Influence of gaseous and particulate species on neutralization processes of polar aerosol and snow — A case study from Ny-Ålesund

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ABSTRACT

The inter-conversion of nitrogen and sulfur species between the gas and particulate phases and their interaction with alkaline species influences the acidity of the aerosols and surface snow. To better understand these processes, a short field campaign was undertaken in Ny-Ålesund, Svalbard, during 13th April 2012 to 24th April 2012. Air measurements were carried out through a particulate sampler equipped with denuders and filter packs for simultaneous collection of trace gases (HNO3, NO2, SO2 and reactive nitrogen compounds) and aerosols, with daily collection of snow samples. Ionic composition of the samples was analyzed using ion chromatography technique. The results suggested that nitrate-rich aerosols are formed when PAN (peroxy acetyl nitrate) disassociates to form NO2 and HNO3 which further hydrolyzes to form pNO3− (particulate nitrate). This resulted in a high contribution of pNO3− (62%) to the total nitrogen budget over the study area. The acidity of the aerosols and snow evaluated through cation/anion ratio (C/A) indicated alkaline conditions with C/A > 2. The bicarbonates/carbonates of Mg2+ played an important role in neutralization processes of surface snow while the role of NH3 was dominant in aerosol neutralization processes. Such neutralization processes can increase the aerosol hygroscopicity causing warming. Chloride depletion in the snow was significant as compared to the aerosols, indicating two important processes, scavenging of coarse sea salt by the snow and gaseous adsorption of SO2 on the snow surface. However, a more systematic and long term study is required for a better understanding of the neutralization processes and chemical interconversions.

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Introduction

The Polar Regions provide a unique site to study the effects of environmental changes because of its variable climatology and chemistry. Long-range transport of contaminants from mid-latitudes is a major source of aerosols in the Arctic, with a winter–spring maximum known as Arctic haze (Rahn, 1981; Quinn et al., 2009). In winter, the absence of solar radiation prevents the primary photochemical production of radical species that initiate many important atmospheric chemical processes. During winter, the lower troposphere is stable and stratified. This hinders any vertical mixing and deposition of particles (Barrie and Platt, 1997). On the contrary, during the polar sunrise, the atmosphere undergoes changes in composition caused by rising temperatures and photo-chemically induced reactions. The snowpack impurities are photolyzed to

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release reactive trace gases into the boundary layer (Grannas et al., 2007). Most of the studies have defined the sunlit months, when the solar radiation starts to increase, as the spring time commences. The Arctic spring time lasts from late March to early June (Schroeder et al., 1998; Beine et al., 2001, 2003; Ianniello et al., 2002; Quinn et al., 2007). Such studies have focused on the important chemical changes in the chemical composition of Arctic aerosols and snow occurring due to photolysis. These studies have suggested that $SO_2^-$ is the dominant component in aerosols during the spring time (Quinn et al., 2007). In the recent years a lot of emphasis has been given to the nitrogen cycling at the air–snow interface specially during the spring season when the increase in radiation initiates a chain of photo-chemical reactions. To better understand such processes in the atmosphere and snow surfaces, simultaneous measurements of many particulate species in aerosols and snow surface and gaseous chemical species, including PAN (peroxy acetyl nitrate), HNO$_3$ or NO$_2$, SO$_2$ were carried out in this study. The conversion mechanisms and rates for the formation of $SO_2^-$ and NO$_2^-$ are important factors in controlling the concentrations of these pollutants. In addition, the rate of conversion of NO$_x$ (NO + NO$_2$) to NO$^+$ affects ozone ($O_3$) formation and the ultimate fate of NO$_x$ in the atmosphere. NO$_x$ and SO$_2$ are oxidized to HNO$_3$ and H$_2$SO$_4$ in the atmosphere, which form sulfate and nitrate salts by neutralization reactions with alkaline components (Matsumoto and Tanaka, 1996).

The study of oxidized nitrogen species is crucial because there are evidences that the deposited HNO$_3$ on the aerosols could be photolytically decomposed to produce nitrous acid (HONO) (Li, 1994). Such reactivation of NO$_2$ may essentially enhance the lifetime of active nitrogen far beyond the few days that are generally accepted as NO$_2$ lifetime. In this way, the spatial and temporal impact of NO$_x$ emissions on atmospheric photochemistry and ozone tropospheric production is increased. Similarly, the rate of oxidation of SO$_2$ to $SO_2^-$ determines its lifetime in the atmosphere. The oxidizing agents such as $O_3$, hydrogen peroxide (H$_2$O$_2$), and reactive free radicals (OH and HO$_2$) play an important role in the atmospheric oxidation of SO$_2$ and NO$_2$ to acids (Monn and Schaeppi, 1993). SO$_2$ is oxidized to H$_2$SO$_4$ by homogeneous gas–phase reactions followed by condensation of H$_2$SO$_4$ on pre-existing aerosol and into new aerosol particles with partial neutralization by ammonia (NH$_3$) (Huntzicker et al., 1984). The complexity of such interconversions of particulate and gaseous species demands further studies of chemical composition of aerosols and gases simultaneously. These interconversions affect the process of neutralization of the aerosols, which can take place when SO$_2$ converts to H$_2$SO$_4$ in the atmosphere and it reacts with ambient NH$_3$ to produce ammonium bisulfate (NH$_4$HSO$_4$) and the very weakly acidic ammonium sulfate (NH$_4$H$_2$SO$_4$) (Matsumoto and Okita, 1998). The proportion of each of the above $SO_2^-$ species in the atmosphere depends upon the meteorological conditions and local concentrations of NH$_3$ (Huntzicker et al., 1980; Lioy and Waldman, 1989). If NH$_3$ is scarce, H$_2$SO$_4$ in aerosols will not be completely neutralized and will remain in more acidic forms such as NH$_4$HSO$_4$ (Millestein et al., 2008). Thus, the study of sulphur and nitrogen chemistry holds a significant place in assessing the changes in springtime Arctic troposphere. The chemistry of nitrogen and sulphur at the air–snow interface is highly complex and intertwined. The uptake or release of nitrogen highly depends on the alkaline or acidic nature of aerosols and snow surface, which in turn is governed by the neutralization of H$_2$SO$_4$ by NH$_3$, or formation of sulphate and nitrate salts of Mg$^{2+}$ and Ca$^{2+}$. Therefore, the arctic aerosol may range from highly acidic to fully neutralized depending on the availability of NH$_3$. A recent study has showed that the such neutralization processes in arctic atmosphere has major implications for aerosol radiative forcing (Fisher et al., 2011). Once aerosol gets neutralized to form ammonium sulphate (NH$_4$)$_2$SO$_4$ at low humidity, its hygroscopicity is reduced. Due to this decrease in water content the direct radiative forcing of $SO_2^-$ aerosol also reduces (Boucher and Anderson, 1995; Wang et al., 2006; Martin et al., 2004), ice-cloud nucleation and heterogeneous chemistry is also affected (Abbatt et al., 2006; Baustian et al., 2010; Eastwood et al., 2009; Fickert et al., 1999). However, there is still dearth of studies focusing on the aerosol and snow neutralization and gas-particle interconversion processes. The neutralization reactions in aerosol become critical as aerosol neutralization also suppresses acid catalyzed heterogeneous bromine reactions thought to be critical in driving ozone and mercury depletion events in Arctic spring (Fickert et al., 1999; Fiot and von Glasow, 2008).

Another important factor that governs chemical composition of the aerosol and snow is the scavenging and deposition of aerosols on the surface snow. The gaseous NO$_x$ and SO$_2$ emitted from Russian or Eurasian sources can be oxidized in the Arctic atmosphere shifting the balance from nitrogen or sulfur gas-phase compounds to their particulate forms. These particulate forms may then reach the surface snow via wet or dry deposition altering the chemical environment and leading to reversible reactions. Studies focusing on the chemical balance between the particulate and gaseous chemical species and simultaneously quantifying the chemical changes occurring in the snow surface are very sparse in Ny–Ålesund. Apparently, only the work of Beine et al. (2001) has focused on the chemistry of ionic species in all the three important reservoirs, trace gases, aerosol, snow, through an experimental study carried out at Zeppelin station. Thus, this brief campaign attempts to provide an independent snapshot overview of the possible chemical reactions and changes occurring in aerosols, trace gases and surface snow simultaneously during the 9 sunlit days of April 2012 in Ny–Ålesund. Present study focuses on the chemical processes of neutralization and gas to particle conversions, specifically of nitrogen and sulphur species.

1. Study area

The Svalbard Archipelago located in the high Arctic is one of the world’s northern most settlements. Ny–Ålesund is situated on the southern shore of the Kongsfjorden, on the west coast of Spitsbergen, which is the largest and only permanently populated island of Svalbard. There are about 15 inhabitants in Ny–Ålesund research village during the winter and up to 100–150 during summer, depending on the research activity and tourism. Therefore, during the summer season the area is more likely to be affected by local pollution in comparison to the winter or the spring season. Gruevbødets atmospheric laboratory (GB), is located at about 10 m above mean sea level (a.m.s.l.), 800 m southwest from the Ny–Ålesund village (Fig. 1). GB is situated away from the main
settlement and is least affected by the local emissions of the Ny-Ålesund village. Air Measurements were carried out at the Gruvebadet atmospheric laboratory, from 13th April 2012 to 24th April 2012 (these 9 sampling days would be marked as S1–S9 in the entire text). The northeast side of this facility is designated as a clean area, where snowmobile traffic and other potentially contaminating activities are forbidden. This sampling location was also not directly affected by the local pollution from the settlement area. Daily (time series) snow samples were collected from the upwind area near the air sampling site.

A hybrid single particle Lagrangian integrated trajectory (HYSPLIT) model was used to analyse the back trajectory using the National Centre for Atmospheric Research (NCAR) re-analysis data at a height of 500 m a.m.s.l. The trajectories were clustered into three clusters using geographic information system (GIS) based software, Trajstat (http://ready.arl.noaa.gov/HYSPLIT). The analysis suggested that 16.7% of the trajectories travelled a considerable distance over the Arctic Ocean and patches of sea ice before entering the sampling site (Fig. 2). Greenland and western Siberian air masses contributed 25% and 58%, respectively (Fig. 2). Therefore, 42% of the air mass in spring 2012 originated from relatively clean sectors.

The meteorological data during sampling period was provided by the Institute for Atmospheric Science and Climate National Research Council of Italy (ISAC-CNR). The average temperature during the study period was \(-9^\circ\)C with a minimum temperature reaching up to \(-12.2^\circ\)C. The average pressure at 10 m a.m.s.l ranged between 995 and 1009 hPa. The wind speed varied between 1.6 and 9.3 m/sec with an average of 3 m/sec. The average relative humidity during the study period was 69% ranging between 54% and 77%. The solar radiation showed much variation with an average radiation of 129 W/m². An average precipitation of 0.3 mm (0.2–1.3 mm) was observed with four precipitation events (including two relatively significant on 16th April 2012 and 22nd April 2012) during the sampling period.

Fig. 1 – Study area: (a) Svalbard Archipelago, (b) Ny-Ålesund and snow sampling site and (c) Gruvedabdet atmospheric laboratory, the air sampling site.
2. Methodology

2.1. Sample collection

The sampling was carried out with a university research glassware corporation (URG) air particulate sampler (2000-01J, URG, USA). The use of dilute acid scrubber has been first suggested by Crider et al. (1969). Since then the method is being continuously used with modifications to achieve more accuracy (Allegrini et al., 1999, 1987; Beine et al., 1996; De Santis et al., 1996; Ianniello et al., 2002). This sampler has a parallel configuration for denuders allowing simultaneous installation of up to eight denuders. However, in this study only two denuders were operated in parallel with a flow of 8 L/min in each denuder (Fig. 3). Each denuder is followed by a 2-staged filter pack. Gases diffuse from a laminar flow regime through the denuder to the walls, where they are absorbed by the specific coating, while aerosols, having significantly smaller diffusion rates, pass through the denuder without being trapped. Before the air enters the denuders, a cyclone was placed to remove any coarse particles which may adhere to the denuder walls, causing sampling artifacts (Fig. 3). The individual annular denuders were made of Pyrex glass, are 24.2 cm long, and have an inner diameter of 3 cm. The filter pack includes a 47 mm Teflon filter (Z2669395, Pall Gelman, USA) for the collection of particles, and a 47 mm Nylon filter (Z66608, Pall Gelman, USA) for the collection of hydrochloric and nitric acid evaporated from the front filter as a result of acid-base exchange between H₂SO₄ and chloride or nitrate salts. Different coating solutions were used for the collection of different gases (Table 1). The NaF coating solution was used for the collection of SO₂, HNO₃, and HCl. This coating were used for the collection of HNO₃ and HCl in the previous studies also (Beine et al., 2001; Ianniello et al., 2002). The alkaline carbon coating was used for the collection of NO₂ and PAN (as NO₂ and NO₃). The alkaline carbon coating was prepared by dissolving 0.5 g of active carbon (Fluka Prod. 05105) in 4 mL of a 2% NaOH and 1% glycerol (w/v) in methanol. Prior to use, carbon was extracted overnight in a Soxhlet extractor with water-methanol 1:1 solution, washed twice with boiling 0.5 mol/L NaOH, twice with boiling water and then dried at about 100°C.

The coating of Na₂CO₃, NaF and NaCl are all good for HNO₃ collection, but all these coatings can suffer from the direct interference of NO₂ (Durham and Stockburger, 1986; Perrino et al., 1990). The flow in each denuder was fixed at 8 L/min. The Na₂CO₃ coating consisted of 1% Na₂CO₃ + 1% glycerol (w/v) in water: methanol 1:1 solution. The NaF coating consisted of 0.08% (weight/volume) NaF in methanol. Prior to the first use of the denuders, they were soaked in 20 g/L NaOH for 12 hr. Before starting the collection of new sample each day, the denuders were soaked for 6 hr in deionized water, rinsed three time with fresh dionized (DI) water and dried with clean bottled air. After coating the denuders with the specific coatings the drying procedure is repeated again. All the lab procedures were carried out under laminar air flow conditions. The collection efficiency of the alkaline denuders was estimated at the flow rate of 8.2 L/min from the first term of the standard Gormley and Kennedy (1949) equation applied to annular geometry according to Winiwarter (1989). The efficiency was calculated to be 99%. To prevent any contamination in samples, proper cleaning protocols (Beine et al., 2001, 2003) for denuders and filters were followed. The filter blanks (FB), denuder-field blank (DFB) and denuder-laboratory blank (DLB) were collected every alternate day.

Daily samples of surface snow were collected up to a depth of 10 cm in a pre-designated clean snow sampling sector, upwind from Gruvebadet atmospheric laboratory. Each day a new sampling pit was dug close to the previous day sampling pit. The surface snow was collected in sterile low density polyethylene (LDPE) whirl-pak bags using fresh, sterile, powder-free and polymer-coated latex gloves and pre-cleaned Teflon scoop. The samples were kept frozen in −20°C until analysis.
2.2. Sample analysis

All filters and denuders were individually extracted in 7 and 10 mL of de-ionized water respectively. De-ionized water containing 0.03% H₂O₂ was used for the extraction of NaF coated denuders to oxidize sulphite to sulphate. The reaction is instantaneous and complete. The extracts were subsequently analyzed for major ions by a reagent-free ion chromatography (RF-IC) system (DX-2500 and ICS-2000, Dionex, USA) placed in a class 100 clean room and equipped with an automated Eluent Generator Module (EG50, Dionex, USA) and conductivity detector (CD25, Dionex, USA). The cations were separated on an IonPac CS17 (4 mm) column with methanesulfonic acid (MSA) as eluent at a flow rate of 1.0 mL/min, using the gradient method and an IonPac CG17 Guard column with a CSRS-ULTRA suppressor. The anions were separated on an IonPac AS11-HC (4 mm) column with potassium hydroxide (KOH) at 1.2 mL/min as eluent, using gradient method and an IonPac AG11-HC Guard column, with an ASRS-ULTRA (4 mm) suppressor. Calibration was done using concentration range of 50–500 ppb IV (Inorganic Ventures, USA) high-purity standards. In order to confirm the quality of measurements, chromatographic standards were analyzed on a daily basis throughout the study. The precision estimated from the standard deviation of repeat measurements of standard and samples was 3% for Na⁺, K⁺, Mg²⁺ and Ca²⁺; 4% for NH₄⁺; 6% for Cl⁻, and 4% for NO₃⁻ and SO₄²⁻. The PAN values obtained by the described method are proxy for all gas-phase organic nitrate species such as peroxyacetyl nitrate as well as

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**Fig. 3 – Schematics of the sampling instrument (adapted from URG 2000-01 J manual). PM10 is the particulate matter with a cut off size of 10 μm.**

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<table>
<thead>
<tr>
<th>Denuder</th>
<th>Major species</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaF</td>
<td>HNO₃(g), HCl(g), SO₂(g)</td>
</tr>
<tr>
<td></td>
<td>Interferents: NO₃(g), Cl⁻(g), SO₄²⁻(g), NO₂(g), NO₂⁻(g), as PAN and alkyl nitrate</td>
</tr>
<tr>
<td>Alkaline carbon</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Filter type</th>
<th>Major species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Filter: Teflon, 47 mm</td>
<td>NO₃(g), Cl⁻(g), SO₄²⁻(g), NO₂(g), Na⁺(g), K⁺(g), Ca²⁺(g), Mg²⁺(g), NH₄⁺(g)</td>
</tr>
<tr>
<td>2nd Filter: Nylasorb, 47 mm</td>
<td>Evaporated species from Teflon filter: HNO₃(g), HCl(g), NH₄(g)</td>
</tr>
</tbody>
</table>

p and g in the parentheses denote particulate and gaseous species, respectively. PAN: peroxy acetyl nitrate.
alkyl nitrates. Their exact speciation cannot be investigated with our method. However, PAN usually comprises 60%–80% of the measured NO₂ in the Arctic (Bottenheim et al., 1993). The limit of detection (LOD) for the species are shown in Table 2.

The LOD for denuder and filter measurements of various particulate and gaseous species (Table 2) are evaluated on the basis of the LOD of the analytical method and of the standard deviations of field blanks (Beine et al., 2003; Iannielli et al., 2002; Perrino et al., 2001). The denuder field blank was housed within the temperature regulated chamber of the sampling equipment for the same time period as the samples but without any air flow. Both the denuder blanks were coated and extracted as the samples with 10 mL de-ionized water. High field blank values of major cations were observed in this study, however, all sample values have been corrected with the field blanks.

2.3. Calculations

The reported mixing ratios are calculated from the contributions of several individual measurements (as per the equations given below).

\[
\text{HNO}_3(\text{ng/m}^3) = \frac{\text{NO}_3^- (\text{NaF denuder})}{\text{Volume (m}^3\text{)}} \times \frac{1}{E} \times \frac{\text{mw}_{\text{HNO}_3}}{\text{mw}_{\text{NO}_3}}
\]

where \(\text{HNO}_3\), \(\text{NO}_3^- (\text{NaF denuder})\) and \(\text{Volume (m}^3\text{)}\) refer to gaseous nitric acid, nitrate collected on sodium fluoride coated denuder and the volume of sample air, respectively. \(E\) (collection efficiency for \(\text{HNO}_3\)) = 0.995, and \(\text{mw}\) is the molecular weight of the species.

\(\text{NO}_3^-\) (particle phase, reported as only the fine fraction, ng/m³) can be calculated as:

\[
\text{NO}_3^- (\text{particle phase, ng/m}^3) = \frac{n(\text{NO}_3^- (\text{Nylon F}))-n(\text{NO}_3^- (\text{N.F.B}))-n(\text{NO}_3^- (\text{Teflon F.B})))}{\text{Volume (m}^3\text{)}}
\]

where \(F\) stands for filter, \(F.B\) denotes filter blank, \(N.F.B\) denotes nylon filter blank, and \(n\) denotes the filter number (1st filter collecting \(\text{NO}_3^-\) on nylon filter, \(n\) is used just for sample identification and not in the calculation for the above equation).

\[\text{NO}_2\] (particle phase, reported as only the fine fraction, ng/m³) can be calculated as:

\[
\text{NO}_2^- (\text{particle phase, ng/m}^3) = \frac{n(\text{NO}_2^- (\text{Alk.carbon Denuder})) \times \text{mw}_{\text{NO}_2^-}}{\text{Volume (m}^3\text{)}}
\]

\[\text{NO}_2\] (gas phase, ng/m³) = \[\text{NO}_2\] (Alk. Carbon Denuder) \times 0.0105

where \[\text{NO}_2\] (Alk. Carbon Denuder) denotes \[\text{NO}_2\] collected on the denuder coated with alkaline carbon and 0.0105 equates to interference factor of 1.05%. This interference factor was established through laboratory test in the work carried out by Beine et al. (2001) to account for the potential interferences from oxidant species, such as ozone which could convert nitrite into nitrate.

The concentrations of gases and aerosols were calculated in ng/m³ and then converted to their mixing ratios in pmol/mol taking into consideration, the measured temperature and pressure during the sampling period. The non-sea salt components of the major ions are important markers of source and transport processes. The high Na⁺ and non-sea salt SO₄²⁻ (nssSO₄⁻) concentrations correspond to transport of oceanic and polluted Arctic air masses respectively (Hara et al., 1997). The non-sea salt potassium (nssK⁺) is attributed to soil dust and is also released during biomass burning (Crimmins et al., 2004). The sea salt Na⁺ (ssNa⁺) is estimated using the following equation (Röthlisberger et al., 2002):

\[\text{ssNa}^+ = (\text{R}_e \times \text{Na}^+ - \text{Ca}^{2+})/(\text{R}_e - \text{R}_m)\]

where \(\text{R}_e = 1.78\) and \(\text{R}_m = 0.038\) are the average ratios of \text{Ca}^{2+}/Na⁺ in crust and marine systems respectively. The Na⁺ and Ca²⁺ are respective total concentrations in aerosol.

The non-sea-salt-concentrations of potassium (nssK⁺), magnesium (nssMg²⁺), calcium (nssCa²⁺), and sulfate (nssSO₄²⁻) were calculated from the following equations (Virkkula et al., 2006):

\[\text{nssNa}^+ = \text{Na}^+ (\text{total}) - \text{ssNa}^+\]

\[\text{nssK}^+ = \text{K}^+ - 0.038 \times \text{ssNa}^+\]

\[\text{nssMg}^{2+} = \text{Mg}^{2+} - 0.12 \times \text{ssNa}^+\]

\[\text{nssCa}^{2+} = \text{Ca}^{2+} - 0.038 \times \text{ssNa}^+\]

\[\text{nssSO}_4^{2-} = \text{SO}_4^{2-} - 0.25 \times \text{ssNa}^+\]

The crustal contributions to the nssSO₄²⁻ concentration (nssSO₄²⁻ crust) was calculated by the following equation (Bove et al., 2016):

\[\text{nssSO}_4^{2-} \text{ crust} = (\text{SO}_4^{2-}/\text{Ca}^{2+}) \text{ crust} \times \text{nssCa}^{2+}\]

where \(\text{SO}_4^{2-}/\text{Ca}^{2+}\) value in dust was estimated to be 0.021 ng/g by Mason (1966).

The sea salt content was calculated as:

\[\text{Sea salt (ng/m}^3\text{)} = \text{Cl}^- (\text{ng/m}^3\text{}) + \text{ssNa}^+ (\text{ng/m}^3\text{)} \times 1.47\]

where Cl⁻ is the chloride ion, ssNa⁺ is the sea salt sodium concentrations in snow, and 1.47 is the mass ratio of

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Blank values of the particulate species collected on Teflon filter (24 hourly samples).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured species</td>
<td>LOD (ng/m³)</td>
</tr>
<tr>
<td>Na⁺</td>
<td>7.95</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>6.63</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>8.61</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>5.12</td>
</tr>
<tr>
<td>K⁺</td>
<td>6.63</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>9.24</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>4.77</td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>4.76</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>2.53</td>
</tr>
<tr>
<td>HCl</td>
<td>3.61</td>
</tr>
<tr>
<td>SO₂⁻</td>
<td>3.59</td>
</tr>
<tr>
<td>HNO₃</td>
<td>4.98</td>
</tr>
<tr>
<td>PAN</td>
<td>5.32</td>
</tr>
<tr>
<td>NO₂</td>
<td>2.81</td>
</tr>
</tbody>
</table>

LOD: limit of detection.
(Na⁺ + K⁺ + Mg²⁺ + Ca²⁺ + SO₄²⁻ + HCO₃⁻) to Na⁺ in seawater (Bates et al., 2001).

The neutralization ratio (NR) is calculated to understand the neutralization of acidic sulphur species in aerosols expressed as mol/mol by the following equations (Fisher et al., 2011):

\[
\text{NR} = \frac{\text{NH}_4^+}{2 \times \text{nssSO}_4^{2-} + \text{NO}_3^-}
\]

\[
\text{NR} = \frac{\text{nssCa}^{2+}}{\text{nssSO}_4^{2-} + \text{NO}_3^-}
\]

\[
\text{NR} = \frac{\text{nssMg}^{2+}}{\text{nssSO}_4^{2-} + \text{NO}_3^-}
\]

The ion balance method was adopted to assess the proton availability and hence evaluate the acidity of aerosols (Hennigan et al., 2015). The cation/anion (C/A) ratio was calculated in the study taking into account the sum of concentrations all cations under study (Na⁺, Ca²⁺, NH₄⁺, Mg²⁺ and K⁺) divided by the molar concentrations of the anions (SO₄²⁻, NO₃⁻ and Cl⁻) in charge equivalents.

To understand the degree of atmospheric conversion of SO₂ to SO₄²⁻ and NO₂ to NO₃⁻ the sulfur conversion ratio (Fs) and nitrogen conversion ratio (Fn) were also calculated through the following equations (Khoder, 2002):

\[
\text{Fs} = \frac{\text{nssSO}_4^{2-}}{\text{SO}_2 + \text{nssSO}_4^{2-}}
\]

where, nssSO₄²⁻ is the non-sea salt sulfate concentration, and SO₂ is the gas phase SO₂ concentration, averaged over the sampling period.

\[
\text{Fn} = \frac{\text{pNO}_3^-}{\text{pNO}_3^- + \text{PAN} + \text{HNO}_3}
\]

where, pNO₃⁻ is the particulate nitrate concentration (as NO₃⁻), and PAN and HNO₃ are the gaseous nitrogen concentration, averaged over the sampling period. PAN is thermally very stable as compared to other nitrogen species (Seinfeld and Pandis, 2016) and HNO₃ is the primary reservoir of nitrogen species in the polar regions; hence play an important role in determining the Fn ratio. NO₂ has been excluded in this calculation as it is chemically very reactive which enters into reaction with ozone to form reactive NO₃⁻ radicals (which ultimately form HNO₃) or it can undergo photolysis to initiate ozone formation reactions (Bottenheim and Barrie, 1996; Thomas et al., 2011, 2012). Therefore, the detected NO₂ with the denuder system may not completely account for the amount of NO₂ present in the atmosphere at a particular time.

3. Results and discussion

3.1. Gas-phase composition during the study period

Among the gaseous species, PAN showed the highest average mixing ratio of 35.5 pmol/mol without any significant scatter in the dataset (Fig. 4). PAN is a long-lived species with little diurnal variation and PAN(g) (along with alkyl nitrates) is the most abundant nitrogen species in the Arctic atmosphere. It usually comprises 70%-80% of the measured reactive nitrogen (NO₃⁻) in the Arctic (Bottenheim et al., 1993). The nitrogen-enriched air masses from the continents can be transported into the remote, nutrient-limited region of Arctic (Dickerson, 1985) primarily in the form of PAN(g), but also as NO₃⁻ and NH₄⁺ aerosol (Kühnel et al., 2013). However, the PAN values in our study was lower than the other values reported in Ny-Ålesund (Beine et al., 2001; Ianniello et al., 2007) (Fig. 4). This could be attributed to the relatively prominent influence of clean air in this study in comparison to other studies mentioned above. Studies have shown that only dry continental air masses carry higher PAN concentrations (Beine et al., 1997; Bottenheim and Sirois, 1996). Studies have also indicated that there could be in situ sources for PAN in the order of 1 pmol/(mol·hr) during spring in the Arctic (Solberg et al., 1997), but such source contributions are negligible when computing the nitrogen budget (Beine and Kroghnes, 2000). PAN is followed by SO₂ (25.8 pmol/mol) with values ranging from 0.42 to 69.3 pmol/mol. Interestingly these two gases form the main component of the Arctic haze (Jaeschke et al., 1999). The concentration of the reservoir species HNO₃ (20.1 pmol/mol) was observed to be comparable with SO₂, NO₂ being a highly reactive gaseous species accounted for a low average concentration of 8.4 pmol/mol during the study period. The concentration of HCl accounted for the lowest average (7.3 pmol/mol). HCl is the primary reservoir species for Cl⁻ in the stratosphere. HCl in itself is generally un-reactive but during the spring time it reacts heterogeneously to form more reactive forms (such as Cl₂ or ClO) (Nooth et al., 1997) that could be responsible for ozone destruction. These lower values during the study period may indicate that most of the HCl could have already been dissociated to form the reactive chlorine.
and its subsequent products. High mean mixing ratios of aerosol NO$_2$ (147.5 pmol/mol) is observed in the study. It was three times higher than the values observed by its gaseous precursors, HNO$_3$, NO$_2$ and PAN, indicating that the inter-conversion of precursor gaseous species to the particulate NO$_2$ was dominant during the study period. Such inter-conversions are discussed in detail in the subsequent sections.

### 3.2. Aerosol chemical composition

The mean aerosol SO$_4^{2-}$ estimated (38.6 pmol/mol) is much lower than the value reported in other studies at Ny-Ålesund (Beine et al., 2001). Salt constitutes just 22.6% of the total aerosol chemical mass, whereas NO$_3$ dominates the total aerosol mass (38.6%). It is interesting to note that Na$^+$ in aerosols is not completely sourced from sea spray. The nssNa$^+$ in aerosols constitute 57% of the total Na$^+$ signifying some additional (crustal or anthropogenic) sources. However, the nssCl$^-$ (non-sea salt chloride) calculated by subtracting the ssCl$^-$ (sea salt chloride) from total Cl$^-$ (nssCl$^-$ = 1.81 x ssNa$^+$, 1.81 w/w sea water ratio, Bowen, 1979) showed that contribution of negligible over the study period. The average Cl$^-$/ssNa$^+$ molar ratio (1.20) was almost equivalent to the sea water ratio (1.16) suggesting no significant Cl$^-$ depletion. Further, it is noted that among the cations, NH$_4^+$ showed the highest concentration contributing nearly 16% towards the aerosol composition. NH$_4^+$ is a major ion which can neutralize the excess acidity in aerosols caused by the presence of H$_2$SO$_4$. The NH$_4^+$ and nssCa$^{2+}$ constitute 28.7% of the total aerosol load, with the crustal proxy like nssCa$^{2+}$ sharing 12.8% of the mass. These two ionic proxies can neutralize the acidity of the aerosols to a large extent. The nssCa$^{2+}$ containing carbonates and bicarbonates constitutes >90% of the total calcium, indicating a significant crustal influence in the aerosols of the region during the study period. The high NH$_4^+$ concentrations found during the study (210.3 pmol/mol) were comparable with the values reported in Arctic spring 1999 (156.2 pmol/mol, Beine et al., 2001). The secondary inorganic-aerosol mass which regulates its acidity with the neutralization reactions, given as the sum of nssSO$_4^{2-}$, NO$_3$ and NH$_4$ (Squizzato et al., 2013) constitutes 57.7%, indicating that the aerosol chemistry during the study period was primarily governed by these secondary ions. The nssSO$_4^{2-}$ constitutes 51% of the total SO$_4^{2-}$ mass indicating that SO$_4^{2-}$ aerosol is the representative of well a mixed aerosol, suggestive of both marine and non-marine (anthropogenic, biogenic, crustal) influence. The nssSO$_4^{2-}$ (crust) formed just 7% of the total nssSO$_4^{2-}$ concentration, indicating that anthropogenic or biogenic sources dominated the nssSO$_4^{2-}$ in aerosol during the study period.

Taking into account the extensive measurement of almost all the nitrogen species during the study period, the nitrogen budget over the study area during the brief period is computed (Table 3) and compared with the two previous studies of spring 1997 and 1999 over the Arctic (Solberg et al., 1997; Beine et al., 2001). These are the only two studies which estimated the nitrogen budget over the study area during the brief period. The total NO$_3$ in Ny-Ålesund remained almost the same when comparing the budget with 1999; however the contribution of pNO$_3$ and PAN to each year’s budget was different. The pNO$_3$ contributed just 13% to the total budget in 1997 and 1999, but this study reports that the contribution of pNO$_3$ to the total nitrogen budget over the study area was 62%. Such a significant contribution of pNO$_3$ implies a high rate of conversion of gaseous nitrogen species (PAN and NO$_2$) to particulate nitrate. The comparison of PAN concentration in these years suggested varying percentage contribution to the total budget with, 44.6% in 1997, 80.4% in 1999 and 14% in 2012. However, it is important to note that the limited time period in this study makes this analysis sensitive to single episodes, and the values given in Table 3 could indicate the mixing ratio levels in air of different origin, which is giving rise to these differences when comparing with other studies. This snapshot during April 2012 was mainly influenced by the humid maritime air, thus bringing in less PAN concentrations (due to increased thermal dissociation of PAN due to warmer temperatures over the oceans) as stated earlier (Beine et al., 1996; Bottenheim and Sirois, 1996). Therefore, the chemistry described here seems to be different from the work of other researchers who have reported their observation during the event of continental air mass surges. However, the conversion of PAN to NO$_3$ and the formation of further inorganic oxidized species (which are dominant in this study) is evaluated in Section 3.5.

### 3.3. Snow chemical composition

The snow chemistry was dominated by sea-salt (Na$^+$, Cl$^-$) with its contribution of 76% to the total ionic mass concentration. Na$^+$ showed the highest concentration with a mean value of 4285 ng/g, showing much variability (Fig. 4). The Na$^+$ during the study time was dominantly sourced from sea spray in the surface snow, as the nssNa$^+$ formed just 4% of the total Na$^+$ concentration. The contribution of nssNa$^+$ in snow is thus considerably low as compared to the nssNa$^+$ in the aerosols, suggesting that the coarse aerosols originated from the sea spray settled on the surface snow enriching the snow in ssNa$^+$, while the Na$^+$ in the fine aerosols enriched by the dust remained in the atmosphere which was collected by the sampler. The Cl$^-$ values were almost half the concentration of Na$^+$, but fairly constant over the study. The calculated concentration of nssCl$^-$ was negligible over the study period. On the contrary, the snow composition in the

| Table 3 – Estimation of nitrogen budget during April 2012 (all values are in pmol/mol). |
|-----------------|----------------|-----------------|----------------|
| Species        | 1997/1998a    | 1999b           | 2012 (present study) | Percentage of total NO$_x$ (%) |
| NO              | –3.00         | –1.00           | 1.00               | 0.45                            |
| HONO           | 8.43          | 2.68            | 2.68               | 1.14                            |
| HNO$_3$        | 8.74          | 4.32            | 20.10              | 8.50                            |
| NO$_2$         | 19.53         | 5.98            | 8.45               | 3.61                            |
| NO$_3$(g)      | 10.96         | 3.09            | 26.88              | 11.33                           |
| NO$_3$(p)      | 15.56         | 29.76           | 147.54             | 62.33                           |
| PAN(g)         | 53.35         | 191.67          | 32.50              | 13.74                           |
| Total NO$_3$   | 119.56        | 238.49          | 236.89             |                                  |

NO and HONO values were estimated from the studies of Beine et al., 2001.

a Solberg et al., 1997.

b Beine et al., 2001.
The present study was much Cl⁻ depleted as compared to the winter snow of 1996/1997 (de Caritat et al., 2005). The Cl⁻/ssNa⁺ molar ratio (0.83) was less than the sea water ratio (1.16) in this study, suggesting some significant Cl⁻ depletions. The Cl⁻ depletion calculated for the snow samples was found to be significantly high (51.5%), indicating that the reactions occurring between the sea salt and the H₂SO₄ (Eq. (1)) present in the snow dominated and formed an important part of the snow chemical reactions during the spring time.

\[
\text{HNO}_3(g) + \text{NaCl}(s) \rightarrow \text{NaNO}_3(s) + \text{HCl}(g) \quad (1)
\]

This suggests a strong interaction, probably gaseous adsorption of the anthropogenic SO₂ present in the Arctic Haze on the surface snow.

Interestingly, the SO₂(g) reveals opposite variation compared to SO₄²⁻ in snow (S) indicating that a greater part of SO₄²⁻ (S) is derived from the direct exchange of SO₂(g) with surface snow. Two major precipitation events were recorded, first on S3 (15th April 2012, 0.7 mm) and the second on S6 (18th April 2012, 1.3 mm). On the higher precipitation day (S6), the SO₄²⁻ (S) concentrations nearly doubled with values from 800 to 1650 ng/g. This was followed by a subsequent decrease in SO₂(g) concentration (43–12 pmol/mol) and a decrease in aerosols SO₄²⁻ concentration (21–15 pmol/mol) as well (Fig. 5). On S3, the SO₄²⁻ (S) concentration increased, but not as drastically as on the higher precipitation day, S6. Therefore, wet scavenging of gaseous and aerosol S-species, with gaseous scavenging dominating the deposition process is suggested to be dominant during this period.

Among the acidic ions, the snow SO₄²⁻ forms 12.9% of the ionic composition, whereas the NO₃⁻ was only 1.5%. The nssSO₄²⁻ contributed 35% to the total sulphate concentration in snow. The nssSO₄²⁻ concentration was corrected for crustal contributions which showed that crustal nssSO₄²⁻ was just 1% of the total nssSO₄²⁻. The rest was either anthropogenic or biogenic. The sources of SO₄²⁻ in the Arctic are not well understood at the surface and they vary with the altitude (Shindell et al., 2008). The high Cl⁻ depletion is also clearly explained by the presence of anthropogenic nssSO₄²⁻ in snow. In the present study, 58% of the trajectory is from the west Siberian sector, which is a dominant contributor of SO₂ to the Arctic region due to anthropogenic and biomass burning activities (Wang et al., 2011; Warneke et al., 2010, 2009). These emissions are transported to the Arctic through low level transport (Marelle et al., 2015; Harrigan et al., 2011; Stohl, 2006). This could contribute significantly to the acidity of the surface snow.

3.4. Acidity of the aerosol and surface snow during the study period

The role of the acidic species (NO₃⁻ and SO₄²⁻) in Cl⁻ depletion was further explored by estimating the aerosol and surface snow acidity through the cation-to-anion ratios in charge equivalents. Although the C/A ratios in both aerosol and surface snow was found to be >1, higher C/A was observed in the aerosols (2.5) suggesting more neutralization reactions taking place in aerosols, as compared to the snow, where the C/A ratio was found to be 1.9. Since the nssNa⁺ and nssCa²⁺

Fig. 5 – SO₂(g) and SO₄²⁻ variations during Spring 2012. (g): gaseous species, (A): aerosol, (S): snow. S1–S9 are the nine sampling days as indicated in Section 1.
was higher in the aerosols, the dust which is rich in alkaline material neutralized the acidic aerosols along with NH₃.

The extent to which the H₂SO₄ in aerosol is neutralized has major implications on aerosol radiative forcing (Fisher et al., 2011). Studies have shown that NH₃ can get absorbed on the acidic SO₄²⁻ aerosol particles forming (NH₄)₂SO₄, thus reducing its acidity and hygroscopicity, especially at low humidity. This reduction in water content of the aerosols reduces its direct radiative forcing (Boucher and Anderson, 1995; Jacobson, 2001; Martin et al., 2004; Wang et al., 2008). Thus, neutralization processes are important for the accurate estimation of the chemical composition of aerosol and surface snow, specifically of a remote and climatically sensitive region like Arctic. Since the carbonate bases of Mg²⁺ and Ca²⁺ along with NH₃ can also contribute to the neutralization of acidic inputs in aerosols (Rastogi and Sarin, 2006), neutralization ratio was calculated for nssMg²⁺, nssCa²⁺ and NH₄⁺ for both the aerosols and surface snow. The percentage contribution of the ions towards the neutralization processes is shown in Fig. 6. The observations suggest that the NR was highest for NH₄⁺ (1.88), suggesting that NH₃ plays the dominant role in neutralizing the aerosols and contributes nearly 71% in the neutralization of aerosols (Fig. 6). This process is followed by neutralization of H₂SO₄ by calcium carbonates and bicarbonates, with calcium contributing to 23% in the neutralization processes in aerosols. The dominance of neutralization reactions of NH₃ and the formation of ammonium salts was inferred by NH₄⁺/nssSO₄²⁻ (Rₛ). The Rₛ for aerosols was found >3 indicating the formation of (NH₄)₂SO₄ in an NH₃ rich atmosphere (Eq. (2)), where after the neutralization of H₂SO₄ in aerosol the remaining NH₃ can remain in the gaseous form (Seinfeld and Pandis, 2016).

\[
\text{H}_2\text{SO}_4(\text{aq}) + 2\text{NH}_3(\text{g}) \rightarrow (\text{NH}_4)_2\text{SO}_4(\text{s})
\]  

(2)  

The NH₄⁺ rich aerosols found in the study appears to have sourced from NH₃ related to biomass emissions and boreal fires from west Siberian region. The fires have been reported in Novosibirsk Region on 14 April 2012 by the moderate resolution imaging spectroradiometer (MODIS) on the Aqua satellite (http://www.fire.unifreiburg.de/GFMCnew/2013/04/29/20130429_ru.htm). Further, fires on 17th April 2012 in the Siberian Federal District has also been reported by the Federal Forest Agency of Russia (Source: http://www.rosleshoz.gov.ru/forest_fires/info/8). The air masses from these regions could be easily mixed with the anthropogenic air masses areas of East Asia, since they follow similar uplift and transport patterns (Fischer et al., 2010). Such neutralization of nssSO₄²⁻ aerosols suppresses the acid catalyzed heterogeneous bromine reactions, which are important regulators of the ozone and mercury depletion events in Arctic (Fickert et al., 1999; Piot and von Glasow, 2008). On the contrary, the Rₛ ratio of 0.56 in surface snow, indicates the formation of NH₄HSO₄ in limited NH₃ conditions (Eq. (3)).

\[
\text{NH}_3(\text{g}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{NH}_4\text{HSO}_4(\text{s})
\]  

(3)  

Further, the contribution of NH₃ in neutralization reactions in surface snow was found to be very less (15%) in this study compared to the neutralization by non sea salt fractions of Mg²⁺ (carbonates and bicarbonates) as indicated by the higher NR of Mg²⁺, 0.8 with a 55% contribution to the neutralization processes in snow (Fig. 6). This observation suggests the possible formation of Mg²⁺ salts in snow. The crustal dust derived nssMg²⁺ in snow being more effective in the neutralization of the snow acidity could lead to the formation compounds like MgSO₄ and MgCl₂. An interesting observation was that despite the fact that nssMg²⁺ concentration is low in the snow as compared to the nssCa²⁺, yet the neutralization process is more significantly affected by the formation of Mg²⁺ salts over the Ca²⁺ salts, probably due to the high dissolution of magnesium and carbonates in the snow when it was melted for analysis. Further, this observation also suggests that post depositional processes are also exerting an important control over the ammonium concentration and the related reactions in the surface snow.

Several studies report an increase of NO₃⁻ concentration for molar NH₃/nssSO₄²⁻ ratio (Rₛ) > 1.5 (Pathak et al., 2004, 2009; Arsene et al., 2011; Huang et al., 2011). Since aerosols in the study region were found to be NO₃ rich and the average NH₃ neutralization ratio in the study was 1.88, indicating a fully neutralized aerosol, the uptake of NO₃⁻ by these aerosols needs to be investigated. The relationship between NO₃⁻ and NH₃ at different levels of nssSO₄²⁻, which is indicative of the pathway of NO₃⁻ formation (Pathak et al., 2004, 2009) was investigated through studying the variation of NH₃/nssSO₄²⁻ with the NO₃⁻ concentration throughout the study period (Fig. 7). The observations showed that on sampling day S3, when the ratio increased sharply from 7.8 to 30.5, indicating an ammonia excess, a simultaneous and significant increase of NO₃⁻ concentration from 46.7 to 269.0 pmol/mol was recorded. On S5 when the ratio decreases from 18.8 to 4.5, the NO₃⁻ concentrations also decreased from 253.7 to 21.4 pmol/mol. Except for sampling day S9, the ratio was directly proportional to NO₃⁻ concentration in the aerosols (Fig. 7).

\[
\text{HNO}_3(\text{aq}) + \text{NH}_3(\text{g}) \rightarrow \text{NH}_4\text{NO}_3
\]  

(4)  

This relationship clearly suggests that the presence of ammonia excess in the aerosols increases the NO₃⁻ uptake which could lead to the formation of NaNO₃ (Eq. (1)) or
NH₄NO₃ (Eq. (2)) as compared to nssSO₄²⁻ rich aerosols which were primarily composed of NH₄HSO₄, with low uptake or release of NO₃ from aerosols (Eq. (4)).

### 3.5. Interaction of ions between nitrogen and sulphur particulate aerosol with their precursor gases

To make more useful interpretation of the interconversions of nitrogen and sulphur species under prevailing meteorological conditions, the degree of atmospheric conversion of SO₂ to nssSO₄²⁻ and NO₂ to NO₃ as well as the sulfur conversion ratio (Fs) and nitrogen conversion ratio (Fn) were also calculated. While the percentage of nitrogen conversion ratio was 65%, only 34% of the sulphur conversion ratio was observed during the study. This finding suggests that sulphur species was mainly present in the gaseous phase as compared to the gas phase of nitrogen species. This observation also supports high contribution of pNO₃ to the nitrogen budget of the study region during Arctic spring. The NO₃ and SO₄²⁻ are formed when NO₂ and SO₂ are oxidized to HNO₃ and H₂SO₄ through O₂ or H₂O₂ in the atmosphere (Mohn and Schaeppi, 1993; Matsumoto and Tanaka, 1996). On the sampling day S6, when lower humidity (54%) as compared to other days and high radiation (167 W/m²) was observed, lowest Nitrogen conversion ratio (Fn) value (0.5) was also noted. This could indicate that low humidity conditions lower the conversion of gaseous nitrogen to aerosol NO₃ (Table 4). The atmospheric oxidation rate of these reactive gases would increase with increasing relative humidity (Fahey et al., 2005; Rattigan et al., 2002). Apparently, HNO₃ or NO₂ uptake is limited in such conditions. Apart from humidity as a limiting factor, low NR and sea salt content also did not favor NO₂ conversion to NO₃ (S6).

The highest NR ratio on the sampling day S7 indicate alkaline ambient conditions with low sulphur conversion ratio (Fs) with a low particulate sulfate concentration in the aerosols. Highly acidic conditions prevailed on day S9, with NR (NH₄⁺) ratio as low as 0.11 and C/A ratio as low as 0.29. Further Fn = 1 on this day suggests that most of the gaseous nitrogen species (HNO₃) was present in the form of aerosol NO₃ (aqueous phase). NO₃ in aerosol can either be sourced by the formation of NH₄NO₃ (during ammonia excess, low temperature, high humidity conditions) or through heterogeneous reactions of HNO₃ with sea salt (Eq. (5)) (Bauer et al., 2007). However, the low NR(NH₄⁺) indicates that nitrate was formed only through the latter process on day S9.

\[
\text{CaCO}_3 + \text{HNO}_3 \rightarrow \text{Ca}^{2+} + \text{NO}_3^- + \text{HCO}_3^-
\]

(5)

Such an observation supports that enrichment of aerosols with sea spray or crustal dust during HNO₃ rich and NH₄ poor ambient conditions can lead to uptake of HNO₃ in aerosols forming nitrate rich-acidic aerosols.

The estimated molar ratio for pNO₃/HNO₃ was the highest (14.2), followed by HNO₃/PAN, indicating that the pNO₃ was mostly formed by the reaction of HNO₃ with the aerosols. The ternary diagram (Fig. 8) shows that as the ratios of NO₂/PAN and HNO₃/PAN decreases, the pNO₃/HNO₃ ratio increases. The finding suggests that PAN forms NO₂ through thermal dissociation (Eq. (6)). However, considering that subzero temperatures were prevailing during the study time that may not have promoted such reaction at the sampling site, it is proposed that this reaction could have occurred during the air mass transport over the continental regions of northwest Russia and over the Arctic Ocean. However, NO₂ being a reactive species, enters into hydrolysis reaction with photochemically active OH radical to form HNO₃ (Eq. (7)) (Bottenheim and Barrie, 1996). The OH radicals are rapidly formed in the Arctic atmosphere during the photolysis

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<th>Table 4 – Relationship of cation/anion (C/A) ratio with the conversion ratios in aerosols for the study period.</th>
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<td>Days</td>
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NR: neutralization ratio; C/A: cation/anion ratio; Fn: nitrogen conversion ratio; Fs: sulfur conversion ratio; Avg.: average; Std.dev.: standard deviation; S1-S9 are the nine sampling days as indicated in Section 1.
of O₃, OH being the major oxidant during day light hours can initiate another series of photochemical reactions where HNO₃(g), can further hydrolyze to form pNO₃ (Eq. (10)) (Finlayson-Pitts and Pitts, 2000). Other mechanisms of HNO₃ formation also do exist in the Arctic atmosphere (Eqs. (8) and (9)), where M is any non-reactive species which can stabilize the product formed by taking up the extra energy. The NO₃ reaction with hydrocarbon (RH) is relatively slower as compared to other reactions during the daytime (Finlayson-Pitts and Pitts, 2000).

\[
\text{PAN} + h\nu \rightarrow \text{CH}_3\text{CO}_3 + \text{NO}_2 \tag{6}
\]

\[
\text{NO}_2 + \text{OH} + M \rightarrow \text{HNO}_3 \tag{7}
\]

\[
\text{NO}_3 + \text{RH} \rightarrow \text{HNO}_3 + \text{products} \tag{8}
\]

\[
\text{NO}_3 + \text{NO}_2 + M + \text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 \tag{9}
\]

\[
\text{HNO}_3 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NO}_3 \tag{10}
\]

where \( h\nu \) is the required energy of the photon. Thus the observation that the pNO₃/HNO₃ ratio is higher in comparison to NO₂/PAN and HNO₃/PAN (decreases simultaneously with increase of pNO₃/HNO₃) and the highest contribution of pNO₃ in the nitrogen budget indicates that chemical reactions during this snapshot period of study leads predominantly to the formation of inorganic oxidation products like pNO₃ and HNO₃.

4. Conclusions

Present study provides a snapshot of aerosol-snow chemical processes during 13th April 2012 to 24th April 2012 in Ny-Ålesund, Svalbard. Among the gaseous species, PAN dominated the study region and the gas to particle conversion of the gaseous nitrogen species was found significantly dominant compared to the sulphur gas to particle conversion. Nitrate-rich aerosols were formed when PAN disassociates to form NO₂ and HNO₃, which further hydrolyze to form pNO₃. The influx of crustal particles (nssNa⁺ and nssCa²⁺) dominated the fine aerosols turning them more neutralized as compared to the surface snow of the region, which was impacted by the coarse sea spray particles. High Cl⁻ depletion in surface snow was also recorded despite the presence of alkaline aerosols. The observation was supported by the gaseous adsorption of SO₂ on the snow surface in the low temperature conditions and precipitation events. The neutralization of aerosols was regulated by NH₄⁺ forming (NH₄)₂SO₄ whereas due to ammonia deficit in snow, the neutralization of the snow was not complete, which formed NH₄HSO₄ salts. Further, the ammonia deficit conditions lead to the formation of the carbonate/bicarbonate salts of nssMg²⁺. The alkaline conditions in the atmosphere also favored the uptake of HNO₃ by the aerosols. Thus, chemistry of surface snow was found to be quite different as compared to the chemistry of the aerosols. The highly alkaline conditions and the mixing of sulphate aerosol with NH₄⁺ can decrease their scattering effect and increase the hygroscopicity, thus causing warming. Such processes of neutralization and scavenging can have significant impact on aerosol radiative forcing. Further, the processes in the overlying atmosphere could be different from the snow chemical processes, if phenomenon of gaseous scavenging is taken into account. It is clearly evident through these observations that while the Polar Regions, may be relatively “clean", but their chemistry is extremely complex. The role of meteorological conditions governing the influx of aerosols and their scavenging, which influences a range of chemical reactions and the processes, could be very significant. Such high variability in the aerosol and snow chemical composition in such a short sampling time suggests the need to critically evaluate their chemistry through a high-resolution real time data for an extended period involving a simultaneous measurement of gases as well as the particulate phase.

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