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3

4 Title: **Nitrate post-depositional processes in Svalbard surface snow**

5

6 Authors: Mats P. Björkman<sup>1,2,3\*</sup>, Carmen P. Vega<sup>4</sup>, Rafael Kühnel<sup>1,2</sup>, Francesca Spataro<sup>5</sup>,  
7 Antonietta Ianniello<sup>5</sup>, Giulio Esposito<sup>5</sup>, Jan Kaiser<sup>6</sup>, Alina Marca<sup>6</sup>, Andy Hodson<sup>7</sup>, Elisabeth  
8 Isaksson<sup>1</sup> and Tjarda J. Roberts<sup>8</sup>

9 <sup>1</sup>Norwegian Polar Institute, Fram Centre, N-9296 Tromsø, Norway.

10 <sup>2</sup>Department of Geosciences, University of Oslo, P.O. Box 1047 Blindern, 0316 Oslo,  
11 Norway.

12 <sup>3</sup>Now at: Department of Earth Sciences, University of Gothenburg, Box 460, SE-40530  
13 Göteborg, Sweden.

14 <sup>4</sup>Department of Earth Sciences, Uppsala University, Villavägen 16, SE-76236, Uppsala,  
15 Sweden.

16 <sup>5</sup>C.N.R.-Istituto sull'Inquinamento Atmosferico (IIA), Via Salaria Km 29.300, I-00015  
17 Monterotondo Scalo (Roma), Italy.

18 <sup>6</sup>School of Environmental Sciences, University of East Anglia, Norwich NR4 7TJ, U.K.

19 <sup>7</sup>Department of Geography, University of Sheffield, Sheffield S10 2TN, U.K.

20 <sup>8</sup>LPC2E, UMR 7328, CNRS-Université d'Orléans, 3A avenue de la Recherche  
21 Scientifique, 45071 Orléans, Cedex 2, France.

22 **\*Corresponding author**

23 Mats P. Björkman, Department of Earth Sciences, University of Gothenburg, Box 460, SE-40530  
24 Göteborg, Sweden.  
25 E-mail: [mats.p.bjorkman@gmail.com](mailto:mats.p.bjorkman@gmail.com)  
26 Telephone number: +46 (0) 730581145

## 27 Key points

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

## 31 Abstract

32 The snowpack acts as a sink for atmospheric reactive nitrogen, but several post-  
33 depositional pathways have been reported to alter the concentration and isotopic composition of  
34 snow nitrate with implications for atmospheric boundary layer chemistry, ice core records and  
35 terrestrial ecology following snow-melt. Careful daily sampling of surface snow during winter  
36 (11 – 15 February, 2010) and spring-time (April 9 – May 5, 2010) near Ny-Ålesund, Svalbard  
37 reveals a complex pattern of processes within the snowpack. Dry deposition was found to  
38 dominate over post-depositional losses, with a net nitrate deposition rate of  $(0.6 \pm 0.2) \mu\text{mol m}^{-2} \text{d}^{-1}$   
39 to homogeneous surface snow. At Ny-Ålesund, such surface dry deposition can either solely  
40 result from long-range atmospheric transport of  $\text{NO}_{x,y}$  or include the re-deposition of  
41 photolytic/bacterial emission originating from deeper snow layers. Our data further confirm that  
42 polar basin air masses bring  $^{15}\text{N}$ -depleted nitrate to Svalbard, while high nitrate  $\delta(^{18}\text{O})$  values  
43 only occur in connection with ozone-depleted air, and show that these signatures are reflected in  
44 the deposited nitrate. Such ozone-depleted air is attributed to active halogen chemistry in the air-  
45 masses advected to the site. However, here the Ny-Ålesund surface snow was shown to have an

46 active role in the halogen dynamics for this region, as indicated by declining bromide  
47 concentrations and increasing nitrate  $\delta(^{18}\text{O})$ , during high BrO (low ozone) events. The data also  
48 indicates that the snow-pack BrO-NO<sub>x</sub> cycling continued in post-event periods, when ambient  
49 ozone and BrO levels recovered.

## 50 1. Introduction

### 51 1.1 Overview

52 Snowpack nitrate (NO<sub>3</sub><sup>-</sup>) can influence the chemical composition of the lower atmospheric  
53 boundary layer through photochemical release of nitrogen oxides (e.g. Honrath et al., 1999,  
54 Domine and Shepson, 2002; Grannas et al., 2007; Morin et al., 2009; Thomas et al., 2012). Even  
55 though snow is a highly reflective material, the shape and small size of snow grains favours a  
56 forward scattering of the light into the snowpack (Domine et al., 2008), creating a photo-active  
57 zone in the surface region of the snow cover (e.g. Qiu et al., 2002; Simpson et al., 2002; Galbavy  
58 et al., 2007). Following polar sunrise, photolysis of surface snow NO<sub>3</sub><sup>-</sup> and the concomitant  
59 emission of nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>) can alter the isotopic composition and  
60 concentration of NO<sub>3</sub><sup>-</sup> in snow and ice (Jarvis et al., 2008; Frey et al., 2009; Erbland et al., 2013).  
61 Furthermore, the removal of NO<sub>3</sub><sup>-</sup> through HNO<sub>3</sub> evaporation from snow can also contribute to  
62 NO<sub>3</sub><sup>-</sup> isotopic and concentration changes (Frey et al., 2009; Erbland et al., 2013). In addition to  
63 these post-depositional processes, dry deposition of pollutants and further accumulation of snow  
64 will influence the isotopic composition and budget of NO<sub>3</sub><sup>-</sup>, where the snow accumulation buries  
65 older layers and prevents further photolytic reactions (Jarvis et al., 2009; Erbland et al., 2013).  
66 Since several pathways have been described for the NO<sub>x</sub> (NO<sub>x</sub> = NO + NO<sub>2</sub>) oxidation to nitric  
67 acid (HNO<sub>3</sub>) in polar regions, e.g. involving ozone (O<sub>3</sub>), hydroxyl (OH) and bromine monoxide  
68 (BrO) species (Russell et al., 1985; Evans et al., 2003; Seinfeld and Pandis, 2006; Morin et al.,

69 2007b), atmospheric boundary layer chemistry is of key importance for the isotopic  $\text{NO}_3^-$   
70 signature found in snow.

71 Here we present a detailed investigation of the processes governing the concentration and  
72 isotopic composition of  $\text{NO}_3^-$  ( $^{15}\text{N}/^{14}\text{N}$  and  $^{18}\text{O}/^{16}\text{O}$ ) in the most photo-active zone (upper 5 cm)  
73 of the snowpack at Ny-Ålesund, Svalbard (Fig. 1). In order to highlight the effects of photolysis,  
74 the sampling period covered both the polar night and springtime during 2010. The data was  
75 analyzed in conjunction with atmospheric flux measurements of oxidized nitrogen;  $\text{NO}$ ,  $\text{NO}_2$ ,  
76  $\text{HNO}_3$  and particulate  $\text{NO}_3^-$  (p- $\text{NO}_3^-$ ), that were conducted directly above the snowpack, and  $\text{O}_3$   
77 concentrations monitored both at Gruvebadet and at the nearby Zeppelin Station (Fig. 1). This  
78 study is used to infer the influence of BrO chemistry upon the snowpack nitrogen cycle for the  
79 first time in Svalbard.

## 80 1.2 Background

### 81 1.2.1 Long-range transport and deposition of oxidized nitrogen

82 Through *long-range atmospheric transport* (Fig. 2) oxidized nitrogen that is emitted at mid-  
83 latitude regions can reach pristine Arctic environments (Rahn et al., 1980; Rahn, 1981;  
84 Dickerson, 1985; Stohl, 2006; Hirdman et al., 2010; Kühnel et al., 2011; Kühnel, 2013), often in  
85 the form of molecules with longer atmospheric residence time such as peroxyacyl nitrates  
86 (PANs) or p- $\text{NO}_3^-$  (Beine et al., 1997; Seinfeld and Pandis, 2006). However, occasional rapid  
87 long-range transport events also occur, as recently identified for Ny-Ålesund in the European  
88 high Arctic (e.g. Hodson et al., 2010, Kühnel 2013), which can transport pollutants with shorter  
89 life-times, such as  $\text{NO}_x$ , (or its oxidation product  $\text{HNO}_3$ ) into the Arctic (Zien et al., 2014). The  
90 original isotopic composition of each  $\text{NO}_x$  source (e.g. forest fires or fossil fuel combustion,  
91 among other) depends on the oxidation process and origin of the nitrogen (N) and oxygen (O)

92 (e.g. Kendall et al., 2007). In the Arctic spring, the long-range transported oxidized nitrogen  
93 pollutants, such as PANs, decompose and undergo local boundary layer *NO<sub>x</sub>-cycling*, involving  
94 O<sub>3</sub>, BrO or hydroperoxyl radicals (HO<sub>2</sub>) and solar radiation (*hν*, Fig. 2). This cycling is followed  
95 by a *NO<sub>x</sub>-removal*, where both a day time (through OH or HO<sub>2</sub>) and a night time (through NO<sub>3</sub>  
96 and dinitrogen pentoxide (N<sub>2</sub>O<sub>5</sub>)) conversion of NO<sub>2</sub> to HNO<sub>3</sub> occurs (Fig. 2, Russell et al.,  
97 1985; Dentener and Crutzen, 1993; Hanson and Ravishankara, 1995; Hanson et al., 1996; Evans  
98 et al., 2003; Morin et al., 2007b; Morin et al., 2008; Thomas et al., 2011; Thomas et al., 2012),  
99 where the N<sub>2</sub>O<sub>5</sub> also can be directly deposited to the snow (e.g. Huff et al., 2011). For Arctic  
100 sites, HNO<sub>3</sub> production via the *BrO-pathway*, involving BrONO<sub>2</sub> (Fig. 2), is particularly  
101 important during episodes of BrO chemistry, which also causes low O<sub>3</sub> levels (e.g. Evans et al.,  
102 2003; Morin et al., 2007b). Nitric acid and p-NO<sub>3</sub><sup>-</sup> will then be removed from the atmosphere by  
103 snow, rain or dry deposition (Cadle, 1991; Bergin et al., 1995; Kuhn, 2001), and be deposited to  
104 the snow as NO<sub>3</sub><sup>-</sup> (Diehl et al., 1995; Abbatt, 1997). The snowpack therefore acts as an important  
105 sink and reservoir for atmospheric reactive nitrogen, with a unique isotopic NO<sub>3</sub><sup>-</sup> composition  
106 and concentration for each snow layer. For the N-isotopic composition, the *initial* snow signature  
107 typically resemble the original source of NO<sub>x</sub>, this since the fractionation during NO<sub>x</sub>-cycling  
108 and removal is considered to be low (Freyer, 1991). For the O-isotopes, the interaction and O-  
109 exchange with O<sub>3</sub>, BrO, and OH during the NO<sub>x</sub>-cycling and NO<sub>x</sub>-removal will strongly  
110 influence the initial snow O-signature, typically masking any other processes or original source  
111 signatures (e.g. Michalski et al., 2003; Jarvis et al., 2009; Morin et al., 2009). Thus the *initial* O-  
112 signature provides insights into the oxidation processes that have occurred prior to deposition.  
113 These initial concentrations and isotopic imprints may, however, be altered by post-depositional  
114 snow processes as will be further outlined below (1.2.2.).

115 In Svalbard, the  $\text{NO}_3^-$  deposition and thereby the snow concentration is governed by wet  
116 deposition, where a few sporadic “strong” events dominate the total annual deposition (Kühnel et  
117 al., 2011). These “strong” deposition events are due to rapid transport of polluted European air  
118 masses (e.g. Hodson et al., 2010), which are occasionally channelled northward between a  
119 blocking anticyclone, situated over Scandinavia and Central Europe, and an incoming cyclone  
120 over the Atlantic (Kühnel, 2013). The typical transport time for such events are about 2 to 5 days  
121 and where the air-masses picks up in speed and humidity just prior to the arrival to Svalbard  
122 (Kühnel 2013). The estimated winter dry deposition of  $\text{NO}_3^-$  in this region is modest (approx. 14  
123 %, Björkman et al., 2013), but nevertheless, of importance for the isotopic composition of  $\text{NO}_3^-$   
124 in snow when studying short term daily variations (Hastings et al., 2004).

#### 125 1.2.2 Snowpack $\text{NO}_3^-$ photolysis and evaporation

126 Due to  $\text{NO}_x$  release from the photo-active zone of the snowpack, the deposited  $\text{NO}_3^-$  can play  
127 an important role in atmospheric boundary layer chemistry after the initial deposition (e.g.  
128 Thomas et al., 2012). The snowpack is therefore an active player in atmospheric chemical  
129 processes and not just a  $\text{NO}_3^-$  sink (Honrath et al., 1999). Snowpack  $\text{NO}_3^-$  photolysis, of  
130 relevance for the  $\text{NO}_3^-$  budget, is believed to occur at the very surface of snow crystals (Boxe and  
131 Saiz-Lopez, 2008), with reaction rates and quantum yields for photolytic processes similar to  
132 those in aqueous solutions (Bartels-Rausch et al., 2014). This region of the ice crystal has  
133 previously been referred to as a quasi-liquid layer (QLL, Kvivlidz et al., 1970), but has lately  
134 been re-described as a disordered interface (DI, Bartels-Rausch et al., 2014). This new term  
135 emphasizes the disordered molecular structure that occurs at the surface of any crystal, created  
136 by the absence of molecular bonds towards its surface (Bartels-Rausch et al., 2014), instead of  
137 involving a liquid state analogy. The photolysis of  $\text{NO}_3^-$  within the DI and subsequent reactions

138 (Fig. 2) lead to the production of  $\text{NO}_2$  and to a lesser extent  $\text{NO}$  (see Jacobi and Hilker, 2007;  
139 Boxe and Saiz-Lopez, 2008 for an overview of reaction pathways). The produced  $\text{NO}_2$  and  $\text{NO}$   
140 can then diffuse out of the DI into firm air and thereafter into the atmospheric boundary layer  
141 (e.g. Honrath et al., 1999; Jones et al., 2000; Beine et al., 2003). This photolytic initiated loss  
142 also alters the isotopic composition of snowpack  $\text{NO}_3^-$ , with an enrichment of  $^{15}\text{N}$  in the residual  
143  $\text{NO}_3^-$  due to photolytic fractionation (Frey et al., 2009; Morin et al., 2009; Erbland et al., 2013).  
144 On the other hand the O-composition of the remaining  $\text{NO}_3^-$  will be strongly influenced by the  
145 isotopic exchange between the photolytic products and OH-radical or  $\text{H}_2\text{O}$  within the DI  
146 (McCabe et al., 2005; Frey et al., 2009). There is also evidence for nitrous acid ( $\text{HONO}$ )  
147 production from irradiated snow (Fig. 2, Zhou et al., 2001; Beine et al., 2002a), due to the  
148 interaction between nitrite ( $\text{NO}_2^-$ ) and a hydrogen ion ( $\text{H}^+$ , e.g. Dominé and Shepson, 2002).  
149 However, several other pathways have also been described; i.e. involving humic acids (e.g.  
150 Beine et al., 2008, Villena et al., 2001) or heterogeneous reactions in the firm (e.g. Jacobi and  
151 Hilker, 2007), although the reaction steps in these pathways are not fully understood (Grannas et  
152 al., 2007; Jacobi and Hilker, 2007; Beine et al., 2008; Boxe and Saiz-Lopez, 2008, Jacobi et al.,  
153 2014) and therefore not included in Fig. 2. Nitrate loss from the snow has also been found to be  
154 due to *evaporation* (Fig. 2) of  $\text{HNO}_3$ , a process also favouring the loss of isotopically light  $\text{NO}_3^-$   
155 (e.g. Frey et al., 2009). A recent study by Erbland et al. (2013) confirms that evaporation is an  
156 active player in post-depositional processes in areas with low snow accumulation rates and high  
157 firm air ventilation, such as central Antarctic sites. However, the process has been shown to be  
158 quantitatively modest compared to the loss through photolysis for these Antarctic sites (Erbland  
159 et al., 2013). Interestingly, laboratory studies of snow and ice have found no evidence for this  
160 evaporative pathway (Chu and Anastasio, 2003; Sato et al., 2008).

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

### 168 1.2.3 Local biogeochemical contribution to snowpack $\text{NO}_3^-$

169 The DI reactions described above mostly involve  $\text{NO}_3^-$  of non-local origin, deposited  
170 following long-range atmospheric transport. However, a more locally produced source of  
171 oxidized nitrogen has been suggested through microbial activity (Brooks et al., 1997; Ma et al.,  
172 2007; Miteva, 2008; Siciliano et al., 2009, Roberts et al., 2010). Svalbard snow is known to  
173 contain a diverse community of microorganisms (Amato et al., 2007; Larose et al., 2010), and  
174 the microbial assimilation of ammonium ( $\text{NH}_4^+$ ) might result in the production of gas phase  $\text{NO}$ ,  
175  $\text{HNO}_3$  and HONO, even during winter (Fig. 2, Amoroso et al., 2010). Isotopic fractionation is  
176 expected through microbial assimilation of nitrogen compounds (e.g. Kendall, 1998), although  
177 during the nutrient limited conditions in a snowpack such nitrogen isotopic fractionation might  
178 not necessarily be expressed in the produced reactive nitrogen emissions (Amoroso et al., 2010).  
179 The resulting snowpack emission, under these conditions, would have an N-isotopic composition  
180 related to the N source (in this case, organic or mineral bound  $\text{NH}_4^+$ ) and an O-isotopic  
181 composition influenced by the surrounding water (Amoroso et al., 2010).

### 182 1.2.4 Re-cycling of $\text{NO}_x$ snowpack emissions

183           The gas phase products of post-depositional and biogeochemical processes are emitted  
184 into the firm air and onwards to the lower atmospheric boundary layer, where further reactions  
185 may lead to a re-deposition of HNO<sub>3</sub> to the snow (Fig. 2, Hastings et al., 2004; Morin et al.,  
186 2007b; Jarvis et al., 2009). During spring and summer conditions, these reactions can have a  
187 diurnal pattern governed by day-time emissions and night-time deposition (Hastings et al., 2004).  
188 The isotopic composition of this re-deposited HNO<sub>3</sub> would then be influenced by the oxidation  
189 pathways undertaken, see Fig. 2 (e.g. Jarvis et al., 2009). Additionally, snow is a highly porous  
190 medium that undergoes a steady exchange of air with the surrounding atmosphere (Sturm and  
191 Johnson, 1991; Albert and Hardy, 1995; Colbeck, 1997; Albert et al., 2002; Frey et al., 2005).  
192 This exchange allows the boundary layer processes in Fig. 2 to occur also within the snowpack  
193 interstitial air pockets.

## 194       2. Methods

### 195       2.1 Field sampling

196       The top 5 cm of the snowpack was sampled close to Gruvebadet, 1 km outside the *Ny-*  
197 *Ålesund International Arctic Research and Monitoring Facility* in Svalbard (78°55' N, 11°55' E,  
198 Fig. 1). Samples were collected between February 11 and 15 (*dark* campaign) and between April  
199 9 and May 5 (*spring* campaign) during 2010. The sampling was undertaken at mid-day (11:00-  
200 13:00) during the *dark* campaign, and every morning (09:00 – 10:00) during the *spring*  
201 campaign. All snow samples were collected by inserting a pre-cleaned acrylic collars (height:  
202 5cm, inner diameter: 10.4 cm, volume: 425 cm<sup>-3</sup>) vertically into the snowpack, and using pre-  
203 cleaned plastic shovels, clean overalls, face masks and powder-free gloves. Triplicate samples  
204 were collected approximately 10 m apart, resulting in a total of 96 samples. To account for  
205 variations in surface snow density throughout the campaign, several collars were filled next to

206 each other at each of the three triplicate sample locations, yielding a total sampled snow volume  
207 between 1.3 L and 3.8 L. The snow was transferred directly into clean black plastic zipper  
208 storage bags to prevent further photolysis, brought into the laboratory in Ny-Ålesund and melted  
209 at room temperature. Each melted snow sample was vacuum filtered (pore size 0.45  $\mu\text{m}$ ,  
210 according to Hodson et al., 2005), bottled in 50 ml-tubes, refrozen and shipped for analysis of  
211 major ions and  $\text{NO}_3^-$  stable isotopes. To minimize contamination between samples, vacuum units  
212 and sample tubes were rinsed three times with sample water or, in the case of low sample  
213 volume, ultra-pure water ( $>18 \text{ M}\Omega$ ). Field-blanks were collected along with the samples to check  
214 for contamination. Blank bags were opened and closed during sampling (without any snow  
215 addition), filled with 100 mL ultra-pure water, and then treated and analysed like the rest of the  
216 samples. Furthermore, during the spring campaign, an extra 50 ml sterile sampling tube was  
217 filled with the top 5 cm surface snow next to each sampling point for an opportunistic  
218 complementary major ion analysis performed on-site.

## 219 2.2 Laboratory analysis

### 220 2.2.1 Major ions

221 The samples were analyzed for  $\text{NO}_3^-$ , chloride ( $\text{Cl}^-$ ) and sodium ( $\text{Na}^+$ ) by ion chromatography  
222 at the Department of Geography, University of Sheffield, UK using two separate systems  
223 (Dionex DX 90 ion chromatographs, 4400 integrators, AS40 autosamplers) with Dionex columns  
224 AS14A and CS12A for anions and cations respectively. Standards (range 100 to 2000  $\mu\text{g L}^{-1}$ )  
225 were prepared every day from 1000  $\text{mg L}^{-1}$  Merck CertiPUR stock standards. The analytical  
226 precision (1 standard deviation,  $1\sigma$ ) estimated from repeat analyses of multi element reference  
227 standards (Merck CertiPUR) were 1.4 and 1.6 %, respectively, for the anions  $\text{Cl}^-$  and  $\text{NO}_3^-$ , and  
228 0.06 % for the cation  $\text{Na}^+$ . Based on repeat analyses of separate filter aliquots, the analytical

229 precision including sample treatment was better than 5 % for each ion. Detection limits (D.L.)  
230 defined as  $3\sigma$  for the analytic blanks were 0.17, 0.21 and 0.34  $\mu\text{mol L}^{-1}$  for  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{Na}^+$ ,  
231 respectively.

232 The complementary spring-time 50 ml-snow samples and the diffusion line preparations  
233 (described below in section 2.3.2) were analyzed for  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{NO}_2^-$  and bromide ( $\text{Br}^-$ ) in  
234 Ny-Ålesund by the Institute of Atmospheric Pollution Research – National Research Council of  
235 Italy (IIA-CNR). Melted snow was analyzed without pre-treatment by ion chromatography  
236 analytical technique (Dionex ICS 90 coupled with an AS50 auto-sampler and using Dionex  
237 AS14 and CS12 columns). A multipoint calibration was performed using six standards in the  
238 range 5 to 1000  $\mu\text{g L}^{-1}$ , obtaining linear responses. Dilutions were carried out for more  
239 concentrated samples. Calibration solutions were prepared every second week from 1000  $\text{mg L}^{-1}$   
240 standard solutions (Merck). Control samples (1000  $\mu\text{g L}^{-1}$  calibration solution) were analyzed  
241 every seven samples in order to re-calibrate the ion chromatograph. The variation in the  
242 concentration of these control samples ranged within 0.5 – 1 %. The analytical precision errors  
243 from repeated analyses of a calibration solution (500  $\mu\text{g L}^{-1}$ ), were 1.13, 0.73, 0.35, 0.43 and  
244 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  
245 and 35.8  $\text{nmol L}^{-1}$  were determined for  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$  and  $\text{Na}^+$ , respectively.

#### 246 2.2.2 $\text{NO}_3^-$ isotopic composition

247 The  $^{15}\text{N}$  and  $^{18}\text{O}$  isotopic composition of  $\text{NO}_3^-$  were analyzed at the School of Environmental  
248 Sciences, University of East Anglia, Norwich, UK, using the bacterial denitrifier method  
249 (Sigman et al., 2001; Coplen et al., 2004; Kaiser et al., 2007) where the *Pseudomonas*  
250 *aureofaciens* strain was utilized. Values presented here are denoted as isotope deltas,  $\delta(^{15}\text{N})$  and

251  $\delta(^{18}\text{O})$  (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  
252 expressed with respect to an international standard in ‰ ( $10^{-3}$ , per mil) (Eq. 1).

$$253 \quad \delta_{\text{sample}} = \frac{R_{\text{sample}} - R_{\text{ref}}}{R_{\text{ref}}} \quad \text{Eq. 1}$$

254 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,  
255 where atmospheric nitrogen (Air- $\text{N}_2$ ) was used as nitrogen reference and Vienna Standard Mean  
256 Ocean Water (VSMOW) was used as oxygen reference. Positive delta values indicate an  
257 enrichment of the heavier isotope (or a depletion of the lighter isotope) compared to the standard.  
258 To calibrate the isotope delta values, the international nitrate reference material IAEA-NO-3 was  
259 used, assuming it has  $\delta(^{15}\text{N}) = 4.7$  ‰ vs. Air- $\text{N}_2$  and  $\delta(^{18}\text{O}) = 25.61$  ‰ vs. VSMOW (Böhlke et  
260 al., 2003). The  $\delta(^{15}\text{N})$  values reported here have not been corrected for any non-mass dependent  
261  $^{17}\text{O}$  contribution to the  $m/z$  45 ion current during mass-spectrometric analysis. However,  $\delta(^{17}\text{O})$   
262 and  $\delta(^{18}\text{O})$  are usually well correlated and the true  $\delta(^{15}\text{N})$  was estimated to be 1-2 ‰ lower than  
263 the reported values. The bacterial denitrifier method requires a minimum of 20 nmol  $\text{NO}_3^-$   
264 (optimum being 50 nmol) in at most 10 mL of solution. Consequently, only samples above this  
265 limit were analyzed ( $n = 87$ ).

## 266 2.3 Air-snow fluxes

### 267 2.3.1 Surface snow net change

268 By following the concentration change in surface snow over time, it is possible to  
269 evaluate the overall net change due to surface snow processes occurring after wet deposition.  
270 This method has previously been used to evaluate  $\text{NO}_3^-$  dry deposition to snow (Cadle et al.,  
271 1985; Johansson and Granat, 1986; Cadle, 1991; Cress et al., 1995). The net change ( $F_{\text{net}}$ ) can be  
272 calculated as (Björkman et al., 2013):

$$273 \quad F_{\text{net}} = -\frac{c_0 V_t - c_t V_t}{At} \quad \text{Eq. 2}$$

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

$$283 \quad F_{\text{net}} (1 + \delta_{\text{net}}) = -k [c_0(1 + \delta_0) - c_t(1 + \delta_t)] \quad \text{Eq. 3}$$

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

$$287 \quad 0 = c_t(\delta_t - \delta_{\text{net}}) - c_0(\delta_0 - \delta_{\text{net}}) \quad \text{Eq. 4}$$

288 which then can be rearranged to give:

$$289 \quad \delta_{\text{net}} = \frac{c_t \delta_t - c_0 \delta_0}{c_t - c_0} \quad \text{Eq. 5}$$

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

### 292 2.3.2 $\text{NO}_x$ , $\text{HNO}_3^-$ and p- $\text{NO}_3^-$ flux measurements

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

295 the snow sampling site) during the period April 9 to 27 in 2010. The NO and NO<sub>2</sub> concentrations  
296 were measured on a 6 minute basis, using a modified commercial two-channel high-sensitivity  
297 chemiluminescence detector (Sonoma Technologies, USA, Beine et al., 2002b; Amoroso et al.,  
298 2010). The two channels sampled air from dual inlets at 0.3 m and 1.5 m above the surface snow,  
299 respectively. Nitric oxide detection was based on the chemiluminescence signal produced by the  
300 reaction between NO and O<sub>3</sub>, which was photolytically generated in a 150 ml min<sup>-1</sup> flow rate of  
301 O<sub>2</sub> by a corona discharge O<sub>3</sub> generator. Nitrogen dioxide was detected as NO following  
302 photolysis between 350 and 420 nm by light-emitting diodes. The instrument was calibrated  
303 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  
304 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  
305 addition of 8.3 nmol mol<sup>-1</sup>. The NO detection limit was determined as 3σ of the observed scatter  
306 in the instrument signal and corresponded to 2.5 pmol mol<sup>-1</sup> for 1 h averages.

307 Measurements of HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> concentrations were made by two independent diffusion  
308 lines (Beine et al., 2001; Perrino et al., 2001; Ianniello et al., 2002; Ianniello et al., 2007) with  
309 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  
310 measured on a 12 h basis from April 10 to 16, while a time resolution of 24 h was used from  
311 April 17 to 27. The diffusion lines used in this study included a denuder train consisting of two  
312 sodium fluoride (1% NaF in 9:1 ethanol/water solution) coated denuders for HNO<sub>3</sub> sampling.  
313 The atmospheric HNO<sub>3</sub> concentrations were calculated by subtracting the analyte mass  
314 (expressed as NO<sub>3</sub><sup>-</sup>) in the second NaF coated denuder from the analyte mass in the first NaF  
315 coated denuder (Febo et al., 1989). The denuder train was followed by a cyclone (2.5 μm  
316 aerodynamic diameter cut-off point) and a filter pack set in series, for the collection of  
317 particulate matter in the coarse and fine fractions, respectively. The filter pack included a Teflon

318 filter (Whatman Teflon, 47 mm, 1  $\mu\text{m}$  pore size), a nylon filter (Nylosorb Gelman, 47 mm, 1  $\mu\text{m}$   
319 pore size), a  $\text{Na}_2\text{CO}_3$ -glycerol impregnated paper filter (Whatman 41) and a  $\text{H}_3\text{PO}_3$  coated paper  
320 filter. The last three filters were used to collect chemical species evaporated from the Teflon  
321 filter (Ianniello et al., 2002; Ianniello et al., 2011; Spataro et al., 2013). The sampling flow rate  
322 was  $15 \text{ L min}^{-1}$ , and typical sampling volumes of  $11.9 \text{ m}^3$  and  $23.5 \text{ m}^3$  were obtained for 12 h and  
323 24 h sampling periods, respectively. After sampling, the denuders, cyclone and filters were  
324 extracted and these samples were analyzed within 24 h by using the IIA-CNR Ion  
325 Chromatography system described in section 2.2.1. Under these conditions, the collection  
326 efficiency for both  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  was  $>99\%$ . The D.L. of  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  (calculated as  
327  $3\sigma$  of field blanks) were  $2.95 \text{ ng m}^{-3}$  and  $1.42 \text{ ng m}^{-3}$ , respectively on a 24 h measurement period,  
328 while the precision errors of these measurements were 2.54 % at  $20 \text{ ng m}^{-3}$  and 0.73 % at  $79 \text{ ng}$   
329  $\text{m}^{-3}$ , respectively. Here we focus only on  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  data, although the diffusion line  
330 sampling system did allow us to also collect other gaseous and particulate compounds, which  
331 will be discussed elsewhere.

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

337 Using the measured concentration differences and the atmospheric eddy diffusivities ( $K$ ) for  
338 the same period, the atmospheric fluxes for  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{HNO}_3$  and coarse and fine particulate  $\text{NO}_3^-$   
339 were derived ( $\text{Flux} = \Delta \times K$ ) as detailed elsewhere (Sozzi et al., 1998; Ianniello et al., 2002;  
340 Beine et al., 2003 and references therein). Diffusivities were obtained from atmospheric

341 turbulence measurements made at a frequency of 10 Hz by using an UVW tripropeller  
342 anemometer (Metek, USA-T1), which was placed at 1.5 m above the snowpack, assuming  
343 neutral boundary layer conditions.

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

### 346 2.3.3 Dry deposition estimates

347 If the atmospheric concentration ( $c_{\text{atm}}$ ) of  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  are measured, the expected dry  
348 deposition flux ( $F_{\text{dry-dep}}$ ) can be modeled as long as the deposition velocities ( $v_d$ ) are known (e.g.  
349 Seinfeld and Pandis, 2006):

$$350 F_{\text{dry-dep}} = v_d c_{\text{atm}} \quad \text{Eq. 6}$$

351 In a recent study covering the same *spring* campaign, the dry deposition of  $\text{HNO}_3$  and  $\text{p-}$   
352  $\text{NO}_3^-$  was both modelled and measured for Ny-Ålesund (Björkman et al., 2013). Median  
353 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  $\text{p-}$   
354  $\text{NO}_3^-$ , particle size  $0.7$  and  $7 \mu\text{m}$  in diameter, respectively (Björkman et al., 2013). The combined  
355 gaseous and particulate dry deposition,  $F_{\text{model(LND)}}$  (referring to the modelled  $\text{HNO}_3$  and  $\text{p-NO}_3^-$   
356 dry deposition rates obtained using a lognormal distribution (LND) for  $\text{NO}_3^-$  aerosols sizes in  
357 Björkman et al., (2013)), will be used here for comparison with the surface snow and flux  
358 measurements, and for further modelling purposes. Björkman et al., (2013) also measured the  
359 actual  $\text{NO}_3^-$  dry deposition ( $F_{\text{tray}}$ ) to snow using a “bucket” approach (e.g. Cress et al., 1995) and  
360 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  
361 will also be used for further modelling purposes. An overview of  $\text{NO}_3^-$  dry deposition in the  
362 Arctic, and a full description of these dry deposition estimates are given by Björkman et al.  
363 (2013).

#### 364 2.3.4 Additional observations

365 Meteorological data from Ny-Ålesund, in particular precipitation data, were provided by the  
366 Norwegian Meteorological Institute (DNMI) and are available at <http://www.eklima.no>. The  
367 atmospheric concentration of O<sub>3</sub> (*c*<sub>O<sub>3</sub></sub>) is continuously measured by the Norwegian Institute for  
368 Air Research (NILU) at the nearby Zeppelin atmospheric research station (474 m a.s.l, Fig. 1),  
369 available at <http://ebas.nilu.no>. During the spring campaign 2010, O<sub>3</sub> concentrations were also  
370 recorded by IIA-CNR at Gruvebadet until April 27. NILU also provides an online base  
371 atmospheric transport model, FLEXTRA (<http://www.nilu.no/projects/ccc/trajectories/>). Using  
372 FLEXTRA air mass back-trajectories arriving to Ny-Ålesund were established for all sampling  
373 days at 00:00 and 12:00, with trajectories spanning 7 days back in time.

374 Additionally, sonic anemometer (Gill R3) and fast hygrometer (Campbell Scientific KH2O  
375 krypton) data from the Amundsen-Nobile Climate Change Tower (Fig. 1) were provided by The  
376 Institute for Atmospheric Science and Climate - National Research Council of Italy (ISAC-CNR,  
377 M. Mazzola and A. Viola, per. com.). The 10 minute average data sampled at 7.5 m above  
378 ground were used to evaluate water vapour flux as an indication of sublimation rates.

### 379 2.4 Models

#### 380 2.4.1 Photolytic model

381 NO<sub>x</sub> production due to photolysis of NO<sub>3</sub><sup>-</sup> has previously been modelled for Ny-Ålesund  
382 snow, using the solar zenith angle ( $\theta_{SZA}$ ) and the surface snow NO<sub>3</sub><sup>-</sup> concentrations, with results  
383 comparable to NO<sub>x</sub> emission measurements (France et al., 2010; France et al., 2011b). This  
384 model assumes that the photolysis of NO<sub>3</sub><sup>-</sup> only follows the reaction  $\text{NO}_3^- + h\nu \rightarrow \text{NO}_2 + \text{O}^-$  and

385 is, according to the reactions in Fig. 2, a simplification of the DI dynamics, but has the potential  
 386 to provide useful insights into the  $\text{NO}_3^-$  loss through photolysis. For the purpose of this study, a  
 387 photolytic rate function considering only the surface snow layer during clear sky conditions  
 388 (France et al., 2010) will be used for comparison to the sampled top 5 cm of the snowpack.  
 389 However, a depth integrated model would be more appropriate if bulk snowpack samples were  
 390 under consideration (see France et al., 2010; France et al., 2011a; France et al., 2011b for further  
 391 details). Here only surface snow was sampled, in order to avoid a potential disturbance of the  
 392 post-depositional processes under investigation.

393 A polynomial function (Eq. 7) was fitted to the photolysis rates ( $J_{\text{NO}_3^-}$ , in  $\text{s}^{-1}$ ) given in  
 394 France et al. (2010) as a function of  $\theta_{\text{SZA}}$  (in  $^\circ$ ), with  $R^2=0.9994$  (Fig S1):

$$395 J_{\text{NO}_3^-} = 1.18e^{-14}\theta_{\text{SZA}}^4 - 1.09e^{-12}\theta_{\text{SZA}}^3 - 3.51e^{-11}\theta_{\text{SZA}}^2 - 8.80e^{-10}\theta_{\text{SZA}} + 3.86e^{-7} \quad \text{Eq. 7}$$

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

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

$$400 F_{J_{\text{NO}_3^-}} = J_{\text{NO}_3^-} c_0 z_{\text{SWE}} \quad \text{Eq. 8}$$

401 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  
 402 surface snow (in m). For lower  $\text{NO}_3^-$  concentrations, or unusually high  $\text{NO}_2$  emissions, the  
 403 surface snow  $\text{NO}_3^-$  concentration might change over the course of the day. To minimize this  
 404 potential source of error, the time resolution of the photolysis calculations was set to 1 h in  
 405 accordance with the  $\theta_{\text{SZA}}$  data. The  $F_{J_{\text{NO}_3^-}}$  emission given by Eq. 8 provides the flux in  $\mu\text{mol m}^{-2}$   
 406  $\text{d}^{-1}$  units.

407 2.4.2 Box models

408 A box model, describing the main sources and sinks of  $\text{NO}_3^-$  in the snow, was applied to  
 409 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  
 410 outgoing fluxes were assumed to be due to photolysis of  $\text{NO}_3^-$ , and all incoming fluxes were  
 411 assumed to be due to  $\text{NO}_3^-$  dry deposition. Hence, this is a simplification of the actual processes,  
 412 which might for example also include evaporation of  $\text{HNO}_3$  (see Fig. 2). However, as an initial  
 413 assumption (and further justified below) photochemistry was assumed to be the major loss  
 414 process for this surface snow study.

415 In the model, the change in  $c_{\text{NO}_3}$  over time when the sun is below the horizon was  
 416 expressed as Eq. 9, while Eq. 10 gives the change when both dry deposition and photolysis are  
 417 present:

$$418 \frac{dc}{dt} = \frac{v_d c_{\text{atm}} A}{V_t} \quad \text{Eq. 9}$$

$$419 \frac{dc}{dt} = \frac{v_d c_{\text{atm}} A}{V_t} - Jc \quad \text{Eq. 10}$$

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

$$425 c_t = \frac{v_d c_{\text{atm}} A t}{V_t} + c_0 \quad \text{Eq. 11}$$

$$426 c_t = \left( \frac{v_d c_{\text{atm}} A}{V_t J} \right) * (1 - e^{-Jt}) + c_0 e^{-Jt} \quad \text{Eq. 12}$$

427 where Eq. 11 and 12 represent periods when the sun is below or above the horizon, respectively.

428 The isotopic composition of  $\text{NO}_3^-$  remaining in the snow ( $\delta_t$ ) can then be expressed as:

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

430 Similarly to Eq. 11 and 12,  $c'_i$  are given by:

431  $c'_t = \frac{v_d c'_{\text{atm}} A t}{V_t} + c'_0$  Eq. 14

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

433 where  $c'_0 = c_0 R_{\text{ref}}(1+\delta_0)$ ,  $c'_{\text{atm}} = c_{\text{atm}} R_{\text{ref}}(1+\delta_{\text{atm}})$ ,  $J' = J(1+\varepsilon)$ , and where  $\delta_0$  and  $\delta_{\text{atm}}$  are the initial  
 434 and atmospheric N or O isotopic composition, respectively, while  $\varepsilon$  is the photolytic fractionation  
 435 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  
 436 ( $^{15}\text{N}$  or  $^{18}\text{O}$ ). The error due to the assumption that the concentration of the major isotope is equal  
 437 to the total nitrate concentration, is negligible (<0.01 ‰).

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

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

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

443 Eq. 17

444 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  
 445 of the instantaneous photolytic product:  $\delta_{\text{photo}} = \delta_0(1+\varepsilon)+\varepsilon$ .

446 Previous studies have suggested a range of  $^{15}\varepsilon$ , from -48 ‰ (Frey et al., 2009) to -12 ‰  
 447 (Blunier et al., 2005), and  $^{18}\varepsilon$  from -34 ‰ (Frey et al., 2009) to between 2 and 7 ‰ (McCabe et  
 448 al., 2005) for the photolytic fractionation in question. However, secondary reactions (e.g.  $\text{NO}_2 +$   
 449  $\text{OH}^- \rightarrow \text{NO}_3^-$ ) following photolysis will generate an exchange of O (see DI reactions in Fig. 2,

450 Jacobi and Hilker, 2007) suggesting that any measured estimation of  $^{18}\epsilon$  will represent the  
451 combined effect of both the photolytic fractionation and secondary reactions (McCabe et al.,  
452 2005; Erbland et al., 2013). For the purpose of this study,  $^{15}\epsilon$  and  $^{18}\epsilon$  were set to  $-48$  and  $2$  ‰,  
453 respectively (McCabe et al., 2005; Frey et al., 2009). Furthermore, a sensitivity test covering a  
454 range from  $0$  to  $-70$  ‰ for  $^{15}\epsilon$  and  $10$  to  $-50$  ‰ for  $^{18}\epsilon$  was also performed to evaluate the actual  
455 influence of different photolytic fractionations on the results.

456 Furthermore, three  $\delta_{\text{atm}}$  deposition scenarios for each isotope composition,  $\delta(^{15}\text{N})$  and  
457  $\delta(^{18}\text{O})$ , were evaluated with the aim of establishing the most likely input source, so called “end-  
458 member”, signatures for any dry deposition. For  $\delta_{\text{atm}}(^{15}\text{N})$  these scenarios were set to resemble: I)  
459 the local biogeochemical signal ( $+5$  ‰), II) the ambient atmospheric signal ( $-13$  ‰) described  
460 for Ny-Ålesund by Amoroso et al. (2010), and III) the influence of Polar basin air ( $-20$  ‰)  
461 suggested by Morin et al. (2009). For  $\delta_{\text{atm}}(^{18}\text{O})$  the scenarios were set to resemble: I) the low  
462  $\delta(^{18}\text{O})$  signal found in  $\text{HNO}_3$  at Summit, Greenland ( $+40$  ‰) due to the interaction with OH  
463 during  $\text{NO}_x$ -cycling and removal (see Fig. 2, Jarvis et al., 2009), II) the mid-latitude  $\text{HNO}_3$  signal  
464 ( $+75$  ‰) found in air arriving at Svalbard (Morin et al., 2009), and III) the uniquely high  $\delta(^{18}\text{O})$   
465 found for  $\text{HNO}_3$  in the polar basin atmosphere during spring due to the influence of the BrO-  
466 pathway (up to  $+100$  ‰, Morin et al., 2009).

467

### 468 3. Results

#### 469 3.1 $\text{NO}_3^-$ concentrations

470 The surface snow  $\text{NO}_3^-$  concentrations ( $c_{\text{NO}_3}$ ) during the *dark* ( $n = 14$ ) and the *spring* ( $n = 79$ )  
471 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  
472 uncertainty denotes the standard error,  $\sigma_{\bar{x}}$ ), with a total concentration range from  $0.6$  to  $6.3$   $\mu\text{mol}$

473  $\text{L}^{-1}$  (Fig. 3e). The variations among the three replicates, sampled approx. 10 m apart, were  
474 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  
475 April 9), as viewed by the occasionally increased  $\sigma_{\bar{x}}$  in Fig. 3e. The  $c_{\text{NO}_3}$  variation found is larger  
476 than the errors expected from IC analysis itself and therefore shows that local variation and the  
477 layering of the surface snow have a large influence. During both the *dark* and the *spring*  
478 campaign, several precipitation events occurred (Fig. 3e) which introduced new snow layers with  
479 event-specific  $\text{NO}_3^-$  concentration and isotopic signature. These events interrupted any trends  
480 that post-depositional processes would have introduced to the surface snow chemistry, and the  
481 spring data were therefore separated into three distinct, precipitation-free periods: April 12-21,  
482 23-26 and April 27 - May 5 (Fig. 3). Periods 1 and 2 were characterized by multiple surface  
483 snow layers, whereas period 3 followed a large ( $> 5 \text{ cm}$ ) precipitation event resulting in a  
484 relatively uniform snow surface (Fig. 3a). Period 3 was therefore considered the most reliable  
485 period for identification of  $c_{\text{NO}_3}$  and isotope composition trends.

486 For the *spring* campaign, linear regression models fitted to all three periods showed  
487 significant increases in the surface snow  $c_{\text{NO}_3}$  (Fig. 3e and Table 1), indicative of net deposition  
488 or snow-water sublimation (see section 3.4). No such changes were found during the short *dark*  
489 sampling campaign due to interrupting precipitation events. In general, all three spring periods  
490 indicated a day to day  $c_{\text{NO}_3}$  variation. To avoid any bias caused by such variation the fitted linear  
491 regression models were used to calculate initial (index: 0) and final (index: t) values of  $c_{\text{NO}_3}$  (and  
492 other relevant parameters) for each period and will be used for modelling purposes (Table 1 and  
493 2).

494 3.2  $\text{NO}_3^-$  isotopic composition

495 The  $\delta(^{15}\text{N})$  of  $\text{NO}_3^-$  ranged between  $-15.9$  and  $-13.7$  ‰ during the *dark* sampling ( $n =$   
496  $12$ ), and between  $-19.9$  and  $0.7$  ‰ during the *spring* campaign ( $n = 71$ ), averaging  $(-14.7 \pm 0.2)$   
497 ‰ and  $(-8.7 \pm 0.5)$  ‰ respectively (Fig. 3d). The  $\delta(^{18}\text{O})$  ranged between  $76.6$  and  $83.7$  ‰ during  
498 the *dark* sampling, and  $76.5$  to  $90.6$  ‰ during the *spring* campaign, averaging  $(79.2 \pm 0.6)$  ‰ and  
499  $(85.1 \pm 0.4)$  ‰ respectively (Fig. 3d). In summary, the *spring* snow has significantly elevated  
500 values of  $\delta(^{15}\text{N})$  and  $\delta(^{18}\text{O})$  compared to the *dark* sampling ( $p\text{-value} < 0.01$ ), although both  
501 periods showed considerable variability.

502 Linear regression models revealed significant increases of  $\delta(^{15}\text{N})$  and  $\delta(^{18}\text{O})$  during  
503 period 3 (Table 1), and to a lesser extent ( $p\text{-value} = 0.08$ ) for  $\delta(^{18}\text{O})$  during period 2 (Fig. 3d and  
504 Table 1). The remaining linear regression models fitted for  $\delta(^{15}\text{N})$  and  $\delta(^{18}\text{O})$  during period 1 and  
505 2 were not significant (Fig. 3d and Table 1). In a similar manner to  $c_{\text{NO}_3}$ , the initial and final  
506  $\delta(^{15}\text{N})$  and  $\delta(^{18}\text{O})$  values were calculated for each period using the linear regression models  
507 (Table 1 and 2) to minimize the effects of daily variability upon further calculations.

### 508 3.3 Snow $\text{Br}^-$ and atmospheric $\text{O}_3$ concentrations

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

## 518 3.4 Sublimation rates

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

## 528 3.5 Air-snow fluxes

### 529 3.5.1 Surface snow net change

530 The increasing trends in surface snow  $c_{\text{NO}_3}$  indicate a net deposition of  $\text{NO}_3^-$  since snow-  
531 water sublimation was found to be low. Hence, this indicated that dry deposition rates overcome  
532 photolytic and evaporative losses. Using the calculated initial and final values of  $c_{\text{NO}_3}$  and  $V$  for  
533 each period (Table 2), all three period were confirmed to have a significant increase due to net  
534 deposition according to Eq. 2 (Table 3). Similarly the isotopic composition for the net change  
535 was calculated according to Eq. 5 (Table 3).

### 536 3.5.2 $\text{NO}_x$ , $\text{HNO}_3^-$ and p- $\text{NO}_3^-$ flux measurements

537 The mean  $\text{NO}_2$  concentrations ( $C_{\text{NO}_2}$ ) during the campaign were  $28.6$  ( $\sigma = 19.3$ )  $\text{pmol}$   
538  $\text{mol}^{-1}$  and  $28.7$  ( $\sigma = 20.3$ )  $\text{pmol mol}^{-1}$  at the upper and lower inlet, respectively (Fig. 4a).  
539 Similarly, the mean  $\text{NO}$  concentrations ( $C_{\text{NO}}$ ) were  $15.2$  ( $\sigma = 12.5$ ) and  $16.6$  ( $\sigma = 17.5$ ) at the  
540 upper and lower inlet respectively (Fig. 4b). The  $C_{\text{NO}}$  and  $C_{\text{NO}_2}$  concentrations showed

541 statistically significant diurnal cycles on some days (9-11 April, 15-16 April, 22-27 April) with  
542 amplitudes of 1-36 pmol mol<sup>-1</sup> and 3-49 pmol mol<sup>-1</sup> for C<sub>NO</sub> and C<sub>NO<sub>2</sub></sub>, respectively (Fig. 4a, b).  
543 The diurnal cycles appeared more or less symmetric with UV radiation, with maximum C<sub>NO</sub> and  
544 C<sub>NO<sub>2</sub></sub> observed between 11:00 and 13:00, reaching minima values during night-time. During  
545 periods without diurnal cycles the maximum NO and NO<sub>2</sub> concentrations were reached between  
546 18:00 and 21:00, with minimum values measured between 06:00 and 12:00 and, hence, delayed  
547 the diurnal irradiance pattern. The turbulence measurements resulted in median eddy diffusivity  
548 (*K*) of 0.2 mol m<sup>-2</sup> s<sup>-1</sup> (with the first and third quartile at 0.14 and 0.22 mol m<sup>-2</sup> s<sup>-1</sup>, respectively),  
549 and the NO<sub>x</sub>, HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> fluxes were calculated as *K* multiplied by the difference between  
550 the two inlets (as detailed in Beine et al., 2003). The 6 min NO<sub>x</sub> fluxes data (Fig. 4c) showed a  
551 median NO emission of -0.73 pmol m<sup>-2</sup> s<sup>-1</sup> (with the first and third quartile at -0.31 and -1.53  
552 pmol m<sup>-2</sup> s<sup>-1</sup>, respectively) with a median NO<sub>2</sub> emission of -0.79 pmol m<sup>-2</sup> s<sup>-1</sup> (with the first and  
553 third quartile at -0.35 and -1.62 pmol m<sup>-2</sup> s<sup>-1</sup>, respectively). The corresponding median NO  
554 deposition rates (Fig. 4c) were 0.61 pmol m<sup>-2</sup> s<sup>-1</sup> (with the first and third quartile at 0.27 and 1.18  
555 pmol m<sup>-2</sup> s<sup>-1</sup>, respectively) while the median NO<sub>2</sub> deposition was 0.83 pmol m<sup>-2</sup> s<sup>-1</sup> (with the first  
556 and third quartile at 0.38 and 1.54 pmol m<sup>-2</sup> s<sup>-1</sup>, respectively). The combined daily fluxes of NO<sub>x</sub>  
557 (*F*<sub>NO<sub>x</sub></sub>), used for comparison to the surface snow concentrations (Fig. 5b), showed an daily  
558 averaged *F*<sub>NO<sub>x</sub></sub> emissions range from -0.2 to -1.8 μmol m<sup>-2</sup> d<sup>-1</sup>, and the daily average *F*<sub>NO<sub>x</sub></sub>  
559 depositions ranged from 0.2 to 1.7 μmol m<sup>-2</sup> d<sup>-1</sup> (Fig. 5b). The resulting daily net fluxes (Σ *F*<sub>NO<sub>x</sub></sub>)  
560 ranged from -0.1 to 0.2 μmol m<sup>-2</sup> d<sup>-1</sup> (Fig. 5b).

561 The mean concentrations of HNO<sub>3</sub>, fine and coarse particulate NO<sub>3</sub><sup>-</sup> were 6.06 ± 5.32,  
562 14.33 ± 13.68 and 15.14 ± 9.53 ppt, respectively. The HNO<sub>3</sub> and the combined fine and coarse  
563 particulate NO<sub>3</sub><sup>-</sup> fluxes (*F*<sub>HNO<sub>3</sub></sub> and *F*<sub>p-NO<sub>3</sub></sub>, Fig. 5c) mostly indicated a deposition, with the mean

564 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  
565 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  $3.2 \text{ } \mu\text{mol m}^{-2}$   
566  $\text{d}^{-1}$  (Fig. 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  
567 dominated  $\Sigma F_{\text{NO}_3}$ , with particularly high rates during the precipitation event between period 2  
568 and 3 (Fig. 5c). The data also shows that fine particles ( $<2.5 \text{ } \mu\text{m}$  diameter) were responsible for  
569 much of the  $\text{p-NO}_3^-$  flux during high flux events. The sampling interval (12 or 24 h) for  $F_{\text{HNO}_3}$   
570 and  $F_{\text{p-NO}_3}$  did not allow a separation of daily emission and deposition estimates, as was achieved  
571 using the 6 minute  $F_{\text{NO}_x}$  data.

### 572 3.6 Box models

573 The photolytic rate function ( $J_{\text{NO}_3^-}$ ) showed clear diurnal variation superimposed upon a  
574 uniformly increasing trend as a consequence of the steadily rising sun (midnight sun commenced  
575 on April 18). The integrated daily surface snow flux ( $F_{J_{\text{NO}_3^-}}$ ), estimated from  $J_{\text{NO}_3^-}$  and  $c_{\text{NO}_3^-}$ ,  
576 showed emission rates of the same order of magnitude as the measured  $\Sigma F_{\text{NO}_x}$ . However,  $F_{J_{\text{NO}_3^-}}$   
577 was considerably lower than the measured  $\text{NO}_x$  emission ( $F_{\text{NO}_x}$ ). This mismatch is likely due to  
578 the estimation of  $\text{NO}_3^-$  photolysis from surface snow only being compared to measured  
579 emissions above the full snowpack.

580 The measured range of the combined  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  fluxes ( $\Sigma F_{\text{NO}_3}$ ) was of the same  
581 order of magnitude as the modelled  $\text{HNO}_3 + \text{p-NO}_3^-$  dry deposition ( $F_{\text{model(LND)}}$ ) during this  
582 *spring* campaign (Björkman et al., 2013), although the measured average  $\text{NO}_3^-$  dry deposition  
583 ( $F_{\text{tray}}$ ) showed higher spring averages than both  $F_{\text{model(LND)}}$  and the  $\Sigma F_{\text{NO}_3}$  (Fig. 5c). However,  
584 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  
585 connection with the precipitation event between period 2 and 3 was not captured by the dry  
586 deposition estimates in Björkman et al. (2013) (Fig. 5c).

## 587 4. Discussion

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

### 596 4.1 Dry deposition vs. post-depositional loss

597 A striking feature during the *spring* sampling is the significant increase of  $c_{\text{NO}_3}$  for all three  
598 sub-periods, in-between precipitation events (Table 1 and Fig. 3e), where a positive net change  
599 ( $F_{\text{net}}$ ) was confirmed for all periods using Eq. 2 (Table 3). Hence, Eq. 2 gives the overall net  
600 increase or decrease of  $c_{\text{NO}_3}$ , where the most likely surplus would be due to an  $\text{NO}_3^-$  addition by  
601 dry deposition as long as snow sublimation is low. The measured sublimation rates during the  
602 three periods were low and could only have changed the daily  $c_{\text{NO}_3}$  by a modest quantity  
603 (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  
604 (average  $11.1 \pm 1.6$  %, for the same periods). Similarly, the model photolysis rate ( $J_{\text{NO}_3^-}$ ) could  
605 only have changed the daily  $c_{\text{NO}_3}$  by a 0.2 to 0.4 % reduction, indicating a very minor influence  
606 of photolysis on these daily variations. Of course,  $\text{HNO}_3$  evaporation and HONO emissions  
607 could further influence the daily variations. However, both these processes require a surplus of  
608  $\text{H}^+$ , whereas Ny-Ålesund snow is typically alkaline (Beine et al., 2003; Amorosso et al., 2006)  
609 with a high sea-salt content given the close proximity to the fjord. Furthermore, the  $\text{NO}_2^-$  levels

610 where below the detection limit of the IC measurements (data not shown) further indicating low  
611 HONO production. The limited occurrence of sublimation, modelled  $J_{\text{NO}_3^-}$  and positive  $F_{\text{net}}$   
612 collectively therefore indicate that the addition of  $\text{NO}_3^-$  through dry deposition outweighed any  
613 changes induced by photolytic and/or evaporative loss processes. The estimated  $F_{\text{net}}$  for the three  
614 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  
615 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  
616 by Björkman et al. (2013). However, these are slightly higher than the average modelled dry  
617 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  
618 slightly higher than the value Beine et al. (2003) found for Ny-Ålesund ( $\sim 0.2 \mu\text{mol m}^{-2} \text{d}^{-1}$ )  
619 during an previous spring, using a diffusion line sampling technique.

620 The  $\delta(^{15}\text{N})$  and  $\delta(^{18}\text{O})$  composition of the net change ( $\delta_{\text{net}}$ ), as calculated by Eq. 5, differed  
621 between the three sub-periods (Table 3). Regarding the  $F_{\text{net}}$ , no major influence of loss processes  
622 was found for periods 1 and 2, since any fractionation during post-depositional loss would have  
623 led to an  $\delta_{\text{net}}(^{15}\text{N})$  increase in  $\text{NO}_3^-$ . In contrast, period 1 and 2 showed negative  $\delta_{\text{net}}(^{15}\text{N})$  values  
624 of  $-8.2 \pm 13.6$  and  $-12.2 \pm 18.8$  ‰, respectively, even though the validity of these estimates are  
625 reduced by the non-significant regressions used for calculation. One might argue that the  
626 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  
627 indicative of post-depositional loss. This would, however, contradict the significant  $c_{\text{NO}_3}$  increase  
628 and positive  $F_{\text{net}}$  observed for this period (Table 3), therefore alternative explanations need to be  
629 considered, as attempted through box modelling below. The  $\text{NO}_3^-$   $\delta_{\text{net}}(^{18}\text{O})$  found for period 1,  
630 even though the linear regression was non-significant, was lower than the isotope delta of the  
631 snow (Table 3), whereas for periods 2 and 3 the  $\delta_{\text{net}}(^{18}\text{O})$  approached the upper limit found for  
632 atmospheric  $\text{HNO}_3$  in this region (100 ‰, Morin et al., 2009). The isotopic signature of snow

633  $\text{NO}_3^-$  is, however, influenced by several co-occurring processes as discussed in the introduction  
634 and viewed in Fig. 2 and will be further investigated in section 4.3.

#### 635 4.2 $\text{NO}_x$ , $\text{HNO}_3^-$ and p- $\text{NO}_3^-$ flux measurements

636 The flux measurements revealed both emissions and deposition fluxes of all the investigated  
637 compounds ( $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{HNO}_3^-$  and p- $\text{NO}_3^-$ , Fig. 4 and 5) and where the mean  $\text{NO}$  and  $\text{NO}_2$   
638 concentrations were in agreement with other measurements in the coastal Arctic boundary layer  
639 during the same time of year (Allegrini et al., 1999; Beine et al., 2001; 2002b; Amoroso et al.,  
640 2010; Sander and Bottenheim, 2012). Although the calculated daily  $\text{NO}$  and  $\text{NO}_2$  fluxes (Fig. 5)  
641 are in the lower region of what has earlier been reported for Ny-Ålesund by Amoroso et al.  
642 (2010), the occasional diurnal cycling of  $\text{NO}$  and  $\text{NO}_2$  observed confirms previous studies  
643 carried out at Ny-Ålesund (Beine et al., 1996 and 1997). Also the daily average  $\text{HNO}_3$  flux  
644 measured in 2010 are within the variability of earlier estimates for Ny-Ålesund (Beine et al.,  
645 2003; Amoroso et al., 2010), but substantially lower than the episode with exceptionally high  
646 deposition fluxes (up to  $1.5 \mu\text{mol m}^{-2} \text{h}^{-1}$ ) reported by Amoroso et al. (2010).

647 Due to coastal location of Ny-Ålesund, the chemical composition of snow was dominated by  
648 a marine influence. As a result of sea salt inputs, and to a lesser extension of dust, the ionic  
649 balance of snow revealed an alkaline character for 44% of the daily snow samples (with pH  
650 values between 7.80 and 8.70) which, according to Beine et al. (2003 and 2008), could lead to a  
651 reduced  $\text{NO}_x$  emission and even to an increased deposition. In addition, it is worth noting that  
652 33% and 41% of all available 6-min  $\text{NO}$  and  $\text{NO}_2$  fluxes (about 5000 values), respectively, were  
653 positive values, indicating that a  $\text{NO}_x$  deposition to the snow surface occurred, as observed in  
654 earlier polar studies (e.g: Beine et al., 2002, Amoroso et al., 2010). It has previously been shown  
655 that the intricate system of  $\text{NO}_3^-$  photolysis and  $\text{NO}_x$  emission is followed by a subsequent  $\text{HNO}_3$

656 deposition, producing a diurnal pattern at Summit, Greenland, with day-time emission and night  
657 time deposition (Hastings et al., 2004). A similar feature can be observed in our 2010 flux data,  
658 were the NO and NO<sub>2</sub> emission during periods of high irradiance can be on the same order of  
659 magnitude as the total HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> deposition. Indicating that, for this almost alkaline  
660 snow environment, the NO<sub>x</sub> emissions were reduced or close to zero. Thus, the measured fluxes  
661 of NO<sub>x</sub>, HNO<sub>3</sub> and p-NO<sub>3</sub><sup>-</sup> are neither sufficient to explain the observed c<sub>NO3</sub> increase. In the  
662 following section we will further focus on separating and explaining the processes influencing  
663 the surface snow, using the box model to find the most likely sources of the observed NO<sub>3</sub><sup>-</sup>  
664 deposition and its isotopic signature.

#### 665 4.3 Reproducing observed trends

666 In the box model used here, describing the main source and sink of NO<sub>3</sub><sup>-</sup> in the snow (section  
667 2.4.2), all outgoing fluxes are assumed to be due to photolysis and all incoming fluxes due to  
668 HNO<sub>3</sub> dry deposition. As a consequence of the day-to-day variability of isotope deltas and c<sub>NO3</sub>,  
669 our comparison between model and measured data focuses on the regression analysis for the  
670 three precipitation-free spring periods, bearing in mind the lower p-values for the trends in δ(<sup>15</sup>N)  
671 and δ(<sup>18</sup>O) of snow NO<sub>3</sub><sup>-</sup> during period 1 and 2 (Table 1 and Fig. 3).

##### 672 4.3.1 Box model using F<sub>NOx</sub> and F<sub>NO3</sub>

673 The box model (Eq. 16) shows that the measured net fluxes of NO<sub>x</sub> (Σ F<sub>NOx</sub>, Fig 5b) and  
674 HNO<sub>3</sub> + p-NO<sub>3</sub><sup>-</sup> (Σ F<sub>NO3</sub>, Fig 5c) were insufficient to alter the surface snow c<sub>NO3</sub> significantly  
675 during periods 1 and 2 (Fig. 6c, noting the atmospheric flux measurements were terminated on  
676 April 27, just prior to period 3). The small change in c<sub>NO3</sub> such daily net fluxes would induce was  
677 below the detection limit of the snow sampling procedure used here. A similar conclusion was

678 reached by Beine et al., (2003) when they compared atmospheric dry deposition estimates with  
679 the surface snow  $\text{NO}_3^-$  concentrations.

680 In spite of the limited ability of the atmospheric flux driven model to reproduce the  
681 surface snow  $c_{\text{NO}_3}$  trends, the modelled influence on  $\delta(^{18}\text{O})$  and  $\delta(^{15}\text{N})$  was more pronounced  
682 (using Eq. 17, Fig. 6). This is especially the case during the first day of period 1, when p- $\text{NO}_3^-$   
683 emission (Fig. 5c) resulted in an increased modelled  $\delta(^{18}\text{O})$ , and where the  $\delta_{\text{atm}}(^{18}\text{O})$  scenarios  
684 +40 and +100 ‰ followed the very lower and upper limit of the data variability for the rest of  
685 period 1 (Fig. 6a). Although particle emission from snow might be limited (Cadle, 1991), some  
686 re-suspension of particles by wind is possible (Barrie et al., 1998). During period 2 neither of the  
687  $\delta_{\text{atm}}(^{18}\text{O})$  scenarios followed the observed  $\delta(^{18}\text{O})$  pattern. For periods 1 and 2, the modelled  $\delta(^{15}\text{N})$   
688 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  
689 fact, model results for all three  $\delta_{\text{atm}}(^{15}\text{N})$  scenarios were well within the data variability and did  
690 not deviate much from each other (Fig. 6b). Overall, none of the  $\delta_{\text{atm}}$  scenarios and emission  
691 fractionations, including the sensitivity test for different fractionations ( $^{15}\epsilon$  and  $^{18}\epsilon$ , section 2.4.2),  
692 reproduced the observed trends in a satisfactory way. This is probably due to the many layers  
693 found in the sampled surface snow during period 1 and 2, that can yield large daily variations in  
694  $\delta(^{15}\text{N})$  and  $\delta(^{18}\text{O})$ . It is especially troublesome that the observed  $c_{\text{NO}_3}$  trends (Table 1) and  
695 calculated dry deposition rates (Table 3) cannot be explained by the atmospheric flux in the box  
696 model. A possible explanation could be a re-deposition of  $\text{NO}_x$ ,  $\text{HNO}_3^-$  and HONO emitted from  
697 deeper within the snowpack, or the soil below, to the surface snow layer. Such a sub-surface  
698 source would then not necessarily need to involve an emission to the atmospheric boundary  
699 layer, thus could impact the surface snow measurements of  $\text{NO}_3^-$  deposition but not the  
700 atmospheric flux measurements as a result.

#### 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 (Eq. 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 modelled photolysis ( $J_{\text{NO}_3^-}$ ) was used in conjunction with  $F_{\text{model(LND)}}$ , Fig. S2. This box modelling attempt, and a third approach, using  $J_{\text{NO}_3^-}$  in conjunction with  $F_{\text{tray}}$ , Fig. 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 (Fig. 7), attributing the addition through dry deposition to have a prevailing role over photolytic and, probably, evaporative loss.

For the isotopic composition the models (Eq. 14 and 15) seems to have had a clear negative influence upon the surface  $\delta(^{15}\text{N})$  signature during periods 1 and 2 (Fig. 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 (Fig. 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 re-deposition 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 mid-latitude spring values for the U.S. (Elliott et al., 2009). For period 3, the air mass back-trajectories are more stagnant

724 around Svalbard, with a south-easterly influence at the end of this period. This indicates that the  
725 high end-member found for period 3 could also be influenced by local or European emission  
726 sources, and is not necessarily solely a biogeochemical signal.

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

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

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

#### 747 4.4 O<sub>3</sub> and BrO interaction

748 During the *spring* campaign several O<sub>3</sub> depletion events (ODE) occurred; on April 13, 21  
749 – 22, 26 – 27 and April 30 – May 1 (Fig. 3b). Such events are known in the Arctic as a result of  
750 active halogen chemistry where Br<sub>2</sub>, BrCl or Cl<sub>2</sub> (ultimately of oceanic origin, whose release is  
751 believed to involve snow and first-year sea-ice) are released in to the boundary layer. Their rapid  
752 photolysis by solar radiation forms Br or Cl radicals, which then initiates a chain reaction  
753 depleting O<sub>3</sub> (Fig. 2, e.g. Foster et al., 2001; Simpson et al., 2007; Abbatt et al., 2012). For Ny-  
754 Ålesund, studies typically observe such events as a consequence of the advection of air masses  
755 already depleted in O<sub>3</sub>, originating from the polar basin (e.g. Barrie and Platt, 1997), where low  
756 levels of boundary layer O<sub>3</sub> are typical during spring (Hopper et al., 1994; Hopper et al., 1998;  
757 Jacobi et al., 2010). This is consistent with the ODEs observed during the spring 2010, where  
758 more northerly air flows occur prior to the ozone depletion episodes (Fig. 3) and where satellite  
759 data (Begoin et al., 2010) reveals increased BrO column abundances concurrent with the ODE's  
760 (Fig. S3). Alongside its impact on boundary layer O<sub>3</sub>, BrO can also influence NO<sub>x</sub>-cycling and  
761 its transformation to HNO<sub>3</sub>, via the formation and hydrolysis of BrONO<sub>2</sub>. This generates a  
762 uniquely high  $\delta(^{18}\text{O})$  (Fig. 2, e.g. Evans et al., 2003; Morin et al., 2007b).

763 For period 2 a northerly airflow was observed which can explain both the low  $\delta(^{15}\text{N})$   
764 (photolytic produced NO<sub>x</sub> from polar basin snowpacks) and the high  $\delta(^{18}\text{O})$  (BrO-pathway) end-  
765 member (Morin et al., 2009). However, for period 3, when the airflow is stagnant or south-  
766 westerly, with only a minor influence of polar basin air, the high  $\delta(^{18}\text{O})$  end-member would need  
767 to have another explanation. Interestingly the Br<sup>-</sup> concentrations ( $c_{\text{Br}^-}$ ) in the surface snow are  
768 high during period 1, decrease during period 2, then remain low and slightly decrease further  
769 during period 3 (Fig. 3b and Table 1). There is also a significant ( $p < 0.05$ ) negative correlation

770 between the daily averages of  $c_{\text{Br}}$  and  $c_{\text{NO}_3}$  ( $R = -0.84$ ) during period 3, as well as between  $c_{\text{Br}}$   
771 and  $\delta(^{15}\text{N})$  and  $\delta(^{18}\text{O})$  ( $R = -0.91$  and  $-0.83$ , respectively). According to the BrO-pathway in Fig.  
772 2, formation of  $\text{BrONO}_2$  from  $\text{BrO} + \text{NO}_2$  can be followed by a photolytic dissociation, or –  
773 particularly under conditions of high surface area – be followed by hydrolysis whereby  $\text{BrONO}_2$   
774 disintegrates into  $\text{HNO}_3$  and  $\text{HOBr}$  on ice crystals (Evans et al., 2003; Morin et al., 2007b). This  
775 latter case thereby converts  $\text{NO}_x$  into  $\text{HNO}_3$ . Assuming that this reaction occurs within the snow  
776 or just above, the newly formed  $\text{HOBr}$  would further react with  $\text{Br}^-$  ions in the DI with a release  
777 of gaseous  $\text{Br}_2$  as a result (e.g. Simpson et al., 2007; Abbatt et al., 2012). In the presence of a  
778  $\text{NO}_x$ ,  $\text{HNO}_3$  or  $\text{HONO}$  supply from deeper within the snowpack (i.e. photolysis, evaporation or  
779 biologic emissions from the snow or soil), this BrO- $\text{NO}_x$  chemistry would rapidly re-deposit the  
780  $\text{NO}_x$  as  $\text{HNO}_3$  in the surface snow. This would then minimize any snowpack emissions and, in  
781 the case of negligible local soil emissions, keep the total snow  $\text{NO}_3^-$  budget un-altered. This  
782 coupled BrO- $\text{NO}_x$  chemistry can explain both the decrease in  $\text{Br}^-$  concentration in the surface  
783 snow as well as the increasing  $\delta(^{18}\text{O})$  and  $c_{\text{NO}_3}$  values observed in the surface snow during period  
784 2 and 3. This is the first time such coupling has been observed in Svalbard, although increasing  
785 BrO levels have earlier been reported above Ny-Ålesund snow following an ODE (Avallone et  
786 al., 2003). To start the BrO production and following chain reactions, an initial pulse (or “seed”)  
787 of reactive halogens is needed (Simpson et al., 2007). It is however, unlikely that the BrO  
788 cycling seen in our  $c_{\text{Br}}$  and  $\delta(^{18}\text{O})$  data, and in the BrO record from Avallone et al., (2003) are  
789 initiated locally. They are likely rather results of polar basin air advection providing “seed”  
790 halogens during the observed ODEs, which then initiate the local BrO production. This  
791 hypothesis is further strengthened by the column content of BrO (Fig. S3) where the atmosphere  
792 above western Svalbard, and eastern parts of the Fram Strait, shows prevailing low BrO levels,

793 which only increases in conjunction with ODE's when surges of BrO moves into the Ny-Ålesund  
794 area. Nevertheless, during period 3, our surface snow bromide, nitrate, and  $\delta(^{18}\text{O})$  observations  
795 provide evidence for continued local (snowpack) BrO-NO<sub>x</sub> cycling, even whilst BrO column  
796 abundances decline and ambient air ozone recovers.

## 797 5. Conclusion

798 Detailed sampling of the photo-active surface zone of the Ny-Ålesund snowpack during  
799 winter and spring-time demonstrates that NO<sub>3</sub><sup>-</sup> dry deposition is the predominant process  
800 determining NO<sub>3</sub><sup>-</sup> concentrations during precipitation free periods and prevails over any NO<sub>3</sub><sup>-</sup>  
801 post-depositional loss via photolysis and HNO<sub>3</sub> evaporation within this layer. The measured dry  
802 deposition in uniform surface snow ( $0.6\pm 0.2 \mu\text{mol m}^{-2} \text{d}^{-1}$ ) is in line with previously reported  
803 values for Ny-Ålesund (Björkman et al., 2013). However, it indicates greater net deposition than  
804 that derived from cumulative NO<sub>x</sub>, HNO<sub>3</sub><sup>-</sup> and p-NO<sub>3</sub><sup>-</sup> fluxes, measured 200 m from the sampling  
805 site. Given its permeable nature, we emphasize that the snowpack should be considered as an  
806 integral part of the atmospheric boundary layer, allowing relevant reactions (Fig. 2) to occur  
807 within interstitial air pockets within the snow. Thus, our observed dry deposition of NO<sub>3</sub><sup>-</sup> could  
808 originate from both the overlying atmosphere and from re-deposition of NO<sub>3</sub><sup>-</sup> released from  
809 deeper within the snowpack.

810 Magnitudes and trends in surface snow  $\delta(^{15}\text{N})$  and  $\delta(^{18}\text{O})$  were compared to back-trajectory  
811 analysis and local ODEs indicative of BrO chemistry. Trajectories originating from the polar  
812 basin were found to bring <sup>15</sup>N-depleted air masses to Svalbard, confirming findings from an  
813 earlier atmospheric study of NO<sub>3</sub><sup>-</sup> in Ny-Ålesund aerosol (Morin et al., 2009), and demonstrating  
814 that such NO<sub>3</sub><sup>-</sup> is deposited to the snowpack. Stagnant air and air masses originating from mid-  
815 latitude regions were related to <sup>15</sup>N-enriched dry NO<sub>3</sub><sup>-</sup> deposition with an end-member of

816 (+7.0±0.7) ‰. Such positive  $\delta(^{15}\text{N})$  values have previously been found in European and U.S. air  
817 (Elliott et al., 2009; Morin et al., 2009), probably as a result of anthropogenic emissions (e.g.  
818 Kendall et al., 2007), but can also result from in-situ biogeochemical cycling of clay-bound  $\text{NH}_4^+$   
819 (Amoroso et al., 2010).

820 The average  $\delta(^{18}\text{O})$  values were lower during the winter-time compared to spring-time, when  
821  $\text{NO}_3^-$  deposition from polar basin air masses only exhibited positive  $\delta(^{18}\text{O})$  trends in conjunction  
822 with low  $\text{O}_3$  levels. These conditions indicate active halogen cycling and demonstrate the  
823 importance of  $\text{NO}_x$  to  $\text{NO}_3^-$  formation via coupled BrO- $\text{NO}_x$  chemistry (as identified in Ny-  
824 Ålesund aerosol: Morin et al., 2009) for snow  $\text{NO}_3^-$  deposition. Furthermore, we identify  
825 evidence for such BrO chemistry occurring within the snowpack (interstitial air pockets) itself,  
826 and demonstrate its active involvement in the  $\text{NO}_3^-$  post-depositional cycling, as evidenced by  
827 steadily decreasing snow  $\text{Br}^-$  content and increasing  $\delta(^{18}\text{O})$  and  $\text{NO}_3^-$  concentration in surface  
828 snow samples. These are the first observations of such snowpack BrO- $\text{NO}_x$  coupling in this part  
829 of the Arctic. However, as indicated both by this and a previous study (Avallone et al., 2003),  
830 local BrO production is concomitant with the arrival of BrO active  $\text{O}_3$ -depleted air, which  
831 contributes the necessary “seed” halogens to get the local production initiated (Simpson et al.,  
832 2007). This production might explain the uniquely high  $\delta(^{18}\text{O})$  end-member (+105.9±72.3 ‰)  
833 found even during stagnant and south-easterly air influences, regions usually associated with  
834 higher  $\text{O}_3$  levels.

835 In summary, our study demonstrates how careful sampling of surface snow can provide  
836 useful insights regarding atmospheric and snow processes controlling the fate of reactive  
837 nitrogen in the Arctic including coupling of BrO- $\text{NO}_x$  chemistry. In particular, our results

838 elucidate the relative importance of these processes for a snowpack located in a coastal region at  
839 low altitude (Ny-Ålesund), in contrast to studies elsewhere (e.g. Greenland).

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1175 *Chemistry and Physics*, 14: 7367-7396.

1176 Table 1. Fitted linear regression models ( $y=kx+m$ ) for the three periods (Fig. 4)\*.

Model	Period	$k$	$m$	$n$	$R^2$	p-value	Unit
$c_{NO_3}$	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	$\mu\text{mol L}^{-1}$
$c_{Br}$	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	<< 0.01	$\text{nmol L}^{-1}$
$c_{Cl}$	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	$\mu\text{mol L}^{-1}$
$c_{Na}$	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	‰
$z_{SWE}$	1	0.1	-8.2	30	0.50	<< 0.01	cm
	2	0.03	-2.0	12	0.02	0.63	cm
	3	0.2	-21.1	26	0.88	<< 0.01	cm
$V$	1	4.0	-346.8	30	0.50	<< 0.01	mL
	2	-0.7	-157.3	12	0.01	0.80	mL
	3	7.8	-896.6	26	0.88	<< 0.01	mL

1177 \*Regression models were analyzed for the  $\text{NO}_3^-$  concentration ( $c_{NO_3}$ ),  $\text{Br}^-$  concentration ( $c_{Br}$ ),  
 1178  $\text{Cl}^-$  concentration ( $c_{Cl}$ ),  $\text{Na}^+$  concentration ( $c_{Na}$ ), the  $\text{NO}_3^-$  isotopic composition ( $\delta(^{15}\text{N})$  and  
 1179  $\delta(^{18}\text{O})$ ), the surface snow water equivalence ( $z_{SWE}$ ), and the sample volume ( $V$ ). Also given are  
 1180 the numbers of measurements ( $n$ ) used for each regression, the multiple  $R^2$  value for the models,  
 1181 and the significance (p-value) of the slope  $k$ .

1182 Table 2. Calculated initial ( $\theta$ ) and final ( $t$ ) values from the regression model in Table 1.

<b>Model</b>	<b>Period</b>	$\theta$	$t$	<b>Unit</b>
$C_{NO_3}$	1	1.1±0.2	1.8±0.2	μmol L <sup>-1</sup>
	2	1.4±0.1	1.9±0.1	μmol L <sup>-1</sup>
	3	1.7±0.1	2.3±0.1	μmol L <sup>-1</sup>
$\delta(^{15}N)$	1	-5.3±1.8	-6.5±1.7	‰
	2	-7.4±1.7	-8.7±1.7	‰
	3	-12.9±0.6	-8.0±0.6	‰
$\delta(^{18}O)$	1	84.0±1.2	83.4±1.2	‰
	2	85.2±0.9	88.0±0.9	‰
	3	83.0±0.9	88.7±0.9	‰
$z_{SWE}$	1	1.3±0.1	2.2±0.1	cm
	2	1.7±0.1	1.8±0.1	cm
	3	0.4±0.1	1.8±0.1	cm
$V$	1	57.2±4.0	92.9±4.0	mL
	2	73.4±5.2	71.2±5.2	mL
	3	15.6±2.9	78.0±2.9	mL

1183

1184 Table 3. Calculated net change of  $\text{NO}_3^-$  ( $F_{\text{net}}$ ) and isotopic signatures ( $\delta(^{15}\text{N})$  and  $\delta(^{18}\text{O})$ ).

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

1185 \* calculated from Eq. 2

1186 # calculated from Eq. 5.

1187

1188 Figure captions:

1189

1190 Figure 1. Maps of a) the Ny-Ålesund region and b) the Svalbard archipelago. Included in a) as a  
1191 star is the surface snow sampling site and "Gruvebadet" (a newly established research site), the  
1192 Amundsen-Nobile Climate Change Tower (CCT) and the Zeppelin Station. In b) the most  
1193 commonly used ice-core drilling sites (Holtedahlfonna, Lomonosovfonna and Austfonna) are  
1194 given along with the major settlements (Longyearbyen, Barentsburg, Svea, Ny-Ålesund and  
1195 Hornsund).

1196

1197 Figure 2. A schematic of the processes important for  $\text{NO}_3^-$  dynamics in Svalbard surface snow.

1198

1199 Figure 3. Nitrate concentrations ( $c_{\text{NO}_3}$ ) and isotopic signatures ( $\delta(^{15}\text{N})$  and  $\delta(^{18}\text{O})$ ) of the daily  
1200 surface snow samples in 2010. Including; a) a schematic sketch of the visible layering found in  
1201 the sampled surface snow; b) the atmospheric  $\text{O}_3$  concentration ( $c_{\text{O}_3}$ ) measured at the Zeppelin  
1202 Station and at Gruvebadet, along with surface snow  $\text{Br}^-$  concentrations ( $c_{\text{Br}^-}$ ); c) a schematic  
1203 sketch of 7 days back-trajectories obtained from the FLEXTRA model, where arrows indicate  
1204 flow paths and circles indicate stagnant air; d) the measured  $\delta(^{15}\text{N})$  and  $\delta(^{18}\text{O})$  in the surface  
1205 snow, and; e) the measured  $c_{\text{NO}_3}$  in the surface snow together with the registered precipitation in  
1206 Ny-Ålesund. Furthermore, error bars indicates standard error ( $\sigma_{\bar{x}}$ ), \* indicate samples where  $\sigma_{\bar{x}}$   
1207 is calculated from only two data points, and symbols without error bars indicates one replicate.  
1208 Solid lines represent significant linear regression models ( $lm$ ,  $p$ -value  $< 0.05$ ), while broken lines  
1209 equal non-significant trends ( $p$ -value  $> 0.05$ ).

1210

1211 Figure 4. Measured flux data (6 minute resolution) from Gruvebadet during the spring campaign  
1212 2010. Including; a) the  $\text{NO}$  concentrations ( $C_{\text{NO}}$ ) at the upper and lower inlets; b) the  $\text{NO}_2$   
1213 concentrations ( $C_{\text{NO}_2}$ ) at the upper and lower inlets; c) the  $\text{NO}$  and  $\text{NO}_2$  flux data ( $F_{\text{NO}}$  and  $F_{\text{NO}_2}$ ,  
1214 respectively) derived from the difference between the upper and lower inlets and the eddy  
1215 diffusivity,  $K$ .

1216

1217 Figure 5. Measured and modelled  $\text{NO}_x$ ,  $\text{HNO}_3$  and  $\text{p-NO}_3^-$  fluxes measured at Gruvebadet.  
1218 Where; a) is the photolytic rate ( $J_{\text{NO}_3^-}$ ) estimated from Eq. 7; b) is the daily average emission and  
1219 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  
1220 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  
1221 Fig. 3e; c) is 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  
1222 the net flux of these ( $\Sigma F_{\text{NO}_3^-}$ ), also included is the measured ( $F_{\text{tray}}$ ) and modelled ( $F_{\text{model(LND)}}$ )  
1223  $\text{NO}_3^-$  dry deposition to Ny-Ålesund given in Björkman et al. (2013).

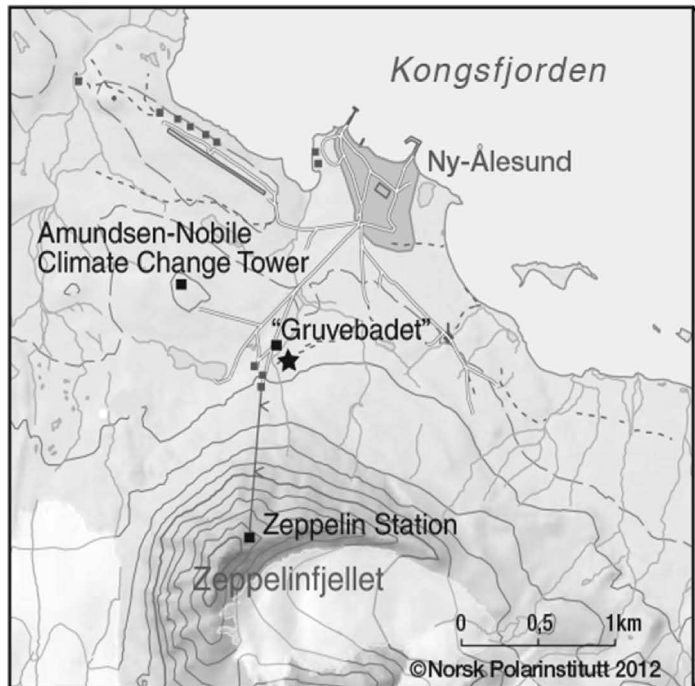
1224

1225 Figure 6. Box model results, using the  $\text{NO}_x$ ,  $\text{HNO}_3^-$  and  $\text{p-NO}_3^-$  flux measurements. Given in a) is  
1226 the modeled  $\delta_t$  for  $^{18}\text{O}$  (Eq. 13) for the three isotopic deposition scenarios ( $\delta_{\text{atm}}$ ) where; + 40 ‰  
1227 resembles the OH signal found in Greenland (Jarvis et al., 2009); + 75 ‰ resembles a mid-  
1228 latitude signal (Morin et al., 2009); and + 100 ‰ resembles the influence of BrO chemistry  
1229 (Morin et al., 2009). Also included in a) is the actual measured  $\delta(^{18}\text{O})$  and co-occurring linear  
1230 regression models ( $lm$ , Table 1). Similarly b) gives the modeled  $\delta_t$  for  $^{15}\text{N}$  (Eq. 13) for the three  
1231 isotopic deposition scenarios ( $\delta_{\text{atm}}$ ) where; - 20 ‰ represents Polar basin air (Morin et al., 2009);

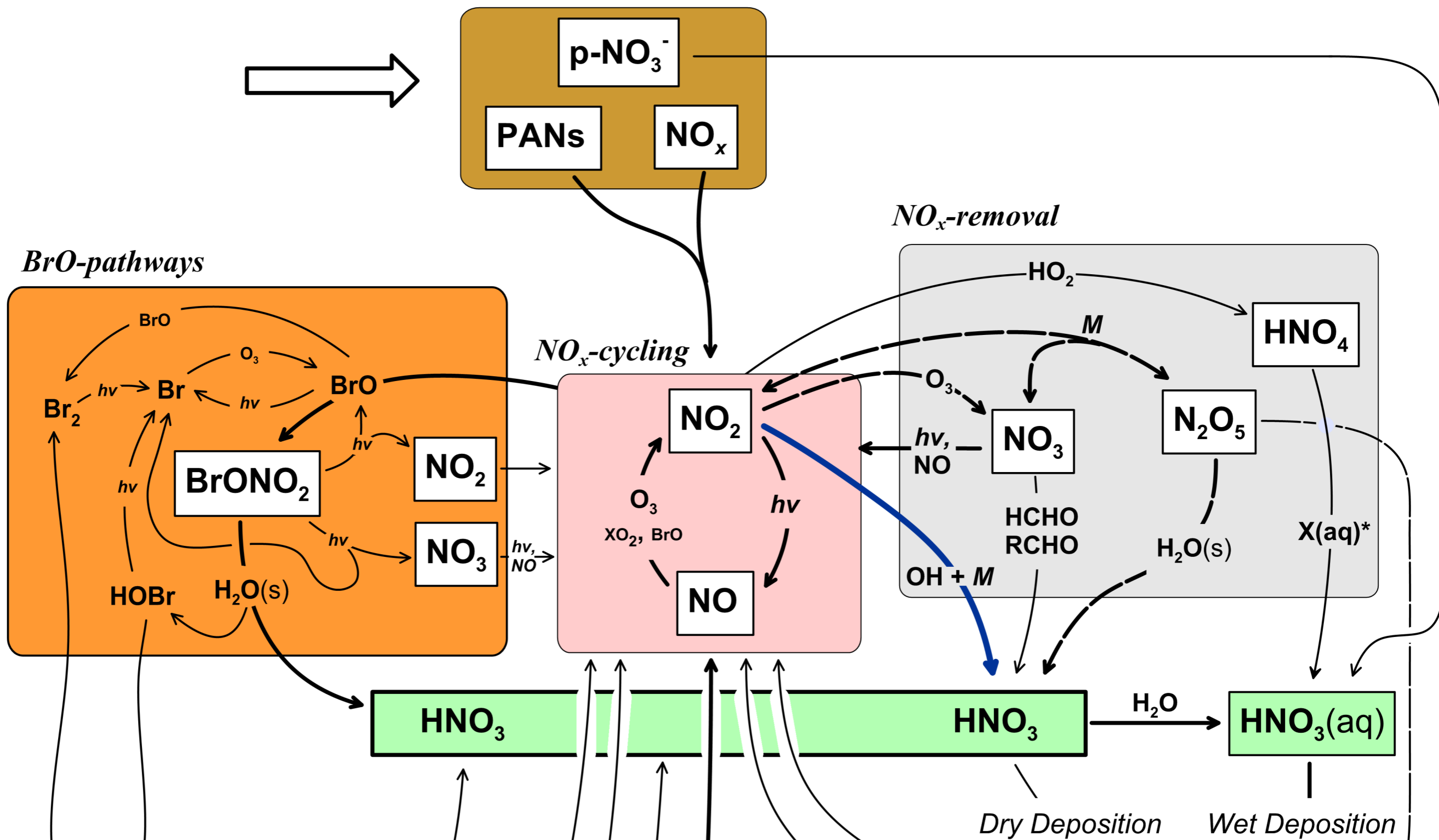
1232 – 13 ‰ represent ambient air (Amoroso et al., 2010); and + 5 ‰ represents a local  
1233 biogeochemical signal (Amoroso et al.,2010). Also included in b) is the measured  $\delta(^{15}\text{N})$  and  
1234 developed  $lm$ 's. Given in c) is the modeled  $c_t$  (Eq. 16) along with the measured  $c_{\text{NO}_3}$  and  $lm$ 's.  
1235 Furthermore, the fractionation sensitivity test is included as shaded areas around the box model  
1236 results in a) and b).

1237 Figure 7. Same as Fig. 6 but where the box model parameterization for three mission of  $\text{NO}_x$   
1238 from the snow-pack is based on the photolytic rate function ( $J_{\text{NO}_3}$ , Eq. 7) and the deposition of  
1239 nitrate from the atmosphere based on the dry deposition rate ( $F_{\text{tray}}$ ) using Eq. 11 and 12.

1240

**a)****b)**

**Atmospheric boundary layer  
snowpack interstitial air pockets**



**Snowpack**

**Biogeochemical cycling**

