Original Article

Behavior Analysis of pH, Dissolved Aluminum and Fluoride Species in Acidified River Environments Rich in Sulfate and Fluoride

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ABSTRACT

In this study, the water quality of typical acidified rivers in Yamagata and Fukushima Pref., Japan (Matsu River, Ara River and Su River) were investigated. These rivers have been receiving an inflow of a treated acid mine drainage leaches or an acidic hot spring water. Effects of dissolved aluminum and fluoride species on the acidified river environments were studied by data analyses on the water quality and chemical equilibrium calculations using the aqueous speciation computer code of the program PHREEQC. The results showed that aluminum ion in river water inhibits a rise in pH (i.e. a pH buffering effect) by alkali consumption with the hydrolysis in processes of aluminum solid-phase formations. The chemical equilibrium calculations indicated that the aluminum solid phases forming in the rivers would be mainly basaluminite ($\text{Al}_4(\text{OH})_{10}\text{SO}_4$) and alunite ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$) and generations of aluminum fluoride species such as AlF^{2+} and AlF_2^+ at the points with fluorine loadings such as the inflow of hot spring water. Moreover, it was suggested that generations of these aluminum fluoride species would be moderating the pH buffering effects with aluminum solid-phase formations by moderation of the hydrolysis of aluminum.

Keywords: aluminum, fluoride, aqueous speciation, chemical equilibrium modeling, acidified river

INTRODUCTION

Acidification of river is caused by contamination of mainly acid mine drainage (AMD). At many AMD sites, the impact of AMD had been mitigated by removal of metals and sulfate using alkaline industrial chemicals [1]. However, AMD still has been presenting a thread for environment by its high acidity and contents of harmful heavy metals since gold mining activities have been rapidly increasing in South America and Africa [2]. AMD results from the oxidization of pyrite and other sulfide minerals exposed to weathering processes [3]. The generation of AMD followed by acidification of river has been greatly accelerated by mining activities such as open-cut mining, mining tailings, and rock stock piles. The stream biota, such as benthic macroinvertebrates and attached algae, can be severely affected by the acidification of river [4,5]. The inflows of hot spring water and/or

wastes from facilities of a hot spring town also often cause the acidification of river and affect the habitation of stream biota. Aluminum is often detected in high concentrations at acidified water environments [6–8]. Inorganic monomeric aluminum is indicated to have high potential toxicity [9–11]. Additionally, Al^{3+} and its hydrolysis products were reported to greatly influence water quality in acidified rivers [6,7,12]. Consequently, the aluminum speciation can be considered a key factor for risk assessments of acidified water environments. Good understanding of the behavior of aluminum is necessary for the sustainable protection and/or mitigation of acidified water environments. Aqueous speciation computer programs and geochemical models are reported to be useful tools for the evaluation of the chemical conditions of soils and surface waters affected by artificial or environmental contaminations. Several aqueous speciation programs have been presented such as PHREEQC [13], WHAM [14], and

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Fig. 1 Locations of stations selected for the investigation in a) Matsu River and b) Ara River and Su River. The map was drawn based on what was published by the Geospatial Information Authority of Japan (GSI).

Visual Minteq [15]. It was reported that these models have been used for assessment of metal toxicity and estimation of effects of acid rain on aluminum mobility [16]. Behavior of aluminum in the water environment is influenced by complexing with water molecules and anions such as chloride, fluoride, sulfate, nitrate, phosphate, and negatively charged functional groups on humic materials and clay [17]. Fluoride has higher affinity for aluminum and is often present at high concentrations in acidified water environments, especially, hot spring water and/or wastes. It was reported that fluoride present under acidic conditions would be almost complexed and dominant Al-F complex at $\text{pH} < 5$ is AlF^{2+} [18,19]. Additionally, the increase in fluoride in solution would cause an increase in total aluminum in solution [19]. However, simultaneous modeling of chemical equilibrium with Al minerals and aluminum speciation focused on binding to fluoride species based on field investigation data has been conducted rarely in acidified surface water. Especially, the behavior analysis of aluminum and fluoride species with the downflow of river by the speciation modeling is quite rare.

This study aims to clarify the behavior of pH, dissolved aluminum and fluoride species in acidified river environments. In this study, the water quality of two typical acidified river basins rich in sulfate and fluoride, in Yamagata and Fukushima Pref., Japan (the basin of Matsu River and the basin of Ara and Su River) were investigated. And then, data analyses on the water quality and chemical equilibrium calculations were conducted using the aqueous speciation

computer code of the program PHREEQC.

MATERIALS AND METHODS

Site description

Matsu River is a typical acidified river of Japan. The source of the river is located near Mount Azuma, overlooking the city of Yonezawa in southeast Yamagata Prefecture. The abandoned Nishiazuma mine is located on Mount Azuma and continues to discharge AMD. Infiltration treatment has been attempted by diverting AMD into the ground through 80 permeable wells of about 80 m in depth. The AMD discharged into the permeable wells is diluted by groundwater and neutralized by cation exchange upon contact with soil and bedrock; the treated AMD leaches out and flows into nearby rivers. Six stations (**Fig. 1 a**) were selected to comprehensively investigate the Matsu River area. Station M1 was located at the infiltration treatment site used to divert AMD into the permeable wells. Station M2 was in a stream that received leachate from the permeable wells. Stations M3 and M4 were located in the transition zone between the mountainous area and the agricultural and urban areas. Stations M5 and M6 received the inflow from several agricultural irrigation canals and snow discharging ditches and were situated in an agricultural or urban area.

On the other hand, the source of Ara and Su River lies at the eastside of Azuma Mountain Range that has active volcanos. The basin of the rivers which are acidified rivers

received the inflows of hot spring water and/or wastes from facilities of a hot spring town. Ara River runs through the urban area of western part of Fukushima City and then flow into Abukuma River after joining several tributaries like Su River, etc. Su River as the biggest tributary of Ara River, at the part of headstream, reserves the inflows of acidic hot spring water and/or wastes from the facilities of the hot spring. Consequently, Ara River has been acidified at the downstream reaches after joining Su River. Seven stations (Fig. 1 b)) were selected. Station A1 was located at the reaches of Su River, upstream of the junction of Su River and Amado River. Station A2 was located at the reaches of Amado River, upstream of the junction. Station A1 and A2 were mainly in the agricultural area. Station A3 and A4 were downstream of the junction, located in the transition zone between the agricultural and urban areas. Station A5 was located in Ara River joining Su River at the downstream of Station A4. Station A6 and A7 were at the downstream end of the reach of Ara River, near the junction of Ara River and Abukuma River.

Field investigation

Sampling of river water at Matsu River was conducted on August 29 and October 31 in 2016 and July 21 and October 11 in 2017. Samplings at Ara and Su River were conducted on May 12, June 16, July 13, September 14, October 24, and December 1 in 2016 and April 24, May 17, June 29, August 29, October 27, November 17, and December 4 in 2017. The pH and electrical conductivity (EC) values were measured on site. River water samples were filtered through 0.45 μm membrane filters. After filtration, water samples were treated with nitric acid, and the dissolved B, Na, Ca, Mg, K, Fe, Al, Mn, Cd, Cr, Cu, Zn and Pb were analyzed by inductively coupled plasma-mass spectrometer (Elan DRCII, PerkinElmer Japan Co., Ltd., Yokohama, Japan) in accordance with standard protocols for analysis of water [20]. Arsenic concentrations were determined by atomic absorption spectrophotometry (AA7000, Shimadzu Corporation, Kyoto, Japan) with a hydride generator (Shimadzu Corporation). Anion (Cl^- , SO_4^{2-} , and NO_3^-) in the water samples were measured by ion chromatography (DX-500, Thermo Fisher Scientific K.K., Tokyo, Japan) after filtration through a 0.45 μm membrane filter. Fluoride concentrations were determined by Lanthanum-alizarin complex spectrophotometric method (ALC) after steam acid distillation. The analyses of fluoride were according to the testing method for industrial wastewater of Japan [21].

Modeling of chemical equilibrium with aluminum minerals and the speciation of aluminum and fluoride

PHREEQCI Version 3 with the thermodynamic datasets: wateq4f.dat was used to calculate the concentrations of aluminum and fluoride species in the river water samples and the chemical equilibrium between the river water samples and most common aluminum minerals predicted to form in acidified river environments and acid sulfate soil environments: amorphous $\text{Al}(\text{OH})_3$, alunite ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$) and basaluminite ($\text{Al}_4(\text{SO}_4)(\text{OH})_{10} \cdot 5\text{H}_2\text{O}$) [22–25]. PHREEQCI Version 3 is a complete Windows-based graphical user interface to the aqueous speciation computer code of the program PHREEQC [13]. PHREEQC is based on an ion association aqueous model and can perform several types of modeling including chemical speciation and equilibrium. PHREEQC has been used for calculation of aqueous speciation, saturation indices [$\text{SI} = \log (\text{ion activity product/solubility product})$] and ion activities at several situations such as in surface and groundwater [26].

The concentrations of aluminum and fluoride species were calculated from the chemical analysis data on the field investigation (pH, water temperature, concentrations of dissolved B, Na, Ca, Mg, K, Fe, Al, Mn, Cd, Cr, Cu, Zn As, Pb, F, Cl^- , SO_4^{2-} , and NO_3^-) as input. Calculated concentrations of the aluminum and fluoride species (Al^{3+} , AlOH^{2+} , $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3$, $\text{Al}(\text{OH})_4^-$, AlF^{2+} , AlF_2^+ , AlF_3 , AlF_4^- , AlSO_4^+ , $\text{Al}(\text{SO}_4)^-$, HF , MgF^+ , CaF^+ , FeF^{2+} , NaF , MnF^+ , $\text{BF}(\text{OH})_3^-$, $\text{BF}_2(\text{OH})_2^-$, BF_3OH^- , BF_4^- , CdF^+ , CdF_2 , CuF^+ , FeF_2^+ , FeF_3 , HF_2^- , PbF^+ , PbF_2 , PbF_3^- , PbF_4^{2-} , ZnF^+ and F^-) had output as the results.

The chemical equilibrium with the aluminum minerals were simulated as follows: The total concentrations of dissolved aluminum in which the river water samples reach the equilibrium with each aluminum mineral was calculated at the saturation indices (SI) of 0. And then, differences of predicted and actual concentrations of dissolved aluminum were evaluated using residual substance standard deviations between those predicted and actual concentrations to determine which of the aluminum minerals is most likely to precipitate in the acidified rivers. During calculations, ionic strength effects on the reactions were taken into accounts with using Debye-Hückel equation by PHREEQC. Equilibrium constants in the thermodynamic datasets: wateq4f.dat were also adjusted for water temperature data on the field investigation by PHREEQC using van't Hoff's equation with the enthalpy of reaction listed in the datasets.

Fig. 2 Mean pH and concentrations of the major elements at each station of Matsu River in 2017.

a) aluminum, fluoride and pH, b) the major elements, and c) sulfate ion

RESULTS AND DISCUSSION

Figure 2 a), b) and c) show the mean pH and concentrations of the major ions at each station of Matsu River in 2017. Additionally, the numerical value and the standard deviation of each element in **Fig. 2** are listed in **Table 1**. The concentration of SO_4^{2-} was more than 400 mg/L at Station M1. It was due to the inflow of AMD with high concentrations of acid and SO_4^{2-} from many discharge spots in the abandoned mine. The concentration of SO_4^{2-} in Station M2 that received leachate from the permeable wells showed a sharp decrease down to 91.7 mg/L. The pH value was 2.61 at Station M1, but drastically increased to 4.49 at Station M2. The concentrations of metals were high at Station M1 (especially Ca: 13 mg/L, Fe: 39.3 mg/L and Al: 15.2 mg/L), and the concentrations of all metals except Ca decreased downstream of Station M2. These decreases in SO_4^{2-} and dissolved metal concentrations and increase in pH were attributable to the infiltration treatment. The increase in Ca was probably due to leaching from soil and bedrock at the infiltration treatment site. On the other hand, Cl^- increased downstream from Station M5. This increase in Cl^- was due to an increase in the inflow of wastewater from domestic, agricultural and livestock sources with a change in the land use from the mountainous areas to the agricultural and urban areas. Downstream after Station M2, the concentrations of SO_4^{2-} , Mg and Mn decreased gradually due to dilution by water inflow of the river's tributaries and the wastewater from domestic, agricultural and livestock sources. Although the river water was diluted from Stations M2 to M4, the pH values did not clearly increase, but remained weakly acidic. However, the pH increased sharply downstream of Station M4. In the weakly acidic region from Stations M2 to M4, the Al concentration remained relatively high (M4: 2.23 mg/L)

compared with those in downstream sites (M5: 0.04 mg/L and M6: 0.74 mg/L). **Table 2 a)** shows the concentrations of the minor ions and dissolved organic carbon (DOC) at each station of Matsu River in 2017. The concentrations of Cu, Zn, Cd, Pb and Cr were especially high at Station M1 compared with the ones at the downstream stations. However, the concentrations of these ions except for fluoride decreased downstream of Station M2. **Figure 3 a), b) and c)** show the mean pH and concentrations of the major ions at each station of Ara River and Su River in 2017. Additionally, the numerical value and the standard deviation of each element in **Fig. 3** are listed in **Table 3**. The concentrations of SO_4^{2-} and Al were relatively high at Station A1 compared with ones at other stations (SO_4^{2-} : 192 mg/L, Al: 9.50 mg/L). Since the acidic hot springs located in the headwaters of Station A1 contained high concentrations of SO_4^{2-} as well as Al, Ca, Mg and Na, it can be said that Station A1 at the upstream reaches of Ara River had been affected by the inflows of the acidic hot spring water and/or wastes from facilities of the hot springs. Thereafter, the concentrations of SO_4^{2-} and Al decreased gradually downstream with the joining of the tributaries such as Amado River (Station A2) and Ara River (Station A5) and the inflow of wastewater from domestic, agricultural and livestock sources. The concentrations of SO_4^{2-} and Al at the most downstream site (Station A7) were 84.1 and 0.05 mg/L, respectively. The pH at Station A1 was 3.81 and increased gradually downstream up to 6.16 at Station A7.

Table 2 b) shows the concentrations of the minor ions and DOC at each station of Ara River and Su River in 2017. Fluoride concentration at Station A1 was higher than the ones at the downstream stations (F: 470 $\mu\text{g/L}$). There were no big differences in the concentrations of Cu, Zn, Cd, Pb and Cr among the stations in Ara River and Su River. Additionally,

Table 1 Mean values and the standard deviations of pH and concentrations of the major elements at each station of Matsu River in 2017.

Station	pH	mg/L																				
		F		Al	Na	Mg	Ca	Mn	Fe	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻										
		Ave.*	S.D.*	Ave.	S.D.	Ave.	S.D.	Ave.	S.D.	Ave.	S.D.	Ave.	S.D.	Ave.	S.D.							
M1	2.6	0.2	0.11	<0.01	15.2	2.95	4.56	1.61	3.32	0.91	13.2	3.55	0.50	0.01	39.4	16.1	0.84	0.05	0.14	<0.01	427	95.1
M2	4.6	0.1	0.10	0.08	4.23	2.88	7.83	4.50	4.01	2.40	25.3	14.8	0.24	0.15	0.72	0.89	1.43	0.06	0.52	0.03	91.7	25.7
M3	4.8	<0.1	0.15	0.03	2.64	2.38	8.39	4.84	3.58	2.18	23.2	14.9	0.19	0.13	0.64	0.82	2.00	0.20	2.39	2.22	76.6	27.3
M4	4.8	<0.1	0.16	<0.01	2.23	2.12	7.34	4.29	3.13	2.02	19.3	13.4	0.19	0.13	0.76	0.85	1.89	0.12	0.75	0.10	62.9	26.9
M5	6.3	0.4	0.09	0.07	0.04	0.01	7.56	3.69	1.97	0.56	11.6	3.11	0.06	<0.01	0.26	0.33	4.02	0.69	1.42	0.53	28.2	6.8
M6	6.7	0.3	0.02	0.03	0.74	1.02	8.36	4.23	2.40	0.79	13.2	4.22	0.04	<0.01	0.31	0.39	4.65	0.60	2.57	0.44	26.9	4.2

* Ave. and S.D. are the mean value and standard deviation, respectively.

fluoride in stations in Ara River and Su River remained at a high concentration compared with the ones in Matsu River. The concentrations of major ions of Takayu Hot Spring which is one of the hot springs flowing into Ara River and Su River are shown in **Table 4** [27]. The hot spring water is notably containing high concentration of fluoride compared with that of the AMD at Station M1 of the abandoned Nishiazuma Mine (See **Table 1**). Fluoride was reported to be emitted as hydrogen fluoride from volcanoes and then removed from the atmosphere by the deposition on land or surface water [18]. Consequently, the high concentrations of fluoride in Ara River and Su River are probably caused by the inflows of the hot spring water containing a large amount of fluoride due to the volcanic activity of Azuma Mountain Range.

Figure 4 a) and **b)** show the relative values of concentrations of the major ions at each station in Matsu River as well as Ara River and Su River, respectively. The relative values of Matsu River, Ara River and Su River in **Fig. 4 a)** and **b)** were calculated based on concentrations for Station M3 and A1, respectively. In Matsu River, relative values of the major ions relating with the AMD (H^+ , Al, Ca, Mn and SO_4^{2-}) decreased apparently between Stations M3 and M5. These decreases in relative values could be due to increase in the inflow of the tributaries and wastewater with a change in the land use from the mountainous areas to the agricultural and urban areas. Moreover, the decreases in the relative values of Al and H^+ ions were similar and greater than those of Mn and SO_4^{2-} .

In Ara River and Su River, relative values of H^+ ion, Al, Mn and SO_4^{2-} also decreased apparently between Stations A1 and A3 similarly. And then, these relative values decreased downstream gradually. These decreases in relative values could be also due to increase in the inflow of the tributaries and wastewater as well as the case of Matsu River. Additionally, both decreases in Al and H^+ ions were also greater than those of Mn and SO_4^{2-} .

The decreases in the relative values of Mn and SO_4^{2-} would reflect how the degree of dilution occurs by the inflow of the tributaries and wastewater, since Mn and SO_4^{2-} are relatively chemically stable in the pH ranges of both rivers (pH range of Matsu River: 4.6 ~ 6.7, Ara River and Su River: 3.8 ~ 6.2) and these ions upstream are especially higher than ones downstream in both rivers. Consequently, the greater decreases in Al and H^+ ions have been indicating that Al and H^+ ions decreased not only due to the dilution but also due to other factors.

In Aka River, which is one of the famous acidified rivers in Japan, the riverbed sediments have been reported to have

Table 2 Concentrations of the minor elements and DOC at each station of a) Matsu River and b) Ara River and Su River in 2017.

Station	a)											
	Cu		Zn		Cd		Pb		Cr		DOC	
	Ave.* S.D.*		Ave. S.D.		Ave. S.D.		Ave. S.D.		Ave. S.D.		Ave. S.D.	
M1	22.0	2.9	66.6	13.1	1.9	0.3	77.8	8.0	16.7	1.0	0.8	< 0.1
M2	2.1	1.0	16.2	8.7	0.5	0.3	2.5	1.1	0.6	0.4	0.7	0.2
M3	1.7	1.0	14.0	8.3	< 0.5	-	1.8	0.9	< 0.5	-	1.0	0.2
M4	1.4	0.8	11.0	6.4	< 0.5	-	1.5	1.0	< 0.5	-	1.2	0.4
M5	0.6	0.2	3.9	0.0	< 0.5	-	< 0.5	-	< 0.5	-	1.1	0.3
M6	0.9	0.5	4.6	1.0	< 0.5	-	< 0.5	-	< 0.5	-	1.0	0.1

* Ave. and S.D. are the mean value and standard deviation, respectively.

Station	b)											
	Cu		Zn		Cd		Pb		Cr		DOC	
	Ave.* S.D.*		Ave. S.D.		Ave. S.D.		Ave. S.D.		Ave. S.D.		Ave. S.D.	
A1	3.0	1.4	30.3	14.2	< 0.5	-	0.7	0.4	0.7	0.3	0.6	0.3
A2	0.8	0.6	4.0	2.2	< 0.5	-	< 0.5	-	< 0.5	-	0.7	0.2
A3	1.9	1.0	20.7	12.2	< 0.5	-	< 0.5	-	< 0.5	-	0.4	0.1
A4	1.8	1.1	16.3	9.4	< 0.5	-	< 0.5	-	< 0.5	-	0.5	0.3
A5	0.6	0.4	5.8	2.1	< 0.5	-	< 0.5	-	< 0.5	-	0.5	0.1
A6	1.0	0.5	11.3	6.0	< 0.5	-	< 0.5	-	< 0.5	-	0.4	0.1
A7	0.9	0.4	10.2	5.9	< 0.5	-	< 0.5	-	< 0.5	-	0.5	0.1

* Ave. and S.D. are the mean value and standard deviation, respectively.

Fig. 3 Mean pH and concentrations of the major elements at each station of Ara River and Su River in 2017.
a) aluminum, fluoride and pH, b) the major elements, and c) sulfate ion

much higher Al content where pH is greater than about 5 [5]. Moreover, authors indicated that products of Al hydrolysis were found to have precipitated onto the riverbed, which supports the hypothesis that Al ions and insoluble products were formed by hydrolysis of Al in Matsu River [7]. Therefore, the observed greater decreases in Al in Ara and Su rivers

were also likely due to the lower solubility of aluminum hydroxide when pH was raised by the dilution. In previous study, authors estimated the main form of Al precipitate in Matsu River according to whether field data of Al concentration fit the curves of solubility diagrams controlled by each mineral: amorphous $\text{Al}(\text{OH})_3$, basaluminite or jurbanite. The

Table 3 Mean values and the standard deviations of pH and concentrations of the major elements at each station of Ara River and Su River in 2017.

Station	pH		mg/L														NO ₃ ⁻	SO ₄ ²⁻				
	F	Al	Na	Mg	Ca	Mn	Fe	Cl ⁻	Ave.	S.D.	Ave.	S.D.	Ave.	S.D.	Ave.	S.D.						
	Ave.*	S.D.*	Ave.	S.D.	Ave.	S.D.	Ave.	S.D.	Ave.	S.D.	Ave.	S.D.	Ave.	S.D.	Ave.	S.D.	Ave.	S.D.				
A1	3.8	0.4	0.47	0.09	9.50	3.52	21.2	8.6	17.5	7.5	40.8	15.3	0.69	0.27	1.23	0.88	22.2	5.9	1.8	0.5	192	44.7
A2	6.6	0.5	0.07	0.07	0.10	0.07	5.06	2.5	3.42	1.7	9.85	3.6	0.02	0.01	0.10	0.18	2.8	0.5	2.3	0.7	13.2	4.4
A3	4.7	0.3	0.30	0.12	4.66	2.79	16.8	7.8	13.7	6.5	28.7	11.1	0.49	0.24	0.51	0.70	16.0	5.1	2.4	0.6	126	41.1
A4	4.8	0.3	0.25	0.11	3.81	2.42	16.7	7.6	13.4	6.3	29.4	10.7	0.46	0.22	0.52	0.66	15.4	4.4	3.1	0.6	117	32.8
A5	7.2	0.2	0.26	0.07	0.07	0.04	12.5	4.9	8.08	3.4	25.9	8.3	0.05	0.03	0.25	0.49	8.2	1.8	0.9	0.1	62.1	11.8
A6	5.7	0.5	0.22	0.13	0.25	0.24	15.0	6.8	11.6	5.4	28.8	9.5	0.27	0.13	0.36	0.61	13.2	3.8	3.2	1.0	88.8	22.0
A7	6.2	0.2	0.21	0.06	0.05	0.06	12.7	6.5	9.3	4.9	28.7	8.9	0.19	0.11	0.32	0.61	12.9	3.3	3.4	0.9	84.1	18.0

* Ave. and S.D. are the mean value and standard deviation, respectively.

results showed that basaluminite would likely be the main form of Al precipitate in Matsu River [6]. Consequently, the consumption of the alkali component (OH⁻) through the hydrolysis of Al ions and the forming of basaluminite as shown in the reactions (1) – (3) likely act as pH buffer with the inhibition of a smooth increase in pH at Matsu River. The middle to lower reaches in Ara River and Su River also would have an occurrence of the pH buffering like that in Matsu River.

However, at Station A3 in which all relative values decreased apparently in Ara River and Su River, the relative values of Al and H⁺ ion remained more than 49% and 10%, respectively, while those of Al and H⁺ ions in Matsu River were less than 2% and 4%, respectively. In addition, the relative values of Al and H⁺ ions continued to decrease downstream. This behavior of Al and H⁺ ions in Ara River and Su River clearly differs from that in Matsu River. This difference in aluminum behavior suggested that the aluminum and pH behaviors in Ara River and Su River have been affected by factors other than the hydrolysis of Al ions.

The most common aluminum minerals predicted to form in AMD and acid sulfate soil environments are amorphous Al(OH)₃, alunite (KAl₃(SO₄)₂(OH)₆), basaluminite (Al₄(SO₄)(OH)₁₀·5H₂O) and jurbanite (Al(OH)SO₄·5H₂O): see reactions (3) – (6) [22–25]. The chemical equilibrium with the most common aluminum minerals was simulated for Matsu River, Ara River and Su River. Dissolved forms of aluminum which can exist in river water were used in the simulations: Al³⁺, AlOH²⁺, Al(OH)₂⁺, Al(OH)₃, Al(OH)₄⁻, AlF²⁺, AlF₂⁺, AlF₃, AlF₄⁻, AlSO₄⁺ and Al(SO₄)₂⁻. The predicted concentration of each dissolved form of aluminum in which the river water samples reach the equilibrium with

Table 4 Concentrations of major elements of Takayu Hot Spring.

pH	F ⁻	Cl ⁻	SO ₄ ²⁻	Na	K	Mg	Ca	Al	Mn
	mg/L								
2.7	1.60	56.7	619	57.2	23.7	26.0	95.2	30.3	1.40

Fig. 4 Relative values of concentrations of the major elements at each station in a) Matsu River and b) Ara River and Su River. **Fig. 5** Root mean square errors (RMSE) between those predicted and actual aluminum concentrations for the aluminum minerals at each station in a) Matsu River and b) Ara River and Su River.

each aluminum mineral was calculated by PHREEQC. And then, the total concentrations of dissolved aluminum (ΣAl) in the equilibrium states were predicted as follows:

$$\begin{aligned} \Sigma\text{Al} = & [\text{Al}^{3+}] + [\text{AlOH}^{2+}] + [\text{Al}(\text{OH})_2^+] + [\text{Al}(\text{OH})_3] + \\ & [\text{Al}(\text{OH})_4^-] + [\text{AlF}_2^{2+}] + [\text{AlF}_2^+] + [\text{AlF}_3] + [\text{AlF}_4^-] + [\text{AlSO}_4^+] \\ & + [\text{Al}(\text{SO}_4)_2^-] \end{aligned} \quad (7)$$

For the following discussions, the total concentration of dissolved aluminum (ΣAl) in the equilibrium states is to be called as the predicted aluminum concentration. On the other hand, the aluminum concentration in the river water

sample is to be called as the actual aluminum concentration. The concentrations of Si were analyzed at all stations in the investigations. The maximum and minimum Si concentration was 62.8 mg/L at Station A1 on Aug. 28 and 11.4 mg/L at Station M5 on Jul. 21. The differences of ΣAl between the model assuming a concentration of 100 mg/L Si and the ones not assuming it were less than 0.1% of predicted aluminum concentrations. Therefore, the Si concentrations were not introduced into the model, since the modeling results were not sensitive to Si in the concentration range observed in both rivers.

Figure 5 a) and b) show the root mean square errors

Fig. 6 Distribution of aluminum species calculated from the data on the field investigation in a) Matsu River and b) Ara River and Su River.

(RMSE) between those predicted and actual aluminum concentrations for the aluminum minerals at each station in a) Matsu River and b) Ara River and Su River. The equation for the calculation of RMSE is as follows:

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^n (\text{predicted } Al_i - \text{actual } Al_i)^2}{n}} \quad (8)$$

where n , *predicted Al_i* and *actual Al_i* represent the number of sampling in each station, predicted and actual aluminum concentration in each sampling, respectively. The RMSE showed as negative logarithm value ($-\log \text{RMSE}$) on the vertical axis in **Fig. 5**. Consequently, the differences of predicted and actual aluminum concentrations were smaller toward the upper side of the vertical axis. At all stations in both rivers, the negative logarithm values of RMSE for basaluminite and alunite were clearly higher than the ones for amorphous $\text{Al}(\text{OH})_3$. This result shows the predicted aluminum concentrations for basaluminite and alunite were closer to actual ones than the predicted ones for amorphous $\text{Al}(\text{OH})_3$ and that the solubility of aluminum was mainly controlled by basaluminite and alunite. Especially, in Matsu River, the negative logarithm values of RMSE for basaluminite greatly increased between Station M4 and M5 in which a sharp increase in pH was confirmed. This increase possibly suggests that primarily basaluminite controlled the solubility of aluminum in Matsu River. The crystallization of gibbsite from amorphous $\text{Al}(\text{OH})_3$ was reported to be greatly inhibited by the presence of SO_4^{2-} [28], and the presence of basaluminite in the precipitates formed upon the neutraliza-

tion of acid sulfate soil leachates were also confirmed by X-ray absorption near-edge structure spectroscopy [22]. These reports can support our suggestions.

The concentrations of aluminum species calculated from the data on the field investigations in both rivers are shown in **Fig. 6 a)** and **b)**. Total height of the bar charts at each station describes the actual aluminum concentration derived from the data on the field investigation. Each pattern in the bar charts shows the calculated concentration of each aluminum species in the explanatory note. In both rivers, the total aluminum concentration was almost occupied by AlSO_4^+ , AlOH^{2+} , Al^{3+} and Al-F complex . There was a report that the dissolved aluminum species contained in extraction water from acidic soil located in woodland in the Netherlands consisted of AlSO_4^+ , AlOH_2^+ , Al^{3+} and Al-F complexes [29]. This report has been supporting our results. However, it also indicated that the composition ratio of the dissolved aluminum species significantly varied depending on the sampling location [29]. Moreover, Mulder *et al.* [29] reported that organically complexed aluminum contributed at about 7% in the soil extraction water such that Al , DOC and pH were 50.2 mg/L, 27.7 mg/L and 3.98, respectively. Additionally, Dahlgren *et al.* [30] indicated that inorganic aluminum species were dominant species when organic C/metal atomic ratios: $\text{DOC mol/L}/\text{sum of all metal mol/L}$, were <50 at the study of aqueous aluminum in leachates from a subalpine Spodosol located in the Cascade Range of Washington State. In this study, DOC in both acidified rivers was sufficiently low compared with that in the Mulder's report (see **Table 2**). Moreover, the organic C/Al atomic ratios at Stations M2 and

Fig. 7 Breakdown of the Al-F complex at each station in a) Matsu River and b) Ara River and Su River.

A3 where the precipitation of basaluminite and alunite had not yet started were 36 and 19, respectively. Consequently, the calculations of aluminum and fluoride species were probably not influenced at the sufficient low DOC conditions.

It is thought that Al-F complexes, especially, AlF^{2+} with a relatively large formation constant, formed preferentially over the others and that AlSO_4^+ and AlOH^{2+} would form followed by the formation of the Al-F complexes (see reactions 1, 9 and 10). Nevertheless, AlSO_4^+ was more than half of the total Al concentration at each station located in the up and middle reaches with a pH range ≤ 5.0 (M3, M4, A3 and A4). The high concentrations of AlSO_4^+ in the up and middle reaches (M3, M4, A3 and A4) would be due to Al and SO_4^{2-} existing in large quantities in the upstream reaches. On the other hand, AlSO_4^+ have decreased drastically in the pH range > 5.0 .

Figure 7 a) and b) show the breakdown of the Al-F complex at each station. AlF^{2+} was the dominant species of Al-F complex at the up and middle reaches (M3, M4, A3 and A4). The abundance ratio of AlF_2^+ increased at the downstream reaches. Additionally, the concentration of Al-F complex in Ara River and Su River decreased downstream mildly compared with that in Matsu River. This result suggests that the Al-F complexes still have been remaining even in the downstream reaches in Ara River and Su River. It would be due to high concentrations of fluoride in both rivers (Table 3). Fluoride speciation was also conducted data on the field investigation in both rivers. All fluoride species which can

be calculated by PHREEQC were considered as listed in the materials and methods section. The Al-F complex occupied almost all fluoride concentrations at each station in both rivers, although their data are not shown in this paper. The other fluoride species consisted less than 1% and 3% of the fluoride concentration in Matsu River and Ara and Su rivers, respectively.

Figure 8 a) and b) show the concentrations of total fluoride, Al-F complex, fluoride ion and pH at each station in both rivers. In Matsu River, the concentrations of fluoride ions (F^-) increased downstream. Additionally, Al-F complex decreased obviously with the increase in fluoride ions at the downstream stations of M4 where pH obviously increased. These results suggest that aluminum ions would be removed from Al-F complex by the aluminum consumptions with the precipitation as basaluminite and that pH would increase rapidly after the consumption of aluminum ions. On the other hand, the concentrations of total fluoride and Al-F complex at all stations in Ara River and Su River were high compared with those in Matsu River. This would be caused by the inflow of hot spring water with high content of fluoride into the upper reaches of Su River and the joining of Ara River (Station A5) with relatively high concentration of fluoride (as shown in Table 3) at the downstream of Station A4. Figure 9 shows scatter graph of the concentration ratio of total fluoride to aluminum for pH value (total F/Al) in both rivers. The plot in Fig. 8 shows not the average values but the individual measured value at each investigation. The concentration ratios of both rivers were less than 0.6 in a pH range ≤ 5.0 . This is because the concentrations of Al were high in this pH range in which the precipitation of basaluminite and alunite had not yet started. Moreover, almost all the concentration ratios

Fig. 8 Concentrations of total fluoride, Al-F complex and fluoride ion and pH at each station in a) Matsu River and b) Ara River and Su River.

Fig. 9 Concentration ratio of total fluoride to aluminum for pH value (total F/Al) in both rivers.

were distributed in more than 5 in a pH range ≥ 6.5 . This is due to the decrease in concentrations of Al in this pH range wherein the hydrolysis of Al ions had almost completed. However, in the pH range > 5.0 and < 6.0 , the concentration ratios of only Ara River and Su River were distributed in $0.2 \sim 8.0$. This result suggested that only Ara River and Su River have high concentration ratios of total fluoride to aluminum in the pH range > 5.0 and < 6.0 wherein the hydrolysis of Al ions has been progressing. Additionally, in **Fig. 3**, Station A3 of Ara River and Su River has clearly high relative values of Al and H⁺ ions compared with the ones at Station M5 of Matsu River, although all relative values decreased apparently at Stations A3 and M5. These results suggest that the abundance of Al-F complex generated in Ara River and Su River would delay the aluminum consumptions by interfering with the formation of basaluminite.

In acidified river environments, aluminum ions were con-

sumed rapidly in the pH range between about 5.0 and 6.0 with a pH buffering state by the progress of the hydrolysis of aluminum ions, in principle [6,17]. However, our results indicated that fluoride forms an abundance of Al-F complex mainly AlF_2^{2+} with aluminum ions in the case with high concentration ratios of fluoride to aluminum and that the Al-F complexes would be delaying the aluminum consumptions by interfering with the hydrolysis of aluminum ions. The delay on the Al consumptions by the Al-F complexes would moderate the pH buffering effect of the hydrolysis of Al ions and moderate the sharp rise of pH observed after the completion of the hydrolysis of Al ions.

CONCLUSIONS

In the present work, the behavior of pH, dissolved aluminum, and fluoride species in acidified river environments rich in sulfate and fluoride was studied.

The modeling of the speciation of aluminum and fluoride with using the field investigation data showed that the dominant aluminum species are $\text{Al}(\text{SO}_4)_4^+$, AlOH^{2+} , Al^{3+} and Al-F complexes in Matsu River as an acidified river rich in sulfate and Ara River and Su River as acidified rivers rich in sulfate and fluoride. In both rivers, AlSO_4^+ was more than half of the total aluminum concentration at each station located in the upper and middle reaches in a pH range ≤ 5.0 , while AlSO_4^+ had decreased drastically in the pH range > 5.0 . The Al-F complexes still have been remaining even in the downstream reaches in Ara River and Su River rich in fluoride. The modeling of chemical equilibrium with the aluminum minerals indicated that aluminum ions have been precipitating as mainly basaluminite and alunite by the hydrolysis.

aluminum ions were consumed rapidly in the pH range between about 5.0 and 6.0 with a pH buffering state such that pH hardly continues by the progressing of the hydrolysis of aluminum ions. However, in Ara River and Su River rich in fluoride, an abundance of Al-F complex mainly AlF^{2+} would be delaying the aluminum consumptions by interfering with the hydrolysis of aluminum ions. The delay on aluminum consumptions by the Al-F complexes would moderate the pH buffering effect of the hydrolysis of aluminum ions and also moderate the sharp rise of pH observed after the completion of the hydrolysis of aluminum ions.

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