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

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Abstract

The NO_X (NO and NO_2) and HO_X (OH and HO_2) budgets of the atmosphere exert a major influence on atmospheric composition, controlling removal of primary pollutants and formation of a wide range of secondary products, including ozone, that can influence human health and climate. However, there remain large uncertainties in the changes to these budgets over recent decades. Due to their short atmospheric lifetimes, NO_X and HO_X are highly variable in space and time, and so the measurements of these species are of limited value for examining long term, large scale changes to their budgets. Here, we take an alternative approach by examining long-term atmospheric trends of alkyl nitrates, the formation of which is dependent on the atmospheric NO/HO_2 ratio. We derive long term trends in the alkyl nitrates from measurements in firn air from the NEEM site, Greenland. Their mixing ratios increased by a factor of 4 – 5 between the 1970s and 1990s. This was followed by a steep decline to the sampling date of 2008. Moreover, we examine how the trends in the alkyl nitrates compare to similarly derived trends in their parent alkanes (i.e. the alkanes which, when oxidised in the presence of NO_X, lead to the formation of the alkyl nitrates). The ratios of the alkyl nitrates to their parent alkanes increase from

around 1970 to the late 1990's consistent with large changes to the [NO]/[HO_2] ratio in the northern hemisphere atmosphere during this period. These could represent historic changes to NO_X sources and sinks. Alternatively, they could represent changes to concentrations of the hydroxyl radical, OH, or to the transport time of the air masses from source regions to the Arctic.

1 Introduction

The NO_X ($NO + NO_2$) and HO_X ($OH + HO_2$) budgets of the troposphere act to control the concentrations of oxidants such as OH, ozone and NO_3 (Fig. 1). These in turn control removal of pollutants from the atmosphere. Emissions of NO_x in the northern hemisphere are mainly anthropogenic, with roughly equal proportions from power generation and transport (Olivier and Berdowski et al., 2001; Olivier et al., 2001). NO_X and HO_X are linked through ozone production, which is positively correlated with NO_X concentrations in the background atmosphere through the photolysis of NO_2 (Reactions R1-R2). The photolysis of ozone in the presence of water vapour then leads to the production of OH (Reactions R3-R4). Removal of NO_X from the atmosphere is controlled by the reaction of NO_2 with OH during the daytime (Reaction R5). This forms nitric acid, HNO_3, which is lost from the atmosphere by wet deposition. At night, and during the winter, the heterogeneous reaction of the NOx reservoir species N_2O_5 (formed from the reaction of NO_2 with NO_3 (Reactions R6-R7) with H_2O on aerosol becomes an important NO_X sink (Reaction R8). OH and HO_2 rapidly interconvert through the reactions of OH with CO and hydrocarbons, such as alkanes, and the reaction of HO_2 with NO (Reaction R9). The reaction of NO with peroxy radicals (HO_2 and RO_2 – Reactions R9-R10) recycles the NO_X back to NO_2. The main removal processes for HOx are the reaction of OH with NO_2 (Reaction R5) and the reaction of HO_2 with peroxy radicals (including self-reaction) (Reactions R11-R12).

HO_X sources

$$\mathrm{NO_2} \rightarrow \mathrm{NO} + \mathrm{O} \tag{R1}$$

$$\mathrm{O} + \mathrm{O_2} \rightarrow \mathrm{O_3} \tag{R2}$$

$$\mathrm{O_3} \rightarrow \mathrm{O(^1D)} + \mathrm{O_2} \tag{R3}$$

$$\mathrm{O(^1D)} + \mathrm{H_2O} \rightarrow 2\mathrm{OH} \tag{R4}$$

NO_X sinks

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

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

$NO_2 + NO_3 \rightarrow N_2O_5$ (R7)

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

NOx and HOx recycling

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

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

HO_X sinks

$HO_2 + RO_2 \rightarrow ROOH$ (R11)

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

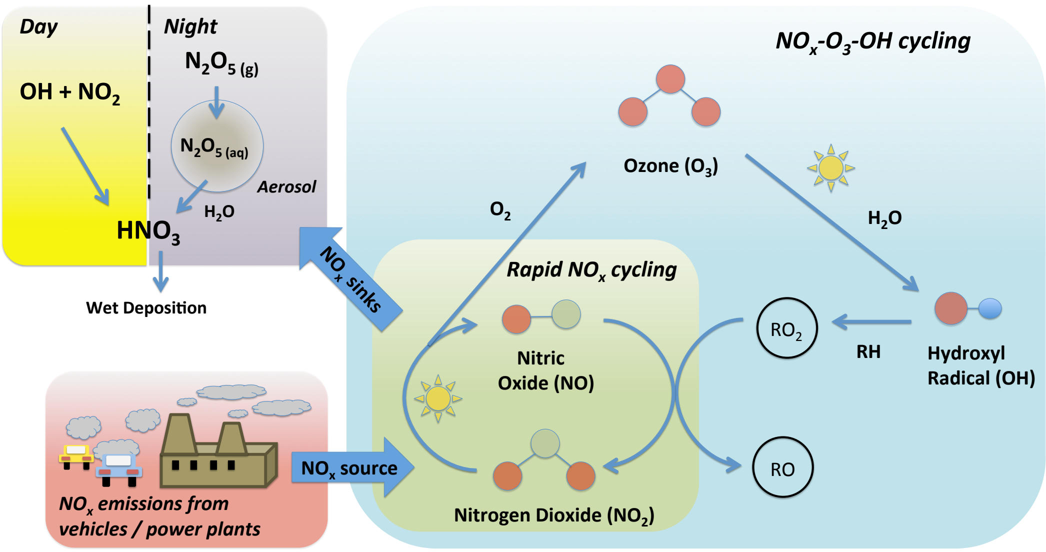

Figure 1 Schematic of the NO_x-O_3-OH relationship in the background troposphere.

However, changes to the atmospheric concentrations of both HO_X and NO_X during the previous century are poorly constrained. This is because all HO_X and NO_X species are short lived, present at low concentrations (0.01 – 10 ppt) and have a high spatial and temporal variability. (e.g.

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

To attempt to study historical trends in HO_X and NO_X we have examined trends in longer living species which are affected by changes to HO_X and NO_X in the atmosphere.

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

1.1 Alkanes

Emissions of butanes (C_4H_{10}) and pentanes (C_5H_{12}) to the atmosphere are almost entirely anthropogenic (> 98 % globally (Pozzer et al., 2010)), associated with fugitive emissions during oil and natural gas drilling and evaporation and combustion of fossil fuels such as in road vehicles (Pozzer et al., 2010; Pétron et al., 2012; Helmig et al., 2014a). The primary removal mechanism of these species from the atmosphere is reaction with the hydroxyl radical, OH (minor sinks include reaction with atomic chlorine, Cl, and the nitrate radical, NO_3). Atmospheric mixing ratios of butanes and pentanes display a large seasonal cycle in mid-high latitudes (*e.g.* Swanson *et al.*, 2003; Helmig *et al.*, 2009) due to changes in their chemical lifetimes (~1 month in the winter and 4 – 5 days in the summer) driven by the seasonal cycle in OH concentration. Emissions are not thought to have a significant seasonal variability (Pozzer et al., 2010).

1.2 Alkyl Nitrates

Alkyl nitrates ($RONO_2$) are secondary oxidation products of the alkanes (RH). Their atmospheric lifetimes are on the order of months in winter and ten days in summer (Clemitshaw et al., 1997). Consequently, they display a strong seasonal cycle in the Arctic, with peaks in the late winter/early spring and minima in the summer (Swanson et al., 2003), similar to the alkanes. Alkyl nitrates are formed when alkanes react with OH to form a peroxy radical, RO_2 (Reaction R13), which subsequently reacts with NO to form an alkyl nitrate (Reaction 14b) (*e.g.* Talukdar et al., 1997). This is a minor channel of the RO_2 + NO reaction (Reaction R14a) which generally leads to ozone production via recycling of NO to NO_2 and the subsequent photolysis of NO_2. RO_2 can also react with HO_2 (the hydroperoxyl radical) (Reaction R11) to form a peroxide (ROOH). The probability of RO_2 reacting with NO (leading to alkyl nitrate production) is thus governed by the ratio $[NO]/[HO_2]$. Alkyl nitrates are lost from the atmosphere by reaction with OH (Reaction R15), photolysis (Reaction R16) and wet/dry deposition.

$$RH + OH \rightarrow RO_2 \tag{R13}$$

$$RO_2 + NO \rightarrow RCHO + NO_2 \tag{R14a}$$

$$\rightarrow RONO_2 \tag{R14b}$$

$$RO_2 + HO_2 \rightarrow ROOH \tag{R11}$$

$$RONO_2 + OH \rightarrow \text{products} \tag{R15}$$

$$RONO_2 \rightarrow \text{products} \tag{R16}$$

2 Methodologies

2.1 Firn Sampling

Firn air samples were collected at the NEEM site, Greenland (77.45°N, 51.07°W, 2484m a.s.l) from two boreholes between 14th and 30th July 2008 ("2008 EU hole" and "2008 US hole"). Further samples were collected from another NEEM borehole during July 2009 ("2009 hole"). The '2008 EU hole' was sampled using the firn air system of the University of Bern (Schwander et al., 1993), and the 'US' hole, sampled using the US firn air system (Battle et al., 1996). The alkane measurements used in this work – originally reported in Helmig et al. (2014b) - come from a combination of the 2008 EU and US holes and the 2009 hole with the exception of the pentanes, which come only from the 2008 EU and US holes. The alkyl nitrate samples come only from the 2008 EU hole. Full sampling details are available in Helmig et al. (2014b) and Buizert et al. (2012).

2.2 Firn Analysis

The firn air samples from the 'EU' hole at NEEM were analysed for alkyl nitrates at UEA using a GC-MS in Negative Ion Chemical Ionisation mode (GC-NICI-MS) (e.g. Worton et al., 2008).

2-pentyl nitrate and 3-pentyl nitrate are presented together as 2+3-pentyl nitrate because the two are not baseline separated in the chromatogram.

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

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

2.3 Firn Modelling

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

For determining the atmospheric history of a gas from firn air measurements, the firn diffusion profiles must first be constrained. This is done using a series of reference gases with well known atmospheric histories. At NEEM the reference gases used were CO_2, CH_4, SF_6, HFC-134a, CFC-11, CFC-12, CFC-113, and CH_3CCl_3, as well as $^{14}CO_2$ (Witrant et al., 2012).

Each gas also has a different diffusion rate through the firn based on its molecular structure, this is called the diffusion coefficient. The diffusion coefficient is calculated relative to a reference gas, generally CO_2. Different methods have been reported for the calculation of these diffusion coefficients (e.g. Chen and Othmer, 1962; Fuller et al., 1966). The diffusion coefficients of the alkyl nitrates were calculated using the method of Fuller et al. (1966) based on the sum of the Le Bas molar volumes of the molecule. Model runs were also performed using diffusion coefficients for the alkyl nitrates calculated using the Chen and Othmer method. These coefficients are ~ 10% lower than those calculated using the Fuller method. However, the atmospheric scenarios derived from the modelling are very similar, well within the 2-σ uncertainty envelopes presented in Figure 2. The diffusion coefficients used for the firn modelling for each molecule within this work are given in Table 1.

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

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

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

Table 1 Diffusion coefficients used in the firn modelling, calculated from Le Bas molecular 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 Alkyl Nitrate Trends

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

Figure 2 also shows the atmospheric histories of the same three alkyl nitrates derived from firn air from North GRIP, Greenland, up to 2001, presented in Worton et al. (2012) (pink shaded area). There is very good agreement between the derived trends at the two sites. Differences can be attributed to the limited number of measurements at both sites, possible drift in the calibration standard used and uncertainties in the firn modelling. Both sites show the same large increase in mixing ratios from the 1970s to the 1990s. Importantly, the NEEM records show that the turnover and subsequent decline in mixing ratios, the beginnings of which were evident in the North GRIP records, appears to continue through the 2000s. However, as noted in Section 2.3, the derived atmospheric history of 2+3-pentyl nitrate is sensitive to the inclusion of the measurement at 34.72 m. The scenario that did not include this measurement was almost flat from 1995 to 2008 rather than declining as in Figure 2.

There are very limited in-situ measurements of alkyl nitrates in the Arctic and even fewer that cover a whole seasonal cycle. Swanson et al. (2003) report the seasonal cycle of 2-butyl nitrate at the Summit station, Greenland (72.34 N, 38.29 W, 3250 m a.s.l), from June 1997 to June 1998 based on samples collected roughly every two days. Dibb et al. (2007) report monthly mean measurements of 2-butyl nitrate for the period June 2000 through to August 2002 based on samples taken roughly weekly also from Summit. In order to compare these in-situ measurements to output derived from the firn measurements the annual mean is taken. This is because the firn smoothes out the seasonality and represents the annual mean of mixing ratios. Calculating the 2-butyl nitrate annual mean for the three periods 1997-1998 (6.8 ppt), 2000-2001 (5.3 ppt), and 2001-2002 (5.0 ppt) gives values that can be compared to the output from the firn model for 2-butyl nitrate. These agree with the firn model output in terms of absolute mixing ratios of 2-butyl nitrate during this period (5 – 8 ppt) (Fig. 2). They also show a declining trend through the period, in agreement with the firn model output, though this is not statistically significant within the errors.

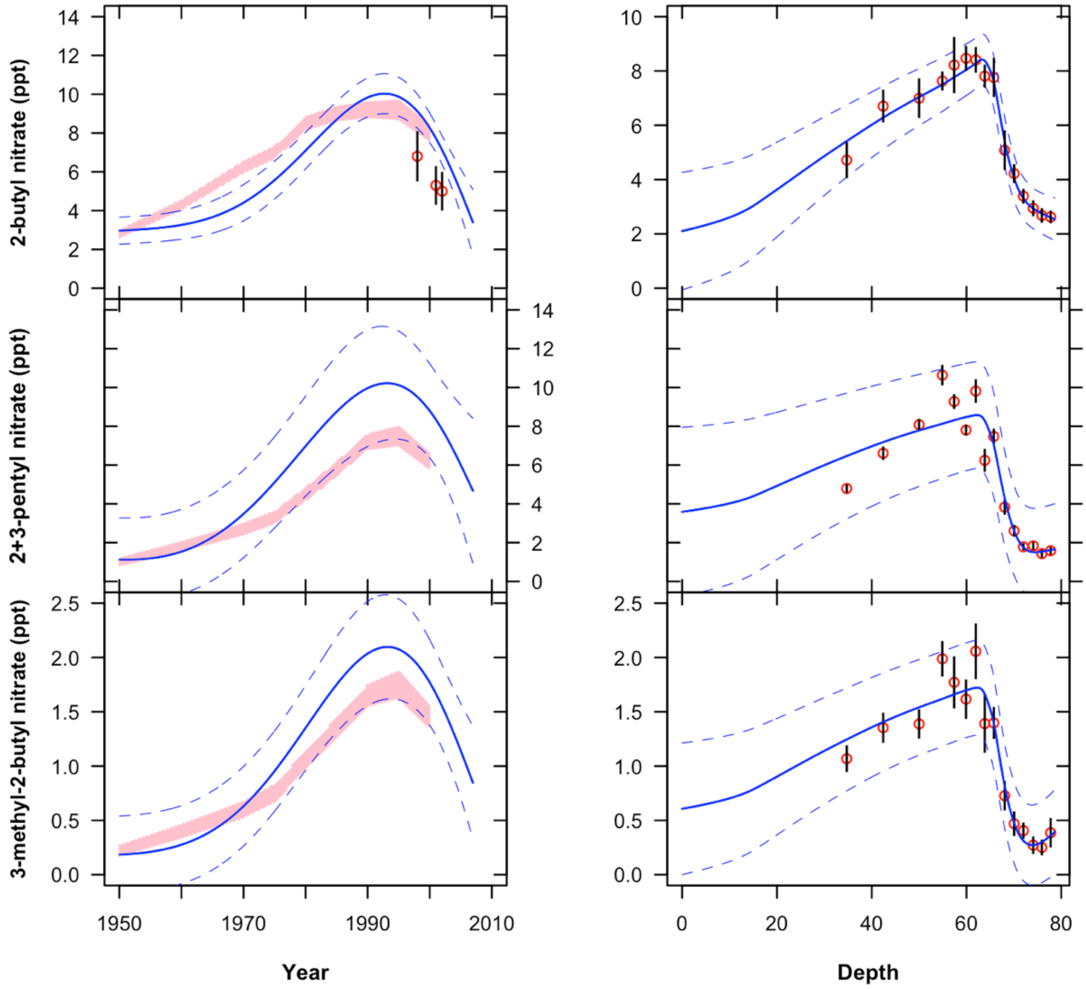

Figure 2 Concentration-depth profiles in the firn and the model derived atmospheric histories. Right panel: The concentration-depth profiles measured in the firn (ppt): red open circles: measured mixing ratios (ppt) with error bars indicating the 2-σ uncertainty; solid blue line: best fit of the firn 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.

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

(i) Changes to the atmospheric mixing ratios of the parent alkanes;

(ii) Changes to [OH].*t*, where *t* is time since emission of the alkane. i.e. the amount of photochemical processing that the air mass in which the alkyl nitrates are being formed undergoes before reaching the Arctic;

(iii) Changes to the production efficiency of the alkyl nitrates, i.e. whether the peroxy radical reacts with NO (Reaction R14) or with HO_2 (Reaction R11;

(iv) Changes to the alkyl nitrate sinks, i.e., changes in [OH] or radiation.

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

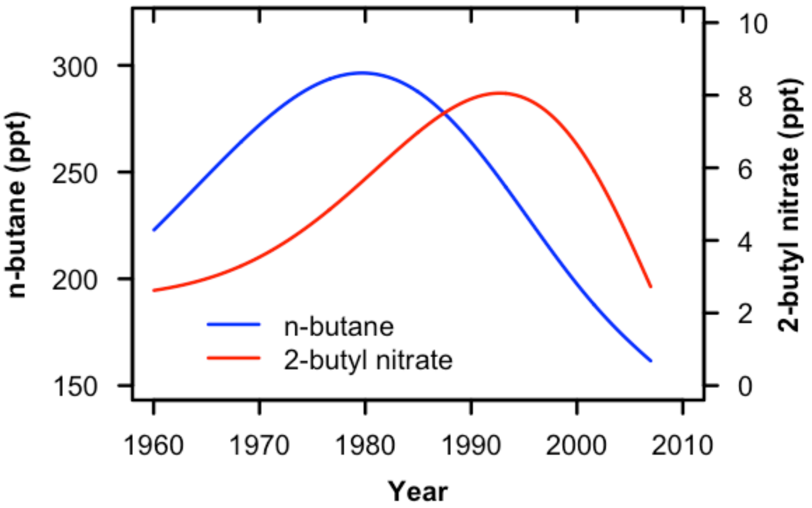

Figure 3 Atmospheric histories of 2-butyl nitrate (red) and its parent alkane, n-butane (blue), derived from firn measurements at NEEM, Greenland.

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

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

4 Ratios of Alkyl Nitrate to Parent Alkane

Bertman et al. (1995) presented a mathematical equation to describe the production of alkyl nitrates in a NO_x rich environment (Equation E1 (assumes an initial zero mixing ratio for alkyl nitrates)).

$$\frac{[\mathrm{RONO_2}]}{[\mathrm{RH}]} = \frac{\beta k_A}{(k_B - k_A)}\left(1 - e^{(k_A - k_B)t}\right) \qquad \text{(E1)}$$

Where $\beta = \alpha_{13}\alpha_{14}$, $k_A = k_{13}[\mathrm{OH}]$, $k_B = k_{15}[\mathrm{OH}] + j_{16}$; subscript numbers refer to reactions given in the Introduction. In this equation, [OH] is assumed to be a constant. Similarly for the purposes of this work, [OH] is assumed to be constant and represents an average [OH] to which the air mass is exposed during transport from the source region to the Arctic.

Bertman et al. (1995) derived Equation E1 by integrating the rate equation for $[\mathrm{RONO_2}]$ assuming a NOx rich environment (Equation E2).

$$\frac{\mathrm{d}[\mathrm{RONO_2}]}{\mathrm{d}t} = \beta k_A[\mathrm{RH}] - k_B[\mathrm{RONO_2}] \qquad \text{(E2)}$$

We extend Equation E2 to include the term $k_{14}[\mathrm{NO}]/(k_{14}[\mathrm{NO}]+k_{11}[\mathrm{HO_2}])$ (Equation E3). This term accounts for the fact that only a fraction of the peroxy radicals will react with NO. This term is assumed to be constant (in the same way as [OH]) during transport and represents an integrated value for this ratio during transport of the air mass from the source region to the Arctic.

$$\frac{\mathrm{d}[\mathrm{RONO_2}]}{\mathrm{d}t} = \frac{\beta k_A[\mathrm{RH}]k_{14}[\mathrm{NO}]}{k_{14}[\mathrm{NO}] + k_{11}[\mathrm{HO_2}]} - k_B[\mathrm{RONO_2}] \qquad \text{(E3)}$$

Since the term $k_{14}[\mathrm{NO}]/(k_{14}[\mathrm{NO}]+k_{11}[\mathrm{HO_2}])$ is assumed to be a constant, integration of Equation E3 gives an equation the same as Equation E1 from Bertman et al. except with addition of the term $k_{14}[\mathrm{NO}]/(k_{14}[\mathrm{NO}]+k_{11}[\mathrm{HO_2}])$ (Equation E4).

$$\frac{[\mathrm{RONO_2}]}{[\mathrm{RH}]} = \frac{\beta k_A}{(k_B - k_A)}\left(1 - \mathrm{e}^{(k_A - k_B)t}\right)\frac{k_{14}[\mathrm{NO}]}{k_{14}[\mathrm{NO}] + k_{11}[\mathrm{HO_2}]} \qquad \text{(E4)}$$

Atmospheric histories of the three parent alkanes of the alkyl nitrates presented in Figure 2 were presented in Helmig et al. (2014b) – Figure 7. These are used here, in conjunction with the alkyl nitrate histories in Figure 2, to determine trends of the ratio $[\mathrm{RONO_2}]/[\mathrm{RH}]$ for each alkyl nitrate-alkane pair. By rearranging Equation E4, we can then probe two of the possible causes for the observed alkyl nitrate trends. Firstly, that the production efficiency (i.e. the integrated $k_{14}[\mathrm{NO}]/(k_{14}[\mathrm{NO}]+k_{11}[\mathrm{HO_2}])$ ratio) has changed over time. Secondly, that the processing of the air mass, i.e. OH concentration ([OH]), multiplied by the transport time from source regions to the Arctic, t (assuming photolysis to have remained constant), has changed.

5 Changes to the Production Efficiency of the Alkyl Nitrates

In an urban environment, daytime [NO] can range from 10 – 1000 ppb. At these mixing ratios the ratio $k_{14}[\mathrm{NO}]/(k_{14}[\mathrm{NO}]+k_{11}[\mathrm{HO_2}])$ is very close to 1, i.e. all of the alkyl peroxy radicals formed in Reaction R13 go on to form alkyl nitrates at a yield determined by the branching ratio α_{13}. However, in rural and more remote regions of the atmosphere, daytime [NO] ranges from 1 – 100 ppt. At these mixing ratios $k_{14}[\mathrm{NO}]/(k_{14}[\mathrm{NO}]+k_{11}[\mathrm{HO_2}])$ varies between around 0.4 – 1, assuming a daytime $[\mathrm{HO_2}] = 2 \times 10^7$ molecules $\mathrm{cm^{-3}}$ (winter time – the alkyl nitrate and alkane signals in the firn are dominated by winter time concentrations). Changes to [NO] or $[\mathrm{HO_2}]$ in these remote environments will affect the production efficiency of the alkyl nitrates. Since the term $k_{14}[\mathrm{NO}]/(k_{14}[\mathrm{NO}]+k_{11}[\mathrm{HO_2}])$ is an average across the whole transport time it reflects both the urban and remote environments.

Equation E5 is a rearrangement of Equation E4 from which historic changes to $[\mathrm{NO}]/[\mathrm{HO_2}]$ can be calculated using the changes to the $[\mathrm{RONO_2}]/[\mathrm{RH}]$ ratio (assuming that the photochemical processing, $[\mathrm{OH}]t$, has remained constant).

$$\frac{[\mathrm{NO}]}{[\mathrm{HO_2}]} = \left[\frac{k_{14}}{k_{11}}\left(\frac{[\mathrm{RH}]\,k_{13}\,\alpha_{13}\,\alpha_{14}\left(1 - e^{(k_{13} - k_{15})[\mathrm{OH}]t}\right)}{[\mathrm{RONO_2}]\,(k_{15} - k_{13})} - 1\right)\right]^{-1} \qquad \text{(E5)}$$

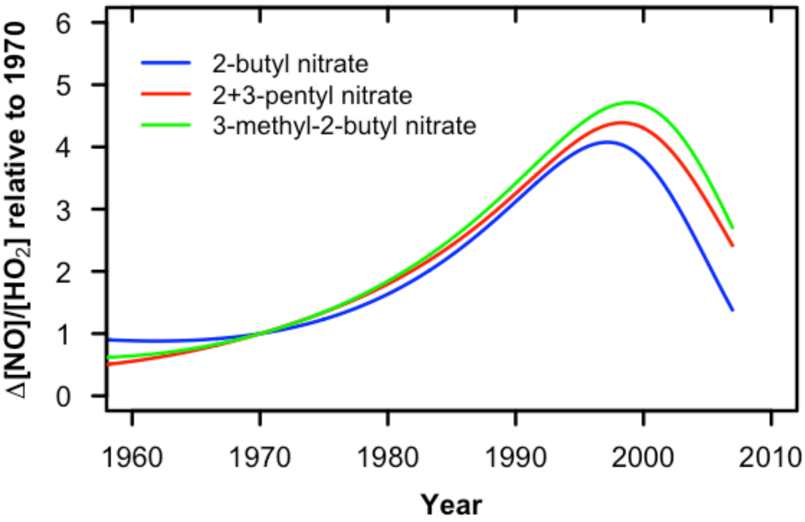

Figure 4 The trend in the $[NO]/[HO_2]$ ratio of the air masses in which the alkyl nitrates were formed, calculated using Equation E5 for each of three alkyl nitrate/alkane pairs. This assumes that the amount of photochemical processing, [OH]*t*, remained constant at 5×10^{11} molecules cm^{-3} s.

Figure 4 shows the trend in the $[NO]/[HO_2]$ ratio derived using Equation E5. A value of 5×10^{11} molecules cm^{-3} s is used for the constant [OH].*t*. This is based on a mean transport time of air masses from Europe (from where the majority of winter-time pollutants are transported to the Arctic – see Section 6.1) to the Arctic in the winter of ten days (Stohl, 2006), and a mean winter-time [OH] of ~ 6×10^5 cm^{-3} (in reasonable agreement with that derived by Derwent et al. (2012) for the North Atlantic in winter-time). Halving the assumed [OH].*t* to 2.5×10^{11} molecules cm^{-3} s increases the magnitude of the relative changes by a factor of ~ 2. Whereas doubling [OH].*t*, only decreases the derived changes by ~ 15 %.

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

This analysis suggests that the observed changes to the $[RONO_2]/[RH]$ ratio in the firn could be explained by changes to the average $[NO]/[HO_2]$ ratio experienced by air masses in transport to the Arctic. We now investigate whether trends in processes that could drive this ratio are consistent with this scenario, i.e. how NO_x and HO_2 concentrations may have changed.

5.1 Changes to atmospheric NO_x concentrations

5.1.1 NO_x sources

The atmospheric NO_X concentration is determined by the relative magnitudes of the sources and sinks. The main sources of NO_X in the northern hemisphere are anthropogenic emissions from fossil fuel use, power stations and transport (Olivier and Berdowski et al., 2001; Olivier et al., 2001).

Figure 5 shows how NO_X emissions from North America, Europe and Russia have varied between 1970 and 2008, taken from the bottom-up estimates of the EDGAR database (EDGAR v4.2, http://edgar.jrc.ec.europa.eu). Emissions were fairly constant between 1970 and 1990 and then fell by about 25 % from 1990 to 2008. This is in good agreement with the NO_X emission trends for OECD Europe presented in Vestreng et al. (2009).

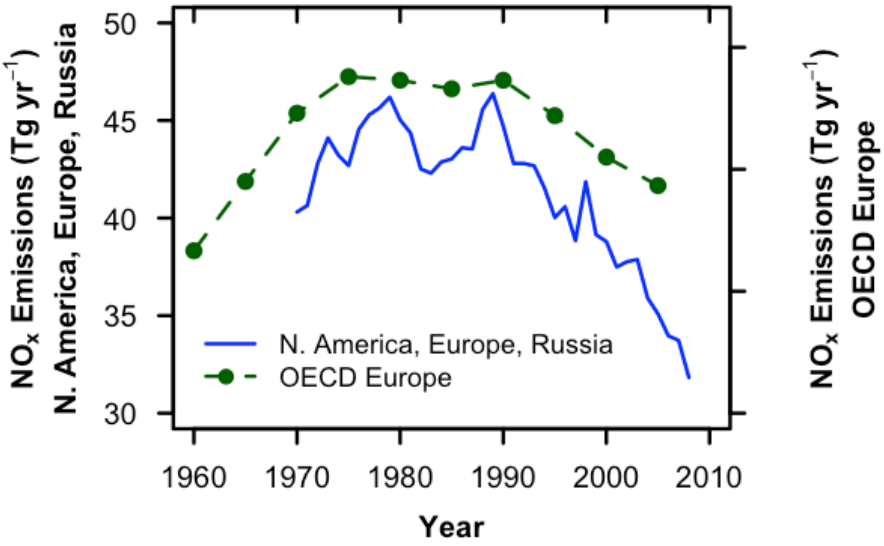

Figure 5 Blue solid line (left axis): The trend in NO_X emissions (Tg yr^{-1}) from North America, Europe and Russia for the period 1970 to 2008 (EDGAR v4.2, http://edgar.jrc.ec.europa.eu). Green points (and dashed line) (right axis): OECD Europe NO_X emissions (Tg yr^{-1}) from Vestreng et al. (2009).

Assuming that these bottom up emissions estimates are correct in the timing of the NO_X emissions changes, it seems unlikely that the increase in the [NO]/[HO_2] ratio derived for the period 1970 to the late 1990s was driven primarily by changing NO_X emissions.

The subsequent decline in [NO]/[HO_2], on the other hand, may well have been driven by decreasing emissions. Measurements at a range of UK sites showed a decrease in NO_X concentrations from 1996 (the beginning of the reported measurements) to 2002 – 2004, of 1 – 3.5 % per year, depending on the site (Carslaw et al., 2011). During the same period, the fraction of the NO_X that is NO_2 (f-NO_2) roughly doubled. Recent trends at many European sites show similar trends with small decreases in NO_x between 1999 and 2007 (the period for which measurements are available) but level or increasing NO_2 through the same period (Carslaw et al., 2011; Gilge et al., 2010) – suggesting that NO has decreased by more than NO_x concentrations.

Declining NO_X emissions have been used to explain these trends in measured concentrations. However, the decline in these ambient concentrations is not as large as would be expected using current emission inventories (Carslaw et al., 2011).

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_2O_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_2O_5. The reaction of N_2O_5 with H_2O 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, though often focussing on remaining uncertainties in the uptake coefficients, have broadly agreed with the magnitude of the changes suggested by Dentener and Crutzen (Brown and Stutz, 2012).

There has been a large decrease in sulfate aerosol observed in Europe and the United States since 1980 (Berglen et al., 2007; Turnock et al., 2015). Figure 6 shows the measured trend in winter-time (DJF) sulfate mass concentration presented in Turnock et al. (2015), with decreases of about 75% from 1979 to 2005. This decreasing trend has been driven by a ~70 % decrease in SO_2 emissions (Smith et al., 2011) from these regions (Figure 6). It is noted that while global SO_2 emissions have only decreased about 15 % from the peak in the 1970s, due to rapidly increasing emissions in East Asia in recent decades, sulfate aerosol has a lifetime of about 5 days in the troposphere (and SO_2 of about 1 day) (Stevenson et al., 2003) and so aerosol concentrations will be largely driven by regional SO_2 emissions.

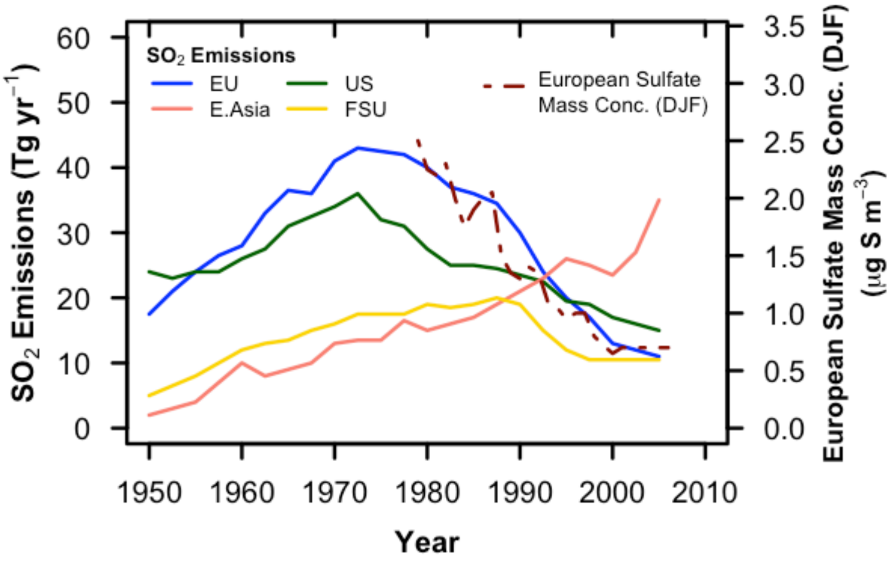

Figure 6 SO_2 emissions (Tg yr^{-1}) 1950-2005 from Smith et al. (2011), and mean European sulfate mass concentration (μg S m^{-3}) in winter (DJF) from Turnock et al. (2015). SO_2 emissions: Blue – Europe; Green – N. America (US + Canada); Gold – Former Soviet Union (Russia, Ukraine, others); Pink – E. Asia (China, Japan, S. Korea, others). Brown dashed line - mean European sulfate mass concentration in winter (DJF).

These large decreases in sulfate aerosol in Europe and the US (the main source regions for air masses arriving in the Arctic in the winter) would be expected to have led to a decrease in NO_X removal by N_2O_5 hydrolysis, and hence to an increase in the NO_X lifetime and atmospheric [NO_X]. The time period of decreasing SO_2 emissions and sulfate aerosol 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.

Equation E6 is a rearrangement of Equation E4 from which historic changes to the photochemical processing, [OH]*t*, can be calculated using the changes to the [RONO$_2$]/[RH] ratio (assuming that the [NO]/[HO$_2$] ratio has remained constant).

$$[\mathrm{OH}]\,\mathrm{t} = \ln\left(1 - \left[\frac{[\mathrm{RONO_2}]\,(k_{15}-k_{13})}{[\mathrm{RH}]\,k_{13}\alpha_{13}\alpha_{14}}\left(\frac{k_{11}\,[\mathrm{HO_2}]}{k_{14}\,[\mathrm{NO}]}+1\right)\right]\right) \div (k_{13}-k_{15}) \qquad \text{(E6)}$$

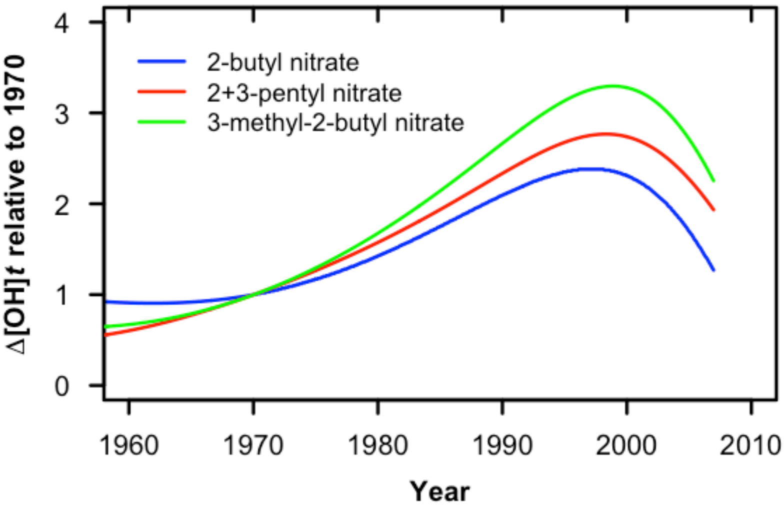

Figure 7 The trend in [OH]*t* calculated using Equation E6 for each of three alkane-alkyl nitrate pairs. This assumes that the ratio [NO]/[HO$_2$] remained constant at 0.5.

Figure 6 shows the trends in [OH].*t* derived from the alkyl nitrate-alkane pairs if a constant value for [NO]/[HO$_2$] is assumed. The value used for the constant [NO]/[HO$_2$] was 0.5. This is in line with the [NO]/[HO$_2$] derived using Equation E5 with a fixed [OH]*t* value of 5×10^{11} molecules cm^{-3} s.

Figure 6 shows that the observed $[RONO_2]/[RH]$ ratios between around 1970 and the late 1990s could be explained by a relative change in $[OH]t$ of a factor of between 2.4 (2-butyl nitrate) and 3.3 (3-methyl-2-butyl nitrate). Increasing the $[NO]/[HO_2]$ value by an order of magnitude, to 5, decreases the derived $[OH]t$ changes by ~ 25 %. Decreasing the $[NO]/[HO_2]$ value by an order of magnitude, to 0.05, increases the derived $[OH]t$ changes by ~ 5 %.

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).

Studies using changes to atmospheric mixing ratios of methyl chloroform (CH_3CCl_3) have suggested that global mean OH concentrations are 'well buffered' (e.g. Montzka et al., 2011). Since the main sink of CH_3CCl_3 in the atmosphere is reaction with OH, and the emission sources and other sinks are thought to be well constrained, the variation in its observed mixing ratios at a number of remote sites can be used to infer variations in global [OH]. Global mean [OH] has been inferred in this way in a number of studies (Prinn et al., 1995, 2001, 2005; Rigby et al., 2008; Montzka et al., 2011). The most recent of these (Montzka et al., 2011) reported little inter-annual variability in mean global atmospheric [OH] estimating roughly 5% variation from the mean value during the period 1997 – 2008, but this does not cover the period of interest here (1970 to later 1990s). Similarly, Kai et al. (2011) inferred a low variability in global [OH] between 1998 and 2005 based on a relatively constant δ-D-CH_4. Earlier work using methyl chloroform (Prinn et al., 2001) reported an increase in NH [OH] of roughly 40% between 1979 and 1991 but this increase has been questioned in more recent work (*e.g.* Montzka et al., 2011).

However, there are a growing number of observational data sets of trace gases in the NH which show trends since 1980 that could be explained, at least in part, by changes to the concentration of the OH sink. E.g. decreasing Arctic alkane mixing ratios (Helmig et al., 2014b; Aydin et al., 2011); decreasing Arctic CO mixing ratios (Petrenko et al., 2013); increasing d^{13}C of methane (Monteil et al., 2011; Sapart et al., 2013); decreasing dC^{16}O of Arctic CO (Wang et al., 2012).

A recent multi-model inter-comparison exercise of seventeen global chemical transport models, showed agreement for a small increasing trend in global mean [OH] of 3.5 (± 2.2) % between 1980 and 2000 and a slightly larger [OH] increase in the northern hemisphere of 4.6 (± 1.9) % (Naik et al., 2013). Dalsøren et al. (2015) determined an increase in global mean [OH] of about 10 % between 1970 and 2006 from modelled increases of the methane lifetime.

7 Discussion

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

A key species of the tropospheric chemistry cycle, tightly linked to NO_X and HO_X, is ozone (Figure 1). Ozone mixing ratios increased at sites across the NH during the second half of the twentieth century, roughly doubling since 1960 (Parrish et al., 2012). Ozone production is positively linked to $[NO_X]$ (at low NO_X concentrations such as the background atmosphere). Hence, an increase in the $[NO]/[HO_2]$ ratio from around 1970 to the mid-1990s is consistent with long-term trends in ozone in the background atmosphere.

Furthermore, while the alkyl nitrate measurements represent changes to the winter-time atmosphere, the ozone trends are seen in both summer and winter. If these are being driven by increases to $[NO_X]$ in the background atmosphere, then this suggests that the chemical changes to the atmosphere may have been present throughout the year and are not just a winter time phenomenon.

This work also implies that there may have been a change in [OH]. Indeed due to the connected nature of the chemistry of NO_X, ozone and OH it seems unlikely, given the implied increases in NO_X suggested here, and the recorded increases in ozone, that there was not a commensurate increase in OH during this period. Furthermore, the primary production of OH, denoted by P(OH), is dependent on ozone mixing ratios, either via photolysis of ozone (Equation E7 - Smith et al., 2006) or via ozonolysis of alkenes (Johnson and Marston, 2008).

$$P(\mathrm{OH}) = 2f[\mathrm{O_3}] \times j(\mathrm{O^1D}) \qquad \text{(E7)}$$

Where f is the fraction of $O(^1D)$ that reacts with water vapour. Ozone has increased at background sites between 1960 and 2000 (Parrish et al., 2012) and measured water vapour has also increased slightly (Hartmann et al., 2013). It therefore seems that the primary production of OH in the background atmosphere must have increased through the final decades of the past century. On the other hand, the primary sink of OH in the background atmosphere, CO, has decreased by about 15% since 1980 (Petrenko et al., 2013), with the secondary sink, CH_4, having increased between 1980 and 2000 by about 15%.

The global growth rate of methane in the atmosphere continually declined throughout the period of the 1970s to 2000, culminating in the 'methane pause' between 1999 and 2006

(Dlugockencky et al. 2009). A possible cause of this change in growth rate in methane could be an increase in OH concentration (e.g. Dalsøren et al. 2016). This is consistent with an increase in [OH] also being the cause of the trend in the ratio of alkyl nitrate to parent alkane seen in this work. It should be noted, though, that the majority of the OH oxidation of methane occurs in the tropics (e.g. Bloss et al. 2005), while any increase in OH suggested by the work herein must be viewed as representative only of the mid-high latitude northern hemisphere and the winter time. However, the processes suggested herein, such as changes to the N_2O_5 sink, have been shown to be effective at a hemispheric scale.

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

Including alkyl nitrate chemistry and using the alkyl nitrate measurements presented herein could provide a valuable constraint for modelling changes to NOx and HOx back to the middle of the twentieth century in global chemical transport models.

8 Conclusions

Time series such as those presented here are fundamental to improving our understanding of trends in atmospheric composition during the twentieth century. The long-term trends of alkyl nitrates presented herein suggest major changes to the chemical state of the atmosphere during the past five decades. The trends were likely driven by changes to the [NO]/[HO_2] ratio during this period. A 4 – 5 fold increase in the [NO]/[HO_2] ratio is suggested between the 1970s and late 1990s. This is not consistent with reported changes to NO_X emissions, but may have been driven by a reduction in the NO_X sink. The recent decreases (since the late 1990s) in alkyl nitrate concentrations are in qualitative agreement with recent decreases in NO_X emissions and in measured NO_X concentrations. Changes to concentrations of the hydroxyl radical, or to the transport time of air masses from source regions to the Arctic may also have contributed to the observed trends.

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