1 **Changes to the chemical state of the northern hemisphere**

2 **atmosphere during the second half of the twentieth century**

3

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13

14 **Abstract**

15 **The NO_X (NO and NO_2) and HO_X (OH and HO_2) 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_X and HO_X**

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_2 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_X, lead to the formation of the**

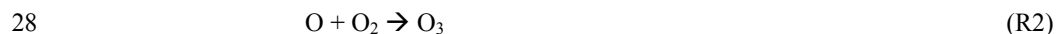29 **alkyl nitrates). The ratios of the alkyl nitrates to their parent alkanes increase from**

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1   **around 1970 to the late 1990's consistent with large changes to the [NO]/[HO$_2$] ratio in**

2   **the northern hemisphere atmosphere during this period. These could represent historic**

3   **changes to NO$_X$ 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$_X$ (NO + NO$_2$) and HO$_X$ (OH + HO$_2$) budgets of the troposphere act to control the

9   concentrations of oxidants such as OH, ozone and NO$_3$ (Fig. 1). These in turn control removal

10   of pollutants from the atmosphere. Emissions of NO$_x$ 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$_X$ and HO$_X$ are linked through the

13   production of ozone, which is positively correlated with NO$_X$ concentrations in the background

14   atmosphere through the photolysis of NO$_2$ (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$_X$ from the atmosphere is controlled by the reaction of NO$_2$ with OH during the daytime

17   (Reaction R5). This forms nitric acid, HNO$_3$, which is lost from the atmosphere by wet

18   deposition. At night, and during the winter, the heterogeneous reaction of the NOx reservoir

19   species N$_2$O$_5$ (formed from the reaction of NO$_2$ with NO$_3$ (Reactions R6-R7) with H$_2$O on

20   aerosol becomes an important NO$_X$ sink (Reaction R8). OH and HO$_2$ rapidly interconvert

21   through the reactions of OH with CO and hydrocarbons, such as alkanes, and the reaction of

22   HO$_2$ with NO (Reaction R9). The reaction of NO with peroxy radicals (HO$_2$ and RO$_2$ –

23   Reactions R9-R10) recycles the NO$_X$ back to NO$_2$. The main removal processes for HOx are

24   the reaction of OH with NO$_2$ (Reaction R9) and the reaction of HO$_2$ with peroxy radicals

25   (including self-reaction) (Reactions R11-R12).

26   *HO$_X$ sources*

27   $$NO_2 \rightarrow NO + O \hspace{4cm} (R1)$$

28   $$O + O_2 \rightarrow O_3 \hspace{4cm} (R2)$$

29   $$O_3 \rightarrow O(^1D) + O_2 \hspace{4cm} (R3)$$

30   $$O(^1D) + H_2O \rightarrow 2OH \hspace{3.5cm} (R4)$$

1

2   *NO_X sinks*

3   *Day:* $NO_2 + OH \rightarrow HNO_3$ (R5)

4   *Night:* $NO_2 + O_3 \rightarrow NO_3 + O_2$ (R6)

5                           $NO_2 + NO_3 \rightarrow N_2O_5$ (R7)

6                           $N_2O_5 + H_2O \rightarrow 2HNO_3$ (R8)

7   ***NOx and HOx recycling***

8                           $NO + HO_2 \rightarrow OH + NO_2$ (R9)

9                           $NO + RO_2 \rightarrow RO + NO_2$ (R10)

10   ***HO_X sinks***

11                          $HO_2 + RO_2 \rightarrow ROOH$ (R11)

12                          $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ (R12)

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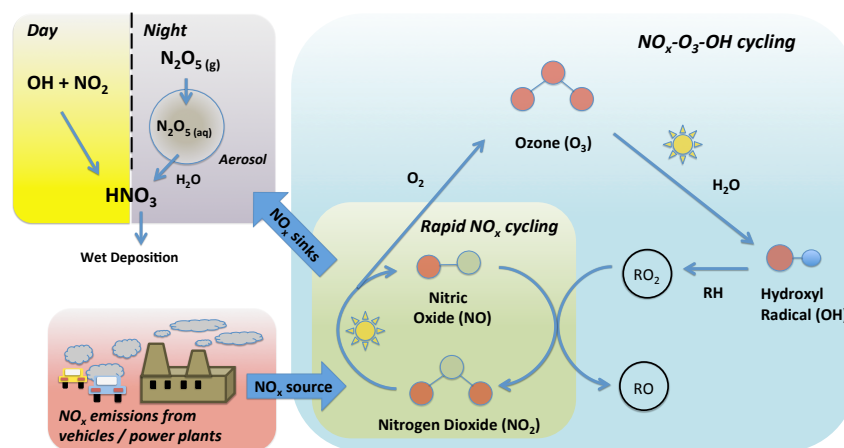
15   Figure 1 Schematic of the NO_x-O_3-OH relationship in the background troposphere.

16

17   However, changes to the atmospheric concentrations of both HO_X and NO_X during the previous

18   century are poorly constrained. This is because all HO_X and NO_X species are short lived, present

19   at low concentrations (0.01 – 10 ppt) and have a high spatial and temporal variability. (e.g.

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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 (± 1.9) %. This modelled increase is driven by increases in

7   the NO_x burden and in the water vapour concentration.

8   To attempt to study historical trends in HO_X and NO_X we have examined trends in longer living

9   species which are affected by changes to HO_X and 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 (C_4H_{10}) and pentanes (C_5H_{12}) to the atmosphere are almost entirely

18 anthropogenic (> 98 % globally (Pozzer 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 (Pozzer 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, 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 (~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 (Pozzer

27 et al., 2010).

28 **1.2   Alkyl Nitrates**

29 Alkyl nitrates ($RONO_2$) 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 (Clemitshaw

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_2

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 $RO_2 + NO$ reaction (Reaction R14a)

6   which generally leads to ozone production via recycling of NO to NO_2 and the subsequent

7   photolysis of NO_2. RO_2 can also react with HO_2 (the hydroperoxyl radical) (Reaction R11) to

8   form a peroxide (ROOH). The probability of RO_2 reacting with NO (leading to alkyl nitrate

9   production) is thus governed by the ratio $[NO]/[HO_2]$. Alkyl nitrates are lost from the

10   atmosphere by reaction with OH (Reaction R15), photolysis (Reaction R16) and wet/dry

11   deposition.

12       $RH + OH \rightarrow RO_2$ (R13)

13       $RO_2 + NO \rightarrow RCHO + NO_2$ (R14a)

14              $\rightarrow RONO_2$ (R14b)

15       $RO_2 + HO_2 \rightarrow ROOH$ (R11)

16       $RONO_2 + OH \rightarrow$ products   (R15)

17       $RONO_2 \rightarrow$ products   (R16)

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 14th and 30th 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

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

2   Buizert et al. (2012).

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).

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.

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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_2, CH_4, SF_6, HFC-134a,

4   CFC-11, CFC-12, CFC-113, and CH_3CCl_3, as well as $^{14}CO_2$ (Witrant 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_2. 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 Witrant 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

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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_2
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

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1   measurements to output derived from the firn measurements the annual mean is taken. This is

2   because the firn 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 firn model for 2-butyl nitrate. These agree with the firn 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 firn model output, though this is not statistically

8   significant within the errors.

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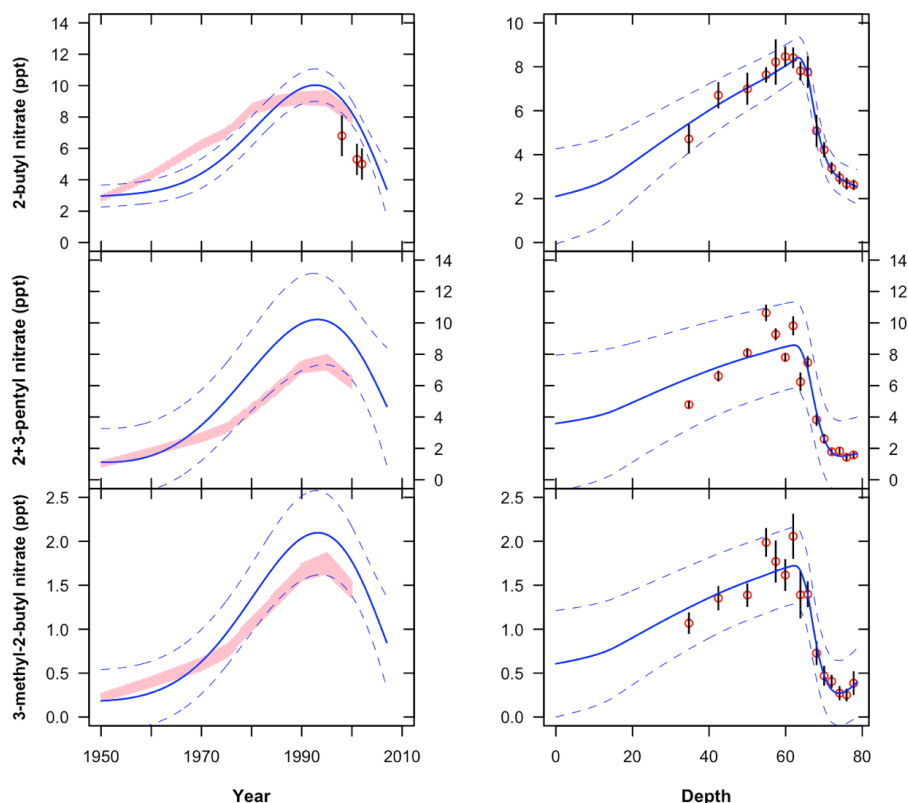
Figure 2 Concentration-depth profiles in the firn and the model derived atmospheric histories. Right panel: The concentration-depth profiles measured in the firn (ppt): red open circles: measured mixing ratios (ppt) with error bars indicating the 2-σ uncertainty; solid blue line: best fit of the firn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

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 [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 HO_2 (Reaction R11;

9   (iv)   Changes to the alkyl nitrate sinks, i.e., changes in [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 (~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 firn 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.

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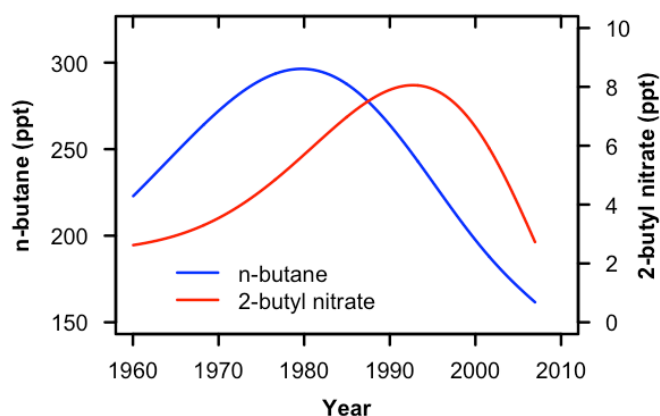
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19   Figure 3 Atmospheric histories of 2-butyl nitrate (red) and its parent alkane, n-butane (blue), derived from firn

20   measurements at NEEM, Greenland.

21

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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_x rich environment (Equation E1 (assumes an initial zero mixing ratio for alkyl

11 nitrates)). We extend Equation E1 to include the term $k_{14}[NO]/(k_{14}[NO]+k_{11}[HO_2])$ (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
$$\frac{[RONO_2]}{[RH]} = \frac{\beta k_A}{(k_B - k_A)}\left(1 - e^{(k_A - k_B)t}\right)$$
(E1)

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

17 in the Introduction.

18
$$\frac{[RONO_2]}{[RH]} = \frac{\beta k_A}{(k_B - k_A)}(1 - e^{(k_A - k_B)t})\frac{k_{14}[NO]}{k_{14}[NO] + k_{11}[HO_2]}$$
(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. ∫[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 $[RONO_2]/[RH]$ 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 $[NO]/[HO_2]$ ratio) has changed over time. Secondly, that the processing of the air mass, i.e. OH

1   concentration ([OH]), 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 [NO] can range from $10 - 1000$ ppb. At these mixing ratios

6   the ratio $k_{14}[NO]/(k_{14}[NO]+k_{11}[HO_2])$ 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 α_{13}. However, in rural and more remote regions of the atmosphere, daytime [NO] ranges

9   from $1 - 100$ ppt. At these mixing ratios $k_{14}[NO]/(k_{14}[NO]+k_{11}[HO_2])$ varies between around

10    $0.4 - 1$, assuming a daytime $[HO_2] = 2 \times 10^7$ molecules cm^{-3} (winter time – the alkyl nitrate and

11   alkane signals in the firn are dominated by winter time concentrations). Changes to [NO] or

12   [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 [NO]/[HO$_2$] can

14   be calculated using the changes to the [RONO$_2$]/[RH] ratio (assuming that the photochemical

15   processing, [OH]t, has remained constant).

$$\frac{[NO]}{[HO_2]} = \left[\frac{k_{14}}{k_{11}} \left(\frac{[RH] k_{13} \alpha_{13} \alpha_{14} \left(1 - e^{(k_{13}-k_{15})[OH]t}\right)}{[RONO_2] (k_{15} - k_{13})} - 1 \right) \right]^{-1}$$

16   (E3)

17
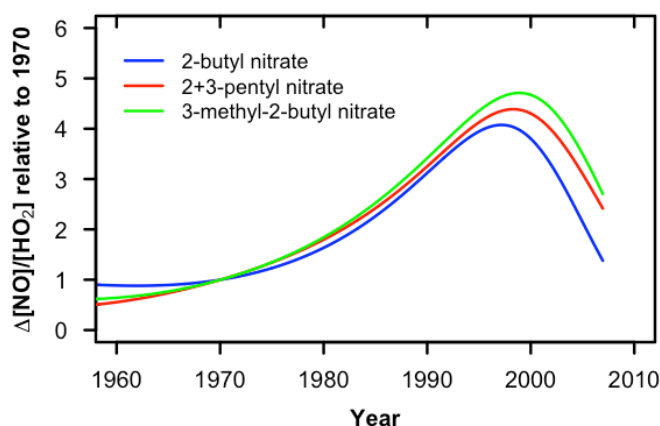
18   Figure 4 The trend in the [NO]/[HO$_2$] ratio of the air masses in which the alkyl nitrates were formed, calculated

19   using Equation E3 for each of three alkyl nitrate/alkane pairs. This assumes that the amount of photochemical

20   processing, [OH]t, remained constant at 5×10^{11} molecules cm^{-3} s.

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2   Figure 4 shows the trend in the [NO]/[HO$_2$] ratio derived using Equation E3. A value of 5 ×

3   10^{11} molecules cm^{-3} s is used for the constant [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 [OH] of ~ 6 × 10^5 cm^{-3} (in reasonable agreement with that derived by Derwent et

7   al. (2012) for the North Atlantic in winter-time). Halving the assumed [OH].t to 2.5 × 10^{11}

8   molecules cm^{-3} s increases the magnitude of the relative changes by a factor of ~ 2. Whereas

9   doubling [OH].t, only decreases the derived changes by ~ 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 [NO]/[HO$_2$] ratio, we shall

13   now examine how the NO$_x$ and HO$_2$ concentrations may have changed.

14   **5.1   Changes to atmospheric NO$_x$ concentrations**

15   5.1.1 NO$_x$ sources

16   The atmospheric NO$_X$ concentration is determined by the relative magnitudes of the sources

17   and sinks. The main sources of 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 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 NO$_X$ emission

24   trends for OECD Europe presented in Vestreng et al. (2009).

25

1
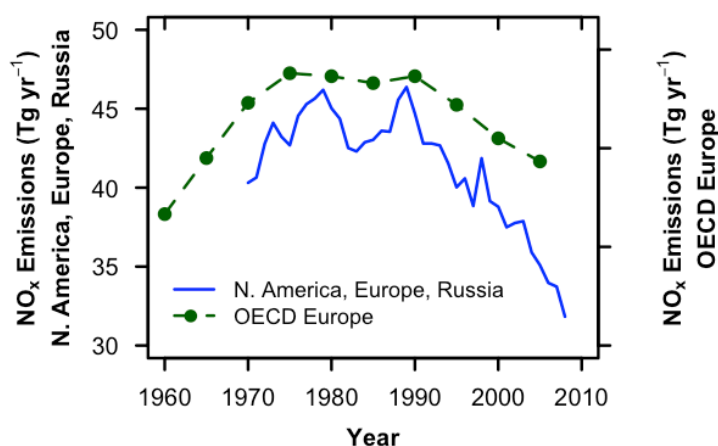
Figure 5 Blue solid line (left axis): The trend in NO_X emissions (Tg yr^{-1}) from North America, Europe and Russia
for the period 1970 to 2008 (EDGAR v4.2, http://edgar.jrc.ec.europa.eu). Green points (and dashed line) (right
axis): OECD Europe NO_X emissions (Tg yr^{-1}) from Vestreng et al. (2009).

5

6   Assuming that these bottom up emissions estimates are correct in the timing of the NO_X

7   emissions changes, it seems unlikely that the increase in the [NO]/[HO$_2$] ratio derived for the

8   period 1970 to the late 1990s was driven primarily by changing NO_X emissions.

9   The subsequent decline in [NO]/[HO$_2$], 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_X

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_X that is NO_2 (f-NO$_2$) roughly doubled. Recent trends at many European sites show

14 similar trends with small decreases in NO_x between 1999 and 2007 (the period for which

15 measurements are available) but level or increasing NO_2 through the same period (Carslaw et

16 al., 2011; Gilge et al., 2010) – suggesting that NO has decreased by more than NO_x

17 concentrations.

18 Declining NO_X 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).

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5.1.2 NO$_x$ sinks

At mid-high latitudes, in the daytime, during the summer, the main sink for NO$_X$ is the reaction of NO$_2$ with OH. This reaction produces nitric acid (HNO$_3$), much of which is then removed from the atmosphere by wet deposition. However, at night and during the winter months, when daily mean [OH] is more than an order of magnitude lower than during the summer (e.g. Derwent et al., 2012), the dominant NO$_X$ sink is conversion of dinitrogen pentoxide (N$_2$O$_5$) to HNO$_3$ on aerosol. This occurs when photolysis is low, allowing NO$_3$ (formed from the reaction of NO$_2$ with O$_3$) to build up. NO$_3$ reacts with NO$_2$ to form N$_2$O$_5$. The reaction of N$_2$O$_5$ with H$_2$O is slow in the gas-phase (Tuazon et al., 1983) but occurs rapidly in aerosol.

A modelling study by Dentener and Crutzen (1993) predicted that changes to the loss of NO$_x$ via sulfate aerosol could have a significant effect on northern hemisphere NO$_x$ concentrations and that these changes would also affect O$_3$ and OH concentrations. Subsequent modelling studies have broadly agreed with the magnitude of the changes suggested by Dentener and Crutzen (Brown and Stutz, 2012). Based on these studies, the large decrease in sulfate aerosol observed in Europe and the United States since 1980 (Berglen et al., 2007; Turnock et al., 2015) (driven by a 60 – 70 % decrease in SO$_2$ emissions (Smith et al., 2011)) would be expected to have led to a decrease in NO$_X$ removal by N$_2$O$_5$ hydrolysis, and hence to an increase in the NO$_X$ lifetime and atmospheric [NO$_X$]. This time period is broadly in line with the derived steep increase in the [NO]/[HO$_2$] ratio.

5.2 The Hydroperoxyl Radical, HO$_2$

The complex nature of the interconnectedness of the chemistry make it difficult to predict how HO$_2$ concentrations will have changed in response to changes in primary emissions.

6 Changes to Photochemical Oxidation

An alternative explanation for the observed alkyl nitrate trends is that the amount of photochemical processing of the air mass changed during the time period. An increase in processing could be caused by a change in either the concentration of the OH radical (assuming photolysis to have remained constant), or by an increase in the transport time of the air mass 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, $[OH]t$, can be calculated using the changes to the $[RONO_2]/[RH]$

3   ratio (assuming that the $[NO]/[HO_2]$ ratio has remained constant).

4

$$[OH]t = \ln\left(1 - \left[\frac{[RONO_2]\,(k_{15}-k_{13})}{[RH]\,k_{13}\,\alpha_{13}\,\alpha_{14}}\left(\frac{k_{11}[HO_2]}{k_{14}[NO]}+1\right)\right]\right) \div (k_{13}-k_{15}) \qquad (E4)$$
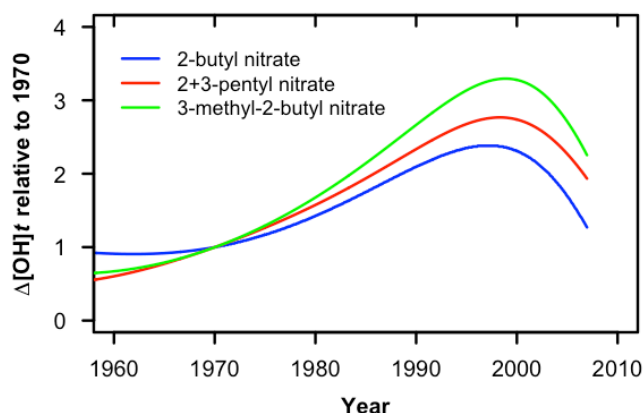
5

6

7

8   Figure 6 The trend in $[OH]t$ calculated using Equation E4 for each of three alkane-alkyl nitrate pairs. This assumes

9   that the ratio $[NO]/[HO_2]$ remained constant at 0.5.

10

11   Figure 6 shows the trends in $[OH].t$ derived from the alkyl nitrate-alkane pairs if a constant

12   value for $[NO]/[HO_2]$ is assumed. The value used for the constant $[NO]/[HO_2]$ was 0.5. This is

13   in line with the $[NO]/[HO_2]$ derived using Equation E3 with a fixed $[OH]t$ value of 5×10^{11}

14   molecules cm^{-3} s.

15   Figure 6 shows that the observed $[RONO_2]/[RH]$ ratios between around 1970 and the late 1990s

16   could be explained by a relative change in $[OH]t$ of a factor of between 2.4 (2-butyl nitrate) and

17   3.3 (3-methyl-2-butyl nitrate). Increasing the $[NO]/[HO_2]$ value by an order of magnitude, to 5,

18   decreases the derived $[OH]t$ changes by $\sim 25\%$. Decreasing the $[NO]/[HO_2]$ value by an order

19   of magnitude, to 0.05, increases the derived $[OH]t$ changes by $\sim 5\%$.

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6.1 Air mass transport time to the Arctic

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

6.2 The Hydroxyl Radical, OH

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

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1   Studies using changes to atmospheric mixing ratios of methyl chloroform (CH_3CCl_3) have

2   suggested that global mean OH concentrations are 'well buffered' (e.g. Montzka et al., 2011).

3   Since the main sink of CH_3CCl_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 δ-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 $d^{13}C$ of methane

18   (Monteil et al., 2011; Sapart et al., 2013); decreasing $dC^{16}O$ 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 (± 2.2) % between

21   1980 and 2000 and a slightly larger [OH] increase in the northern hemisphere of 4.6 (± 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 NO_X and 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

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1   positively linked to [NO$_X$] (at low NO$_X$ concentrations such as the background atmosphere).

2   Hence, an increase in the [NO]/[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 [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 [OH]. Indeed due to the connected

10   nature of the chemistry of NO$_X$, ozone and OH it seems unlikely, given the implied increases

11   in 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(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        $P(\mathrm{OH}) = 2f[\mathrm{O}_3] \times j(\mathrm{O}^1\mathrm{D})$ (E5)

16   Where f is the fraction of O(^{1}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, 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   (Dlugockencky 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 [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 N$_2$O$_5$ sink,

32   have been shown to be effective at a hemispheric scale.

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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 NOx and HOx 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 $[NO]/[HO_2]$ ratio during

16   this period. A 4 – 5 fold increase in the $[NO]/[HO_2]$ ratio is suggested between the 1970s and

17   late 1990s. This is not consistent with reported changes to NO_X emissions, but may have been

18   driven by a reduction in the NO_X sink. The recent decreases (since the late 1990s) in alkyl

19   nitrate concentrations are in qualitative agreement with recent decreases in NO_X emissions and

20   in measured NO_X 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**

6

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