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Assessment of the geochemical conditions for the release of arsenic, iron and copper into groundwater in the coastal aquifer at Yumigahama, western Japan

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Abstract

Arsenic contamination in groundwater is a hazard worldwide, and Japan is no exception. Arsenic has been detected in perched groundwater in the Holocene Yumigahama sandbar, where such water should be As-free due to prevailing oxidizing conditions. Groundwater drawn from shallow hand-pump wells is used for agriculture in the area. This study aims to evaluate the geochemical conditions of the Yumigahama aquifer by examining mobilization of As, Fe and Cu in soil under extreme pH conditions, and also the influence of fermentation. Soil samples were eluted with 1M HCl and 0.5M NaOH, and fermented with 0.28M glucose. Groundwater and treated samples were analysed for As, Fe and Cu by atomic absorption spectrophotometry. Bulk soils were analysed by X-ray fluorescence. Groundwater has near-neutral pH (6.1-7.9) and As, Fe and Cu ranges are 0.01-42.2μg/L, 0.01-65.4mg/L and 0.7-73.6μg/L respectively. Based on an average of 5.4mg/L As in the soil, about 5% of As was eluted after treatment with HCl or NaOH, whereas 0.3% was removed by glucose fermentation. Lower pH favoured Fe elution (0.1%-0.6% of 36,354mg/L Fe in the soil), whereas at higher pH, 1% to 5% of the 10.7mg/L of Cu in soil was easily mobilized. From the experimental results, As is probably hosted by FeOOH when acidic conditions prevail and by organic matter in alkaline conditions, whereas Fe is released from FeOOH (lower pH). Nitrate and phosphate from fertilizers probably contribute to modification of the aquifer redox conditions. Change of redox conditions due to agricultural practice, presence of even low concentrations of organic compounds and microbial activity can influence the release of As, Fe and Cu from soil into water.

1 Introduction

High As concentrations in groundwater and its toxic impact on human health have recently been reported from many parts of the world. In West Bengal, Bangladesh, and China, arsenic pollution of groundwater has caused skin lesions, skin cancer and other serious health problems in many local people [1, 2].

Chandrasekharam *et al.* [3], Sahu *et al.*[4], and others have studied the As release process by the correlation between arsenic and iron oxides under certain oxi-reduction conditions. In addition, adsorption and dissolution processes, availability of organic matter and bacterial activity are other key factors in the understanding of As occurrence. However, most well waters that contain high concentrations of dissolved iron have no As enrichment. Changes of pH also contribute to mobilization of As, Cu^{2+}, Zn^{2+} and other toxic trace elements [5, 6].

The original geochemical equilibria of aquifers can be modified according to the land use. Therefore, evaluation of the geochemical interaction between groundwater and the geological environment is important to understand the migration processes of the chemical pollutants into aquifers.

This study aims to evaluate the geochemical conditions of the Yumigahama sand deposit (Tottori, western Japan), where groundwater has been largely used for agriculture. Mobilization of As, Fe and Cu in soils was verified under higher and lower pH conditions and under influence of glucose fermentation.

2 Regional setting

Yumigahama Peninsula is located in Tottori Prefecture, western Japan (Fig. 1). The peninsula was formed in the Early Holocene (about 8,000 years B.P.), during worldwide transgression [7, 8]. Yumigahama is a sand deposit up to 70 m thick, and is composed by Holocene sand, Holocene mud and Pleistocene sand layers, in descending order [9, 10]. The deposits overlie Pleistocene basalt and Tertiary sediments [9, 11].

Groundwater replenishment occurs mainly by direct precipitation, and also from artificial irrigation canals from the Yonegawa River, the main drainage of the region. The rainfall recorded in Sakaiminato in 2001 was 2,155 mm, with minimum and maximum monthly precipitation of 34.5 mm (April) and 306.0 mm (June) respectively. Water levels were measured from hydrants at different sites between July and November 1999. Water levels varied between 1.40 m (topographic level of 2 m) and 4.50 m (5 m) above mean sea level [12].

3 Methodology

Previous work [12, 13] has shown that groundwater from some wells in the central part and the extremities of the peninsula contained some As (0.01-0.2 mg/L), low NO_3^- concentrations (<10mg/L) and some enrichment in Fe (0.5 mg/L). This is consistent with locally reducing conditions in the aquifer.

Conversely, nitrate-rich, arsenic-free and iron-poor waters are present in the rest of the peninsula, reflecting oxidizing conditions.

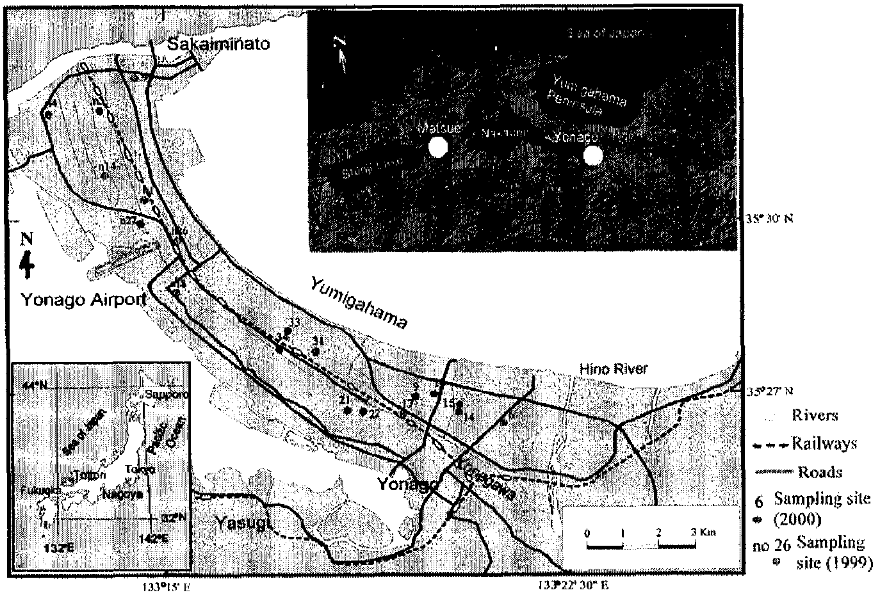


Figure 1: Location map of the groundwater and soil sampling sites (Yumigahama Peninsula, Western Japan).

Based on this previous work, 19 sample sites of Yumigahama (Fig. 1) were selected for a new field program. Groundwater was sampled in December 2001 (autumn) and February 2002 (winter). Soil was collected once from the same sites, during the second phase.

3.1 Fieldwork

Groundwater samples were taken from hand-pump wells, after pumping for several minutes to remove standing water from the well tube. At each site, 300 ml of pumped sample was stored in a clean plastic bottle, and acidified with 2.29 ml of nitric acid (1.31mol/L HNO_3) to prevent oxidation and precipitation [14].

One-kilogram soil samples were collected 20 cm below ground surface, and placed in polythene bags. Both groundwater and soil samples were stored in a cooler with ice packs for transport to the laboratory.

Temperature (°C), pH, ORP (mV), electrical conductivity (µS/cm), and DO (mg/L) were measured in first work phase using portable probes.

3.2 Laboratory procedures

About 50 g of soil sample were dried at 110°C, and later powdered using an automatic agate pestle and mortar for 25-30 min. Bulk soil analyses were determined by XRF. The soils were also subjected to elution and fermentation tests.

The elution and fermentation tests were performed to examine mobilization of As, Fe and Cu under three different conditions. Solutions of 1M HCl, 0.5M NaOH and 0.28M glucose were prepared to simulate extreme pH conditions (very low and very high pH values) and the influence of fermentation, respectively. For each test, about 10 g of soil from each site were treated with 50 ml of the respective solutions. Samples treated with HCl and NaOH were agitated for 30 minutes. In the case of the fermented samples, they were agitated for 1 minute, and later had a treatment time of 20 hours. Afterwards samples were centrifuged at a speed of 3,000 rpm for 5 minutes. Supernatant liquids were stored in polythene bottles and subsequently analysed for As, Fe and Cu by AAS.

Arsenic, Fe and Cu contents in groundwater were determined by AAS.

4 Results

4.1 Field parameters

Measured water temperatures varied from 15.10°C to 19.20°C (average 17.09°C), pH ranged between 6.09-7.87 (average 6.84), and electrical conductivity varied from 137 µS/cm to 583 µS/cm (average 347 µS/cm). Oxi-reduction potential ranged from –70 mV to 94 mV (average 27.53 mV), and DO from 1.5 to 4.0 mg/L (average 2.89 mg/L).

4.2 Groundwater analyses

Results of the groundwater analysis are summarized in Table 1.

Arsenic concentration in groundwater from the first sampling ranged from 0.7 µg/L to 42.2 µg/L; those in the second sampling ranged between 0.01 µg/L and 38.3 µg/L. The highest concentrations were from sites no.18 (23.5 µg/L, first sampling; 17.5 µg/L, second sampling), no.26 (42.2 µg/L; 38.3 µg/L) and 9 (12.7 µg/L, first sampling only). These results exceed 10 µg/L, the provisional limit recommended by WHO for drinking water quality [15].

Iron contents ranged from 0.02 mg/L to 20.2 mg/L in the first fieldwork sampling, and from 0.01 mg/L to 65.4 mg/L in the second sampling. Most sites had concentrations above the WHO guideline of 0.3 mg/L, except sites no.1, no.4, no.14, 21, ,31, 33 and 40, and first sampling at site 22.

Cupper concentrations ranges in the first and second samplings were 5.2-17.7 µg/L and 0.7-73.6 µg/L respectively, below the provisional limit of 2 mg/L defined by WHO [15].

Table 1. Analyses of groundwater, soil and elutants, Yumigahama (I, first fieldwork; II, second fieldwork). Soil samples treated with 1M HCl, 0.5M NaOH and 0.28M glucose solutions. Samples tabulated from west to east.

	Groundwater						Soil				Soil				Soil			
	[As] µg/L		[Fe] mg/L		[Cu] µg/L		[As]	As elution (µg/L)			[Fe_2O_3]	Fe elution (mg/L)			[Cu]	Cu elution (µg/L)		
Sample	(I)	(II)	(I)	(II)	(I)	(II)	(mg/L)	HCl	NaOH	Glucose	(mg/L)	HCl	NaOH	Glucose	(mg/L)	HCl	NaOH	Glucose
40	4.4	1.7	0.02	0.01	10.4	0.8	6.7	227.5	122.2	14.3	25767	132.8	13.5	3.5	10.3	86.6	311.6	7.1
no 4	1.1	2.9	0.1	0.1	10.0	0.7	6.0	1836	1109	7.02	36104	103.5	14.2	1.6	8.1	46.9	257.5	2.5
no 3	1.4	1.4	0.9	3.2	5.9	1.9	8.4	1027	476.4	13.8	32331	92.7	64.2	8.4	10.3	76.8	381.3	1.4
no 14	0.7	3.0	0.1	0.1	9.5	1.3	4.0	318.7	369.5	31.2	32802	171.6	34.8	9.1	12.0	80.5	247.2	2.3
no 1	1.4	2.9	0.03	0.03	8.1	0.8	5.5	219.4	123.1	7.7	32491	113.3	8.7	2.9	10.8	106.5	116.0	7.4
no 27	0.7	1.2	6.9	7.8	5.2	2.2	4.1	188.2	107.9	7.0	33393	120.7	7.2	0.9	11.4	102.3	377.1	4.1
no 26	42.2	38.3	19.8	65.4	5.8	2.0	5.7	134.3	119.6	23.2	32397	147.7	16.4	8.1	18.8	210.0	543.6	7.8
no 18	23.5	17.5	9.8	34.6	6.2	1.3	4.4	264.9	265.6	10.3	39804	73.2	2.4	1.0	13.7	146.3	380.5	9.0
33	1.4	0.01	0.3	0.2	8.4	1.5	6.7	304.2	173.6	13.1	40291	158.9	16.6	6.0	8.3	45.5	194.2	4.5
34	2.1	1.9	0.3	0.4	17.7	11.4	8.2	232.0	112.0	26.6	41765	166.4	5.8	6.3	11.0	58.8	238.9	5.8
31	1.7	0.01	0.02	0.3	11.1	5.9	3.1	192.2	127.2	5.8	47714	25.1	1.1	1.2	8.8	14.1	158.4	1.4
21	1.0	1.4	0.1	0.1	8.4	1.1	6.2	265.1	122.4	9.5	36922	144.7	18.8	1.6	13.6	70.9	370.8	5.1
22	1.5	1.5	0.3	4.1	8.5	73.6	5.2	182.9	102.6	22.8	49367	108.9	2.9	5.2	12.7	39.0	194.9	6.9
17	6.0	3.5	6.5	22.3	9.3	5.6	4.0	186.5	109.4	24.1	43016	108.0	4.7	7.3	10.9	30.0	156.4	6.7
9	12.7	2.7	10.5	28.6	6.0	1.2	5.0	264.0	156.4	9.2	32092	100.4	34.1	3.8	9.9	101.0	472.8	6.3
10	2.9	3.2	7.8	19.1	9.4	7.1	2.7	229.9	123.1	7.9	32723	36.8	2.9	0.7	4.8	35.0	180.9	3.3
15	2.2	2.5	13.7	33.8	9.1	3.0	3.6	220.6	100.8	11.8	22375	59.1	7.1	4.8	6.0	55.7	147.0	3.8
14	1.1	1.6	20.2	49.3	10.5	6.2	5.9	238.6	281.7	5.5	43050	110.1	28.1	4.2	10.5	120.8	341.5	2.0
6	2.7	1.3	12.9	31.3	7.2	2.0	6.7	162.8	164.6	35.3	36319	208.6	33.2	10.5	10.7	48.0	223.0	1.9

4.3 Elution and fermentation tests

After treating Yumigahama soils with 1M HCl solution, the pH of the elutants was 1.2 (highly acidic). Arsenic concentrations in the elutants ranged from 134 to 1,836 μg/L; highest values were from sites no.3 and no.4 (1,027 and 1,836 μg/L respectively). Iron contents varied from 25 mg/L to 210 mg/L, whereas Cu contents were 14 μg/L to 210 μg/L. Analyses are listed in Table 1.

Elutants from soils treated with 0.5M NaOH had pH values of 13. Arsenic, Fe and Cu ranges were 100.8-1,109 μg/L; 1.1-64.2 mg/L; 116-543.6 μg/L respectively (Table 1).

Supernatant liquids from soils treated with 0.28M glucose had pH ranging from 4.65 to 6.88 (average 5.83). Arsenic contents ranged from 5.5 to 35.3 μg/L; Fe from 0.7 to 10.5 mg/L; and Cu from 1.4 to 9 μg/L (Table 1).

5 Discussion

5.1 Groundwater and samples treated with HCl, NaOH and glucose

From the physical-chemical data obtained in the field, the shallow aquifer at Yumigahama can be characterized as slightly anoxic to oxic. In such domains groundwater has near-neutral pH and low DO.

No correlation between As and Fe, As and Cu, and Fe and Cu was observed in the groundwater samples analysed by AAS.

In the eluted samples, there is a possible positive correlation between As and Fe for samples treated with NaOH and glucose solutions. However, no clear relationship was verified for other associations.

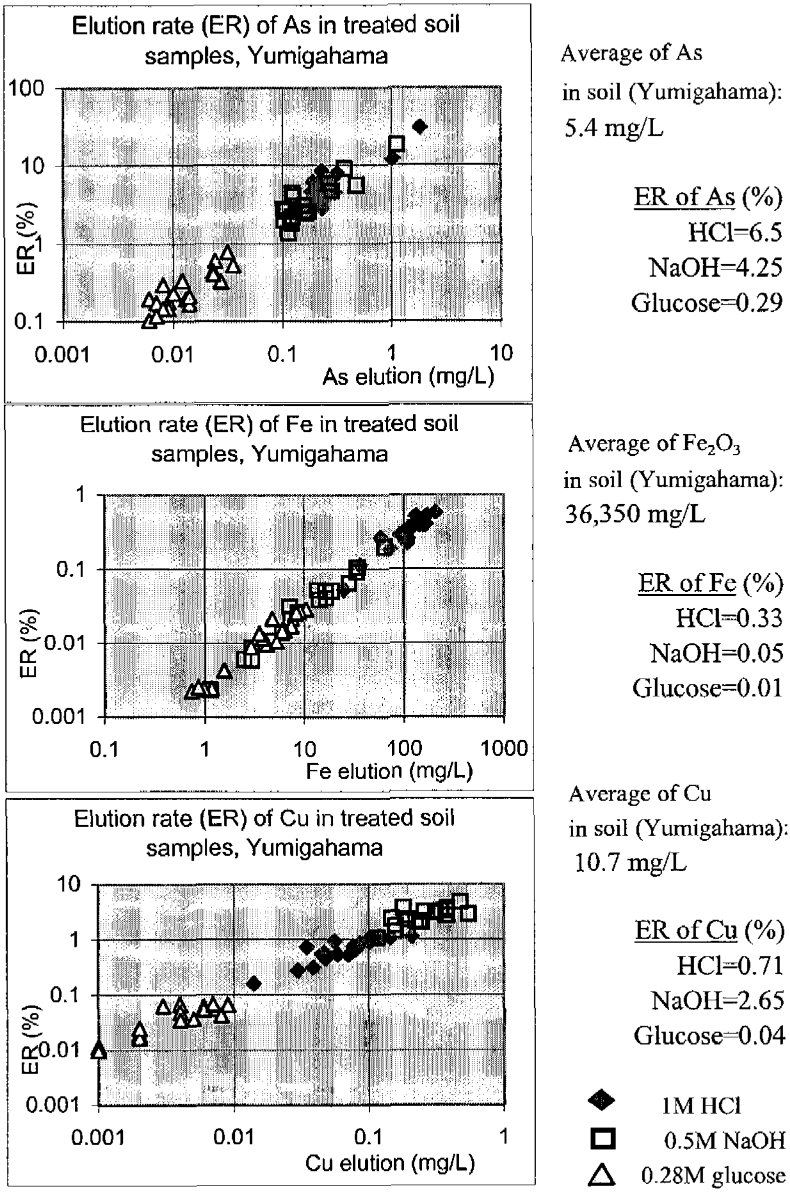
Compared to the groundwater analyses, As concentrations were much higher in the elutants after treating the soils with 0.28M glucose, 0.5M NaOH and 1M HCl, in sequence of increasing content. The highest Fe concentrations were obtained from the HCl elution test, and the lowest by glucose fermentation. However, in the fermentation test Fe was released even at sample sites where the groundwater contained less than 0.3 mg/L. In the case of Cu, the highest values occured in the elution tests with 0.5 M NaOH (alkaline conditions), and the lowest contents were released with fermentation test.

5.2 Elution rate (ER)

Elution rate (ER) is the proportion between the eluted element and its concentration in soil:

$$ER = \frac{\text{concentration of the eluted element}}{\text{concentration of the element in soil}} \times 100\ \%$$

Arsenic concentrations in the soils averaged 5.4 mg/L, and around 5% of this was eluted by both HCl and NaOH solutions. The ER of samples treated with 0.28M glucose was 0.29 %. These results show that As can be mobilized



Average of As
in soil (Yumigahama):
5.4 mg/L

ER of As (%)
HCl=6.5
NaOH=4.25
Glucose=0.29

Average of Fe_2O_3
in soil (Yumigahama):
36,350 mg/L

ER of Fe (%)
HCl=0.33
NaOH=0.05
Glucose=0.01

Average of Cu
in soil (Yumigahama):
10.7 mg/L

ER of Cu (%)
HCl=0.71
NaOH=2.65
Glucose=0.04

◆ 1M HCl
□ 0.5M NaOH
△ 0.28M glucose

Figure 2: Relationship between ER and As, Fe and Cu eluted with HCl, NaOH and glucose (Yumigahama).

from soils in either acidic or alkaline conditions, and the availability of organic compounds (such as glucose or organic matter) in the aquifer can also contribute to As release into the groundwater (Fig. 2). This corroborates other studies related to processes of As release [1, 4, 5]. Arsenic may have two different host matters: organic matter (when prevailing higher pH) and iron oxyhydroxide minerals (lower pH). Under alkaline conditions, As is desorbed from organic matter. In acidic conditions, Fe oxyhydroxide is dissolved releasing Fe^{2+} and As into water.

Iron in soils (average of 36,354 mg/L) was easily mobilized by HCl solution at an average rate of 0.33 %, whereas average elution rates in the NaOH and glucose treatments decreased to 0.05 % and to 0.01% respectively (Fig. 2). Sandy aquifers are generally abundant in iron oxides and oxyhydroxides, which have a strong binding affinity [5]. Under prevailing acidic conditions, Fe oxyhydroxides are dissolved and As and Fe are mobilized from soils into groundwater.

Copper, which has an average concentration of 10.7 mg/L in the soils, was eluted at an average rate of 2.65 % after NaOH treatment. This treatment was more effective than HCl (average elution rate of 0.71%) and glucose (average of 0.04%) in mobilizing Cu (Fig. 2). These results contrast to those from the literature, which states Cu usually becomes more insoluble as pH increases [1, 16]. Our results may be due to the presence of bacteria that live under strong alkaline conditions and, thus, release Cu from soil. However, our present data cannot attest such supposition.

5.3 Human activity

Based on the XRF data, Yumigahama soils at 20 cm depth contain an average of 1,130 mg/L phosphorus, whereas underlying sands average 480 mg/L [17]. This excess in the upper soils could be explained by the high phosphate levels in fertilizers used in local cultivation. Nitrate pollution (over 10mg/L N) has also been reported from Yumigahama groundwater [12, 13].

High levels of nitrate and phosphate may be strongly influenced by human activity, not only by application of nitrogen or phosphorus fertilizers, but also by septic tank discharges and domestic wastewater [18, 19]. Because there is a competitive sorption between phosphates and arsenic in soil, phosphate from fertilizers may also augment mobility of As in groundwater [20, 21].

A schematic reconstruction of the Yumigahama area shows a well passing through a lens of sedimentary organic matter (Fig. 3). The available organic matter may be decomposed by microbial oxidation. Dissolved oxygen and NO_3^- are consumed, and anoxic conditions are established in the aquifer, favouring reduction of arseniferous iron oxihydroxides and the release of As, Fe and other elements into the groundwater.

6 Conclusions

Because most trace elements are susceptible to changes of pH and redox equilibrium, it is important to evaluate the physical-chemical conditions of aquifer systems, and consider the influence of human activity in the area. Agricultural practices in the Yumigahama area may have changed the original chemical conditions of the aquifer by introducing higher contents of nitrate and phosphate from fertilizers to the soils. Tests with HCl, NaOH and glucose solutions simulated change of the natural conditions of the soil, considering higher and lower pH conditions and the availability of organic matter.

Yumigahama groundwater has a prevailing oxidizing character, near-neutral pH and low DO. It also has detectable levels of As (less than 6 µg/L). At 3 sites in particular (9, no.18 and no.26), As concentration exceeded 10 µg/L, the WHO guideline value for arsenic in drinking water. High Fe and Cu contents are not correlated with As occurrence. According to the elution and fermention tests, As is easily mobilized under strong acidic (low pH) and alkaline (high pH) conditions, and probably has two different host matters in the aquifer: FeOOH (in acidic conditions) and organic matter (alkaline conditions). High iron contents in the elutants suggest dissolution from Fe oxides-hydroxides, favoured by low pH. Copper may be released from soil to groundwater especially under strong alkaline conditions and, perhaps, by influence of specific bacteria.

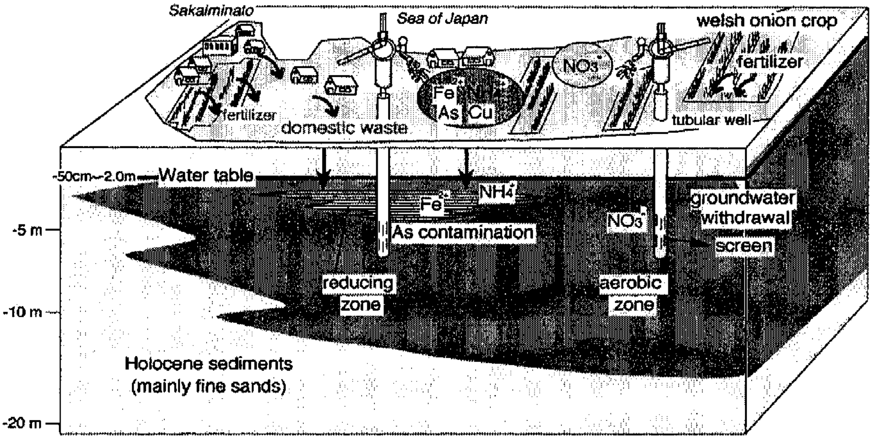


Figure 3: Schematic diagram of the release process of As, Fe and Cu (modified from Ito *et al.*, [12]).

Based on the analytical results of groundwater and soil, each site at Yumigahama may have specific geological and geochemical conditions that create a favourable environment for As release. Besides local pH and prevailing redox reactions, organic matter, bacterial activity and excess of phosphate (from fertilizers) may also make an important contribution to this process.

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