10.5 INVESTIGATION OF CHEMICAL COMPONENTS IN SOLID PRECIPITATION AND ENVIRONMENTAL ATMOSPHERE AT NY-ALESUND

(ON ABILITIES OF NO_3^- IN SOLID PRECIPITATION PARTICIPATING IN LONG RANGE TRANSPORT)

T. Endoh[1]*, T. Takahashi[2], I. Noguchi[3], S. Koga[4], N. Kurita[5], N. Tanaka[5], and M. Wada[6],

[1]Institute of Low Temperature Science, Hokkaido University, Sapporo
[2]Hokkaido University of Education, Sapporo,
[3]Hokkaido Institute of Environmental Science, Sapporo
[4]National Institute for Resources and Environment and Resource Research, Tsukuba
[5]Earth Frontia, Tokyo
and
[6]National Institute of Polar Research, Tokyo

1. INTRODUCTION

Up to the present, tremendous numbers of studies have been performed about acid rain, however it is very scarce to be seen about acid snow. Snowflakes have much more information about their history of growth than raindrops. Furthermore, we should recognize that almost raindrops in the world become from solid precipitation melting. Therefore, a clarification of chemistry of solid precipitation is required for a comprehensive understanding of the formation mechanism of acid precipitation. From our previous results of observations at urban and suburbs of Sapporo city, non-rimed snow crystals contain relatively greater concentration of NO_3^- rather than rimed snow crystals (Takahashi *et al*., 1996). These results are coincident with that of laboratory work reported by Diehl *et al*. (1996). The snow particles fell through the air stream polluted by urban air. Therefore, it has been considered that the NO_3^- ion detected from non-rimed snow crystals was affected from anthropogenic air pollution below cloud base.

It had been observed and marked that non-rimed snow crystals have preferentially higher concentration of NO_3^- ion than rimed snow crystals as reported by Takahashi et al. (1996). Such results are seen in coinciding to the results obtained in the laboratory experiments by Mitra et al. (1992) and Diehl et al. (1996). At that time, the component of NO_3^- in solid precipitation without frozen cloud droplets were considered to be taken by the atmospheric scavenging of an anthropogenic contamination of air in land breeze below cloud base. One of the reasons why they took place in these processes as their origin was thought that NO_3^- was brought in short range transport. To verify that, same kind of observation and sampling were carried out in a remote area, Moshiri (Japan) where environmental atmosphere was extremely clean like in the polar region. The concentration of NO_3^- in solid precipitation was however, observed not to be in the lower level expected but in the considerably greater values. Therefore, these results made us to consider about the abilities of NO_3^- in solid precipitation participating in long range transport like as SO_4^{2-} ion. To examine and verify these hypotheses, this study was carried out at Ny-Alesund (Spits Bergen) of the polar region as one of the most remote area of the world.

2. METHODS

Solid precipitation particles were sampled with receiving directly as a natural snowfall with several clean-up containers in the center floor surrounded by a screening net wind-shelter avoiding not to be contaminated by drifting snow. Inside of the shelter, two instruments were installed i.e. a measuring system for snowfall rate with an electric balance and a recording system of snow particle shapes, sizes and species by a time lapse video microscopic camera. The environmental atmosphere was introduced from inlet pipes set in the outdoor and connected to a system commercially called low volume air sampler with a virtual filter at the diameter in 2 micron dividing into two size ranges i.e. fine and coarse particles. Each air was filtrated with some doping filters and they were analyzed to the chemical components, species and concentration.

These snow samples had been kept in a freezing room until the time of nonstop analysis, which were done by ion chromatography, automated colorimeter, atomic absorption spectrometer and isotopic mass analyzer.

3. RESULTS

An observational research had been carried out at the arctic, Ny-Alesund (79N, 12E) as one of the most remote areas of northern hemisphere, from 16th December 1998 to 9th January 1999. Solid precipitation particles were sampled at and analyzed by means of mainly chemical methods with some isotopic ones. Atmospheric gaseous and particle materials in the environmental atmosphere were also sampled by a system of low volume air sampler.

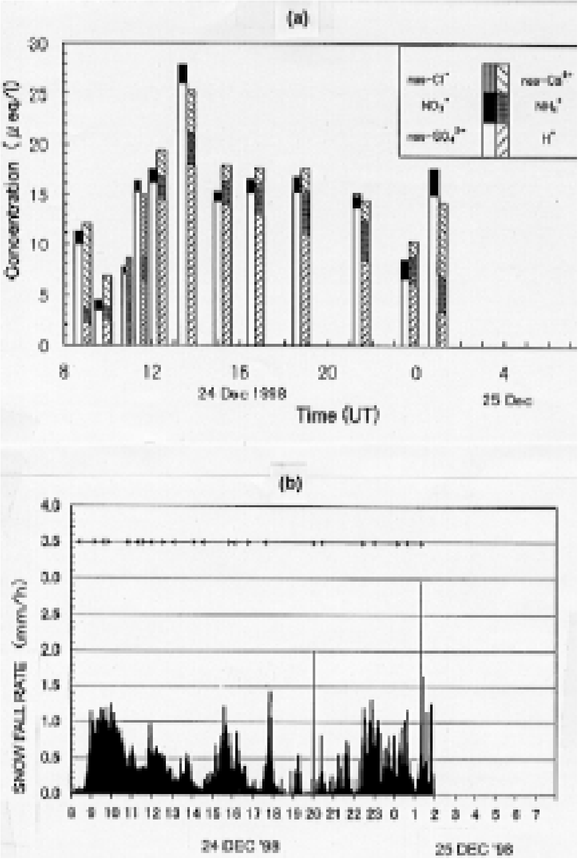

Fig. 1. Temporal changes of (a) chemical components in solid precipitation and (b) snow fall rate in Ny-Alesund in Case 1 for 24th-25th December 1998.

Although seven series of definite snowfall had been observed for the observational duration, four characteristic cases are selected for discussion of this presentation as shown in Figs. 1, 2, 3 and 4. Over the whole duration of snow fall season over there, we had used to have almost rimed snow particles which had been observed to contain nss-SO_4^{2-} ions predominantly as shown as open columns in Figs. 1a and 3a.

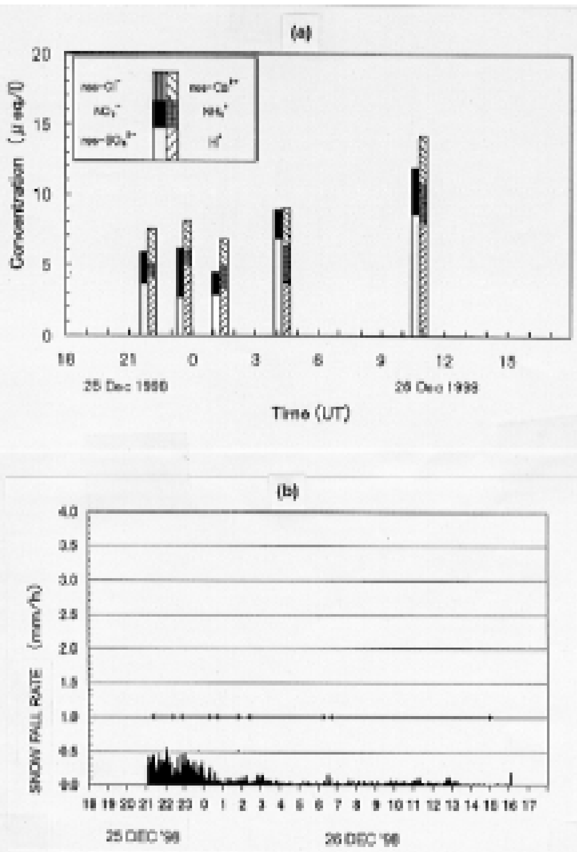

Fig. 2. Temporal changes of (a) chemical components in solid precipitation and (b) snow fall rate in Ny-Alesund in Case 2 for 25th-26th December 1998.

Almost similar results were reported previously by Parungo *et al*. (1987) and Takahashi *et al*. (1996). In these cases, winds were almost all southeasterly wind which is thought to bring abundant vapor or a lot of super cooled cloud droplets. These cloud droplets are easily considered to intake SO_4^{2-} and provide it to rimed snow crystals. In very shorter period, non-rimed snow crystals were observed with north-westerly wind which were thought to bring no abundant cloud droplets as the relatively dryer air stream from sea ice covered ocean area where the supply of water vapor were not sufficient. Those samples of solid precipitation have been analyzed and revealed for them to contain much higher concentration of NO_3^- ions than the rimed snow crystals as shown in Fig.2a comparing with Figs.1a and 3a.

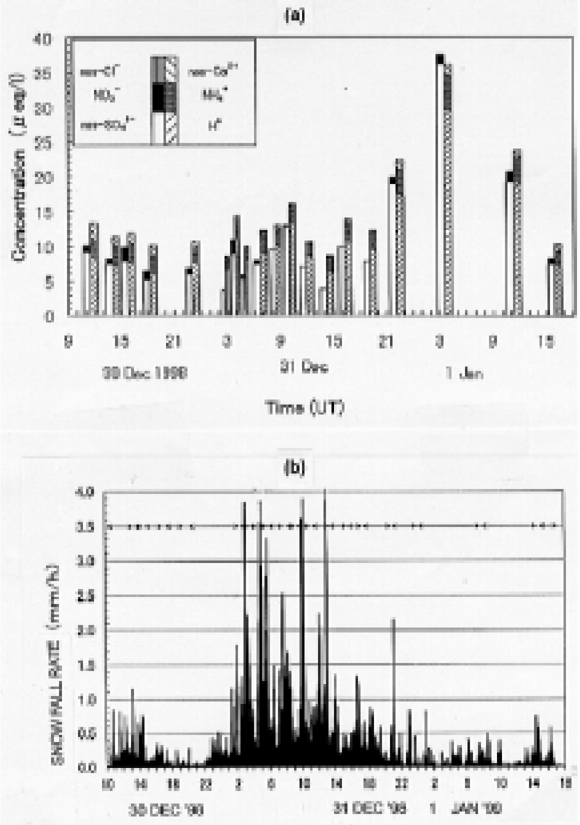

Fig. 3. Temporal changes of (a) chemical components in solid precipitation and (b) snow fall rate in Ny-Alesund in Case 3 from 30th December 1998 to 1st February 1999.

Those samples of solid precipitation have been analyzed and revealed for them to contain much higher concentration of NO_3^- ions than the rimed snow crystals as shown in Fig.2a comparing with Figs.1a and 3a.

For the duration of a series of a long lasting snowfall in Case 3 shown in Fig 3a, rimed snow crystal were observed continuously over the whole duration. Predominant chemical component in cation were also remarked to be nss-SO_4^{2-} shown as open columns in Fig. 3a as similar as in Fig. 1a. In the same figure, it seems interesting that concentration of NO_3^- in snow particles shown as solid columns were seemed to decrease with the time lapse and finally to become vanished into lower values below the threshold of detection.

Another new finding was pointed out the highest concentration of NO_3^- detected in solid

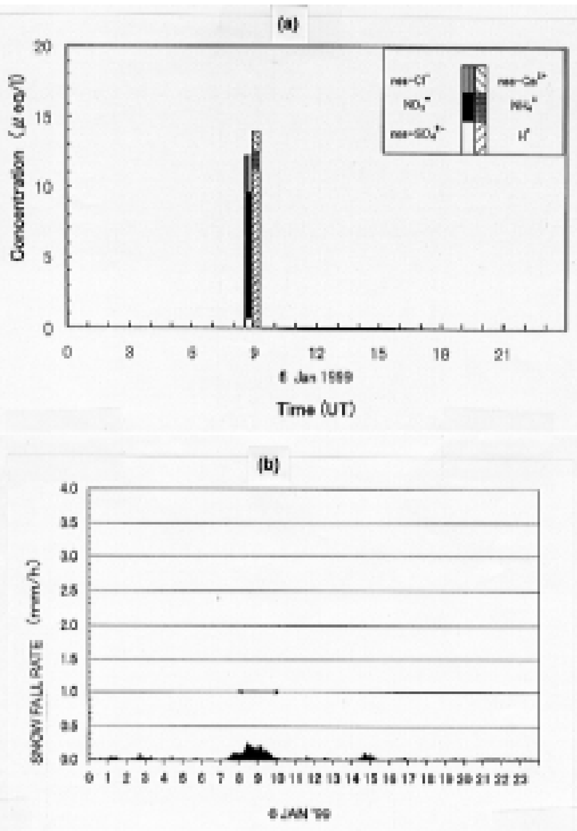

Fig. 4. Temporal changes of (a) chemical components in solid precipitation and (b) snow fall rate in Ny-Alesund in Case 4 on 6th February 1999.

precipitation of this observation as shown by solid columns in Fig. 4a. This precipitation was thought to be brought by an isolated cloud. It may be the most interesting remark that ion concentration in solid precipitation of are NO_3^- and H^+ are almost same values. These result means that the snow crystals obtained had to intake those ions as the shape of HNO_3 gas.

The temporal changes of concentration of cation and anion in coarse and fine aerosols are shown in Fig. 5a and 5b and same ones in gas are also shown in Fig. 6. In these figures, duration on non-rimed snow fall of Case 2 is corresponding to 3rd column from left hand side in each figure and a noted depression or loss of NO_3^- are found out in only fine aerosol particles in Fig. 5b rather than those in coarse aerosol particles in Fig. 6a and HNO_3 gas in Fig. 6

4. DISCUSSION

It was reconfirmed that concentrations of SO_4^{2-} and NO_3^- are predominantly higher in solid precipitation of snowfall with rimed and non-rimed snow crystals, respectively in the most typical phenomena of Case1, 3 and Case2 especially. The former and latter cases of the solid precipitations were corresponding to the snowfalls with southeasterly wind and northwesterly wind respectively. The former and latter directing winds are thought to bring abundant and poor vapor from open sea over the Gulf Stream and ice covered sea ice field over Arctic Sea. These differences are thought to make the solid precipitation particles to rimed and non-rimed snow crystals in the clouds respectively. It may be considered that frozen cloud droplets on rimed snow crystals provide higher concentration of SO_4^{2-}. It may be also considered that super cooled cloud droplets intake SO_2 gas and provide the scene of aquatic reaction help preferentially oxidization processes. Therefore, frozen cloud droplets provide higher concentration of SO_4^{2-} onto the rimed snow crystals.

As shown in Fig. 3 on the way of a series of snowfall lasting for a long time, the concentration of NO_3^- in the precipitation were seen to decrease with the time lapse and arrive to the lowest value which is not detected ones over the latter stage of the whole duration of long lasting snowfall. NO_3^- in the precipitation was seen to decrease with the time lapse and arrived to the lowest value which is not detected ones over the latter stage of the whole duration of long lasting snowfall.

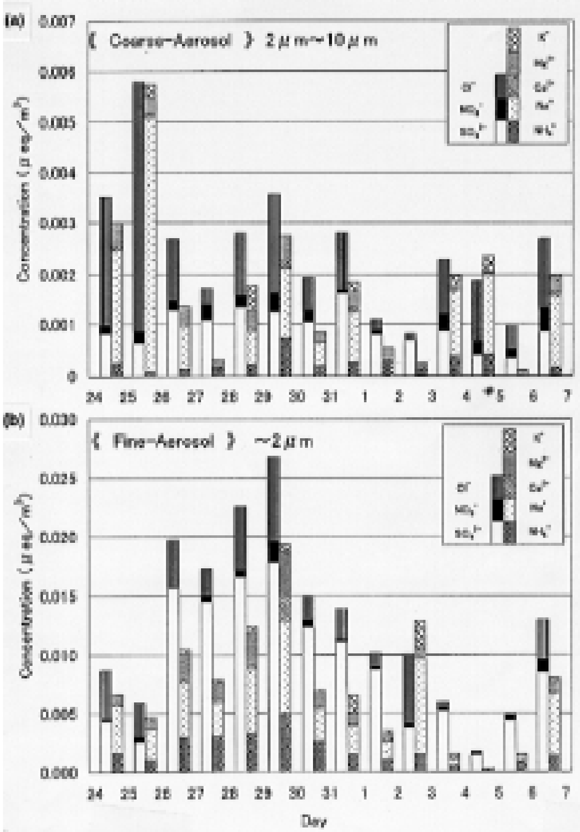

Fig. 5 Temporal changes of chemical components in (a) coarse and (b) fine particles of the environmental atmosphere.

These phenomena may be considered to suggest that concentration of NO_3^- is decreasing in the atmosphere in the long range transport. These results made us to suspect that NO_3^- are consumed and lost along the migration in long range transport. On the other hand, NO_3^- in the environmental atmosphere was observed not to be in the lower values rather than that in the mid-latitude. These make us to uptake that NO_3^- in solid precipitation are considered in the worth of admiration in participating in long range transport.

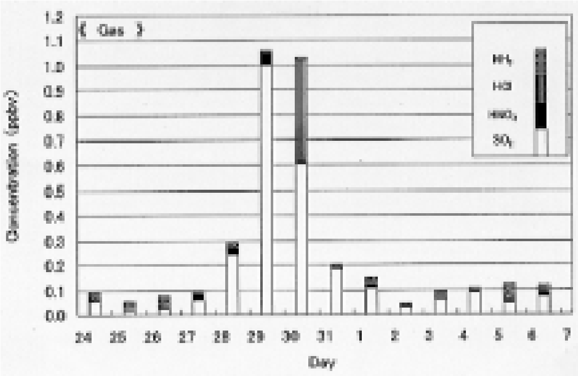

Fig. 6 Temporal changes of chemical components in gaseous materials of the environmental atmosphere.

In another previous repot by Endoh et al. (1998), a similar speculations were presented as follows. Concentration of NO_3^- in fewer rimed snow crystals was also observed to be proportional to that of surrounding atmosphere. It means to be undeniable that NO_3^- ion observed are considered affected from anthropogenic air pollution below cloud base. However, some certain quantities of NO_3^- ions may be thought to compose in the core part of solid precipitation particles and may be considered formed and contained in cloud processes. Therefore, we should appreciate NO_3^- ions to participate to the species of long-range transport substances like as SO_4^{-2}.

To examine cause or origin of the highest concentration of NO_3^- in solid precipitation observed in the duration and there, which had been brought from an isolated snowstorm, some analyses of back trajectory analyses were performed and one of the results which is the most close to the duration are shown in Fig. 7. In schematics of vertical cross section, a distinct separation of air stream is seen between pressure level of lower below 800hPa level and higher above 700hPa. Air streams of these upper and lower levels are seen to correspond to two different back trajectories from North America via Greenland and North European coastal region of Arctic Sea respectively in the upper plane view of Fig. 7. It may be considered that air stream of such high contents of NO_3^- had come from Northern European Continent with higher concentration by 5 days. Accordingly, it may be also suggested that it is one of reasons for NO_3^- to be considered belong to long range transported materials.

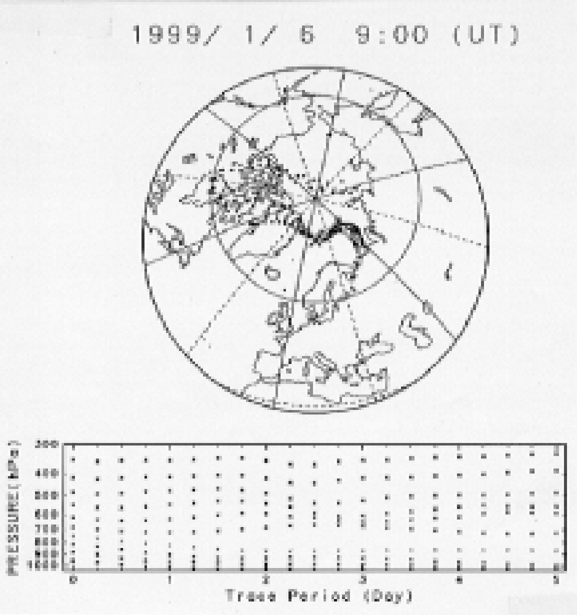

Fig. 7 Back trajectory analyses of the site (x) for 5 days from 09 UT 6th February 1999. Upper: plane view. Lower: vertical cross section.

5. CONCLUDING REMARKS

The remarked findings are summarized as followings.

1) It may be recognized again and confirmed that rimed and non-rimed snow crystals have predominantly higher concentration of SO_4^{2-} and NO_3^-, respectively.

2) In the period non-rimed snow crystals fall, noted depressions of NO_3^- were observed in temporal changes of fine aerosols among HNO_3 gas and coarse aerosols of the environmental atmosphere.

3) Therefore, it may be considered that some scavenging mechanisms are more predominantly efficient than those of gaseous absorption or coalescence of coarse aerosols for the intake mechanism of NO_3^- toward the ice interface. On the other hand, it was observed that non-rimed snow crystals intake NO_3^- ion as HNO_3 gas in some case.

4) Concentration of NO_3^- in solid precipitation had been observed to decrease almost up to the value of the limit of detection within the time lapse in a long lasting snowfall.

5) Considerably higher concentration of NO_3^- was detected in solid precipitation, which was thought to migrate from North Europe by 5 days back trajectory analyses.

6) Summarizing over all concluding remarks, it may be speculated comprehensively that NO_3^- is seen as long range transport material since NO_3^- ion was observed in solid precipitation at such remote area.

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