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## Chemical Characteristics of Rainwater at Motooka, Fukuoka

by

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### Abstract

Rainwater was collected with bulk samplers for two years from September 1998 to June 2000 at Motooka, Fukuoka, where a new campus of Kyushu University is under construction. Two rainwater samplers of open-air type for bulk sampling were set in the area. The rainwater stored in the tank was collected and chemically analyzed at an interval of two weeks during this monitoring period. Lowest pH of 4.0 was observed once, and relatively low pH, lower than the average pH of rainwater in Japan (pH 4.7), were measured 17 times out of 45 times in total. Concentrations of  $\text{NO}_3^-$  and non-sea salt (nss)  $\text{SO}_4^{2-}$  showed seasonal variations such that higher values during wintertime compared with other three seasons. Deposited amounts of these ions were calculated to be relatively constant for  $\text{NO}_3^-$  when precipitation for one observation period, two weeks, exceeded 40 to 50 mm, but varied in a wide range for  $\text{SO}_4^{2-}$  regardless of precipitation.

**Keywords:** Rainwater, Chemical characteristics, pH, Motooka

### 1. Introduction

Motooka area is situated in the western most part of Fukuoka City, where a new campus of Kyushu University is under construction. The area is located inside of Itoshima Peninsula that faces to the sea. A distance from the eastern boundary of the property of the new campus to the sea shore of Hakata Bay is only 1.5 km. Chemical compositions of rainwater in this area, therefore, may be affected by sea salt. At the same time, acidic materials originated  $\text{NO}_x$  gas may also affect the chemistry of rainwater as the area is located relatively close to the urban area of Fukuoka City.

Insufficient fresh water supply from the local government is expected. Thus, surface and ground waters can be alternative sources of fresh water supply to the new campus. Rainwater is a main source of groundwater so that elucidating chemical characteristics of rainwater and its seasonal variations is of importance for evaluation of their effects on the quality of water resources in this area. Two rainwater samplers of open-air type and of filtering type were set at two different places in the area. Stored rainwater was collected and chemically analyzed at an interval of two

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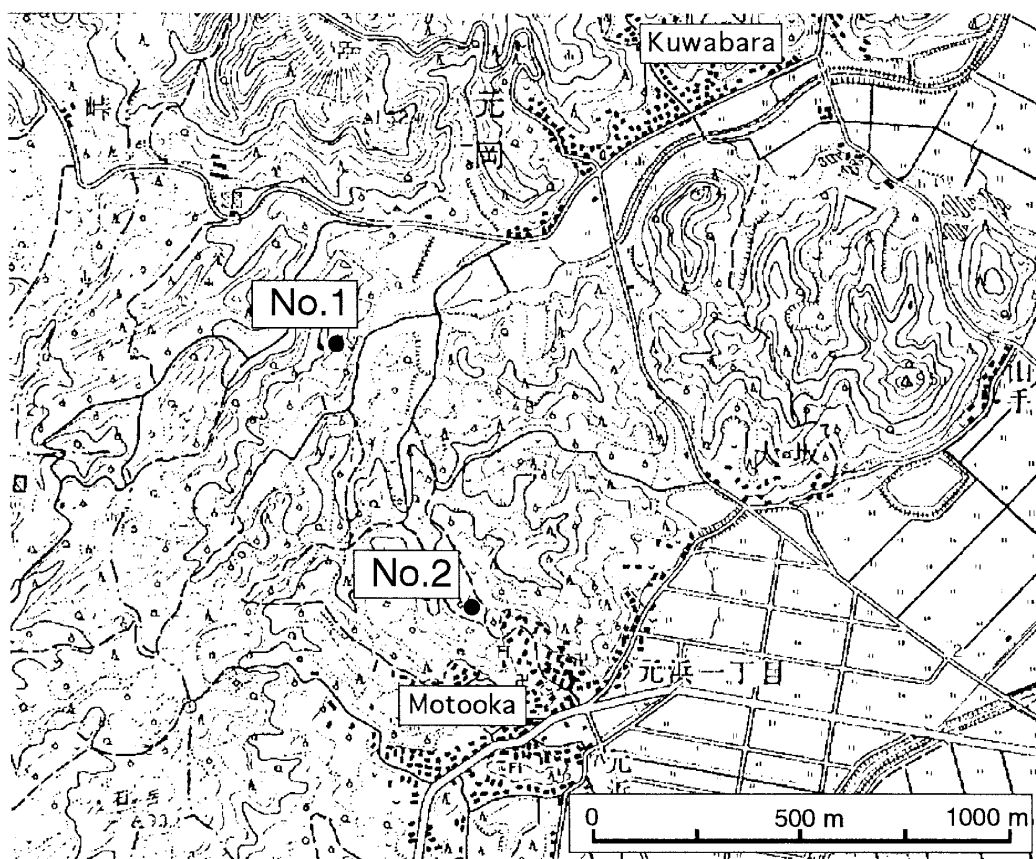
weeks for about two years from 1998 to 2000 when no development for construction work commenced. The chemical characteristics of rainwater and their variations with time are presented. The results obtained from this study can represent rainwater chemistry unaffected by the development of the area.

## 2. Sampling and analysis methods of rainwater

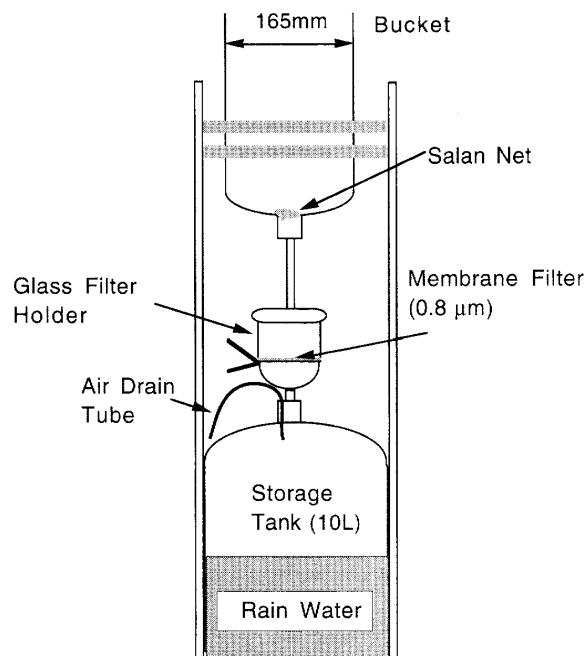
The location map of rainwater sampler is shown in **Fig. 1**. Solid circles represent the location of the rain samplers: No. 1 and No. 2. Sampler No. 1 was located on the hillside of gently sloped southward, and the slope was covered with low shrubs without any tall trees nearby. That of No. 2 was set in a small pasture along narrow road running north to south in the area, and the pasture was surrounded with tall bamboo and trees.

The rain samplers were made in accordance with a design of sampler of filtering type designated by the Ministry of Environment<sup>1)</sup>. A schematic of the sampler is shown in **Fig. 2**. It consists of a cylindrical plastic bucket that catches rainwater (165 mm diameter and 230 mm height), a glass filter holder, and a polyethylene storage tank (10 L). The bucket and the filter holder are connected with silicon tube. A piece of salan net is fitted at the bottom of the bucket and then a plastic net is set on it so that insects and/or solid materials such as fallen leaves would not enter into the filter holder. A membrane filter of 0.8  $\mu\text{m}$  is fitted at the filter holder. The tube connecting the bucket and the glass holder, and the glass holder are covered with aluminum foil, and the tank with plastic bag in black both to avoid the effects of sunlight along the tube wall as well as stored rainwater in the tank.

Rainwater monitoring was carried out for two years from the middle of September 1998 to the



**Fig. 1** Location map of rain sampler at Motooka, Fukuoka.



**Fig. 2** Schematic diagram of rain sampler of open air and filtering type.

late June 2000. During this period, rainwater stored in the tanks was collected at a time interval of two weeks. On collection, the stored water was measured with a mess cylinder at each location. After measuring the volume of water, the rainwater was stored in a polyethylene bottle ( $250 \text{ cm}^3$ ) that was rinsed with the rainwater if enough amount of water was stored. Then the bucket, the filter holder and the tank were carefully rinsed with deionized water and the salan net and the membrane filter paper were replaced for the next sampling of rainwater. Precipitation was calculated by dividing the measured water volume with the cross sectional area of the bucket ( $213.8 \text{ cm}^2$ ).

The rainwater was chemically analyzed the next day of the collection, otherwise stored in a refrigerator until analysis. The rainwater was measured for pH and Electrical Conductivity (EC). A part of the water was filtered with a membrane filter of  $0.45 \mu\text{m}$  and then analyzed for anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) and cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) with Ionchromatography (Dionex AQ).

### 3. Results and discussion

In the following, the results for the rainwater collected at No. 1 are presented as the precipitation and the chemical concentrations are similar between the samples of No. 1 and No. 2. When the rainwater in the tank of No. 1 was apparently contaminated with bird droppings, the results are substituted by those of No. 2. This contamination occurred seven times during the whole monitoring period. The results of chemical analyses are presented as of the date of rainwater collection, but they represent the average values of rainwater deposited during the one monitoring period, basically two weeks, since the preceding collection of the rainwater.

#### 3.1 Precipitation and pH

**Figure 3** represents changes in the precipitation and pH of the rainwater with time. The lowest pH was measured to be 4.0 on November 16, 1998, and no rainwater lower than pH 4.0 was sampled. Values of pH lower than 4.7, the average pH of rainwater in Japan<sup>2)</sup>, were measured 14 times. They occurred mainly in the period from November to March. An average precipitation for one monitoring period, two weeks, was  $59 \text{ mm}/(2\text{wks})$ , and very low precipitation, less than  $2 \text{ mm}/(2$

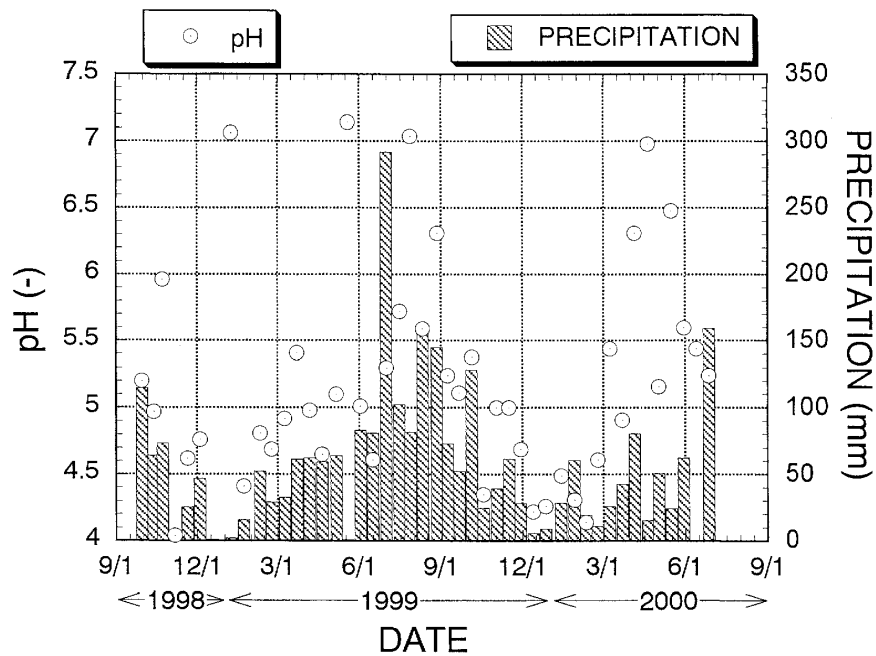


Fig. 3 Changes in pH and precipitation with time.

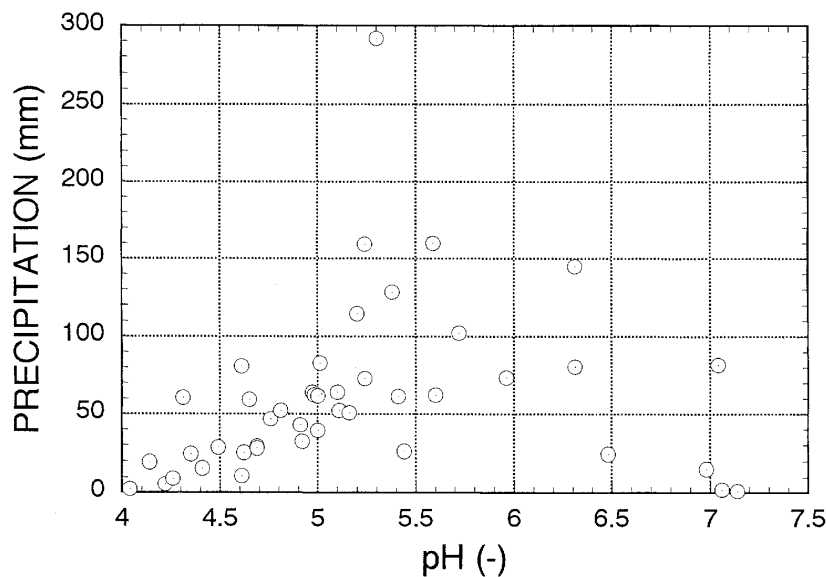


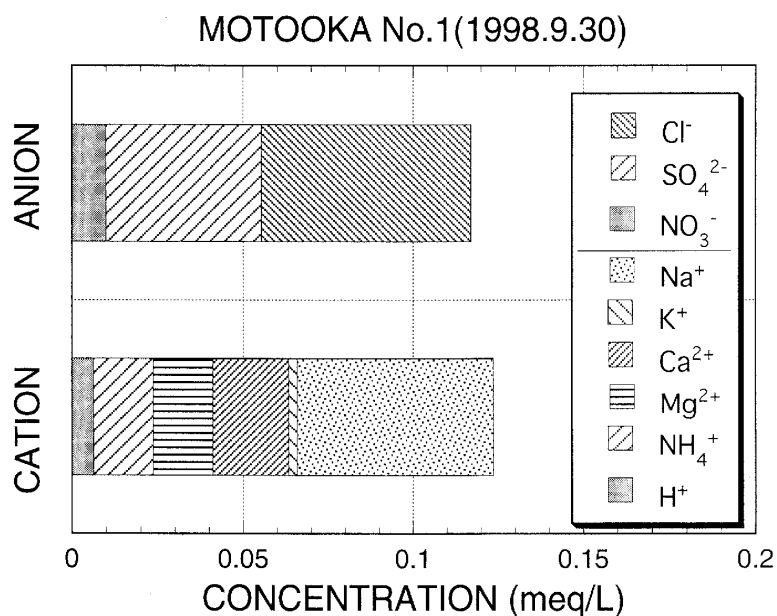
Fig. 4 Relationship between pH of rainwater and precipitation.

wks) was recorded for three times only in 1998. The largest precipitation of 291 mm/(2wks) was observed for a period from June 16 to July 1, 1999.

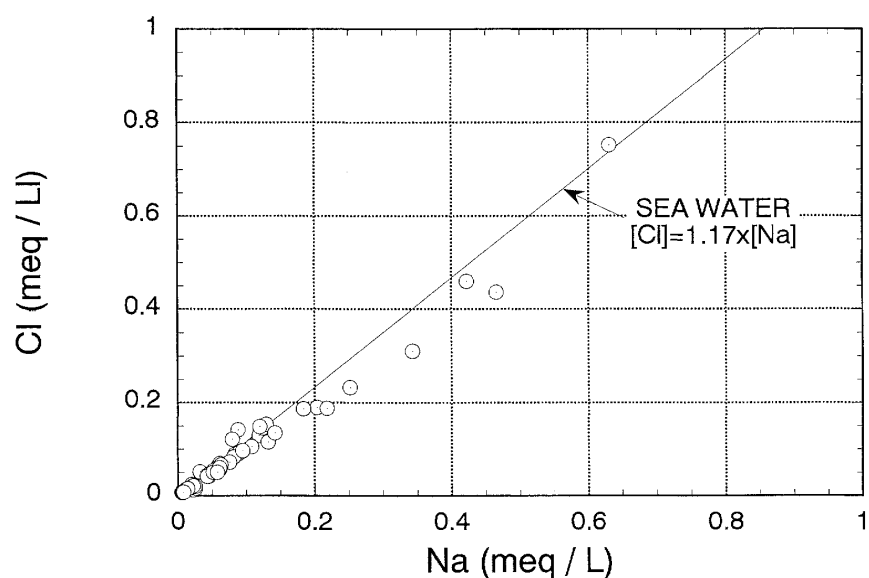
Figure 4 shows precipitation versus pH. Values of pH generally increase as precipitation increases. Rainwater of pH lower than 4.7 mainly deposited when precipitation was less than 30 mm/(2wks). Values of pH higher than 6.5 were also measured in spite of low precipitation. This relatively high pH can be attributed to that rainwater was neutralized by reacting with soil dusts and/or ammonium ( $\text{NH}_3$ ) in the atmosphere while depositing on the surface. However, rainwater with pH higher than 7.0 has small precipitation: 1-2 mm/(2wks).

### 3.2 Ion constituents of rainwater

Concentrations of ion component for anion and cation of rainwater are shown in Fig. 5. Sodium ion ( $\text{Na}^+$ ) dominates the concentrations of cation whereas chloride ( $\text{Cl}^-$ ) and sulfate ( $\text{SO}_4^{2-}$ )



**Fig. 5** Components of cation and anion of rainwater sampled between September 16 and 30, 1998.



**Fig. 6** Comparison of concentrations of sodium ion ( $\text{Na}^+$ ) and chloride ion ( $\text{Cl}^-$ ) of rainwater and ratio of these ions of seawater (solid line).

ions those of anion.  $\text{Cl}^-$  can be originated from  $\text{HCl}$  gas discharged from incinerators and volcanoes, and also from seawater. This area locates close to the sea, and the rainwater can be well affected by sea salt derived from seawater. In order to evaluate the effects of seawater on rainwater chemistry, on equivalent ratio of  $\text{Na}^+$  to  $\text{Cl}^-$  of the rainwater samples is plotted against that of seawater. The results are shown in **Fig. 6**. The solid line indicates the concentration ratio of these ions for seawater. Most rainwater samples are plotted on the line implying  $\text{Na}^+$  and  $\text{Cl}^-$  in the rainwater are derived mostly from sea salt.

### 3.3 Concentrations of nitrate and sulfate ions

Concentrations of nitrate ( $\text{NO}_3^-$ ) and sulfate ( $\text{SO}_4^{2-}$ ) ions among anions reflect the amount of nitric and sulfuric acids that are main and strong acids, which lower pH of rainwater. Nitric acid

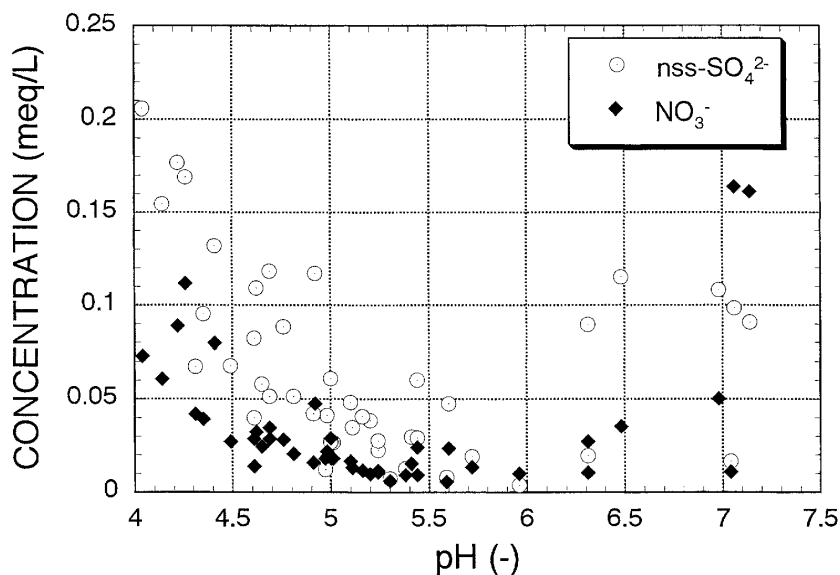


Fig. 7 Relationship between pH and concentrations of nitrate ion ( $\text{NO}_3^-$ ) and non-sea salt sulfate ion ( $\text{nss-SO}_4^{2-}$ ).

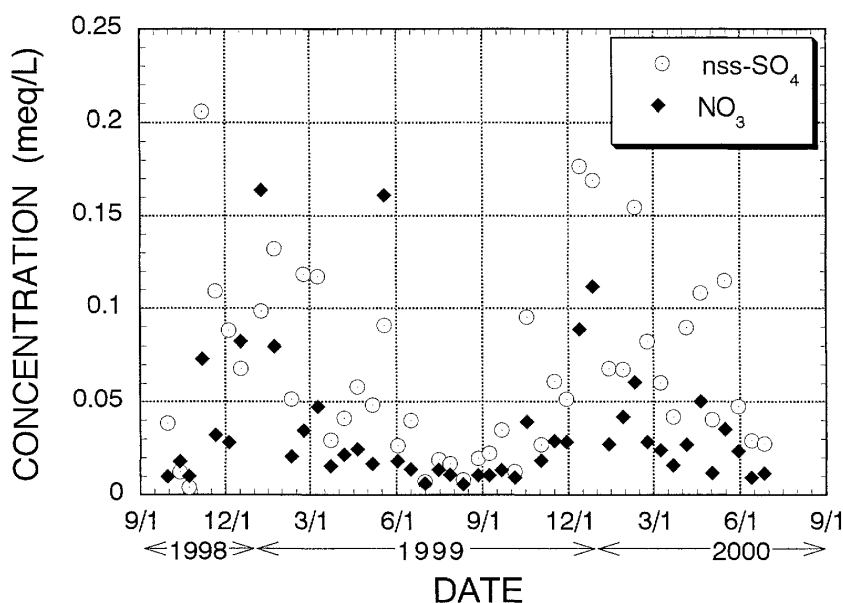
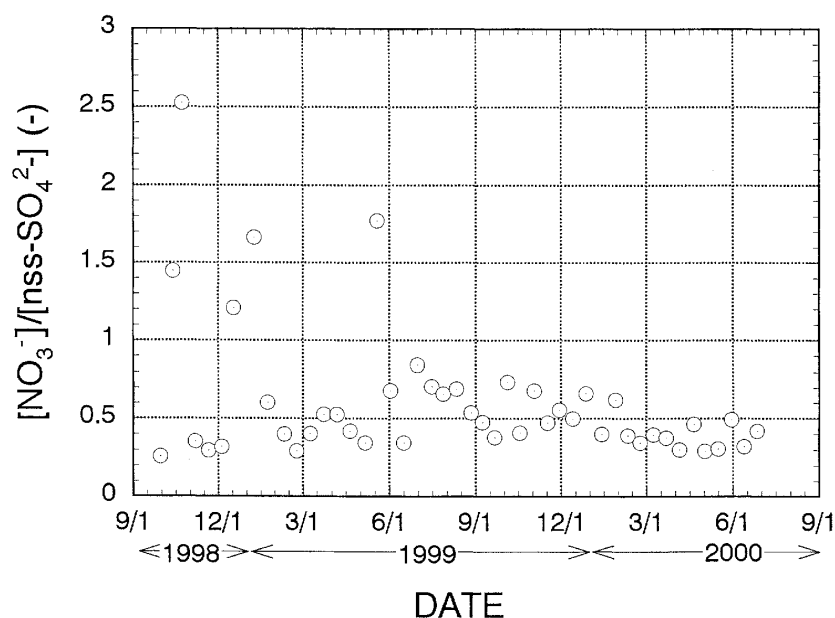


Fig. 8 Concentrations of  $\text{NO}_3^-$  and  $\text{nss-SO}_4^{2-}$  with time.

mainly contributes to lowering pH of rainwater in urban areas, and sulfuric acid in rural and other areas<sup>3)</sup>. Thus, the effects of these ions on lowering pH of rainwater are examined. For this purpose, concentration of  $\text{SO}_4^{2-}$  originated in sea salt should be removed from the analyzed concentration. Magnitude of contribution of sea salt on  $\text{SO}_4^{2-}$  concentration can be determined on the assumption that all  $\text{Na}^+$  in rainwater is originated in sea salt with a conserved equivalent ratio of  $\text{Na}^+$  to  $\text{SO}_4^{2-}$ <sup>4)</sup>. Then,  $\text{SO}_4^{2-}$  concentration unaffected by sea salt (non-sea salt (nss)- $\text{SO}_4^{2-}$ ) can be calculated by subtracting the concentration of  $\text{SO}_4^{2-}$  originated in sea salt from the analyzed value.

Figure 7 shows the relationship between pH and concentrations of  $\text{NO}_3^-$  and  $\text{nss-SO}_4^{2-}$  in equivalent. Values of pH apparently decrease as concentrations of these ions increase. The concentration of  $\text{nss-SO}_4^{2-}$  generally shows higher value over a wide range of pH compared with that of  $\text{NO}_3^-$ . A few data points show high pH of about 7 in spite of relatively high concentrations of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ . This implies that acids in rainwater are sufficiently neutralized. In Fig. 8, concentrations



**Fig. 9** Ratio of  $\text{NO}_3^-$  to  $\text{nss-SO}_4^{2-}$  in equivalent concentration with time.

of  $\text{NO}_3^-$  and  $\text{nss-SO}_4^{2-}$  with time are plotted. Concentrations of  $\text{nss-SO}_4^{2-}$  show some fluctuations, and they are relatively high mainly during the period from October to March. These high concentrations during wintertime may be attributed to sulfur dioxide ( $\text{SO}_2$ ) transported from the countries of East Asia by northwesterly monsoon<sup>5)</sup>. High values of about 0.1 meq/L were also observed from April to May in 2000. Volcanoes in southern Kyushu such as Sakurajima and Aso discharge a large amount of  $\text{SO}_2$  that is transported northward by southerly and results in acidification of rainwater in northern Kyushu<sup>6)</sup>. This may be a reason of high concentrations of  $\text{SO}_4^{2-}$  during this springtime.

Then, most concentrations of  $\text{NO}_3^-$  show below 0.05 meq/L except eight data points with higher values mainly observed from November to February. When these high  $\text{NO}_3^-$  concentrations were observed, precipitation was less than 20 mm/(2wks) that is lower than the average precipitation of 59 mm/(2wks) of the whole monitoring period. In particular, precipitations are only 1.1 and 2.1 mm/(2wks) when  $\text{NO}_3^-$  concentration is higher than 0.15 meq/L. This is because that rainwater washes out most acidic materials in the atmosphere during the early stage of rainfall. If no subsequent rainfall occurs except this early rainfall, rainwater of high concentration of  $\text{NO}_3^-$  would remain in the tank. On the other hand, subsequent and sufficient rainfall may dilute the stored rainwater in the tank resulted in a low concentration of  $\text{NO}_3^-$ .

Changes in equivalent ratio of  $\text{NO}_3^-$  to  $\text{nss-SO}_4^{2-}$  with time are illustrated in **Fig. 9**. Excluding a few values higher than 1.0, ratios are generally high from June to December in 1998 and relatively low in other periods. Seasonal characteristics are not evident in this ratio. However, the high ratio suggests that rainwater accepts more effects of  $\text{NO}_3^-$  than  $\text{SO}_4^{2-}$  on its acidification. An average ratio over the whole monitoring period is calculated to be 0.48, excluding values more than 1.0. This is higher than the average value of 0.34 in Japan<sup>7)</sup>. This suggests that  $\text{nss-SO}_4^{2-}$  dominates acidification of the rainwater at Motooka. Similar values are reported such as 0.5 at Sendai and 0.51 at Tokyo(Koto-ku). However, lower values at Nagasaki and Oomura in Kyushu are reported to be 0.22 and 0.23, respectively<sup>7)</sup>.

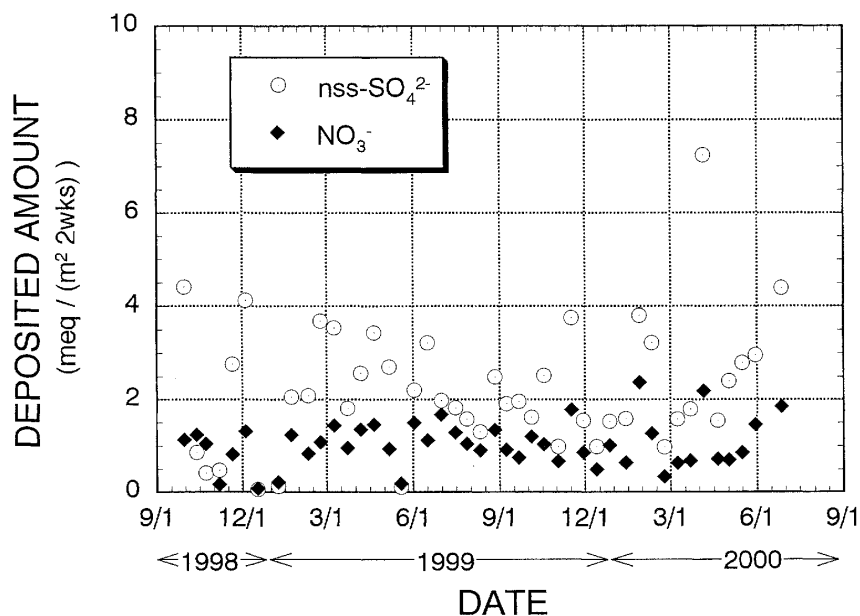
Precipitation was extremely small such as in a range from 0.47 and 2.3 mm/(2wks) for the three rain samples with the ratios above 1.0 after December 1998. Rainwater sampled at each rainfall event in Kobe showed low pH and high  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  concentrations, which frequently occurred when precipitation of one rainfall was less than 2 mm<sup>8)</sup>. Similar characteristics were found in rainwater at Motooka.



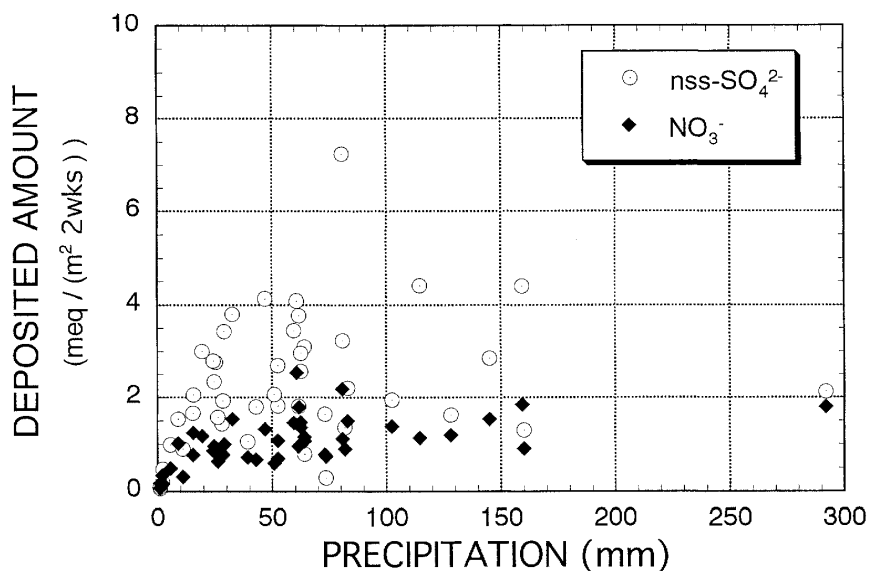
### 3.4 Deposited amount of nitrate and sulfate ions

Deposited amounts of  $\text{NO}_3^-$  and  $\text{nss-SO}_4^{2-}$  are calculated using concentrations and precipitation for one sampling period. The deposited amount of  $\text{NO}_3^-$  remains in a range from 0.5 to 2.0  $\text{meq}/(\text{m}^2 \text{ 2wks})$  and its fluctuation is rather small as shown in **Fig. 10**. On the other hand, that of  $\text{nss-SO}_4^{2-}$  also shows small values, but varies in a wide range. Values larger than 3.0  $\text{meq}/(\text{m}^2 \text{ 2wks})$  appear chiefly during wintertime from November to March. When precipitation is less than 2 mm/(2wks), deposited amounts of both ions are small in spite of high concentrations as shown in **Fig. 8**.

**Figure 11** presents the relationship between precipitation and deposited amounts of  $\text{NO}_3^-$  and  $\text{nss-SO}_4^{2-}$ . The deposited amount of  $\text{NO}_3^-$  increases as an increase of precipitation. It remains, however, in a range from 0.5 to 2.0  $\text{meq}/(\text{m}^2 \text{ 2wks})$  when precipitation is larger than 50 mm/(2wks). That of  $\text{nss-SO}_4^{2-}$  also increases as an increase in precipitation, but varies in a wide range. This



**Fig. 10** Deposited amounts of  $\text{NO}_3^-$  and  $\text{nss-SO}_4^{2-}$  with time.

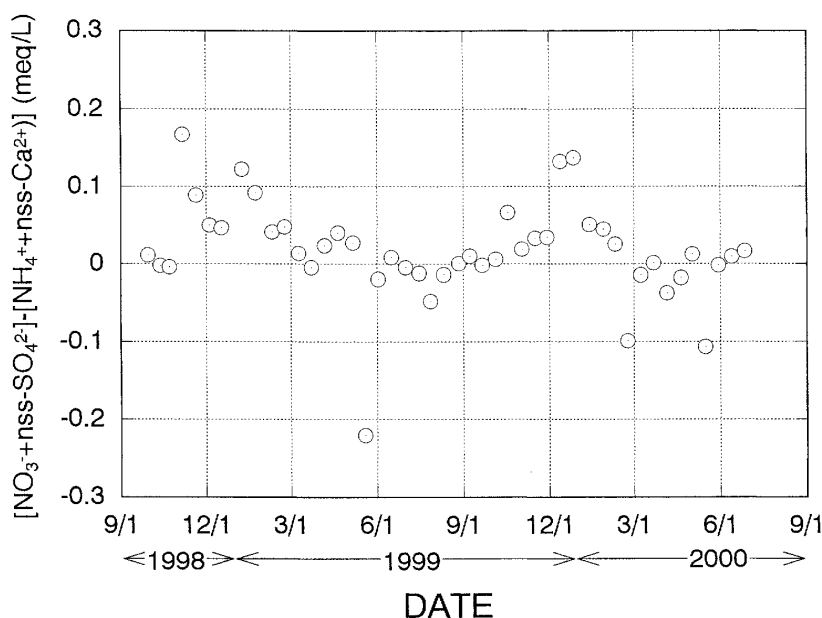


**Fig. 11** Relationship between deposited amounts of  $\text{NO}_3^-$  and  $\text{nss-SO}_4^{2-}$ , and precipitation.

implies that nitric acid in the atmosphere originated in urban area may be thoroughly washed out when rainfall event occurs, then no nitric acid is available to be washed out by the following rain fall. Thus, the deposited amount of  $\text{NO}_3^-$  shows relatively constant even precipitation increases. However,  $\text{nss-SO}_4^{2-}$  derived from sulfuric acid is well affected by  $\text{SO}_2$  discharged and transported a long distance from volcanoes as well as that from East Asia. Thus, the magnitude of effects of  $\text{SO}_2$  from these sources on rainwater may control the deposited amount of  $\text{SO}_4^{2-}$ .

### 3.5 Potentials of acidity and neutralization

Anions of  $\text{NO}_3^-$  and  $\text{nss-SO}_4^{2-}$  are derived from nitric and sulfuric acids that are partly or fully neutralized while adsorbed into rainwater or depositing directly onto the ground surface. Ammonia and calcium in the atmosphere play as a neutralizer<sup>9)</sup>. In order to evaluate the effects of neutralization of rainwater or to examine the difference of chemical component of rainwater, the total concentrations of  $\text{NO}_3^-$  and  $\text{nss-SO}_4^{2-}$  as  $[\text{NO}_3^- + \text{nss-SO}_4^{2-}]$  and those of  $\text{NH}_4^+$  and non-sea salt calcium ( $\text{nss-Ca}^{2+}$ ) as  $[\text{NH}_4^+ + \text{nss-Ca}^{2+}]$  are used as indices. The concentrations are indicated by equilibrium. Tsuruta defined these total concentrations as acidic potential and neutralization potential, respectively<sup>5)</sup>. The differences of these potentials with time are shown in **Fig. 12**. Most values show positive, indicating acidic potential predominates over the monitoring period. This also implies that rainwater is not fully neutralized. Periodic variations are also observed such that higher values during wintertime. This variation matches well with changes in pH with time shown in **Fig. 3**.



3) Deposited amount of  $\text{NO}_3^-$  remains relatively constant when precipitation exceeded 50 mm/(2 wks), but that of  $\text{SO}_4^{2-}$  varies in a wide range regardless of precipitation.

4) Acidic potential of rainwater dominates over neutralization potential throughout the monitoring period.

Finally, chemical characteristics of rainwater obtained through this study represent those unaffected by the development of this area for a new campus of Kyushu University.

### Acknowledgements

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