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Atmospheric Chemistry and Physics Discussions

# *Interactive comment on* "Changes to the chemical state of the northern hemisphere atmosphere during the second half of the twentieth century" *by* Mike J. Newland et al.

**Anonymous Referee #1**

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Summary:

This manuscript presents a very valuable data set of historical changes in alkyl nitrates and their parent hydrocarbons. Assuming 1) that the measurements of the concentrations of these species in the firn air are valid, and 2) that the conversion of firn air concentrations as a function of depth to ambient concentrations as a function of year are valid, then the results of Sections 1 through 3 are worthy of publication. However, the analysis of the ratios of alkyl nitrate to parent alkane is flawed and does not justify the very far reaching conclusions given in this paper, i.e., the analysis does not establish that the chemical state of the northern hemisphere atmosphere changed during the second half of the twentieth century. The analysis, discussion and conclusions in



Sections 4-8 must be reconsidered and modified as necessary. When the analysis is reconsidered, it may not be possible to reach significant general conclusions. Specific issues are detailed below.

Major issues:

1) The fatal problem with this paper is that the derivation of Equations E2 and E3 is flawed. Thus, the conclusions of this paper that are based on these equations are also flawed. For this paper to be acceptable for publication, the authors must reconsider all analyses based on these equations, and revise the conclusions accordingly. Bertman et al. [1995] derived Equation E1 by integrating the differential equation for the time rate of change of the alkyl nitrate concentration, which required approximations that were valid in an NOx rich environment. To extend Equation E1 to yield Equation E2 as the authors have done is not valid. To be valid, the original differential equation of Bertman et al. [1995] must be properly modified to include Reaction 11, and then properly integrated.

As it stands, it is clear that Equation E2 cannot be correct. The left side of the equation is a ratio that is determined by long time scale evolution, while the right side depends on NO and HO2 concentrations, which are variables that vary on very short time scales. For example, if the NO concentration were suddenly increased by fresh emissions, Equation E2 indicates that the [RONO2]/[RH] ratio would change, which is obviously incorrect. It might be (or might not be) that a proper integration of the appropriate differential equation could yield an equation that looks like Equation E2, where the NO and HO2 concentrations would be weighted time integrals, but those weightings are likely to be different for each species. How those weightings might be calculated is not clear. Equation E3 is derived from Equation E2, so the problems in the latter propagate to the former. The left side is now a ratio of highly variable species, while the right side depends on concentrations that change relatively slowly. The authors are evidently implicitly assuming that the NO and HO2 concentrations are some sort of remote, hemisphere wide average (as indicated by the statement on lines 11-12 of page 13).

However, this is far from clearly correct, as the production of the alkyl nitrates may well be dominated by relatively rapid photochemistry in the urban, NOx-rich, higher OH environment, rather than photochemistry in the remote environment. Hence, properly integrating the differential equations describing the photochemical processes is critical to correct analysis. That integration may not be possible to carry out analytically.

2) It is unclear whether the uncertainties in the estimated diffusion coefficients of the alkyl nitrates have an important impact on the atmospheric history reconstructions. This should be discussed.

3) On page 7 "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 most shallow measurement used). The scenarios presented in this work are based on including this measurement." Is this an important issue? The authors should discuss the effect on the final conclusions if this measurement is excluded.

Minor issues:

1) Abstract lines 18-21 - I disagree with the statement "Due to their short atmospheric lifetimes, NOx and HOx are highly variable in space and time, and so the measurements of these species are of very limited value for examining long term, large scale changes to their budgets." If measurements of either HOx or NOx were measured in a given region in an extensive enough manner to characterize average ambient concentrations (e.g., during an intensive aircraft deployment such as NASA DC-8 studies), and if those extensive measurements were repeated after the passage of a decade or so, then it should be possible to quantify the long term, large scale changes to their concentrations. I suggest that this statement be removed, as it is superfluous to the paper.

2) Page 2, lines 13 and 14. I also disagree with the phrase "which is positively correlated with NOx concentrations in the background atmosphere through the photolysis



of NO2 (Reactions R1-R2)." Ozone is certainly correlated with total NOy concentrations, but since ozone and NOx have very different lifetimes, they are in general only poorly correlated, because any correlation resulting from production through the photolysis of NO2 is destroyed by removal or fresh emissions of NOx, even in the remote troposphere. Here and elsewhere throughout the paper, I suggest that very careful consideration be given to the veracity of each sentence.

3) Page 2, lines 23 and 24 - The phrase "The main removal processes for HOx are the reaction of OH with NO2 (Reaction R9) ..." has an error. Evidently this reaction has not been separately listed in the paper.

4) Page 4, line - Should be "on-road" vehicles.

5) Page 6 - Sentence on lines 18-21 is not clear.

6) Page 8 - Line 12 - The Worton et al. (2010) reference is not in the References list; should be Worton et al. (2012)?

7) Page 12, lines 19-22 are not exactly correct: In Equation E1, taken from Bertman et al. (1995), [OH] is assumed to be the average over the time t. This is exactly what the authors are doing as well. This should be clarified, i.e. the term [OH]t represents the time integral of [OH] over the period during transport from the source region to the Arctic.

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