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## 学 位 論 文 要 旨

### Abstract

Two concerns about acid rain in the Hokuriku district have been studied. One was to evaluate the contributions of transported non sea-salt sulfate ions and nitrate ions from the Asian Continent to those in winter precipitation in the Hokuriku district. The other was to discuss the features and causes of acidified stream on both Imizu Hill and Kureha Hill.

The contributions of acidic constituents originating from the Asian Continent to the winter precipitation in the Hokuriku district were larger for non sea-salt sulfate ions than for nitrate ions. The contributions of both types of ions originated from the Asian Continent decreased from seacoast areas to inland areas. The contribution of nitrate ions of domestic origin to the winter precipitation in Hokuriku district was larger than the Asian contribution, even in the seacoast area.

The cause of acidification of stream water in Kureha Hill was considered to be nitrate ions leaching from the soil. The present results showed that nitrate ions deposited in Kureha Hill mainly originated from domestic pollutants. Therefore, if nitrate depositions of domestic origin were decreased, the nitrate concentrations in stream water in Kureha Hill might drop. However, cations leaching from soils in Kureha Hill and Imizu Hill were not controlled because sulfuric acid in the soil was the main cause of cations leaching into the stream waters in both Hills. The sulfuric acid was derived from pyrite, which might be present in tuff in the soils of both Hills.

## Introduction

Acid rain has been observed in Europe, North America and East Asia including Japan<sup>1)</sup>. Damage to the environment and the ecological system by acid rain includes destruction of forests and acidification of soils<sup>2)</sup>. Moreover, the deposition of nitrogen by nitrate ions and ammonium ions, which are dissolved in acid rain as acidic and neutralizing constituents, causes nitrogen saturation in the forest ecosystem<sup>3,4)</sup>.

One of the concerns about acid rain in the Hokuriku districts is transportation of non sea-salt sulfate ions from the Asian Continent. In winter, there is a northwestern wind that transports part of the sulfur oxides originating in China to districts along the Sea of Japan. China is thought to be the source of 88% of the sulfur oxides emitted in East Asian regions<sup>5)</sup>. Moreover, nitrate ions, derived from nitrogen oxide, might be transported from the Asian Continent accompanied by non sea-salt sulfate ions originating from those areas<sup>6)</sup>.

However, the difference of transported acidic constituents (non sea-salt sulfate ions and nitrate ions) concentrations in winter precipitation between Ishikawa Prefecture and Toyama Prefecture (Figure 1) is not revealed. Therefore, the

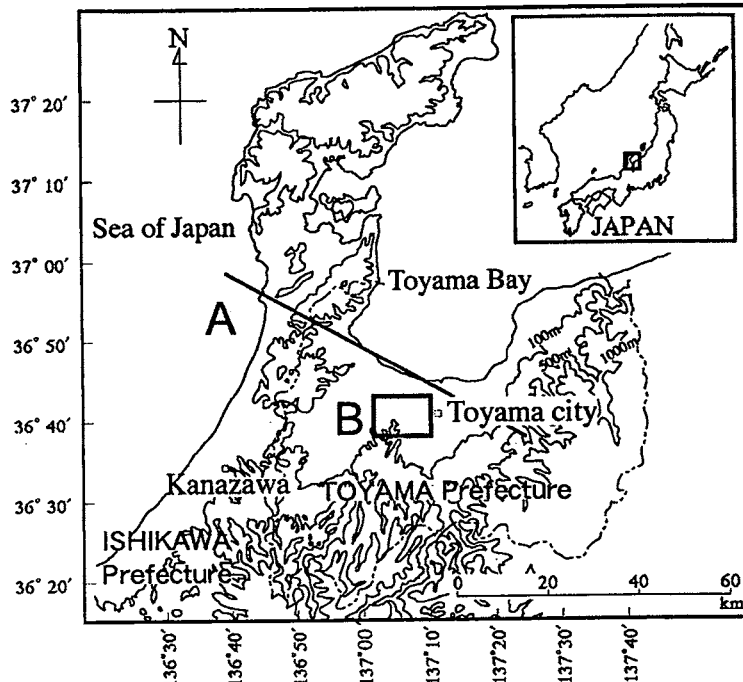


Figure 1 Locations of studying area

- A: Study on Origin and contribution of acidic constituents and neutralizing constituents in winter precipitation.
- B: study on acidification of stream water in the hills in Toyama Prefecture.

differences of contribution of transported acidic constituents to observed concentrations in Ishikawa Prefecture and Toyama Prefecture are not evaluated.

Meanwhile, another concern is how much damage do acid rain and acid depositions cause to the environment in the Hokuriku district.

In 1982 a salamander, *Hynobius Takedai* (Hokuriku Sanshouo) was discovered to be living and breeding in a small pond on Kureha Hill in Toyama city (Figure 1)<sup>7</sup>. The pond was fed by spring water with a low pH and high concentrations of nitrate ions<sup>8</sup>. This was the first investigation of the Toyama Science Museum. It was later found that water with low pH, low alkalinity, low concentrations of cations and high concentrations of nitrate ions flowed in almost all the streams on the western side of Kureha Hill. This was published in "Report on Kureha Hill Environment Investigation Program (1992-94)" by Toyama Science Museum<sup>9</sup>. Recently, the same type of water, with low pH, low alkalinity and low concentrations of cations but low concentrations of nitrate ions, was found in the streams on Imizu Hill (in Toyama city, Kosugi town, Fuchyu Town, Daimon town and Takaoka city) (Figure 1) in the "Satoyama Environment Investigation Programs" in progress by Toyama Science Museum. However, a previous report on the Gejo River, whose watershed is on the Imizu Hill, showed that the water with low alkalinity and low concentrations of cations had already flowed in this river in 1969<sup>10</sup>. Kureha Hill is located at the eastern end of Imizu Hill and runs to northeast from Imizu Hill. Moreover, the geological features of the two hills are almost the same between both Hills.

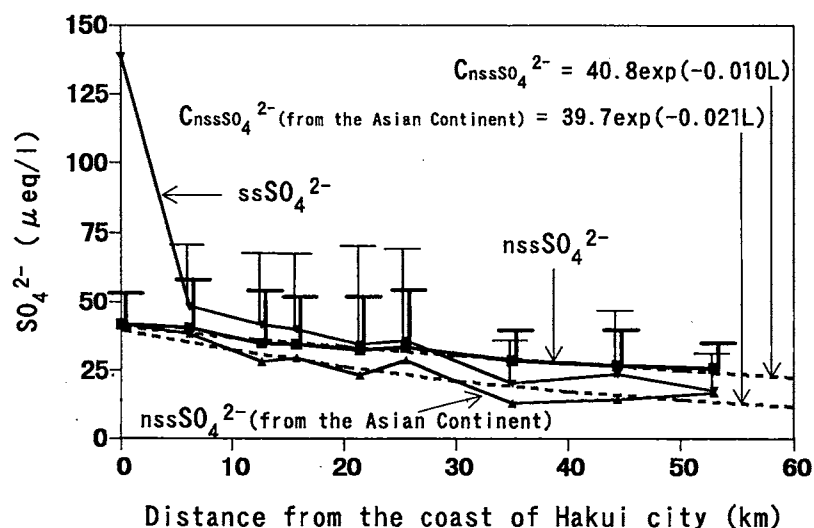
The stream waters on both hills are similar to water that has been acidified by acid rain. Moreover, the high concentrations of nitrate ions in the stream waters in Kureha Hill are similar to those of water in a nitrate-saturated forest watershed. However, the cause of acidification of the stream waters on both hills and the cause of "nitrogen saturation" on the Kureha Hill are not known.

Therefore, the purpose of this report is to discuss two concerns about acid rain in the Hokuriku district. One is to evaluate the contributions of transported non sea-salt sulfate ions and nitrate ions from the Asian Continent to those in winter precipitation in the Hokuriku district, and the other is to discuss the features and causes of acidified stream on both Imizu Hill and Kureha Hill.

## Result

### **Origin and contribution of acidic constituents and neutralizing constituents in winter precipitation.**

- ① In fresh snow samples, non sea-salt sulfate ions were the only constituent of which concentration exponentially decreased (Figure 2). In contrast to non sea-salt sulfate ions, concentrations of nitrate ions, ammonium ions and non sea-salt



**Figure 2** Spatial profiles of sea-salt and non sea-salt sulfate ions

Each plot and vertical bar indicate the mean value and S.D., respectively of five to ten samples.

calcium ions in fresh snow samples, did not decrease from Hakui city to Toyama city. The main origin of these constituents except for non sea-salt sulfate ions in fresh snow in leeward areas of Hakui city, Ishikawa Prefecture was domestic.

- ② The concentrations of non sea-salt sulfate ions and nitrate ions originating from the Asian Continent in fresh snow samples decreased with a decrease coefficient similar to that of sea-salt sulfate ions and sodium ions. This fact indicates that non sea-salt sulfate ions and nitrate ions that originated from the Asian Continent were removed from the atmosphere by the rainout process, because it was previously reported that sea-salt constituents are removed from atmosphere by rainout process.
- ③ In bulk samples collected from October 1999 to March 2000, the contribution of non sea-salt sulfate ions and nitrate ions of the Asian Continent origin to total concentrations were calculated to be 0.78 and 0.29, respectively, on the coast of Hakui city in Ishikawa Prefecture. In Toyama city, 52 km from the coast of Hakui city, the contribution of non sea-salt sulfate ions and nitrate ions originating from the Asian Continent to those were 0.29 and 0.12, respectively (Figure 3).
- ④ The contributions of non sea-salt sulfate ions and nitrate ions originating from the Asian continent to the total concentrations were larger in fresh snow samples than those in bulk snow samples. Conversely, the contribution of domestic non sea-salt sulfate ions and nitrate ions to the total concentration was larger in the bulk sampler than in fresh snow.

#### **On acidification of stream water in the hills in Toyama Prefecture.**

- ① The average pH and ANC of stream water at Hyakumakidani, one of the most

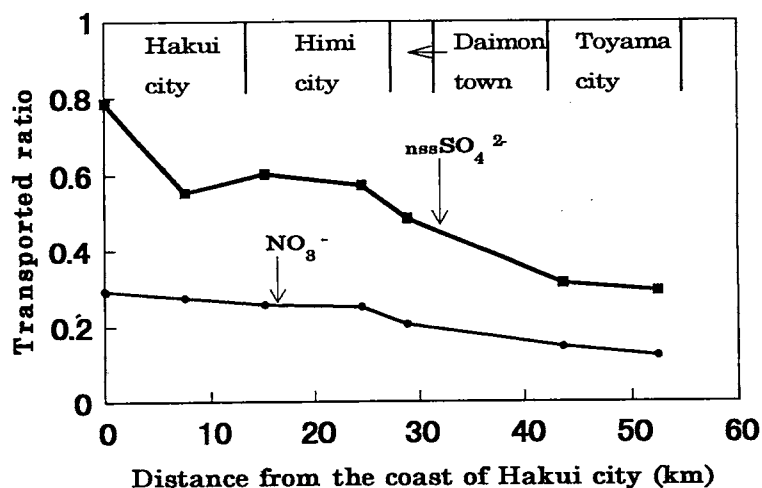


Figure 3 Contribution ratios of transported  $\text{nssSO}_4^{2-}$  and nitrate

acidic streams in Kureha Hill in Toyama city, were  $5.2$  and  $-8 \mu \text{ eq/l}$ , respectively. The concentrations of nitrate ions remained high throughout the year. The average concentration was  $125 \mu \text{ eq/l}$ .

- ② Sulfate ion concentrations in stream water were higher than those in bulk precipitation. High sulfate ion concentrations are sometimes observed in stream water in Kureha Hill and Imizu Hill, indicating the existence of an internal source of sulfate. It is likely that the sulfate originates from the oxidation of pyrite. The acidity caused by the internal sulfate might have leached cations from the soil, which would have resulted in low concentrations of cations, a low pH and a low ANC in the stream water.
- ③ Nitrate ions caused acidification of stream water in an episodic event at Hyakumakidani, because, concentrations of nitrate ions increased with increased discharge, while pH and sulfate concentrations decreased (Figure 4).
- ④ A two-stage tank model simulation indicated that the flow-path changed in the soil during high-discharge periods and the increased subsurface flow containing high concentrations of nitrate contributed to the increased nitrate concentrations.
- ⑤ The Hyakumakidani watershed already is at the final stage of nitrogen saturation according to Stoddard's definition. However, according to Aber's definition, the watershed is in Stage 2 because no visible attenuation has been observed.
- ⑥ The only difference between the Hyakumakidani watershed and the watershed in Imizu Hill (under nitrogen-limiting conditions) was the proportion of net nitrification rate to net nitrogen mineralization rate. The high proportion could be one of the reasons that Hyakumakidani leached high concentrations of nitrate into the streams (Table 1).

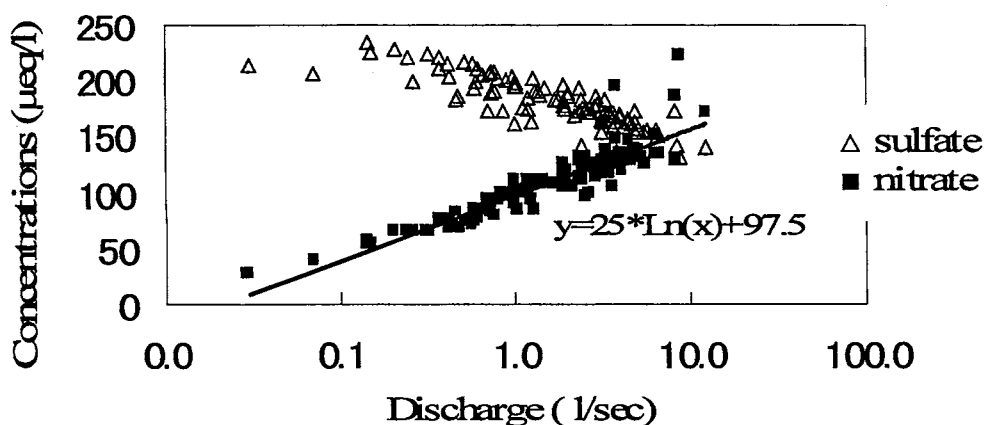


Figure 4 Relationships between the nitrate and sulfate concentrations and discharge.

Table 1 Net nitrogen mineralization and net nitrification of soils at different depths.

	Hyakumaki			Sannokuma		
	0-5 <sup>a)</sup>	5-15 <sup>a)</sup>	15-30 <sup>a)</sup>	0-5 <sup>a)</sup>	5-15 <sup>a)</sup>	15-30 <sup>a)</sup>
Net nitrogen mineralization ( $\mu\text{mol } 100\text{g}^{-1} \text{ dry soil } 4 \text{ weeks}^{-1}$ )	143	31	23	75	20	6
Net nitrification ( $\mu\text{mol } 100\text{g}^{-1} \text{ dry soil } 4 \text{ weeks}^{-1}$ )	150	32	23	11	2	1
Net nitrification / Net mineralization	1.05	1.03	1.00	0.15	0.10	0.17

a) Depth (cm)

## Conclusion

The contributions of acidic constituents originating from the Asian continent to the winter precipitation in the Hokuriku district were larger for non sea-salt sulfate ions than for nitrate ions. The contributions of both types of ions originated from the Asian Continent decreased from seacoast areas to inland areas. The contribution of nitrate ions of domestic origin to the winter precipitation in Hokuriku district was larger than the Asian contribution, even in the seacoast area. In Toyama city, 52 km from the seacoast of Hakui city, the main sources of domestic pollutants are vehicles, factories and thermal power stations. Controlling the emission of acidic constituents from these sources might lessen the winter acid rain in Toyama city.

The cause of acidification of stream water in Kureha Hill was considered to be nitrate ions leaching from the soil. The present results showed that nitrate ions

deposited in Kureha Hill mainly originated from domestic pollutants. Therefore, if nitrate and ammonium ion depositions of domestic origin were decreased, the nitrate concentrations in stream water in Kureha Hill might drop below the saturation levels. However, cations leaching from soils in Kureha Hill and Imizu Hill were not controlled because sulfuric acid in the soil was the main cause of cations leaching into the stream waters in both Hills. The sulfuric acid was derived from pyrite, which might be present in tuff in the soils of both Hills. Cations leaching from the soils in both Hills might have started after the formation of both Hills (about 700,000 years ago).

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## 学位論文審査結果の要旨

〔審査経過〕平成14年1月22日の第1回審査委員会で審査方針を決定した。基礎学力を確認し、各委員による面接と諮問を行い、2月1日に口頭発表（最終試験）を行った。引き続き、第2回審査委員会を開催し、協議の結果以下のとおり判定した。

〔審査結果〕北陸地方では冬季にアジア大陸で発生した酸性物質の飛来に起因する酸性雨・雪が観察されることが広く知られている。しかし、国内に存在する発生源を無視したまま、中国大陸起源との関連のみで語られることが多かった。本研究は、北陸地方で観察される冬季の酸性雨・雪を羽咋市海岸から富山市内にわたって密に配置した観測地点で採取し、羽咋市海岸からの距離による中国大陸起源の硫酸イオンと硝酸イオンの寄与の大きさを明らかにすることを試みた。さらに、富山市呉羽丘陵に観察される溪流水の酸性化の原因を明らかにすることを試みた。その結果、北陸地方の冬季降水中の酸性物質に占める中国大陸起源の寄与は、硝酸イオンより硫酸イオンの方が大きく、いずれも羽咋市海岸で最も大きく海岸からの距離に依存してその割合は減少することを明らかにした。さらに、富山市呉羽丘陵に観察される溪流水の酸性化の原因が土壌からの硝酸イオンの浸出によることを明らかにした。

以上のように、本論文は北陸地方特有の酸性雨・雪現象を解析した成果を有しており、審査委員会は博士（薬学）に値すると判定した。