(20.7)	0(0)	0.005(8.6)	0.041(70.7)	0.058
	B	0(0)	0(0)	0(0)	0.027(100)	0.027

found for sample A. The difference of the fractionation patterns between Th and U seems to arise from the differences of their chemical forms in the river water. It is well known that U tends to form the soluble sexivalent species UO_2^{2+} in most natural water.[39–41] But for Th, a quadrivalent species is the only stable form, which is probably coprecipitated with the hydroxides of Fe and Al in water.[42]

Conclusion

Using the size fractionation technique and NAA method, it was possible to obtain some knowledge about the chemical species of the trace elements existing in the Tama River water. One of the factors that governed the size distribution patterns of the trace elements was the TOC concentration in the river water. The high TOC concentration largely contributed to the dissolution of Rb, Cs, Ba, Al, U, the transition elements, and the heavier REEs. Fe, Sc, Th, and the light REEs, which tend to precipitate as the hydroxides, however, were predominantly distributed in the particulate size fraction. Na, K, Mg, Ca, Sr, Ni, As, Se, Mo, Sb, and W, which easily form the various soluble inorganic ions, on the other hand, were found only in the smallest size fraction, regardless of the TOC concentration in the river water.

Several tedious problems, however, still remain to be examined concerning the size fractionation technique. It must be kept in mind that adsorptive losses of trace elements onto the filter[43] and contamination from the filter materials[44] may occur during the filtration, which may lead to erroneous analytical results. Equilibrium conditions on chemical species of trace elements kept in the river water may be upset at the time of filtration, so that rapid treatments of the samples are required. Filters are not 100% efficient with respect to their size selectivety characteristics,[9] and the effective pore size decreases during the filtration because of filter clogging. Such problems are more insidious and require consideration in greater detail to minimize analytical errors. In order to determine exactly the chemical species of trace elements in river water, further studies will be necessary.

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