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WASHOUT CHARACTERISTICS OF ARSENIC COMPOUNDS IN THE TOYOHIRA RIVER

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SYNOPSIS

Hot spring water and mine effluents flow into the Toyohira River, which runs through the center of Sapporo, Japan. In the river, concentrations of components originating from hot spring water and mine effluent change in accordance with a certain flow regime. This phenomenon must be addressed in water quality management. The authors have examined the seasonal fluctuations in arsenic in accordance with flow regime (ordinary-water, snowmelt and rainfall periods), as well as its downflow behavior and runoff characteristics. During low-water periods, the arsenic that originates from hot-spring water tends to wash out as *dilute* pollution or *constant-concentration* pollution. During periods of snowmelt and rainfall flood, that arsenic tends to wash out as *diffuse* pollution. The tendency for the type of pollution to differ in accordance with the flow regime is greater downstream of the dam than upstream of the dam.

A dissolved form of arsenic dominates during the ordinary-water period, whereas a suspended form dominates during the high-water (snowmelt and rainfall) periods, clearly indicating a tendency for arsenic runoff to fluctuate with changes in flow regime. We found that the arsenic runoff is largely affected by arsenic suspensibility during downflow, by accumulations in the bottom sediment, and by flood-induced re-suspension from bottom sediment.

INTRODUCTION

We studied the Toyohira River, where arsenic originating in hot-spring water is of growing concern. Since this problem is related to the water supply of Sapporo, the behavior of arsenic is an important issue that has to be addressed in water quality management. This research ultimately aims to protect the water supply source and to conserve the water environment through water quality management of the Toyohira River. Researchers focused on the behavior of arsenic contained in the hot spring water, we analyzed arsenic loads, runoff characteristics, the mechanism of qualitative changes, and other factors. From past water quality surveys during the ordinary-water period, found that hot spring water contains dissolved arsenic in high concentrations. After running off into the Toyohira River, it is absorbed by silt and clay and accumulates in high concentrations in the bottom sediment of dams. Runoff characteristics of arsenic vary from point source (dilution) to non-point source (diffused) in its downstream flow from small tributaries to dams and to rivers (Tatsumi et al. (9)). Furthermore, during the rainfall flood period, suspended arsenic washes out in high concentrations due to the agitation of the bottom sediment (Tatsumi et al. (10)). This paper analyzes comprehensively the seasonal fluctuations in arsenic according to flow regime (ordinary-water, snowmelt and rainfall periods) and examines arsenic downflow behavior and runoff characteristics in the snowmelt period in a snowy region.

METHOD OF RESEARCH

Conditions of the water area under study

The Toyohira River, which originates in Mt. Koizaridake (1,235m), has a catchment area of 904.8 km^2 and a total channel length of 72.5 km. It flows into the Ishikari River after running through Jozan Lake, Jozankei Hot Spring Resort, Misumai and the urban area of Sapporo (Figure 1). Jozankei Hot Spring, a muriated spring, is at the upper reaches of the catchment basin. At the upper reaches of the Shirai River, a secondary tributary of the Toyohira River, the Toyoha Mine is located, which produces lead and zinc. Its effluents pollute the river. At the middle reaches are located Ichinosawa Dam, Toyama Dam and Moiwa Dam. They were built for several purposes: 1) to prevent erosion and to control sediments, and 2) to provide electric power generation and water supply. Water from the Jozankei Hot Spring contains large amounts of arsenic (As), Na^+ and Cl^- (3). Since the mean arsenic content is $3.1 mg \cdot l^{-1}$ (Satou et al. (6)), its level sometimes exceeds the water quality standard for drinking water at the intake point (T-3) at the lower reaches of the Toyohira River. The movement of arsenic as it flows down the river was brought to the attentions of researchers by (Tatsumi et al. (9); Satou et al. (6)). Sulfuric acid effluents produced in ore dressing at the Toyoha Mine has been treated; however, there have been cases where heavy metal components such as Fe, Mn and Cd have posed problems (Hanya (2)).

Survey method

Figure 1 shows the five water quality survey points. Four of them are in the Toyohira River (from upper reaches downward: T-10, T-9, T-7, and T-3) and one point (S-1) is in the Shirai River, a tributary of the Toyohira River. The Jozankei Hot Spring Resort is between survey points T-10 and T-9. Surveys were conducted once or twice a week during the snowmelt period from April to May 2002. (Water was sampled ten times at each survey point in Toyohira River. Hereinafter, the surveies conducted from April to May are referred to as "snowmelt-flood surveies.") During the rainfall from August 21 through 24, 2001 (79 mm) and from October 1 through 3 (97 mm), water was sampled approximately every two hours at different discharges. Samples of water were taken before the rainfall started. (Water was sampled 17 times at each survey point for the both survey periods. Hereinafter, the survey for the rainfall period is referred to as "rainfall-flood survey.") Water sampling for the period when the water level is normal and stable was done once a month from June 2002 to March 2003. Water was sampled nine times at each of the four survey points on the Toyohira River. Hereinafter, water sampling during the ordinary and stable-flow regime is referred to as "ordinary-water survey."

Bottom sediment surveys were conducted in the three dam reservoirs (Ichinosawa Dam, Toyama Dam and Moiwa Dam) shown in Figure 1. At Toyama Dam and Moiwa Dam, sediment was taken at three points: the upper, middle and lower reaches of the reservoirs. At the Ichinosawa Dam, sediment was taken at seven points in view of impacts from the inflowing tributary.

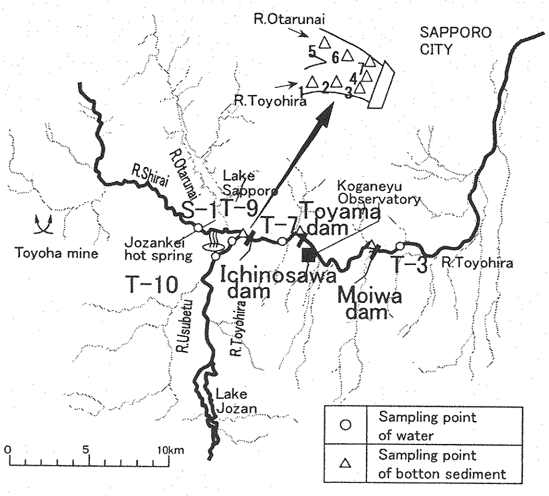

Fig. 1 Studied area and survey points of the Toyohira river

Water and sediment quality analysis items and analytical method

Water temperature, air temperature and electric conductivity (EC) were measured onsite at the time of sampling. Samples were kept at low temperature while being transported to the laboratory and were refrigerated until analysis. Samples for arsenic analysis were stored after nitric acid had been added to adjust the pH to 1. Approximately 30 items of water quality components were analyzed. We analyzed organic components (COD and TOC), nutrient salts (TN and TP), heavy metal components (Fe, Mn, As and Pb), SS, and the main inorganic components. Dissolved components were analyzed after filtration using a membrane filter with 0.45-μm pore size. We used symbols to represent the analyzed items. To represent the difference in sample form (i.e., samples with suspended sediment (total sample) vs. filtered samples (dissolved form)), we used T for the former and F for the latter. For samples of suspended components (the remainder after subtracting the concentration in dissolved form from the concentration as a total sample), P was used. Water quality analysis was performed according to JIS-K0102 for industrial effluent tests. Arsenic was measured by hydride generation atomic absorption spectrometry after organic matter had been decomposed in pretreatment.

Bottom sediment analysis was performed for arsenic content and granular composition with grains of a diameter of 75 μm or larger were sieved, and those smaller than the sieved grains (<75 μm) were measured by sedimentation particle-size analysis based on Stokes' law. To measure the arsenic content, samples were divided into two categories: grains with diameter of 2 mm or smaller (hereinafter: "bottom sediment [<2 mm]") and fine-grained silt·clay with diameter of smaller than 0.02 mm (hereinafter: "bottom sediment [silt·clay]"). In the bottom sediment analyses, the soil test method was used to analyze granular composition, and the sediment monitoring method was used to analyze arsenic content.

Hydrologic and meteorological data

For discharge at each survey point, we used values automatically observed at the Jozankei Discharge Observatory and Shiraikawa Discharge Observatory (T-9 and S-1) of the Ishikari River Development and Construction Department, Hokkaido Regional Development Bureau; outflow discharge from Hokkaido Electric Power Co.'s Jozankei intake weir (T-10); inflow discharge at Toyama Dam (T-7); and outflow discharge from Moiwa Dam (T-3). For precipitation, we used data from the Meteorological Agency (Koganeyu Observatory near Toyama Dam).

RESULTS AND DISCUSSION

Changes in discharge and general water quality conditions

Figure 2 shows daily precipitation, discharge at T-3, and mean daily values of turbidity and EC during the survey. Survey periods are indicated by "○ (ordinary-water survey)", "△ (snowmelt-flood survey)" and "× (rainfall-flood survey)". The discharge peaks during the snowmelt period, then decreases in summer and increases with rainfall in autumn, which indicates a typical runoff pattern in a snowy region. Turbidity shows concentration changes in accordance with discharge and rainfall, and suspended components are washed out in high concentrations during the snowmelt- and rainfall-flood periods. EC is high during the dry season and declines sharply when discharge increases.

Arsenic concentrations and forms (dissolved, suspended)

Figure 3(a) shows arsenic concentrations (As_T) at different points during the ordinary-water period. Arsenic concentrations are low (0.004 $mg \cdot l^{-1}$) at the upper reaches (T-10). The arsenic concentration is much greater at points immediately downstream of this survey point. At T-9, which is downstream of the Jozankei Hot Spring Resort, the mean value is 0.22 $mg \cdot l^{-1}$ (the largest value observed in this survey). This is due to point-source inflow of hot spring water with high As_T concentrations (2.7 - 3.3 (3.1 on average) $mg \cdot l^{-1}$) (Satou et al. (6)). Figure 3(b) shows the proportions of suspended arsenic (As_P) and dissolved (As_F) arsenic. Although all the arsenic originating from hot-spring water is in dissolved form, a proportion of the suspended form gradually increases in the course of downflow, approaching 12% at T-7. At T-3, a point downstream of T-7, the proportion of the suspended form falls to about 6%, which may be attributed to the removal of suspended arsenic from river water through accumulation on the riverbed and in the reservoir.

Figure 4(a) shows the concentration changes during the snowmelt period at T-9 and 3. Arsenic concentrations during the snowmelt period when discharge increases were lower than those at the ordinary-water period. However, when the water level peaked on April 17th and 25th, the arsenic concentrations rose. The correlation between arsenic concentration and discharge was not clear. In contrast, at T-3, where there is inflow from the Shirai River and other tributaries with lower As_T concentrations, the arsenic concentration is low (0.01 - 0.03 $mg \cdot l^{-1}$), and the fluctuations are smaller than those at T-9. Figure 4(b) shows the ratio of suspended arsenic (As_p) to dissolved arsenic (As_F). The ratios of dissolved arsenic are high at both survey points when the discharge is small. However, suspended arsenic comes to accounts for about 60% to 80% of the total arsenic on the two days with high discharge (April 17th and 25th). The form of arsenic runoff greatly depends on the flow regime. Concentrations of dissolved arsenic decrease with increase in discharge, and the contribution of suspended arsenic increases during flooding.

Figures 5(a) shows concentration of arsenic during the rainfall period. Figure 5(b) shows the ratios of suspended to dissolved arsenic during the same period. Although the arsenic concentration during the rainfall period decreases with increase in discharge before increasing remarkably around the maximum discharge. The highest values of arsenic concentration at both survey points were recorded during the period with maximum discharge. A reduction in concentrations was then observed with decrease in discharge at both points. The percentage of dissolved arsenic to total arsenic was more than 90% at the both survey points during the low discharge period (Surveys ① and ④). During the high-discharge period (Survey ⑧) the proportion of suspended arsenic increases, reaching about 60% to 90% near the maximum discharge (Surveys ⑪ and ⑬).

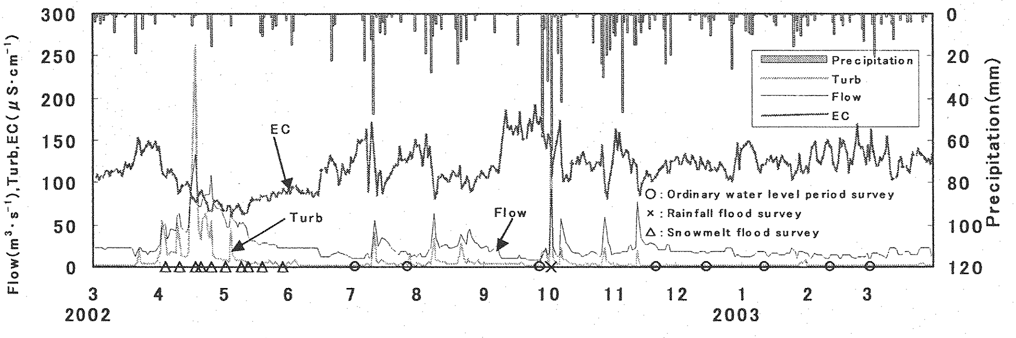

Fig. 2 Changes in flow, EC, turbidity, and precipitation during the survey period at T-3

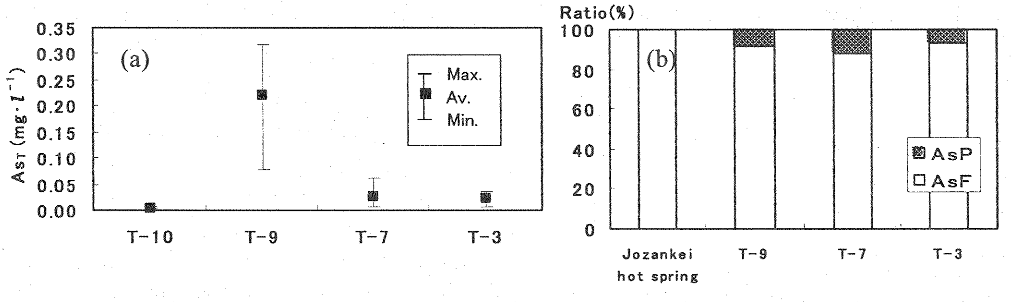

Fig. 3 (a)Arsenic concentrations (As_T) at different points during the ordinary-water period

(b) Ratio of suspended arsenic (As_p) to dissolved arsenic (As_F)

General conditions of the bottom sediment

Table 1 shows the arsenic content in the bottom sediment [<2 mm] and in the bottom sediment [silt·clay], and Table 2 shows the grain size distribution according to the Atterberg scale. Arsenic content (mean value) in the bottom sediment [<2 mm] is low (19.6 $mg \cdot kg^{-1}$) at survey points No. 5, 6, and 7 in the reservoir on the Otarunai River side of Ichinosawa Dam, where the influence of the hot spring water inflow is small, but it is considerable (185 $mg \cdot kg^{-1}$) at survey points No. 1, 2, 3, and 4 in the reservoir on the Toyohira River side, which is influenced by the hot spring water inflow. Further down, at the Toyama Dam and Moiwa Dam, arsenic content gradually decreases to 66.3 $mg \cdot kg^{-1}$ and 33.5 $mg \cdot kg^{-1}$ respectively. Arsenic content in the bottom sediment [silt·clay] is 164 $mg \cdot kg^{-1}$ at survey points No. 1, 2, 3, and 4 in Ichinosawa Dam, and arsenic contained in the bottom sediment [<2 mm] is about the same level.

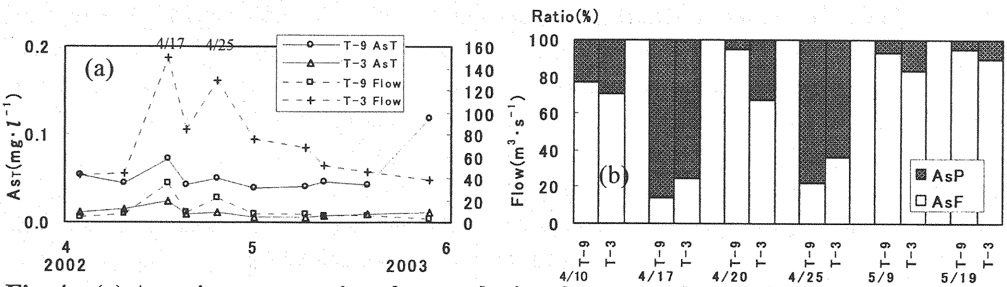

Fig. 4 (a) Arsenic concentration changes during the snowmelt period at T-9 and 3
(b) Ratio of suspended arsenic (As_p) to dissolved arsenic (As_F)

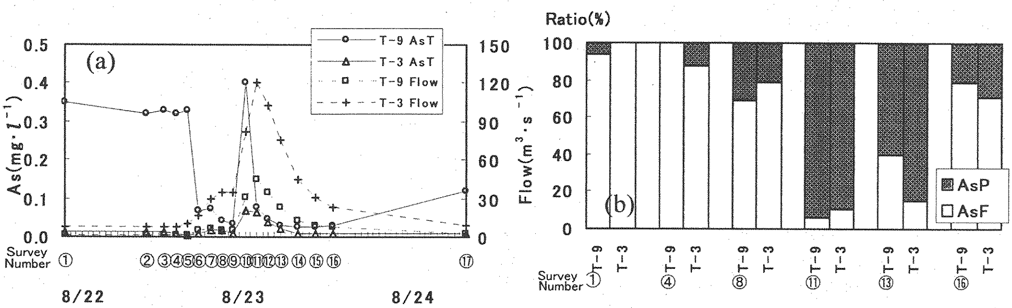

Fig. 5 (a) Concentration of arsenic during the rainfall period at T-9 and 3
(b) Ratio of suspended arsenic (As_p) to dissolved arsenic (As_F)

At Toyama Dam and Moiwa Dam, the arsenic content of bottom sediment [silt·clay] is 143 mg·kg^{-1} and 88.7 mg·kg^{-1}, respectively, and is higher than that of the bottom sediment [<2 mm]. The arsenic content in the fine-grained bottom sediment (silt and clay) remains high upstream of Moiwa Dam, which is at the lower reaches of the Toyohira River. This indicates widespread arsenic pollution of the bottom sediment. This finding supports the phenomenon discussed earlier that arsenic suspended in river water during the ordinary-water period settles and accumulates in the river channel and in the dam reservoir. At the Ichinosawa Dam, fluctuations of arsenic content in the bottom sediment are great and are dependent on the local influence of the hot spring water inflow. At the Toyama Dam and Moiwa Dam, where the inflowing water is homogeneous, local differences within the reservoir are small. Evidence of arsenic content in the bottom sediment of 10.2 - 148 (mg·kg^{-1}) in the main stream of the Shiraoi River in Hokkaido, which is influenced by Nittetsu Mine (Numabe et al. (5)), of 2.5 - 32.9 (mg·kg^{-1}) in the Inagawa River system in Hyogo, which has an influx of spring water containing arsenic (Ashida et al. (1)), and of 1.3 - 3.2 (mg·kg^{-1}) in the Hayakawa River in Hakone, Kanagawa, which has an influx of hot spring water (Kaise (4)). The arsenic content in the bottom sediment of the Toyohira River is as high or higher than any of these.

Table 1 Arsenic content in the bottom sediment

St.	unit	Ichinosawa dam (No.1～4)	Ichinosawa dam (No.5～7)	Toyama dam	Moiwa dam
Bottom sediment (<2mm)**	mg·kg^{-1}	123～244 (185)*	10.1～30.7 (19.6)*	15.2～94.7 (66.3)*	32.6～34.4 (33.5)*
Bottom sediment (Silt·Clay)***	mg·kg^{-1}	98.0～225 (164)*	29.7～54.7 (42.0)*	127～154 (143)*	83.0～95.2 (88.7)*

* Figures in parentheses are arithmetic means.
** Range of grain diameter: 0–2 mm.
*** Range of grain diameter: 0–0.02 mm.

Table 2 Ratio of Grain size of botton sediments

unit:%

		Ichinosawa dam						
	No.	1	2	3	4	5	6	7
Sand	(0.02–2mm)	91	67	76	81	94	94	92
Silt·Clay	(<0.02mm)	9	33	24	19	6	6	8

		Toyama dam			Moiwa dam		
		Upper point	Middle point	Lower point	Upper point	Middle point	Lower point
Sand	(0.02–2mm)	98	72	79	66	73	50
Silt·Clay	(<0.02mm)	2	28	21	34	27	50

Runoff characteristics of arsenic

Runoff characteristics of arsenic were examined from a viewpoint of the relationship between specific discharge and specific discharge load of components. To clarify differences in arsenic runoff mechanism between locations, the discharge and runoff load were recalculated per unit area of the basin.

$$Y = c X^n \qquad (1)$$

〈1〉 $n > 1$: diffuse pollution
〈2〉 $n \fallingdotseq 1$: constant concentration pollution
〈3〉 $n < 1$: dilution pollution

Water quality data of the same points obtained by regular surveys in 1996 - 1997 (17 times in total) were included in this analysis (Tatsumi et al. (9), (10)). Figure 6 shows the above relationship concerning T-9 and T-3. Table 3 shows the constant n when the equation $Y = c \cdot X^n$ is applied to each period (whole survey period, low-water period, snowmelt-flood period, rainfall-flood period) concerning T-9, T-7 and T-3, as well as the correlation coefficient r between log Y and log X. In this equation, Y is specific runoff load in $g \cdot km^{-2} \cdot s^{-1}$, X is specific discharge in $m^3 \cdot km^{-2} \cdot s^{-1}$, c and n are coefficients. Considering how the water quality components vary in concentration with time and with discharge, the runoff characteristics of water quality components can be roughly classified using the constant n as follows (Tachibana (8), Sevens and Smith (7)).

Table 3 Relationships between specific discharge and specific loading of Arsenic ($Y=C \cdot X^n$, Y : $g \cdot km^{-2} \cdot s^{-1}$, X : $m^3 \cdot km^{-2} \cdot s^{-1}$, C,n : Constant)

St.	Period	n	r[1)]	N[2)]
T−9	Whole survey period	0.56	0.75 **	69
	Low water level period	0.40	0.55 **	33
	Snowmelt flood period	1.15	0.95 **	11
	Rainfall flood period	1.28	0.85 **	25
T−7	Whole survey period	1.02	0.91 **	68
	Low water level period	1.17	0.92 **	33
	Snowmelt flood period	1.48	0.84 **	9
	Rainfall flood period	2.20	0.92 **	26
T−3	Whole survey period	1.16	0.94 **	68
	Low water level period	1.15	0.95 **	30
	Snowmelt flood period	1.40	0.88 **	11
	Rainfall flood period	2.05	0.95 **	27

* : $P<0.05$, ** : $P<0.01$ 1) r : Correlation coefficient 2) N : Sample number

A close correlation was found between specific discharge and specific discharge loads at each survey point when the whole survey period and all the data collected during our survey were used. However, it was not a simple linear relationship at T-9. The relationship between discharge and loads showed different tendencies between the low-water period and the flood period, as loads stayed at almost the same level when discharge was low, but they rapidly rose when discharge increases. Specific runoff loads showed great increases at and beyond discharges equivalent to 95-day water discharge ($4m^3 \cdot s^{-1}$ (logQ ≒ -1.74)). Low water is defined as discharge of less than 4 $m^3 \cdot s^{-1}$, snowmelt flood as discharge exceeding 4 $m^3 \cdot s^{-1}$ between April and May, and rainfall flood as discharge exceeding 4 $m^3 \cdot s^{-1}$ between June and December.

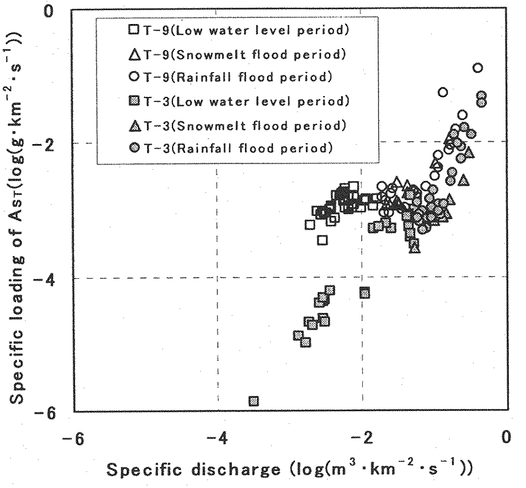

Fig. 6 Relationship between specific discharge ($\log(m^3 \cdot km^{-2} \cdot s^{-1})$) and specific loading ($\log(g \cdot km^{-2} \cdot s^{-1})$) of Arsenic at T-3 and T-9

During the low-water-level period, immediately after hot spring water flowed in, the value of n was smaller than 1 at T-9, and no remarkable changes in the runoff load were observed. The correlation coefficient was also low, indicating that arsenic runoff in the river is dominated by effluents from the hot spring resort, and that it is washed out as dilution pollution. In contrast, at T-7 and T-3, downstream of the dam, n is around 1, and runoff loads increased following the increase in discharge. The correlation coefficient also shows a high positive value, indicating that arsenic runoff shifts to a stable constant concentration level of pollution.

During the flood period, arsenic is washed out as a constant concentration and diffuse pollution, in which n is greater than 1 at each survey point, and a high correlation between log L and log Q is observed. T-7 and T-3 have higher n values than T-9, which indicates that arsenic runoff for these two points is washout runoff, and also shows the influence of the dam reservoir. During the rainfall-flood period, in particular, the arsenic washout pattern is that of a higher-order function whose n is 2 or larger, and the concentration increases by a much greater factor than the discharge. The reason for this is that the arsenic that has accumulated in the bottom sediment during the ordinary-water period is washed out again into the river by agitation of bottom sediment during the flood period. A dam reservoir is believed to be a stable supplier of arsenic. The values of n at each point during the rainfall-flood period exceed those during the snowmelt-flood period. During the autumn rainfall-flood periods, there are remarkable differences in discharge between periods of rainfall and other times, and the arsenic accumulated during the ordinary-water period is washed out in a relatively short time span.

During the snowmelt-flood period, when flooding lasts for a long time, runoff fluctuations level out and runoff of water quality components becomes relatively stable. This is a characteristic of runoff in cold, snowy regions.

Classification of runoff characteristics by principal component analysis

Principal water components were analyzed for T-9, T-7 and T-3 using the water quality data from points downstream from the hot spring water inflow. Figure 7(a) shows loads of principal components of each water quality item. The primary principal components (contribution rate 48%) indicate differences in the pollution source. Loads of principal components of items originating in the point-source hot spring, such as Na^+, Cl^- and As_F, distribute as positive values on the x axis, while those of diffuse items resulting mainly from surface runoff and agitation of the bottom sediment, such as POC, SS, suspended nitrogen (PN), suspended iron (Fe_p) and As_p, distribute as negative values on the x axis. The secondary principal components (contribution rate 28%) are related to changes in discharge. Components such as POC, SS, PN, Fe_p, As_p, Na^+, Cl^- and As_F, which fluctuate greatly with the flow regime, distribute as positive values, whereas components with fewer fluctuations, such as pH and DO, distribute as negative values.

Figure 7(b) shows scores of principal components of each point. At T-9, they distribute as positive values on the x axis, and the primary principal component during the ordinary-water period with low discharge is strongly influenced by the hot spring water as a point source.

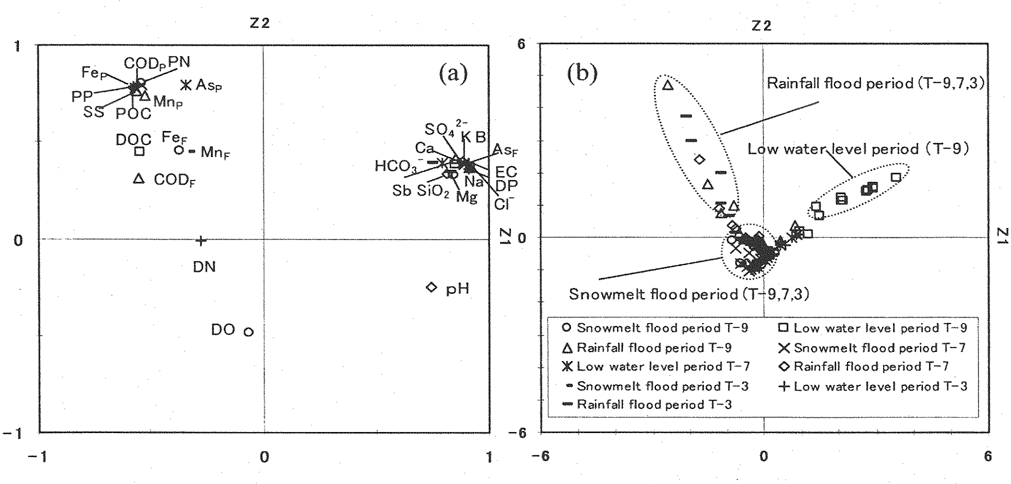

Fig. 7 Results of principle components analysis at T-9, T-7 and T-3
(a) Plot of factor loading of first two principle components. (1st component:48%, 2st component:28%) (b) Plot of factor score of first two principle components.

During snowmelt- and rainfall-flood periods, however, they distribute in the second and third quadrants, which indicate a strong tendency for them to diffuse runoff. At T-7 and T-3, they also distribute in the second and third quadrants during the flood period, showing runoff as diffuse pollution. The primary principle components distribute positively against the secondary principal components at every point during the rainfall-flood period. In contrast, during the snowmelt-flood period when flood lasts for a long time, they distribute near the origin, indicating a smaller washout than during the rainfall-flood period.

The arsenic pollution originates in the hot spring water, whose main components are Na^+ and Cl^-. When the water level is low, it washes out as dilution pollution at T-9, but during flooding it washes out as diffuse pollution at every point, showing behavior typical of suspended components such as SS and POC.

CONCLUSIONS

Hot spring water and mine effluents flow into the Toyohira River, which runs through the center of Sapporo, Japan. In this river, the concentrations of components originating from hot spring water and mine effluents vary according to the flow regime. This phenomenon must be addressed to maintain good water quality management. We studied the behavior of arsenic originating from hot spring water, focusing mainly on the characteristics and mechanism of its runoff and on the relationship between the seasonal changes in arsenic concentration and the changes in flow regime. We found that when the water level is low, the arsenic originating in hot-spring water washes out as dilution pollution or as polluted water whose arsenic concentration remains constant. Downstream from the dam, the arsenic that washes out during flooding results in diffuse pollution. The flow-regime-dependent difference in washout is likely attributed to arsenic accumulation in the bottom sediment at times of low water. The arsenic that accumulates in large amounts in the dam reservoir is stably supplied to the river. During flooding, however, agitation of the bottom sediment increases the washout of suspended arsenic, and so the pattern of arsenic runoff differs depending on the flooding duration in the snowmelt and rainfall periods.

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APPENDIX — NOTATION

The following symbols are used in this paper:

X = Specific discharge;
Y = Specific loading; and
C , n = Constant.

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