VARIATION OF MERCURY CONTENT AND ITS CHEMICAL FORMS ASSOCIATED WITH FLOW OF RIVER WATER

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VARIATION OF MERCURY CONTENT AND ITS CHEMICAL FORMS ASSOCIATED WITH FLOW OF RIVER WATER

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Abstract

The mercury content of low polluted river water is very low, being as little as ppt level. It is very difficult to get precise and reliable value on them. It is, therefore, necessary to pre-concentrate for the determination of mercury at ppt levels in river water.

The recommended procedures are as follows; (I) River water sample is acidified with sulfuric acid and then mercury is reduced with thin (II) chloride. Nitrogen gas is passed through the sample solution and any mercury evolved is trapped on a porous gold collector and determined by cold vapor atomic absorption spectrometry. (II) River water sample is treated with sodium hydroxide, copper (II) ions and tin (II) chloride, and the mercury is determined as in (I). (III) River water sample is treated with a mixture of nitric acid and potassium permanganate solution and heated on a water bath, followed by (I).

Dissolved inorganic mercury, dissolved inorganic mercury and dissolved organic mercury, and the total mercury can be determined by methods (I), (II) and (III), respectively.

River water samples were collected from main river in Kagoshima prefecture. Variation of mercury content and its chemical forms associated with flow of river water were investigated.

Levels of mercury content by methods (I), (II) and (III) were found to be in the range of 0.8～3.1 ng/l (geometric mean 1.8 ng/l), 2.8～42.$_0$ ng/l (geometric mean 4.8 ng/l) and 3.4～50.$_3$ ng/l (geometric mean 5.8 ng/l) for 15 samples taken from the three rivers, respectively.

The mercury chemical forms in clean river water is almost conceivable as dissolved inorganic mercury. In polluted river water, 90% over of total mercury was adsorbed mercury to suspended matter. Along with flow of river water, dissolved inorganic mercury was gradually decreased.

Introduction

As an attention is paid to environmental problem, determinated values of mercury content of land water (rain, river, lake, ground water, etc.) are increasing. However, report regarding to the chemical forms of mercury is small. This is related to that content of mercury is very low, being as little as ppt level. Accordingly, it is very difficult to obtain precise analytical results.

Conventionally, inorganic mercury is determined by cold vapor atomic absorption spectrophotometry[1)-5)]. Also, to determine the organic mercury content gaschromato-

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graph method has been widely employed[6)7)]. The concomitant use of two methods require time and labor. Authors added improvement to the analytical methods of Magos[8)], Umezaki[9)] and Kamada et al.[10)]. These methods[11)12)] were sucessfully applied to the determination of mercury in land water samples.

This report describes the results of mercury content and its chemical forms associated with flow of river.

Experimental

Sampling of River Water and Preservation.

Sampling stations of river water in Kagoshima prefecture are shown in Fig. 1; the station numbers and distance from the estuary are tabulated in Table 1.

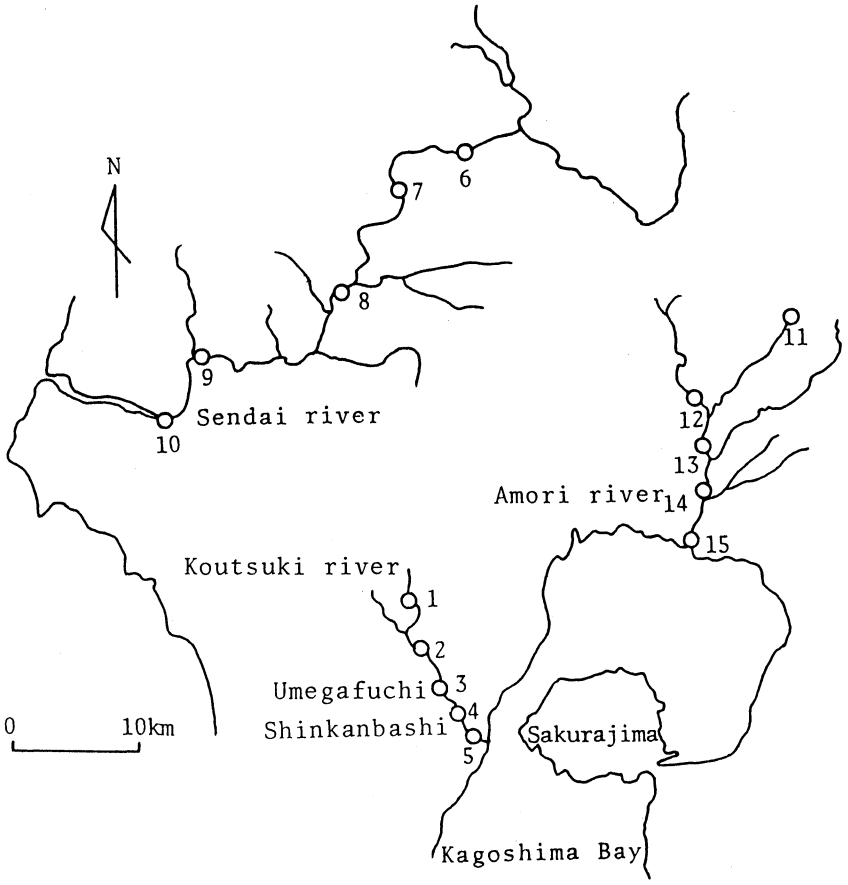

Fig. 1 Sampling stations of river water.

River water samples used for the determination of mercury content was kept in hard glass bottles (1 liter) with teflon packing, which was exuded beforehand by approximately 3 mol/l nitric acid for two weeks and then washed throughly with water. 10 ml of (1 : 1) sulfuric acid was added to each 1 liter of sample at the sampling place as quickly as possible. Samples were then brought back to the laboratory and analyzed.

Apparatus and Reagents.

Apparatus. The apparatus used reforming Mercury Auto monitor by Nippon Instruments.

Reagents. All reagents (exclude acid and potassium permanganate) used analytical grade of marketing. The acids (hydrochloric acid, sulfuric acid, nitric acid) and the potassium permanganate, which were used all analytical special reagent grade for the measurement of the toxic metals.

Determination Method of Mercury in River Water.

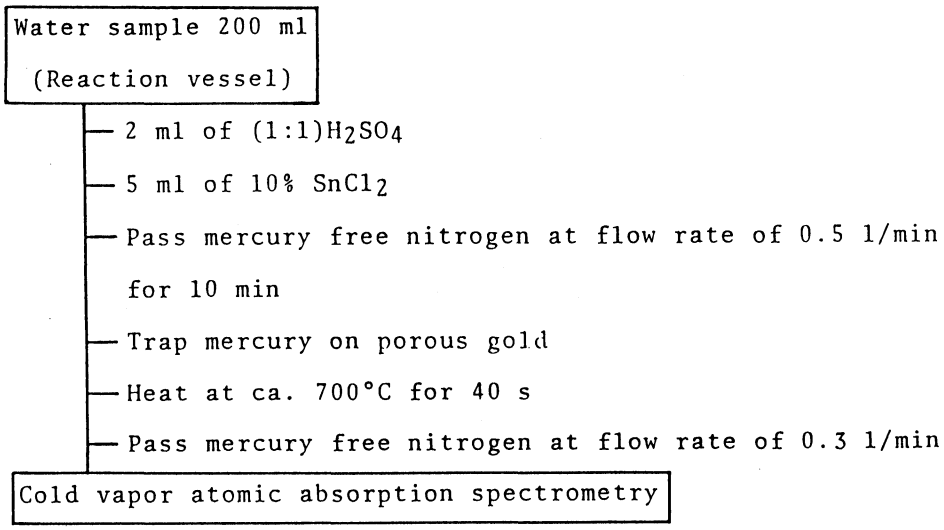

Fig. 2 Analytical procedure of dissolved inorganic mercury in water sample. [Method I].

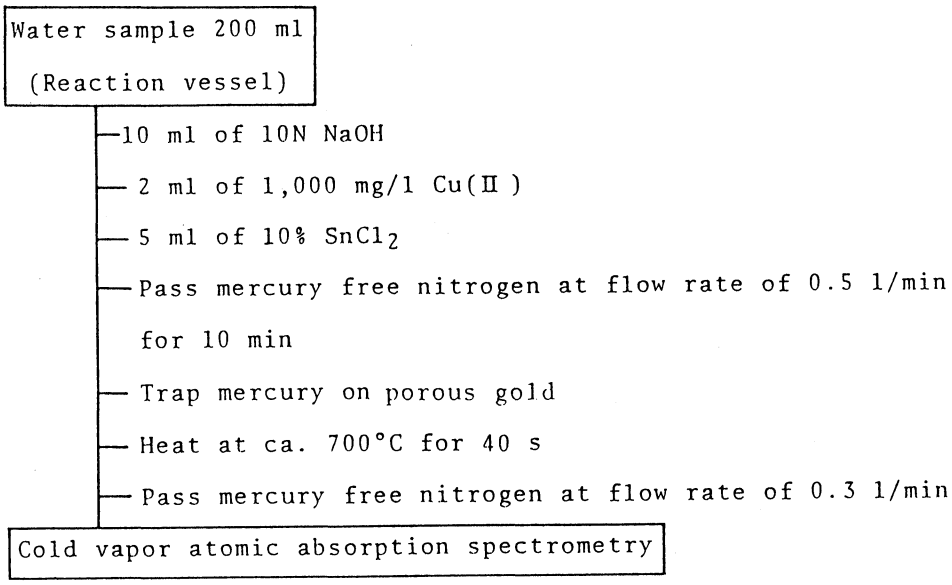

Fig. 3 Analytical procedure of dissolved inorganic mercury and dissolved organic mercury in water sample. [Method II].

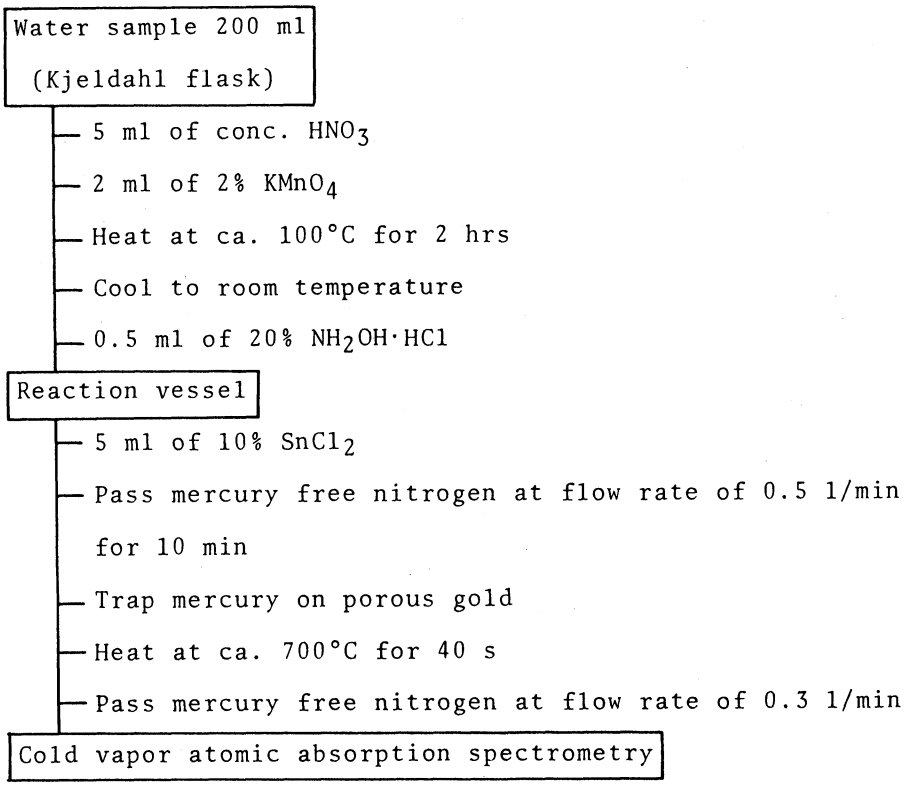

Fig. 4 Analytical procedure of total mercury in water sample. [Method III].

Porous gold collector was used for the separation and concentration of ultratrace amounts of mercury. The differential determination methods of mercury for river water are shown in Fig. 2~4.

Dissolved inorganic mercury, dissolved inorganic mercury and dissolved organic mercury, and the total mercury can be determined by methods (I), (II) and (III), respectively.

Results and Discussion

Mercury Content in Land Water.

Mercury content and chemical forms in land water were determined by methods I, II and III. The results are shown in Table 1.

As for mercury content of clean land water, differences by methods I, II and III are almost nonexistent. However, total mercury content is occasionally about 10 times of dissoved inorganic mercury in the koutsuki river water (flow through Kagoshima City) and Unagi pond. And then turbid sample filtered with milipore filter of 0.45 μm. 10 ml of (1 : 1) sulfuric acid was added to each 1 liter of sample at the sampling place or laboratory as quickly as possible, mercury was determined. The analytical results of mercury content and its chemical forms are shown in Table 2. Table 2 shows comparison of total mercury in samples that filtered and does not filtered with miliporefilter of 0.45 μm. Total mercury of

Table 1. Analytical results of mercury in land water

Sample	Locality	Date	Inorg. Hg*	Inorg. Hg** +Org. Hg	Total Hg***
			(ng/l)	(ng/l)	(ng/l)
Rain water	Kagoshima Univ.	Apr. 12. '80	4.9	9.0	—
〃 〃	〃 〃	May. 8. 〃	2.1	2.6	7.8
〃 〃	〃 〃	Jul. 16. 〃	4.1	4.4	4.8
River water	Kooriyama chō	Apr. 3. 〃	2.7	3.2	3.4
〃 〃	Umegafuchi	〃 〃 〃	2.1	2.6	35.5
〃 〃	Takenohashi	〃 〃 〃	2.7	2.6	14.2
Ground water	Miedake	〃 6. 〃	2.8	3.0	3.0
〃 〃	Kakinokibira	〃 〃 〃	2.6	2.2	3.0
Lake water 0 m	Unagiike	Mar. 18. 〃	2.8	3.5	8.4
〃 〃 −30 m	〃	〃 〃 〃	3.0	3.4	3.2
〃 〃 −50 m	〃	〃 〃 〃	2.6	3.8	38.4

*: Method (I), **: Method (II), ***: Method (III)

Table 2. Effect of filtration for mercury determination in land water

Sample	Date	Inorg. Hg	Inorg. Hg +Org. Hg	Total Hg
		(ng/l)	(ng/l)	(ng/l)
Koutsuki river (Umegafuchi)	Apr. 3. '80	2.1	2.6	35.5
〃 〃	〃 〃 〃	2.0*	2.4*	5.3*
〃 〃	May. 7. 〃	2.0	2.5	3.5
〃 〃	〃 〃 〃	2.3*	2.6*	2.8*
Koutsuki river (Takenohashi)	Apr. 3. 〃	2.7	2.6	14.2
〃 〃	〃 〃 〃	2.7*	2.9*	6.0*
〃 〃	May. 7. 〃	1.9	3.2	7.1
〃 〃	〃 〃 〃	1.6*	2.6*	3.3*

*: Filtration (0.45 μm)

filtered samples are nonexistent abnormally. Accordingly, abnormally big mercury content caused by suspended matter.

Change of Mercury Content and Its Chemical Forms Associated with Flow of River Water.

Along with flow of river, the water quality varies with influence of geology, industrial activity and human activity. The mercury content of low polluted river water is order of 1 ~3 ng/l. Accordingly, it is very difficult to get presise and reliable value on mercury associated with flow of river water.

In this research, we were investigated the Sendai river, the Amori river and the Koutsuki river which flow through center of Kagoshima City.

The sampling stations are shown in Fig. 1. Also, change of mercury content and its chemical forms associated with flow of river water are shown in Table 3.

Levels of mercury content by methods (I), (II) and (III) were found to be in the range of

Table 3. Analytical results of mercury associated with flow of river water

Sample	Station. No.	Distance(km)*	Date	Inorg. Hg	Inorg. Hg +Org. Hg	Total Hg
				(ng/l)	(ng/l)	(ng/l)
Koutsuki river	1	19.8	Jul. 21. '80	2.7	3.2	3.4
〃 〃	2	12.8	〃 〃 〃	3.1	3.1	4.5
〃 〃	3	8.4	〃 〃 〃	2.5	3.8	3.7
〃 〃	4	5.5	〃 〃 〃	1.1	4.4	5.2
〃 〃	5	1.9	〃 〃 〃	0.8	6.2	6.4
Sendai river	6	64.1	〃 22. 〃	2.1	2.9	3.2
〃 〃	7	50.2	〃 〃 〃	2.1	2.8	5.2
〃 〃	8	39.5	〃 〃 〃	1.8	3.3	5.5
〃 〃	9	18.5	〃 〃 〃	1.8	4.6	5.0
〃 〃	10	11.2	〃 〃 〃	1.2	4.1	5.2
Amori river	11	34.7	〃 〃 〃	3.1	42.0	50.3
〃 〃	12	18.1	〃 〃 〃	1.7	5.0	5.6
〃 〃	13	13.8	〃 〃 〃	1.5	5.5	5.8
〃 〃	14	6.7	〃 〃 〃	1.7	4.8	5.5
〃 〃	15	1.8	〃 〃 〃	2.3	5.4	6.6

*: Distance from the estuary

0.8～3.1 ng/l (geometric mean 1.8 ng/l), 2.8～$42._0$ ng/l (geometric mean 4.8 ng/l) and 3.4 ～$50._3$ ng/l (geometric mean 5.8 ng/l) for 15 samples taken the tree rivers, respectively.

Along with flow of river water dissolved inorganic mercury plus dissolved organic mercury and total mercury content of the Koutsuki river are gradually increasing. On the other hand, dissolved inorganic mercury content is gradually decreasing. Such trend is seen even at the Sendai river and the Amori river. Accordingly, we are conceivable that dissolved inorganic mercury adsorbed to suspended matter. Differences between dissolved inorganic mercury and total mercury are small in upstream that an industrial activity and an influence of human activity are little.

Time Change of Mercury Content of River Water at Fixed Point.

We chose the Koutsuki river as object river. The river is about 30 km long and valley area is about 105 km^2. This river is flowing southeast through the central part of Kagoshima City. Also, source of water supply of Kagoshima city is taken at Kogashira about 11 km upstream from the estuary. A flow rate of the Koutsuki river is comparatively small (4 m^3/sec)[13]. Sampling station was chosen at Shinkanbashi about 4 km upstream from the estuary. As for surroundings of the river, the housing land is going on. Accordingly, a human activity is exerting an influence on the water quality of the river. A supply to the river of a pollutant changes corresponding to human life. Accordingly, the water quality of such river water is changing continually. Kamada et al.[14] has been reported positive correlation between zinc content of the Koutsuki river and traffic density of the national load number 3 that are going along in the Koutsuki river. Also, a relation between phosphorus in the Koutsuki river and human activity has been reported[15].

Thereupon, we checked about relevancy of human activity and mercury content of river water with time. River water was collected at Shinkanbashi of the Koutsuki river at 2 hours intervals until 6th from August 5 in 1980.

The results are shown in Fig. 5. As can be seen from the figure, a fairly high degree of positive correlation exists between total mercury and human activity from 10 to 14 o'clock.

Fig. 5 is showing the maximum of total mercury content of the midnight. As for this, an influence of human activity can not consider.

Increase of total mercury of the midnight depends to muddiness of river water by rain of around 22 o'clock.

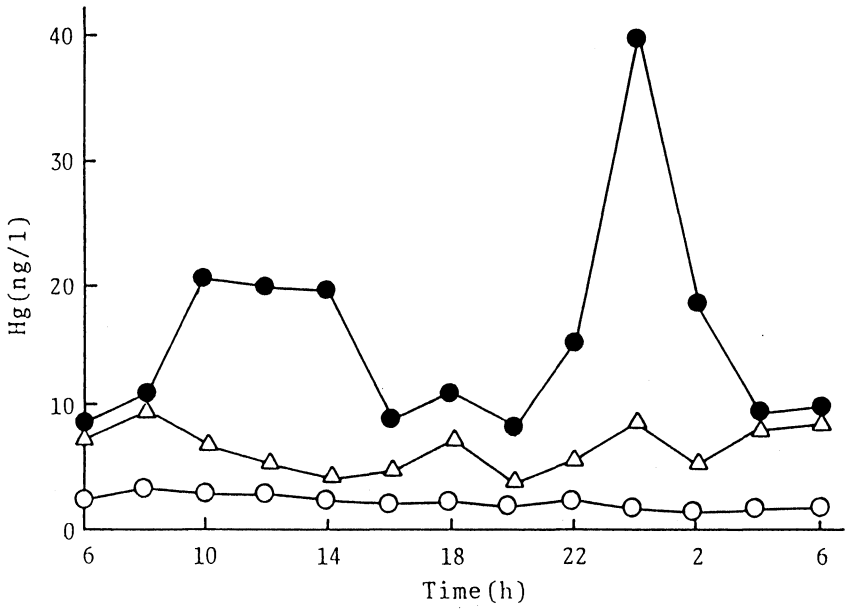

Fig. 5 Variation of mercury content with time.
Sample: Koutsuki river (Shinkanbashi), (Aug. 5–6, '80).
○: Dissolved inorganic mercury.
△: Dissolved inorganic mercury and dissolved organic mercury.
●: Total mercury.

Recovery of Mercury from Spiked River Water.

Water sample was used surface water at Umegafuchi of the Koutsuki river. The water sample divided into the sample that filtered and did not filtered with milipore filter of 0.45 μm. 10 ml of (1 : 1) sulfuric acid and inorganic mercury 50 ng were added to each 1 liter water sample and preserved in hard glass bottle. Then, the change in mercury content and its chemical forms were examined during storage. The analytical results are shown in Fig. 6.

Recovery of dissolved inorganic mercury without filtration has decreased sharply within a day. In regard to dissolved inorganic mercury, recovery below 15% are obtained. Recovery of mercury by method (II) and (III) are about 80% obtained, does not take part in

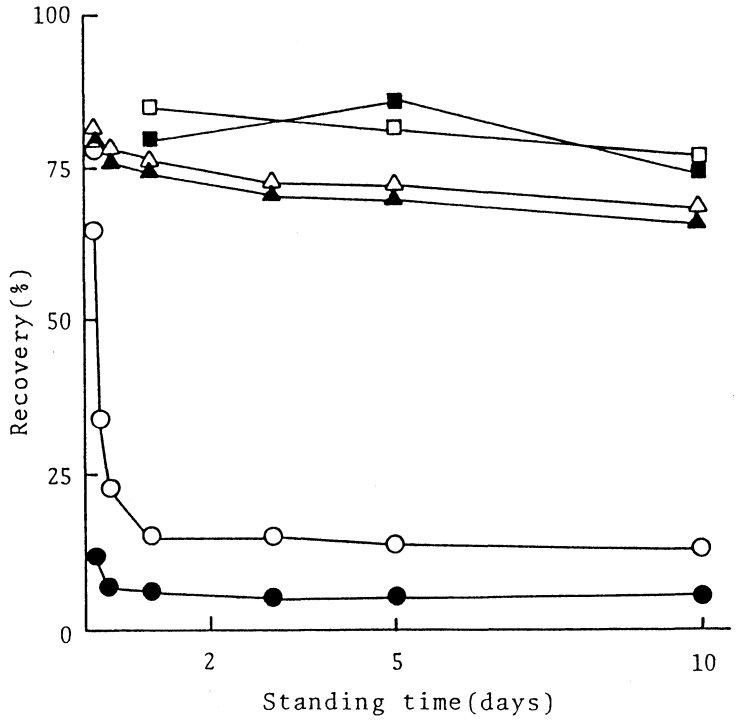

Fig. 6 Recovery of mercury from spiked river water in glass bottle.
Sample: Koutsuki river (Umegafuchi).
Mercury: 50 ng/l as Hg ($HgCl_2$).
○, △, □: Filtration; ●, ▲, ■: Without filtration.
H_2SO_4: (1:1) H_2SO_4 10 ml/l.
○, ●: Dissolved inorganic mercury [Method I].
△, ▲: Dissolved inorganic mercury and dissovled organic mercury [Method II].
■, □: Total mercury [Method III].

the filtration.

However, recoveries of mercury by method (II) and (III) are gradually decreasing with increase of days. It is conceivable that about 20% of added inorganic mercury vaporize or adsorbs to device wall in short period.

Conclusion

Mercury content and chemical forms of mercury associated with flow of river water were investigated. The mercury content in clean river water is 1～5 ng/l. The mercury chemical forms of such river water is almost conceivable as dissolved inorganic mercury. On the other hand, 90% over of total mercury is containing in suspended matter in polluted river water. Samples that filtered with milipore filter of 0.45 μm did not show abnormally big mercury content.

When suspended matter increases along with flow of river water, dissolved inorganic mercury content gradually decreased. Accordingly, mercury was almost containing in dissolved organic material and suspended matter. Also, recovery of mercury was checked from spiked river water. Although dissolved inorganic mercury decreased in a short period,

a part of total mercury did not change during 10 days.

Also, we checked about the relevancy between a human activity and mercury content. As for in pattern of mercury content and human activity, an agreement was not necessarily obtained.

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