High Aluminum Levels Accompanied by Near-Neutral pH in Outflow from a Forest Watershed in Aichi Prefecture, Japan

愛知県の森林流域における高濃度 Al の流出

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We found a high concentration of dissolved aluminum accompanied by almost neutral pH in stream water within a suburban secondary forest underlain by granite bedrock. We aimed to clarify the characteristics of the high Al levels in runoff by observing the chemical properties of spring water, stream water and surface soils. The mean pH values of spring water and stream water were 6.09 and 6.44, and the mean concentrations of dissolved Al of each after filtration with 0.45 μm membrane were 66 $\mu\text{mol/L}$ and 41 $\mu\text{mol/L}$, respectively. The concentrations of dissolved Al in these waters were extremely high for such pH levels. There was no relationship between dissolved Al concentration and dissolved organic carbon (DOC) which, if it did exist, would be considered an indicator of organic species of Al in the stream water. The concentration of dissolved Al was highly correlated with Fe concentration but not with Si. The total concentration of water-soluble Al in soil extracts from the surface soils around the stream was extremely high, and the concentrations of dissolved Al, Fe and Si were highly correlated. These results suggest that the high concentration of Al in the spring water and stream water are derived from weathering of aluminosilicates and that Al might be dissolving in water as inorganic colloidal species.

Key words: Spring water, Stream water, Al, DOC, pH, Acidification

本研究では、愛知県内の花崗岩地域の二次林から流出する渓流水の pH が中性に近い値であるにもかかわらず、高い濃度の Al を含むことを見出し、その Al 流出の化学的な特徴を明らかにすることを目的として、湧水と渓流水の溶存 Al と他の溶存成分の関係、および表層土壌の化学性について調べた。湧水、渓流水の平均 pH 値は 6.09, 6.44 であり、0.45 μm メンブレンフィルタでろ過した湧水、渓流水の平均溶存 Al 濃度はそれぞれ 66, 41 $\mu\text{mol/L}$ であった。このような中性に近い pH の渓流水としては、きわめて高い濃度の Al が存在することが明らかとなった。有機態 Al の指標である溶存有機炭素 (DOC) と溶存 Al 濃度との間には関係は見られなかった。また、溶存 Al と Fe 濃度との高い相関には見られたが、Si との間には相関が見られなかった。一方、溪流周辺の表面土壌には、水溶性 Al 濃度が非常に高い値を示す試料があり、溶存 Al と Fe, Si 濃度の間には高い相関関係が認められた。これらの結果は、渓流水と湧水の Al がケイ酸塩鉱物の風化によって流出していること、さらには無機態コロイド状 Al で存在している可能性を示している。

キーワード: 湧水、渓流水、アルミニウム (Al)、溶存有機炭素 (DOC)、pH、酸性化

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I. Introduction

In forest ecosystems, soil acidification caused by acid deposition results in aluminum (Al) dissolution into soil solution and has been considered a major mechanism of forest decline over recent decades (Lawrence *et al.*, 1988; Chapman *et al.*, 1993; Sullivan and Drever, 2001; Walker *et al.*, 1990). It has been well established that the toxicity and geochemical mobility of dissolved Al in natural aquatic systems depend strongly on the chemical species of Al present, and that the species in which dissolved Al exists varies with solution pH (Driscoll, 1984). In Europe, especially in Scandinavia, soil acidification has induced increases in Al concentration in stream water with toxic effects on aquatic organisms (Cronan *et al.*, 1986; Harriman *et al.*, 1987; Christophersen *et al.*, 1990; Mulder and Stein, 1994; Boudot *et al.*, 2000; Herrmann, 2001; Stutter *et al.*, 2001; Lydersen and Lofgren, 2002; Mol *et al.*, 2003). On the other hand, few instances of acidification of stream water have been reported in Japan (Kaneko *et al.*, 2003; Umemura *et al.*, 2003) because of the high pH buffering capacity of Japanese soils, nevertheless the atmospheric loads of acidic materials are comparable between Europe and Japan. Consequently, the low concentrations of Al in stream water in Japan have led to a general perception that the effects of acidic deposition on aquatic systems are not so serious (Kaneko *et al.*, 2003).

However, we found a high concentration of dissolved Al accompanied by almost neutral pH in stream water in Foresta Hills, Aichi Prefecture, within a suburban secondary forest; Al concentrations were 10-100 times higher than in stream water from other forest watersheds in Japan (Kaneko *et al.*, 2003) while pH values remained similar (Ohrui and Mitchell, 1998; Toda *et al.*, 2000).

In the current work, we aimed to clarify the characteristics of the high Al levels in runoff by observing spatial and temporal changes in the chemical properties of spring water and stream water in Foresta Hills. Since elevated Al levels in water are generally accompanied by low pH or dissolved organic materials which bind to Al, we focused not

only on pH, but also on the concentration of dissolved organic carbon (DOC) as an indicator of organic species of Al. In addition, we compared the chemical properties of the water samples with those of water soluble components in the surface soils especially on iron (Fe) and silicon (Si) which are the major mineral-derived elements we would expect to see.

II. Materials and Methods

1. Experimental location

Foresta Hills is located in Toyota city, Aichi Prefecture, Japan (137°11'27"E, 35°02'00"N) and varies from 40 m to 105 m in altitude (Fig. 1). The catchment area is 0.0147 km² and the stream is a first-order tributary of the Yahagi River. The surveyed area consists of temperate secondary forest, where the dominant tree species are *Quercus serrata*, *Q. variabilis* and *Evodiopanax innovans*. The soil has formed in-situ from granite bedrock. In the study area, the annual precipitation was 1272 mm and the mean temperature was 16.8 °C in 2001. The soil type is a slightly dry brown forest soil (B₂-B₃) (Committee of Forest Soil of Japan, 1983).

2. Sampling and analysis

In the catchment, spring water and stream wa-

Fig. 1 Location of the study area.

ter were collected once a week from May 2002 to April 2003 (stream water 46 times, spring water 45 times). The stream water was sampled at five sites at 20-m intervals from the sampling site of the spring water (Fig. 1). To measure water soluble elements in soil, soil samples were collected from surface (0-5 cm depth from A horizon) and sub-surface (20-25 cm depth from B horizon) at six sites (Fig. 1) since the depth of A horizon in this slope ranged from 5 to 15 cm. Soil sampling was performed on June 26, 2002. After air-dried and sieving with 2 mm mesh, soil samples were shaken with 2.5 fold distilled water (soil 50g (D. W): water 125 ml) and then centrifuged. All water samples were filtered with a 0.45- μ m membrane filter and stored at 4 °C. Stream discharge in the catchment was measured continuously with a V-notch weir. Precipitation was measured using a rain gage (OTA, model NO34-T (RA-I)).

The pH and EC of water samples were measured using a dual probe meter, (TOA, model WM-

22WP). Al, Fe and Si in water samples were analyzed using an Inductively Coupled Plasma Spectrophotometer (Nippon Jarrell Ash, IRIS ICP). Dissolved organic carbon (DOC) was analyzed using a total organic carbon analyzer (Shimadzu, TOC-V CSV).

III. Results and Discussion

Fig. 2 shows the hydrograph during the study period. Total precipitation and runoff were 1268.9 mm and 252.0 mm (19.9%) in the study period.

Fig. 2 Hydrograph during the study period.

Fig. 3 Variations in the pH, EC values, dissolved Al, Fe, Si and DOC concentrations of spring water and stream water.

(from May 2002 to April 2003) respectively. The runoff ratio during the study period was lower than the one from 2000 to 2001 (31.8%) Stream discharge was closely related to precipitation for rainfall events exceeding 20 mm total rainfall.

The variations in pH and EC values and dissolved Al, Fe, Si and DOC concentrations of spring water and stream water during the observation period are shown in Fig. 3. In this figure, it is apparent that a high concentration of dissolved Al (max: 0.26 mmol/L) was observed in both spring water and stream water. The mean concentration of dissolved Al in spring water and stream water were 0.066 and 0.041 mmol/L, respectively. Such high Al concentrations in stream water reported previously in Europe and America have usually been accompanied by low pH values (3-5 (Mulder and Stein, 1994; Soulsby, 1995; Dise *et al.*, 2001; Stutter *et al.*, 2001; Lydersen and Löfgren, 2002) Dise *et al.* (2001) indicated that Al^{3+} released from soil when pH of soil solution decline below about 4.5. The pH values of spring water and stream water in our observations ranged from 5.51 to 6.96 and the mean values were 6.09 and 6.44, respectively. Though these values were lower than the average value of stream water in various Japanese forests (7.1) reported by Toda *et al.* (2000) it is obvious that the acidity of spring water or stream water was not enough low to dissolve Al^{3+} ion. Since the filter size used in our measurements (0.45 μm) was the same as that used in the previous studies on chemical characteristics of stream water (Neal, 1995; Sullivan and Drever, 2001) the high concentration of dissolved Al accompanied by relatively high pH of 5.51-6.81 in Foresta Hills seems to be unusual phenomenon.

Many researchers have reported that Al and Fe ions were dissolved as organic species into soil solution and stream water in forest ecosystems (Browne and Driscoll, 1993; Muscutt *et al.*, 1993; Chapman *et al.*, 1993; Berggren and Mulder, 1995; Kopáček *et al.*, 2000) Browne and Driscoll (1993) and Berggren and Mulder (1995) reported that aqueous Al species bind strongly to DOC. Also, Muscutt *et al.* (1993) Chapman *et al.* (1993) and

Fig. 4 The relationships among DOC, dissolved Al and Fe concentrations in stream water and spring water.

Kopáček *et al.*, (2000) found that a correlation between organic Al or organic Fe concentration and DOC when the concentration level of Al was low (under 0.009 mmol/L). On the contrary, our results show no relationship between DOC and dissolved Al or Fe concentration accompanied by high pH (about 6.5 (Fig. 4)) and higher Al concentration and comparable DOC compared with the levels in the previous reports. This observation suggests that the main species of Al in the waters from Foresta Hills, even if a small part is possible, should not be organic form.

In order to clarify spatial changes in the chemical characteristics of the stream water, the mean values of pH, EC, Al, Fe, Si and DOC in stream water were plotted according to distance from the springhead with 20 m interval (Fig. 5). Although there was no significant difference, among sampling sites, trends towards increasing pH values and decreasing EC values with distance from the spring were found. The increase in pH in stream water with distance from a spring water source has been observed in many catchments and was interpreted as being a result of the degassing of CO_2 due to the change in partial pressure (Collins and Jenkins, 1996; Ohte *et al.*, 2001; Stutter and Billett, 2003). The decrease in EC value means removal of ionic species from water and the degassing of CO_2 should be a possible mechanism of this by decrease

Fig. 5 The change in chemical characteristics with distance of stream flow from the springhead. (Error bar illustrates the standard deviation)

of proton and bicarbonate ion in water. In addition, the Al and Si concentrations showed a slight decrease trend due to water flow in Fig. 5. This suggests that coagulation of ionic species of Al such as aluminum hydroxide ions or colloidal species of Al or Si might occur through pH increase. However, it is noteworthy that about 0.03 mmol/L of Al was still found in the stream water 5. On the contrary, the concentrations of Fe and DOC did not change significantly over the distance of water flow measured. These facts indicate that Al found in the waters did not always behave with Fe or dissolved

organic matter.

Fig. 6 illustrates the relationship among dissolved Al, Fe and Si in the soil extracts of surface soil (0-5 cm depth) and sub-surface soil (20-25 cm depth). Although the concentrations of these elements in the soil extracts varied widely depending on the sampling sites, we found a clear correlation among these elements with a molar ratio of Al: Fe: Si of 1: 0.22: 0.45 in both surface soil and sub-surface soil, where the mean pH values of the soil extracts were 4.89 and 4.86, respectively. These results mean that the soils are acidic and that the water-soluble Al in soil extracts seems to be derived from aluminosilicate minerals of granite parent material.

In order to understand the origin of Al in stream water in Foresta Hills, concentrations of dissolved Al were plotted against concentrations of Si and Fe for stream water and spring water (Fig. 7). The lines in the figure show the corresponding relationship between pairs of elements found from soil extracts shown in Fig. 6. In the relation between dissolved Al and Si, the concentrations of dissolved Al were lower than for comparative Si values in the soil extract relationships. In general, concentration of SiO_2 in stream water reflects degree of weathering (Ohruai and Mitchell, 1998). The significant deviation of each plot from the correlation line obtained by soil extract indicates a subsequent dis-

Fig. 6 The relationships among dissolved Al, Fe and Si in the soil extracts of surface and sub-surface soils.

Fig. 7 The relationship between dissolved Al concentration and Fe or Si concentrations in spring water and stream water (straight lines illustrate the corresponding regression from soil extracts of surface and sub-surface soils)

solution of SiO_2 due to weathering during water infiltration through the surface soil to deeper layer in bedrock. In the case of the relation between Al and Fe, it can be seen that some plots follow the same relationships as the soil extracts, but that other plots seem to show a new correlation line. It is suggested that Al and Fe behave similarly within certain ratios from 0.07 to 0.22 in spring water and stream water. One possibility for the form of Al and also Fe is existence as colloidal particle smaller than $0.45 \mu m$. The fact was accorded with Mitchell *et al.* (2001) suggested Al and Fe would exist primarily in a solid colloidal form in stream water. More detailed research on the chemical form of Al would be necessary to understand this rare case of Al outflow accompanied by relatively high pH, i.e., over 6.

IV. Conclusions

In Foresta Hills, we found a high concentration of dissolved Al in spring and stream waters nevertheless the mean pH values of spring water and stream water were 6.09 and 6.44, respectively; the corresponding mean dissolved Al concentrations were 0.066 and 0.041 mmol/L. Until now, such high dissolved Al concentrations have not been found in

Japanese watersheds. In our study, the concentration of dissolved Al was highly correlated with Fe concentration but not with Si and there was no relationship between dissolved Al concentration and DOC, while the concentrations of dissolved Al, Fe and Si in soil extracts from the surface soils were closely correlated. These various pieces of evidence all combine to suggest that the high concentration of dissolved Al in the spring water and stream water should be derived from the weathering of aluminosilicates, and that main Al species might be an inorganic colloidal species in water. Further research on the chemical species of Al is necessary to clarify the mechanism of such a high concentration of Al runoff.

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