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## RESEARCH ARTICLE

10.1002/2013JD021234

## Key Points:

- $\text{NO}_3^-$  deposition and snowpack processes quantified by surface snow sampling
- $\text{NO}_3^-$  dry deposition dominates over postdeposition loss in Ny-Ålesund surface snow
- Br decreases while  $\text{NO}_3^- \delta(^{18}\text{O})$  increases, suggesting tied BrO- $\text{NO}_x$  chemistry

## Supporting Information:

- Readme
- Figure S1
- Figure S2
- Figure S3

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## Nitrate postdeposition processes in Svalbard surface snow

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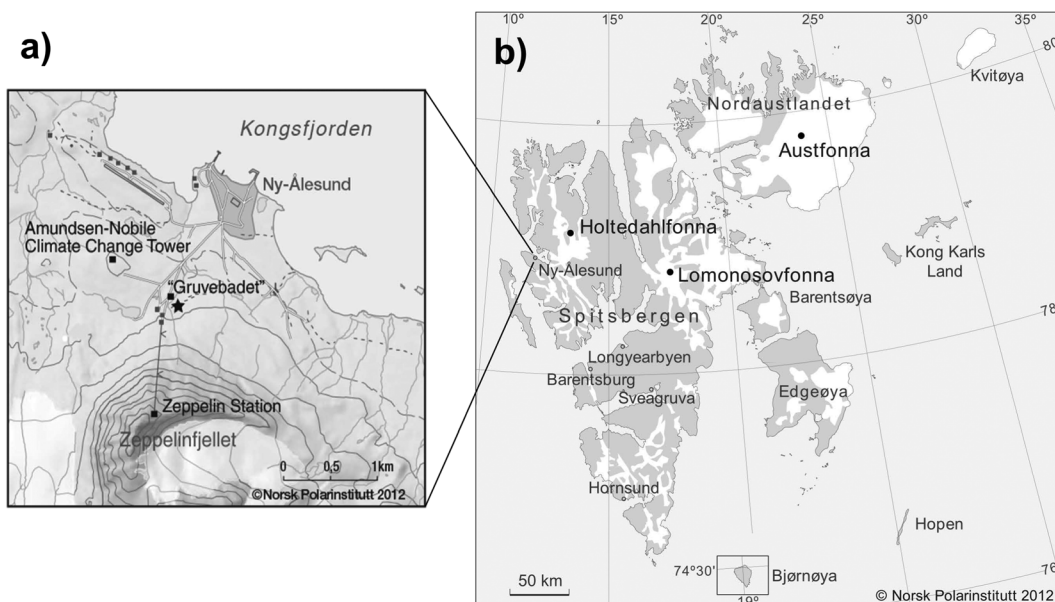
**Abstract** The snowpack acts as a sink for atmospheric reactive nitrogen, but several postdeposition pathways have been reported to alter the concentration and isotopic composition of snow nitrate with implications for atmospheric boundary layer chemistry, ice core records, and terrestrial ecology following snow melt. Careful daily sampling of surface snow during winter (11–15 February 2010) and springtime (9 April to 5 May 2010) near Ny-Ålesund, Svalbard reveals a complex pattern of processes within the snowpack. Dry deposition was found to dominate over postdeposition losses, with a net nitrate deposition rate of  $(0.6 \pm 0.2) \mu\text{mol m}^{-2} \text{d}^{-1}$  to homogeneous surface snow. At Ny-Ålesund, such surface dry deposition can either solely result from long-range atmospheric transport of oxidized nitrogen or include the redeposition of photolytic/bacterial emission originating from deeper snow layers. Our data further confirm that polar basin air masses bring <sup>15</sup>N-depleted nitrate to Svalbard, while high nitrate  $\delta(^{18}\text{O})$  values only occur in connection with ozone-depleted air, and show that these signatures are reflected in the deposited nitrate. Such ozone-depleted air is attributed to active halogen chemistry in the air masses advected to the site. However, here the Ny-Ålesund surface snow was shown to have an active role in the halogen dynamics for this region, as indicated by declining bromide concentrations and increasing nitrate  $\delta(^{18}\text{O})$ , during high BrO (low-ozone) events. The data also indicate that the snowpack BrO- $\text{NO}_x$  cycling continued in postevent periods, when ambient ozone and BrO levels recovered.

## 1. Introduction

### 1.1. Overview

Snowpack nitrate ( $\text{NO}_3^-$ ) can influence the chemical composition of the lower atmospheric boundary layer through photochemical release of nitrogen oxides [e.g., Honrath et al., 1999; Domine and Shepson, 2002; Grannas et al., 2007; Morin et al., 2009; Thomas et al., 2012]. Even though snow is a highly reflective material, the shape and small size of snow grains favors a forward scattering of the light into the snowpack [Domine et al., 2008], creating a photoactive zone in the surface region of the snow cover [e.g., Qiu et al., 2002; Simpson et al., 2002; Galbavy et al., 2007]. Following polar sunrise, photolysis of surface snow  $\text{NO}_3^-$  and the concomitant emission of nitric oxide (NO) and nitrogen dioxide ( $\text{NO}_2$ ) can alter the isotopic composition and concentration of  $\text{NO}_3^-$  in snow and ice [Jarvis et al., 2008; Frey et al., 2009; Erbland et al., 2013]. Furthermore, the removal of  $\text{NO}_3^-$  through  $\text{HNO}_3$  evaporation from snow can also contribute to  $\text{NO}_3^-$  isotopic and concentration changes [Frey et al., 2009; Erbland et al., 2013]. In addition to these postdeposition processes, dry deposition of pollutants and further accumulation of snow will influence the isotopic composition and budget of  $\text{NO}_3^-$ , where the snow accumulation buries older layers and prevents further photolytic reactions [Jarvis et al., 2009; Erbland et al., 2013]. Since several pathways have been described for the  $\text{NO}_x$  ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ) oxidation to nitric acid ( $\text{HNO}_3$ ) in polar regions, e.g., involving ozone ( $\text{O}_3$ ), hydroxyl (OH), and bromine monoxide (BrO) species [Russell et al., 1985; Evans et al., 2003; Seinfeld and Pandis, 2006; Morin et al., 2007b], atmospheric boundary layer chemistry is of key importance for the isotopic  $\text{NO}_3^-$  signature found in snow.

Here we present a detailed investigation of the processes governing the concentration and isotopic composition of  $\text{NO}_3^-$  (<sup>15</sup>N/<sup>14</sup>N and <sup>18</sup>O/<sup>16</sup>O) in the most photoactive zone (upper 5 cm) of the snowpack at



**Figure 1.** Maps of (a) the Ny-Ålesund region and (b) the Svalbard archipelago. Included in Figure 1a as a star is the surface snow sampling site and “Gruvebadet” (a newly established research site), the Amundsen-Nobile Climate Change Tower, and the Zeppelin Station. In Figure 1b the most commonly used ice core drilling sites (Holteedahlfonna, Lomonosovfonna, and Austfonna) are given along with the major settlements (Longyearbyen, Barentsburg, Svea, Ny-Ålesund, and Hornsund).

Ny-Ålesund, Svalbard (Figure 1). In order to highlight the effects of photolysis, the sampling period covered both the polar night and springtime during 2010. The data were analyzed in conjunction with atmospheric flux measurements of oxidized nitrogen;  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{HNO}_3$ , and particulate  $\text{NO}_3^-$  ( $\text{p-NO}_3^-$ ), that were conducted directly above the snowpack, and  $\text{O}_3$  concentrations monitored both at Gruvebadet and at the nearby Zeppelin Station (Figure 1). This study is used to infer the influence of BrO chemistry upon the snowpack nitrogen cycle for the first time in Svalbard.

## 1.2. Background

### 1.2.1. Long-Range Transport and Deposition of Oxidized Nitrogen

Through *long-range atmospheric transport* (Figure 2) oxidized nitrogen that is emitted at midlatitude regions can reach pristine Arctic environments [Rahn *et al.*, 1980; Rahn, 1981; Dickerson, 1985; Stohl, 2006; Hirdman *et al.*, 2010; Kühnel *et al.*, 2011; Kühnel, 2013], often in the form of molecules with longer atmospheric residence time such as peroxyacyl nitrates (PANs) or  $\text{p-NO}_3^-$  [Beine *et al.*, 1997; Seinfeld and Pandis, 2006]. However, occasional rapid long-range transport events also occur, as recently identified for Ny-Ålesund in the European high Arctic [e.g., Hodson *et al.*, 2010; Kühnel, 2013], which can transport pollutants with shorter lifetimes, such as  $\text{NO}_x$ , (or its oxidation product  $\text{HNO}_3$ ) into the Arctic [Zien *et al.*, 2014]. The original isotopic composition of each  $\text{NO}_x$  source (e.g., forest fires or fossil fuel combustion, among other) depends on the oxidation process and origin of the nitrogen (N) and oxygen (O) [e.g. Kendall *et al.*, 2007]. In the Arctic spring, the long-range transported oxidized nitrogen pollutants, such as PANs, decompose and undergo local boundary layer  $\text{NO}_x$  cycling, involving  $\text{O}_3$ , BrO, or hydroperoxyl radicals ( $\text{HO}_2$ ) and solar radiation ( $h\nu$ , Figure 2). This cycling is followed by a  $\text{NO}_x$  removal, where both a day time (through OH or  $\text{HO}_2$ ) and a nighttime (through  $\text{NO}_3$  and dinitrogen pentoxide ( $\text{N}_2\text{O}_5$ )) conversion of  $\text{NO}_2$  to  $\text{HNO}_3$  occurs (Figure 2) [Russell *et al.*, 1985; Dentener and Crutzen, 1993; Hanson and Ravishankara, 1995; Hanson *et al.*, 1996; Evans *et al.*, 2003; Morin *et al.*, 2007b; Morin *et al.*, 2008; Thomas *et al.*, 2011; Thomas *et al.*, 2012], where the  $\text{N}_2\text{O}_5$  also can be directly deposited to the snow [e.g., Huff *et al.*, 2011]. For Arctic sites,  $\text{HNO}_3$  production via the BrO pathway, involving  $\text{BrONO}_2$  (Figure 2), is particularly important during episodes of BrO chemistry, which also causes low  $\text{O}_3$  levels [e.g., Evans *et al.*, 2003; Morin *et al.*, 2007b]. Nitric acid and  $\text{p-NO}_3^-$  will then be removed from the atmosphere by snow, rain, or dry deposition [Cadle, 1991; Bergin *et al.*, 1995; Kuhn, 2001], and be deposited to the snow as  $\text{NO}_3^-$  [Diehl *et al.*, 1995; Abbatt, 1997]. The snowpack therefore acts as an important sink and reservoir for atmospheric reactive nitrogen, with a unique isotopic  $\text{NO}_3^-$  composition and

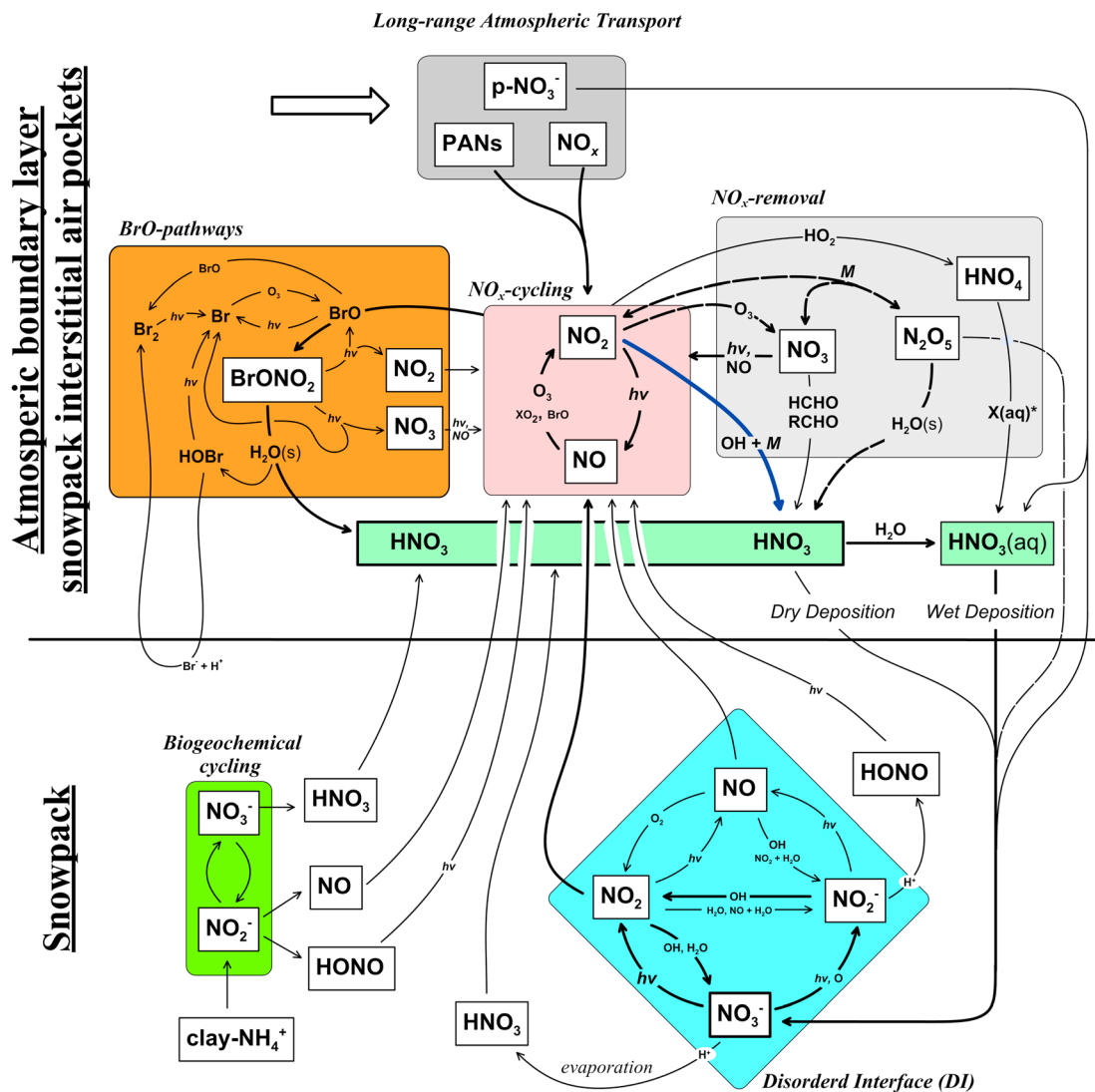


Figure 2. A schematic of the processes important for  $\text{NO}_3^-$  dynamics in Svalbard surface snow.

concentration for each snow layer. For the N-isotopic composition, the *initial* snow signature typically resembles the original source of  $\text{NO}_x$ , this since the fractionation during  $\text{NO}_x$  cycling and  $\text{NO}_x$  removal is considered to be low [Freyer, 1991]. For the O isotopes, the interaction and O exchange with  $\text{O}_3$ , BrO, and OH during the  $\text{NO}_x$  cycling and  $\text{NO}_x$  removal will strongly influence the initial snow O signature, typically masking any other processes or original source signatures [e.g., Michalski et al., 2003; Jarvis et al., 2009; Morin et al., 2009]. Thus the *initial* O signature provides insights into the oxidation processes that have occurred prior to deposition. These initial concentrations and isotopic imprints may, however, be altered by postdeposition processes as will be further outlined below (section 1.2.2).

In Svalbard, the  $\text{NO}_3^-$  deposition and thereby the snow concentration is governed by wet deposition, where a few sporadic “strong” events dominate the total annual deposition [Kühnel et al., 2011]. These strong deposition events are due to rapid transport of polluted European air masses [e.g., Hodson et al., 2010], which are occasionally channeled northward between a blocking anticyclone, situated over Scandinavia and Central Europe, and an incoming cyclone over the Atlantic [Kühnel, 2013]. The typical transport time for such events are about 2 to 5 days and where the air masses picks up in speed and humidity just prior to the arrival to Svalbard [Kühnel, 2013]. The estimated winter dry deposition of  $\text{NO}_3^-$  in this region is modest (approximately 14%) [Björkman et al., 2013], but nevertheless, of importance for the isotopic composition of  $\text{NO}_3^-$  in snow when studying short term daily variations [Hastings et al., 2004].

### 1.2.2. Snowpack $\text{NO}_3^-$ Photolysis and Evaporation

Due to  $\text{NO}_x$  release from the photoactive zone of the snowpack, the deposited  $\text{NO}_3^-$  can play an important role in atmospheric boundary layer chemistry after the initial deposition [e.g., Thomas *et al.*, 2012]. The snowpack is therefore an active player in atmospheric chemical processes and not just a  $\text{NO}_3^-$  sink [Honrath *et al.*, 1999]. Snowpack  $\text{NO}_3^-$  photolysis, of relevance for the  $\text{NO}_3^-$  budget, is believed to occur at the very surface of snow crystals [Boxe and Saiz-Lopez, 2008], with reaction rates and quantum yields for photolytic processes similar to those in aqueous solutions [Bartels-Rausch *et al.*, 2012]. This region of the ice crystal has previously been referred to as a quasi-liquid layer [Kvlividz *et al.*, 1970], but has lately been redescribed as a disordered interface (DI) [Bartels-Rausch *et al.*, 2012]. This new term emphasizes the disordered molecular structure that occurs at the surface of any crystal, created by the absence of molecular bonds toward its surface [Bartels-Rausch *et al.*, 2012], instead of involving a liquid state analogy. The photolysis of  $\text{NO}_3^-$  within the DI and subsequent reactions (Figure 2) lead to the production of  $\text{NO}_2$  and to a lesser extent  $\text{NO}$  (see Jacobi and Hilker [2007]; Boxe and Saiz-Lopez [2008] for an overview of reaction pathways). The produced  $\text{NO}_2$  and  $\text{NO}$  can then diffuse out of the DI into firn air and thereafter into the atmospheric boundary layer [e.g. Honrath *et al.*, 1999; Jones *et al.*, 2000; Beine *et al.*, 2003]. This photolytic initiated loss also alters the isotopic composition of snowpack  $\text{NO}_3^-$ , with an enrichment of  $^{15}\text{N}$  in the residual  $\text{NO}_3^-$  due to photolytic fractionation [Frey *et al.*, 2009; Morin *et al.*, 2009; Erbland *et al.*, 2013]. On the other hand the O composition of the remaining  $\text{NO}_3^-$  will be strongly influenced by the isotopic exchange between the photolytic products and OH-radical or  $\text{H}_2\text{O}$  within the DI [McCabe *et al.*, 2005; Frey *et al.*, 2009]. There is also evidence for nitrous acid (HONO) production from irradiated snow (Figure 2) [Zhou *et al.*, 2001; Beine *et al.*, 2002a], due to the interaction between nitrite ( $\text{NO}_2^-$ ) and a hydrogen ion ( $\text{H}^+$ ) [e.g., Dominé and Shepson, 2002]. However, several other pathways have also been described; i.e. involving humic acids [e.g., Beine *et al.*, 2008; Villena *et al.*, 2011] or heterogeneous reactions in the firn [e.g., Jacobi and Hilker, 2007], although the reaction steps in these pathways are not fully understood [Grannas *et al.*, 2007; Jacobi and Hilker, 2007; Beine *et al.*, 2008; Boxe and Saiz-Lopez, 2008; Jacobi *et al.*, 2014] and therefore not included in Figure 2. Nitrate loss from the snow has also been found to be due to evaporation (Figure 2) of  $\text{HNO}_3$ , a process also favoring the loss of isotopically light  $\text{NO}_3^-$  [e.g., Frey *et al.*, 2009]. A recent study by Erbland *et al.* [2013] confirms that evaporation is an active player in postdeposition processes in areas with low snow accumulation rates and high firn air ventilation, such as central Antarctic sites. However, the process has been shown to be quantitatively modest compared to the loss through photolysis for these Antarctic sites [Erbland *et al.*, 2013]. Interestingly, laboratory studies of snow and ice have found no evidence for this evaporative pathway [Chu and Anastasio, 2003; Sato *et al.*, 2008].

Snowpack  $\text{NO}_x$  emissions, according to the above postdeposition processes, have been estimated for Arctic, Antarctic, and midlatitude snow [Dibb *et al.*, 1998; Honrath *et al.*, 1999, 2000; Jones *et al.*, 2000, 2001; Beine *et al.*, 2002a]. However, these studies are not necessarily directly applicable to the snowpack in Ny-Ålesund, Svalbard (European high Arctic), where substantially lower snowpack  $\text{NO}_x$ ,  $\text{HNO}_3$ ,  $\text{p-NO}_3^-$ , and HONO emissions have been reported in comparison to the other investigated regions [Beine *et al.*, 2003; Amoroso *et al.*, 2006, 2010].

### 1.2.3. Local Biogeochemical Contribution to Snowpack $\text{NO}_3^-$

The DI reactions described above mostly involve  $\text{NO}_3^-$  of nonlocal origin, deposited following long-range atmospheric transport. However, a more locally produced source of oxidized nitrogen has been suggested through microbial activity [Brooks *et al.*, 1997; Ma *et al.*, 2007; Miteva, 2008; Siciliano *et al.*, 2009; Roberts *et al.*, 2010]. Svalbard snow is known to contain a diverse community of microorganisms [Amato *et al.*, 2007; Larose *et al.*, 2010], and the microbial assimilation of ammonium ( $\text{NH}_4^+$ ) might result in the production of gas phase  $\text{NO}$ ,  $\text{HNO}_3$ , and HONO, even during winter (Figure 2) [Amoroso *et al.*, 2010]. Isotopic fractionation is expected through microbial assimilation of nitrogen compounds [e.g., Kendall, 1998], although during the nutrient-limited conditions in a snowpack such nitrogen isotopic fractionation might not necessarily be expressed in the produced reactive nitrogen emissions [Amoroso *et al.*, 2010]. The resulting snowpack emission, under these conditions, would have an N isotopic composition related to the N source (in this case, organic or mineral bound  $\text{NH}_4^+$ ) and an O isotopic composition influenced by the surrounding water [Amoroso *et al.*, 2010].

### 1.2.4. Recycling of $\text{NO}_x$ Snowpack Emissions

The gas phase products of postdeposition and biogeochemical processes are emitted into the firn air and onward to the lower atmospheric boundary layer, where further reactions may lead to a redeposition of

HNO<sub>3</sub> to the snow (Figure 2) [Hastings *et al.*, 2004; Morin *et al.*, 2007b; Jarvis *et al.*, 2009]. During spring and summer conditions, these reactions can have a diurnal pattern governed by daytime emissions and nighttime deposition [Hastings *et al.*, 2004]. The isotopic composition of this redeposited HNO<sub>3</sub> would then be influenced by the oxidation pathways undertaken, see Figure 2 [e.g., Jarvis *et al.*, 2009]. Additionally, snow is a highly porous medium that undergoes a steady exchange of air with the surrounding atmosphere [Sturm and Johnson, 1991; Albert and Hardy, 1995; Colbeck, 1997; Albert *et al.*, 2002; Frey *et al.*, 2005]. This exchange allows the boundary layer processes in Figure 2 to occur also within the snowpack interstitial air pockets.

## 2. Methods

### 2.1. Field Sampling

The top 5 cm of the snowpack was sampled close to Gruvebadet, 1 km outside the Ny-Ålesund International Arctic Research and Monitoring Facility in Svalbard (78°55'N, 11°55' E, Figure 1). Samples were collected between 11 and 15 February (*dark* campaign) and between 9 April and 5 May (*spring* campaign) during 2010. The sampling was undertaken at midday (11:00–13:00) during the dark campaign, and every morning (09:00–10:00) during the spring campaign. All snow samples were collected by inserting a precleaned acrylic collars (height: 5 cm, inner diameter: 10.4 cm, and volume: 425 cm<sup>3</sup>) vertically into the snowpack, and using precleaned plastic shovels, clean overalls, face masks, and powder-free gloves. Triplicate samples were collected approximately 10 m apart, resulting in a total of 96 samples. To account for variations in surface snow density throughout the campaign, several collars were filled next to each other at each of the three triplicate sample locations, yielding a total sampled snow volume between 1.3 L and 3.8 L. The snow was transferred directly into clean black plastic zipper storage bags to prevent further photolysis, brought into the laboratory in Ny-Ålesund and melted at room temperature. Each melted snow sample was vacuum filtered (pore size 0.45 μm, according to Hodson *et al.* [2005]), bottled in 50 ml tubes, refrozen, and shipped for analysis of major ions and NO<sub>3</sub><sup>−</sup> stable isotopes. To minimize contamination between samples, vacuum units and sample tubes were rinsed 3 times with sample water or, in the case of low sample volume, ultrapure water (>18 MΩ). Field blanks were collected along with the samples to check for contamination. Blank bags were opened and closed during sampling (without any snow addition), filled with 100 mL ultrapure water, and then treated and analyzed like the rest of the samples. Furthermore, during the spring campaign, an extra 50 ml sterile sampling tube was filled with the top 5 cm surface snow next to each sampling point for an opportunistic complementary major ion analysis performed on-site.

### 2.2. Laboratory Analysis

#### 2.2.1. Major Ions

The samples were analyzed for NO<sub>3</sub><sup>−</sup>, chloride (Cl<sup>−</sup>), and sodium (Na<sup>+</sup>) by ion chromatography at the Department of Geography, University of Sheffield, UK using two separate systems (Dionex DX 90 ion chromatographs, 4400 integrators, AS40 autosamplers) with Dionex columns AS14A and CS12A for anions and cations, respectively. Standards (range 100 to 2000 μg L<sup>−1</sup>) were prepared every day from 1000 mg L<sup>−1</sup> Merck CertiPUR stock standards. The analytical precision (1 standard deviation, 1σ) estimated from repeat analyses of multielement reference standards (Merck CertiPUR) were 1.4 and 1.6%, respectively, for the anions Cl<sup>−</sup> and NO<sub>3</sub><sup>−</sup>, and 0.06% for the cation Na<sup>+</sup>. Based on repeat analyses of separate filter aliquots, the analytical precision including sample treatment was better than 5% for each ion. Detection limits (DL) defined as 3σ for the analytic blanks were 0.17, 0.21, and 0.34 μmol L<sup>−1</sup> for Cl<sup>−</sup>, NO<sub>3</sub><sup>−</sup>, and Na<sup>+</sup>, respectively.

The complementary springtime 50 ml snow samples and the diffusion line preparations (described below in section 2.3.2) were analyzed for NO<sub>3</sub><sup>−</sup>, Cl<sup>−</sup>, Na<sup>+</sup>, NO<sub>2</sub><sup>−</sup>, and bromide (Br<sup>−</sup>) in Ny-Ålesund by the Institute of Atmospheric Pollution Research-National Research Council of Italy (IIA-CNR). Melted snow was analyzed without pretreatment by ion chromatography analytical technique (Dionex ICS 90 coupled with an AS50 autosampler and using Dionex AS14 and CS12 columns). A multipoint calibration was performed using six standards in the range 5 to 1000 μg L<sup>−1</sup>, obtaining linear responses. Dilutions were carried out for more concentrated samples. Calibration solutions were prepared every second week from 1000 mg L<sup>−1</sup> standard solutions (Merck). Control samples (1000 μg L<sup>−1</sup> calibration solution) were analyzed every seven samples in order to recalibrate the ion chromatograph. The variation in the concentration of these control samples ranged within 0.5–1%. The analytical precision errors from repeated analyses of a calibration

solution ( $500 \mu\text{g L}^{-1}$ ), were 1.13, 0.73, 0.35, 0.43, and 1.31%, respectively, for  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ , and  $\text{Na}^+$ . Detection limits of 46.5, 14.3, 4.9, 6.9, and  $35.8 \text{ nmol L}^{-1}$  were determined for  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ , and  $\text{Na}^+$ , respectively.

### 2.2.2. $\text{NO}_3^-$ Isotopic Composition

The  $^{15}\text{N}$  and  $^{18}\text{O}$  isotopic composition of  $\text{NO}_3^-$  were analyzed at the School of Environmental Sciences, University of East Anglia, Norwich, UK, using the bacterial denitrifier method [Sigman *et al.*, 2001; Coplen *et al.*, 2004; Kaiser *et al.*, 2007] where the *Pseudomonas aureofaciens* strain was utilized. Values presented here are denoted as isotope deltas,  $\delta(^{15}\text{N})$  and  $\delta(^{18}\text{O})$  (IUPAC nomenclature:  $\delta(^{15}\text{N}, ^{14}\text{N}, \text{NO}_3^-)$  and  $\delta(^{18}\text{O}, ^{16}\text{O}, \text{NO}_3^-)$ , respectively), and expressed with respect to an international standard in ‰ ( $10^{-3}$ , per mil) (equation (1)).

$$\delta_{\text{sample}} = \frac{R_{\text{sample}} - R_{\text{ref}}}{R_{\text{ref}}} \quad (1)$$

Here  $R$  represents the  $^{15}\text{N}/^{14}\text{N}$  or  $^{18}\text{O}/^{16}\text{O}$  ratio in the sample ( $_{\text{sample}}$ ) and reference ( $_{\text{ref}}$ ) respectively, where atmospheric nitrogen ( $\text{Air-N}_2$ ) was used as nitrogen reference and Vienna Standard Mean Ocean Water (VSMOW) was used as oxygen reference. Positive delta values indicate an enrichment of the heavier isotope (or a depletion of the lighter isotope) compared to the standard. To calibrate the isotope delta values, the international nitrate reference material IAEA-NO-3 was used, assuming it has  $\delta(^{15}\text{N}) = 4.7\text{‰}$  versus  $\text{Air-N}_2$  and  $\delta(^{18}\text{O}) = 25.61\text{‰}$  versus VSMOW [Böhrlke *et al.*, 2003]. The  $\delta(^{15}\text{N})$  values reported here have not been corrected for any nonmass-dependent  $^{17}\text{O}$  contribution to the  $m/z$  45 ion current during mass spectrometric analysis. However,  $\delta(^{17}\text{O})$  and  $\delta(^{18}\text{O})$  are usually well correlated and the true  $\delta(^{15}\text{N})$  was estimated to be 1–2‰ lower than the reported values. The bacterial denitrifier method requires a minimum of  $20 \text{ nmol NO}_3^-$  (optimum being  $50 \text{ nmol}$ ) in at most  $10 \text{ mL}$  of solution. Consequently, only samples above this limit were analyzed ( $n = 87$ ).

## 2.3. Air-Snow Fluxes

### 2.3.1. Surface Snow Net Change

By following the concentration change in surface snow over time, it is possible to evaluate the overall net change due to processes occurring after wet deposition. This method has previously been used to evaluate  $\text{NO}_3^-$  dry deposition to snow [Cadle *et al.*, 1985; Johansson and Granat, 1986; Cadle, 1991; Cress *et al.*, 1995]. The net change ( $F_{\text{net}}$ ) can be calculated as [Björkman *et al.*, 2013]:

$$F_{\text{net}} = -\frac{c_0 V_t - c_t V_t}{At} \quad (2)$$

where  $c$  is the molar  $\text{NO}_3^-$  concentration in snow,  $V$  the melted volume of the sample,  $A$  the surface area of the snow sample (in this study equal to the cross-section area of the sampling collar), and where  $t$  is the exposure time between the initial sample (index: 0) and the final sample (index:  $t$ ). In Björkman *et al.* [2013], the dry deposition was calculated as an atmospheric loss, giving negative numbers, whereas here the surface gain is of interest; hence, a negative sign is used in equation (2) to account for this. Furthermore, equation (2) will be valid as a pure dry deposition estimate only if no other  $\text{NO}_3^-$  postdeposition processes take place and snow water sublimation is negligible. In all other cases, equation (2) will describe the net effect of the various processes. In terms of the isotopic composition, equation (2) can be written as:

$$F_{\text{net}} (1 + \delta_{\text{net}}) = -k [c_0(1 + \delta_0) - c_t(1 + \delta_t)] \quad (3)$$

where  $k$  is the deposition velocity given as:  $k = V_t / (At)$ ,  $\delta_{\text{net}}$  is the isotopic composition of the net change, whereas  $\delta_0$  and  $\delta_t$  are the initial and final isotopic composition of  $\text{NO}_3^-$ . Equation (3) can be expressed as

$$0 = c_t(\delta_t - \delta_{\text{net}}) - c_0(\delta_0 - \delta_{\text{net}}) \quad (4)$$

which then can be rearranged to give

$$\delta_{\text{net}} = \frac{c_t \delta_t - c_0 \delta_0}{c_t - c_0} \quad (5)$$

equation (5) then gives the change in the isotopic signature ( $\delta_{\text{net}}$ ) and is equal to the isotopic composition of the dry deposited  $\text{NO}_3^-$  if other postdeposition processes are negligible.

### 2.3.2. $\text{NO}_x$ , $\text{HNO}_3^-$ , and $\text{p-NO}_3^-$ Flux Measurements

In addition to the snow sampling, atmospheric flux measurements of  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{HNO}_3$ , and  $\text{p-NO}_3^-$  to and from the snowpack were conducted by IIA-CNR outside Gruvebadet ( $200 \text{ m}$  from the snow sampling site)

during the period 9 to 27 April in 2010. The NO and NO<sub>2</sub> concentrations were measured on a 6 min basis, using a modified commercial two-channel high-sensitivity chemiluminescence detector (Sonoma Technologies, USA) [Beine *et al.*, 2002b; Amoroso *et al.*, 2010]. The two channels sampled air from dual inlets at 0.3 m and 1.5 m above the surface snow, respectively. Nitric oxide detection was based on the chemiluminescence signal produced by the reaction between NO and O<sub>3</sub>, which was photolytically generated in a 150 mL min<sup>-1</sup> flow rate of O<sub>2</sub> by a corona discharge O<sub>3</sub> generator. Nitrogen dioxide was detected as NO following photolysis between 350 and 420 nm by light-emitting diodes. The instrument was calibrated daily with 5.0 μmol mol<sup>-1</sup> of gaseous NO (NIST traceable NO standard, Scott-Marrin, in N<sub>2</sub>) at a flow rate of 2.0 mL min<sup>-1</sup> into the sampling flow (about 1200 mL min<sup>-1</sup>), corresponding to a NO addition of 8.3 nmol mol<sup>-1</sup>. The NO detection limit was determined as 3σ of the observed scatter in the instrument signal and corresponded to 2.5 pmol mol<sup>-1</sup> for 1 h averages.

Measurements of HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> concentrations were made by two independent diffusion lines [Beine *et al.*, 2001; Perrino *et al.*, 2001; Ianniello *et al.*, 2002, 2007] with inlets also at 0.3 and 1.5 m above the snow surface. The HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> concentration was measured on a 12 h basis from 10 to 16 April, while a time resolution of 24 h was used from 17 to 27 April. The diffusion lines used in this study included a denuder train consisting of two sodium fluoride (1% NaF in 9:1 ethanol/water solution) coated denuders for HNO<sub>3</sub> sampling. The atmospheric HNO<sub>3</sub> concentrations were calculated by subtracting the analyte mass (expressed as NO<sub>3</sub><sup>-</sup>) in the second NaF coated denuder from the analyte mass in the first NaF coated denuder [Febo *et al.*, 1989]. The denuder train was followed by a cyclone (2.5 μm aerodynamic diameter cutoff point) and a filter pack set in series, for the collection of particulate matter in the coarse and fine fractions, respectively. The filter pack included a Teflon filter (Whatman Teflon, 47 mm, 1 μm pore size), a nylon filter (Nylosorb Gelman, 47 mm, 1 μm pore size), a Na<sub>2</sub>CO<sub>3</sub> glycerol-impregnated paper filter (Whatman 41) and a H<sub>3</sub>PO<sub>3</sub> coated paper filter. The last three filters were used to collect chemical species evaporated from the Teflon filter [Ianniello *et al.*, 2002, 2011; Spataro *et al.*, 2013]. The sampling flow rate was 15 L min<sup>-1</sup>, and typical sampling volumes of 11.9 m<sup>3</sup> and 23.5 m<sup>3</sup> were obtained for 12 h and 24 h sampling periods, respectively. After sampling, the denuders, cyclone, and filters were extracted and these samples were analyzed within 24 h by using the IIA-CNR Ion Chromatography system described in section 2.2.1. Under these conditions, the collection efficiency for both HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> was >99%. The DL of HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> (calculated as 3σ of field blanks) were 2.95 ng m<sup>-3</sup> and 1.42 ng m<sup>-3</sup>, respectively, on a 24 h measurement period, while the precision errors of these measurements were 2.54% at 20 ng m<sup>-3</sup> and 0.73% at 79 ng m<sup>-3</sup>, respectively. Here we focus only on HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> data, although the diffusion line sampling system did allow us to also collect other gaseous and particulate compounds, which will be discussed elsewhere.

The fluxes of NO, NO<sub>2</sub>, HNO<sub>3</sub>, and p-NO<sub>3</sub><sup>-</sup> (hereafter  $F_{\text{NO}}$ ,  $F_{\text{NO}_2}$ ,  $F_{\text{HNO}_3}$ , and  $F_{\text{p-NO}_3^-}$ , respectively) were determined combining the two height gradient sampling with atmospheric turbulence measurements. The difference between the measured concentrations at the two sampling heights is in this work referred to a concentration difference ( $\Delta$  = lower height – upper). Hence, a positive difference implies emission of the measured species from the snow surface.

Using the measured concentration differences and the atmospheric eddy diffusivities ( $K$ ) for the same period, the atmospheric fluxes for NO, NO<sub>2</sub>, HNO<sub>3</sub>, and coarse and fine particulate NO<sub>3</sub><sup>-</sup> were derived ( $\text{Flux} = \Delta \times K$ ) as detailed elsewhere [Sozzi *et al.*, 1998; Ianniello *et al.*, 2002; Beine *et al.*, 2003, and references therein]. Diffusivities were obtained from atmospheric turbulence measurements made at a frequency of 10 Hz by using an sonic anemometer (Metek, USA-T1), which was placed at 1.5 m above the snowpack, assuming neutral boundary layer conditions.

For the purpose of this study these fluxes have been averaged to daily emissions, depositions, and net fluxes (from 09:00 onward) for comparison with the surface snow data.

### 2.3.3. Dry Deposition Estimates

If the atmospheric concentration ( $c_{\text{atm}}$ ) of HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> are measured, the expected dry deposition flux ( $F_{\text{dry-dep}}$ ) can be modeled as long as the deposition velocities ( $v_d$ ) are known [e.g., Seinfeld and Pandis, 2006]:

$$F_{\text{dry-dep}} = v_d c_{\text{atm}} \quad (6)$$

In a recent study covering the same spring campaign, the dry deposition of HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> was both modeled and measured for Ny-Ålesund [Björkman *et al.*, 2013]. Median deposition velocities were estimated



to be  $0.63 \text{ cm s}^{-1}$  for  $\text{HNO}_3$  and  $0.0025$  or  $0.16 \text{ cm s}^{-1}$  for  $\text{p-NO}_3^-$ , particle size  $0.7$  and  $7 \mu\text{m}$  in diameter, respectively [Björkman *et al.*, 2013]. The combined gaseous and particulate dry deposition,  $F_{\text{model(LND)}}$  (referring to the modeled  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  dry deposition rates obtained using a lognormal distribution (LND) for  $\text{NO}_3^-$  aerosols sizes in Björkman *et al.* [2013]), will be used here for comparison with the surface snow and flux measurements, and for further modeling purposes. Björkman *et al.* [2013] also measured the actual  $\text{NO}_3^-$  dry deposition ( $F_{\text{tray}}$ ) to snow using a “bucket” approach [e.g., Cress *et al.*, 1995] and found an average deposition of  $(0.04 \pm 0.02) \text{ mg m}^{-2} \text{ d}^{-1}$  (equal to  $(0.7 \pm 0.3) \mu\text{mol m}^{-2} \text{ d}^{-1}$ ) which will also be used for further modeling purposes. An overview of  $\text{NO}_3^-$  dry deposition in the Arctic, and a full description of these dry deposition estimates are given by Björkman *et al.* [2013].

#### 2.3.4. Additional Observations

Meteorological data from Ny-Ålesund, in particular precipitation data, were provided by the Norwegian Meteorological Institute (DNMI) and are available at <http://www.eklima.no>. The atmospheric concentration of  $\text{O}_3$  ( $c_{\text{O}_3}$ ) is continuously measured by the Norwegian Institute for Air Research (NILU) at the nearby Zeppelin atmospheric research station (474 m above sea level, Figure 1), available at <http://ebas.nilu.no>. During the spring campaign 2010,  $\text{O}_3$  concentrations were also recorded by IIA-CNR at Gruebadet until 27 April. NILU also provides an online base atmospheric transport model, FLEXTRA (<http://www.nilu.no/projects/ccc/trajectories/>). Using FLEXTRA air mass back trajectories arriving to Ny-Ålesund were established for all sampling days at 00:00 and 12:00, with trajectories spanning 7 days back in time.

Additionally, sonic anemometer (Gill R3) and fast hygrometer (Campbell Scientific KH2O krypton) data from the Amundsen-Nobile Climate Change Tower (Figure 1) were provided by The Institute for Atmospheric Science and Climate-National Research Council of Italy (ISAC-CNR, M. Mazzola, and A. Viola, personal communication, 2013). The 10 min average data sampled at 7.5 m above ground were used to evaluate water vapor flux as an indication of sublimation rates.

### 2.4. Models

#### 2.4.1. Photolytic Model

$\text{NO}_x$  production due to photolysis of  $\text{NO}_3^-$  has previously been modeled for Ny-Ålesund snow, using the solar zenith angle ( $\theta_{\text{SZA}}$ ) and the surface snow  $\text{NO}_3^-$  concentrations, with results comparable to  $\text{NO}_x$  emission measurements [France *et al.*, 2010, 2011b]. This model assumes that the photolysis of  $\text{NO}_3^-$  only follows the reaction  $\text{NO}_3^- + h\nu \rightarrow \text{NO}_2 + \text{O}^-$  and is, according to the reactions in Figure 2, a simplification of the DI dynamics but has the potential to provide useful insights into the  $\text{NO}_3^-$  loss through photolysis. For the purpose of this study, a photolytic rate function considering only the surface snow layer during clear-sky conditions [France *et al.*, 2010] will be used for comparison to the sampled top 5 cm of the snowpack. However, a depth-integrated model would be more appropriate if bulk snowpack samples were under consideration (see France *et al.* [2010, 2011a, 2011b] for further details). Here only surface snow was sampled, in order to avoid a potential disturbance of the postdeposition processes under investigation.

A polynomial function (equation (7)) was fitted to the photolysis rates ( $J_{\text{NO}_3^-}$ , in  $\text{s}^{-1}$ ) given in France *et al.* [2010] as a function of  $\theta_{\text{SZA}}$  (in degrees), with  $R^2 = 0.9994$  (Figure S1 in the supporting information):

$$J_{\text{NO}_3^-} = 1.18e^{-14}\theta_{\text{SZA}}^4 - 1.09e^{-12}\theta_{\text{SZA}}^3 - 3.51e^{-11}\theta_{\text{SZA}}^2 - 8.80e^{-10}\theta_{\text{SZA}} + 3.86e^{-7} \quad (7)$$

where  $\theta_{\text{SZA}}$  was extracted for Ny-Ålesund (<http://www.esrl.noaa.gov/gmd/grad/neubrew/>) with 1 h resolution. Furthermore, to not induce any error from equation (7) when the Sun is close to or below the horizon,  $J_{\text{NO}_3^-}$  was set to zero for  $\theta_{\text{SZA}} > 89.77^\circ$ .

The upper limit for the surface snow  $\text{NO}_2$  emission ( $F_{J_{\text{NO}_3^-}}$ ) can then be calculated as

$$F_{J_{\text{NO}_3^-}} = J_{\text{NO}_3^-} c_0 z_{\text{SWE}} \quad (8)$$

where  $c_0$  is the concentration of  $\text{NO}_3^-$  (in  $\text{mol m}^{-3}$ ) and  $z_{\text{SWE}}$  is the snow water equivalence of the surface snow (in meters). For lower  $\text{NO}_3^-$  concentrations, or unusually high  $\text{NO}_2$  emissions, the surface snow  $\text{NO}_3^-$  concentration might change over the course of the day. To minimize this potential source of error, the time resolution of the photolysis calculations was set to 1 h in accordance with the  $\theta_{\text{SZA}}$  data. The  $F_{J_{\text{NO}_3^-}}$  emission given by equation (8) provides the flux in  $\mu\text{mol m}^{-2} \text{ d}^{-1}$  units.

### 2.4.2. Box Models

A box model, describing the main sources and sinks of  $\text{NO}_3^-$  in the snow, was applied to predict changes in concentration ( $c_{\text{NO}_3}$ ),  $\delta(^{15}\text{N})$ , and  $\delta(^{18}\text{O})$  of  $\text{NO}_3^-$ . In this box model all outgoing fluxes were assumed to be due to photolysis of  $\text{NO}_3^-$ , and all incoming fluxes were assumed to be due to  $\text{NO}_3^-$  dry deposition. Hence, this is a simplification of the actual processes, which might, for example, also include evaporation of  $\text{HNO}_3$  (see Figure 2). However, as an initial assumption (and further justified below) photochemistry was assumed to be the major loss process for this surface snow study.

In the model, the change in  $c_{\text{NO}_3}$  over time when the Sun is below the horizon was expressed as equation (9), while equation (10) gives the change when both dry deposition and photolysis are present

$$\frac{dc}{dt} = \frac{v_d c_{\text{atm}} A}{V_t} \quad (9)$$

$$\frac{dc}{dt} = \frac{v_d c_{\text{atm}} A}{V_t} - Jc \quad (10)$$

Here  $v_d c_{\text{atm}}$  equals the dry deposition rates according to equation (8) and was attributed to the  $F_{\text{model(LND)}}$  or  $F_{\text{tray}}$  in Björkman *et al.* [2013], while the product of photolytic rate ( $J$ ) and snowpack concentration ( $c$ ) constitutes the loss process. Note, in equation (10) and the following equations the photolytic rate of  $\text{NO}_3^-$  ( $J_{\text{NO}_3}$  in equation (7)) has been substituted with  $J$  to keep the equations simple. Equations (9) and (10) can be integrated to give the new concentration ( $c_t$ ):

$$c_t = \frac{v_d c_{\text{atm}} A t}{V_t} + c_0 \quad (11)$$

$$c_t = \left( \frac{v_d c_{\text{atm}} A}{V_t J} \right) * (1 - e^{-Jt}) + c_0 e^{-Jt} \quad (12)$$

where equations (11) and (12) represent periods when the Sun is below or above the horizon, respectively. The isotopic composition of  $\text{NO}_3^-$  remaining in the snow ( $\delta_t$ ) can then be expressed as

$$\delta_t = \left( \frac{c'_t}{c_t} - 1 \right) / R_{\text{ref}} \quad (13)$$

Similar to equations (11) and (12),  $c'_t$  are given by

$$c'_t = \frac{v_d c'_{\text{atm}} A t}{V_t} + c'_0 \quad (14)$$

$$c'_t = \left( \frac{v_d c'_{\text{atm}} A}{V_t J'} \right) * (1 - e^{-J't}) + c'_0 e^{-J't} \quad (15)$$

where  $c'_0 = c_0 R_{\text{ref}}(1 + \delta_0)$ ,  $c'_{\text{atm}} = c_{\text{atm}} R_{\text{ref}}(1 + \delta_{\text{atm}})$ , and  $J' = J(1 + \varepsilon)$ , and where  $\delta_0$  and  $\delta_{\text{atm}}$  are the initial and atmospheric N or O isotopic composition, respectively, while  $\varepsilon$  is the photolytic fractionation for  $^{15}\text{N}/^{14}\text{N}$  ( $^{15}\varepsilon$ ) and  $^{18}\text{O}/^{16}\text{O}$  ( $^{18}\varepsilon$ ). Primed quantities refer to the less abundant isotopic species ( $^{15}\text{N}$  or  $^{18}\text{O}$ ). The error due to the assumption that the concentration of the major isotope is equal to the total nitrate concentration, is negligible ( $<0.01\%$ ).

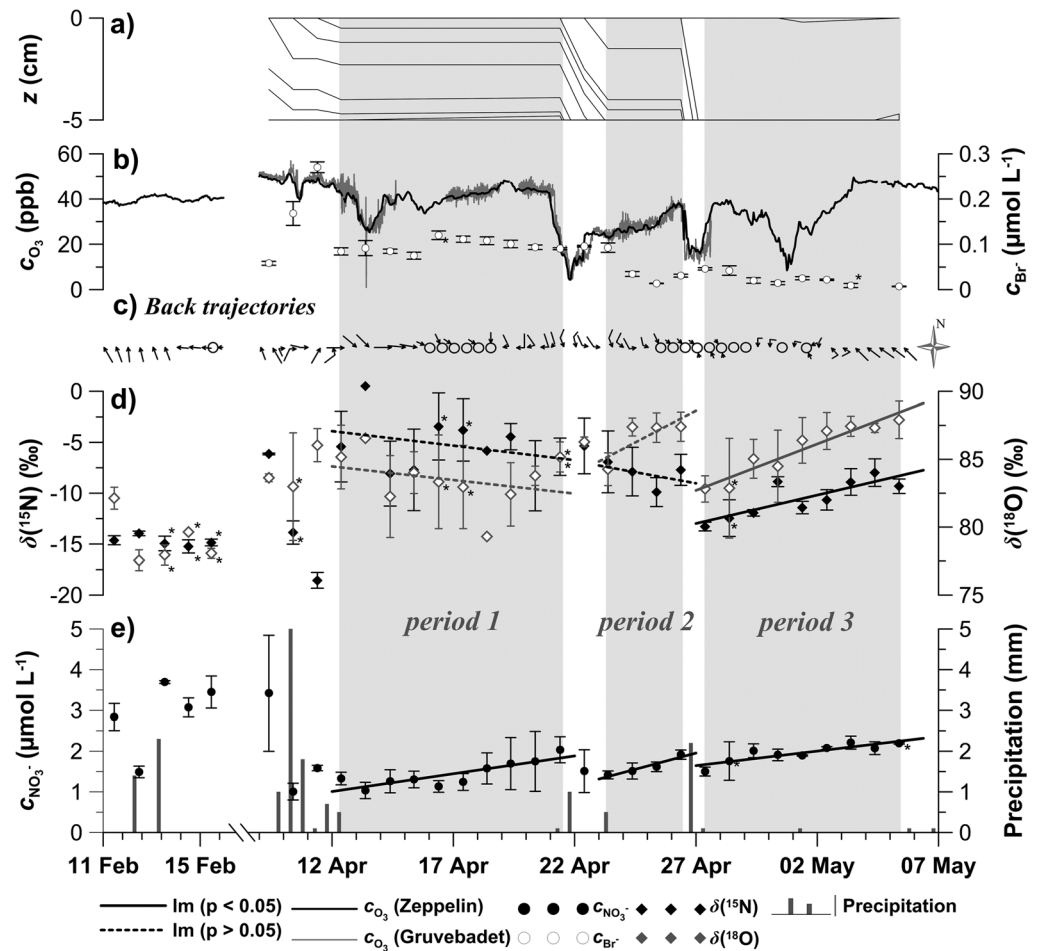
In order to evaluate the daily  $\delta(^{15}\text{N})$ ,  $\delta(^{18}\text{O})$ , and  $c_{\text{NO}_3}$  changes induced from the  $\text{NO}_x$ ,  $\text{HNO}_3^-$ , and  $\text{p-NO}_3^-$  flux measurements (section 2.3.2), the daily averaged emissions ( $F_{\text{emi}}$ ) and deposition ( $F_{\text{dep}}$ ) were evaluated in a similar way:

$$c_t = \frac{F_{(\text{dep})} A t}{V_t} - \frac{F_{(\text{emi})} A t}{V_t} + c_0 \quad (16)$$

$$c'_t = \frac{F'_{(\text{dep})} A t}{V_t} - \frac{F'_{(\text{emi})} A t}{V_t} + c'_0 \quad (17)$$

where  $F'_{(\text{dep})} = F_{(\text{dep})} R_{\text{ref}}(1 + \delta_{\text{atm}})$ ,  $F'_{(\text{emi})} = F_{(\text{emi})} R_{\text{ref}}(1 + \delta_{\text{photo}})$ , and  $\delta_{\text{photo}}$  is the isotopic composition of the instantaneous photolytic product:  $\delta_{\text{photo}} = \delta_0(1 + \varepsilon) + \varepsilon$ .

Previous studies have suggested a range of  $^{15}\varepsilon$ , from  $-48\%$  [Frey *et al.*, 2009] to  $-12\%$  [Blunier *et al.*, 2005], and  $^{18}\varepsilon$  from  $-34\%$  [Frey *et al.*, 2009] to between 2 and 7‰ [McCabe *et al.*, 2005] for the photolytic



**Figure 3.** Nitrate concentrations ( $c_{\text{NO}_3}$ ) and isotopic signatures ( $\delta(^{15}\text{N})$  and  $\delta(^{18}\text{O})$ ) of the daily surface snow samples in 2010, including (a) a schematic sketch of the visible layering found in the sampled surface snow; (b) the atmospheric  $\text{O}_3$  concentration ( $c_{\text{O}_3}$ ) measured at the Zeppelin Station and at Gruebadet, along with surface snow  $\text{Br}^-$  concentrations ( $c_{\text{Br}^-}$ ); (c) a schematic sketch of 7 days back trajectories obtained from the FLEXTRA model, where arrows indicate flow paths and circles indicate stagnant air; (d) the measured  $\delta(^{15}\text{N})$  and  $\delta(^{18}\text{O})$  in the surface snow; and (e) the measured  $c_{\text{NO}_3}$  in the surface snow together with the registered precipitation in Ny-Ålesund. Furthermore, error bars indicate standard error ( $\sigma_{\bar{x}}$ ), asterisks indicate samples where  $\sigma_{\bar{x}}$  is calculated from only two data points, and symbols without error bars indicate one replicate. Solid lines represent significant linear regression models ( $\text{lm}$ ,  $p$  value  $< 0.05$ ), while broken lines equal non-significant trends ( $p$  value  $> 0.05$ ).

fractionation in question. However, secondary reactions (e.g.,  $\text{NO}_2 + \text{OH}^- \rightarrow \text{NO}_3^-$ ) following photolysis will generate an exchange of O (see DI reactions in Figure 2) [Jacobi and Hilker, 2007] suggesting that any measured estimation of  $^{18}\epsilon$  will represent the combined effect of both the photolytic fractionation and secondary reactions [McCabe et al., 2005; Erbland et al., 2013]. For the purpose of this study,  $^{15}\epsilon$  and  $^{18}\epsilon$  were set to  $-48$  and  $2\text{‰}$ , respectively [McCabe et al., 2005; Frey et al., 2009]. Furthermore, a sensitivity test covering a range from 0 to  $-70\text{‰}$  for  $^{15}\epsilon$  and 10 to  $-50\text{‰}$  for  $^{18}\epsilon$  was also performed to evaluate the actual influence of different photolytic fractionations on the results.

Furthermore, three  $\delta_{\text{atm}}$  deposition scenarios for each isotope composition,  $\delta(^{15}\text{N})$  and  $\delta(^{18}\text{O})$ , were evaluated with the aim of establishing the most likely input source, so called “end-member,” signatures for any dry deposition. For  $\delta_{\text{atm}}(^{15}\text{N})$  these scenarios were set to resemble the following: (i) the local biogeochemical signal ( $+5\text{‰}$ ), (ii) the ambient atmospheric signal ( $-13\text{‰}$ ) described for Ny-Ålesund by Amoroso et al. [2010], and (iii) the influence of Polar basin air ( $-20\text{‰}$ ) suggested by Morin et al. [2009]. For  $\delta_{\text{atm}}(^{18}\text{O})$  the scenarios were set to resemble the following: (i) the low  $\delta(^{18}\text{O})$  signal found in  $\text{HNO}_3$  at Summit, Greenland ( $+40\text{‰}$ ), due to the interaction with OH during  $\text{NO}_x$  cycling and removal (see Figure 2) [Jarvis et al., 2009], (ii) the

**Table 1.** Fitted Linear Regression Models ( $y = kx + m$ ) for the Three Periods (Figure 4)<sup>a</sup>

Model	Period	$k$	$m$	$n$	$R^2$	$p$ value	Unit
$c_{\text{NO}_3}$	1	0.1	-7.8	30	0.17	< 0.03	$\mu\text{mol L}^{-1}$
	2	0.2	-18.1	12	0.50	0.01	$\mu\text{mol L}^{-1}$
	3	0.1	-6.5	26	0.34	< 0.01	$\mu\text{mol L}^{-1}$
$c_{\text{Br}}$	1	1.5	-61.3	29	0.06	0.18	$\text{nmol L}^{-1}$
	2	-20.6	2100.4	12	0.56	< 0.01	$\text{nmol L}^{-1}$
	3	-4.5	566.2	23	0.56	$\ll$ 0.01	$\text{nmol L}^{-1}$
$c_{\text{Cl}}$	1	2.4	-206.6	29	0.09	0.11	$\mu\text{mol L}^{-1}$
	2	3.4	-348.0	12	0.04	0.56	$\mu\text{mol L}^{-1}$
	3	3.1	-339.7	26	0.45	< 0.01	$\mu\text{mol L}^{-1}$
$c_{\text{Na}}$	1	1.0	-70.8	30	0.02	0.42	$\mu\text{mol L}^{-1}$
	2	2.7	-279.4	12	0.06	0.43	$\mu\text{mol L}^{-1}$
	3	3.2	-354.8	27	0.40	< 0.01	$\mu\text{mol L}^{-1}$
$\delta(^{15}\text{N})$	1	-0.1	8.8	23	0.01	0.67	‰
	2	-0.4	41.6	12	0.02	0.65	‰
	3	0.6	-85.1	26	0.49	< 0.01	‰
$\delta(^{18}\text{O})$	1	-0.1	90.2	23	0.00	0.78	‰
	2	0.9	-20.7	12	0.28	0.08	‰
	3	0.7	-0.4	26	0.37	< 0.01	‰
$z_{\text{SWE}}$	1	0.1	-8.2	30	0.50	$\ll$ 0.01	cm
	2	0.03	-2.0	12	0.02	0.63	cm
	3	0.2	-21.1	26	0.88	$\ll$ 0.01	cm
$V$	1	4.0	-346.8	30	0.50	$\ll$ 0.01	mL
	2	-0.7	-157.3	12	0.01	0.80	mL
	3	7.8	-896.6	26	0.88	$\ll$ 0.01	mL

<sup>a</sup>Regression models were analyzed for the  $\text{NO}_3^-$  concentration ( $c_{\text{NO}_3}$ ),  $\text{Br}^-$  concentration ( $c_{\text{Br}}$ ),  $\text{Cl}^-$  concentration ( $c_{\text{Cl}}$ ),  $\text{Na}^+$  concentration ( $c_{\text{Na}}$ ), the  $\text{NO}_3^-$  isotopic composition ( $\delta(^{15}\text{N})$  and  $\delta(^{18}\text{O})$ ), the surface snow water equivalence ( $z_{\text{SWE}}$ ), and the sample volume ( $V$ ). Also given are the numbers of measurements ( $n$ ) used for each regression, the multiple  $R^2$  value for the models, and the significance ( $p$  value) of the slope  $k$ .

midlatitude  $\text{HNO}_3$  signal (+75‰) found in air arriving at Svalbard [Morin *et al.*, 2009], and (iii) the uniquely high  $\delta(^{18}\text{O})$  found for  $\text{HNO}_3$  in the polar basin atmosphere during spring due to the influence of the BrO pathway (up to +100‰, Morin *et al.*, 2009).

### 3. Results

#### 3.1. $\text{NO}_3^-$ Concentrations

The surface snow  $\text{NO}_3^-$  concentrations ( $c_{\text{NO}_3}$ ) during the dark ( $n = 14$ ) and the spring ( $n = 79$ ) campaign averaged  $(2.9 \pm 0.2) \mu\text{mol L}^{-1}$  and  $(1.7 \pm 0.1) \mu\text{mol L}^{-1}$ , respectively (where the uncertainty denotes the standard error,  $\sigma_{\bar{x}}$ ), with a total concentration range from 0.6 to  $6.3 \mu\text{mol L}^{-1}$  (Figure 3e). The variations among the three replicates, sampled approximately 10 m apart, were moderate (average  $\sigma_{\bar{x}} = 0.3 \mu\text{mol L}^{-1}$ ) with some exceptions (maximum  $\sigma_{\bar{x}} = 1.4 \mu\text{mol L}^{-1}$  on 9 April), as viewed by the occasionally increased  $\sigma_{\bar{x}}$  in Figure 3e. The  $c_{\text{NO}_3}$  variation found is larger than the errors expected from IC analysis itself and therefore shows that local variation and the layering of the surface snow have a large influence. During both the dark and the spring campaign, several precipitation events occurred (Figure 3e) which introduced new snow layers with event-specific  $\text{NO}_3^-$  concentration and isotopic signature. These events interrupted any trends that postdeposition processes would have introduced to the surface snow chemistry, and the spring data were therefore separated into three distinct, precipitation-free periods: 12–21, 23–26, and 27 April to 5 May (Figure 3). Periods 1 and 2 were characterized by multiple surface snow layers, whereas period 3 followed a large (>5 cm) precipitation event resulting in a relatively uniform snow surface (Figure 3a). Period 3 was therefore considered the most reliable period for identification of  $c_{\text{NO}_3}$  and isotope composition trends.

For the spring campaign, linear regression models fitted to all three periods showed significant increases in the surface snow  $c_{\text{NO}_3}$  (Figure 3e and Table 1), indicative of net deposition or snow water sublimation (see section 3.4). No such changes were found during the short dark sampling campaign due to interrupting precipitation events. In general, all three spring periods indicated a day to day  $c_{\text{NO}_3}$  variation. To avoid any bias caused by such

**Table 2.** Calculated Initial ( $t_0$ ) and Final ( $t_f$ ) Values From the Regression Model in Table 1

Model	Period	$t_0$	$t_f$	Unit
$c_{\text{NO}_3}$	1	$1.1 \pm 0.2$	$1.8 \pm 0.2$	$\mu\text{mol L}^{-1}$
	2	$1.4 \pm 0.1$	$1.9 \pm 0.1$	$\mu\text{mol L}^{-1}$
	3	$1.7 \pm 0.1$	$2.3 \pm 0.1$	$\mu\text{mol L}^{-1}$
$\delta(^{15}\text{N})$	1	$-5.3 \pm 1.8$	$-6.5 \pm 1.7$	‰
	2	$-7.4 \pm 1.7$	$-8.7 \pm 1.7$	‰
	3	$-12.9 \pm 0.6$	$-8.0 \pm 0.6$	‰
$\delta(^{18}\text{O})$	1	$84.0 \pm 1.2$	$83.4 \pm 1.2$	‰
	2	$85.2 \pm 0.9$	$88.0 \pm 0.9$	‰
	3	$83.0 \pm 0.9$	$88.7 \pm 0.9$	‰
$z_{\text{SWE}}$	1	$1.3 \pm 0.1$	$2.2 \pm 0.1$	cm
	2	$1.7 \pm 0.1$	$1.8 \pm 0.1$	cm
	3	$0.4 \pm 0.1$	$1.8 \pm 0.1$	cm
$V$	1	$57.2 \pm 4.0$	$92.9 \pm 4.0$	mL
	2	$73.4 \pm 5.2$	$71.2 \pm 5.2$	mL
	3	$15.6 \pm 2.9$	$78.0 \pm 2.9$	mL

variation, the fitted linear regression models were used to calculate initial (index: 0) and final (index:  $t$ ) values of  $c_{\text{NO}_3}$  (and other relevant parameters) for each period and will be used for modeling purposes (Tables 1 and 2).

### 3.2. $\text{NO}_3^-$ Isotopic Composition

The  $\delta(^{15}\text{N})$  of  $\text{NO}_3^-$  ranged between  $-15.9$  and  $-13.7$ ‰ during the dark sampling ( $n = 12$ ) and between  $-19.9$  and  $0.7$ ‰ during the spring campaign ( $n = 71$ ), averaging  $(-14.7 \pm 0.2)$ ‰ and  $(-8.7 \pm 0.5)$ ‰, respectively (Figure 3d). The  $\delta(^{18}\text{O})$  ranged between  $76.6$  and  $83.7$ ‰ during the dark sampling and  $76.5$  to  $90.6$ ‰ during

the spring campaign, averaging  $(79.2 \pm 0.6)$ ‰ and  $(85.1 \pm 0.4)$ ‰, respectively (Figure 3d). In summary, the spring snow has significantly elevated values of  $\delta(^{15}\text{N})$  and  $\delta(^{18}\text{O})$  compared to the dark sampling ( $p$  value  $< 0.01$ ), although both periods showed considerable variability.

Linear regression models revealed significant increases of  $\delta(^{15}\text{N})$  and  $\delta(^{18}\text{O})$  during period 3 (Table 1), and to a lesser extent ( $p$  value = 0.08) for  $\delta(^{18}\text{O})$  during period 2 (Figure 3d and Table 1). The remaining linear regression models fitted for  $\delta(^{15}\text{N})$  and  $\delta(^{18}\text{O})$  during period 1 and 2 were not significant (Figure 3d and Table 1). In a similar manner to  $c_{\text{NO}_3}$ , the initial and final  $\delta(^{15}\text{N})$  and  $\delta(^{18}\text{O})$  values were calculated for each period using the linear regression models (Tables 1 and 2) to minimize the effects of daily variability upon further calculations.

### 3.3. Snow $\text{Br}^-$ and Atmospheric $\text{O}_3$ Concentrations

In contrast to  $c_{\text{NO}_3}$ , surface snow concentration of  $\text{Br}^-$  ( $c_{\text{Br}}$ ) showed an overall linear decline, particularly during periods 2 and 3 (Figure 3b and Table 1). This decline was in clear contrast to the observed sea salt deposition, as shown by the linear regression models fitted to the surface snow  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations ( $c_{\text{Na}}$  and  $c_{\text{Cl}}$ , respectively, in Table 1). The most likely explanation for this  $c_{\text{Br}}$  depletion involves  $\text{BrO}$  chemistry (discussed in section 4.4), which is typically connected to changes in atmospheric  $\text{O}_3$  concentration ( $c_{\text{O}_3}$ ). The ambient  $c_{\text{O}_3}$  showed evidence for several ozone depletion events (ODEs) during the spring campaign. These ODEs mainly occurred during periods 2 and 3 and were commonly associated with air mass back trajectories arriving from the polar basin (Figures 3b and 3c).

### 3.4. Sublimation Rates

The measurement of water vapor fluxes during the campaign was challenging due to riming or fog on the optical windows of the fast hygrometer, meaning that calibration was not always possible, which reduced the number of valid measurements. The removal of outliers from the sonic anemometer data further reduced the data to a final count of 282 measurements throughout the precipitation-free subperiods. Nevertheless, the data confirm a low sublimation rate: the water vapor fluxes indicated an average sublimation rate of  $(-0.042 \pm 0.002)$   $\text{mm d}^{-1}$  ( $n = 282$ ), where the total water vapor flux spanned between  $-0.007$  and  $0.008$   $\text{mm h}^{-1}$  (negative flux indicates surface loss). This sublimation rate has a very small impact on surface snow  $\text{NO}_3^-$  concentration as discussed below.

### 3.5. Air-Snow Fluxes

#### 3.5.1. Surface Snow Net Change

The increasing trends in surface snow  $c_{\text{NO}_3}$  indicate a net deposition of  $\text{NO}_3^-$  since snow water sublimation was found to be low. Hence, this indicated that dry deposition rates overcome photolytic and evaporative losses. Using the calculated initial and final values of  $c_{\text{NO}_3}$  and  $V$  for each period (Table 2), all three periods

**Table 3.** Calculated net Change of  $\text{NO}_3^-$  ( $F_{\text{net}}$ ) and Isotopic Signatures ( $\delta(^{15}\text{N})$  and  $\delta(^{18}\text{O})$ )

Period	$F_{\text{net}}^{\text{a}}$ ( $\mu\text{mol m}^{-2} \text{d}^{-1}$ )	$\delta(^{15}\text{N})^{\text{b}}$ (‰)	$\delta(^{18}\text{O})^{\text{b}}$ (‰)
1	$0.9 \pm 0.4$	$-8.2 \pm 13.6$	$82.7 \pm 87.9$
2	$1.4 \pm 0.6$	$-12.2 \pm 18.8$	$95.4 \pm 110.6$
3	$0.6 \pm 0.2$	$7.0 \pm 5.6$	$105.9 \pm 72.3$

<sup>a</sup>Calculated from equation (2).

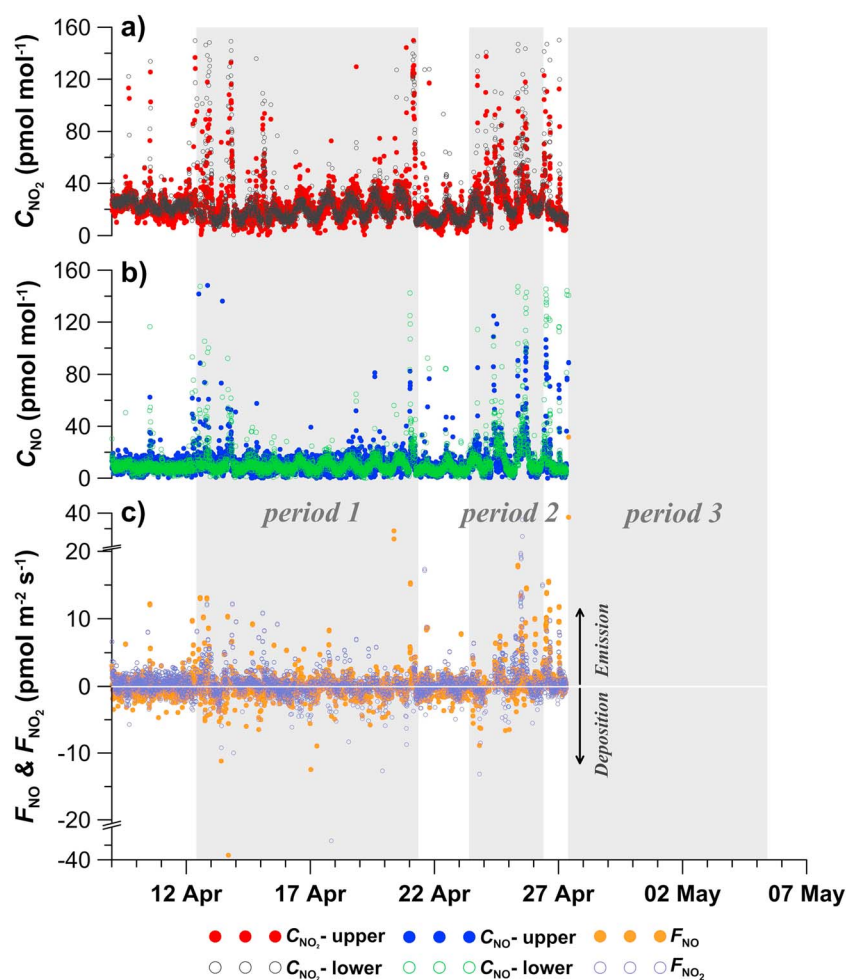
<sup>b</sup>Calculated from equation (5).

were confirmed to have a significant increase due to net deposition according to equation (2) (Table 3). Similarly, the isotopic composition for the net change was calculated according to equation (5) (Table 3).

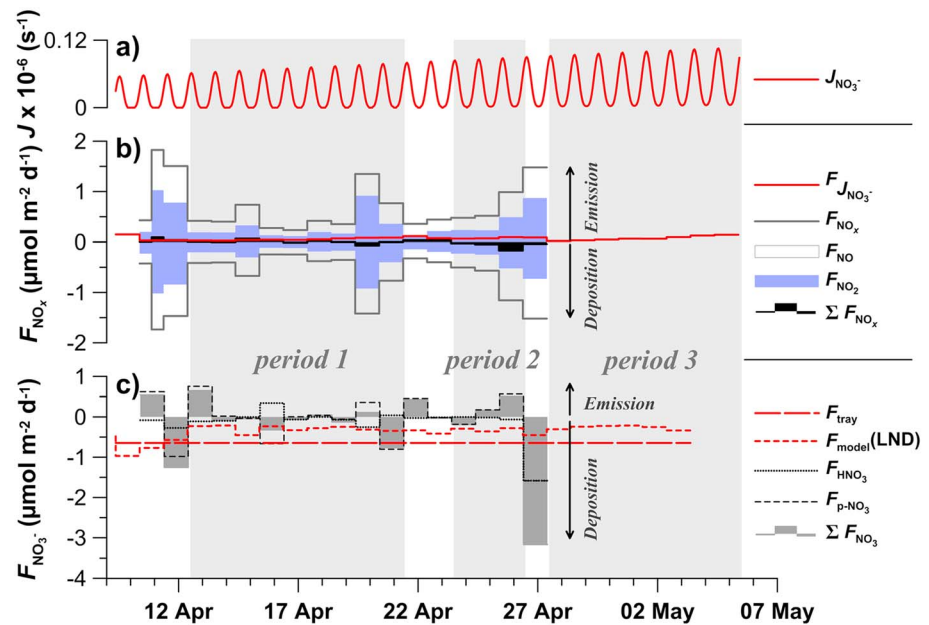
### 3.5.2. $\text{NO}_x$ , $\text{HNO}_3^-$ and $\text{p-NO}_3^-$ Flux Measurements

The mean  $\text{NO}_2$  concentrations ( $C_{\text{NO}_2}$ ) during the campaign were  $28.6$  ( $\sigma = 19.3$ )  $\text{pmol mol}^{-1}$  and

$28.7$  ( $\sigma = 20.3$ )  $\text{pmol mol}^{-1}$  at the upper and lower inlet, respectively (Figure 4a). Similarly, the mean  $\text{NO}$  concentrations ( $C_{\text{NO}}$ ) were  $15.2$  ( $\sigma = 12.5$ ) and  $16.6$  ( $\sigma = 17.5$ ) at the upper and lower inlet respectively (Figure 4b). The  $C_{\text{NO}}$  and  $C_{\text{NO}_2}$  concentrations showed statistically significant diurnal cycles on some days (9–11, 15–16, and 22–27 April) with amplitudes of 1–36  $\text{pmol mol}^{-1}$  and 3–49  $\text{pmol mol}^{-1}$  for  $C_{\text{NO}}$  and  $C_{\text{NO}_2}$ , respectively (Figures 4a and 4b). The diurnal cycles appeared more or less symmetric with UV radiation, with maximum  $C_{\text{NO}}$  and  $C_{\text{NO}_2}$  observed between 11:00 and 13:00, reaching minima values during nighttime. During periods without diurnal cycles the maximum  $\text{NO}$  and  $\text{NO}_2$  concentrations were reached



**Figure 4.** Measured flux data (6 min resolution) from Gruvebadet during the spring campaign 2010, including (a) the  $\text{NO}$  concentrations ( $C_{\text{NO}}$ ) at the upper and lower inlets; (b) the  $\text{NO}_2$  concentrations ( $C_{\text{NO}_2}$ ) at the upper and lower inlets; and (c) the  $\text{NO}$  and  $\text{NO}_2$  flux data ( $F_{\text{NO}}$  and  $F_{\text{NO}_2}$ , respectively) derived from the difference between the upper and lower inlets and the eddy diffusivity,  $K$ .



**Figure 5.** Measured and modeled  $\text{NO}_x$ ,  $\text{HNO}_3$ , and  $\text{p-NO}_3^-$  fluxes measured at Gruebadet. (a) The photolytic rate ( $J_{\text{NO}_3^-}$ ) estimated from equation (7); (b) the daily average emission and deposition of  $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{NO}_x$  ( $F_{\text{NO}}$ ,  $F_{\text{NO}_2}$ , and  $F_{\text{NO}_x}$ ) and the daily  $\text{NO}_x$  net flux ( $\Sigma F_{\text{NO}_x}$ ). Also included is the estimated photolytic  $\text{NO}_2$  flux ( $F_{J_{\text{NO}_3^-}}$ ) using  $J_{\text{NO}_3^-}$  in (a) and the measured  $c_{\text{NO}_3}$  in Figure 3e; (c) the daily average emission and deposition of  $\text{HNO}_3$  ( $F_{\text{HNO}_3}$ ) and  $\text{p-NO}_3^-$  ( $F_{\text{p-NO}_3^-}$ ) and the net flux of these ( $\Sigma F_{\text{NO}_3}$ ), also included is the measured ( $F_{\text{tray}}$ ) and modeled ( $F_{\text{model(LND)}}$ )  $\text{NO}_3^-$  dry deposition to Ny-Ålesund given in Björkman et al. [2013].

between 18:00 and 21:00, with minimum values measured between 06:00 and 12:00 and, hence, delayed the diurnal irradiance pattern. The turbulence measurements resulted in median eddy diffusivity ( $K$ ) of  $0.2 \text{ mol m}^{-2} \text{ s}^{-1}$  (with the first and third quartile at  $0.14$  and  $0.22 \text{ mol m}^{-2} \text{ s}^{-1}$ , respectively), and the  $\text{NO}_x$ ,  $\text{HNO}_3$ , and  $\text{p-NO}_3^-$  fluxes were calculated as  $K$  multiplied by the difference between the two inlets (as detailed in Beine et al. [2003]). The 6 min  $\text{NO}_x$  fluxes data (Figure 4c) showed a median  $\text{NO}$  emission of  $-0.73 \text{ pmol m}^{-2} \text{ s}^{-1}$  (with the first and third quartile at  $-0.31$  and  $-1.53 \text{ pmol m}^{-2} \text{ s}^{-1}$ , respectively) with a median  $\text{NO}_2$  emission of  $-0.79 \text{ pmol m}^{-2} \text{ s}^{-1}$  (with the first and third quartile at  $-0.35$  and  $-1.62 \text{ pmol m}^{-2} \text{ s}^{-1}$ , respectively). The corresponding median  $\text{NO}$  deposition rates (Figure 4c) were  $0.61 \text{ pmol m}^{-2} \text{ s}^{-1}$  (with the first and third quartile at  $0.27$  and  $1.18 \text{ pmol m}^{-2} \text{ s}^{-1}$ , respectively) while the median  $\text{NO}_2$  deposition was  $0.83 \text{ pmol m}^{-2} \text{ s}^{-1}$  (with the first and third quartile at  $0.38$  and  $1.54 \text{ pmol m}^{-2} \text{ s}^{-1}$ , respectively). The combined daily fluxes of  $\text{NO}_x$  ( $F_{\text{NO}_x}$ ), used for comparison to the surface snow concentrations (Figure 5b), showed an daily averaged  $F_{\text{NO}_x}$  emissions range from  $-0.2$  to  $-1.8 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$ , and the daily average  $F_{\text{NO}_x}$  depositions ranged from  $0.2$  to  $1.7 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$  (Figure 5b). The resulting daily net fluxes ( $\Sigma F_{\text{NO}_x}$ ) ranged from  $-0.1$  to  $0.2 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$  (Figure 5b).

The mean concentrations of  $\text{HNO}_3$ , fine and coarse particulate  $\text{NO}_3^-$  were  $6.06 \pm 5.32$ ,  $14.33 \pm 13.68$ , and  $15.14 \pm 9.53 \text{ pmol mol}^{-1}$ , respectively. The  $\text{HNO}_3$  and the combined fine and coarse particulate  $\text{NO}_3^-$  fluxes ( $F_{\text{HNO}_3}$  and  $F_{\text{p-NO}_3^-}$ , Figure 5c) mostly indicated a deposition, with the mean values of  $1.59 \pm 1.32 \text{ pmol m}^{-2} \text{ s}^{-1}$  and  $4.84 \pm 3.52 \text{ pmol m}^{-2} \text{ s}^{-1}$ , respectively. The resulting daily net flux of the total  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  ( $\Sigma F_{\text{NO}_3}$ ) showed variable rates, from  $-0.6$  to  $3.2 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$  (Figure 5c), where the flux of  $\text{p-NO}_3^-$  ( $F_{\text{p-NO}_3^-}$ ) exceeded that of  $\text{HNO}_3$  ( $F_{\text{HNO}_3}$ ) and thus dominated  $\Sigma F_{\text{NO}_3}$ , with particularly high rates during the precipitation event between periods 2 and 3 (Figure 5c). The data also show that fine particles ( $<2.5 \text{ } \mu\text{m}$  diameter) were responsible for much of the  $\text{p-NO}_3^-$  flux during high flux events. The sampling interval (12 or 24 h) for  $F_{\text{HNO}_3}$  and  $F_{\text{p-NO}_3^-}$  did not allow a separation of daily emission and deposition estimates, as was achieved using the 6 min  $F_{\text{NO}_x}$  data.

### 3.6. Box Models

The photolytic rate function ( $J_{\text{NO}_3^-}$ ) showed clear diurnal variation superimposed upon a uniformly increasing trend (Figure 5a) as a consequence of the steadily rising Sun (midnight Sun commenced on 18 April). The integrated daily surface snow flux ( $F_{J_{\text{NO}_3^-}}$ ), estimated from  $J_{\text{NO}_3^-}$  and  $c_{\text{NO}_3}$ , showed emission rates

of the same order of magnitude as the measured  $\Sigma F_{\text{NO}_x}$  (Figure 5b). However,  $F_{J_{\text{NO}_3^-}}$  was considerably lower than the measured  $\text{NO}_x$  emission ( $F_{\text{NO}_x}$ ). This mismatch is likely due to the estimation of  $\text{NO}_3^-$  photolysis from surface snow only being compared to measured emissions above the full snowpack.

The measured range of the combined  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  fluxes ( $\Sigma F_{\text{NO}_3}$ ) was of the same order of magnitude as the modeled  $\text{HNO}_3$  +  $\text{p-NO}_3^-$  dry deposition ( $F_{\text{model(LND)}}$ ) during this spring campaign [Björkman *et al.*, 2013], although the measured average  $\text{NO}_3^-$  dry deposition ( $F_{\text{tray}}$ ) showed higher spring averages than both  $F_{\text{model(LND)}}$  and the  $\Sigma F_{\text{NO}_3}$  (Figure 5c). However, the substantial atmospheric fluxes of  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  ( $F_{\text{HNO}_3}$  and  $F_{\text{p-NO}_3^-}$ ) observed in connection with the precipitation event between periods 2 and 3 was not captured by the dry deposition estimates in Björkman *et al.* [2013] (Figure 5c).

#### 4. Discussion

Here we present a discussion of the trends and influences on  $\text{NO}_3^-$  concentrations and isotopic composition found for Ny-Ålesund surface snow. We argue that the main process during precipitation-free periods is the addition of  $\text{NO}_3^-$  through dry deposition, which dominates over  $\text{NO}_3^-$  postdeposition losses via photolysis and evaporation. However, this dry deposition can be influenced both by atmospheric sources, as well as  $\text{NO}_x$ ,  $\text{HNO}_3$ , and HONO emitted from deeper within the snowpack, processes which therefore require consideration. An active involvement of halogen chemistry was also inferred from the surface snow measurements, and so we discuss the role of surface snow as a contributor in the production of boundary layer BrO.

##### 4.1. Dry Deposition Versus Postdeposition Loss

A striking feature during the spring sampling is the significant increase of  $c_{\text{NO}_3}$  for all three subperiods, in-between precipitation events (Table 1 and Figure 3e), where a positive net change ( $F_{\text{net}}$ ) was confirmed for all periods using equation (2) (Table 3). Hence, equation (2) gives the overall net increase or decrease of  $c_{\text{NO}_3}$ , where the most likely surplus would be due to an  $\text{NO}_3^-$  addition by dry deposition as long as snow sublimation is low. The measured sublimation rates during the three periods were low and could only have changed the daily  $c_{\text{NO}_3}$  by a modest quantity (average  $0.31 \pm 0.03\%$ , range 0.2 to 0.8%), which is well below the day to day  $c_{\text{NO}_3}$  variations (average  $11.1 \pm 1.6\%$ , for the same periods). Similarly, the model photolysis rate ( $J_{\text{NO}_3^-}$ ) could only have changed the daily  $c_{\text{NO}_3}$  by a 0.2 to 0.4% reduction, indicating a very minor influence of photolysis on these daily variations. Of course,  $\text{HNO}_3$  evaporation and HONO emissions could further influence the daily variations. However, both these processes require a surplus of  $\text{H}^+$ , whereas Ny-Ålesund snow is typically alkaline [Beine *et al.*, 2003; Amoroso *et al.*, 2006] with a high sea salt content given the close proximity to the fjord. Furthermore, the  $\text{NO}_2^-$  levels were below the detection limit of the IC measurements (data not shown) further indicating low HONO production. The limited occurrence of sublimation, modeled  $J_{\text{NO}_3^-}$  and positive  $F_{\text{net}}$  collectively therefore indicate that the addition of  $\text{NO}_3^-$  through dry deposition outweighed any changes induced by photolytic and/or evaporative loss processes. The estimated  $F_{\text{net}}$  for the three periods, with a daily weighted average of  $0.9 \pm 0.4 \mu\text{mol m}^{-2} \text{d}^{-1}$  (Table 3), is also consistent with the measured dry deposition rate ( $F_{\text{tray}}$ ,  $0.7 \pm 0.3 \mu\text{mol m}^{-2} \text{d}^{-1}$ ) estimated for the same time period by Björkman *et al.* [2013]. However, these are slightly higher than the average modeled dry deposition ( $F_{\text{model(LND)}}$ ,  $0.3 \pm 0.1 \mu\text{mol m}^{-2} \text{d}^{-1}$ ) for this period [Björkman *et al.*, 2013], and also slightly higher than the value Beine *et al.* [2003] found for Ny-Ålesund ( $\sim 0.2 \mu\text{mol m}^{-2} \text{d}^{-1}$ ) during a previous spring, using a diffusion line sampling technique.

The  $\delta(^{15}\text{N})$  and  $\delta(^{18}\text{O})$  composition of the net change ( $\delta_{\text{net}}$ ), as calculated by equation (5), differed between the three subperiods (Table 3). Regarding the  $F_{\text{net}}$ , no major influence of loss processes was found for periods 1 and 2, since any fractionation during postdeposition loss would have led to an  $\delta_{\text{net}}(^{15}\text{N})$  increase in  $\text{NO}_3^-$ . In contrast, periods 1 and 2 showed negative  $\delta_{\text{net}}(^{15}\text{N})$  values of  $-8.2 \pm 13.6$  and  $-12.2 \pm 18.8\%$ , respectively, even though the validity of these estimates are reduced by the nonsignificant regressions used for calculation. One might argue that the significant positive  $\delta_{\text{net}}(^{15}\text{N})$  value of  $(7.0 \pm 0.7)\%$  calculated for the  $\text{NO}_3^-$  in period 3 could be indicative of postdeposition loss. This would, however, contradict the significant  $c_{\text{NO}_3}$  increase and positive  $F_{\text{net}}$  observed for this period (Table 3), therefore alternative explanations need to be considered, as attempted through box modeling below. The  $\text{NO}_3^-$   $\delta_{\text{net}}(^{18}\text{O})$  found for period 1, even though the linear regression was nonsignificant,



was lower than the isotope delta of the snow (Table 3), whereas for periods 2 and 3 the  $\delta_{\text{net}}(^{18}\text{O})$  approached the upper limit found for atmospheric  $\text{HNO}_3$  in this region (100‰) [Morin *et al.*, 2009]. The isotopic signature of snow  $\text{NO}_3^-$  is, however, influenced by several cooccurring processes as discussed in the section 1 and viewed in Figure 2 and will be further investigated in section 4.3.

#### 4.2. $\text{NO}_x$ , $\text{HNO}_3^-$ , and $\text{p-NO}_3^-$ Flux Measurements

The flux measurements revealed both emissions and deposition fluxes of all the investigated compounds ( $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{HNO}_3^-$ , and  $\text{p-NO}_3^-$ , Figures 4 and 5) and where the mean  $\text{NO}$  and  $\text{NO}_2$  concentrations were in agreement with other measurements in the coastal Arctic boundary layer during the same time of year [Allegrini *et al.*, 1999; Beine *et al.*, 2001, 2002b; Amoroso *et al.*, 2010; Sander and Bottenheim, 2012]. Although the calculated daily  $\text{NO}$  and  $\text{NO}_2$  fluxes (Figure 5) are in the lower region of what has earlier been reported for Ny-Ålesund by Amoroso *et al.* [2010], the occasional diurnal cycling of  $\text{NO}$  and  $\text{NO}_2$  observed confirms previous studies carried out at Ny-Ålesund [Beine *et al.*, 1996, 1997]. Also, the daily average  $\text{HNO}_3$  flux measured in 2010 are within the variability of earlier estimates for Ny-Ålesund [Beine *et al.*, 2003; Amoroso *et al.*, 2010], but substantially lower than the episode with exceptionally high deposition fluxes (up to  $1.5 \mu\text{mol m}^{-2} \text{h}^{-1}$ ) reported by Amoroso *et al.* [2010].

Due to the coastal location of Ny-Ålesund, the chemical composition of snow was dominated by a marine signature. As a result of sea salt inputs, and to a lesser extension of dust, the ionic balance of snow revealed an alkaline character for 44% of the daily snow samples (with pH values between 7.80 and 8.70) which, according to Beine *et al.* [2003, 2008], could lead to a reduced  $\text{NO}_x$  emission and even to an increased deposition. In addition, it is worth noting that 33% and 41% of all available 6 min  $\text{NO}$  and  $\text{NO}_2$  fluxes (about 5000 values), respectively, indicated a  $\text{NO}_x$  deposition to the snow surface, as observed in earlier polar studies [e.g., Beine *et al.*, 2002; Amoroso *et al.*, 2010]. It has previously been shown that the intricate system of  $\text{NO}_3^-$  photolysis and  $\text{NO}_x$  emission is followed by a subsequent  $\text{HNO}_3$  deposition, producing a diurnal pattern at Summit, Greenland, with daytime emission and nighttime deposition [Hastings *et al.*, 2004]. A similar feature can be observed in our 2010 flux data, where the  $\text{NO}$  and  $\text{NO}_2$  emission during periods of high irradiance can be on the same order of magnitude as the total  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  deposition. Indicating that, for this almost alkaline snow environment, the  $\text{NO}_x$  emissions were reduced or close to zero. Thus, the measured fluxes of  $\text{NO}_x$ ,  $\text{HNO}_3$ , and  $\text{p-NO}_3^-$  are neither sufficient to explain the observed  $c_{\text{NO}_3}$  increase. In the following section we will further focus on separating and explaining the processes influencing the surface snow, using the box model to find the most likely sources of the observed  $\text{NO}_3^-$  deposition and its isotopic signature.

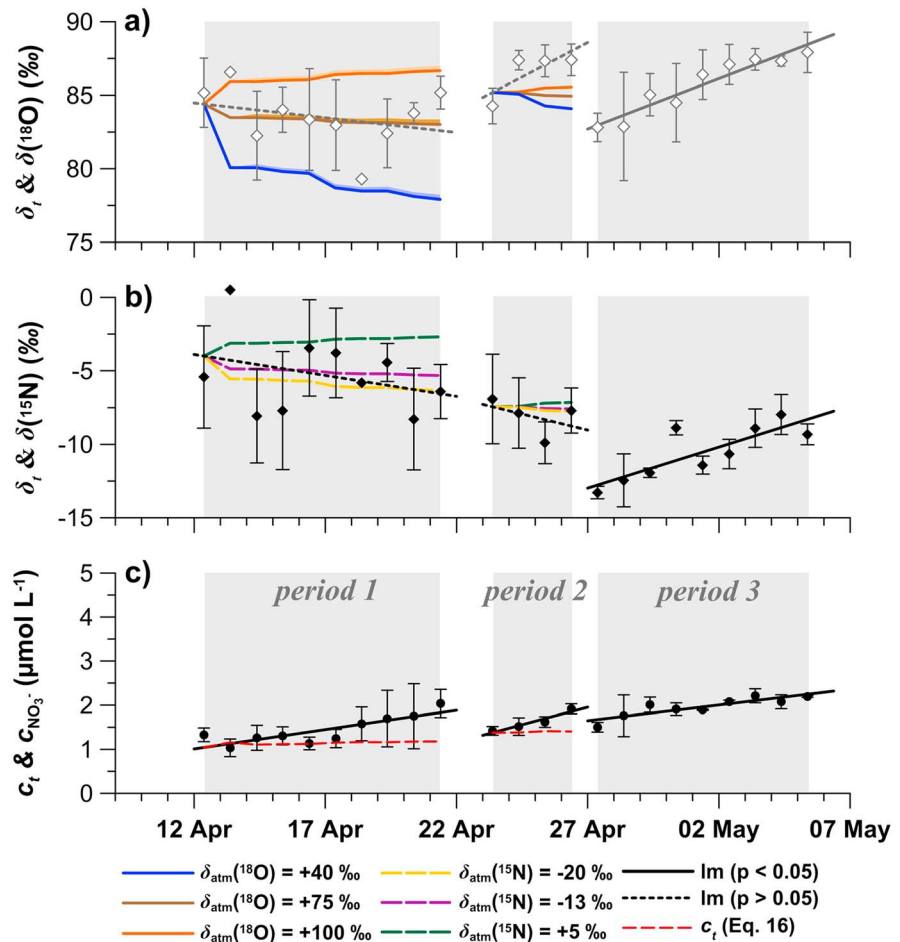
#### 4.3. Reproducing Observed Trends

In the box model used here, describing the main source and sink of  $\text{NO}_3^-$  in the snow (section 2.4.2), all outgoing fluxes are assumed to be due to photolysis and all incoming fluxes due to  $\text{HNO}_3$  dry deposition. As a consequence of the day-to-day variability of isotope deltas and  $c_{\text{NO}_3}$ , our comparison between model and measured data focuses on the regression analysis for the three precipitation-free spring periods, bearing in mind the lower  $p$  values for the trends in  $\delta(^{15}\text{N})$  and  $\delta(^{18}\text{O})$  of snow  $\text{NO}_3^-$  during periods 1 and 2 (Table 1 and Figure 3).

##### 4.3.1. Box Model Using $F_{\text{NO}_x}$ and $F_{\text{NO}_3}$

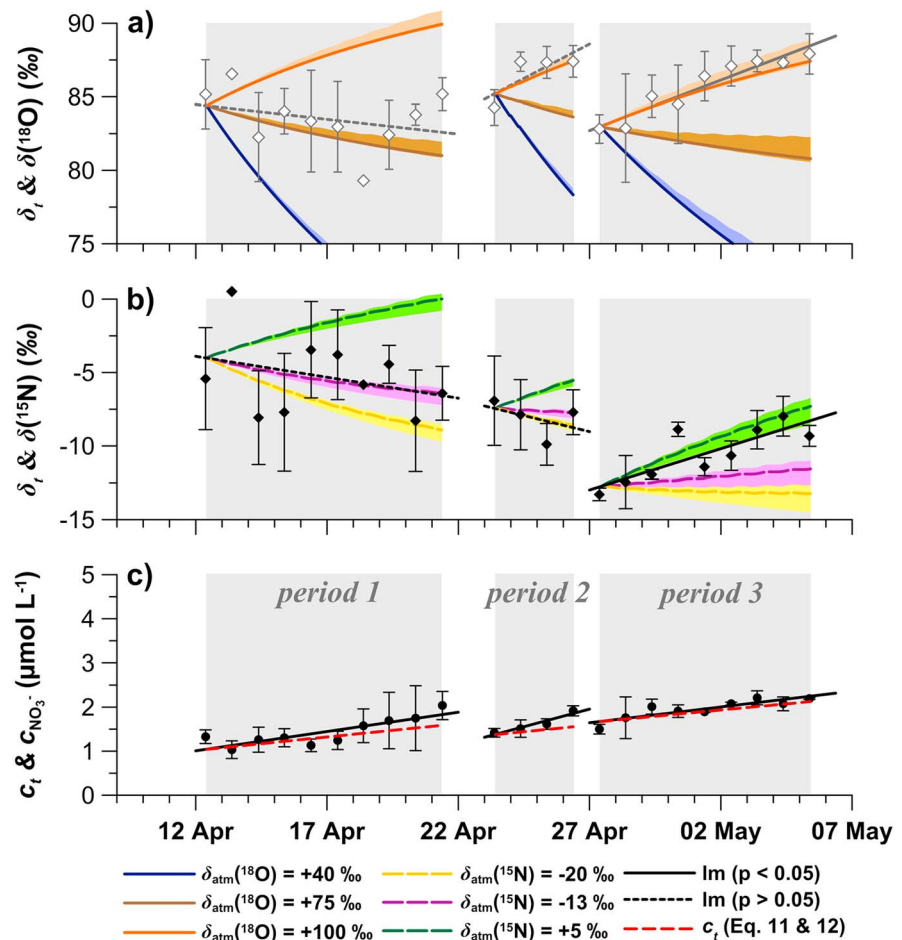
The box model (equation (16)) shows that the measured net fluxes of  $\text{NO}_x$  ( $\Sigma F_{\text{NO}_x}$ , Figure 5b) and  $\text{HNO}_3 + \text{p-NO}_3^-$  ( $\Sigma F_{\text{NO}_3}$ , Figure 5c) were insufficient to alter the surface snow  $c_{\text{NO}_3}$  significantly during periods 1 and 2 (Figure 6c, noting the atmospheric flux measurements were terminated on 27 April, just prior to period 3). The small change in  $c_{\text{NO}_3}$  such daily net fluxes would induce was below the detection limit of the snow sampling procedure used here. A similar conclusion was reached by Beine *et al.* [2003] when they compared atmospheric dry deposition estimates with the surface snow  $\text{NO}_3^-$  concentrations.

In spite of the limited ability of the atmospheric flux driven model to reproduce the surface snow  $c_{\text{NO}_3}$  trends, the modeled influence on  $\delta(^{18}\text{O})$  and  $\delta(^{15}\text{N})$  was more pronounced (using equation (17), Figure 6). This is especially the case during the first day of period 1, when  $\text{p-NO}_3^-$  emission (Figure 5c) resulted in an increased modeled  $\delta(^{18}\text{O})$ , and where the  $\delta_{\text{atm}}(^{18}\text{O})$  scenarios +40 and +100‰ followed the very lower and upper limit of the data variability for the rest of period 1 (Figure 6a). Although particle emission from



**Figure 6.** Box model results, using the  $\text{NO}_x$ ,  $\text{HNO}_3^-$ , and  $\text{p-NO}_3^-$  flux measurements. (a) The modeled  $\delta_f$  for  $^{18}\text{O}$  (equation (13)) for the three isotopic deposition scenarios ( $\delta_{\text{atm}}$ ), where +40‰ resembles the OH signal found in Greenland [Jarvis et al., 2009], +75‰ resembles a midlatitude signal [Morin et al., 2009], and +100‰ resembles the influence of BrO chemistry [Morin et al., 2009]. Also included in Figure 6a is the actual measured  $\delta(^{18}\text{O})$  and cooccurring linear regression models (lm, Table 1). (b) The modeled  $\delta_f$  for  $^{15}\text{N}$  (equation (13)) for the three isotopic deposition scenarios ( $\delta_{\text{atm}}$ ), where -20‰ represents polar basin air [Morin et al., 2009], -13‰ represent ambient air [Amoroso et al., 2010], and +5‰ represents a local biogeochemical signal [Amoroso et al., 2010]. Also included in Figure 6b is the measured  $\delta(^{15}\text{N})$  and developed lm's. (c) The modeled  $c_f$  (equation (16)) along with the measured  $c_{\text{NO}_3^-}$  and lm's. Furthermore, the fractionation sensitivity test is included as shaded areas around the box model results in Figures 6a and 6b.

snow might be limited [Cadle, 1991], some resuspension of particles by wind is possible [Barrie et al., 1998]. During period 2 neither of the  $\delta_{\text{atm}}(^{18}\text{O})$  scenarios followed the observed  $\delta(^{18}\text{O})$  pattern. For periods 1 and 2, the modeled  $\delta(^{15}\text{N})$  was not as sensitive to the choice of  $\delta_{\text{atm}}(^{15}\text{N})$  scenarios (+5, -13, and -20‰), as for  $\delta(^{18}\text{O})$ . In fact, model results for all three  $\delta_{\text{atm}}(^{15}\text{N})$  scenarios were well within the data variability and did not deviate much from each other (Figure 6b). Overall, none of the  $\delta_{\text{atm}}$  scenarios and emission fractionations, including the sensitivity test for different fractionations ( $^{15}\epsilon$  and  $^{18}\epsilon$ , section 2.4.2), reproduced the observed trends in a satisfactory way. This is probably due to the many layers found in the sampled surface snow during period 1 and 2, that can yield large daily variations in  $\delta(^{15}\text{N})$  and  $\delta(^{18}\text{O})$ . It is especially troublesome that the observed  $c_{\text{NO}_3^-}$  trends (Table 1) and calculated dry deposition rates (Table 3) cannot be explained by the atmospheric flux in the box model. A possible explanation could be a redeposition of  $\text{NO}_x$ ,  $\text{HNO}_3^-$ , and  $\text{HONO}$  emitted from deeper within the snowpack, or the soil below, to the surface snow layer. Such a subsurface source would then not necessarily need to involve an emission to the atmospheric boundary layer, thus could impact the surface snow measurements of  $\text{NO}_3^-$  deposition but not the atmospheric flux measurements as a result.



**Figure 7.** Same as Figure 6 but where the box model parameterization for the emission of  $\text{NO}_x$  is based on the photolytic rate function ( $J_{\text{NO}_3^-}$ , equation (7)) and the deposition of  $\text{NO}_3^-$  from the atmosphere based on the dry deposition rate ( $F_{\text{tray}}$ ) using equations (11) and (12).

**4.3.2. Box Model Using  $J_{\text{NO}_3^-}$  and  $F_{\text{model(LND)}}$  or  $F_{\text{tray}}$**

As a second attempt to reproduce the observed surface snow trends (equations (11) and (12)) and to also address the observations of period 3, which can be considered most reliable as the surface snow was one homogeneous layer, the modeled photolysis ( $J_{\text{NO}_3^-}$ ) was used in conjunction with  $F_{\text{model(LND)}}$ , Figure S2. This box modeling attempt, and a third approach, using  $J_{\text{NO}_3^-}$  in conjunction with  $F_{\text{tray}}$ , Figure 7, captured the  $c_{\text{NO}_3}$  trends far better than the atmospheric flux measurements. This was particularly the case with the third attempt, which reproduced the observed  $c_{\text{NO}_3}$  increase during period 3 in a sufficient manner (Figure 7c), attributing the addition through dry deposition to have a prevailing role over photolytic and, probably, evaporative loss.

For the isotopic composition the models (equations (14) and (15)) seems to have had a clear negative influence upon the surface  $\delta(^{15}\text{N})$  signature during periods 1 and 2 (Figures S2 and 7), with a  $\delta_{\text{atm}}(^{15}\text{N})$  close to the ambient atmospheric ( $-13\text{‰}$ ) [Amoroso et al., 2010] and the Polar Basin signals ( $-20\text{‰}$ ) [Morin et al., 2009]. This also corresponds well to the main back trajectories observed during these periods (Figure 3c). In contrast, period 3 indicated the influence of a positive end-member ( $+7.0 \pm 0.7\text{‰}$ , Table 3) that cannot be explained by a photolytic and/or evaporative  $\text{NO}_3^-$  loss, hence indicates dry deposition seems to have occurred. This positive  $\delta(^{15}\text{N})$  signature is more in line with the  $+5\text{‰}$  previously described for snowpack biogeochemical processes in this region [Amoroso et al., 2010], indicating a redeposition of  $\text{NO}_x$ ,  $\text{HNO}_3^-$ , and HONO emitted deeper within (or below) the snowpack. However, anthropogenic  $\text{NO}_x$  emissions are also in general slightly positive [e.g., Hastings, 2010], with the exception of agricultural soils [Felix and Elliott, 2013]. For example, Morin et al. [2009] found an atmospheric nitrate signal of  $+5.9\text{‰}$  from European air in the English Channel, a value also consistent with midlatitude spring values for the U.S. [Elliott et al., 2009]. For

period 3, the air mass back trajectories are more stagnant around Svalbard, with a southeasterly influence at the end of this period. This indicates that the high end-member found for period 3 could also be influenced by local or European emission sources, and is not necessarily solely a biogeochemical signal.

For period 1, the  $\delta(^{18}\text{O})$  end-member is close to the midlatitude scenario (+75‰, Figures S2 and 7), which is also the post-1950 background value for this region as indicated by Svalbard ice core averages ( $+75.1 \pm 4.1\%$ ) [Vega, 2014], in spite of a northerly airflow which was assumed to bring a  $\delta(^{18}\text{O})$  signal around +100‰. The  $\delta(^{18}\text{O})$  end-member for periods 2 and 3 is on the other hand more in line with air masses from the Polar Basin [Morin *et al.*, 2009], for which the uniquely high  $\delta(^{18}\text{O})$  has been found to result from an active atmospheric BrO interaction (Figure 2) [Morin *et al.*, 2007a, 2007b]. This is especially surprising for period 3, where the back trajectories are stagnant or southeasterly oriented, with only a minor influence of Polar air (Figure 3c). Under these circumstances a midlatitude  $\delta(^{18}\text{O})$  scenario would be expected for period 3, rather than the +100‰ evidenced here. The reason for this deviation is probably due to a local snow-determined BrO-NO<sub>x</sub> interaction, the first such observation of its kind in this region, and will be further discussed in section 4.

The sensitivity test performed (shaded ranges in Figures 6, 7, and S2) indicates that the actual photolytic fractionation used in the box modeling has little influence on the outcome, probably due to the prevailing dry deposition regime in our surface snow.

In summary, period 1 shows evidence of a polar basin/ ambient atmospheric influence on  $\delta(^{15}\text{N})$  and a  $\delta(^{18}\text{O})$  signature that resembles midlatitudinal air. Period 2 shows a polar basin influence upon both the  $\delta(^{15}\text{N})$  and the  $\delta(^{18}\text{O})$  signatures; while period 3 has a  $\delta(^{15}\text{N})$  similar to that which is expected from either biogeochemical cycling of NH<sub>4</sub><sup>+</sup> in the snowpack, or local/European emissions, along with the BrO influenced  $\delta(^{18}\text{O})$  signature.

#### 4.4. O<sub>3</sub> and BrO Interaction

During the spring campaign several O<sub>3</sub> depletion events (ODE) occurred; on 13, 21–22, 26–27, and 30 April to 1 May (Figure 3b). Such events are known in the Arctic as a result of active halogen chemistry where Br<sub>2</sub>, BrCl, or Cl<sub>2</sub> (ultimately of oceanic origin, whose release is believed to involve snow and first-year sea ice) are released in to the boundary layer. Their rapid photolysis by solar radiation forms Br or Cl radicals, which then initiates a chain reaction depleting O<sub>3</sub> (Figure 2) [e.g., Foster *et al.*, 2001; Simpson *et al.*, 2007; Abbatt *et al.*, 2012]. For Ny-Ålesund, studies typically observe such events as a consequence of the advection of air masses already depleted in O<sub>3</sub>, originating from the polar basin [e.g., Barrie and Platt, 1997], where low levels of boundary layer O<sub>3</sub> are typical during spring [Hopper *et al.*, 1994, 1998; Jacobi *et al.*, 2010]. This is consistent with the ODEs observed during the spring 2010, where more northerly air flows occur prior to the ozone depletion episodes (Figure 3) and where satellite data [Begoïn *et al.*, 2010] reveals increased BrO column abundances concurrent with the ODE's (Figure S3). Alongside its impact on boundary layer O<sub>3</sub>, BrO can also influence NO<sub>x</sub> cycling and its transformation to HNO<sub>3</sub>, via the formation and hydrolysis of BrONO<sub>2</sub>. This generates a uniquely high  $\delta(^{18}\text{O})$  (Figure 2) [e.g., Evans *et al.*, 2003; Morin *et al.*, 2007b].

For period 2 a northerly airflow was observed which can explain both the low  $\delta(^{15}\text{N})$  (photolytic produced NO<sub>x</sub> from polar basin snowpacks) and the high  $\delta(^{18}\text{O})$  (BrO pathway) end-member [Morin *et al.*, 2009]. However, for period 3, when the airflow is stagnant or southwesterly, with only a minor influence of polar basin air, the high  $\delta(^{18}\text{O})$  end-member would need to have another explanation. Interestingly, the Br<sup>-</sup> concentrations ( $c_{\text{Br}}$ ) in the surface snow are high during period 1, decrease during period 2, then remain low and slightly decrease further during period 3 (Figure 3b and Table 1). There is also a significant ( $p < 0.05$ ) negative correlation between the daily averages of  $c_{\text{Br}}$  and  $c_{\text{NO}_3}$  ( $R = -0.84$ ) during period 3, as well as between  $c_{\text{Br}}$  and  $\delta(^{15}\text{N})$  and  $\delta(^{18}\text{O})$  ( $R = -0.91$  and  $-0.83$ , respectively). According to the BrO pathway in Figure 2, formation of BrONO<sub>2</sub> from BrO + NO<sub>2</sub> can be followed by a photolytic dissociation, or—particularly under conditions of high surface area—be followed by hydrolysis whereby BrONO<sub>2</sub> disintegrates into HNO<sub>3</sub> and HOBr on ice crystals [Evans *et al.*, 2003; Morin *et al.*, 2007b]. This latter case thereby converts NO<sub>x</sub> into HNO<sub>3</sub>. Assuming that this reaction occurs within the snow or just above, the newly formed HOBr would further react with Br<sup>-</sup> ions in the DI with a release of gaseous Br<sub>2</sub> as a result [e.g., Simpson *et al.*, 2007; Abbatt *et al.*, 2012]. In the presence of a NO<sub>x</sub>, HNO<sub>3</sub>, or HONO supply from deeper within the snowpack (i.e., photolysis, evaporation, or biologic emissions from the snow or soil), this BrO-NO<sub>x</sub> chemistry would rapidly redeposit the NO<sub>x</sub> as HNO<sub>3</sub> in the surface snow. This would then minimize any snowpack emissions and, in the

case of negligible local soil emissions, keep the total snow  $\text{NO}_3^-$  budget unaltered. This coupled BrO- $\text{NO}_x$  chemistry can explain both the decrease in  $\text{Br}^-$  concentration in the surface snow as well as the increasing  $\delta(^{18}\text{O})$  and  $c_{\text{NO}_3}$  values observed in the surface snow during periods 2 and 3. This is the first time such coupling has been observed in Svalbard, although increasing BrO levels have earlier been reported above Ny-Ålesund snow following an ODE [Avallone *et al.*, 2003]. To start the BrO production and following chain reactions, an initial pulse (or “seed”) of reactive halogens is needed [Simpson *et al.*, 2007]. It is however, unlikely that the BrO cycling seen in our  $c_{\text{Br}}$  and  $\delta(^{18}\text{O})$  data, and in the BrO record from Avallone *et al.* [2003] are initiated locally. They are likely rather results of polar basin air advection providing seed halogens during the observed ODEs, which then initiate the local BrO production. This hypothesis is further strengthened by the column content of BrO (Figure S3) where the atmosphere above western Svalbard, and eastern parts of the Fram Strait, shows prevailing low BrO levels, which only increases in conjunction with ODEs when surges of BrO moves into the Ny-Ålesund area. Nevertheless, during period 3, our surface snow bromide, nitrate, and  $\delta(^{18}\text{O})$  observations provide evidence for continued local (snowpack) BrO- $\text{NO}_x$  cycling, even while BrO column abundances decline and ambient air ozone recovers.

## 5. Conclusion

Detailed sampling of the photoactive surface zone of the Ny-Ålesund snowpack during winter and springtime demonstrates that  $\text{NO}_3^-$  dry deposition is the predominant process determining  $\text{NO}_3^-$  concentrations during precipitation-free periods and prevails over any  $\text{NO}_3^-$  postdeposition loss via photolysis and  $\text{HNO}_3$  evaporation within this layer. The measured dry deposition in uniform surface snow ( $0.6 \pm 0.2 \mu\text{mol m}^{-2} \text{d}^{-1}$ ) is in line with previously reported values for Ny-Ålesund [Björkman *et al.*, 2013]. However, it indicates greater net deposition than that derived from cumulative  $\text{NO}_x$ ,  $\text{HNO}_3^-$ , and  $\text{p-NO}_3^-$  fluxes, measured 200 m from the sampling site. Given its permeable nature, we emphasize that the snowpack should be considered as an integral part of the atmospheric boundary layer, allowing relevant reactions (Figure 2) to occur within interstitial air pockets within the snow. Thus, our observed dry deposition of  $\text{NO}_3^-$  could originate from both the overlying atmosphere and from redeposition of  $\text{NO}_3^-$  released from deeper within the snowpack or soil below.

Magnitudes and trends in surface snow  $\delta(^{15}\text{N})$  and  $\delta(^{18}\text{O})$  were compared to back trajectory analysis and local ODEs indicative of BrO chemistry. Trajectories originating from the polar basin were found to bring  $^{15}\text{N}$ -depleted air masses to Svalbard, confirming findings from an earlier atmospheric study of  $\text{NO}_3^-$  in Ny-Ålesund aerosol [Morin *et al.*, 2009], and demonstrating that such  $\text{NO}_3^-$  is deposited to the snowpack. Stagnant air and air masses originating from midlatitude regions were related to  $^{15}\text{N}$ -enriched dry  $\text{NO}_3^-$  deposition with an end-member of  $(+7.0 \pm 0.7)\%$ . Such positive  $\delta(^{15}\text{N})$  values have previously been found in European and U.S. air [Elliott *et al.*, 2009; Morin *et al.*, 2009], probably as a result of anthropogenic emissions [e.g., Kendall *et al.*, 2007], but can also result from in situ biogeochemical cycling of clay-bound  $\text{NH}_4^+$  [Amaroso *et al.*, 2010].

The average  $\delta(^{18}\text{O})$  values were lower during the wintertime compared to springtime, when  $\text{NO}_3^-$  deposition from polar basin air masses only exhibited positive  $\delta(^{18}\text{O})$  trends in conjunction with low  $\text{O}_3$  levels. These conditions indicate active halogen cycling and demonstrate the importance of  $\text{NO}_x$  to  $\text{NO}_3^-$  formation via coupled BrO- $\text{NO}_x$  chemistry (as identified in Ny-Ålesund aerosol: Morin *et al.* [2009]) for snow  $\text{NO}_3^-$  deposition. Furthermore, we identify evidence for such BrO chemistry occurring within the snowpack (interstitial air pockets) itself, and demonstrate its active involvement in the  $\text{NO}_3^-$  postdeposition cycling, as evidenced by steadily decreasing snow  $\text{Br}^-$  content and increasing  $\delta(^{18}\text{O})$  and  $\text{NO}_3^-$  concentration in surface snow samples. These are the first observations of such snowpack BrO- $\text{NO}_x$  coupling in this part of the Arctic. However, as indicated both by this and a previous study [Avallone *et al.*, 2003], local BrO production is concomitant with the arrival of BrO active  $\text{O}_3$ -depleted air, which contributes the necessary seed halogens to get the local production initiated [Simpson *et al.*, 2007]. This production might explain the uniquely high  $\delta(^{18}\text{O})$  end-member  $(+105.9 \pm 72.3\%)$  found even during stagnant and southeasterly air influences, regions usually associated with higher  $\text{O}_3$  levels.

In summary, our study demonstrates how careful sampling of surface snow can provide useful insights regarding atmospheric and snow processes controlling the fate of reactive nitrogen in the Arctic including coupling of BrO- $\text{NO}_x$  chemistry. In particular, our results elucidate the relative importance of these processes for a snowpack located in a coastal region at low altitude (Ny-Ålesund), in contrast to studies elsewhere (e.g., Greenland).

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