

Dear Professor McClaren,

Firstly, thank you for taking the time to closely consider the reviewers' comments and to thoroughly review the paper yourself. We appreciate that the reviewers' contrasting comments puts you in a difficult position so we are grateful that you have given us this further opportunity to improve the quality and clarity of the paper.

We of course agree with the reviewer who suggested that the paper should be published, allowing others to read it, include our new data in their own research and to consider our analysis of that data. The paper presents measurements which appears to shed light on an issue that is absolutely central to the community's understanding of historical trends in the chemical composition of the troposphere. Only in the last few weeks, two other papers have been published in PNAS on this subject (Rigby et al., Role of atmospheric oxidation in recent methane growth; Turner et al., Ambiguity in the causes for decadal trends in atmospheric methane and hydroxyl). In those papers they used atmospheric measurements of methyl chloroform and $\delta^{13}\text{CH}_4$ to derive a trend for OH. Their conclusion was that a change in the oxidising capacity could be partially responsible for the accelerated growth in methane post 2007, but they too had to accept that no change in OH was still consistent with their results given the large uncertainties. The trend in oxidizing capacity of the atmosphere is proving difficult to determine given all the uncertainties in measurements, emission inventories and modelling techniques. However, we firmly believe that our data and analysis provide a new angle to this debate and, whilst it too comes with large uncertainties which we openly acknowledge, we think it is important to get published so that it can contribute to solving this important issue.

To summarise how we see what we have done in the paper: we present a new data set (alkyl nitrate trends), and then ask why the trends look as they do. We combine the alkyl nitrate trends with existing data sets (parent alkanes) to gain more insight, and then present a range of possible explanations that could explain the observed trends. We are clear where assumptions have had to be made. Neither reviewer presents any alternative explanations for the observed trends beyond those we posit. As we see it, this is everything that should be done in a paper. That the paper may cause discussion and debate over its conclusions can only be seen as a good thing, hopefully leading to further work in the area and ultimately improving our understanding of tropospheric chemistry.

I note that the title, abstract and conclusions taken together were somewhat inconsistent. The title and the conclusions explicitly suggested that the observations presented in the paper were driven by changes to the chemical state of the atmosphere whereas the abstract presents all possibilities equally. The conclusions have been altered to give a more equal weight to all possibilities.

We hope that you will feel that we have addressed your comments satisfactorily and will agree to publishing our manuscript.

Below we respond to each of your comments (in bold) in turn. Our comments are inset. Altered text from the manuscript is inset and italicised. We then refer to specific lines from this section in our responses.

Major uncertainty

It is well known that the major sources of the parent compounds (iC₄, nC₄, iC₅ alkanes as well as n-pentane) derive from fuel and fuel evaporation sources. These species are among the most volatile in gasoline products and as such they make up a major fraction of the vapor pressure of gasoline (or at least historically they did), typically expressed as the Reid Vapor Pressure (RVP). It is also well known that prior to late 80's/early 90's the % composition of gasoline was very high in these C₄/C₅ components due to carburetor's being very common and that refineries typically adjusted the RVP of gasoline according to the season (high in winter to help cold start; low in summer to avoid vapor lock) and according to the latitude of the market; where one major parameter that refineries used to adjust the RVP was *the % composition of C₄ and C₅ components of the gasoline*. Thus there were major changes to the seasonal composition of the major source of C₄ and C₅ alkanes to the atmosphere; this was far from being constant seasonally in the 70's, 80's, 90's. Furthermore, in the 90's when vapor regulations started to come in to affect in a big way to control the tropospheric O₃ problem, especially in North America (presumably Europe as well, I am not clear on this) the regulations dictated that RVP of gasoline be reduced significantly (down to RVP = 6 or 7 psi in California as I recall). As far as I understand there were major reductions in the C₄/C₅ components in gasoline at this time. Thus, sources of C₄/C₅ emissions changed significantly, and likely they changed both in magnitude and the spatiotemporal patterns changed (southern areas reduced RVP more than northern areas, California was first). This could conceivably have changed not just the sources of C₄/C₅ alkanes to the atmosphere but also the temporal transport times to the arctic.

I see virtually no discussion of the points raised above, including major reformulations in gasoline that have taken place historically due to changing technology (Carburetor to Fuel injection vehicles) and changing regulations (reduced RVP and increased vapor recovery in southern locations), other than page 4, line 26/27, which says that *"Emissions are not thought to have a significant seasonal variability (Pozzer et al, 2010)"*. While this statement may currently be the case, it certainly was not the case in the past and it does not address the temporal changes in emissions over decades from 1970 onward, and any potential spatio-temporal change in the emissions pattern that resulted from changing regulations. Thus not only [RH] changes seasonally and over decadal periods, but the ratio [RONO₂]/[RH] could change over decades also due to changing emissions and emission patterns. Thus changes in [RONO₂]/[RH] could partially be driven by changes in emissions. Likewise changes in Δ[NO]/[HO₂] and Δ[OH]t (Figures 4 and 6) could partially arise from changes in emissions as well. While what I lay out above is somewhat speculative (changing spatiotemporal patterns), the changes in emissions, reformulations and changes in regulations that affect C₄/C₅ precursor hydrocarbons are not. I think this should be addressed before a conclusion is made that the chemical state of the atmosphere has changed.

We think that much of this concern has derived from our inclusion of the line, *"Emissions are not thought to have a significant seasonal variability (Pozzer et al, 2010)"*. We agree that we have no evidence of this beyond citing Pozzer et al. and will remove the line. However, any seasonal variability of emissions driven by changes in

fuel composition in US cities is of little relevance to the Arctic measurements presented, hence the reason we haven't discussed it in the paper. We shall explain below:

- (i) The observed alkyl nitrate and alkane signals captured in the Arctic firn are caused almost entirely by winter time (October-May) emissions (alkanes) and chemical production (alkyl nitrates). This is seen in the seasonal cycles of the alkanes and alkyl nitrates at Summit (Swanson et al., 2003) where the winter maxima dominate over the summer minima, because of the short lifetimes of the alkanes and alkyl nitrates in the summer. Whereas, “EPA regulates the vapor pressure of gasoline sold at retail stations during the summer ozone season (June 1 to September 15)” (<https://www.epa.gov/gasoline-standards/gasoline-reid-vapor-pressure>). Hence this summer time mix of alkanes will have minimal impact on the smooth Arctic signal.

To demonstrate this point further, the Arctic records of the C4 and C5 alkanes presented in Helmig et al. (2014) show very similar trends. I believe that the main summer-time change to US fuel composition was to greatly reduce n-butane content (rather than iso-butane, n-pentane or iso-pentane) see e.g. Gentner et al., 2009, ES&T. However, there is no change in the Arctic n-butane record relative to the other alkanes at the time of the implementation of these measures (early 1990s).

Further to all of this is that numerous studies have suggested that Europe is the main winter time contributor to Arctic pollutants and as far as I am aware, no similar policy to that in the US has ever been implemented in European countries.

Further again, as stated above, this US legislation only comes in from 1990 (in California where it was introduced first). We see most of the increases in alkyl nitrate mixing ratios and changes in ratios with their parent alkanes before any of these measures were introduced.

So while we propose to put in a few lines clarifying why these well-known seasonal variations to fuel composition in US cities have no bearing on our work, I hope that the editor sees why we do not consider that the issue requires a major discussion in the paper.

In the Introduction (Section 1.1), we will add the lines,

“Butane and pentane emissions will be dependent on fuel composition, with evaporative emissions also dependent on temperature. Many areas in the United States are part of ‘ozone attainment areas’ and during summer months (June-September 15) have been required by law since 1989 to provide a gasoline blend with a low Reid vapour pressure (RVP) to reduce the ozone production potential (www.epa.gov). This reduction in RVP is generally achieved by reducing the fuel’s butane content relative to winter-time fuel (e.g.

Gentner et al., 2009). Measurements in firn air from Greenland (Aydin et al., 2011; Worton et al., 2012; Helmig et al., 2014) suggest northern hemisphere C2-C5 alkane mixing ratios increased through the middle of the past century to a peak in ~1980 (~1970 for ethane). In-situ measurements from the urban areas of London (1993 – 2008) (Dollard et al., 2007; von Schneidemesser et al., 2010) and Los Angeles (1960 – 2010) (Warneke et al., 2012) show steadily decreasing alkane mixing ratios, as do measurements at the semi-rural site of Hohenpeissenberg, Germany (von Schneidemesser et al., 2010). Emission estimates from the ACCMIP global emission inventory (Lamarque et al., 2010) (available at <http://eccad.sedoo.fr>) show non-methane VOC emissions in Europe and North America increasing steadily between 1950 and 1980 before falling again to roughly 1965 levels by 2000.”

- (ii) The great benefit of the method of analysis presented in this paper, looking at the ratio of the alkyl nitrates to their parent alkanes, is that it is not affected by long term changes to alkane emissions driven by changes in technology etc., unless these changes happened at different times in different countries / states. i.e. if these changes significantly alter the transport/processing time between the source region and the Arctic.

The point that fuel compositions may have been changed at different times in different locations is of course relevant. Changing the source regions of the alkanes will affect the amount of processing time between the source region and the Arctic (i.e. $\overline{[OH]t}$) (as we discuss in Section 6.1).

Another driver of this sort of spatial change could have been either of the points that you raise, i.e. inter-annual (rather than intra-annual) changes to fuel composition driven either by technology or regulation in different places (i.e. European countries / US states) at different times could have had an effect on spatial distribution of emissions. However there is no evidence for this, with estimates of butane and pentane emissions from ACCMIP (<http://eccad.sedoo.fr>) for the two regions displaying very similar trends.

Furthermore, my understanding is that RVP was largely controlled in the US by changes to butanes specifically (not pentanes). The fact that we are seeing a very similar trend for the butanes compared to the pentanes again suggests that summer-time fuel composition changes are having little/no effect on the signal we see in the Arctic.

So while these are all indeed possibilities, there seems little evidence for them. However, we now include a discussion on these possibilities in Section 6.1 with more possible reasons behind changes to atmospheric transport time/source regions.

“Concerning (ii), changes to the relative distribution of the major source regions of the alkanes could have occurred for a number of reasons. Fuel composition has changed through time as a response to technological development of vehicles. Clean air legislation has led to the development of cars with progressively lower evaporative and tailpipe emissions (e.g. Wallington et al., 2006), through developments such as catalytic converters. In addition emissions may have changed simply due to a change in vehicle usage. If such changes were to have occurred in more northerly regions significantly earlier than in more southerly regions, this could have increased the mean transport time of air masses to the Arctic.

For many areas in the United States, the Reid vapour pressure of fuel is regulated in the summer season (June 1 - September 15) (epa.gov.uk), leading to sale of a different fuel mix in summer compared to winter. This is generally achieved by producers reducing the butane content of the fuel (Gentner et al., 2006). This legislation came in in 1990. However, the observed alkane and alkyl nitrate signals in Greenland are almost entirely winter-time signals (e.g. Swanson et al., 2003), and so such seasonal variation in fuel composition would not be expected affect the firn measurements.

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 followed a similar declining trend in recent years (Lamarque et al., 2010; von Schneidemesser et al., 2010; Warneke et al., 2012;), thus the relative contribution from each region will not have changed dramatically.”

To summarise our response to your major concern, we don't feel that seasonal changes to fuel composition (and thus emissions) in the US, will have any effect on our results. We agree that changes to winter-time emissions, driven by technology or legislation, at different times in different countries in Europe or states in the US (or Canada) could change the atmospheric processing time of air masses arriving in the Arctic, but have found no evidence of such changes.

Other Major Concerns and Uncertainties

P12L20 – what is the effect in this term of ignoring RO2-RO2 self reactions.

Effectively the production efficiency term, which we now represent explicitly in Equations E4, E5 and E6, represents $k_{14}[\text{NO}]/\text{total sinks}$, where total sinks = $k_{14}[\text{NO}] + k_{11}[\text{HO}_2] + \Sigma k[\text{RO}_2] + \text{etc.}$

However, in the background environment, the only other peroxy radical possibly present at high enough concentrations to compete with NO and HO₂ as a sink is CH₃O₂, which is thought to be present at similar concentrations to HO₂. However, the reaction

rate of CH_3O_2 with other alkyl peroxy radicals is $< 2 \times 10^{-13} \text{ cm}^{-3} \text{ s}^{-1}$ (http://iupac.pole-ether.fr/htdocs/show_datasheets.php?category=Gas-phase+organics%3A+ROO), i.e. two orders of magnitude slower than Butyl peroxy + HO_2 ($2.1 \times 10^{-11} \text{ cm}^{-3} \text{ s}^{-1}$, MCMv3.3.1). In an urban environment the term $k_{14}[\text{NO}]$ would be expected to dominate. Hence we present γ simply as $k_{14}[\text{NO}] / (k_{14}[\text{NO}] + k_{11}[\text{HO}_2])$.

We have added comments to this effect to Section 4:

“We extend Equation E2 to include the possibility of alkyl nitrate production at less than 100% efficiency, in a non-NO_x-rich environment, i.e. that the peroxy radical, RO₂, formed may react with something other than NO. This is achieved by the inclusion of the term $k_{14}[\text{NO}] / (k_{14}[\text{NO}] + \text{other RO}_2 \text{ sinks})$. In high-NO_x environments, this value is $\cong 1$. However, in lower NO_x environments, other sinks for the peroxy radical, RO₂, will compete with NO. In reality the term $k_{11}[\text{HO}_2]$ is likely to dominate the ‘other RO₂ sinks’ term in a background environment, with the only other species likely to be present at high enough concentrations to compete, being the methyl peroxy radical (CH_3O_2), which may be present at similar concentrations to HO_2 , but the reaction rate of CH_3O_2 with other alkyl peroxy radicals larger than CH_3O_2 is $\leq 2 \times 10^{-13} \text{ cm}^{-3} \text{ s}^{-1}$ (IUPAC), two orders of magnitude slower than the reaction with HO_2 (IUPAC). Hence in Equation E3 we extend Equation E2 by including the term $k_{14}[\text{NO}] / (k_{14}[\text{NO}] + k_{11}[\text{HO}_2])$.”

P13L1: it is not good enough to just say that we assume the γ is constant, since we know that γ is not constant and that it changes as the air mass transports from source regions to the arctic. You must justify the statement by telling us what the estimated effect is ...perhaps by telling us in a few lines what was present in Table T1 (your response to reviewer.)

We have added some of the comment to Reviewer #1 into Section 4 (see below). and have included most of the comment with some plots in Supplementary Information. The values in Table S1/T1 have changed (decreased) as we now include the photolysis sink as throughout the rest of the paper.

*“For the purposes of our calculations, $k_{14}[\text{NO}] / (k_{14}[\text{NO}] + k_{11}[\text{HO}_2])$ is assumed (in the same way as $[\text{OH}]$) to represent an integrated value for this ratio during transport of the air mass from the source region to the Arctic, i.e. $1/t * \int k_{14}[\text{NO}] / (k_{14}[\text{NO}] + k_{11}[\text{HO}_2]) . dt$. This is represented by the term γ in Equation E4.*

$$\gamma = \left(\frac{k_{14}[\text{NO}]}{k_{14}[\text{NO}] + k_{11}[\text{HO}_2]} \right) = \text{Mean alkyl nitrate production efficiency}$$

$k_{14}[\text{NO}] / (k_{14}[\text{NO}] + k_{11}[\text{HO}_2])$ would not be expected to be constant in reality since $[\text{NO}]$ is likely to change by orders of magnitude during transport, with values on the order of $2.5 \times 10^{11} \text{ cm}^{-3}$ close to the emissions source falling to $\sim 1 \times 10^8 \text{ cm}^{-3}$ further from source. However, while changes to the ratio $k_{14}[\text{NO}] / (k_{14}[\text{NO}] + k_{11}[\text{HO}_2])$ at different times along the air mass trajectory will affect $d[\text{RONO}_2] / dt$ at that time differently because $d[\text{RONO}_2] / dt$ is also driven by $[\text{RH}]$ which is a function of time, the uncertainties introduced by the assumption of γ as an integrated value on

[RONO₂]/[RH] calculated at time t = 10 days are on the order of 5 % (see Supplementary Information). The observed changes in [RONO₂]/[RH] in the firm are considerably larger than this, on the order of a factor of 3 – 5. Hence we consider the assumption of γ as a constant to be a reasonable assumption for the sake of making the problem tractable and that the changes to γ that we calculate in the paper are not an artefact of this assumption.”

Table T1 : Your scenarios should probably have extended [OH] at least to the generally accepted day and night global average [OH] level, [OH] = 1.2x10⁶ molec cm⁻³, as a sensitivity test. Obviously the changes in [RONO₂]/[RH] in this case would be larger than 5% for both A and B scenarios. The uncertainties you discuss in this response to the reviewer should be added to the paper as a few lines and perhaps to Supplemental.

The air which we are sampling has not been exposed to global mean [OH], it has been exposed to the winter-time mean for northern hemisphere mid-high latitudes (as evidenced from in-situ measurements of the seasonal cycles of both alkanes and alkyl nitrates from Summit in Swanson et al. (2003).

However, extending this analysis to [OH]=1.2x10⁶ gives only slightly larger changes of 8.1% for Scenario A and 5.8% for Scenario B. So the point made, that these are very small compared to the factor of 4-5 changes seen in the alkyl nitrate scenarios, still holds.

A brief discussion of this is now included in the manuscript, with further discussion in Supplementary Information (see response to point above).

P13 L28: Equation 13. [NO]/[HO₂] should be presented with some sort of average symbol that is different from what you have now, which implies an instantaneous average of concentrations instead of a long term average. ie [NO]~ ∫ [NO]dt or [NO]/[HO₂] = ∫ [NO]/[HO₂] dt

We agree, firstly we will replace the term $k_{14}[NO]/(k_{14}[NO]+k_{11}[HO_2])$ in Equations E4-E6 with the term γ , which we will define as the mean $k_{14}[NO]/(k_{14}[NO]+k_{11}[HO_2])$ to which the air masses are exposed during transport from source region to the Arctic. I.e.

$$1/t * \int k_{14}[NO]/(k_{14}[NO]+k_{11}[HO_2]).dt$$

We now do not now explicitly calculate changes to [NO]/[HO₂] but when in places we do refer to this ratio we are careful to define precisely where these are relevant to / what we mean.

We have removed Figure 4, the plot of $\Delta[NO]/[HO_2]$, and we now have a plot of γ , i.e. the mean alkyl nitrate production efficiency, $1/t * \int k_{14}[NO]/(k_{14}[NO]+k_{11}[HO_2]).dt$. We agree that it is incorrect to then determine a mean [NO]/[HO₂] ratio from a rearrangement of,

$$\gamma = \left(\frac{k_{14}[\text{NO}]}{k_{14}[\text{NO}] + k_{11}[\text{HO}_2]} \right)$$

to something such as

$$\left(\frac{[\text{NO}]}{[\text{HO}_2]} \right) = \frac{k_{14}}{k_{11}} \left(\frac{1}{\gamma} - 1 \right)$$

Hence Figure 4 is now a plot of $\Delta\gamma$ relative to 1970. This has little effect on our conclusions and γ then feeds in to Equation 6.

E3: The [NO]/[HO2] average you calculate and present in Figure 4 depends (perhaps critically so) on the values of all rate constants and branching ratios in the equations. The constants assumed should be presented somewhere in the paper and/or you should tell us at what temperature you calculated the rate constants (since T likely changes 30-40 oC as the air mass is transported from source regions to the arctic the region). What is the uncertainty in assuming a constant T. What is sensitivity of Figure 4 to using different T?

All rate constants and branching ratios are now given in a table which I have put in Supplementary Information, while commenting in the manuscript that all rate constants and branching ratios are taken from the MCMv3.3.1 for a temperature of 273K.

“All rate constants and branching ratios used in the calculations are taken from MCMv3.3.1 (mcm.leeds.ac.uk) assuming a temperature of 273K.”

We assume a constant T of 273 K. Changing the temperature (but keeping it as a constant) has no effect on the relative change in γ (i.e. Fig. 4 would be unchanged). Reducing the constant T by 15 K to 258 K, increases the calculated peak relative change in [OH].t (i.e. the results in Fig. 8) from a factor of 2.47 to 2.56 for 2-butyl nitrate, and from 2.89 to 3.05 for 2+3-pentyl nitrate (the [OH].t calculated from 3-methyl-2-butyl nitrate is unchanged because the iso-pentane+OH rate constant from MCMv3.3.1 is not T dependent). Increasing the constant T by 15 K to 288 K, decreases the [OH].t peak from 2.47 to 2.41 for 2-butyl nitrate and from 2.89 to 2.77 for 2+3-pentyl nitrate.

I cannot see that changing temperature could have had much of an effect, with an increase of ~1 K in NH mean winter time temperatures between the beginning and end of our record. Though temperatures may have changed a little more in the Arctic, processing is basically finished by the time the air mass reaches the Arctic because there is no sunlight and hence no photochemistry.

Changing source regions and hence transport time would likely also change the temperature profile to which the air mass was exposed but as shown above, changing temperature has a small effect on the calculations and the main effect would be the change to processing time rather than any change in temperature.

Figure 14L4 (Figure 4 caption). Why is photochemical age $\int [\text{OH}]dt = 5 \times 10^{11}$? This is about 5 days averaging at global average $[\text{OH}]$. How does figure change as you change the photochemical processing?

As described in the text:

“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 $[\text{OH}]$ of $\sim 6 \times 10^5 \text{ cm}^{-3}$ (in reasonable agreement with that derived by Derwent et al. (2012) for the North Atlantic in winter-time).”

We are not considering mean global $[\text{OH}]$, we are considering a mean $[\text{OH}]$ in mid-high latitude northern hemisphere winter-time (see comment above).

See discussion on next point for sensitivity analysis.

p17E6 – I believe this equation is derived presuming that alkyl nitrates do not photolyze. Considering that $\sim 50\%$ of loss of 2-butyl nitrate is photolysis, what is the effect on the calculations and the results in Figure 6 resulting from this assumption.

Yes, you are correct and we can (and should) include the photolysis sink. This has no effect on the conclusions of the paper. It changes the magnitude of the calculated **absolute** values for γ but not the relative changes (i.e. Figure 4). For $[\text{OH}]t$ it changes both the calculated absolute and relative changes.

For the sake of reducing the number of assumptions we have to make we include the photolysis sink, j_{16} , in the ratio, λ , where $\lambda = j_{16}/k_{15}[\overline{\text{OH}}]$, i.e. the ratio of the photolysis sink to the OH sink. Presenting it like this allows us to not have to assume a value for j_{16} and means that $[\text{OH}]$ drops out of the equation meaning we move from the equation below,

$$\gamma = \frac{[\text{RONO}_2](k_{15}[\text{OH}] + j_{16} - k_{13}[\text{OH}])}{[\text{RH}][\text{OH}]\beta k_{13}(1 - e^{(k_A - k_B)t})} \quad (\text{E5a})$$

to that now presented in the paper, Equation E5.

$$\gamma = \frac{[\text{RONO}_2](k_{15}(1 + \lambda) - k_{13})}{[\text{RH}]\beta k_{13}(1 - e^{(k_A - k_B)t})} \quad (\text{E5})$$

In the Supplementary Information we show the sensitivity of the calculated relative changes to $[\text{OH}]t$ to the assumed value of λ (as stated above, relative changes to γ , and hence $[\text{NO}]/[\text{HO}_2]$, are not affected by the inclusion of photolysis).

In Equation E5, λ is assumed to be constant through the period of study (1960-2007) as $[\text{OH}]_t$ is constant. We assume a value of 1 for λ in Figure 4 and look at the sensitivity of the calculated trend in γ to this value.

In Equation E6, $[\text{OH}]$ is still present on the right hand side of the equation in the term λ . A calculation is initially done assuming λ to be constant through time and = 1. Applying the derived relative $[\text{OH}]$ temporal trend obtained (as part of $[\text{OH}]_t$) from this calculation to λ gives a temporal trend in λ . The calculation is then redone applying this temporal trend and assuming that λ in 1970 = 1. This process is repeated and we iteratively converge on a unique solution for the trend in $[\text{OH}]_t$.

(All of this serves to reduce the calculated changes in $[\text{OH}]_t$ only slightly compared to the previous Figure 6).

The sensitivity of the calculated trend in $[\text{OH}]_t$ to various assumed values for λ in 1970, and to assuming λ to be a constant value, are shown in the Supplementary Information.

This is now described in the paper as,

“Figure 7 shows the trends in $[\overline{\text{OH}}]_t$ derived from the alkyl nitrate-alkane pairs if a constant value for γ is assumed. The value used for the constant γ for each alkyl nitrate was the mean value derived in Figure 4 for the period 1960 – 2007 (0.31 for 2-butyl nitrate, 0.34 for 2+3-pentyl nitrate, 0.17 for 3-methyl-2-butyl nitrate).

Equation E6 also has $[\text{OH}]$ terms on the right hand side of the equation, incorporated in λ . The results in Figure 7 are determined through an iterative process of fitting a polynomial to the trend calculated using an a-priori assumption that $\lambda = 1$ for the whole time period. The calculation is then redone with a temporally varying value for λ using this fit to determine the changes. This converges towards the unique solution presented in Figure 7. E.g. In Figure 7 for 2-butyl nitrate, in 1970 the assumed value of λ is 1, at the peak of $\Delta[\overline{\text{OH}}]_t$ in 1997, when $\Delta[\overline{\text{OH}}]_t = 2.1$, the value of λ is 0.46 (1/2.1).”

Also why is $[\text{NO}]/[\text{HO}_2]$ presumed to be 0.5. Reference? rationale? Sensitivity?

Equation E6 is now presented as,

$$[\overline{\text{OH}}]_t = \ln \left(1 - \frac{[\text{RONO}_2](k_{15}(1 + \lambda) - k_{13})}{[\text{RH}]\gamma\beta k_{13}} \right) \div (k_{13} - k_{15}(1 + \lambda))$$

The $[\text{NO}]$ and $[\text{HO}_2]$ are thus incorporated within γ . For each alkyl nitrate we then use the mean value of γ between 1960-2007 calculated using Equation E5 (using a fixed value of $[\text{OH}]_t$ of $5 \times 10^{11} \text{ cm}^{-3} \text{ s}$, the rationale for this value is given in our answer two

points above – although as stated in the paper, the relative change in γ is actually unaffected by changing $[\text{OH}]_t$).

In the Supplementary Information we show the sensitivity of the calculated relative changes to $[\text{OH}]_t$ to the assumed value of γ .

Minor Points

p2L23-24: by removal, are you presuming $\text{CH}_4 + \text{OH}$ and $\text{CO} + \text{OH}$ regenerate OH catalytically. In any case, please provide a reference for such statements.

Yes, we are talking about primary sources of OH. However, you are right we should provide more detail. For both this point and the next, what we are trying to do in the Introduction is to provide a succinct summary of tropospheric $\text{NO}_x\text{-HO}_x\text{-O}_3$ chemistry, which I'm sure you appreciate is something of a challenge.

We have added the following text to the Introduction,

“Other reactions, such as alkene ozonolysis (Johnson and Marston, 2008) and photolysis of HONO (formed from heterogeneous reactions of NO_2 (Stone et al. 2012)) may also be important primary sources of HO_x , particularly in winter (e.g. Heard et al., 2004).”

“The main removal process for HO_x in urban regions is the reaction of OH with NO_2 (Reaction R5) (Stone et al., 2012) while HO_2 self-reaction and reaction with RO_2 (in particular $\text{CH}_3\text{O}_2 + \text{HO}_2$) (Reactions R11-R12) dominate in low NO_x environments (Stone et al., 2012).”

page 2 - HO_x Sources: In winter regions, O_3 photolysis may not be the main source of OH. There is lots of recent evidence for this.

Yes, we should mention this in the introduction (we do mention alkene ozonolysis as a major source of OH Pg21, line 21.) Additionally we will mention that HONO, may be a primary source of OH, although there are still very large uncertainties in the role of HONO and much of it also likely comes from $\text{OH} + \text{NO}$.

See point above for text added to the Introduction.

Page 2-3 and throughout: The chemical equations are not presented with care. Three body reactions should be presented as such (R2 for example). Photolysis reactions should be indicated as photolysis reactions. (R1, R3, etc). R7 is an equilibrium reaction. Reaction 13 is not balanced, namely because it is actually 2 reactions. R14a does not exclusively give aldehydes as shown, it also give ketones (ie- MEK from butane). R14b involves a rearrangement that is apparently highly temperature dependent that is not mentioned.

Apologies for this, it was the result of having written and re-written the paper numerous times. These will be tidied up and corrected as suggested.

p4L26 – Emissions definitely did have seasonal patterns in the past. I am not sure about today.

See discussion on Major Concern.

p7L27 – Your answer to the question by a reviewer about the effect of the 34.7m sample was not convincing. If this sample was removed, do your conclusions change; regardless of whether it should be removed or not. The historical state of the atmosphere should not rest on a single point.

No, our conclusions would not change.

Firstly, we primarily focus on the stark difference between alkyl nitrate mixing ratios in the 60s-70s and those in the mid-1990s. This is a trend that is seen very clearly in the records of all three alkyl nitrates presented here and is also seen in trend of the same three alkyl nitrates taken from the NGRIP site in Greenland seven years earlier, presented in Worton et al. (2010).

Removing the measurement at 34.7 m has no effect on this.

Secondly, if this measurement is removed, the scenario for 2-butyl nitrate remains rather similar (falling to ~4.2 ppt by the end of the record rather than 3.5 ppt), 3-methyl-2-butyl nitrate falls to ~1.2 ppt rather than 0.8 ppt. It is only 2+3-pentyl nitrate for which the post 1995 part of the reconstruction would change significantly, remaining almost flat rather than decreasing as for the other two.

The pentyl nitrate measurements have a greater scatter in the peak region than the butyl nitrate measurements. This is reflected in the larger 2-sigma uncertainty envelopes of the atmospheric reconstructions.

Figure 3 – how many points are represented in the curve for n-butane in this figure. How uncertain is the peak year, or put another way, what is the uncertainty in the difference between the peak year for n-butane and 2-butyl nitrate. I presume that the shape of Figures 4 and Figures 6 depend critically on the relative temporal trend of n-butane measured in the firn from the other paper. Does the shape of n-butane in Figure 3 make sense given the temporal changes in hemispheric emissions of n-butane...can it be corroborated with other sources of hydrocarbon measurements in northern hemisphere cities or other sites??

The output is from the firn model. Hence the output frequency can be set at whatever we want. The output frequency for the curve shown is monthly. Of course the firn model output represents a smoothed temporal average and cannot represent seasonal or short scale inter-annual variations, particularly in the earlier part of the

record. It represents the temporal trend in surface atmospheric concentrations above the firm that best reproduces the measurement depth profile.

The peak timing of all of the atmospheric scenarios derived for the C3-C5 alkanes (propane - 1979, n-butane - 1980, iso-butane - 1980, n-pentane - 1981, iso-pentane - 1981) measured at NEEM in Helmig et al. (2014) agree to within two years. They also agree to within five years (propane - 1980, n-butane - 1977, iso-butane - 1977, n-pentane - 1976, iso-pentane - 1978) with the peaks derived in Worton et al. (2012) measured at a different Arctic site, North GRIP.

Emission estimates for the butanes and pentanes are available from the ACCMIP data set, available from the ECCAD website (eccad.sedoo.fr). These suggest very similar emissions trends for the regions Europe and North America with emissions rising steadily from the 1950s to 1980, before declining to about 1965 levels 2000. This trend in alkane emissions is broadly consistent with the atmospheric concentrations derived from the firm air.

p11L4. At least once in this paper you should acknowledge that $[OH]_t$ is not a constant, it represents $\int [OH] dt$, and perhaps it would better be presented as an average symbol.

Lines 6 - 8 in the new version of Section 4 now reads,

*“Similarly for the purposes of this work, $[OH]$ is assumed to represent an average $[OH]$ to which the air mass is exposed during transport from the source region to the Arctic, i.e. $1/t * \int [OH].dt$.”*

We now present $[OH]$ when used as $\overline{[OH]}$.

p13L15 – $[NO]$ can range from 1ppb to ??? I have never seen the upper end of your range, 1000 ppb?? Provide a reference if so.

The DEFRA Air Quality Expert Group 2004 report “Nitrogen Dioxide in the United Kingdom” available from <http://www.defra.gov.uk/environment/airquality/aqeg> gives NO_x concentrations that range typically up to a few hundred $\mu g m^{-3}$ ($\mu g m^{-3} \sim 2 * ppb$ for NO_2) and in extreme cases going up to 3000 $\mu g m^{-3}$ (i.e. $\sim 1.5 ppm$).

However, since we refer to $[NO]$, we have changed this line to,

“In an urban environment, daytime $[NO]$ can range from ten to a few hundred ppb.”

P15 Figure 5 –for comparison, both y-axis should extended to zero. Units missing on right axis.

The units are now included on the right hand axis and both axes extend to zero.

p16L20 Section 5.2. Does 1 sentence deserve its own section?

No, perhaps not. We have moved this line to the end of Section 5.0.

p20L12-15: other primary sources of O₃. HCHO? HONO??

I'm not sure what you are referring to with this page and line reference. I'm guessing you mean other primary sources of OH? If so, we will extend the discussion here in a similar way to in the introduction.

“Another primary OH source is via the ozonolysis of alkenes (Johnson and Marston, 2008). A third source of OH that may be important is photolysis of HONO (e.g. Stone et al., 2012). There is still considerable uncertainty about the sources of HONO, with formation from heterogeneous conversion of NO₂ via a range of postulated processes appearing to dominate over the HO_x/NO_x recycling reaction OH + NO (e.g. Michoud et al., 2014). This again would be a primary source of OH which would be expected to correlate positively with NO_x concentrations.”