

Interactive comment on “Alkyl nitrate production and persistence in the Mexico City Plume” by A. E. Perring et al.

A. E. Perring et al.

anne.perring@noaa.gov

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ACPD Response to reviewer #2

We thank reviewer 2 for their time and consideration and address specific concerns as outlined below:

Comment: It seems that photochemical age calculations based on 2-butyl nitrate to butane is based on an estimated and daily averaged OH concentration. Why did the authors not use the OH measurements aboard the DC-8?

Response: The photochemical age is based on estimated and daily-averaged OH concentrations because the quantity of interest is the integrated amount of aging an air parcel has undergone up to the point of sampling rather than the instantaneous rate of

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aging occurring at the time of sampling. See also our response to reviewer #1.

Comment: Page 23762, 3rd para: -HNO₃: there is an old reference to measurements at Summit. How were these measurements adjusted for airborne measurements? – NO, O₃: it seems the scientists who produced this data is neither mentioned in the list of authors nor acknowledged. – HCHO: what data was finally used: NCAR or URI data? –H₂O₂: I assume this data has been used at least in the P(HO_x) calculations. Why is URI not at least acknowledged? – CO: Who measured CO and how? – NO_y: there is no explicit word on who measured NO_y and how? – 2-butyl nitrate: it should be mentioned explicitly what group was responsible for this measurement and how they were performed. A publication specifically referencing these measurements would be helpful.

Response: We will modify the paragraph to include detailed references to all of the instruments in question and to clarify that NO_y is defined as the sum of individual reactive nitrogen observations.

Comment: Page 23763, 2nd para: What were the reasons to use these criteria to discriminate the data? Does this kind of selection introduce bias into the data set?

Response: We assume that reviewer #2 is referring to our sentence “We use the ratio...to sort the MCMA plume points”. We did not use this ratio to “discriminate” the data as we did not reject any data based on the observed 2-butyl nitrate/butane ratio but rather we took data that were selected based on back-trajectory criteria as described in the manuscript and put them in order of increasing photochemical age based on the ratio of 2-butyl nitrate/butane. The rationale behind using this metric was to be able to look at the chemical evolution of the Mexico City plume despite the fact that the plume traveled at different velocities and in different directions on different days.

Comment: Page 23763, lines 13-14: Can Mexico City be considered an isolated point source considering its large spatial extension?

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Response: We believe this approximation is conceptually useful and sufficiently accurate to warrant the level of analysis presented in this paper.

Comment: Page 23769, lines 11-12: The VOC regimes in Mexico City and especially Houston are quite different. How can the authors use n-heptane measurements in Houston as a base to estimate other alkanes in Mexico City?

Response: Observations from many cities described in recent papers by Parrish et al and by others previously indicate that emission ratios (as inferred from observed hydrocarbon ratios) vary little from city to city even though emission rates vary dramatically. We will add a reference to these papers.

Comment: Page 23757, lines 10-11: remove “a wide suite...” It seems 30 hydrocarbons were measured (page 23769, line 8) which is quite a normal range.

Response: We will amend the text as suggested—we were not intending to compare the range to other measurements but to indicate that the suite covered a sufficient range to be representative of the VOC.

Comment: Page 23770, line 13 and page 23772, line 28: remove “observed”, since most of the hydrocarbons were estimated, not measured.

Response: In line 13 of page 23770, we are talking about the relationship of the observed concentrations of C1-C5 nitrates to the observed concentrations of sigma(A_Ns). Both are observed quantities and neither has to do with unmeasured hydrocarbons for which we estimated concentrations. In line 28 of page 23772 we will edit the sentence to read “observed and estimated hydrocarbons” but we note that most of the hydrocarbons were, indeed measured (30) while a minority of them (6) were estimated.

Comment: References: The following papers are either in submission or preparation. It is up to the editor, but personally I do not like these kinds of references, since the reader has no access to this literature: Farmer et al., submitted to PNAS, Fuchs et al, submitted to Atmos. Meas. Tech., Wooldridge et al., in preparation, Atmos. Meas.

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Response: We will add complete citations to the published manuscripts and remove citations to the work not yet publically available. We note that both AMT papers were publically available during the review period.

Comment: Figure 3: why are the DC-8 flight 7 and DC-8 flight 8 highlighted?

Response: As discussed in the text (p23765, lines 2-6) Flights 7 and 8 are highlighted to illustrate that much of the scatter in the calculated age as a function of distance is due to differing wind speeds on different days and that, for any given flight, the relationship between distance and photochemical age is much cleaner.

Comment: Also, assuming that the Mexico City area extends 100km around the Mexico City center (see dashed black circle in figure 2) and cutting off these first 100km in figure 3 the remaining data would not yield any good correlation.

Response: Figure 3 is not intended to show a simple correlation but rather to give the reader a sense for how our calculated age relates to distance from the source, which is a more intuitive (although chemically less exact) measure of plume processing.

Comment: Figure 6: This figure needs additional information, e.g. r^2 and regression equations including error estimates for slopes in order to verify if the regimes differ significantly from each other. Also, I only see two dotted lines for the intermediate age ranges but according to the authors there should be three (see page 23767, lines 14-15).

Response: We will include r^2 and error estimates for the 5 fit-lines shown in Figure 6 in the revised text. There are three dotted lines for intermediate age ranges but the lines representing fits for 5-15 hours and 15-25 hours are very similar and lie practically on top of one another.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 23755, 2009.

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