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ENVIRONMENTAL EFFECTS OF VOLCANIC GASES ON REGIONAL RAINWATER CHEMISTRY AT KUJU, JAPAN

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SUMMARY – Sampling and chemical analysis of rainwater at Kuju volcano were made for ten years from **1992** to examine the effects of volcanic gases on acidification of rainwater and the relationship with volcanic activity. Rainwaters in the near vicinity of the fumarolic area were acidified by HCl, H_2SO_4 and HF. Concentration of Cl^- quickly decreases with distance whereas that of SO_4^{2-} gradually decreases in spite of larger discharge rate of SO_2 relative to HCl from the fumaroles. This implies that HCl preferentially dissolves into rainwater and deposits in the vicinity of the fumarole. Eruptive activity accompanying increase in discharge rates of acidic gases resulted in lowering pH of rainwater only in the near vicinity of fumarolic area. No appreciable effect was detected at distant places.

1. INTRODUCTION

Kuju volcano is located in the Shimabara-Beppu graben, Kyushu Island, and fumarolic areas called Kuju-Iwoyama are located on the northern flank of Mt.Hossho. An eruptive episode started on October 11, **1995,** accompanying ash ejection and new vents formed about **300** m to the south from the centre of the fumarolic areas (Fig.1). The vents and the fumaroles discharged volcanic gases.

Volcanic gases comprise mainly H_2O followed by CO_2, SO_2, H_2S, HCl, HF and other minor gases. One of the natural hazards derived from the volcano is the discharge of these acidic gases that acidify rainwater. Volcanic gases such as HCl and HF are preferentially dissolved into rainwater, and deposit in the vicinity of volcano (Fujita, **1993).** The discharge rates are **26** t/d of SO_2 and **3.1** t/d of **HCl** at Kuju-Iwoyama (Ehara et al., **1981),** and the SO_2 oxidizes in atmosphere to form SO_4^{2-}. This reaction rate is relatively slow (Fujita, **1993).** Thus, SO_2 is transported a long distance, acidifying rainwater across a large area.

Volcanic activity lasts for years and its intensity varies with time. Nevertheless, a long-term loading of acid on the surface may significantly affect on ecological systems in the regional area. Damage of soil in terms **of** loss of neutralization capacity eventually acidifies the regional groundwater.

In order to evaluate the effects of acidification on rainwater due to acidic gases at Kuju volcano, we have collected and chemically analysed rainwater for the last ten years since **1992.**

Fig.1 Location map of Kuju-Iwoyama, and site of rain collector.

2. SAMPLING AND ANALYSIS

Kuju-Iwoyama has specific topographic and climatic features. The fumarolic area is located within the U-shaped crater and is exposed to the north. During the wet season from March to December the weather patterns come from the south. As a result, volcanic gases discharged from the fumaroles disperse toward the north along a valley like topography. Rain collectors of open air type were set at sixteen sites within an area of **3.3** km by **3** km mainly northward from the fumarolic area as shown in Fig.1. The sites of the rain collectors are labeled with numbers starting from No.1 to No.16. Rain collectors for No.5,6,7,15 and 16 were set after the 1995 eruption. Three rain collectors were set at sites further north until 1997. The fumarolic area is indicated by a shaded zone in the bottom right corner of Figure 1, near an area of newly formed craters or vents after the 1995 eruption. Figure **2** illustrates a schematic of rain collector that consists of a cylindrical bucket 60 mm in diameter and a 2L polyethylene tank. **A** piece of saran net was screwed into the polyethylene pipe, connecting the bucket and the tank to avoid contaminating by solids. During 1994 to 1997, a rain collector of filtering type that consists of a cylindrical bucket of 160mm diameter, a glass filter holder for a 0.8μm membrane filter, and a polyethylene **tank** of 10L was used at all sites except No.1.

The rainwater stored in the tank was sampled regularly at intervals of two weeks. On sampling, the rain collector was checked for the mixing of visible dust and insects in the **tank** and the tank was tightly screwed with a cap. The volume of stored water was measured in the laboratory with a measuring cylinder and stored in a 250 cc polyethylene bottle. The 250 cc bottle was well rinsed with the water in the tank before sampling. Then, the bucket and tank were well rinsed with distilled and deionized water, and dried at room temperature for the next sampling. The samples were filtered through 0.45 μm membrane filter and chemically analysed with an ion chromatograph (Dionex **AQ)** for anions (F^-, Cl^-, NO_3^-, SO_4^{2-}) and cations (Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}). pH and EC were also measured.

3. RESULTS AND DISCUSSION

3.1 Ion Components

Figure **3** shows the concentrations of anion and cation components of rainwater sampled at sites No.1, 2, 8 and 10 on June **30,** 1995. Site **No.1** is located in the near vicinity of the fumarolic area, and site No.2 is close to the northern periphery of the fumarolic area. Site No.8 and 10 are located 1.5 **km** and 2.6 km northward from the main fumarolic area, respectively. At both sites No.1 and No.2, H^+ dominates cations, whereas Cl^- dominates anions followed by SO_4^{2-}, and F^- for No.2. This suggests that very reactive gases of **HCl** and HF preferentially dissolve into rainwater and deposit in the vicinity of the fumarolic area. At site No.8, the total ion concentrations are lower than those of **No.1** and **2,** but H^+ still dominates among cations. NO_3^- concentrations are negligibly small relative to other anions at these three sites.

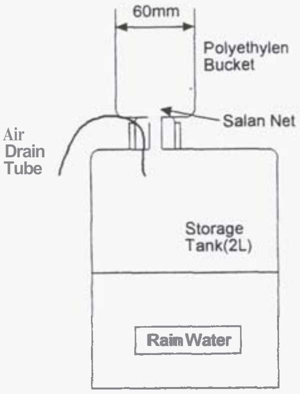


Fig.2 Rain collector.

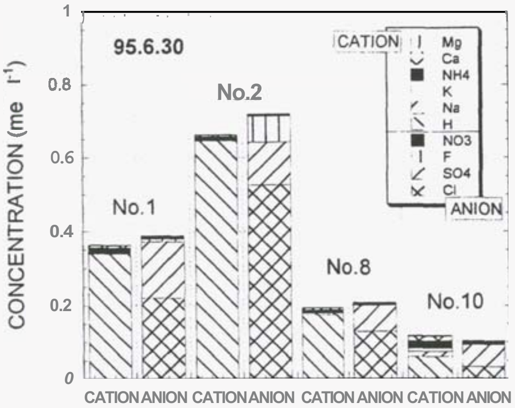


Fig.3 Ion component of rainwater at No.1, 2, **8** and 10 sampled on June 30, 1995.

At further distal sites such as No.10, the total concentration of ions is about one third those of No.1. At this site, H^+ is still a major cation, but other components such as NH_4^+, Na^+, Ca^{2+} occupies other half. Cl^- has lower concentration compared with SO_4^{2-} whereas an inverse relationship in concentration is observed at other three sites. This figure also indicates that Cl^- concentration quickly decreases with distance. On the other hand, decrease of SO_4^{2-} with distance seems to be much slower compared with that of Cl^-. Therefore, HCl quickly deposits due to its enhanced solubility and is the main acid in rainwater in the vicinity of the fumarolic area.

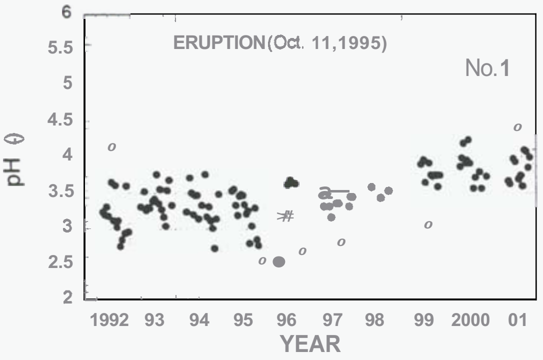
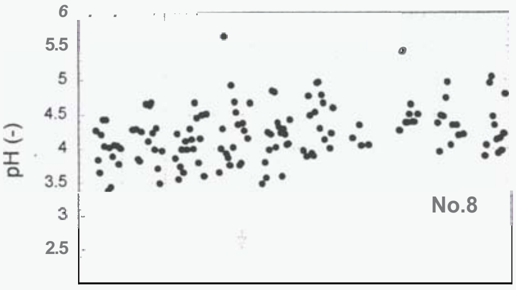


Fig.4 pH of rainwater with time at site No.1. Arrow indicates the onset of the 1995 eruption.



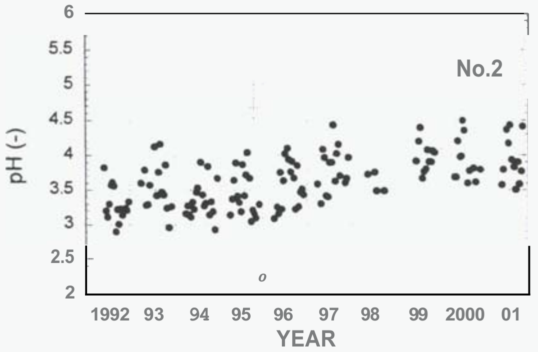


Fig.5 pH of rainwater with time at site No.2.

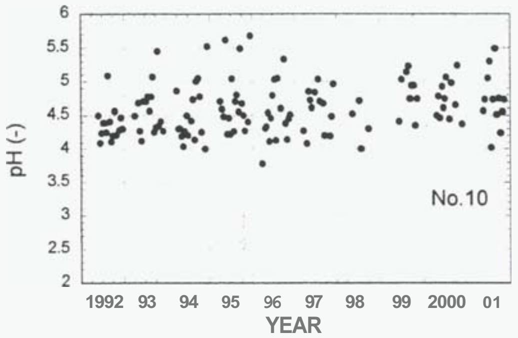


Fig.7 pH of rainwater with time at site No. 10.

3.2 pH of rainwater

Figures 4 to 7 represent pH values of rainwater at sites of No.1, 2, 8 and 10 from 1992 to 2001. The data are plotted on the date of sampling of rainwater stored in the tank, thus these values represent those of average of rainwater collected for the last two weeks before the sampling. Most pH values of No.1 range from 2.7 to 3.7 during 1992 to 1995. The pH remained above 3.5 since 1999. The lowest pH of 2.5 was measured on April 2nd, 1996.

Site No.2 shows pH ranging from 2.9 to 4.2 between 1992 and 1995 (Fig.5). No appreciable drop in pH was observed after the start of the 1995 eruption except pH 2.23 on December 19, 1995. This low pH may be caused by HCl adsorbed on volcanic ash deposited on the bucket that was washed by the next rain and contaminated the stored rainwater. Values of pH gradually increase with time from 1996 to 1998, after which pH remains in a range between 3.5 and 4.5 from 1999 to 2001.

At site No.8 (Fig.6), pH ranges from **3.4** to **4.4** in 1992 and remains as such until 1996. In 1997, the pH increases to 4.0 and remains above that **in** the subsequent years. No marked change in pH was observed during the 1995 eruption.

The majority of the pH values at site **No.** 10 from 1992 to 1998 show 4.0 to ***5.5*** and no appreciable decrease was observed during the period of eruptive activity. The average pH of rainwater in Japan was reported to be 4.7(Tamaki et al., 1991). Thus, rainwaters at No.10 are comparable to the average rain in Japan in terms of pH.

pH values at sites No.1 and 2 in 2001 range from 3.5 to 4.0 that is the same as at No.8 in 1992. This means that effects of acidification by volcanic gases have been moderated even at very close vicinity to the fumarolic area. Site No.8 is located 1.5 km from the fumarolse and the surface has been fully covered with bamboo grass whereas the soil surface at No.2 used to be exposed. Vegetation has been natural and gradually recovering at site No.2 during the last few years, which might be because of less acidification of rainwater as well as fog.

3.3 Concentrations of chemical component

Concentrations of Cl at No.1, 2 and 8 are shown in Figs.8 to 10. High concentrations, up to 2.6 meq l^{-1} were measured at site No. 1 in 1992, then the value remains below 0.7 meq l^{-1} in the subsequent three years. A sharp increase in Cl was observed at the start of the 1995 eruption that implies the discharge rate of HCl increased along with its volcanic activity. However, its concentration decreases sharply with time. Hirabayashi et al. (1996) also reported that discharge rate of HCl from Kuju-Iwoyama quickly increased immediately after the start of eruption

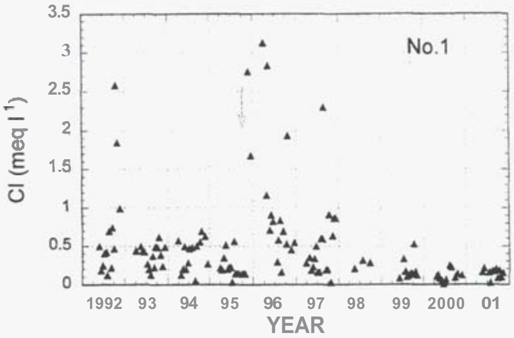


Fig.8 Cl concentration of rainwater at site No.1 with time.

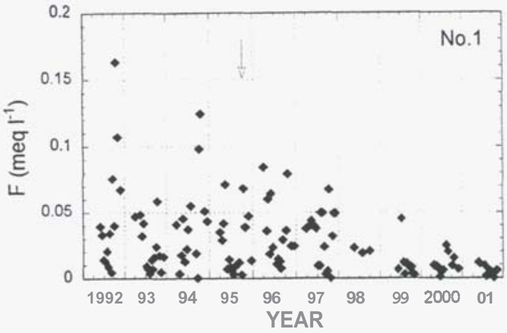


Fig. 11 F concentration of rainwater at site No. 1 with time.

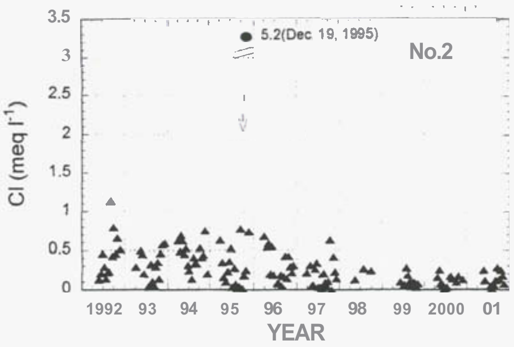


Fig.9 Cl concentration of rainwater at site No.2 with time.

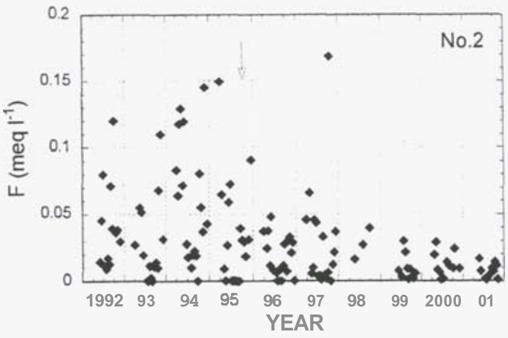
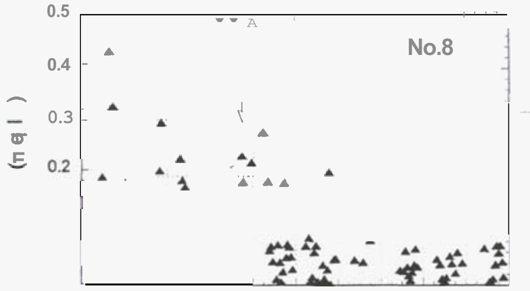


Fig.12 F concentration of rainwater at site No.2 with time.



and decreased with time in early 1996. Most of the Cl concentration during the last three years remains below about 0.3 meq l^{-1} that is about half of the concentration before the 1995 eruption.

The Cl concentration at site No.2 (Fig.9) also shows a similar change with time as No.1, but without a marked increase during 1995 to 1996. A high concentration of **5.2** meq l^{-1} on December 19, 1995, corresponds to low pH of **2.2** in Fig.5. Concentrations in the last three years are about the half that before the 1995 eruption.

At site **No.8(Fig.10)**, Cl is below 0.5 meq l^{-1} for the whole monitoring period. Concentrations decrease with time with a reducing rate of variation. At site No.10, the concentration is below 0.1 meq l^{-1} throughout the monitoring period except for several jumps in 1995 and 1996.

Relatively low concentrations at all sites from 1999 to 2001 suggest that discharge rates of HCl from fumaroles have decreased accompanying less effects of acidification of rainwater in this area.

Fluoride (F$^-$) concentrations at No.1 and 2 are shown in Figs. 11 and 12. At site No.1, concentrations continuously decrease with time and does not show any notable change during the 1995 eruption. Concentrations of F at No.2 show higher values than No.1 throughout the monitoring period. Fumaroles located between these two sites may discharge more HF than those close to site No.1. However, concentrations at No.2 also decrease with time. At No 8, concentrations show similar decreasing behaviour as **No.1** and 2 with values below 0.02 meq l^{-1}. F$^-$ is not detected during the monitoring period for most of the rainwater at No. 10. This suggests that most of HF deposits mainly within 1.5 km from the fumarolic area.

SO_4^{2-} concentrations with time at sites No. 1, 2 and 10 are illustrated in Figs.13 to 15. Large variations in concentration with time intervals of about one year are observed before the 1995 eruption both at sites No. 1 and **2.** Afterwards, they tend to increase until 1997. Concentrations remain below 0.2 meq l^{-1} from 1998 to 2001. Concentration at site No.10 (Fig.15) shows **below** 0.2 meq l^{-1} for the whole observation period, and no marked change was observed with respect to the 1995 eruption. Concentration differences among the sites from 1998 to 2001 are relatively small. This suggests that the effects of SO_2 on acidification of local rainwater have turned to be insignificant relative to the distances from the fumarolic area.

4.CONCLUSIONS

Rainwater was sampled and chemically analyzed for 10 years at Kuju volcano where eruptive activity occurred in 1995. Acidic gases of HCl and HF are preferentially dissolved into rainwater and deposit in the vicinity of fumarolic area. They contribute lowering pH. The concentration difference in SO_4^{2-} with distance from the fumaroles is not significant compared with those in Cl^- and F^-. This is because the oxidation rate of SO_2 is relatively slow. After the 1995 eruption, pH of rainwater increases with time irrespective of the distance from the fumaroles. Consequently, the effects of volcanic gases on acidification of regional rainwater have been moderated.

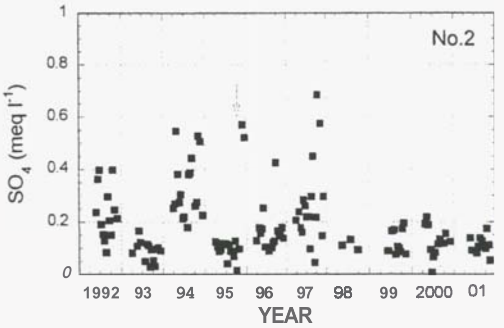
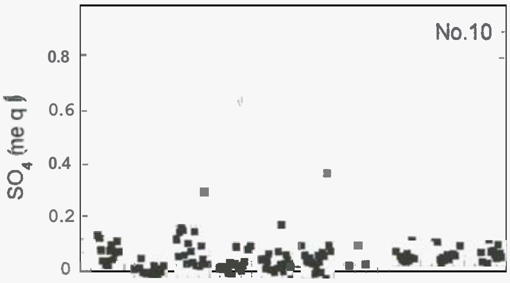


Fig.14 Concentration of SO_4 at site No.2 with time.



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