

Evaluation of Metal Contents in River Water Using a Simple Fractionation Method

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In this study, we performed fractional partition and determination of metals in river water by filtering the sample through a membrane filter with pore size of 0.22 μm immediately after sampling. We considered that the total amount of metal was contained in the nonfiltered sample, and fractional determination was performed separately using atomic absorption spectrometry of the metal in both the filtered and nonfiltered samples. The results showed a different pattern of aluminum distribution compared with other elements.

Key words — metal, river, water, sea, fractionation, filtration

INTRODUCTION

Environmental water, such as river water, well water, and sea water, is used for drinking water or for agricultural use. Many are apprehensive about the influence on humans since substances such as heavy metals contained in the water may be toxic in the body and the detailed mechanism of absorption is not yet understood.^{1–4)} In particular, the toxicity when absorbed in chemical form and the water solubility of heavy metals remain to be elucidated and concern has been growing about the contamination of water supplies with these and other metals.^{5,6)} In this study, simple fractionation partition and determination of the presence of several metals were performed using a membrane filter for environmental water, such as river water and sea water, and the results are discussed.

MATERIALS AND METHODS

Sampling of River Water and Sea Water — Samples were taken five times between October 2000 and February 2001. Ten sites in four Asano River valleys were sampled (the upper reaches of

the lower stream; upper region A1; middle region A2–3; and downstream region A4), where the river flows through Kanazawa city, Ishikawa, and into the Sea of Japan (the Uchinada seashore, A5), and in the four Kakehashi River valleys (the upper reaches of the lower stream; upper region B1; middle region B2–3; and downstream region B4) where the river flows through Komatsu city, Ishikawa and into the Sea of Japan (the Ataka seashore, B5). In addition, samples were taken on days without rain to avoid the possible influence of precipitation on water quality. Table 1 lists sampling sites and conditions. The sampling containers and preservation containers were predipped in detergent and diluted nitric acid and rinsed with Milli-Q water. At the time of sampling, water temperature (alcoholic thermometer) and air temperature (digital hygrometer, SIBATA TH-2 type) were also recorded.

Pretreatment of Samples — A portion of each sample was passed through a membrane filter with pore size of 0.22 μm (Millipore OR type). Subsequently, concentrated nitric acid was added to reach a concentration of 0.1 M, and the samples were stored in polyethylene containers in a cool dark place.⁷⁾ Nonfiltered samples were processed similarly. Electrical conductivity (Horiba DS-14 type conductivity meter) and pH (Yokogawa PH82 type pH meter) were measured in the remaining sample portions.

Metal Analysis — Atomic absorption spectrometry was performed for metal analysis using ant Hitachi Z-8000-type atomic absorption spectropho-

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Table 1. Basic Conditions at Sampling Sites

Sample	Air Temp. (°C)	Water Temp. (°C)	pH	Electronic Conductivity (mS/cm)
A1	13.6±4.3	10.8±4.7	6.78±0.20	1.050± 0.156
A2	15.6±6.0	12.2±5.0	7.07±0.51	1.404± 0.213
A3	16.7±6.4	12.8±5.0	7.37±0.51	1.386± 0.268
A4	15.0±6.4	12.0±6.4	7.01±0.60	4.062± 1.305
A5	16.4±5.6	16.4±4.6	7.72±0.26	> 199.9
B1	15.4±6.2	12.0±4.4	7.25±0.43	1.161± 0.182
B2	16.0±6.9	12.4±5.7	7.00±0.20	1.032± 0.375
B3	17.2±6.0	12.3±5.0	6.97±0.12	1.209± 0.354
B4	15.4±5.5	12.7±4.6	6.94±0.18	19.294± 19.109
B5	15.5±5.0	15.9±4.3	7.66±0.21	>199.9

Table 2. Metal Contents in River and Sea Water Samples

Sample	Filtration	Metal (ppb)					
		Al	Cr	Mn	Cd	Cu	
A1	-	113.59± 126.31	0.89±0.91	5.11± 3.52	— ^{a)}	5.17 ^{b)}	
	+	12.47± 18.01	0.22 ^{b)}	2.87± 1.06	— ^{a)}	— ^{a)}	
A2	-	58.56± 41.08	0.49±0.34	12.61± 7.06	— ^{a)}	1.10± 0.34	
	+	7.54± 7.21	0.24 ^{b)}	11.47± 7.20	— ^{a)}	0.51 ^{b)}	
A3	-	55.70± 24.09	1.09±1.43	13.34± 7.63	— ^{a)}	11.09 ^{b)}	
	+	7.57± 9.54	0.26±0.04	11.98± 7.76	— ^{a)}	— ^{a)}	
A4	-	262.59± 56.62	0.36±0.15	328.60±251.59	0.060 ^{b)}	4.48± 6.31	
	+	5.88± 0.82	— ^{a)}	290.10±255.12	0.053 ^{b)}	1.61± 1.42	
A5	-	25.88± 11.00	0.57±0.30	19.00± 5.26	0.616±0.232	298.99±290.03	
	+	4.49± 5.14	0.52±0.26	13.73± 4.03	0.501±0.286	91.15± 55.05	
B1	-	35.73± 17.46	0.91 ^{b)}	26.25± 12.18	0.791±0.236	17.62± 8.98	
	+	4.93± 3.22	— ^{a)}	25.75± 12.09	0.439±0.095	12.83± 7.03	
B2	-	40.03± 7.96	— ^{a)}	23.78± 7.57	0.336±0.076	10.96± 10.74	
	+	5.14± 1.43	— ^{a)}	22.56± 8.42	0.187±0.090	5.28± 2.97	
B3	-	69.98± 41.32	1.35 ^{b)}	47.57± 14.23	0.281±0.139	6.57± 2.71	
	+	4.03± 1.26	— ^{a)}	45.56± 14.10	0.217±0.106	4.83± 2.44	
B4	-	72.78± 22.74	0.28±0.06	65.32± 13.86	0.153±0.085	7.67± 6.45	
	+	2.25± 0.95	— ^{a)}	62.19± 15.57	0.124±0.079	2.49± 1.37	
B5	-	22.15± 10.94	0.56±0.40	24.47± 10.00	0.701±0.274	78.78± 25.54	
	+	— ^{a)}	0.64±0.35	19.45± 11.12	0.616±0.266	63.11± 29.28	

Data shown as mean ($n \leq 5$) ± S.D. a) not calculated since the value was less than the determination limit. b) $n = 1$.

tometer. Five elements were measured: aluminum (Al); cadmium (Cd); chromium (Cr); copper (Cu); and manganese (Mn). To measure the metal in the samples from the viewpoint of contamination from the surrounding environment and the concentration of the five metals in a sample, the measurement was

carried out in the order Al → Mn → Cd → Cu → Cr. In addition, sea water samples or samples suspected to contain sea water, and samples deviating from the maximum range of the calibration curve were measured again after dilution with 0.1 M nitric acid.

Table 3. Proportions of Filtered Metals in River and Sea Water Samples

Sample	Proportion of metals filtered fractions (%) ^{a)}				
	Al	Cr	Mn	Cd	Cu
A1	4.85 ± 4.57	14.38 ^{b)}	64.90 ± 21.47	— ^{c)}	— ^{c)}
A2	12.40 ± 11.73	96.00 ^{b)}	86.03 ± 13.52	— ^{c)}	— ^{c)}
A3	10.48 ± 10.23	97.93 ± 13.40	83.19 ± 16.83	— ^{c)}	— ^{c)}
A4	2.44 ± 0.84	— ^{c)}	82.50 ± 19.08	88.33 ^{b)}	40.62 ± 30.95
A5	4.34 ^{b)}	77.46 ± 2.03	72.63 ± 12.44	77.30 ± 17.36	44.47 ^{b)}
B1	14.34 ± 5.93	— ^{c)}	97.42 ± 3.10	61.47 ± 27.18	73.91 ± 11.65
B2	12.47 ± 3.57	— ^{c)}	93.36 ± 6.21	61.29 ± 37.34	59.10 ± 19.88
B3	8.24 ± 4.65	— ^{c)}	95.55 ± 2.65	79.68 ± 21.79	72.68 ± 10.08
B4	2.87 ± 1.54	— ^{c)}	94.43 ± 5.26	80.29 ± 3.88	39.80 ± 18.40
B5	— ^{c)}	87.33 ± 0.94	75.91 ± 17.75	87.43 ± 8.28	78.21 ± 15.21
Mean	8.1	74.6	84.6	76.5	58.4
S.D.	4.6	34.6	10.9	11.1	16.8

a) Data shown as mean ($n \leq 5$) ± S.D. b) $n = 1$. c) Not calculated since the value was less than the determination limit.

RESULTS AND DISCUSSION

The results of determination of metal contents are shown in Table 2. Measurements of lead and nickel were below the level of sensitivity in all samples (Pb, 2 ppb; nickel, 1 ppb). The concentration of each element differed by sampling site. Concentrations in the filtered and nonfiltered samples were as follows: Al, 22.2–262.6 ppb (nonfiltered sample)/< 0.5–12.5 ppb (filtered sample); Cr, < 0.2–1.1 ppb/< 0.2–0.64 ppb; Mn, 5.1–328.6 ppb/2.9–290.1 ppb; Cd, < 0.05–0.79 ppb/< 0.05–0.62 ppb; and Cu, 1.1–299.0 ppb/< 0.5–91.2 ppb. The variations were considered to reflect elution from soil, artificial contamination, and changes in the form of the metals over time. In particular, it was hypothesized that contamination would be more marked in the downstream sites (A4 and B4) of the rivers because of the formation of tidal flats and water stagnation. This hypothesis correlated with the color and quantity of residue on the filters at the time of filtration. Most metals were detected in both filtered and nonfiltered samples, and the high-polymer or insoluble fractions were larger than soluble (low molecular weight) fractions that can pass through 0.22 μm pore size filter. In the comparison of elements, aluminum showed a pattern different from other elements: the partition of the water-soluble fractions (A5 and B5) of sea water was very low (Table 3). Since conditions (temperature, pH, time until it enters water from soil, etc.) were consistent in sea water, it was thought that high polymerization (formation of huge particles) was occurring.⁸⁾

Moreover, the soluble fraction was 12% or less, which supports the occurrence of high polymerization. The percentage of aluminum in the filtered samples corresponds with the results in our previous reports.⁵⁾

Thus, although the fractionation and determination of elements of all molecular weights and of soluble/insoluble fractions were not performed, it was possible to collect a large amount of useful data simply and quickly using the current method compared with the column method or dialyzing method.⁹⁾ Although not used in this investigation, we believe that if an acid-proof filter such as polytetrafluoroethylene (PTFE) is used then filtration after acid processing would also be possible. In addition, even if atomic absorption spectrometry is used alone, variable fractionation analysis such as of the acid-soluble/insoluble fractions is expected to become possible.

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