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Thorium Isotope Content in River Water in Japan

by

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Abstract

Concentrations of thorium isotopes ^{232}Th, ^{230}Th and ^{228}Th were determined in the river water collected at ten main rivers in Japan. The concentration of dissolved ^{232}Th in river water was one order of magnitude higher than that in the Pacific surface waters. The weighted averages were 2.7×10^{-8} g/l for ^{232}Th and 2.8×10^{-13} g/l for ^{230}Th. The constancy in ^{232}Th and ^{230}Th concentration with time was observed, but the concentration of ^{228}Th in river water was quite variable. Accordingly, ^{228}Th/^{232}Th activity ratio showed a wide range of variation from 37 to 0.65 during the period of study.

1. Introduction

Concerning the thorium content in river waters in Japan, MIYAKE, SUGIMURA and TSUBOTA (1964) previously gave the weighted average of 2.7×10^{-8} g/l in ten representative rivers in Japan. Recently MOORE (1967) reported the thorium content of continental waters of 9.8×10^{-8} g/l for the Amazon, and 4.4×10^{-8} g/l for the Mississippi, which is the same order of magnitude as that in Japanese rivers.

With respect to the thorium isotope content in river waters, CHERDYNTSEV *et al.* (1963, 1964) and KAZACHEVSKY *et al.* (1964) reported the average activity ratio of 1.4 for ^{230}Th/^{232}Th and 1.0 for ^{228}Th/^{232}Th in Russian rivers. According to MOORE (1967), ^{230}Th/^{232}Th ratio is 0.74 for the Amazon and 1.3 for the Mississippi, and ^{228}Th/^{232}Th ratio is 1.4 for the Amazon and 1.2 for the Mississippi.

The present report gives the results of determination of the content of thorium isotopes and their activity ratio (^{230}Th/^{232}Th and ^{228}Th/^{232}Th) in water collected at ten main rivers in Japan.

2. Samples and method of analysis

The name of rivers at which water samples were collected are Ishikari (Hokkaido Island), Mogami, Kitakami, Shinano, Tone, Kiso, Yodo, Asahi (Honshu Island) and Yoshino (Shikoku Island) and Chikugo (Kyushu Island). Collection of water samples was done in the summer of 1961, 1966, 1967 and fall of 1966. The locations of the

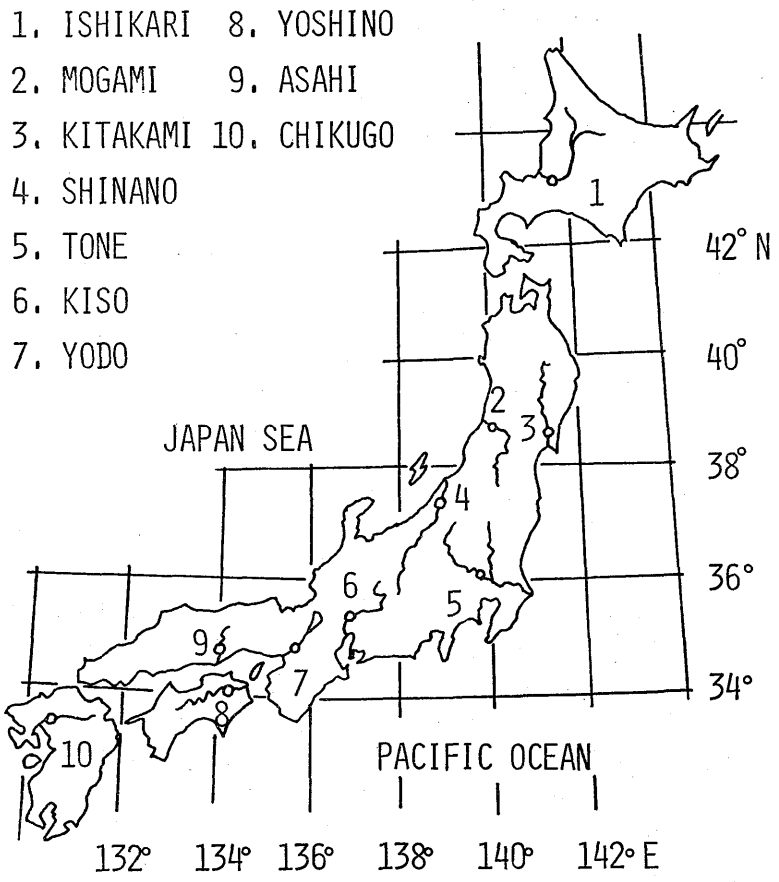

Fig. 1. Location and water sampling site of rivers in Japan.

rivers and the sampling sites are shown in Fig. 1. Sampling sites were selected so as to avoid industrial and urban pollution as well as inflowing sea water.

Analysis of thorium isotopes

Each 500 liters of river water was subjected to the analysis. A water sample was filtered through a membrane filter (Millipore filter HA type). Thorium isotopes were coprecipitated with ferric hydroxide by adding NH_4OH solution to the filtrate. In 8 M HNO_3 solution, thorium isotopes were retained in a column of Dowex 1 ion exchange resin, after other nuclides and a carrier were eluted using successive washes of 8 M HNO_3. Thorium is then eluted from the column with 10 M HCl.

Further purification was done by using a mixed solvent of 5 M HNO_3 and CH_3OH (1:9) in a column of Dowex 1 ion exchange resin. Elution of thorium from the resin was done with 1 M HNO_3 and finally thorium was electroplated on a silver disk (30 mm dia. and 0.5 mm thick).

Measurement of alpha-ray intensities of ^{232}Th (3.98 Mev), ^{230}Th (4.61 Mev) and

^{228}Th (5.42, 5.35 Mev) was done with an alpha-ray spectrometer which consists of a Frisch grid ion chamber or a solid state detector coupled with a multichannel pulse-height analyzer. ^{234}Th, beta-emitter with a half-life of 24.1 days was used as a yield tracer for the chemical separation.

The thorium content in suspended matters was analyzed with the same procedure as in the water analyses after dissolving the suspended matters in HCl, HNO_3 and HF and then adding a yield tracer to the solution.

3. Results and discussion

Tables 1. and 2. give the results of determination of thorium concentration and

Table 1. Contents of thorium isotopes in river waters in Japan (1961 samples).

Name of River	Sample size l	Water temp. ℃	pH	^{232}Th 10^{-8} g/l	^{230}Th 10^{-13} g/l	^{228}Th 10^{-17} g/l
Ishikari	200	23.6	6.6	0.87±0.13	0.50±0.07	1.0 ±0.11
Mogami	200	26.0	7.1	1.2 ±0.14	0.83±0.08	0.11±0.02
Kitakami	200	24.4	7.0	2.7 ±0.41	2.9 ±0.44	14 ±0.95
Shinano	100	22.8	7.3	3.7 ±0.51	4.0 ±0.47	2.7 ±0.34
Tone	400	14.3	7.2	1.3 ±0.09	0.95±0.06	1.8 ±0.08
Kiso	100	22.8	7.2	2.3 ±0.30	1.9 ±0.21	2.3 ±0.24
Yodo	200	27.8	7.2	4.8 ±0.46	2.7 ±0.27	5.0 ±0.39
Yoshino	200	23.6	7.2	3.9 ±0.70	4.1 ±0.46	18 ±1.2
Asahi	200	26.9	7.3	4.8 ±0.61	2.4 ±0.33	3.4 ±0.39
Chikugo	200	25.1	7.2	3.1 ±0.29	2.0 ±0.18	6.4 ±0.37
	weighted mean			2.6 ±1.4	2.2 ±1.2	3.1 ±6.8

Table 2. Activity rations of ^{230}Th/^{232}Th and ^{228}Th/^{232}Th in Japanese River waters (1961 samples).

Name of River	Activity ratio	
	^{230}Th/^{232}Th	^{228}Th/^{232}Th
Ishikari	1.0 ±0.20	8.5 ±1.5
Mogami	1.2 ±0.18	0.65±0.14
Kitakami	1.9 ±0.35	37 ±5.8
Shinano	1.9 ±0.32	5.4 ±0.98
Tone	1.4 ±0.15	10 ±0.87
Kiso	1.4 ±0.23	7.2 ±1.2
Yodo	0.96±0.12	7.6 ±0.72
Yoshino	1.8 ±0.32	34 ±5.1
Asano	0.85±0.15	5.2 ±0.86
Chikugo	1.1 ±0.18	15 ±2.9
mean	1.4 ±0.38	13 ±11

the activity ratio of isotope, $^{230}Th/^{232}Th$ and $^{228}Th/^{232}Th$ in river waters collected in 1961 at ten main rivers in Japan in which the concentration of ^{232}Th was reported in the previous report (MIYAKE, SUGIMURA and TSUBOTA, 1964).

The weighted average values were 2.7×10^{-8} g/l for ^{232}Th, 2.2×10^{-13} g/l for ^{230}Th and 3.1×10^{-17} g/l for ^{228}Th. With respect to the activity ratio of thorium isotope, 13 ± 11 and 1.4 ± 0.38 were obtained respectively for $^{228}Th/^{232}Th$ and $^{230}Th/^{232}Th$.

The results of analysis of thorium content in river waters collected in 1966 and 1967 at eight rivers are summarized in Tables 3 and 4.

Table 3. Contents of thorium isotopes in river waters in Japan (1966 and 1967 samples).

Name of River	Sample size l	Water temp. ℃	pH	^{232}Th 10^{-8} g/l	^{230}Th 10^{-13} g/l	^{228}Th 10^{-17} g/l
Kitakame	500	19.7	7.2	3.3±0.16	2.7 ±0.10	1.0 ±0.08
Shinano	500	16.3	7.3	1.1±0.04	0.76±0.03	0.24±0.02
Tone	500	3.9	7.2	2.5±0.12	0.81±0.03	0.32±0.02
Kiso	500	17.0	7.1	2.5±0.20	1.7 ±0.08	0.72±0.05
Yodo	500	29.2	7.3	4.1±0.18	2.7 ±0.25	0.83±0.06
Yoshino	500	26.9	7.4	2.0±0.10	2.0 ±0.08	0.38±0.04
Asahi	500	28.0	7.4	5.8±0.32	4.7 ±0.25	2.5 ±0.15
Chikugo	500	29.2	7.0	4.9±0.30	3.6 ±0.20	0.64±0.06
	weighted mean			2.7±1.7	2.8 ±1.3	0.62±0.71

Table 4. Activity ratios of $^{230}Th/^{232}Th$ and $^{228}Th/^{232}Th$ in Japanese river waters (1966 and 1967 samples).

Name of River	Activity ratio	
	$^{230}Th/^{232}Th$	$^{228}Th/^{232}Th$
Kitakami	1.4±0.13	2.2 ±0.19
Shinano	1.3±0.31	1.6 ±0.35
Tone	1.1±0.11	1.8 ±0.24
Kiso	1.3±0.15	2.2 ±0.24
Yodo	1.3±0.27	1.7 ±0.33
Yoshino	1.7±0.17	1.4 ±0.14
Asahi	1.4±0.43	3.2 ±0.89
Chikugo	1.4±0.17	0.92±0.13
mean	1.3±0.17	1.8 ±0.64

The weighted averages were 2.7×10^{-18} g/l for ^{232}Th, 2.8×10^{-13} g/l for ^{230}Th and 0.62×10^{-17} g/l for ^{228}Th. The results showed little variation with time in ^{232}Th and ^{230}Th content in river water, but the concentration of ^{228}Th was much smaller than the previous values in 1961 samples.

Thorium isotopes in suspended matters in river waters:

The concentration of thorium isotopes and the activity ratio of $^{228}Th/^{232}Th$ and $^{230}Th/^{232}Th$ in suspended matters in river water were shown in Tables 5 and 6. It is to be noticed that the content of thorium isotope in suspended matter was twice to ten times higher than that in soluble form of thorium in river water.

Table 5. Contents of thorium isotopes in suspended matter in Japanese river waters.

Name of River	Amount of Suspended matter mg/l	^{232}Th 10^{-8} g/l	^{230}Th 10^{-13} g/l	^{228}Th 10^{-17} g/l
Mogami	49	33 ±1.6	17 ±0.8	4.9 ±0.2
Kitakami	33	14 ±1.2	8.6±0.9	2.2 ±0.2
Shinano	24	15 ±1.5	8.5±0.8	2.8 ±0.2
Tone	13	2.8±0.1	1.4±0.1	0.55±0.02
Kiso	7.1	11 ±0.6	6.0±0.3	2.3 ±0.1
Yodo	26	7.7±0.4	3.7±0.2	0.78±0.04
Yoshino	4.9	3.5±0.1	2.7±0.1	0.83±0.02
Asahi	11	13 ±1.0	6.6±0.5	1.6 ±0.1
Chikugo	25	7.6±0.8	3.6±0.4	1.5 ±0.15
	weighted mean	7.2±8.6	7.2±4.5	2.2 ±1.3

Table 6. Activity rativity of $^{230}Th/^{232}Th$ and $^{228}Th/^{232}Th$ in suspended matter in Japanese river waters.

Name of River	Activity ratio	
	$^{232}Th/^{232}Th$	$^{228}Th/^{232}Th$
Mogami	0.88±0.05	1.1 ±0.06
Kitakami	1.1 ±0.14	1.1 ±0.15
Shinano	0.99±0.09	1.4 ±0.11
Tone	0.91±0.05	1.4 ±0.06
Kiso	0.92±0.06	1.5 ±0.08
Yodo	0.92±0.06	1.2 ±0.07
Yoshino	1.4 ±0.38	1.8 ±0.45
Asahi	0.95±0.08	0.92±0.08
Chikugo	0.87±0.10	1.5 ±0.15
mean	0.98±0.16	1.3 ±0.25

The total amount of annual discharge through river waters in Japan of thorium isotopes in soluble form is estimated to be 14.5 tons for ^{232}Th, 12 g for ^{230}Th and 17 mg for ^{228}Th assuming that the rate of total runoff of river water is 5.6×10^{14} liter per year. On the other hand, as the amount of discharge of thorium isotopes in suspended form are two to ten times larger than that in soluble form, the average discharge of thorium isotopes in suspended form is 72.8 tons for ^{232}Th, 400 g for ^{230}Th and 12 mg for ^{228}Th.

$^{230}Th/^{232}Th$ and $^{228}Th/^{232}Th$ ratio:

With respect to the activity ratio of $^{230}Th/^{232}Th$ is 1.4 and 1.3 respectively in 1961 and 1966. While in the suspended matter, the ratio of $^{230}Th/^{232}Th$ is 0.98 on an average, which is close to the value of 1.0 in the land material in Japan, assuming the ratio of 3:2 for the igneous and sedimentary rocks that cover the surface of Japan with 2 ppm of uranium and 6 ppm of thorium as mean contents.

On the other hand, as to the activity ratio of $^{228}Th/^{232}Th$ in river water, larger values as high as 37 were found in the Kitakami river, with a weighted average of 13 ± 11 in 1961. In the 1966 samples, however, the smaller value of 1.8 ± 0.6 was obtained which suggests the large fluctuation in $^{228}Th/^{232}Th$ ratio in river water.

At any rate, it is to be noticed that the mean content of ^{228}Th in river is higher than the equilibrium value to ^{232}Th. On the other hand, the activity ratio of $^{228}Th/^{232}Th$ in the suspended matter is 1.3 ± 0.25 ranging from 0.9 to 1.8, which is close to the equilibrium ratio. Generally, $^{228}Th/^{232}Th$ ratio in the suspended matter is lower than that in soluble form. A similar relationship is reported by the present authors (MIYAKE, SUGIMURA and YASUJIMA, 1970) in sea water and suspended matter in the western North Pacific.

The enrichment of ^{228}Th in river waters occurs by the preferential dissolution of ^{228}Ra, a parent nuclide of ^{228}Th, from the land material into river waters during the weathering process, and the smaller retention factor in river water of radium than that of thorium (MIYAKE, SUGIMURA and TSUBOTA, 1964).

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本邦河川水中のトリウム同位体含量

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本邦の10主要河川（石狩川，最上川，北上川，信濃川，利根川，木曾川，淀川，旭川，吉野川および筑後川）の河川中のトリウム同位体；^{232}Th，^{230}Th および ^{228}Th の含量を測定した。河川水中の溶存 ^{232}Th の濃度は，太平洋の海水における濃度よりも1桁高く，平均$2.7\times10^{-8}g/l$を示す。1961年および1966～1967年の採水試料を比較すると，^{232}Th および ^{230}Th の含量は，ほとんど変化がないのに対し，^{228}Th の含量は大巾に変動することが明らかになった。$^{228}Th/^{232}Th$ の放射能比は，上記期間に37から0.65までの変動巾を示している。また，溶存状態のトリウム同位体にくらべ，懸濁状態のトリウム同位体は，2倍から10倍も多く存在することがわかった。