

Geochemical distribution and fate of arsenic in water and sediments of rivers from the Hokusetsu area, Japan



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ABSTRACT

Study region: Hokusetsu Region in Osaka, Japan.

Study focus: The As contamination was investigated through the geochemical mapping and analysis of river waters and bed sediments over an area of 440 km². Sulfur from sulfides in rocks and dissolved sulfates in water were compared *via* isotopic analysis to assess their origin and the subsequently released As. The fate of As (transport, binding on settling particles) was evaluated through the total and dissolved fractions of As and trace metals Fe, Mn and Al in river waters.

New hydrological insights for the region: The geochemical mapping showed that As in river water exceeded the maximum limit concentration of 10 ppb in several places. The highest As levels (waters and sediments) correlated well with the surface geologies, concentrating in a halo around granitic intrusion and nearby faults. The isotopic analysis of sulfur revealed the occurrence of two kinds of sulfide mineralizations responsible for As contamination: one from Late Paleozoic submarine volcanism in sedimentary rocks, and one from Late Cretaceous igneous activities in contact-metamorphosed rocks disseminated with sulfides. The transport of As along river courses occurred mainly as a dissolved species rather than adsorbed on Fe/Mn/Al particles, signifying the least role of iron oxy-hydroxides in As adsorption.

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1. Introduction

Arsenic (As) is a minor but ubiquitous element in the shallow crust of the Earth and its hydrosphere. Numerous studies of As contamination of groundwaters and river systems have been published because of the critical role of these reservoirs in the supply of drinking water, agriculture, and the large scale of the affected populations (Fendorf et al., 2010; Smedley and Kinniburgh, 2002). In 1993, the government of Japan adopted the WHO standard value of 10 ppb as a national standard for the maximum concentration limit (MCL) of As in drinking and environmental waters.

Since 1994, As concentrations chronically exceeding the MCL limit have been reported in river and ground waters of the Hokusetsu area, north of Osaka Prefecture (Ogoshi et al., 1996; Tonokai and Mitamura, 1998; Masuda et al., 1999; Ashida et al., 2001; Ito et al., 2003). The As contamination was plausibly derived from pyrite hosted by the Paleozoic-Mesozoic

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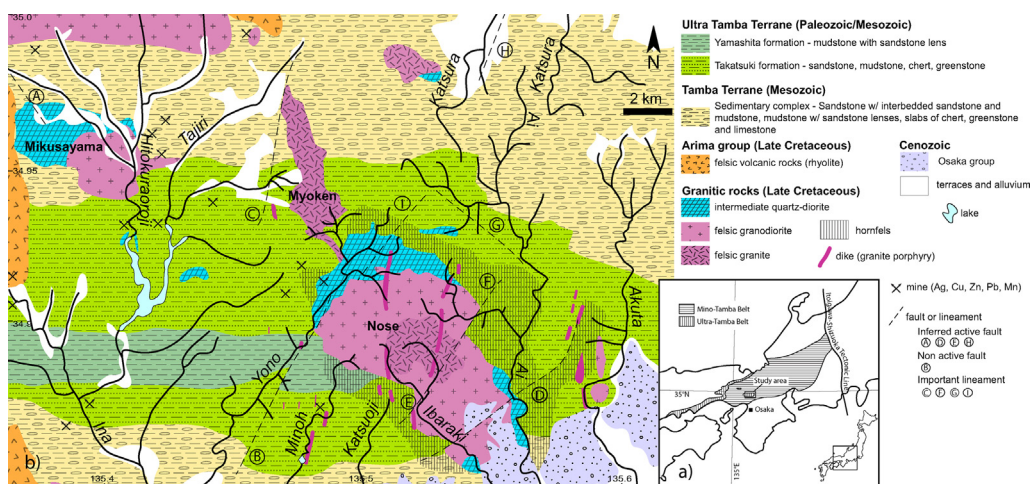


Fig. 1. Context map of the study area (a) and its surface geology (b). The basement geology is composed of Paleozoic/Mesozoic sedimentary rocks intruded by Late Cretaceous felsic and intermediate igneous rocks. Hornfels are found around the Ibaraki Granitic Complex, but their occurrence extends possibly over the shaded area on (b). Mines of hydrothermal veins and skarn deposits are indicated. Faults are designated with letters A to I. B (Satsukiyama fault) has not been active during the Quaternary; sharp lineaments are likely fossil faults. After Miyamura et al. (1972), Matsuura et al. (1995), Okada and Togo (2000) and Miyachi et al. (2005).

sedimentary formations (Ito et al., 2003). However, it was not clear why the pyrite caused such elevated concentrations of As and how wide the contaminated area was.

As-bearing pyrite is a well-known factor responsible for the occurrence of As in water reservoirs. The dissolution of this mineral, induced by oxic conditions, has been incriminated in many cases of groundwater and river contamination (Heinrichs and Udluft, 1999; Berg et al., 2001; Ryan et al., 2011). The Paleozoic-Mesozoic sedimentary rocks mentioned above are widely present in the Hokusetsu area and may host As-bearing pyrite on a large scale, causing As contamination in the shallow groundwater and river water. To understand the natural cycle of As in the hydrosphere and the epigeosphere, it is important to document the mechanism of water contamination and its extent in relation to the water-rock interaction. For this purpose, the Hokusetsu area is suitable because the river chemistry is mainly controlled by the river baseflow, and the geology is thus a constraining factor of the surrounding hydrosphere. This study discusses the distribution of As in the water and bed sediments of rivers in the Hokusetsu area, the mechanisms of its accumulation in the host rocks, and its release into the hydrosphere.

2. Study area and geology

2.1. Geology of the study area

The investigated rivers are tributaries of the Yodo and Ina River systems in Osaka and Hyogo Prefectures, Southwest Japan (Fig. 1a). These streams flow through forest and rural landscapes within their natural riverbed, in the eastern part of the low Hokusetsu Mountains. The magnitude of the discharge of the studied streams varies from river spring (<1 l/s) to large stream (>1.5 m³/s) (MLIT, 2013). The study area is part of the Tamba Belt, a Paleozoic and Mesozoic sedimentary formation that is divided into the Mesozoic Tamba Terrane in the north of the study site and the Paleozoic-to-Mesozoic Ultra-Tamba Terrane in the south (Fig. 1b). These Permian-to-Jurassic terranes are composed of pelagic and terrigenous sediment complexes accreted during the Late Triassic to the Jurassic (Sakaguchi, 1961; Nakae, 1993; Miyachi et al., 2005; Sugamori, 2006). The Tamba Belt formations are overlain in the south by the Quaternary Osaka Group, which is composed of unconsolidated Pleistocene to Holocene sediments. In the west, the formations are overlain by the Late Cretaceous volcanogenic rocks of the Arima group composed of several rhyolitic lavas and tuffaceous formations (Kasama and Yoshida, 1976).

The sedimentary complexes of the Tamba Terrane are mainly composed of sandstone and mudstone, with slabs of chert, greenstone and limestone. The Ultra-Tamba terrane overlies the younger Tamba terrane and comprises the Takatsuki and Yamashita formations. The Takatsuki formation is composed of calcareous or siliceous sandstone, black and red mudstone, and interbedded sandstone and mudstone. The Yamashita formation is mostly composed of bedded mudstone with sandstone laminae and interbedded mudstone with sandstone.

Several plutons intruded into the Tamba Belt during the late Cretaceous (Ishizaka, 1971). In the study area, the main granitic bodies are the Ibaraki and the Mikusayama granitic complexes that intruded around the same time (90–80 Ma; Tainosho et al., 1977). The Ibaraki complex, which had mainly intruded the Ultra-Tamba Terrane, is divided into the northern felsic granite Myoken pluton and the southern Nose pluton. Tainosho (1971) described the Nose pluton as being formed through sequential intrusions of the same parental magma with differential crystallizations from intermediate quartz-diorite

to felsic granodiorite and to granite toward the inner part. The Mikusayama complex, which mainly intruded the Tamba Terrane, is composed of pyroxene quartz-gabbro, granodiorite and granophyre. The chemical and modal compositions of both granitic complexes are very similar, although the Ibaraki quartz-diorite seems richer in biotite than the Mikusayama quartz-gabbro. Both complexes were derived from a dioritic or tholeiitic parental magma, from the same series of magmatism (Tainosho et al., 1977). The study area also bears numerous granite-porphyritic dikes that intruded during the late Cretaceous as well but are likely posterior to the granitic intrusions (Matsuura et al., 1995; Miyachi et al., 2005). In some places, the Tamba sedimentary rocks were metamorphosed into hornfels and quartzite by contact with these intrusive rocks (Miyamura et al., 1972; Matsuura et al., 1995; Miyachi et al., 2005).

Two types of ore mineralizations can be recognized in the Inner Zone of Southwest Japan, where the study area is located. The first type of ore deposit is identified as stratiform Cu-sulfide and bedded Mn deposits that formed with intense submarine volcanism during the Late Paleozoic/Early Mesozoic prior to the accretion of the present Mino-Tamba belt (Sato and Kase, 1996; Tatsumi et al., 1970). The other type of mineralization is associated with the magmatic activities from the Late Cretaceous to Early Paleogene, including the plutons described above and the volcanic rocks of the Arima Group. This magmatism led to the formation of W-Sn, Cu-Ag-Au and Cu-Pb-Zn ores, mainly as hydrothermal veins, including the Tada and Ohtani mines in the study area. Most of the mines exploiting these ore deposits were of modest size, and all of them were closed in the 1980's. These abandoned mines near the studied rivers are indicated in Fig. 1b.

There are a number of faults and lineaments in the study area (Okada and Togo, 2000) (Fig. 1b). Tainosho (1971) and Matsuura et al. (1995) reported a fault (I) running through the northeastern part of the Nose pluton that could be a continuation of the Satsukiyama fault (B), although it was not described in the inventory report by Okada and Togo (2000). While most of the faults are not active, they constitute potential pathways for the infiltration of meteoric waters and the circulation of groundwater within the host rocks.

2.2. Previous studies

Groundwater contaminated with As (10–60 ppb) has been reported in 300-m-deep wells drilled into the Osaka Group formations in Takatsuki City (southeastern edge of Fig. 1b) of which the sediments contained up to 400 ppm As (Tonokai and Mitamura, 1998). The As in the host sediments was thought to be derived from ore minerals transported from the aforementioned ore deposits occasionally found in the hinterland. After the Kobe earthquake in 1995, As concentrations of the Ina River (western part of Fig. 1b) peaked at 42 ppb due to the inflow of highly As-contaminated saline spring water, which was thought to be residual water related to the ore mineralization. The change in the inflow flux of As-contaminated water was likely triggered by changes in pathways of deep groundwater along the faults crossing the mineralized region (Ashida et al., 2001; Ogoshi et al., 1996).

As-contaminated groundwater issued at springs (~25 ppb) was also observed near the Todoromi and Fushio villages on the Yono River (Masuda et al., 1999). The dissolution of sulfide minerals (mainly pyrite) in the host sedimentary rocks was the presumed source of dissolved As. Indeed, Ito et al. (2003) found that the bulk sedimentary rocks contained between 4.2 and 16.4 ppm As, and the separated pyrite minerals contained up to 0.73 wt% As. The geochemical data of dissolved As and sulfates in those spring waters had a clear correlated behavior, whereas the analysis of the S isotopic ratio from SO_4^{2-} and the surrounding rocks indicated the sulfidic origin of the dissolved sulfates (Ito et al., 2003).

In their geochemical mapping work of Central Japan, Ohta et al. (2005) concluded that As in the riverbed sediments derived from the Jurassic accretionary complex rocks was likely due to the Paleozoic/Mesozoic deep sea-floor hydrothermal activity that led to the formation of the Cu and Mn deposits described by Sato and Kase (1996) and mentioned in Section 2.1. Therefore, the accumulation of arsenic in the host rocks of the study area and the subsequent contamination must also be examined through mineralizations related to this volcanogenic process.

3. Methods

3.1. Sample collection

3.1.1. Waters samples

A total of 163 water samples were collected from the Ai, Akuta, Hitokuraoraji, Ibaraki, Katsuoji, Katsura, Minoh and Yono Rivers between 2011 and 2015 (see sampling locations in Fig. 2a). The waters were sampled from the middle of the stream whenever possible. All rivers are small enough for the bottom and surface waters to be well-mixed, and the sampling depth was not considered for the water chemistry. At each sampling station, a set of water samples was collected as follows: samples for major anion analysis were filtered with 0.45 μm glass filters and not acidified, and samples for major cations, As and trace element analysis were preserved with 1:2 (v/v) HNO_3 . Among them, samples for analysis of the dissolved concentrations were filtered with 0.45 μm glass filters, whereas those for total concentrations were directly sampled from the stream. All water samples were collected with as little dead space as possible in polyethylene bottles soaked overnight in HNO_3 and rinsed 3 times with ultrapure water. The physico-chemical parameters of the river waters were measured *in situ* during the sampling with adequate probes plunged into the stream for temperature, pH, electrical conductivity, oxidation-reduction potential and dissolved oxygen.

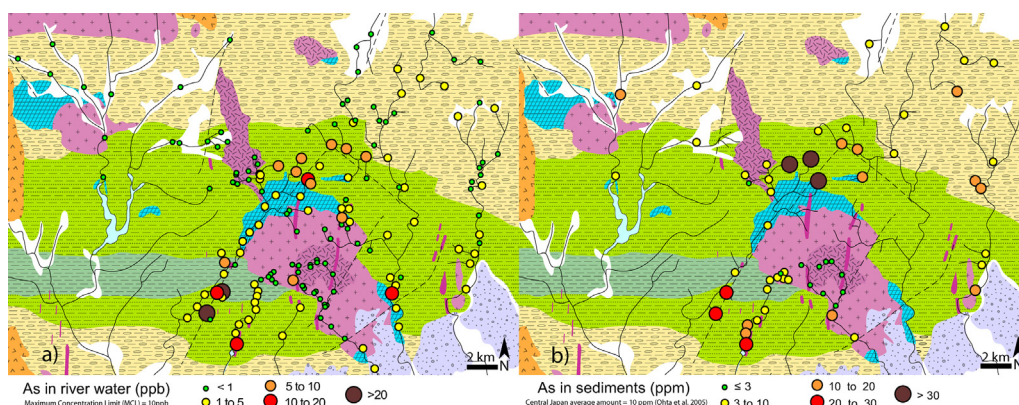


Fig. 2. Distribution of As concentrations in riverwaters (a) and in riverbed sediments (b). The highest concentrations (maximum: 38.3 ppb As in water and 55.2 ppm As in sediments) are distributed in a halo around the Ibaraki Granitic Complex.

3.1.2. Sediments samples

Riverbed sediments can be used as a proxy to elucidate the elemental distribution in surface geology (Salminen et al., 1998; Halamić et al., 2001; Imai et al., 2004; Ohta et al., 2005). During the water sampling, riverbed sediments were also collected at 56 of the 163 locations on the aforementioned rivers (see sediments sampling locations in Fig. 2b). The sediments were collected from the riverbed with a scoop and stored in zipped bags until arrival at the laboratory on the evening of sampling day.

3.1.3. Sulfur isotopes samples

Ito et al. (2003) used the isotopic ratio of sulfur to specify the source of dissolved sulfates in contaminated spring waters. Sulfur isotopes are useful tools for distinguishing the sources of sulfates in an aquatic environment (Yang et al., 1996; Nordstrom et al., 2007). The isotopic signature of S in rocks is also used to define the origin of sulfides (Field, 1966; Seal, 2006). Many papers have reported the isotopic signatures of the various sulfur reservoirs (mineral weathering, soil, air, etc.) in the Inner Zone of Southwest Japan (Yamamoto, 1974; Miyoshi et al., 1988; Ishihara and Sasaki, 1991; Mizota and Sasaki, 1996; Sato and Kase, 1996). These studies are thus also useful for identifying the source of SO_4^{2-} in the studied waters in relation to the As-bearing sulfide minerals. Therefore, in December 2014, river waters for sulfur isotope analysis were sampled from selected points to evaluate the origin of sulfates in As-contaminated rivers. At each location, 1 l of river water was collected. A rock sample of quartzite with large pyrite grains (~ 1 mm) was also collected at the location where the As concentration in sediments was the highest (the upper reach of the Yono River).

3.2. Analytical methods

3.2.1. Water analysis

The water samples were analyzed for alkalinity by HCl titration on the day of sampling, for major anions by Ion Chromatography (IC Dionex 120), and for major cations by Atomic Adsorption Spectrometry (AAS630 Shimadzu). The AAS analysis of Ca^{2+} and Mg^{2+} was enhanced with the addition of LaCl to suppress interferences with others elements (Al, Si, SO_4) as advised by Koga et al. (2004).

In addition to the spatial distribution of As in rivers, the fate of this element along the river course was addressed. Its concentrations would be controlled by adsorption-desorption reactions with suspended matter or sediments of the river system, which may blur the primary As content of sediments derived from source-rock. Thus, As and trace elements such as Al, Fe and Mn commonly found in adsorptive matter, were analyzed for the filtered and unfiltered waters to assess any sorption/deposition process and the exchanges of these elements in the water column. The partitioning of these elements was evaluated with the Dissolved Transport Index (DTI) defined by Martin and Meybeck (1979) using the total and dissolved concentrations for each element. The DTI indicates the percentage of an element present as a dissolved species and is calculated as follows:

$$\text{DTI} = \frac{\text{dissolved concentration}}{\text{total concentration}} \times 100 \quad (1)$$

The dissolved concentration was determined for the $0.45 \mu\text{m}$ filtered waters. This filter size is large enough to analyze the dissolved components although colloidal materials cannot be completely removed (e.g., Nielsen, 2005 and references therein). The DTI is then regarded as the maximum ratio of the dissolved concentration of an element relative to its total concentration in river water. Trace elements in the filtered and unfiltered water fractions were analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS SPQ9700 Hitachi).

Table 1
Arsenic concentrations in standard reference materials (SRMs) used during alkali fusion.

SRM	Measured (ppm As)	Certified (ppm As)	Difference (%)
JSd-1	1.59	2.42	–21
JSd-1	1.63	2.42	–20
JSd-1	1.63	2.42	–19
JSd-1	1.66	2.42	–19
JSd-1	1.74	2.42	–16
JSd-1	1.77	2.42	–16
JSd-1	1.81	2.42	–14
JSd-1	2.61	2.42	+4
JSI-1	12.61	14.9	–8
JSI-1	13.00	14.9	–7
JSI-1	13.91	14.9	–3
JSd-2	33.81	38.6	–7
JSd-2	33.98	38.6	–6

3.2.2. Sediments analysis

Upon arrival at the laboratory, sediments ranging from fine fractions to coarse sand grains were frozen and then vacuum-dried to prevent the redox sensitive minerals (e.g., sulfide minerals) from chemical alterations. A dried aliquot was sieved (#80 mesh, 250 μm , Nichika) and milled to a very fine powder with an automatic agate mortar. The As content of the sediments was determined by alkali fusion. Briefly, the powdered samples were fused with granular Na_2CO_3 at a 1:10 ratio and at 900 °C for 45 min. The fused material was dissolved with 1:1 (v/v) HNO_3 and ultra-pure water, brought to 100 ml completion, and stored until analysis (Seddique et al., 2008). The obtained solutions were diluted to 1:50 and analyzed by ICP-MS (SPQ9700 Hitachi) in a Collision-Reaction Interface cell with H_2 gas. For checking the accuracy of the fusion and the analysis, the Standard Reference Materials (SRMs) of riverbed sediments JSd-1 and JSd-2, as well as slate JSI-1 (Geological Survey of Japan), were processed in the same manner together with the samples. The measured As concentrations from these duplicate or triplicate SRMs were mostly within 8% error, whereas the maximum error was approximately 21% when the As concentration appeared to be low (e.g., JSd-1, 2.42 ppm As) (Table 1).

3.2.3. Sulfur isotopes analysis

The river waters sampled for S isotopes were filtered in the laboratory just after coming back from the field, then they were processed according to Yanagisawa and Sakai (1983). As for the quartzite, small pieces of the rock were crushed and milled manually into fine powder in a tungsten carbide mortar. Pyrite in the powder was oxidized with H_2O_2 (30%, Wako Ind. Japan) until bubbling ceased, acidified with 10 ml of 10% (v/v) HCl, and left on a hot plate for 2 h. The obtained solution was filtered to retain the non-oxidized matrix and 10% (v/v) HNO_3 was added to dissolve the remaining iron oxides.

For both the river water and quartzite samples, 0.5 M BaCl_2 was added to the obtained solutions, which were put on a hot plate overnight to let the BaSO_4 precipitates mature. For each sample, BaSO_4 was individually collected on a 0.45 μm cellulose filter and dried at 60 °C. The isotopic ratio of sulfur of the precipitates was analyzed after decomposition to release SO_2 using an Element Analyzer (IsoPrime EA, Micromass) coupled to a Gas-Mass Spectrometer (GV Instrument, Ltd.).

4. Results

4.1. Arsenic distribution in river waters and bed sediments

The analytical results for the waters and sediments are grouped by rivers and summarized in Table 2. We analyzed major and minor elements; however, only the As and its related composition are discussed here. The spatial distributions of As in river waters and riverbed sediments are shown in Fig. 2.

4.1.1. As in river waters

The As was maldistributed in rivers of the study area. Notably, concentrations greater than 5 ppb appeared in a halo around the Ibaraki Granitic Complex especially at the quartz-diorite margins, in contrast with waters sampled in sedimentary rocks far from the plutons. However, similar distributions of high As concentrations were not observed around the Mikusayama granitic complex, despite the occurrence in this complex of pyroxene quartz-gabbro with chemical compositions similar to the Ibaraki quartz-diorite.

Concentrations of As were less than 1 ppb in river waters originating from or flowing through the felsic parts of the Ibaraki Granitic Complex in both the Nose and Myoken plutons, except for a spring water sample (5.9 ppb) on the upper reach of the Ibaraki River. The As concentrations of water were also low in rivers flowing in the northern and eastern parts of the sedimentary formations. In these areas, concentrations consistently remained less than 3 ppb, which would be the background concentration of arsenic in rivers flowing through sedimentary formations of the Hokusetsu area.

Six water samples exceeded the WHO standard of 10 ppb As, and four of them were from the Yono River. Among those, the most contaminated waters (38.3 and 34.1 ppb) were taken in the source area of two small Yono tributaries, in the

Table 2
Chemical and isotopic composition of riverwater and riverbed sediments of small streams in the Hokusetsu area.

River		Temperature (°C)			pH			EC at 25 °C (μS/cm)			SO ₄ ²⁻ (ppm)			As (ppb)			As in sediments (ppm)			δ ³⁴ S (‰CDT)				
		Min	Max	Med	Min	Max	Med	Min	Max	Med	Min	Max	Med	Min	Max	Med	Min	Max	Med	Water	Rock			
Ai R.	(n=38)	11.5	28.2	17.1	5.2	9.1	8.1	37	462	130	1.6	43.5	5.7	0.2	10.9	1.0	(n=6)	6.1	19.9	9.2				
Akuta R.	(n=17)	13.1	22.0	17.0	7.1	8.8	8.4	74	200	149	1.6	33.5	7.1	0.6	3.4	1.0	(n=6)	1.0	14.6	12.2				
Ibaraki R.	(n=25)	7.9	15.9	12.1	6.9	8.1	7.8	43	172	96	2.6	13.3	6.9	0.1	5.9	0.5	(n=12)	1.0	13.5	2.1	+3.9			
Ina R.	(n=13)	13.3	18.2	16.4	7.3	8.7	8.3	48	163	85	3.0	10.1	5.6	0.5	1.0	0.6	(n=12)	4.9	11.2	7.2				
Katsuoji R.	(n=2)	12.4	14.1	13.3	7.7	7.9	7.8	111	496	303	4.9	170.9	87.9	2.0	4.6	3.3								
Katsura R.	(n=12)	12.4	20.5	17.4	4.3	8.8	8.1	49	205	130	1.9	23.8	7.5	0.3	1.6	0.7	(n=5)	5.8	13.5	7.1				
Minoh R.	(n=18)	8.6	13.6	12	7.2	8.1	7.7	64	151	112	3.4	10.9	7.4	0.2	11.5	1.5	(n=11)	2.8	20.8	8.1	+8.9	+5.0	+3.7	
Yono R.	(n=42)	6.7	26.1	12.1	6.9	8.9	7.8	22	238	65	1.0	31.7	6.6	n.d.	38.3	2.0	(n=12)	2.6	55.2	8.1	+2.6	+6.8	+6.4	-8.8

Bold numbers indicate As concentrations above the WHO limit (10 ppb).

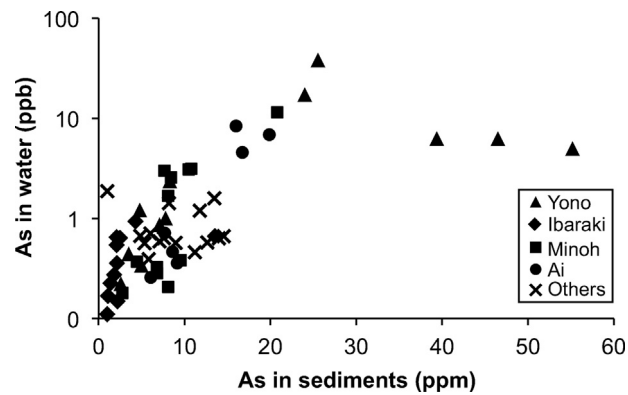


Fig. 3. As concentrations in river bed sediments and waters. Samples with water concentrations >3 ppb As correlated positively, except for Yono River samples from the hornfels area (triangles on the right). Samples with water concentrations <3 ppb As showed a more scattered behavior. Others rivers are Akuta, Hitokuraoroji, Katsuoji, Katsura and Tajiri Rivers.

Todoromi village. Masuda et al. (1999) had previously reported the As contamination of the local spring waters (*i.e.*, resurging groundwater) along these tributaries. In the present study, a large increase in As concentrations (from 1.2 to 34.1 ppb) was observed in the tributaries waters, in association with an increase of water temperature (from 6.7 to 12.1 °C), EC (from 24 to 58 $\mu\text{S}/\text{cm}$), HCO_3^- (from 15 to 47 ppm) and SO_4^{2-} (from 4.6 to 9.3 ppm). Those correlated increases indicated the mixing of the young river waters with the inflow of a more mineralized water that obviously created the As contamination. Other samples with As concentrations greater than 10 ppb were found on the upper reach of the Yono River (10.7 ppb), the lower reach of the Ai River (10.9 ppb), and the lower reach of the Minoh River (11.5 ppb) where an local increase of As, EC, and SO_4^{2-} was also observed.

Overall, the waters containing more than 5 ppb As were observed in relation to the following geology: (1) waters from the upper reach of the Yono River (5.0–10.7 ppb) were flowing in the hornfels area of the contact-metamorphosed quartzite near the quartz-diorite intrusion; (2) waters from the middle reach tributary (8.4 ppb) and the lower reach (10.9 ppb) of the Ai River were located at the margin of the quartz-diorite/granodiorite intrusion and in the vicinity of the quartz-diorite intrusion, respectively; and (3) waters from the lower reach of the Minoh River (11.5 ppb) were located in an area marked by magmatic intrusion. In addition, highly As-contaminated river waters were commonly found near faults and lineaments. The anomalous increase of As concentrations at Todoromi appeared where the Satsukiyama non-active fault (B in Fig. 1b) is running across the tributaries. On the Ai River, the high As concentrations appeared where the I and G faults cross the stream course. This implies that these fracture zones are pathways of As-containing groundwaters.

4.1.2. As in riverbed sediments

The As concentration of riverbed sediments ranged from <1 to 55.2 ppm with an average concentration of 10.3 ppm, which is consistent with the typical average As concentration of 5 to 10 ppm in sedimentary rocks (Smedley and Kinniburgh, 2002), and concordant with that of riverbed sediments from Central Japan (8 ppm) (Ohta et al., 2005). The highest As concentrations (39.4 to 55.2 ppm) were observed in the sediments derived from hornfels and quartzite at the upper reach of the Yono River. The quartzite was heavily disseminated with pyrite, but the river waters taken from the same location had As concentrations of less than 10 ppb. On the other hand, no such elevated As contents were measured in bed sediments (11 ppm) near the Mikusayama complex with the quartz-gabbro intrusion in contact with sedimentary rocks (Tainosho et al., 1977) or nearby small hydrothermal Cu veins.

At the Todoromi tributaries, the As concentrations of the sediments derived from sandstone and mudstone averaged 24.8 ppm. This was higher than the concentration of whole rocks containing pyrite (4–16 ppm As) measured by Ito et al. (2003). At the anomaly location on the Minoh River, sediments had 20.8 ppm As, whereas As concentrations of sediments taken upstream remained less than 11 ppm. There, contact-metamorphosed rocks and large dikes were observed, and a small, now closed, mine of hydrothermal Cu vein was also reported upstream. Thus, the As occurrence may be related to the mineralization induced by the localized magmatism.

Apart from the high As-bearing samples, riverbed sediments derived from the sedimentary rocks of the Tamba Belt commonly had a median As content of 8.4 ppm ($n=33$). When excluding samples with suspected mineralization, this is in accord with the median concentration (8 ppm As) of sediments derived from the accretionary complex in Central Japan, as computed by Ohta et al. (2005). Bed sediments of the Ibaraki River taken from the granitic center of the Nose pluton were depleted in As, with concentrations less than 3 ppm. A sediment sample containing 13.5 ppm As was taken in the granodiorite area, but the As concentration of water from the same location was low (0.7 ppb).

The relationship between the As concentrations of river waters and riverbed sediments (Fig. 3) generally showed a positive correlation. The correlation was especially noticeable for waters with As concentrations greater than 5 ppb in the Ai, Minoh, and Yono Rivers taken from the sedimentary formations. The outlying group of low As concentrations in water associated

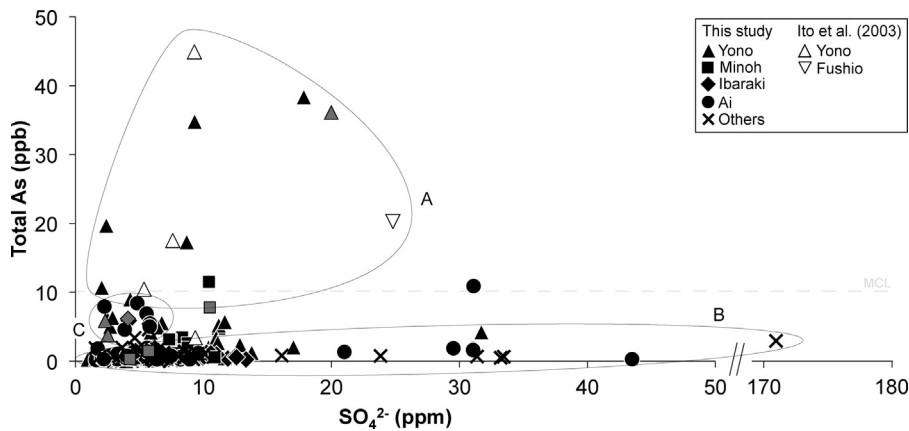


Fig. 4. Dissolved SO_4^{2-} and As concentrations in river waters. Data include river water samples from this study (black symbols), samples for sulfur isotopes analysis from this study (grey symbols) and Ito et al. (2003) (open symbols). Others rivers are Akuta, Hitokuraoroji, Katsuoji, Katsura and Tajiri Rivers. For the enclosed areas A, B and C, see in the text.

with As-rich sediments (>40 ppm As) corresponded to the samples from the area of hornfels and quartzite disseminated with pyrite.

4.2. Dissolved sulfates and sulfur isotopic ratios

The As concentrations of river waters were high in areas where sulfide mineralization was suspected (e.g., a mine near the Minoh river or sulfides in the Todoromi sandstone and greenrock). It was previously hypothesized that the As-contaminated water formed *via* dissolution of pyrite, which contained up to 0.73 wt% As (Ito et al., 2003). Thus, the concentrations of As and dissolved SO_4^{2-} , as well as the sulfur isotope ratio of SO_4^{2-} of waters, were examined to evaluate the effect of pyrite oxidation as a common source of As in the rivers of this study area.

The relationship between the dissolved SO_4^{2-} and As concentrations is shown in Fig. 4. The plot comprises samples of river waters collected during this study (black and grey symbols) and spring waters reported by Ito et al. (2003) (open symbols). The plots show two distinctive groups (A and B in the figure) and an intersecting one (C).

Group A comprises the As-contaminated waters with low dissolved sulfate concentrations (<25 ppm), with the exception of a sample from the Ai River (10.9 ppb As; 31 ppm SO_4^{2-}). Samples containing As concentrations >10 ppb exhibited a positive correlation between As and SO_4^{2-} implying pyrite dissolution, as suggested by Ito et al. (2003). However, once entering the river streams, the As-contaminated spring waters were diluted with ambient meteoric water containing SO_4^{2-} derived from different sources, and the relationship of these two components became ambiguous.

Group B shows low concentrations of As irrelevant to the SO_4^{2-} concentrations. Most of the samples collected far from the plutonic intrusion belong to this group and have SO_4^{2-} that clustered between 0 and 15 ppm. The waters with elevated concentrations of SO_4^{2-} were sampled near anthropogenic activities such as a stone quarry, a waste treatment plant (171 ppm SO_4^{2-}), a landfill, fish farming, highway works, and household wastewaters. The effluents from those activities were almost free of As, and anthropogenic inputs of this element could be excluded from the studied rivers. The concentrations of As less than 3 ppb were then due to mineral dissolution, as the surrounding geological formations still contain small amounts of As (Ohta et al., 2005).

Group C is at the intersection of the contaminated waters of group A and the low-As waters of group B. The samples of this group were without serious anthropogenic SO_4^{2-} inputs and exhibited a mild As contamination.

Fig. 5 shows the map of the $\delta^{34}\text{S}$ values (as ‰_{CDT}) of dissolved SO_4^{2-} in selected river waters and the $\delta^{34}\text{S}$ values of rock sulfides. Fig. 6 plots the relationship between $\delta^{34}\text{S}$ and its related SO_4^{2-} concentrations, showing a decreasing trend in $\delta^{34}\text{S}$ with increasing SO_4^{2-} concentration, plausibly due to the increasing contribution of pyrite dissolution.

The $\delta^{34}\text{S}$ values of SO_4^{2-} ranged from +2.6 to +8.9‰, which corresponds to the $\delta^{34}\text{S}$ ranges for sulfide-sulfur in Paleozoic stratiform deposits (0 to +5.0‰) (Sato and Kase, 1996) and the sulfate-sulfur in native inland Japanese soils (+1.7 to +8.9‰) (Mizota and Sasaki, 1996).

The $\delta^{34}\text{S}$ value (−8.8‰) of the pyrite in quartzite rock was much lower than those of the sedimentary rocks analyzed by Ito et al. (2003), and in the range of igneous sulfides. The waters from the quartzite area had sulfate- $\delta^{34}\text{S}$ values of +6.8‰ and +6.4‰, which are much higher than the $\delta^{34}\text{S}$ of pyrite in this rock.

The waters from the uppermost reaches of rivers yielded $\delta^{34}\text{S}$ values greater than +5‰, and they contained very low concentrations of SO_4^{2-} and As (Fig. 4), suggesting a small contribution to the water chemistry of anthropogenic SO_4^{2-} or SO_4^{2-} and As originating from pyrite dissolution. Thus, the $\delta^{34}\text{S}$ of these young waters must be that of the background sulfates, *i.e.*, those of inland soils.

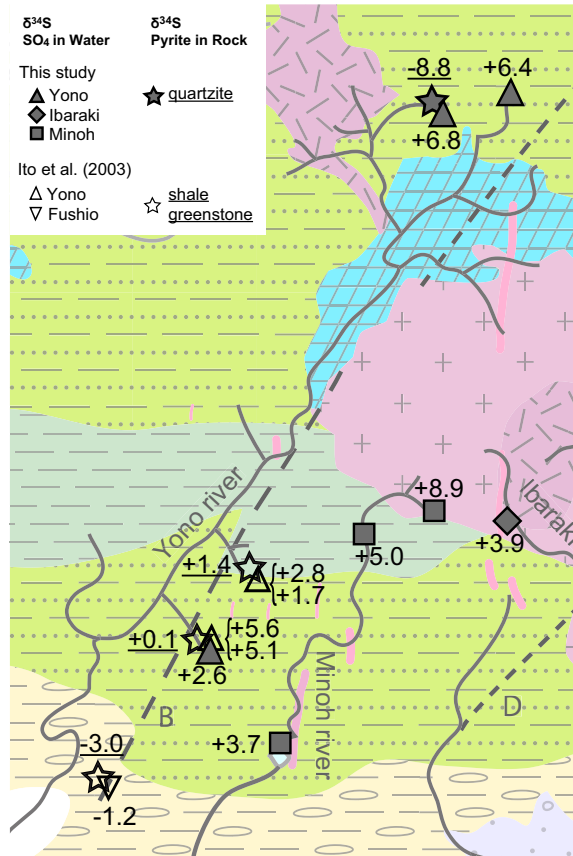


Fig. 5. Mapping of $\delta^{34}\text{S}$ isotopic ratio from pyrite in rocks of the study area (star) and from dissolved sulfates in water (other symbols). Grey symbols: data from this study. Open symbols: data from Ito et al. (2003).

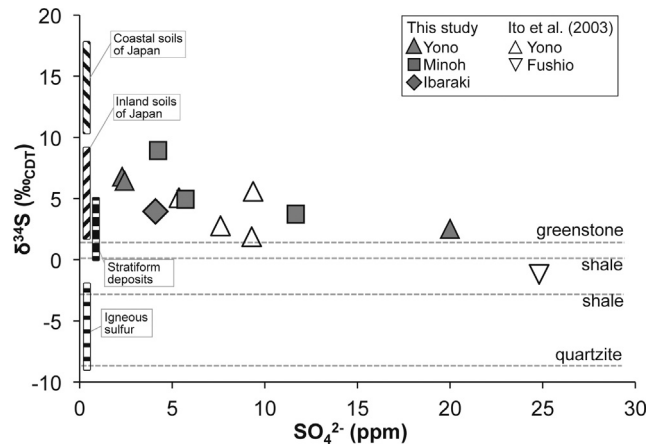


Fig. 6. Biplot of SO_4^{2-} concentrations of river water and their corresponding $\delta^{34}\text{S}$ isotopic ratio. Dashed lines represent the $\delta^{34}\text{S}$ isotopic ratio of pyrite from rocks of the study area. Data show a general mixing process between high $\delta^{34}\text{S}$ ($>+5\%$) from young waters impacted by sulfur soil infiltrations to $\delta^{34}\text{S}$ ($<0\%$) from pyrite dissolution in rocks. After Mizota and Sasaki, 1996 (soil data), Sato and Kase (1996) (stratiform deposits) and Ishihara and Sasaki, 1991 (igneous sulfur).

The $\delta^{34}\text{S}$ of the other river waters and the contaminated spring waters reported by Ito et al. (2003) plotted within the range of $\delta^{34}\text{S}$ of stratiform deposits, although it overlapped with the $\delta^{34}\text{S}$ of inland soils. Data for water containing As concentrations greater than 10 ppb (Group A on Fig. 4) have $\delta^{34}\text{S}$ closer to that of stratiform deposits. One spring water, with 19 ppb As, 8 ppm SO_4^{2-} and $\delta^{34}\text{S} +2.8\%$, was clearly caused by pyrite dissolution, as this water issued directly from the

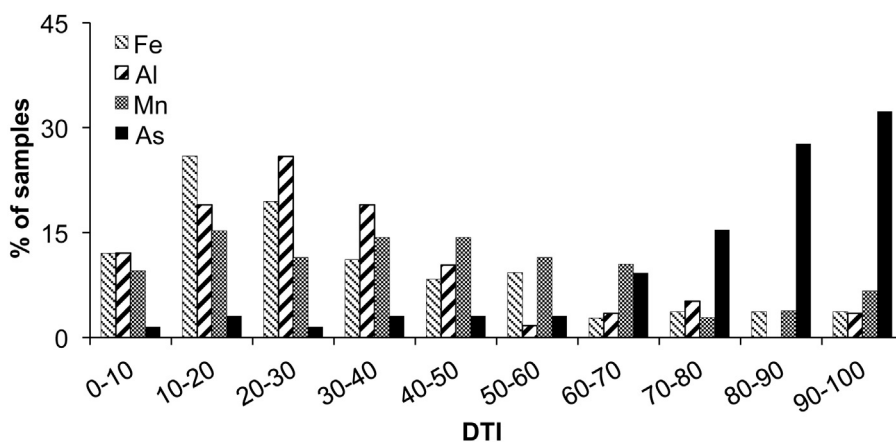


Fig. 7. Distribution of Dissolved Transport Index (DTI) for Fe, Al, Mn and As. Most of DTI_{As} range between 70 and 100, while DTI_{Fe} , DTI_{Al} and DTI_{Mn} range mostly below 40. Fe n = 107; Al n = 56; Mn n = 104; As n = 66. DTI = Dissolved ($<0.45 \mu\text{m}$) conc./Total conc. $\times 100$.

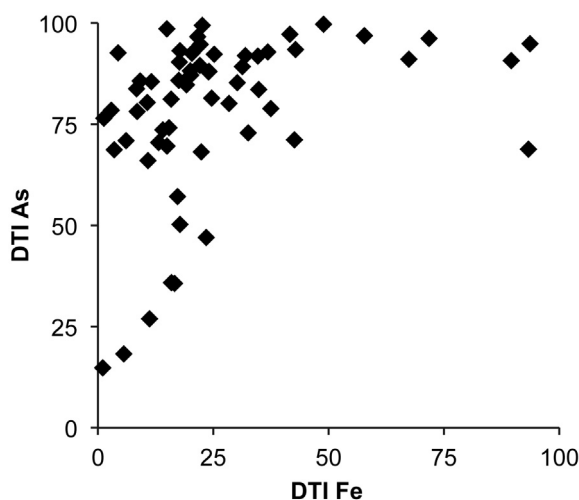


Fig. 8. Biplot of DTI_{Fe} and DTI_{As} . Most of DTI_{As} plot between 70 and 100, meaning that As is mainly present as a dissolved phase in water. For $DTI_{As} < 50$, DTI_{Fe} and DTI_{As} behave together, showing that for low As concentrations (<1 ppb, samples from Ibaraki River), most of the element is adsorbed on Fe particles.

basement rock (Ito et al., 2003). Thus, the $\delta^{34}\text{S}$ values less than $+2.8\%$ of As-contaminated waters must be explained by the large contributions of dissolved pyrite in the host-rocks.

4.3. Partitioning of Fe, Al, Mn, and As

Amorphous Fe-, Al-, and Mn- hydroxides/oxyhydroxides/oxides are known to be adsorbents of As at neutral pH (Dixit and Hering, 2003), especially under oxic conditions. The concentrations of Fe, Al, Mn, and As were compared in filtered and unfiltered river waters, as an assessment of partitioning between the particulate and dissolved fractions, by the mean of the DTI. Fig. 7 represents the distribution of the DTI for Fe, Al, Mn, and As. It shows that DTI_{As} is greater than 70 for 75% of the samples, meaning that for $\frac{3}{4}$ of the samples, at least 70% of As was in the dissolved phase rather than adsorbed on $>0.45 \mu\text{m}$ particles. But the percentages of samples with a $DTI \geq 70$ fell to 11%, 9%, and 13% for Fe, Al, and Mn, respectively. Most of the samples had DTIs <40 for these elements, and their respective median DTI reckoned at 24, 25 and 40. Therefore, As exists primarily as a dissolved species in water, whereas most of the Fe, Mn, and Al is present within the $>0.45 \mu\text{m}$ particulate fraction, likely as clay particles, amorphous oxides, and/or colloids. The adsorptive behavior of As onto Fe particles could be estimated in Fig. 8 with the plot of DTI_{Fe} and DTI_{As} . No relationship between the two quantities is observable, except for low DTI that corresponded to the very low concentrations of As (<1 ppb) in the waters sampled from the upper reaches of the Ibaraki and Yono Rivers that flow through As-depleted granite. These results suggest that the adsorption of As on Fe-particles is minimal and it would remain in the dissolved fraction of the water column.

5. Discussion

5.1. Role of the geology in the arsenic distribution

The distribution of As in river waters is concordant with the distribution of the subsurface geology and consequently, with that of riverbed sediments derived from regolith (Fig. 3). This means that the water chemistry is mainly controlled by the baseflow chemistry *via* water-rock interactions. In the study area, the background As concentration of river waters flowing in the sedimentary rock areas is less than 3 ppb.

Most of the high As concentrations appear in a halo around the Ibaraki Granitic complex, implying that the As contamination is related to the magmatic intrusion. However, As is scarce in river waters and bed sediments near the Mikusayama complex, despite both complexes having a similar magmatic origin. This can be explained by the following three possibilities: 1) a lack of contact-metamorphosed sedimentary rocks that contain disseminated As-bearing pyrite, 2) a discharge ($>0.5 \text{ m}^3/\text{s}$ (MLIT, 2013)) large enough to dilute inputs of As-contaminated groundwater (measured at approximately 0.61/s near the Ibaraki complex), and 3) no prominent fault or lineament to work as an infiltration path for oxic groundwater.

The high (>10 ppb) As concentrations of river water are not solely due to the presence of mineralization. For example, the sediments derived from the quartzite heavily disseminated with sulfides had a high As level (55 ppm), which indicates an enrichment of this element at the time of the contact-metamorphism. But the As concentrations of river waters at this location were less than 10 ppb. The high As concentrations. The As would not be mobilized easily because of the induration of the quartzite matrix compared with the non-metamorphosed sedimentary rocks of the study area. The contamination is apparent at locations where a deeper contaminated groundwater flows into rivers of small discharge and in the area of non-metamorphosed rocks, in which the pyrite oxidation-dissolution would occur, but still in the vicinity of the plutonic intrusion.

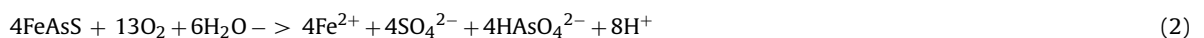
Faults play an important role in the oxidation of pyrite, as seen with the Satsukiyama fault, because they promote the percolation of oxygenated meteoric waters through sheared sedimentary formations that have a higher specific surface area contact. The reaction of pyrite dissolution is then enhanced, and the release of As loads becomes higher than in unfractured host-rocks

5.2. Role of sulfide dissolution in arsenic contamination

The $\delta^{34}\text{S}$ values of sulfides reported for the geologic terrain including the study area can be grouped into two different ranges, according to the type of sulfide deposit. The sulfur isotopes of sulfides largely fractionate in the sediments due to the variable redox conditions and the associated biological activities. But the sulfur isotope ratio of sedimentary sulfides fixed in oceanic crust also changed with geological settings and time; the $\delta^{34}\text{S}$ of those from the Permian to the Jurassic were -10 to -30% on average (Canfield, 2004), whereas sulfide minerals found in massive subseafloor sulfide deposits during the same period were within 0 to $+8\%$ (Seal, 2006). The Mino-Tamba sedimentary formations, to which the study area belongs, were accreted from the Permian to the Jurassic (Charvet, 2013; Isozaki, 1997) and host some of these massive stratiform Cu deposits, with $\delta^{34}\text{S}$ of sulfides ranging from 0 to $+5\%$ (Sato and Kase, 1996). From Ito et al. (2003), two of the $\delta^{34}\text{S}$ values of sulfides from the Paleozoic/Mesozoic greenstone and shale ($+0.1$ and $+1.4\%$, respectively) are in this range, suggesting the sulfides are classified as this type of deposit.

The Hokusetsu area belongs to the Tertiary W-Sn-Cu mineralized province of Japan (Ishihara, 1978) and bears many hydrothermal polymetallic veins enriched with chalcopyrite and pyrite. The ore deposits were induced by the late Cretaceous/Paleogene intrusion of granites and have a range of $\delta^{34}\text{S}$ for sulfide of -9% to -2% (Ishihara and Sasaki, 1991). The quartzite sulfides and the pyrite in the Fushio shale had negative $\delta^{34}\text{S}$ (-8.8% (this study) and -3.0% (Ito et al., 2003), respectively) in the range of igneous $\delta^{34}\text{S}$, but still in contrast with one another. Based on the ranges of sulfur isotopic compositions of sulfide minerals from important mines in southwest Japan, Miyoshi et al. (1988) established a distinction between the ore deposits of subvolcanic origin (e.g., Tada Mine in the study area, with $\delta^{34}\text{S}$ ranging from -3.5 to -2.2%) and the ore deposits of plutonic origin (e.g., Ohtani Mine, with $\delta^{34}\text{S}$ ranging from -10.5 to -8.6%). The quartzite was formed by contact metamorphism with the granitic intrusion of the Nose pluton. Its S isotopic ratio is concordant with the Ohtani ore minerals, which clearly shows that the sulfides were disseminated in relation to the intrusion of the pluton. As noted above, sulfides in the quartzite did not considerably increase the level of As in the surrounding water, suggesting that the type of mineralization and its degree of crystallization play an important role in determining the As levels of the studied river waters.

SO_4^{2-} is a product of the oxidation-dissolution of As-bearing pyrite, which occurs in oxic aquatic environments as follows:



Ito et al. (2003) confirmed this reaction based on a positive correlation between the SO_4^{2-} and As concentrations in spring waters in the Todoromi area. In this study, the behavior between the dissolved sulfates and As could not be established through a simple stoichiometry due to the dilution of the As load in all rivers and the mixing of SO_4^{2-} derived from different sources.

In this study, the highest As concentrations had the lowest $\delta^{34}\text{S}$ values ($+2.6\%$) similar to the $\delta^{34}\text{S}$ of pyrite in the greenstone ($+1.4\%$) and shale ($+0.1\%$). This close $\delta^{34}\text{S}$ relationship was also observed at Fushio for the sulfates of spring

waters (-1.2‰) and the ambient shale (-3.0‰) by Ito et al. (2003). Field (1966), confirmed later by Toran and Harris (1989), emphasized that a small degree of fractionation leading to ^{34}S depletion of a few ‰ in waters occurs during sulfide oxidation. This would explain the discrepancy between the ratios of the host-rocks and the lighter ratios in waters. Therefore, in the present study, waters with As concentrations greater than 10 ppb have low $\delta^{34}\text{S}$ affected by the sulfates derived from the oxidation of pyrite and other sulfides in the ore-deposits described above.

5.3. Fate of arsenic along the river course

The fate of As along the river courses is an important factor in the cycle of this element in the hydrosphere. Many studies emphasized the role of amorphous Al, Mn, and Fe oxides, hydroxides, and oxyhydroxides as a salient absorbent of As. This is especially the case for arsenate, the main As species present under oxic and pH-neutral conditions, as found in the rivers of this study (Bowell, 1994; Grosbois et al., 2011; Zhang et al., 2012). However, results show that adsorption of As onto suspended particles of river waters and sediments is not an important mechanism for As transport in the river waters of this study. Previous studies have already pointed out that As in surface waters is present as a dissolved species rather than in association with suspended particles (Martin and Meybeck, 1979; Tanizaki et al., 1992; Foster and Charlesworth, 1996; Pokrovsky et al., 2005). The present study supports those latter observations. Our data showed a totally different behavior between As, and Fe, Al and Mn, throughout the entire studied river system. Indeed, As dominantly (at least >70%) exists as the dissolved phase, whereas the other elements were predominant in the particulate phase. The particles that would settle are not an important factor controlling the As distribution in the studied rivers. In the studied river system, As is transported down along the river course and does not accumulate in sediments pools.

Previous studies examined the model adsorption capacities of oxides (either as pure or binary Fe oxides) and clays (Pierce and Moore, 1982; Manning and Goldberg, 1997; Zeng, 2004), and they showed a severe decrease in the absorption of As(V) from pH of 7. The adsorption of As onto suspended particles or riverbed sediments is prominent, *i.e.* with a noticeable decrease of As concentration in water, only when the As concentrations are very low (<1 ppb), as in the upper reaches of streams flowing through granitic areas (Ibaraki and Yono rivers). The exchange of As between the aqueous and adsorbing/solid phases in the water column would actually be constrained by competition with other chemical species present in the water, such as sulfates (Wilkie and Hering, 1996). Therefore, only the dilution of contaminated water by an As-free inflow would be effective for the auto-remediation of As in the studied river system.

6. Conclusion

The geochemical mapping of As in the waters and sediments of rivers in the Hokusetsu area of Japan demonstrated the concordant distribution of this element with the surface geology. This indicates that the baseflow, of which the chemistry was formed from the water-rock interaction, is the primary factor determining the distribution of As in the river system. The highest As contamination of river waters occurred in areas of non-metamorphosed sedimentary formations nearby igneous intrusion. The As contamination is generated by the oxidation-dissolution of pyrite in the Paleozoic/Mesozoic sedimentary rocks. The pyrite in the study area has two different origins: the Paleozoic subseafloor hydrothermal activity and the Late Cretaceous/Paleogene magmatism during which plutons intruded. Severe As contamination of river waters only appears where fossil faults occur in the sedimentary rock formations. The fracture zone of these faults must play an important role in the infiltration of oxic surface water into the host rocks to promote the sulfide dissolution. Also, the pyrite disseminated in the Paleozoic/Mesozoic sedimentary rocks would be dissolved more easily than sulfides with higher crystallinity hosted in the magma and/or thermal-altered rocks.

As is transported down to the stream mostly as the dissolved phase, and only minor amounts of this element are adsorbed and accumulated onto the suspended particles. Thus, Fe oxyhydroxides/oxides, Al hydroxides, and/or clay particles are not the major controlling factors determining the level of As in the river waters.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ejrh.2016.09.008>.

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