



**HAL**  
open science

## Changes to the chemical state of the northern hemisphere atmosphere during the second half of the twentieth century

Mike Newland, Patricia Martinerie, Emmanuel Witrant, Detlev Helmig, David Worton, Chris Hogan, William Sturges, Claire Reeves

► **To cite this version:**

Mike Newland, Patricia Martinerie, Emmanuel Witrant, Detlev Helmig, David Worton, et al.. Changes to the chemical state of the northern hemisphere atmosphere during the second half of the twentieth century. Atmospheric Chemistry and Physics Discussions, 2016, 10.5194/acp-2016-927. hal-01411413

**HAL Id: hal-01411413**

**<https://hal.science/hal-01411413>**

Submitted on 17 Mar 2022

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License



1 **Changes to the chemical state of the northern hemisphere**  
2 **atmosphere during the second half of the twentieth century**

3  
4 **Mike J. Newland<sup>1</sup>, Patricia Martinerie<sup>2</sup>, Emmanuel Witrant<sup>3</sup>, Detlev Helmig<sup>4</sup>, David**  
5 **R. Worton<sup>5</sup>, Chris Hogan<sup>1</sup>, William T. Sturges<sup>1</sup>, Claire E. Reeves<sup>1</sup>**

6 [1] {Centre for Ocean and Atmospheric Sciences, School of Environmental Sciences,  
7 University of East Anglia, Norwich, UK}

8 [2] {Univ. Grenoble Alpes/CNRS, LGGE, F-38000 Grenoble, France}

9 [3] {Univ. Grenoble Alpes/CNRS, GIPSA-Lab, F-38000 Grenoble, France}

10 [4] {Institute of Arctic and Alpine Research, University of Colorado, Boulder, Colorado, USA}

11 [5] {National Physical Laboratory, Teddington, Middlesex, UK}

12 Correspondence to: M. J. Newland (m.newland@uea.ac.uk)

13

14 **Abstract**

15 **The NO<sub>x</sub> (NO and NO<sub>2</sub>) and HO<sub>x</sub> (OH and HO<sub>2</sub>) budgets of the atmosphere exert a major**  
16 **influence on atmospheric composition, controlling removal of primary pollutants and**  
17 **formation of a wide range of secondary products, including ozone, that can influence**  
18 **human health and climate. However, there remain large uncertainties in the changes to**  
19 **these budgets over recent decades. Due to their short atmospheric lifetimes, NO<sub>x</sub> and HO<sub>x</sub>**  
20 **are highly variable in space and time, and so the measurements of these species are of very**  
21 **limited value for examining long term, large scale changes to their budgets. Here, we take**  
22 **an alternative approach by examining long-term atmospheric trends of alkyl nitrates, the**  
23 **formation of which is dependent on the atmospheric NO/HO<sub>2</sub> ratio. We derive long term**  
24 **trends in the alkyl nitrates from measurements in firn air from the NEEM site, Greenland.**  
25 **Their mixing ratios increased by a factor of 4 – 5 between the 1970s and 1990s. This was**  
26 **followed by a steep decline to the sampling date of 2008. Moreover, we examine how the**  
27 **trends in the alkyl nitrates compare to similarly derived trends in their parent alkanes**  
28 **(i.e. the alkanes which, when oxidised in the presence of NO<sub>x</sub>, lead to the formation of the**  
29 **alkyl nitrates). The ratios of the alkyl nitrates to their parent alkanes increase from**



1 **around 1970 to the late 1990's consistent with large changes to the [NO]/[HO<sub>2</sub>] ratio in**  
2 **the northern hemisphere atmosphere during this period. These could represent historic**  
3 **changes to NO<sub>x</sub> sources and sinks. Alternatively, they could represent changes to**  
4 **concentrations of the hydroxyl radical, OH, or to the transport time of the air masses from**  
5 **source regions to the Arctic.**

6

## 7 **1 Introduction**

8 The NO<sub>x</sub> (NO + NO<sub>2</sub>) and HO<sub>x</sub> (OH + HO<sub>2</sub>) budgets of the troposphere act to control the  
9 concentrations of oxidants such as OH, ozone and NO<sub>3</sub> (Fig. 1). These in turn control removal  
10 of pollutants from the atmosphere. Emissions of NO<sub>x</sub> in the northern hemisphere are mainly  
11 anthropogenic, with roughly equal proportions from power generation and transport (Olivier  
12 and Berdowski et al., 2001; Olivier et al., 2001). NO<sub>x</sub> and HO<sub>x</sub> are linked through the  
13 production of ozone, which is positively correlated with NO<sub>x</sub> concentrations in the background  
14 atmosphere through the photolysis of NO<sub>2</sub> (Reactions R1-R2). The photolysis of ozone in the  
15 presence of water vapour then leads to the production of OH (Reactions R3-R4). Removal of  
16 NO<sub>x</sub> from the atmosphere is controlled by the reaction of NO<sub>2</sub> with OH during the daytime  
17 (Reaction R5). This forms nitric acid, HNO<sub>3</sub>, which is lost from the atmosphere by wet  
18 deposition. At night, and during the winter, the heterogeneous reaction of the NO<sub>x</sub> reservoir  
19 species N<sub>2</sub>O<sub>5</sub> (formed from the reaction of NO<sub>2</sub> with NO<sub>3</sub> (Reactions R6-R7) with H<sub>2</sub>O on  
20 aerosol becomes an important NO<sub>x</sub> sink (Reaction R8). OH and HO<sub>2</sub> rapidly interconvert  
21 through the reactions of OH with CO and hydrocarbons, such as alkanes, and the reaction of  
22 HO<sub>2</sub> with NO (Reaction R9). The reaction of NO with peroxy radicals (HO<sub>2</sub> and RO<sub>2</sub> –  
23 Reactions R9-R10) recycles the NO<sub>x</sub> back to NO<sub>2</sub>. The main removal processes for HO<sub>x</sub> are  
24 the reaction of OH with NO<sub>2</sub> (Reaction R9) and the reaction of HO<sub>2</sub> with peroxy radicals  
25 (including self-reaction) (Reactions R11-R12).

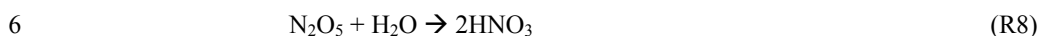
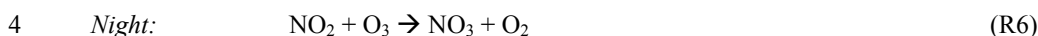
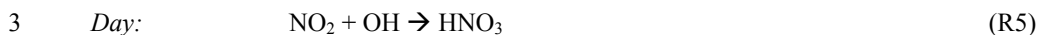
### 26 ***HO<sub>x</sub> sources***





1

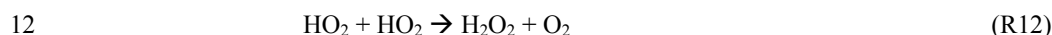
2 ***NO<sub>x</sub> sinks***



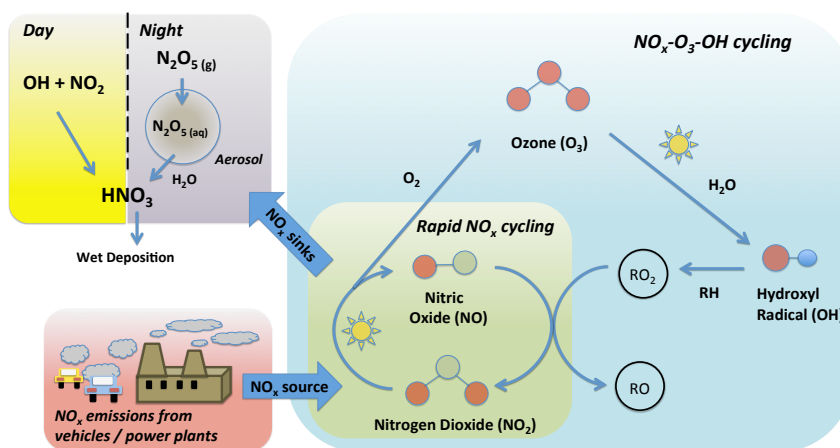
7 ***NO<sub>x</sub> and HO<sub>x</sub> recycling***



10 ***HO<sub>x</sub> sinks***



13



14

15 Figure 1 Schematic of the NO<sub>x</sub>-O<sub>3</sub>-OH relationship in the background troposphere.

16

17 However, changes to the atmospheric concentrations of both HO<sub>x</sub> and NO<sub>x</sub> during the previous  
 18 century are poorly constrained. This is because all HO<sub>x</sub> and NO<sub>x</sub> species are short lived, present  
 19 at low concentrations (0.01 – 10 ppt) and have a high spatial and temporal variability. (e.g.



1 Stone et al., 2012). This makes them difficult to measure and trends difficult to identify (based  
2 on spatially and temporally variable data sets). Furthermore, a range of state of the art  
3 atmospheric chemistry transport models give no consensus of even the sign of OH change  
4 between 1850 and 2000 (Naik et al., 2013). However, the models do agree that between 1980  
5 and 2000 there has been an increase in northern hemisphere OH concentrations, with the best  
6 estimate of the increase being  $4.6 (\pm 1.9) \%$ . This modelled increase is driven by increases in  
7 the  $\text{NO}_x$  burden and in the water vapour concentration.

8 To attempt to study historical trends in  $\text{HO}_x$  and  $\text{NO}_x$  we have examined trends in longer living  
9 species which are affected by changes to  $\text{HO}_x$  and  $\text{NO}_x$  in the atmosphere.

10 In this paper we report long term atmospheric trends of three alkyl nitrates derived from Arctic  
11 firn air. These are chemically produced in the atmosphere from the oxidation of alkanes and  
12 subsequent reaction of the peroxy radical formed with NO. The alkyl nitrate records are  
13 combined with previously reported trends of their parent alkanes from the same Arctic firn site.  
14 These records provide a proxy from which we can learn about the chemical state of the  
15 atmosphere in which they were formed.

## 16 **1.1 Alkanes**

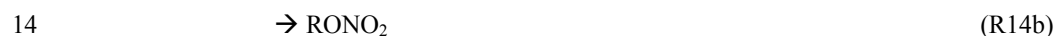
17 Emissions of butanes ( $\text{C}_4\text{H}_{10}$ ) and pentanes ( $\text{C}_5\text{H}_{12}$ ) to the atmosphere are almost entirely  
18 anthropogenic ( $> 98 \%$  globally (Poizzer et al., 2010)), associated with fugitive emissions during  
19 oil and natural gas drilling and evaporation and combustion of fossil fuels such as in road  
20 vehicles (Poizzer et al., 2010; Pétron et al., 2012; Helmig et al., 2014a). The primary removal  
21 mechanism of these species from the atmosphere is reaction with the hydroxyl radical, OH  
22 (minor sinks include reaction with atomic chlorine, Cl, and the nitrate radical,  $\text{NO}_3$ ).  
23 Atmospheric mixing ratios of butanes and pentanes display a large seasonal cycle in mid-high  
24 latitudes (e.g. Swanson *et al.*, 2003; Helmig *et al.*, 2009) due to changes in their chemical  
25 lifetimes ( $\sim 1$  month in the winter and 4 – 5 days in the summer) driven by the seasonal cycle in  
26 OH concentration. Emissions are not thought to have a significant seasonal variability (Poizzer  
27 et al., 2010).

## 28 **1.2 Alkyl Nitrates**

29 Alkyl nitrates ( $\text{RONO}_2$ ) are secondary oxidation products of the alkanes (RH). Their  
30 atmospheric lifetimes are on the order of months in winter and ten days in summer (Clemishaw



1 et al., 1997). Consequently, they display a strong seasonal cycle in the Arctic, with peaks in the  
2 late winter/early spring and minima in the summer (Swanson et al., 2003), similar to the  
3 alkanes. Alkyl nitrates are formed when alkanes react with OH to form a peroxy radical, RO<sub>2</sub>  
4 (Reaction R13), which subsequently reacts with NO to form an alkyl nitrate (Reaction 14b)  
5 (e.g. Talukdar et al., 1997). This is a minor channel of the RO<sub>2</sub> + NO reaction (Reaction R14a)  
6 which generally leads to ozone production via recycling of NO to NO<sub>2</sub> and the subsequent  
7 photolysis of NO<sub>2</sub>. RO<sub>2</sub> can also react with HO<sub>2</sub> (the hydroperoxyl radical) (Reaction R11) to  
8 form a peroxide (ROOH). The probability of RO<sub>2</sub> reacting with NO (leading to alkyl nitrate  
9 production) is thus governed by the ratio [NO]/[HO<sub>2</sub>]. Alkyl nitrates are lost from the  
10 atmosphere by reaction with OH (Reaction R15), photolysis (Reaction R16) and wet/dry  
11 deposition.



18

## 19 **2 Methodologies**

### 20 **2.1 Firn Sampling**

21 Firn air samples were collected at the NEEM site, Greenland (77.45°N, 51.07°W, 2484m a.s.l.)  
22 from two boreholes between 14<sup>th</sup> and 30<sup>th</sup> July 2008 (“2008 EU hole” and “2008 US hole”).  
23 Further samples were collected from another NEEM borehole during July 2009 (“2009 hole”).  
24 The ‘2008 EU hole’ was sampled using the firn air system of the University of Bern (Schwander  
25 et al., 1993), and the ‘US’ hole, sampled using the US firn air system (Battle et al., 1996). The  
26 alkane measurements used in this work – originally reported in Helmig et al. (2014b) - come  
27 from a combination of the 2008 EU and US holes and the 2009 hole with the exception of the  
28 pentanes, which come only from the 2008 EU and US holes. The alkyl nitrate samples come



1 only from the 2008 EU hole. Full sampling details are available in Helmig et al. (2014b) and  
2 Buizert et al. (2012).

### 3 **2.2 Firn Analysis**

4 The firn air samples from the 'EU' hole at NEEM were analysed for alkyl nitrates at UEA using  
5 a GC-MS in Negative Ion Chemical Ionisation mode (GC-NICI-MS) (e.g. Worton et al., 2008).  
6 2-pentyl nitrate and 3-pentyl nitrate are presented together as 2+3-pentyl nitrate because the  
7 two are not baseline separated in the chromatogram.

8 The NEEM samples were analysed using the UEA calibration scale. This was converted to the  
9 NCAR scale (against which the North GRIP 2-butyl nitrate and 2+3-pentyl nitrate samples are  
10 calibrated) for direct comparison with the North GRIP atmospheric histories from Worton et al.  
11 (2012) and with the in-situ measurements at Summit by UCI (Swanson et al., 2003; Dibb et al.,  
12 2007). This scaling was based on an inter-comparison between the UEA and NCAR standards  
13 in 2005 and 2012/13. These led to a rescaling of the UEA 2-butyl nitrate values by 1.245 and  
14 2+3-pentyl nitrate by 1.409. The measurements of 3-methyl-2-butyl nitrate were not rescaled  
15 as the North GRIP measurements were made on the UEA scale.

16 Firn air samples from the 'EU' hole at NEEM were analysed for alkanes at the Max Planck  
17 Institute Laboratory (MPI) by gas chromatography with flame ionisation detection (GC-FID)  
18 (see Baker et al., 2010 for further details). At the Institute of Arctic and Alpine Research  
19 (INSTAAR) firn air samples were analysed samples from both the 'EU' and 'US' holes at  
20 NEEM for alkanes by GC-FID (see Pollmann et al., 2008 and Helmig et al., 2014b for further  
21 details).

### 22 **2.3 Firn Modeling**

23 The air sampled from any given depth in the firn column is representative of a range of ages  
24 because of the inter-connected nature of the firn. Firn models can be used to derive the  
25 atmospheric history of a gas from measurements of air trapped in the firn. The extent and rate,  
26 at which the gas diffuses through the firn, depends on the diffusivity profile of the firn, the  
27 diffusivity coefficient of the gas, and on the gravitational fractionation (caused by the molecular  
28 weight) of the gas. The diffusion profile is different for every firn site.



1 For determining the atmospheric history of a gas from firn air measurements, the firn diffusion  
2 profiles must first be constrained. This is done using a series of reference gases with well known  
3 atmospheric histories. At NEEM the reference gases used were CO<sub>2</sub>, CH<sub>4</sub>, SF<sub>6</sub>, HFC-134a,  
4 CFC-11, CFC-12, CFC-113, and CH<sub>3</sub>CCl<sub>3</sub>, as well as <sup>14</sup>CO<sub>2</sub> (Wittrant et al., 2012).

5 Each gas also has a different diffusion rate through the firn based on its molecular structure,  
6 this is called the diffusion coefficient. The diffusion coefficient is calculated relative to a  
7 reference gas, generally CO<sub>2</sub>. Different methods have been reported for the calculation of these  
8 diffusion coefficients (e.g. Chen and Othmer, 1962; Fuller et al., 1966). The diffusion  
9 coefficients of the alkyl nitrates were calculated using the method of Fuller et al. (1966) based  
10 on the sum of the Le Bas molar volumes of the molecule. The diffusion coefficients used for  
11 the firn modelling for each molecule within this work are given in Table 1.

12 The inverse model used for the atmospheric history reconstructions was the most recent version  
13 of the LGGE-GIPSA atmospheric trend reconstruction model described in Wittrant and  
14 Martinerie (2013).

15 The atmospheric mole fraction derived from the firn reconstructions represents an annual mean.  
16 The alkanes and alkyl nitrates examined in this work have a strong atmospheric seasonality due  
17 to changes in their chemical lifetimes driven by seasonal variability in OH concentration in the  
18 air masses in which they are transported to the Arctic. Thus the seasonal cycle of both species  
19 follows a roughly sinusoidal curve with a peak in the late winter (March) and a trough in mid-  
20 summer (July-August) (Swanson et al. 2003). Consequently, changes to the firn derived mole  
21 fractions are likely to be dominated by changes to winter-time atmospheric concentrations.

22 This model cannot take into account the seasonality in the signal that is preserved in the upper  
23 part of a firn profile. Therefore, measurements above a certain depth must be excluded from the  
24 model input. It is noted that the latter part (post-1995) of the model derived scenarios for 2+3-  
25 pentyl nitrate is rather sensitive to the inclusion or exclusion of the measurement at 34.72 m  
26 (the most shallow measurement used). The scenarios presented in this work are based on  
27 including this measurement.

28

29

30





1 Table 1 Diffusion coefficients used in the firn modeling, calculated from Le Bas molecular  
2 volumes using the method of Fuller *et al.* (1966).

Compound	Diffusion Coefficient relative to CO <sub>2</sub>
2-butyl nitrate	0.467
2+3-pentyl nitrates	0.428
3-methyl-2-butyl nitrate	0.428

3

### 4 **3 Alkyl Nitrate Trends**

5 Atmospheric histories of the three alkyl nitrates 2-butyl nitrate, 2+3-pentyl nitrate, and 3-  
6 methyl-2-butyl nitrate (formed from n-butane, n-pentane, and iso-pentane, respectively)  
7 derived from firn air measurements at NEEM are shown in Figure 2. The records of all three  
8 alkyl nitrates show similar features (as would be expected from the similar sources and sinks).  
9 All show a steep increase in mixing ratio from the 1970s to the 1990s with increases of a factor  
10 of 4 – 5. The peak in the 1990s is followed by a steep decline to the sampling date of 2008.

11 Figure 2 also shows the atmospheric histories of the same three alkyl nitrates derived from firn  
12 air from North GRIP, Greenland, up to 2001, presented in Worton *et al.* (2010) (pink shaded  
13 area). There is very good agreement between the derived trends at the two sites. Differences  
14 can be attributed to the limited number of measurements at both sites, possible drift in the  
15 calibration standard used and uncertainties in the firn modelling. Both sites show the same large  
16 increase in mixing ratios from the 1970s to the 1990s. Importantly, the NEEM records show  
17 that the turnover and subsequent decline in mixing ratios, the beginnings of which were evident  
18 in the North GRIP records, appears to continue through the 2000s. However, as noted in Section  
19 2.3, the derived atmospheric history of 2+3-pentyl nitrate is sensitive to the inclusion of the  
20 measurement at 34.72 m. The scenario that did not include this measurement was almost flat  
21 from 1995 to 2008 rather than declining as in Figure 2.

22 There are very limited in-situ measurements of alkyl nitrates in the Arctic and even fewer that  
23 cover a whole seasonal cycle. Swanson *et al.* (2003) report the seasonal cycle of 2-butyl nitrate  
24 at the Summit station, Greenland (72.34 N, 38.29 W, 3250 m a.s.l), from June 1997 to June  
25 1998 based on samples collected roughly every two days. Dibb *et al.* (2007) report monthly  
26 mean measurements of 2-butyl nitrate for the period June 2000 through to August 2002 based  
27 on samples taken roughly weekly also from Summit. In order to compare these in-situ



1 measurements to output derived from the firm measurements the annual mean is taken. This is  
2 because the firm smoothes out the seasonality and represents the annual mean of mixing ratios.  
3 Calculating the 2-butyl nitrate annual mean for the three periods 1997-1998 (6.8 ppt), 2000-  
4 2001 (5.3 ppt), and 2001-2002 (5.0 ppt) gives values that can be compared to the output from  
5 the firm model for 2-butyl nitrate. These agree with the firm model output in terms of absolute  
6 mixing ratios of 2-butyl nitrate during this period (5 – 8 ppt) (Fig. 2). They also show a declining  
7 trend through the period, in agreement with the firm model output, though this is not statistically  
8 significant within the errors.

9

10

11

12

13

14

15

16

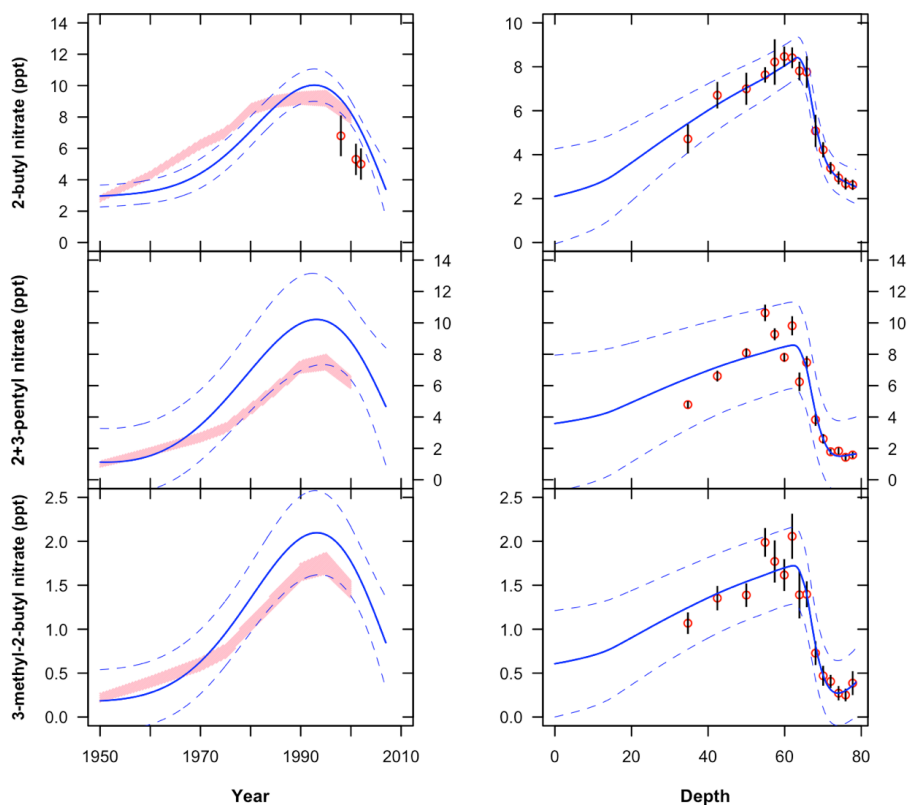
17

18

19

20

21



1

2 Figure 2 Concentration-depth profiles in the firm and the model derived atmospheric histories. Right panel: The  
3 concentration-depth profiles measured in the firm (ppt): red open circles: measured mixing ratios (ppt) with error  
4 bars indicating the 2- $\sigma$  uncertainty; solid blue line: best fit of the firm model, dashed blue lines indicate the 2- $\sigma$   
5 combined analytical and model uncertainties. Left panel: Atmospheric histories of the alkyl nitrates derived from  
6 the firm air measurements using the inverse modelling technique described within (solid blue lines). Dashed lines  
7 represent the 2- $\sigma$  confidence margins of the model calculations, combining the analytical and model uncertainties.  
8 Pink shaded area: atmospheric histories presented in Worton et al. (2012) derived from firm air measurements at  
9 North GRIP, Greenland. Red open circles: Annual average of in-situ measurements at Summit, Greenland (see  
10 text for details) with 1- $\sigma$  uncertainty.

11

12

13

14

15

16

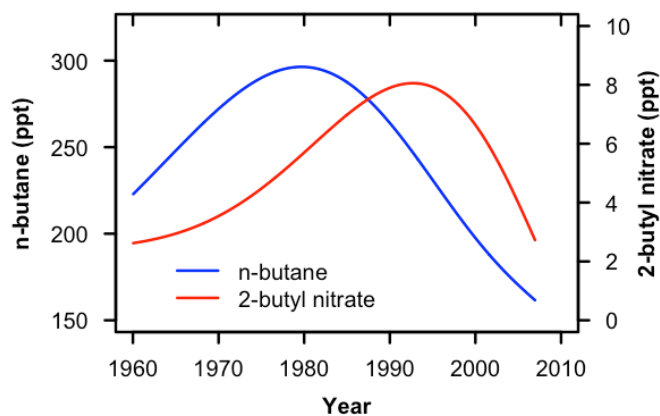


1 Considering Reactions R13 – R16, the trends in the alkyl nitrate mixing ratios (Fig. 2) could be  
2 caused by:

- 3 (i) Changes to the atmospheric mixing ratios of the parent alkanes;
- 4 (ii) Changes to  $[\text{OH}]_t$ , where  $t$  is time since emission of the alkane. i.e. the amount  
5 of photochemical processing that the air mass in which the alkyl nitrates are  
6 being formed undergoes before reaching the Arctic;
- 7 (iii) Changes to the production efficiency of the alkyl nitrates, i.e. whether the peroxy  
8 radical reacts with NO (Reaction R14) or with  $\text{HO}_2$  (Reaction R11);
- 9 (iv) Changes to the alkyl nitrate sinks, i.e., changes in  $[\text{OH}]$  or radiation.

10 Concerning point (i), the peak in alkyl nitrate mixing ratios in the 1990s is not contemporaneous  
11 with that of the parent alkanes ( $\sim 1980$  – Figure 3). This suggests that the changes to the alkyl  
12 nitrate mixing ratios are not being primarily driven by changes to the parent alkane. By  
13 considering the ratio of the alkyl nitrate to its parent hydrocarbon, using the firm derived alkane  
14 trends from NEEM presented in Helmig et al. (2014b), we can effectively remove the effect of  
15 changes to the parent hydrocarbon from the alkyl nitrate signal. This is done in Sections 4, 5  
16 and 6, when points (ii) and (iii) are explored further.

17



18

19 Figure 3 Atmospheric histories of 2-butyl nitrate (red) and its parent alkane, n-butane (blue), derived from firm  
20 measurements at NEEM, Greenland.

21



1 Concerning point (iv), there is evidence for global dimming (i.e. a decrease in surface solar  
2 radiation) of about 5 % between 1960 and 1990 in the northern hemisphere. However, this  
3 began to turn around during the mid 1980s and there was a brightening trend between 1985 and  
4 2000 (Wild et al., 2005). This minor change to the alkyl nitrate sink is unlikely to have had a  
5 noticeable effect on mixing ratios.

6 Points (ii) and (iii) are discussed in the following sections.

7

#### 8 **4 Ratios of Alkyl Nitrate to Parent Alkane**

9 Bertman et al. (1995) presented a mathematical equation to describe the production of alkyl  
10 nitrates in a NO<sub>x</sub> rich environment (Equation E1 (assumes an initial zero mixing ratio for alkyl  
11 nitrates)). We extend Equation E1 to include the term  $k_{14}[\text{NO}]/(k_{14}[\text{NO}]+k_{11}[\text{HO}_2])$  (Equation  
12 E2). This term accounts for the fact that only a fraction of the peroxy radicals will react with  
13 NO. It represents an integrated value for this ratio during transport of the air mass from the  
14 source region to the Arctic.

$$15 \quad \frac{[\text{RONO}_2]}{[\text{RH}]} = \frac{\beta k_A}{(k_B - k_A)} (1 - e^{-(k_A - k_B)t}) \quad (\text{E1})$$

16 Where  $\beta = \alpha_{13}\alpha_{14}$ ,  $k_A = k_{13}[\text{OH}]$ ,  $k_B = k_{15}[\text{OH}] + j_{16}$ ; subscript numbers refer to reactions given  
17 in the Introduction.

$$18 \quad \frac{[\text{RONO}_2]}{[\text{RH}]} = \frac{\beta k_A}{(k_B - k_A)} (1 - e^{-(k_A - k_B)t}) \frac{k_{14}[\text{NO}]}{k_{14}[\text{NO}] + k_{11}[\text{HO}_2]} \quad (\text{E2})$$

19 In Equation E1, taken from Bertman et al. (1995), [OH] is assumed to be a constant. However,  
20 in reality, and for the purposes of this work, it is noted that the [OH] in the term [OH]t represents  
21 the integrated [OH] (i.e.  $\int[\text{OH}].dt$ ) to which the air mass is exposed during transport from the  
22 source region to the Arctic.”

23 Atmospheric histories of the three parent alkanes of the alkyl nitrates presented in Figure 2 were  
24 presented in Helmig et al. (2014b) – Figure 7. These are used here, in conjunction with the alkyl  
25 nitrate histories in Figure 2, to determine trends of the ratio [RONO<sub>2</sub>]/[RH] for each alkyl  
26 nitrate-alkane pair. By rearranging Equation E1, we can then probe two of the possible causes  
27 for the observed alkyl nitrate trends. Firstly, that the production efficiency (i.e. the integrated  
28 [NO]/[HO<sub>2</sub>] ratio) has changed over time. Secondly, that the processing of the air mass, i.e. OH



1 concentration ( $[\text{OH}]t$ ), multiplied by the transport time from source regions to the Arctic,  $t$   
2 (assuming photolysis to have remained constant), has changed.

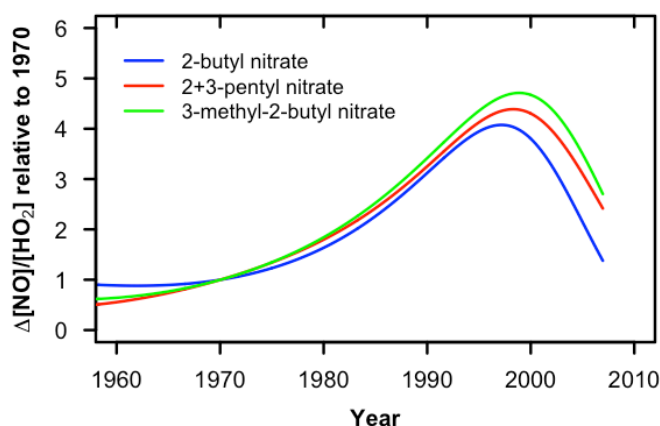
3

#### 4 **5 Changes to the Production Efficiency of the Alkyl Nitrates**

5 In an urban environment, daytime  $[\text{NO}]$  can range from 10 – 1000 ppb. At these mixing ratios  
6 the ratio  $k_{14}[\text{NO}]/(k_{14}[\text{NO}]+k_{11}[\text{HO}_2])$  is very close to 1, i.e. all of the alkyl peroxy radicals  
7 formed in Reaction R13 go on to form alkyl nitrates at a yield determined by the branching  
8 ratio  $\alpha_{13}$ . However, in rural and more remote regions of the atmosphere, daytime  $[\text{NO}]$  ranges  
9 from 1 – 100 ppt. At these mixing ratios  $k_{14}[\text{NO}]/(k_{14}[\text{NO}]+k_{11}[\text{HO}_2])$  varies between around  
10 0.4 – 1, assuming a daytime  $[\text{HO}_2] = 2 \times 10^7$  molecules  $\text{cm}^{-3}$  (winter time – the alkyl nitrate and  
11 alkane signals in the firm are dominated by winter time concentrations). Changes to  $[\text{NO}]$  or  
12  $[\text{HO}_2]$  in these remote environments will affect the production efficiency of the alkyl nitrates.

13 Equation E3 is a rearrangement of Equation E2 from which historic changes to  $[\text{NO}]/[\text{HO}_2]$  can  
14 be calculated using the changes to the  $[\text{RONO}_2]/[\text{RH}]$  ratio (assuming that the photochemical  
15 processing,  $[\text{OH}]t$ , has remained constant).

$$16 \quad \frac{[\text{NO}]}{[\text{HO}_2]} = \left[ \frac{k_{14}}{k_{11}} \left( \frac{[\text{RH}] k_{13} \alpha_{13} \alpha_{14} (1 - e^{(k_{13}-k_{15})[\text{OH}]t})}{[\text{RONO}_2] (k_{15} - k_{13})} - 1 \right) \right]^{-1} \quad (\text{E3})$$



17

18 Figure 4 The trend in the  $[\text{NO}]/[\text{HO}_2]$  ratio of the air masses in which the alkyl nitrates were formed, calculated  
19 using Equation E3 for each of three alkyl nitrate/alkane pairs. This assumes that the amount of photochemical  
20 processing,  $[\text{OH}]t$ , remained constant at  $5 \times 10^{11}$  molecules  $\text{cm}^{-3}$  s.



1

2 Figure 4 shows the trend in the  $[\text{NO}]/[\text{HO}_2]$  ratio derived using Equation E3. A value of  $5 \times$   
3  $10^{11}$  molecules  $\text{cm}^{-3}$  s is used for the constant  $[\text{OH}].t$ . This is based on a mean transport time of  
4 air masses from Europe (from where the majority of winter-time pollutants are transported to  
5 the Arctic – see Section 6.1) to the Arctic in the winter of ten days (Stohl, 2006), and a mean  
6 winter-time  $[\text{OH}]$  of  $\sim 6 \times 10^5$   $\text{cm}^{-3}$  (in reasonable agreement with that derived by Derwent et  
7 al. (2012) for the North Atlantic in winter-time). Halving the assumed  $[\text{OH}].t$  to  $2.5 \times 10^{11}$   
8 molecules  $\text{cm}^{-3}$  s increases the magnitude of the relative changes by a factor of  $\sim 2$ . Whereas  
9 doubling  $[\text{OH}].t$ , only decreases the derived changes by  $\sim 15\%$ .

10 The trend shows similar features to those of the alkyl nitrate trends. The ratio increases from  
11 the 1970s to the late 1990s and then subsequently declines.

12 To investigate the drivers that might have led to these changes in  $[\text{NO}]/[\text{HO}_2]$  ratio, we shall  
13 now examine how the  $\text{NO}_x$  and  $\text{HO}_2$  concentrations may have changed.

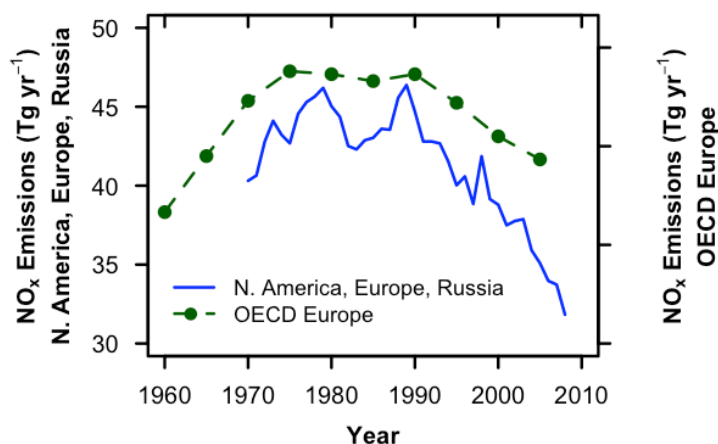
## 14 **5.1 Changes to atmospheric $\text{NO}_x$ concentrations**

### 15 **5.1.1 $\text{NO}_x$ sources**

16 The atmospheric  $\text{NO}_x$  concentration is determined by the relative magnitudes of the sources  
17 and sinks. The main sources of  $\text{NO}_x$  in the northern hemisphere are anthropogenic emissions  
18 from fossil fuel use, power stations and transport (Olivier and Berdowski et al., 2001; Olivier  
19 et al., 2001).

20 Figure 5 shows how  $\text{NO}_x$  emissions from North America, Europe and Russia have varied  
21 between 1970 and 2008, taken from the bottom-up estimates of the EDGAR database (EDGAR  
22 v4.2, <http://edgar.jrc.ec.europa.eu>). Emissions were fairly constant between 1970 and 1990 and  
23 then fell by about 25 % from 1990 to 2008. This is in good agreement with the  $\text{NO}_x$  emission  
24 trends for OECD Europe presented in Vestreng et al. (2009).

25



1

2 Figure 5 Blue solid line (left axis): The trend in NO<sub>x</sub> emissions (Tg yr<sup>-1</sup>) from North America, Europe and Russia  
3 for the period 1970 to 2008 (EDGAR v4.2, <http://edgar.jrc.ec.europa.eu>). Green points (and dashed line) (right  
4 axis): OECD Europe NO<sub>x</sub> emissions (Tg yr<sup>-1</sup>) from Vestreng et al. (2009).

5

6 Assuming that these bottom up emissions estimates are correct in the timing of the NO<sub>x</sub>  
7 emissions changes, it seems unlikely that the increase in the [NO]/[HO<sub>2</sub>] ratio derived for the  
8 period 1970 to the late 1990s was driven primarily by changing NO<sub>x</sub> emissions.

9 The subsequent decline in [NO]/[HO<sub>2</sub>], on the other hand, may well have been driven by  
10 decreasing emissions. Measurements at a range of UK sites showed a decrease in NO<sub>x</sub>  
11 concentrations from 1996 (the beginning of the reported measurements) to 2002 – 2004, of 1 –  
12 3.5 % per year, depending on the site (Carslaw et al., 2011). During the same period, the fraction  
13 of the NO<sub>x</sub> that is NO<sub>2</sub> (f-NO<sub>2</sub>) roughly doubled. Recent trends at many European sites show  
14 similar trends with small decreases in NO<sub>x</sub> between 1999 and 2007 (the period for which  
15 measurements are available) but level or increasing NO<sub>2</sub> through the same period (Carslaw et  
16 al., 2011; Gilge et al., 2010) – suggesting that NO has decreased by more than NO<sub>x</sub>  
17 concentrations.

18 Declining NO<sub>x</sub> emissions have been used to explain these trends in measured concentrations.  
19 However, the decline in these ambient concentrations is not as large as would be expected using  
20 current emission inventories (Carslaw et al., 2011).





## 1 5.1.2 NO<sub>x</sub> sinks

2 At mid-high latitudes, in the daytime, during the summer, the main sink for NO<sub>x</sub> is the reaction  
3 of NO<sub>2</sub> with OH. This reaction produces nitric acid (HNO<sub>3</sub>), much of which is then removed  
4 from the atmosphere by wet deposition. However, at night and during the winter months, when  
5 daily mean [OH] is more than an order of magnitude lower than during the summer (e.g.  
6 Derwent et al., 2012), the dominant NO<sub>x</sub> sink is conversion of dinitrogen pentoxide (N<sub>2</sub>O<sub>5</sub>) to  
7 HNO<sub>3</sub> on aerosol. This occurs when photolysis is low, allowing NO<sub>3</sub> (formed from the reaction  
8 of NO<sub>2</sub> with O<sub>3</sub>) to build up. NO<sub>3</sub> reacts with NO<sub>2</sub> to form N<sub>2</sub>O<sub>5</sub>. The reaction of N<sub>2</sub>O<sub>5</sub> with  
9 H<sub>2</sub>O is slow in the gas-phase (Tuazon et al., 1983) but occurs rapidly in aerosol.

10 A modelling study by Dentener and Crutzen (1993) predicted that changes to the loss of NO<sub>x</sub>  
11 via sulfate aerosol could have a significant effect on northern hemisphere NO<sub>x</sub> concentrations  
12 and that these changes would also affect O<sub>3</sub> and OH concentrations. Subsequent modelling  
13 studies have broadly agreed with the magnitude of the changes suggested by Dentener and  
14 Crutzen (Brown and Stutz, 2012). Based on these studies, the large decrease in sulfate aerosol  
15 observed in Europe and the United States since 1980 (Berglen et al., 2007; Turnock et al., 2015)  
16 (driven by a 60 – 70 % decrease in SO<sub>2</sub> emissions (Smith et al., 2011)) would be expected to  
17 have led to a decrease in NO<sub>x</sub> removal by N<sub>2</sub>O<sub>5</sub> hydrolysis, and hence to an increase in the NO<sub>x</sub>  
18 lifetime and atmospheric [NO<sub>x</sub>]. This time period is broadly in line with the derived steep  
19 increase in the [NO]/[HO<sub>2</sub>] ratio.

## 20 5.2 The Hydroperoxyl Radical, HO<sub>2</sub>

21 The complex nature of the interconnectedness of the chemistry make it difficult to predict how  
22 HO<sub>2</sub> concentrations will have changed in response to changes in primary emissions.

23

## 24 6 Changes to Photochemical Oxidation

25 An alternative explanation for the observed alkyl nitrate trends is that the amount of  
26 photochemical processing of the air mass changed during the time period. An increase in  
27 processing could be caused by a change in either the concentration of the OH radical (assuming  
28 photolysis to have remained constant), or by an increase in the transport time of the air mass  
29 from the source region to the Arctic.

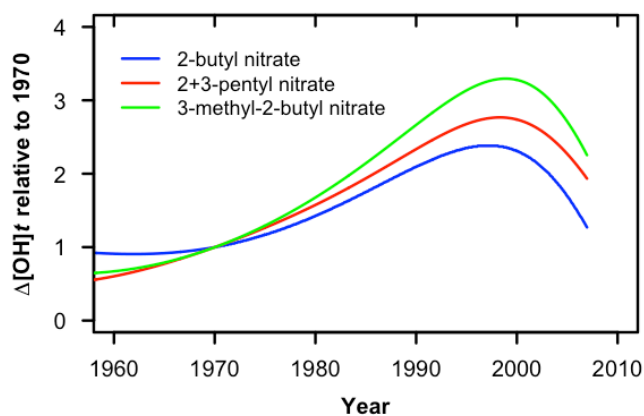


1 Equation E4 is a rearrangement of Equation E2 from which historic changes to the  
 2 photochemical processing,  $[\text{OH}]_t$ , can be calculated using the changes to the  $[\text{RONO}_2]/[\text{RH}]$   
 3 ratio (assuming that the  $[\text{NO}]/[\text{HO}_2]$  ratio has remained constant).

4

$$5 \quad [\text{OH}]_t = \ln \left( 1 - \left[ \frac{[\text{RONO}_2]}{[\text{RH}]} \frac{(k_{15} - k_{13})}{k_{13} \alpha_{13} \alpha_{14}} \left( \frac{k_{11} [\text{HO}_2]}{k_{14} [\text{NO}]} + 1 \right) \right] \right) \div (k_{13} - k_{15}) \quad (\text{E4})$$

6



7

8 Figure 6 The trend in  $[\text{OH}]_t$  calculated using Equation E4 for each of three alkane-alkyl nitrate pairs. This assumes  
 9 that the ratio  $[\text{NO}]/[\text{HO}_2]$  remained constant at 0.5.

10

11 Figure 6 shows the trends in  $[\text{OH}]_t$  derived from the alkyl nitrate-alkane pairs if a constant  
 12 value for  $[\text{NO}]/[\text{HO}_2]$  is assumed. The value used for the constant  $[\text{NO}]/[\text{HO}_2]$  was 0.5. This is  
 13 in line with the  $[\text{NO}]/[\text{HO}_2]$  derived using Equation E3 with a fixed  $[\text{OH}]_t$  value of  $5 \times 10^{11}$   
 14 molecules  $\text{cm}^{-3}$  s.

15 Figure 6 shows that the observed  $[\text{RONO}_2]/[\text{RH}]$  ratios between around 1970 and the late 1990s  
 16 could be explained by a relative change in  $[\text{OH}]_t$  of a factor of between 2.4 (2-butyl nitrate) and  
 17 3.3 (3-methyl-2-butyl nitrate). Increasing the  $[\text{NO}]/[\text{HO}_2]$  value by an order of magnitude, to 5,  
 18 decreases the derived  $[\text{OH}]_t$  changes by  $\sim 25\%$ . Decreasing the  $[\text{NO}]/[\text{HO}_2]$  value by an order  
 19 of magnitude, to 0.05, increases the derived  $[\text{OH}]_t$  changes by  $\sim 5\%$ .



## 1 **6.1 Air mass transport time to the Arctic**

2 The transport time,  $t$ , of pollutants to the Arctic from source is dependent on (i) the atmospheric  
3 transport patterns, and (ii) the source regions of the pollutants. Concerning (i), Kahl et al. (1999)  
4 have suggested that there is a decadal scale (4 – 14 years) variability in transport patterns of  
5 pollutants from the NH to the Arctic but note no long term trend. Hirdman et al. (2010) note  
6 that while changes to transport patterns can explain much of the inter-annual variability of  
7 Arctic concentrations of black carbon and sulfate aerosol (pollutants with similar source regions  
8 to the alkanes), they played only a minor role in long term changes. Eckhardt et al. (2003) have  
9 shown that transport of pollutants to the Arctic from European and US source regions is more  
10 rapid during positive phases of the weather pattern, the North Atlantic Oscillation (NAO).  
11 During the period 1960 – 1980 the NAO was predominantly in a negative phase in winter,  
12 between 1980 and 2000 it was predominantly in a positive phase, and since 2000 neither phase  
13 has been dominant (Hurrell and Deser, 2010). This suggests that there was more rapid transport  
14 of pollutants to the Arctic during the period 1980 – 2000 compared to the preceding and  
15 succeeding periods. This would mean a shorter processing time for the air masses and hence  
16 less alkyl nitrate production and lower alkyl nitrate to alkane ratios. This is the opposite to what  
17 we observe in the firm records, suggesting that changes to the NAO are unlikely to be  
18 responsible for the observed alkyl nitrate trends. Concerning (ii), the main sources of  
19 anthropogenic emissions to the Arctic of gases with lifetimes on the order of a few weeks,  
20 particularly during the winter, have been identified as being northern Eurasia (*e.g.* Shindell et  
21 al., 2008; Stohl et al., 2007; Klonecki et al., 2003). Emissions from Europe and North America  
22 have likely followed a similar declining trend in recent years (*e.g.* Warneke et al., 2012), thus  
23 the relative contribution from each region will not have changed dramatically.

## 24 **6.2 The Hydroxyl Radical, OH**

25 The alternative explanation for an increase in photochemical processing is an increase in [OH].  
26 This would represent a regional trend in [OH] representative of only regions from and through  
27 which air masses are transported to the Arctic, and would relate primarily to the winter (since  
28 the alkyl nitrate and alkane signals in the firm are dominated by winter time concentrations). It  
29 is noted that the increased chemical processing observed could also result from an increase in  
30 an oxidant other than OH, *e.g.* atomic chlorine, as suggested in Helmig et al. (2014b).



1 Studies using changes to atmospheric mixing ratios of methyl chloroform ( $\text{CH}_3\text{CCl}_3$ ) have  
2 suggested that global mean OH concentrations are ‘well buffered’ (e.g. Montzka et al., 2011).  
3 Since the main sink of  $\text{CH}_3\text{CCl}_3$  in the atmosphere is reaction with OH, and the emission  
4 sources and other sinks are thought to be well constrained, the variation in its observed mixing  
5 ratios at a number of remote sites can be used to infer variations in global [OH]. Global mean  
6 [OH] has been inferred in this way in a number of studies (Prinn et al., 1995, 2001, 2005; Rigby  
7 et al., 2008; Montzka et al., 2011). The most recent of these (Montzka et al., 2011) reported  
8 little inter-annual variability in mean global atmospheric [OH] estimating roughly 5% variation  
9 from the mean value during the period 1997 – 2008, but this does not cover the period of interest  
10 here (1970 to later 1990s). Similarly, Kai et al. (2011) inferred a low variability in global [OH]  
11 between 1998 and 2005 based on a relatively constant  $\delta\text{-D-CH}_4$ . Earlier work using methyl  
12 chloroform (Prinn et al., 2001) reported an increase in NH [OH] of roughly 40% between 1979  
13 and 1991 but this increase has been questioned in more recent work (e.g. Montzka et al., 2011).  
14 However, there are a growing number of observational data sets of trace gases in the NH which  
15 show trends since 1980 that could be explained, at least in part, by changes to the concentration  
16 of the OH sink. E.g. decreasing Arctic alkane mixing ratios (Helmig et al., 2014b; Aydin et al.,  
17 2011); decreasing Arctic CO mixing ratios (Petrenko et al., 2013); increasing  $d^{13}\text{C}$  of methane  
18 (Monteil et al., 2011; Sapart et al., 2013); decreasing  $d\text{C}^{16}\text{O}$  of Arctic CO (Wang et al., 2012).  
19 A recent multi-model inter-comparison exercise of seventeen global chemical transport models,  
20 showed agreement for a small increasing trend in global mean [OH] of  $3.5 (\pm 2.2) \%$  between  
21 1980 and 2000 and a slightly larger [OH] increase in the northern hemisphere of  $4.6 (\pm 1.9) \%$   
22 (Naik et al., 2013). Dalsøren et al. (2015) determined an increase in global mean [OH] of about  
23 10 % between 1970 and 2006 from modelled increases of the methane lifetime.

24

## 25 7 Discussion

26 The alkyl nitrate trends presented herein suggest a profound change to the chemical state of the  
27 northern hemisphere mid-high latitude atmosphere in winter between the 1970s and the late  
28 1990s and then again between the late 1990s and the mid-2000s.

29 A key species of the tropospheric chemistry cycle, tightly linked to  $\text{NO}_x$  and  $\text{HO}_x$ , is ozone  
30 (Figure 1). Ozone mixing ratios increased at sites across the NH during the second half of the  
31 twentieth century, roughly doubling since 1960 (Parrish et al., 2012). Ozone production is



1 positively linked to  $[\text{NO}_x]$  (at low  $\text{NO}_x$  concentrations such as the background atmosphere).  
2 Hence, an increase in the  $[\text{NO}]/[\text{HO}_2]$  ratio from around 1970 to the mid-1990s is consistent  
3 with long-term trends in ozone in the background atmosphere.

4 Furthermore, while the alkyl nitrate measurements represent changes to the winter-time  
5 atmosphere, the ozone trends are seen in both summer and winter. If these are being driven by  
6 increases to  $[\text{NO}_x]$  in the background atmosphere, then this suggests that the chemical changes  
7 to the atmosphere may have been present throughout the year and are not just a winter time  
8 phenomenon.

9 This work also implies that there may have been a change in  $[\text{OH}]$ . Indeed due to the connected  
10 nature of the chemistry of  $\text{NO}_x$ , ozone and OH it seems unlikely, given the implied increases  
11 in  $\text{NO}_x$  suggested here, and the recorded increases in ozone, that there was not a commensurate  
12 increase in OH during this period. Furthermore, the primary production of OH, denoted by  
13  $P(\text{OH})$ , is dependent on ozone mixing ratios, either via photolysis of ozone (Equation 5 - Smith  
14 et al., 2006) or via ozonolysis of alkenes (Johnson and Marston, 2008).

$$15 \quad P(\text{OH}) = 2f[\text{O}_3] \times j(\text{O}^1\text{D}) \quad (\text{E5})$$

16 Where  $f$  is the fraction of  $\text{O}^1\text{D}$  that reacts with water vapour. Ozone has increased at  
17 background sites between 1960 and 2000 (Parrish et al., 2012) and measured water vapour has  
18 also increased slightly (Hartmann et al., 2013). It therefore seems that the primary production  
19 of OH in the background atmosphere must have increased through the final decades of the past  
20 century. On the other hand, the primary sink of OH in the background atmosphere, CO, has  
21 decreased by about 15% since 1980 (Petrenko et al., 2013), with the secondary sink,  $\text{CH}_4$ ,  
22 having increased between 1980 and 2000 by about 15%.

23 The global growth rate of methane in the atmosphere continually declined throughout the period  
24 of the 1970s to 2000, culminating in the ‘methane pause’ between 1999 and 2006  
25 (Dlugokencky et al. 2009). A possible cause of this change in growth rate in methane could  
26 be an increase in OH concentration (e.g. Dalsøren et al. 2016). This is consistent with an  
27 increase in  $[\text{OH}]$  also being the cause of the trend in the ratio of alkyl nitrate to parent alkane  
28 seen in this work. It should be noted, though, that the majority of the OH oxidation of methane  
29 occurs in the tropics (e.g. Bloss et al. 2005), while any increase in OH suggested by the work  
30 herein must be viewed as representative only of the mid-high latitude northern hemisphere and  
31 the winter time. However, the processes suggested herein, such as changes to the  $\text{N}_2\text{O}_5$  sink,  
32 have been shown to be effective at a hemispheric scale.



1 In a recent inter-model comparison project, ACCMIP, it was shown that models failed to  
2 capture the measured magnitude of the increase in ozone over recent decades (Parrish et al.,  
3 2014), in particular the steep increase seen between 1980 and 2000. This failure to capture  
4 measured changes to ozone may suggest that models are likely to under-estimate changes to  
5 OH production, from ozone photolysis or reactions of ozone with alkenes, over the same period  
6 (i.e. they may be larger than the  $4.6 (\pm 1.9)$  % reported in Naik et al. (2013) for the NH).

7 Including alkyl nitrate chemistry and using the alkyl nitrate measurements presented herein  
8 could provide a valuable constraint for modelling changes to NO<sub>x</sub> and HO<sub>x</sub> back to the middle  
9 of the twentieth century in global chemical transport models.

10

## 11 **8 Conclusions**

12 Time series such as those presented here are fundamental to improving our understanding of  
13 trends in atmospheric composition during the twentieth century. The long-term trends of alkyl  
14 nitrates presented herein suggest major changes to the chemical state of the atmosphere during  
15 the past five decades. The trends were likely driven by changes to the [NO]/[HO<sub>2</sub>] ratio during  
16 this period. A 4 – 5 fold increase in the [NO]/[HO<sub>2</sub>] ratio is suggested between the 1970s and  
17 late 1990s. This is not consistent with reported changes to NO<sub>x</sub> emissions, but may have been  
18 driven by a reduction in the NO<sub>x</sub> sink. The recent decreases (since the late 1990s) in alkyl  
19 nitrate concentrations are in qualitative agreement with recent decreases in NO<sub>x</sub> emissions and  
20 in measured NO<sub>x</sub> concentrations. Changes to concentrations of the hydroxyl radical, or to the  
21 transport time of air masses from source regions to the Arctic may also have contributed to the  
22 observed trends.

23

## 24 **Acknowledgements**

25 This work was supported by funding from the UK Natural Environment Research Council  
26 (NE/F021194/1 & NE/M003248/1). NEEM is directed and organized by the Centre of Ice and  
27 Climate at the Niels Bohr Institute and US NSF, Office of Polar Programs. It is supported by  
28 funding agencies and institutions in Belgium (FNRS-CFB and FWO), Canada (NRCan/GSC),  
29 China (CAS), Denmark (FIST), France (IPEV, CNRS/INSU, CEA and ANR), Germany (AWI),  
30 Iceland (RannIs), Japan (NIPR), South Korea (KOPRI), The Netherlands (NWO/ALW),  
31 Sweden (VR), Switzerland (SNF), the United Kingdom (NERC) and the USA (USNSF, Office



1 of Polar Programs) and the EU Seventh Framework programs. We are indebted to Jakob  
2 Schwander of the Physics Institute at the University of Bern, Switzerland for collecting the firm  
3 air samples at NEEM, and Thomas Blunier of the Centre for Ice and Climate at University of  
4 Copenhagen, Denmark for leading the NEEM gas consortium. We thank Chelsea Thompson  
5 for useful discussions.

6

## 7 **References**

8 Baker, A., Slemr, F., and Brenninkmeijer, C. A. M.: Analysis of non-methane hydrocarbons in  
9 air samples collected aboard the CARIBIC passenger aircraft, *Atmos. Meas. Tech.*, **3**, 311-321,  
10 2010.

11 Battle, M., Bender, M., Sowers, T., Tans, P. P., Butler, J. H., Elkins, J. W., Ellis, J. T., Conway,  
12 T., Zhang, N., Lang, P., and Clarke, A. D.: Atmospheric gas concentrations over the past  
13 century measured in air from firm at the South Pole, *Nature*, **383**, 231-235, 1996.

14 Berglen, T. F., Myhre, G., Isaksen, I. S. A., Vestreng, V., and Smith, S. J.: Sulphate trends in  
15 Europe: Are we able to model the recent observed decrease?, *Tellus B*, **59**, 773-786, 2007.

16 Bertman, S. B., Roberts, J. M., Parrish, D. D., Buhr, M. P., Goldan, M. P., Kuster, W. C.,  
17 Fehsenfeld, F. C., Montzka, S. A., and Westberg, H.: Evolution of alkyl nitrates with air mass  
18 age, *J. Geophys. Res.*, **100**, 22805-22813, 1995.

19 Bloss, W. J., Evans, M. J., Lee, J. D., Sommariva, R., Heard, D. E., and Pilling, M. J.: The  
20 oxidative capacity of the troposphere: Coupling of field measurements of OH and a global  
21 chemistry transport model, *Faraday Discuss.*, **130**, 425-436, 2005.

22 Brown, S. S., and Stutz, J., Nighttime radical observations and chemistry, *Chem. Soc. Rev.* **41**,  
23 6405-6447, 2012.

24 Buizert, C., Martinerie, P., Petrenko, V. V., Severinghaus, J. P., Trudinger, C. M., Witrant, E.,  
25 Rosen, J. L., Orsi, A. J., Rubino, M., Etheridge, D. M., Steele, L. P., Hogan, C., Laube, J. C.,  
26 Sturges, W. T., Levchenko, V. A., Smith, A. M., Levin, I., Conway, T. J., Dlugokencky, E. J.,  
27 Lang, P. M., Kawamura, K., Jenk, T. M., White, J. W. C., Sowers, T., Schwander, J., and  
28 Blunier, T.: Gas transport in firm: multiple-tracer characterisation and model intercomparison  
29 for NEEM, Northern Greenland, *Atmos. Chem. Phys.*, **12**, 4259-4277, 2012.



- 1 Carslaw, D. C., Beever, S. D., Westmoreland, E., Williams, M. L., Tate, J. E., Murrells, T.,  
2 Stedman, J., Li, Y., Grice, S., Kent, A., and Tsagatakis, I.: Trends in NO<sub>x</sub> and NO<sub>2</sub> emissions  
3 and ambient measurements in the UK. Version: July 2011., 2011.
- 4 Chen, N. H., and Othmer, D. F.: New generalized equation for gas diffusion coefficient, J.  
5 Chem. Eng. Data, 7, 37–41, 1962.
- 6 Clemitshaw, K. C., Williams, J., Rattigan, O. V., Shallcross, D. E., Law, K. S., and Cox, R. A.:  
7 Gas phase ultraviolet absorption cross sections and atmospheric lifetimes of several C2-C5  
8 alkyl nitrates, J. Photochem. Photobiol. A, 102, 117-126, 1997.
- 9 Dalsøren, S. B., Myhre, C. L., Myhre, G., Gomez-Pelaez, A. J., Søvde, O. A., Isaksen, I. S. A.,  
10 Weiss, R. F., and Harth, C. M.: Atmospheric methane evolution the last 40 years, Atmos. Chem.  
11 Phys., 16, 3099-3126, 2016.
- 12 Dentener, F. J. and Crutzen, P.: Reaction of N<sub>2</sub>O<sub>5</sub> on Tropospheric Aerosols: Impact on the  
13 Global Distributions of NO<sub>x</sub>, O<sub>3</sub>, and OH, J. Geophys. Res. 98, 7149-7163, 1993.
- 14 Derwent, R. G., Simmonds, P. G., O'Doherty, S., Grant, A., Young, D., Cooke, M. C.,  
15 Manning, A. J., Utembe, S. R., Jenkin, M. E., and Shallcross, D. E.: Seasonal cycles in short-  
16 lived hydrocarbons in baseline air masses arriving at Mace Head, Ireland, Atmos. Environ., 62,  
17 89-96, 2012.
- 18 Dibb, J. E., Albert, M., Courville, Z., Anastasio, C., Galbavy, E. S., Atlas, E., Beyersdorf, A.  
19 J., Blake, D. R., Meinardi, S., Sherwood Rowland, F., Swanson, A. L., Blake, N. J., Bocquet,  
20 F., Cohen, L., Helmig, D., Burkhardt, J. F., Frey, M. M., Friel, D. K., Hutterli, M. A., Chen, G.,  
21 Conway, T. J., and Oltmans, S. J.: An overview of air-snow exchange at Summit, Greenland:  
22 Recent experiments and findings, Atmos. Environ., 41, 4995-5006, 2007.
- 23 Dlugokencky, E. J., Bruhwiler, L., White, J. W. C., Emmons, L. K., Novelli, P. C., Montzka,  
24 S. A., Masarie, K. A., Lang, P. M., Crotwell, A. M., Miller, J. B., and Gatti, L. V.: Observational  
25 constraints on recent increases in the atmospheric CH<sub>4</sub> burden, Geophys. Res. Lett., 36, art. no.  
26 L18803, 2009.
- 27 EC-JRC/PBL (European Commission, Joint Research Centre/ Netherlands Environmental  
28 Assessment Agency): Emission Database for Global Atmospheric Research (EDGAR), release  
29 version 4.2: available at: <http://edgar.jrc.ec.europa.eu> (last access: April 2014), 2011.





- 1 Eckhardt, S., Stohl, A., Beirle, S., Spichtinger, N., James, P., Forster, C., Junker, C., Wagner,  
2 T., Platt, U., and Jennings, S. G.: The North Atlantic Oscillation controls air pollution transport  
3 to the Arctic, *Atmos. Chem. Phys.*, 3, 1769-1778, doi:10.5194/acp-3-1769-2003, 2003.
- 4 Fuller, E. N., Schettler, P. D., and Giddings, J. C.: A new method for prediction of binary gas-  
5 phase diffusion coefficients, *Ind. Eng. Chem.*, 58, 19-27, 1966.
- 6 Gilge, S., Plass-Duelmer, C., Fricke, W., Kaiser, A., Ries, L., Buchmann, B., and Steinbacher,  
7 M.: Ozone, carbon monoxide and nitrogen oxides time series at four alpine GAW mountain  
8 stations in central Europe, *Atmos. Chem. Phys.*, 10, 12295-12316, 2010.
- 9 Hartmann, D. L., Klein Tank, A. M. G., Rusticucci, M., Alexander, L. V., Brönnimann, S.,  
10 Charabi, Y., Dentener, F. J., Dlugokencky, E. J., Easterling, D. R., Kaplan, A., Soden, B. J.,  
11 Thorne, P. W., Wild, M., and Zhai, P. M.: Observations: Atmosphere and Surface. In: *Climate*  
12 *Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth*  
13 *Assessment Report of the Intergovernmental Panel on Climate Change* [Stocker, T.F., D. Qin,  
14 G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M.  
15 Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York,  
16 NY, USA. 2013.
- 17 Helmig, D., Thompson, C. R., Evans, J., Boylan, P., Hueber, J., and Park, J. -H.: Highly  
18 elevated atmospheric levels of volatile organic compounds in the Uintah basin, Utah, *Environ.*  
19 *Sci. Technol.*, 48, 4707-4715, 2014a.
- 20 Helmig, D., Petrenko, V., Martinerie, P., Witrant, E., Röckmann, T., Zuiderweg, A., Holzinger,  
21 R., Hueber, J., Thompson, C., White, J. W. C., Sturges, W., Baker, A., Blunier, T., Etheridge,  
22 D., Rubino, M., and Tans, P.: Reconstruction of Northern Hemisphere 1950-2010 atmospheric  
23 non-methane hydrocarbons, *Atmos. Chem. Phys.*, 14, 1463-1483, 2014b.
- 24 Helmig, D., Bottenheim, J., Galbally, I. E., Lewis, A., Milton, M. J. T., Penkett, S., Plass-  
25 Duelmer, C., Reimann, S., Tans, P., and Thiel, S.: Volatile Organic Compounds in the Global  
26 Atmosphere, *Eos Trans., AGU*, 90, Feature, 2009.
- 27 Hirdman, D., Burkhart, J. F., Sodemann, H., Eckhardt, S., Jefferson, A., Quinn, P. K., Sharma,  
28 S., Ström, J., and Stohl, A.: Long-term trends of black carbon and sulphate aerosol in the Arctic:  
29 changes in atmospheric transport and source region emissions, *Atmos. Chem. Phys.*, 10, 9351-  
30 9368, 2010.



- 1 Hurrell, J. W., and Deser, C.: North Atlantic climate variability: The role of the North Atlantic  
2 Oscillation, *J. Marine Syst.*, 79, 231-244, 2010.
- 3 Johnson, D., and Marston, G.: The gas-phase ozonolysis of unsaturated volatile organic  
4 compounds in the troposphere, *Chem. Soc. Rev.*, 37, 699–716, 2008.
- 5 Kahl, J. D. W., Galbraith, J. A., and Martinez, D. A.: Decadal-scale variability in long range  
6 atmospheric transport to the Summit of the Greenland Ice Sheet, *Geophys. Res. Lett.*, 26, 481-  
7 484, 1999.
- 8 Kai, F. M., Tyler, S. C., Randerson, J. T, and Blake, D. R.: Reduced methane growth rate  
9 explained by decreased Northern Hemisphere microbial sources, *Nature*, 476, 194-197, 2011.
- 10 Klonecki, A., Hess, P., Emmons, L., Smith, L., Orlando, J., and Blake, D.: Seasonal changes in  
11 the transport of pollutants into the Arctic troposphere – model study, *J. Geophys. Res.*, 108,  
12 doi:10.1029/2002JD002199, 2003.
- 13 Monteil, G., Houweling, S., Dlugokenky, E. J., Maenhout, G., Vaughn, B. H., White, J. W.  
14 C., and Rockmann, T.: Interpreting methane variations in the past two decades using  
15 measurements of CH<sub>4</sub> mixing ratio and isotopic composition, *Atmos. Chem. Phys.*, 11, 9141-  
16 9153, 2011.
- 17 Montzka, S. A., Krol, M., Dlugokenky, E., Hall, B., Jöckel, P., and Lelieveld, J.: Small  
18 Interannual Variability of Global Atmospheric Hydroxyl, *Science*, 331, 67-69, 2011.
- 19 Naik, V., Voulgarakis, A., Fiore, A. M., Horowitz, L. W., Lamarque, J.-F., Lin, M., Prather, M.  
20 J., Young, P. J., Bergmann, D., Cameron-Smith, P. J., Cionni, I., Collins, W. J., Dalsøren, S.  
21 B., Doherty, R., Eyring, V., Faluvegi, G., Folberth, G. A., Josse, B., Lee, Y. H., MacKenzie, I.  
22 A., Nagashima, T., van Noije, T. P. C., Plummer, D. A., Righi, M., Rumbold, S. T., Skeie, R.,  
23 Shindell, D. T., Stevenson, D. S., Strode, S., Sudo, K., Szopa, S., and Zeng, G.: Preindustrial to  
24 present-day changes in tropospheric hydroxyl radical and methane lifetime from the  
25 Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP), *Atmos.*  
26 *Chem. Phys.*, 13, 5277-5298, 2013.
- 27 Olivier, J.G.J., Berdowski, J.J.M.: Global emissions sources and sinks. In: Berdowski, J., et al.  
28 (Eds.), *The Climate System*. A.A. Balkema/Swets and Zeitlinger, Lisse, The Netherlands, pp.  
29 33-78, 2001.



- 1 Olivier, J.G.J., Berdowski, J.J.M., Peters, J.A.H.W., Bakker, J., Visschedijk, A.J.H., Bloos,  
2 J.P.J.: Applications of EDGAR. Including a Description of EDGAR 3.0: Reference Database  
3 with Trend Data for 1970-1995. RIVM, Biltoven, 2001.
- 4 Parrish, D. D., Law, K. S., Staehelin, J., Derwent, R., Cooper, O. R., Tanimoto, H., Volz-  
5 Thomas, A., Gilge, S., Scheel, H.-E., Steinbacher, M., and Chan, E.: Long-term changes in  
6 lower tropospheric baseline ozone concentrations at northern mid-latitudes, Atmos. Chem.  
7 Phys., 12, 11485-11504, 2012.
- 8 Parrish, D. D., Lamarque, J. -F., Naik, V., Horowitz, L., Shindell, D. T., Staehelin, J., Derwent,  
9 R., Cooper, O. R., Tanimoto, H., Volz-Thomas, A., Gilge, S., Scheel, H.-E., Steinbacher, M.,  
10 and Froehlich, M.: Long-term changes in lower tropospheric baseline ozone concentrations:  
11 Comparing chemistry-climate models and observations at northern mid-latitudes, J. Geophys.  
12 Res. Atmos., 119, doi:10.1002/2013JD021435, 2014.
- 13 Petrenko, V. V., Martinerie, P., Novelli, P., Etheridge, D. M., Levin, I., Wang, Z., Blunier, T.,  
14 Chappellaz, J., Kaiser, J., Lang, P., Steele, L. P., Hammer, S., Mak, J., Langenfelds, R. L.,  
15 Schwander, J., Severinghaus, J. P., Witrant, E., Pétron, G., Battle, M. O., Forster, G., Sturges,  
16 W. T., Lamarque, J.-F., Steffen, K., and White, J. W. C.: A 60 yr record of atmospheric carbon  
17 monoxide reconstructed from Greenland firn air, Atmos. Chem. Phys., 13, 7567-7585, 2013.
- 18 Pétron, G., Frost, G., Miller, B. R., Hirsch, A. I., Montzka, S. A., Karion, A., Trainer, M.,  
19 Sweeney, C., Andrews, A. E., Miller, L., Kofler, J., Bar-Ilan, A., Dlugokencky, E. J., Patrick,  
20 L., Moore, C. T., Ryerson, T. B., Siso, C., Kolodzey, W., Lang, P. M., Conway, T., Novelli, P.,  
21 Masarie, K., Hall, B., Guenther, D., Kitzis, D., Miller, J., Welsh, D., Wolfe, D., Neff, W., and  
22 Tans, P.: Hydrocarbon emissions characterization in the Colorado Front Range: A pilot study,  
23 J. Geophys. Res. Atmos., 117, doi:10.1029/2011JD016360, 2012.
- 24 Pollmann, J., Helmig, D., Hueber, J., Plass-Duelmer, C., and Tans, P.: Sampling, storage, and  
25 analysis of C2-C7 non-methane hydrocarbons from the US National Oceanic and Atmospheric  
26 Administration Cooperative Air Sampling Network glass flasks, J. Chromatogr. A, 1188, 75-  
27 87, 2008.
- 28 Pozzer, A., Pollmann, J., Taraborrelli, D., Jöckel, P., Helmig, D., Tans, P., Hueber, J., and  
29 Lelieveld, J.: Observed and simulated global distribution and budget of atmospheric C2-C5  
30 alkanes, Atmos. Chem. Phys., 10, 4403-4422, 2010.



- 1 Prinn, R. G., Weiss, R. F., Miller, B. R., Huang, J., Aleya, F. N., Cunnold, D. M., Fraser, P. J.,  
2 Hartley, D. E., and Simmonds, P. G.: Atmospheric trends and lifetime of  $\text{CH}_3\text{CCl}_3$  and global  
3 OH concentrations, *Science*, 269, 187-192, 1995.
- 4 Prinn, R. G., Huang, J., Weiss, R. F., Cunnold, D. M., Fraser, P. J., Simmonds, P. G.,  
5 McCulloch, A., Harth, C. M., Salameh, P. K., O'Doherty, S., Wang, R. H. J., Porter, L., and  
6 Miller, B. R.: Evidence for substantial variations of atmospheric hydroxyl radicals in the past  
7 two decades, *Science*, 292, 1882–1888, 2001.
- 8 Prinn, R. G., Huang, J., Weiss, R. F., Cunnold, D. M., Fraser, P. J., Simmonds, P. G.,  
9 McCulloch, A., Harth, C. M., Reimann, S., Salameh, P. K., O'Doherty, S., Wang, R. H. J.,  
10 Porter, L. W., Miller, B. R., and Krummel P. B.: Evidence for variability of atmospheric  
11 hydroxyl radicals over the past quarter century, *Geophys. Res. Lett.*, 32, L07809,  
12 doi:10.1029/2004GL022228, 2005.
- 13 Rigby, M., Prinn, R. G., Fraser, P. J., Simmonds, P. G., Langenfelds, R. L., Huang, J.,  
14 Cunnold, D. M., Steele, L. P., Krummel, P. B., Weiss, R. F., O'Doherty, S., Salameh, P. K.,  
15 Wang, H. J., Harth, C. M., Mühle, J., and Porter, L. W.: Renewed growth of atmospheric  
16 methane, *Geophys. Res. Lett.*, 35, Article number L22805, 2008.
- 17 Sapart, C. J., Martinerie, P., Witrant, E., Chappellaz, J., van de Wal, R. S. W., Sperlich, P., van  
18 der Veen, C., Bernard, S., Sturges, W. T., Blunier, T., Schwander, J., Etheridge, D., and  
19 Röckmann, T.: Can the carbon isotopic composition of methane be reconstructed from multi-  
20 site firn air measurements?, *Atmos. Chem. Phys.*, 13, 6993-7005, 2013.
- 21 Schwander, J., Barnola, J. –M., Andrié, C., Leuenberger, M., Ludin, A., Raynaud, D., and  
22 Stauffer, B.: The age of the air in the firn and the ice at Summit, Greenland. *J. Geophys. Res.*  
23 98, 2831-2838, 1993.
- 24 Shindell, D. T.: A multi-model assessment of pollution transport to the Arctic, *Atmos. Chem.*  
25 *Phys.*, 8, 5353-5372, 2008.
- 26 Smith, S. C., Lee, J. D., Bloss, W. J., Johnson, G. P., Ingham, T., and Heard, D. E.:  
27 Concentrations of OH and  $\text{HO}_2$  radicals during NAMBLEX: Measurements and steady state  
28 analysis, *Atmos. Chem. Phys.*, 6, 1435-1453, 2006.
- 29 Smith, S. J., van Aardenne, J., Klimont, Z., Andres, R. J., Volke, A., and Delgado Arias, S.:  
30 Anthropogenic sulfur dioxide emissions: 1850 – 2005, *Atmos. Chem. Phys.*, 11, 1101-1116,  
31 2011.



- 1 Stohl, A.: Characteristics of atmospheric transport into the Arctic troposphere, *J. Geophys. Res.*  
2 *Atmos.*, 111, D11306, doi:10.1029/2005JD006888, 2006.
- 3 Stohl, A., Berg, T., Burkhardt, J. F., Fjærraa, A. M., Forster, C., Herber, A., Hov, Ø., Lunder, C.,  
4 McMillan, W. W., Oltmans, S., Shiobara, M., Simpson, D., Solberg, S., Stebel, K., Ström, J.,  
5 Tørseth, K., Treffeisen, R., Virkkunen, K., and Yttri, K. E.: Arctic smoke – Record high air  
6 pollution levels in the European Arctic due to agricultural fires in Eastern Europe in spring  
7 2006, *Atmos. Chem. Phys.*, 7, 511-534, 2007.
- 8 Stone, D., Whalley, L. K. and Heard, D. E.: Tropospheric OH and HO<sub>2</sub> radicals: field  
9 measurements and model comparisons, *Chem. Soc. Rev.*, 41, 6348-6404, 2012.
- 10 Swanson, A., Blake, N., Atlas, E., Flocke, F., Blake, D. R., and Sherwood, F.: Seasonal  
11 variation of C<sub>2</sub>–C<sub>4</sub> nonmethane hydrocarbons and C<sub>1</sub>–C<sub>4</sub> alkyl nitrates at the Summit research  
12 station in Greenland, *J. Geophys. Res.*, 108, ACH 7-1 ACH 7-19, 2003.
- 13 Talukdar, R. K., Herndon, S. C., Burkholder, J. B., Roberts, J. M., and Ravishankara, A. R.:  
14 Atmospheric fate of several alkyl nitrates. 1. Rate coefficients of the reactions alkyl nitrates  
15 with isotopically labelled hydroxyl radicals, *J. Chem. Soc. Faraday T.*, 93, 2787-2796, 1997.
- 16 Tuazon, E. C., Atkinson, R., Plum, N. C., Winer, A. M., and Pitts, J. N.: The reaction of gas-  
17 phase N<sub>2</sub>O<sub>5</sub> with water vapour, *Geophys. Res. Lett.*, 10, 953-956, 1983.
- 18 Turnock, S. T., Spracklen, D. V., Carslaw, K. S., Mann, G. W., Woodhouse, M. T., Forster, P.  
19 M., Haywood, J., Johnson, C. E., Dalvi, M., Bellouin, N., and Sanchez-Lorenzo, A.: Modelled  
20 and observed changes in aerosols and surface solar radiation over Europe between 1960 and  
21 2009, *Atmos. Chem. Phys.*, 15, 9477-9500, 2015.
- 22 Vestreng, V., Ntziachristos, L., Semb, A., Reis, S., Isaksen, I. S. A., and Tarrasón, L.: Evolution  
23 of NO<sub>x</sub> emissions in Europe with focus on road transport control measures, *Atmos. Chem.*  
24 *Phys.*, 9, 1503-1520, 2009.
- 25 Wang, Z., Chappellaz, J., Martinerie, P., Park, K., Petrenko, V., Witrant, E., Emmons, L. K.,  
26 Blunier, T., Brenninkmeijer, C. A. M., and Mak, J. E.: The isotopic record of Northern  
27 Hemisphere atmospheric carbon monoxide since 1950: Implications for the CO budget, *Atmos.*  
28 *Chem. Phys.*, 12, 4365-4377, 2012.
- 29 Warneke, C., De Gouw, J. A., Holloway, J. S., Peischl, J., Ryerson, T. B., Atlas, E., Blake, D.,  
30 Trainer, M., and Parrish, D. D.: Multiyear trends in volatile organic compounds in Los Angeles,



- 1 California: Five decades of decreasing emissions, *J. Geophys. Res.*, 117,  
2 doi:10.1029/2012JD017899, 2012.
- 3 Wild, M., Gilgen, H., Roesch, A., Ohmura, A., Long, C. N., Dutton, E. G., Forgan, B., Kallis,  
4 A., Russak, V., and Tsvetkov, A.: From dimming to brightening: decadal changes in solar  
5 radiation at earth's surface, *Science*, 308, 847–850, 2005.
- 6 Witrant, E., Martinerie, P., Hogan, C., Laube, J. C., Kawamura, K., Capron, E., Montzka, S.  
7 A., Dlugokencky, E. J., Etheridge, D., Blunier, T., and Sturges, W. T.: A new multi-gas  
8 constrained model of trace gas non-homogeneous transport in firn: evaluation and behaviour at  
9 eleven polar sites, *Atmos. Chem. Phys.*, 12, 11465-11483, 2012.
- 10 Witrant, E. and Martinerie, P.: Input Estimation from Sparse Measurements in LPV Systems  
11 and Isotopic Ratios in Polar Firms, *Proc. of the 5th IFAC Symposium on System Structure and*  
12 *Control*, Grenoble, France, Feb. 4-6, 2013.
- 13 Worton, D. R., Mills, G. P., Oram, D. E., and Sturges, W. T.: Gas chromatography negative ion  
14 chemical ionization mass spectrometry: application to the detection of alkyl nitrates and  
15 halocarbons in the atmosphere, *J. Chromatogr. A*, 1201, 112-119, 2008.
- 16 Worton, D. W., Sturges, W. T., Reeves, C. E., Newland, M. J., Penkett, S. A., Atlas, E., Stroud,  
17 V., Johnson, K., Schmidbauer, N., Solberg, S., Schwander, J., and Barnola, J. -M.: Evidence  
18 from firn air for recent decreases in non-methane hydrocarbons and a 20th century increase in  
19 nitrogen dioxides in the northern hemisphere, *Atmos. Environ.*, 54, 592-602, 2012.