

## VARIATIONS OF WATER QUALITY ALONG ACIDIC RIVERS IN VOLCANIC AREAS OF EASTERN JAPAN

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**ABSTRACT:** There are many acidic rivers in Japan, due to acid mine drainage (AMD) and drainage from acidic hot springs. Low pH values and relatively high concentrations of heavy metals and other trace elements are often detected in the acidic rivers. In this study, water quality parameters including pH and concentrations of major cations and anions, heavy metals, and other trace elements were investigated in nine acidic river basins located in volcanic areas of Eastern Japan. The study included both untreated river basins and basins where neutralization treatment is carried out. Variations of water quality along two acidic river basins and the mechanisms controlling the variations in water quality were also discussed. Generally, the pH values ranged from 1.31 to 5.45 in the nine river basins. Positive effects from neutralization treatment were observed along the Agatsuma river basin where pH values markedly increased and the concentrations of As, Pb, F, Fe, and Al dramatically decreased. In comparison, along the untreated Nagase river basin, the pH values gradually increased and the concentrations of As, Pb, F, Fe, and Al steadily decreased, mainly due to the dilution effect caused by mixing with other rivers. In these two river basins, harmful elements such as As, Pb, and F were probably coprecipitated with Fe and Al hydroxides. The sediments deposited in the Nagase river bed and Lake Inawashiro may therefore contain much higher concentrations of harmful elements including As, Pb, and F as were previously reported on the Shinaki Dam of the Agatsuma river basin.

*Keywords: Water quality, pH, Heavy metals and other trace elements, Acidic rivers, Eastern Japan*

### 1. INTRODUCTION

Acid mine drainage (AMD) is one of the most serious environmental challenges, resulting in the discharge of water with low pH values and relatively high concentrations of heavy metals and other trace elements. The AMD is naturally produced, typically from the oxidation (i.e., weathering) of sulfide minerals including pyrite reacting with air and water. The mining activities can highly accelerate the amount of the discharge by an increase in possibility for sulfide mineral oxidation. The production of AMD sometimes continues for a long time even after mine closure [1-5].

Also, there are many acidic hot springs associated with volcanic activities especially in Japan. The drainage from acidic hot springs also shows low pH values and relatively high concentrations of heavy metals and other trace elements such as As (arsenic), Pb (lead), and F (fluorine). The acidic drainage produced from mines and hot springs discharges into rivers causing acidic rivers.

There are possible negative impacts of the acidic rivers on natural environment and human activity. For example, the acidic water significantly affects the degradation of infrastructures mainly composed of concrete and iron materials in rivers. Because of high acidity

and relatively high concentrations of heavy metals and other trace elements, there are unfavorable risks for the biosphere including human beings in acidic river basins.

In Japan, more than 5,000 mines were operated in the past [6]. In 2013, treatment for AMD was being carried out in approximately 80 mines [7]. In some of acidic hot springs of Japan, treatment for the acidic water is also being performed. The conventional treatment technique is a combination of neutralization and precipitation using lime or similar neutralizing agents to reduce the acidity and the concentrations of heavy metals and other trace elements [2, 8]. The problem with applying neutralization treatment is a high cost because the neutralizing agents must be continuously applied. Since neutralizers such as lime represent natural and scarce resources, it is highly important to reduce their usage. Therefore, alternative neutralizers which have low cost and high neutralization capacity need to be developed.

For developing alternative neutralizers, fundamental knowledge about water quality parameters and their spatial variations along acidic river basins is needed. Presently, there is a lack of research extensively investigating variations of water quality along acidic river basins. The objectives of this study were therefore: (i) to investigate water quality parameters including pH and concentrations of major cations and anions,

heavy metals, and other trace elements in nine representative acidic river basins located in volcanic areas of Eastern Japan and (ii) to discuss variations of water quality along two acidic river basins and the controlling mechanisms for the water quality variations.

## 2. MATERIALS AND METHODS

### 2.1 Study Areas

Water quality investigation was carried out in nine acidic river basins: Urakawa (Nagano Prefecture), Matsukawa (Nagano Prefecture), Yonako (Nagano Prefecture), Iougawa (Niigata Prefecture), Nagase (Fukushima Prefecture), Agatsuma (Gunma Prefecture), Sukawa (Yamagata Prefecture), Tamagawa (Akita Prefecture), and Matsukawa (Iwate Prefecture) (Figs. 1 and 2). All nine river basins are situated in volcanic areas of Eastern Japan. In the nine river basins, a total of around 70 sampling locations were selected. The water quality investigation was conducted between one to four times in each river basin (from 2017 to 2019).

Neutralization treatment using lime is being applied in the upstream parts of the Agatsuma, Tamagawa, and Matsukawa (Iwate Prefecture) river basins, while in other six river basins, there are no specific treatments applied towards increasing river pH values.

### 2.2 Field Works and Laboratory Analyses

After taking river water samples, on-site measurements of water temperature, pH, electric conductivity (EC), and turbidity were immediately performed using portable analyzers (WM-32EP, DKK-TOA CORPORATION, Japan, and 2100P Potable Turbidimeter, HACH, USA) calibrated for each measurement.

In the laboratory, the sampled river water was filtered using a 0.20  $\mu\text{m}$  membrane filter (DISMIC-25CS, Toyo Roshi Kaisha, Ltd., Japan). Major cations and anions ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ ), dissolved inorganic carbon (DIC), and heavy metals and other trace elements (Li, Al, Si, Cr, Mn, Fe, Ni, Cu, Zn, Se, Sr, Cd, and Pb) were analyzed using an ion chromatograph (ICS-1500, Nippon Dionex K.K., Japan), TOC analyzer (TOC-V CSH, SHIMADZU CORPORATION, Japan), and inductivity coupled plasma (ICP) mass spectrometer (MS) (ICPM-8500, SHIMADZU CORPORATION, Japan) or atomic absorption spectrophotometer (AA-6200, SHIMADZU CORPORATION, Japan), respectively. For the DIC, there are three main

chemical forms of  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ . Their relative abundance ratios depend on the pH values in water environment [9]. In this study, the concentration of  $\text{HCO}_3^-$  was calculated using pH, ionic strength, activity coefficient, and equilibrium constant.

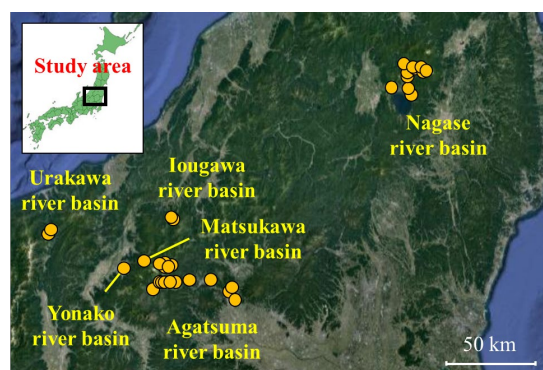


Fig. 1 Study areas of the Urakawa, Matsukawa, Yonako, Iougawa, Nagase, and Agatsuma river basins (orange circles show water sampling locations). The base map was taken from Google Maps.

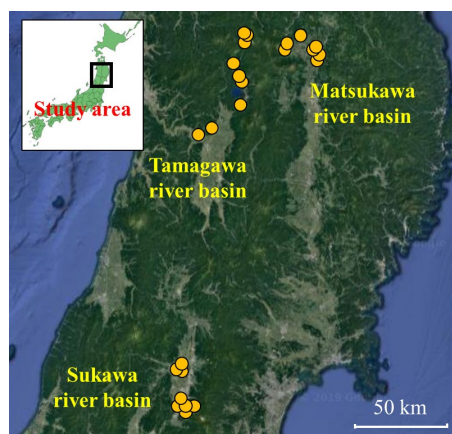


Fig. 2 Study areas of the Sukawa, Tamagawa, and Matsukawa river basins (orange circles show water sampling locations). The base map was taken from Google Maps.

## 3. RESULTS AND DISCUSSION

### 3.1 Levels of Acidity in Nine Acidic River Basins of Eastern Japan

The pH values were 5.45 (October 2019), 3.02 (August 2018), 3.62 (April 2018), and 4.32 (August 2018) in the upstream parts of the Urakawa, Matsukawa (Nagano Prefecture), Yonako, and Iougawa river basins, respectively. Very low pH values of 1.93 (May 2019), 1.66 (July 2017), 1.82 (June 2017), 1.31 (July 2018),

and 3.41 (July 2018) were observed in the upstream parts of Sukawa, Nagase, Agatsuma, Tamagawa, and Matsukawa (Iwate Prefecture) river basins, respectively. In the upstream of the Matsukawa (Iwate Prefecture) river basin, the mentioned pH value of 3.41 was obtained in the sampling location after the neutralization treatment plant. Therefore, the original pH value is expected to be significantly lower.

In the following sections, variations of water quality along the Agatsuma river basin as an example of neutralization treatment being applied and Nagase river basin as an example of no specific treatment being applied are discussed based on the acquired water quality data in June 2017 and July 2017, respectively.

### 3.2 Variations of Water Quality Along the Agatsuma River Basin

In the upstream of the Agatsuma river basin, the Kusatsu hot spring as one of the most famous acidic hot springs in Japan and closed sulfur mines are located at the Eastern foot of an active volcano, Mt. Kusatsu-Shirane. Around this volcanic area, there are several acidic rivers. Especially, the Yukawa river dominated by the discharged water from the Kusatsu hot spring shows the lowest pH value, usually less than pH 2.0. Therefore, the neutralization treatment using lime has been applied by the Ministry of Land, Infrastructure, Transport and Tourism, Government of Japan, over 50 years [10, 11]. The resulting compounds from the treatment are continuously produced and finally deposited in an artificial lake named Shinaki Dam located approximately 3 km downstream of the neutralization treatment plant (Fig. 3). Two more acidic rivers (the Yazawa and the Osawa rivers) are also being neutralized and the neutralized water continuously flows into the Shinaki Dam. A pH value of 2.57 was observed in the Yazawa river. The water from the Shinaki Dam finally discharges to the Tone river (via the mainstream of the Agatsuma river) which is the biggest water resource for the Tokyo Metropolitan area of Japan having a population more than 30 million. In the following section, variations of water quality along the Agatsuma river basin are discussed based on seven sampling locations (Fig. 3).

Figure 4 presents variations of water quality parameters for pH, EC, and the concentrations of As, Pb, F, Fe (iron), and Al (aluminum) from the upstream to downstream along the Agatsuma river basin. Spatial variations in the concentrations of major cations and anions as Stiff diagrams are also illustrated in Fig. 5. A pH value of 1.82 was observed in the Yukawa river before the neutralization treatment plant. After the treatment,

the pH value markedly increased to 4.3. Subsequently, the water from the Shinaki Dam discharges to the mainstream of the Agatsuma river where the pH increased to a neutral value (7.38), while the concentrations of As, Pb, and F dramatically decreased. The Fe and Al concentrations also decreased significantly after the neutralization treatment as shown in Fig. 4. These elements were almost not detected in the mainstream of the Agatsuma river. The metal hydroxides, especially Fe and Al, are in general easy to precipitate by increasing the pH value in the water. One of the most harmful elements, As, can be simultaneously coprecipitated with metal hydroxides [12, 13]. Therefore, in addition to As, other harmful elements such as Pb and F were probably coprecipitated with the Fe and Al hydroxides during the neutralization process. In agreement with this, the river deposits in the Shinaki Dam contain extremely high concentrations of these harmful elements as reported in annual monitoring data by the Ministry of Land, Infrastructure, Transport and Tourism [14].

The EC values significantly decreased (Fig. 4) as many elements including harmful elements were removed by the neutralization treatment. The water quality type was also changed to a Ca-SO<sub>4</sub> dominant type with the addition of calcium carbonate (CaCO<sub>3</sub>) as the neutralizer (Fig. 5). After discharging into the mainstream of the Agatsuma river, the EC values markedly decreased due to the dilution effect mixed with other rivers. The water quality type was, however, still maintained as a Ca-SO<sub>4</sub> dominant type even in the most downstream of the Agatsuma river. Thus, harmful elements from the Shinaki Dam will likely be significantly diluted when discharged into the mainstream of the Agatsuma river.

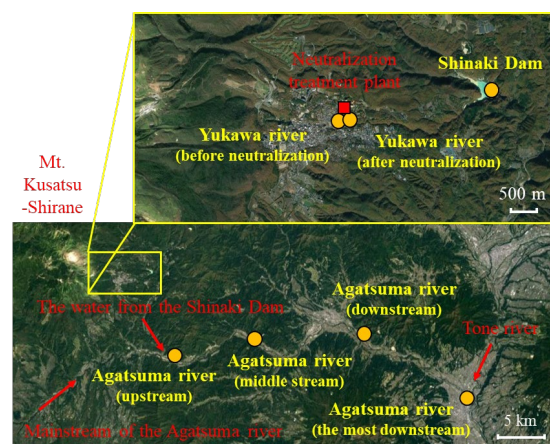


Fig. 3 Study area of the Agatsuma river basin (orange circles show water sampling locations). The base map was taken from Google Maps.

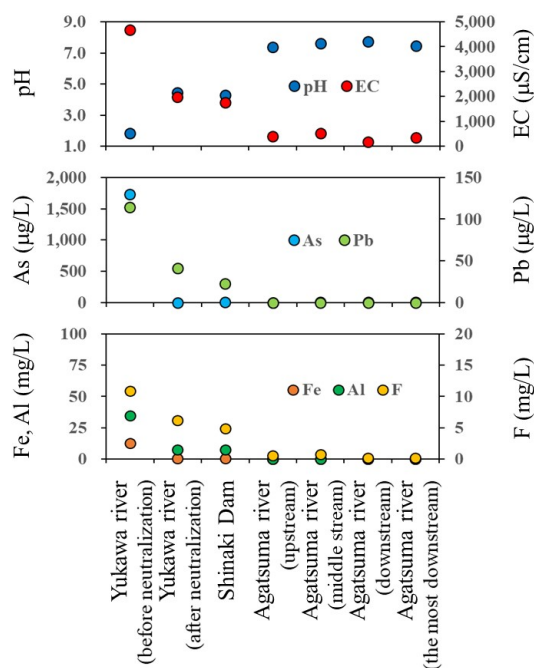


Fig. 4 Variations of pH, EC, and concentrations of As, Pb, F, Fe, and Al from upstream to downstream along the Agatsuma river basin (water sampling locations are shown in Fig. 3).

### 3.3 Variations of Water Quality Along the Nagase River Basin

In the upstream of the Nagase river basin, acidic hot springs and closed sulfur mines are located at the Western foot of Mt. Adatara that is an active volcano. Around this volcanic area, there are also several acidic rivers. The Iougawa river is dominated by the acidic hot spring water and showed the lowest pH value of 1.66. The pH value was almost in the same range as the Yukawa river in the Agatsuma river basin, however, there are no specific treatments applied in the Nagase river basin towards increasing river pH values. The water from the Iougawa river discharges to the Lake Inawashiro (via the mainstream of the Nagase river) (Fig. 6). Then, the water from the

lake discharges to Nippashigawa river and finally flows into the Agano river which is one of the biggest rivers in Japan. In the following section, variations of water quality along the Nagase river basin are discussed based on six sampling locations as shown in Fig. 6.

Figure 7 presents variations of water quality parameters for pH, EC, and the concentrations of As, Pb, F, Fe, and Al from the upstream to downstream along the Nagase river basin. Spatial variations in the concentrations of major cations and anions as Stiff diagrams are also illustrated in Fig. 8. The mentioned pH value of 1.66 in the Iougawa river is due to inflow of the acidic hot spring water. After that, the pH values gradually increased along the river. In the most downstream part of the Nagase river, before discharging into the Lake Inawashiro, the pH still showed a low value of 4.06. However, pH finally became almost neutral (6.78) in the Nippashigawa river. Simultaneously, the As, Pb, F, Fe, and Al concentrations gradually decreased along the river. Especially, in the most downstream part of the Nagase river, very low concentrations of all these elements were observed. The harmful elements such as As, Pb, and F were probably coprecipitated with the Fe and Al hydroxides by increasing the pH values, as also observed in the Agatsuma river basin. The pH value of 4.06 was almost in the same range with the Shinaki dam (pH value of 4.3). The Fe hydroxide was clearly deposited in the river bed (Fig. 9). Similarly, in the Nagase river basin, the sediments in the river bed probably contain high concentrations of harmful elements including As, Pb, and F. Based on previous studies [15, 16], the reaction sediments are also deposited in the bottom of the Lake Inawashiro. The EC values gradually decreased and the Stiff diagrams (Ca-SO<sub>4</sub> dominant type water quality) also became reduced in size (Figs. 7 and 8). The dilution effect due to the mixing with other rivers significantly affects the increase of the pH values in the Nagase river basin, resulting in the removal of harmful elements from the river water.

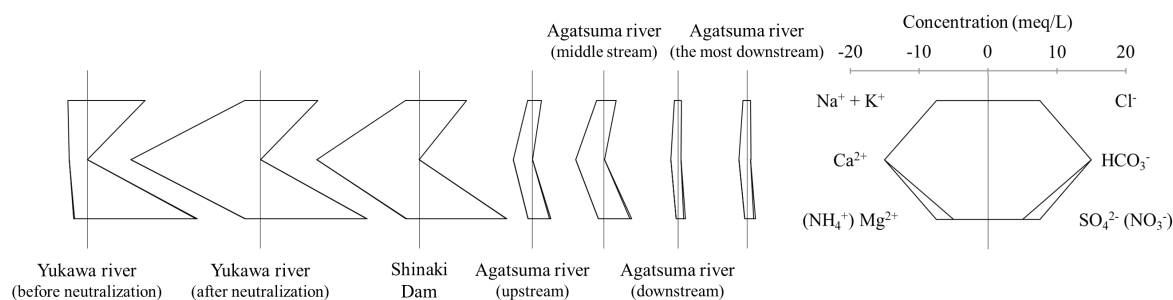


Fig. 5 Variations in concentrations of major cations and anions (shown as Stiff diagrams) from upstream to downstream along the Agatsuma river basin (water sampling locations are shown in Fig. 3).



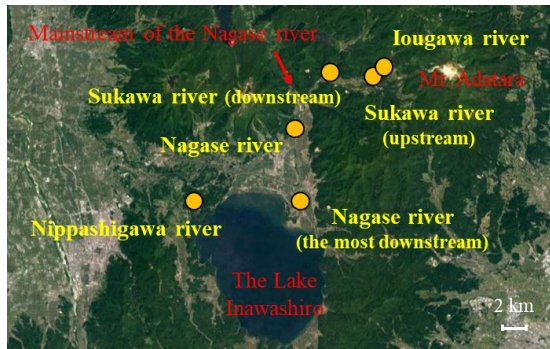


Fig. 6 Study area of the Nagase river basin (orange circles show water sampling locations). The base map was taken from Google Maps.

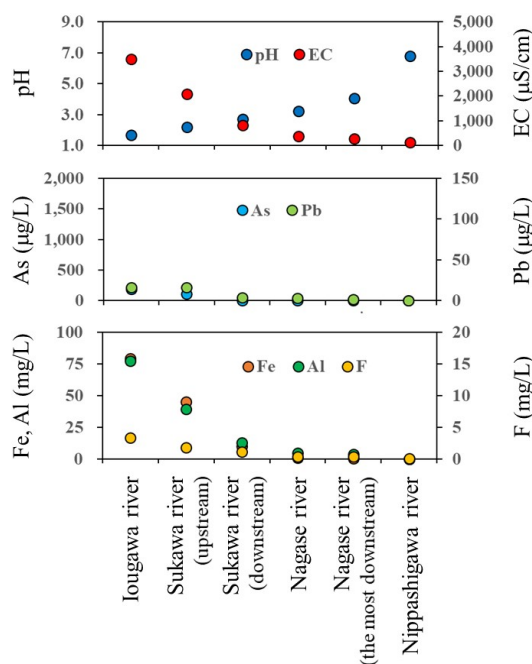


Fig. 7 Variations of pH, EC, and concentrations of As, Pb, F, Fe, and Al from upstream to downstream along the Nagase river basin (water sampling locations are shown in Fig. 6).

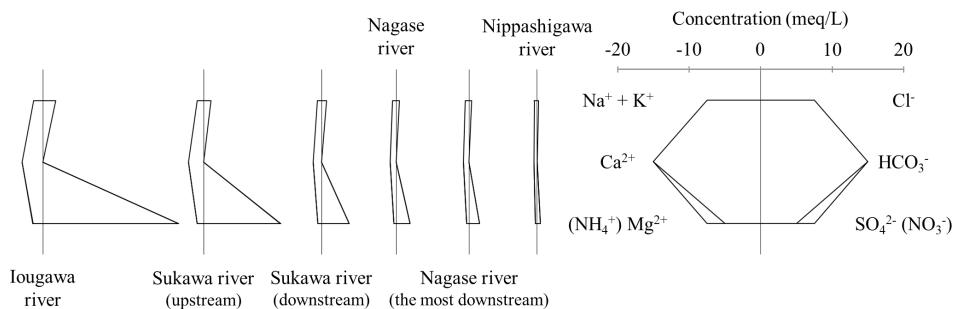


Fig. 8 Variations in concentrations of major cations and anions (shown as Stiff diagrams) from upstream to downstream along the Nagase river basin (water sampling locations are shown in Fig. 6).

The next step of the investigation is to evaluate the chemical stability of these harmful elements in reaction sediments of the river bed in the Nagase river basin and of the Shinaki Dam in the Agatsuma river basin. The sediment in the Shinaki Dam is regularly dredged and disposed into a controlled final landfill site. However, the sediment in the Nagase river basin and the Lake Inawashiro always continue to be accumulated. Therefore, the chemical stability assessment for these sediments is highly needed.

#### 4. CONCLUSION

Water quality parameters including pH and concentrations of major cations and anions, heavy metals, and other trace elements were investigated in nine representative acidic river basins located in volcanic areas of Eastern Japan. Variations of water quality along two acidic river basins (the Agatsuma and the Nagase river basins) and the mechanisms controlling the water quality were also discussed. Generally, the pH values ranged from 1.31 to 5.45 in the nine river basins.

In the Agatsuma river basin with neutralization treatment, the pH values markedly increased and the concentrations of As, Pb, F, Fe, and Al dramatically decreased. In the untreated Nagase river basin, the pH values gradually increased and the concentrations of As, Pb, F, Fe, and Al steadily decreased along the river, mainly due to the dilution by the mixing with other rivers.

In these two acidic river basins, harmful elements of As, Pb, and F were probably coprecipitated with the Fe and Al hydroxides. The sediments deposited in the river bed of the Nagase river basin and the Lake Inawashiro might therefore contain much higher concentrations of harmful elements including As, Pb, and F as were previously reported on the Shinaki Dam of the Agatsuma river basin. The next step is to evaluate the chemical stability of the harmful elements in the sediments.



Fig. 9 The river bed conditions in (a) Sukawa river (upstream) and (b) Nagase river of the Nagase river basin (the locations of the photos correspond to the water sampling locations in Fig. 6).

## 5. ACKNOWLEDGMENTS

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