Author reply

(note: page and line numbers referenced by the referees are as appeared on the ACPD typeset, while page and line numbers in the author responses are associated with the re-submitted manuscript file)

Referee #1

Specific comments:

1. Page 17409, line 20: Are the amounts of aromatics reacted high enough that this source of alkyl nitrates could be significant if the alkyl nitrate yields from reactions of the ring-opened products (which are typically > 90% of the OH reaction products) are a few percent?

Author reply:
The total OH reactivity of aromatic compounds measured by GC-MS is generally 10% of the total OH reactivity due to alkanes (Table 1). Given the overall alkyl nitrate yield from alkanes of 22% (Table 2) and assuming an upper limit to the nitrate yield from aromatic compounds of ~35% (as a C7 secondary peroxy radical at 273K), the organic nitrate contribution from aromatics is only 14% of the contribution from alkanes. Therefore, organic nitrate production from alkanes still dominates.

Correction to page 8 line 19
It is noted that even by assuming an upper-limit nitrate yield of 0.35, the contribution from aromatic compounds to alkyl nitrate production is minor (14%) relative to the production from alkanes.

2. Page 17415, line 1–4: It might be useful to remind the reader that small and large alkanes have different effects on the ratio because alkyl nitrate yields increase with carbon number.

Author reply:
Add to page 13 line 13
… heavier organics. This is consistent with the understanding that alkyl nitrate yield increases with the carbon number of the precursor alkane. By comparison …

Technical comments:

1. Page 17408, line 25: I believe there should be "constant" after "rate".

Author reply:
Correction page 7 line 24
… reaction rate constant and …

2. Page 17411, line 1: Should either be "calculations proceed" or "calculation proceeds".

Author reply:
Correction page 9 line 24
The calculations proceed as follows …

3. Page 17419, line 23: It looks like the subscript 4 is a typo.

Author reply:
Correction page 17 line 16
…) = 0.021. Note the correction …

Referee #2

Major comment

1. My only major comment is that I would like to see a more thorough error analysis. The calculations are based on measurement data that is at times subject to corrections in excess of 50%. Assumptions are made about background mixing ratios to estimate dilution. OH production rates are estimated using filter radiometer measurements (see below). In addition, the alkyl nitrate yields for the larger, and branched alkanes were calculated to take into account secondary AN production down-chain and from secondary oxygenates. It would be nice to see an attempt to carry all these errors and uncertainties through to the final numbers in tables 2 and 3. This would allow the reader to put the significance of the difference between 57 and 64 ppb of ozone into perspective.

Author reply:
An error estimate was not given for the nitrate branching ratio estimation method given by Carter and Atkinson, 1989. A simple estimation from comparisons between predicted and experimental values listed in Table 1 of the said paper suggests a margin of ~15% near ambient conditions. The current uncertainty estimate of the O_3 pyrolysis correction is up to 15% of the reported ΣAN concentration, as estimated from the absolute errors associated with the empirical fit to the laboratory data. The uncertainty in estimated OH concentration is in general 22%, proportional to the uncertainty in J values and OH reactivity data. This results in an uncertainty of ensemble averaged nitrate yield of 28% (oxidation-production method, section 3.2.2), as a result of uncertainties in alkyl nitrate production rate (18%) and dilution rate (26%).

However, the main point in Table 3 is to demonstrate the difference in O_3 concentration predicted when temperature dependence of alkyl nitrate yield is accounted for properly. The associated uncertainty of this estimate correlates with the uncertainty due to the temperature parameterization of alkyl nitrate yields. As an upper limit estimate of the uncertainty associated with the relative ratio of alkyl nitrate yield between 300K and 273K, we treat both uncertainties as un-correlated which gives a net uncertainty of 21% in the predicted 273K nitrate yield with respective to the 300K yield. This corresponds to a variation of 11% in the resulting OH radical chain length and also the net O_3 production rate. Overall, this gives a concentration difference in the range of 7±4 ppb for UBWOS 2012 base condition and 25±15 ppb for snow cover condition.

Replace page 25 Table 3

Table 3. Expected maximum O

Condition	UBWOS 2012 base condition	photolysis × 2 & mixing ÷ 2
α calculated at 273K	57 ppb	140 ppb
α calculated at 300K	64 ppb	165 ppb
difference	7±4 ppb	25±15 ppb

[a] Assuming background O
[b] Carter and Atkinson, 1989.
[c] Uncertainty due to temperature dependence parameterization of alkyl nitrate yield.

Minor comment

1. OH production rates are calculated using measurements of O1D and JNO2. Are those filter radiometer measurements? If yes, how were the photolysis rates of the other OH sources calculated and what is the uncertainty of these calculations?

Author reply:
The photolysis rates are based on 3 individual filter radiometer measurements, of O_3 (O1D), NO_2 and NO_3. They are manufactured by Metcon Inc. with a cited uncertainty of 20%. Photolysis rates of organic species such as formaldehyde are calculated using linear combination of $J(O_3)$ and $J(NO_2)$ values, similar to the method of (Stark et al., 2007).

Addition page 9 line 29
Photolysis rates for O_3, NO_2 and NO_3 are measured directly with filter radiometers. For other species they are estimated using linear combination of photolysis rates of O_3 and NO_2.

2. While I like the analysis done here and appreciate the idea behind this paper, I think that the importance for including temperature dependent production rates for ANs into regional models is probably limited to unique environments like this one. In most other parts of the world the ozone production from alkanes (for which there is sufficient kinetic data available to include in models) is very small to negligible. The authors might consider pointing this out in the conclusions.

Author reply:
It is true that reactions of biogenic alkenes dominate the greater part of the global tropospheric environment. However, we expect similar temperature dependence of organic nitrate yield form the associated peroxy radicals since the underlying requirement of collisional stabilization remains the same. We agree with the referee that better characterizing the temperature

dependence of organic nitrate formation from isoprene and monoterpenes is the crucial step in generalizing this correction to a global scale.

Other corrections

1. Correction page 3 line 20
   … using a pulsed tunable laser …

2. Correction page 3 line 24
   … under a residence time of ~0.17 seconds. The air sample passing through the heated regions were under near ambient atmospheric pressure before entering a restrictive orifice into low pressure transfer line to the LIF cell. Simultaneous …

3. Correction page 3 line 30
   Laboratory experiments carried out after the deployment indicate that the ΣANs channel had been set to a temperature that was higher than necessary to fully dissociate alkyl nitrates. The O_3 pyrolysis and subsequent O atom-initiated chemistry that is usually a very minor negative interferences (Day et al., 2002) resulted in a large enough effect to require a correction term for this dataset. The correction …

4. Correction page 10 line 21
   … is presented in Figure 5 as …

5. Deletion page 14 line 17
   deleted: It was necessary to correct for apparent negative signals observed in the ΣANs signal (ΣANs channel showing less signal level than the ΣPNs channel).

6. Correction page 14 line 27
   … the reaction rate k_{R5} and k_{R6} (…

7. Addition page 15 line 10
   The proper setting for ΣANs observations would be in the 250°C to 280°C range in this instance.

8. Replace page 26 figure 1
   (to editor: the original ΣANs trace has not yet been subtracted of $ClNO_2$ contribution. However, the analysis used the corrected data and is unchanged.)

9. Correction page 27 line 5
   … been corrected for O_3 interference and the $ClNO_2$ contribution has been subtracted (see text).
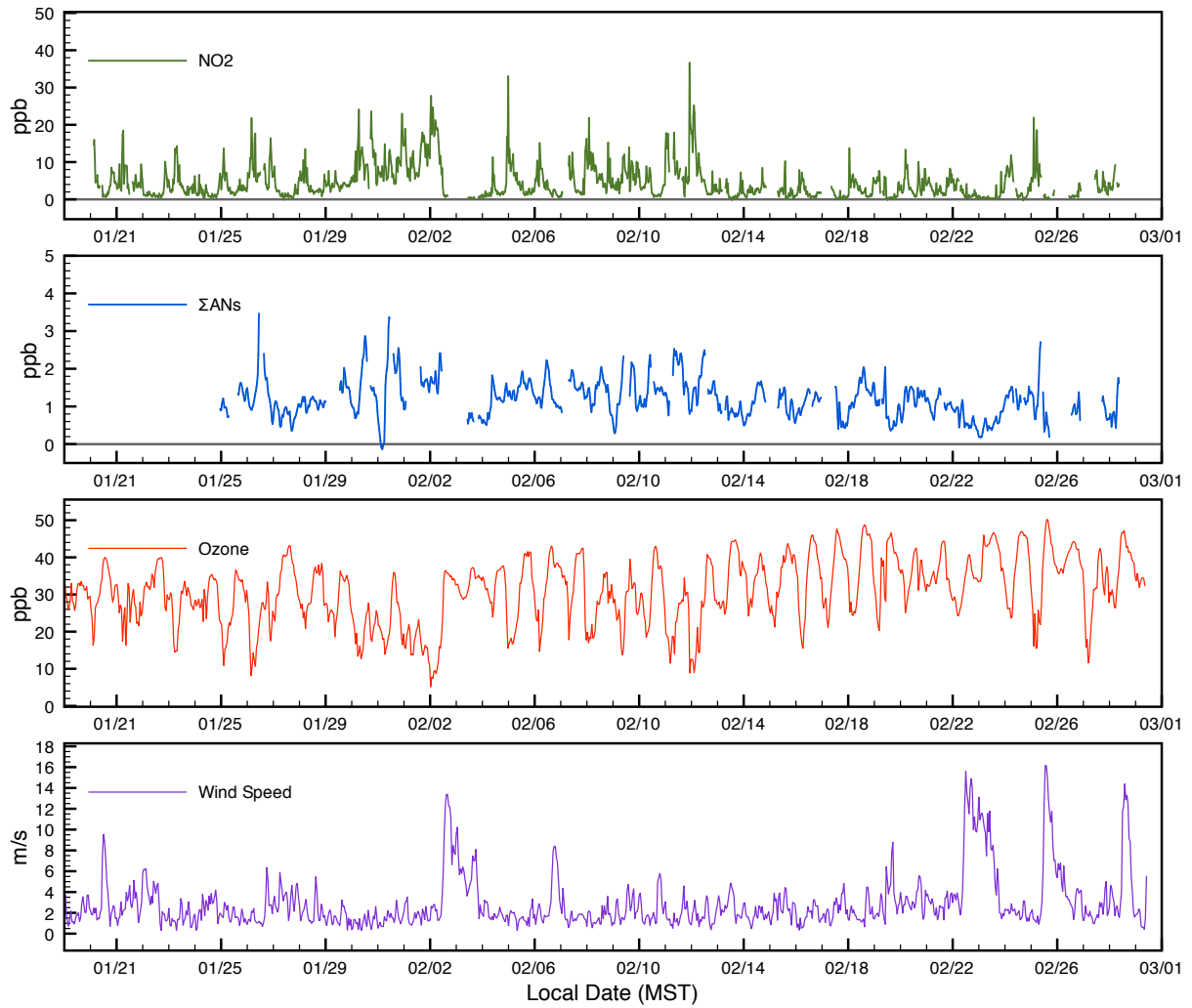
Stark, H., Lerner, B. M., Schmitt, R., Jakoubek, R., Williams, E. J., Ryerson, T. B., Sueper, D. T., Parrish, D. D., and Fehsenfeld, F. C.: Atmospheric in situ measurement of nitrate radical (NO3) and other photolysis rates using spectroradiometry and filter radiometry, J. Geophys. Res.-Atmos., 112, 11, 10.1029/2006jd007578, 2007.