

I am in a bit of a conundrum here. One of the reviewers has suggested rejecting this paper. The second reviewer has suggested publishing the paper "as is", to essentially let the chips fall where they may. I agree with the one reviewer who suggested that the alkyl nitrate firn measurements should be published, however the second half of the publication is by no means without uncertainty (several). I agree that with the current uncertainties in the paper, it difficult to see convincing evidence to make conclusion that the chemical state of the northern hemisphere has changed. I find many of the arguments in the current version of the paper to be uncertain, with many assumptions untested that raise many questions. I think that this is a potentially very important paper but if it is to be published, changes will still need to be made to address the uncertainties that still exist. If you can address these concerns, especially my major uncertainty (see below), then send a revised paper to me to consider.

I have several small concerns, some that are shared with the reviewer(s) and one major uncertainty that has not been raised by either reviewer.

Robert McLaren  
Co-editor ACP

### **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 [RONO<sub>2</sub>]/[RH] could change over decades also due to changing emissions and emission patterns. Thus changes in [RONO<sub>2</sub>]/[RH] could partially be driven by changes in emissions. Likewise changes in  $\Delta[\text{NO}]/[\text{HO}_2]$  and  $\Delta[\text{OH}]t$  (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.

### **Other Major Concerns and Uncertainties**

P12L20 – what is the effect in this term of ignoring RO<sub>2</sub>-RO<sub>2</sub> self reactions.

P13L1: it is not good enough to just say that we assume the  $\gamma$  is constant, since we know that  $\gamma$  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.) Table T1 : Your scenarios should probably have extended [OH] at least to the generally accepted day and night global average [OH] level,  $[\text{OH}] = 1.2 \times 10^6 \text{ molec cm}^{-3}$ , as a sensitivity test. Obviously the changes in [RONO<sub>2</sub>]/[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.

P13 L28: Equation 13.  $[\text{NO}]/[\text{HO}_2]$  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  $[\text{NO}] \sim \int [\text{NO}]dt$  or  $[\text{NO}]/[\text{HO}_2] = \int [\text{NO}]/[\text{HO}_2] dt$

E3: The  $[\text{NO}]/[\text{HO}_2]$  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 °C 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?

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 [OH]. How does figure change as you change the photochemical processing?

p17E6 – I believe this equation is derived presuming that alkyl nitrates do not photolysis. Considering that ~ 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. Also why is  $[\text{NO}]/[\text{HO}_2]$  presumed to be 0.5. Reference? rationale? Sensitivity?

### **Minor Points**

p2L23-24: by removal, are you presuming CH<sub>4</sub> + OH and CO + OH regenerate OH catalytically. In any case, please provide a reference for such statements.

page 2 - HOx Sources: In winter regions, O<sub>3</sub> photolysis may not be the main source of OH. There is lots of recent evidence for this.

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.

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

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.

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 firm 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??

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

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

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

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

p20L12-15: other primary sources of O<sub>3</sub>. HCHO? HONO??