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AN OBSERVATIONAL STUDY ON THE SCAVENGING OF HNO_3 AND HCl VAPOR BY SNOW CRYSTALS

Tsuneya Takahashi *
Hokkaido University of Education, Sapporo, Japan

Tatsuo Endoh
Institute of Low Temperature Science, Hokkaido University, Sapporo, Japan

Izumi Noguchi
Hokkaido Institute of Environmental Sciences, Sapporo, Japan

1. INTRODUCTION

Until the 1980s, it had been accepted that solid hydrometeors did not significantly remove foreign gases from the air while falling in the atmosphere. However, recent laboratory experiments have revealed that ice surfaces are capable of taking up SO_2, HNO_3 and HCl vapor (For review, see Pruppacher and Klett 1997.). Mitra et al. (1990) showed that SO_2 is scavenged quite efficiently with small amounts of H_2O_2 during the depositional growth of a snow crystal. Diehl et al. (1995, 1996) showed that a snow crystal is capable of scavenging significant amounts of HNO_3 and HCl vapor from ambient air. However, they concluded that the gases seemed to enter cloud ice particles mainly by riming because the uptake of the gases by snow crystals was negligibly smaller than that by cloud droplets and raindrops at typical atmospheric gas concentrations.

Takahashi et al. (1996) collected solid hydrometeors at intervals of approximately 1 hr and found that the samples, even those that had been formed only by vapor depositional growth, were acidic. They found that NO_3^- and nss-Cl^- contributed to the acidification of unrimed snow crystals, and they suggested that these ions originated not in aerosol but in HNO_3 and HCl gases because the concentration of NH_4^+ was much lower than those of NO_3^- and nss-Cl^-. In the atmosphere, snow crystals probably scavenge HNO_3 and HCl vapor from ambient air.

If so, the further question is which these gases that are scavenged by snow crystals originate in, a local urban pollutants or pollutants that are transported great distances. To approach this question, further observations were carried out at two sites. In this paper, we report the cases where unrimed snow crystals were observed. Those have an advantage for clarifying the gas-scavenging process by solid hydrometeors: it is not necessary to consider the accretion of supercooled droplets in which vapor was dissolved.

2. OBSERVATIONS

Observations were carried out in January 1997 at Moshiri, located in a remote area in northern Japan, and from January to March 1998 at Mitoi (where Takahashi et al. (1996) also carried out observations), located in a sparsely populated suburban area of Sapporo City in northern Japan. There are few local air pollution sources around the former observation site. The locations of the observation sites are shown in Figure 1. Hereafter, these two sites are referred to as the remote site and the suburban site, respectively.

Solid precipitation particles were collected at intervals of approximately 1 hr in polyethylene containers by the method described by Takahashi et al. (1996). The samples were melted at room temperature within about three months after collecting, and pH, electrical conductivity and concentrations of major ions (SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Ca^+, Mg^{2+}, K^+ and Na^+) were measured by means of an ion chromatograph.

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* *Corresponding author address:* Tsuneya Takahashi, Hokkaido Univ. of Educ., Int. Ctr. for Educ. Res. & Training, Sapporo 002-8501, JAPAN;
e-mail: takahasi@sap.hokkyodai.ac.jp

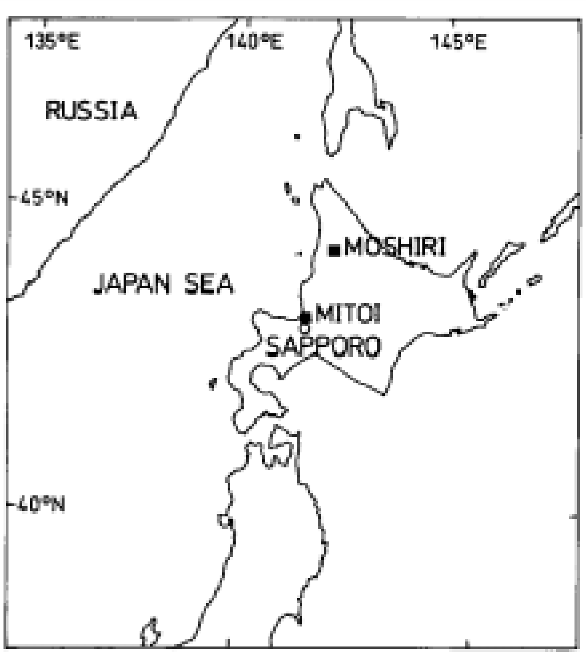

Fig. 1. Map showing locations of observation sites.

The shapes of falling particles that had been directly received on a glass slide or collecting in a vessel during each sampling period were observed under a microscope. The characteristics of the particles were also continuously monitored by two video cameras (Takahashi and Endoh, 1998). The snowfall intensity was monitored every minute by a snow gauge using an electric balance (Konishi et al., 1988).

The concentration of HNO_3 vapor in the atmosphere at ground level was measured, and the concentration of HCl vapor was also measured at the suburban site. When air was sucked, the HNO_3 gas in the air was trapped on a nylon filter after NO_3^- particles had been collected on a Teflon filter. After sampling for 6 hrs or more, both filters were immersed in distilled water, and the extracts were analyzed by ion chromatography. The concentration of HCl was automatically measured by an ion electrode method (Kyoto Electronics model HL19) and displayed as an hourly average.

3. RESULTS AND DISCUSSION

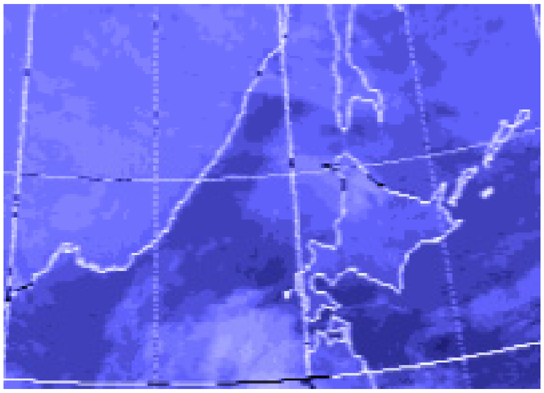

Fig. 2. Satellite infrared image taken on 22 JST, January 28, 1997.

The contributions from sea salt particles were excluded, and thus the concentrations of nss-SO_4^{2-}, NO_3^-, nss-Cl^-, H^+, NH_4^+ and nss-Ca^+ were considered. The concentration of each ion that did not originate from sea salt particles was calculated using the following equation:

$$[\text{nss-X}] = [X]_{mea} \quad [X/Na^+]_{sw} \times [Na^+]_{mea},$$

where X is SO_4^{2-}, Cl^- and Ca^+, and nss-, mea and sw denote non-sea salt, measured concentration in a snow sample and concentration in seawater, respectively.

3.1 Observation at the Remote Site

Figure 2 shows a satellite image when snow crystals were observed at the remote site on January 28, 1997. A southwesterly wind brought snowfall clouds from the Japan Sea. Figure 3 shows examples of snow crystals colected during the observation period. Unrimed

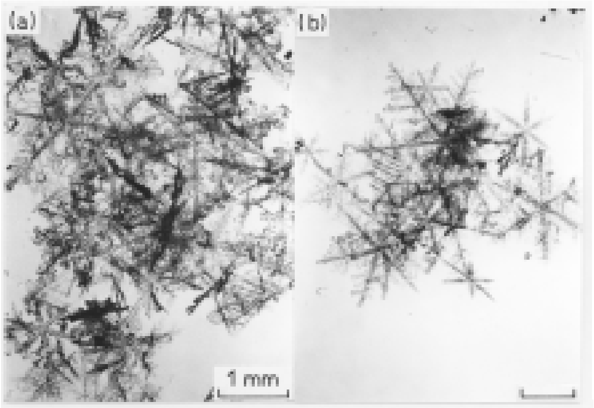

Fig. 3. Photographs of snow crystals that were collecting in a vessel during a sampling period from 21:25 to 23:25 hours on January 28, 1997 (a) and directly received on a glass slide at 23:43 on January 28, 1997 (b).

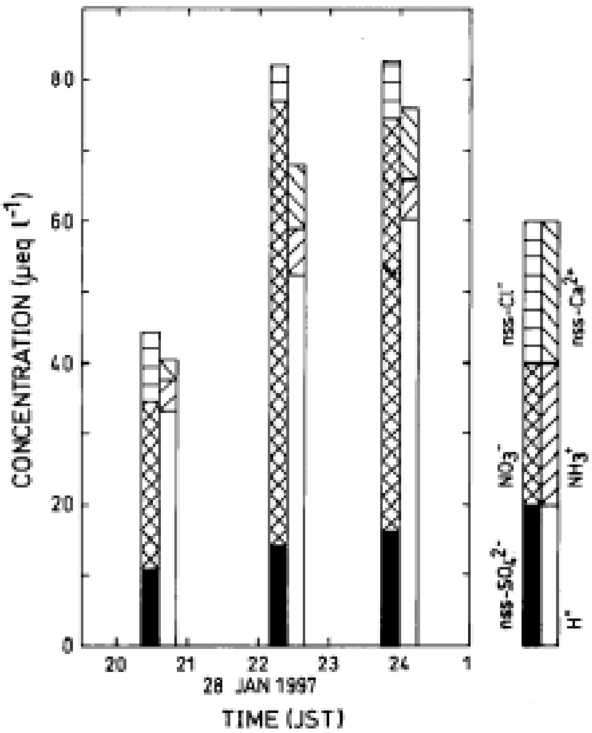

Fig. 4. Concentrations of ions excluding sea salt components (nss-SO$_4^{2-}$, NO$_3^-$, nss-Cl$^-$, H$^+$, NH$_4^+$ and nss-Ca$^+$) in snow samples collected at the remote site on January 28, 1997.

aggregates composed of dendritic crystals were observed. The equivalent ion concentrations in melted snow samples are shown in Figure 4. The concentration of NO$_3^-$ was considerably higher than that of nss-SO$_4^{2-}$. NO$_3^-$ may have accumulated in the snow samples by scavenging of nitrate aerosol particles or of HNO$_3$ vapor by snow crystals. NO$_3^-$ ions did not originate in aerosol particles because the concentration of NO$_3^-$ was much higher than those of NH$_4^+$ and nss-Ca^{2+} in the samples. Thus, it was thought that HNO$_3$ vapor was scavenged in air by snow crystals, as was shown by Takahashi et al. (1996).

The observation of uptake of HNO$_3$ vapor by snow crystals is qualitatively supported by the results of laboratory experiments (Diehl et al., 1995, 1996). According to the experimental results of uptake of HNO$_3$ vapor, the concentration of HNO$_3$ vapor in air should be over 250 ppb in order for the NO$_3^-$ concentration in the melted snow samples to have reached the concentration measured, but the actual average concentration of HNO$_3$ vapor in air sampled over a period of 24 hrs from 9:49 a.m. on January 28 was only 0.02 ppb. Thus, the measured concentration of HNO$_3$ vapor was much lower than the estimated value.

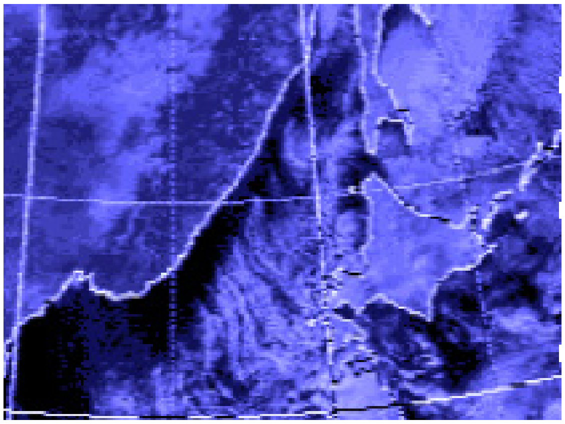

Fig. 5. Satellite visible image taken on 11 JST, February 17, 1998.

3.2 Observation at the Suburban Site

Figure 5 shows a satellite image when samples were collected at the suburban site on February 17, 1998. The snowfall was caused by a cloud band that developed over the Japan Sea in a region where a monsoon from Siberia was passing over a warm current. As shown in Figure 6, unrimed snow crystals of various forms such as column, plate, plate, sector and side plane were observed.

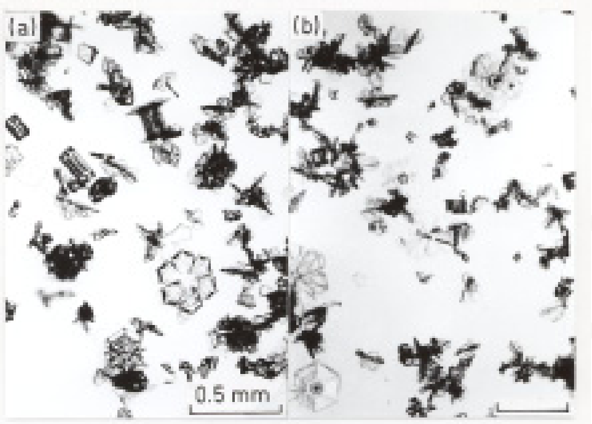

Fig. 6. Photographs of snow crystals that were collected in a vessel during a sampling period from 8:50 a.m. to 10:00 a.m. hours (a) and from 10:05 to 11:32 hours (b) on February 17, 1998.

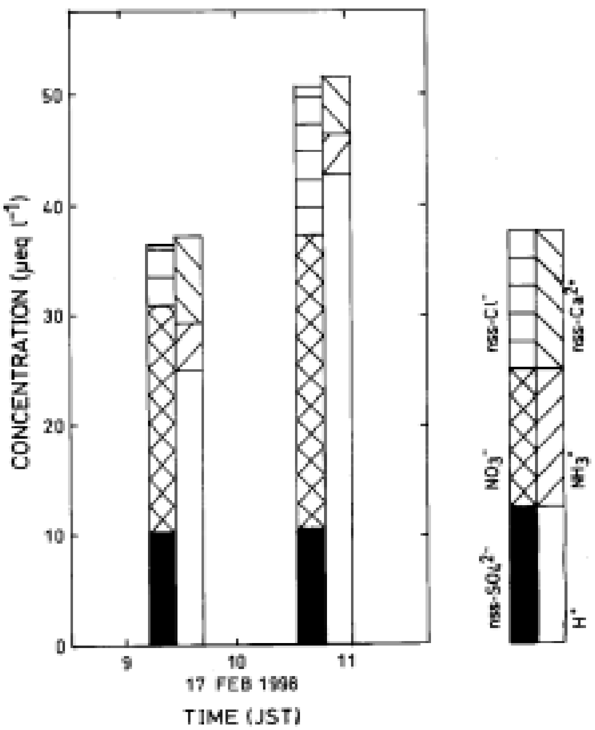

Fig. 7. Concentrations of ions excluding sea salt components (nss-SO_4^{2-}, NO_3^-, nss-Cl^-, H^+, NH_4^+ and nss-Ca^+) in snow samples collected at the suburban site on February 17, 1998.

Figure 7 shows the equivalent ion concentrations in melted snow samples. The concentration of NO_3^- was higher than that of nss-SO_4^{2-}, as was also found at the remote site. It is likely that nss-SO_4^{2-} is not efficiently transferred to falling snow particles without a riming process. Based on the above-mentioned logic, it was thought that snow crystals scavenged HNO_3 vapor. In the latter sample, $[Cl^-/Na^+]_{mes}$ to $[Cl^-/Na^+]_{sw}$ was 1.6, and thus nss-Cl^- also contributed to the acidification of snow crystals. The nss-Cl^- in the snow crystals might have originated from aerosol particles or from HCl gas scavenged by snow crystals. The nss-Cl^- ions did not originate in aerosol particles because the concentration of nss-Cl^- was higher than those of NH_3^- and nss-Ca^{2+} in the samples. Thus, it was thought that HCl vapor in air was scavenged by snow crystals, as was suggested by Takahashi et al. (1996). In some other snow samples, it was found that HNO_3 and HCl vapor contributed to the acidification of rimed snow crystals and graupel particles as well as to the acidification of unrimed snow crystals. In the rimed cases, HNO_3 and HCl vapor was probably taken up by supercooled cloud droplets before accretion or by rime ice. Also, HNO_3 might be formed on cloud droplets that N_2O_5 came in contact with.

The wind direction at an altitude of up to 400 m was easterly, according to the 9 JST 17 February sounding at Sapporo Meteorological Observatory. The land breeze might bring urban polluted air to the observation site, as was suggested by Takahashi et al. (1996). However, the average concentration of HNO_3 vapor in air sampled over a period of 6 hrs from 9:03 a.m. on February 17 was only 0.12 ppb, and the maximum 1-hr average concentration of HCl vapor during the sampling period was 1.5 ppb from 10:00 a.m. on February 17. According to the experimental results of Diehl et al. (1995), the concentrations of HNO_3 vapor and HCl vapor in the air should be 30 and 60 ppb, respectively, to explain the NO_3^- and nss-Cl^- concentrations in the melted snow samples.

Since the measured concentrations of HNO_3 and HCl vapor in the air did not agree with the concentrations estimated from experimental results, it was thought that the HNO_3 and HCl vapor scavenged by unrimed snow crystals did not originate in the local air pollution at ground level but was transported long distances. HNO_3 and HCl vapor may have been stored in cloud droplets due to their high degrees of solubility in water. When the droplets evaporated, the vapor may have been released into air and then scavenged by snow crystals.

4. CONCLUSIONS

Falling unrimed snow samples were collected at a remote site and at a suburban site of Sapporo City and chemically analyzed. The concentrations of HNO_3 and HCl vapor in the atmosphere at ground level were measured.

The concentration of NO_3^- in unrimed samples was considerably higher than that of nss-SO_4^{2-}. NO_3^- and nss-Cl^- contributed to the acidification of snow crystals. It was thought that snow crystals scavenged HNO_3 and HCl vapor, which finding is supported by the results of laboratory experiments (Diehl et al., 1995). The concentrations of HNO_3 and HCl vapor measured in air at ground level were much lower than the values estimated from the above experimental results. It is possible that HNO_3 and HCl vapor in cloud droplets were released into the air and scavenged by snow crystals when the droplets evaporated.

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