Polar Night Investigation of Chemical Components in Fresh Snow Particles and Aerosol/Gas in the Atmosphere at Ny-Ålesund (On Abilities of NO₃⁻ in Solid Precipitation Participating in Long Range Transport) (Extended Abstract)

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1. Introduction

It had been observed and marked that non-rimed snow crystals have preferentially higher concentration of NO3- 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 NO3⁻ 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 NO3- 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 NO3⁻ 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-Ålesund (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.

3. Results

An observational research had been carried out at the arctic, Ny-Ålesund (79°N,



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



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

12'E) 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.

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. 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



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

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.

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



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

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 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 HNO₃ gas.

4. Discussion

Since it was complete polar night, photo-chemical processes and existence of OH

were not considered to be there. Only aqueous phase reaction is considered to take place there. Therefore, oxidization to SO_4^{2-} is corresponding to riming processes. Accordingly over there, if snow crystals are rimed, so that the snow crystals have preferentially higher concentration of SO_4^{2-} . Conversely when it is found that from chemical analysis, solid precipitation contains higher concentration of SO_4^{2-} , it may be expected to be composed of rimed snow crystal.

Therefore, SO_4^{2-} ion in precipitation may be considered to be a kind of tracer of riming under such polar night. SO_2 is usually oxidized into SO_4^{2-} in two major chemical reaction as follows.

1. Gaseous phase chemical reaction.

 $OH \leftarrow photo-chemical reaction.$

$$SO_2 + OH \rightarrow HOSO_2$$
 (1)

$$HOSO_2 + O_2 \rightarrow SO_3 + HO_2 \tag{2}$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$
 (3)

2. Aqueous phase chemical reaction.

 SO_2 is solved easily into the liquid of cloud droplets and reach to some equilibrium state,

$$SO_{2} + H_{2}O = HSO_{3}^{-} + H^{+} = SO_{3}^{2-} + 2H^{+}.$$

$$HSO_{3}^{-} + H_{2}O_{2} \rightarrow SO_{4}^{2-} + H^{+} + H_{2}O$$

$$SO_{3}^{-} + O_{3} \rightarrow SO_{4}^{2-} + O_{2}$$
(4)
(4)

Oxidization of NO_2 to NO_3^- are usually considered to be divided into daytime and nighttime processes as followings.

Daytime

$$NO_2 + OH + M \rightarrow HNO_3 + M$$
 (6)

Nighttime

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{7}$$

$$NO_3 + NO_2 = N_2O_5 \tag{6}$$

$$NO_3 + RCHO \rightarrow HNO_3 + RCO \tag{9}$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \tag{10}$$

Here, R is H or CH_3 .

Here again, since it was complete polar night, OH is not considered to exist. Reaction of (6) may be thought not to occur. Oxidization processes to NO_3^- were considered to be limited to proceed in reaction (7) with O_3 . In Case 3, noted depression of NO_3^- was observed in long lasting snowfall. If we had a sunrise in that morning there, such depression might not be found out.

5. Concluding Remarks

The remarked findings are summarized as followings.

(1) It may be also recognized and confirmed there that rimed and non-rimed snow crystals have predominantly higher concentration of SO_4^{2-} and NO_3^{-} , respectively with lower values than those in mid-latitude by one order.

(2) In a duration of such non-rimed snowfall, noted depressions of NO_3^- were observed in temporal changes of fine aerosols rather than those of gas (HNO₃) and coarse aerosols in the environmental atmosphere.

(3) On the other hand, it was observed that a considerably higher concentration of NO_3^- was detected in non-rimed solid precipitation, coexisting with H⁺ ion with nearly equal concentration (New !!). It may be thought for non-rimed snow crystals to intake NO_3^- ion as HNO_3 gas in some absorption mechanisms.

(4) In the duration of a considerably long lasting snowfall, concentration of NO_3^- in solid precipitation was observed to decrease with time lapse up to almost limited value of detection.

(5) 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.