

We would like to thank both referees for their helpful comments and for acknowledging the effort involved with collecting and analyzing the various data sets included in our manuscript. Our responses to both reviews are in a single document. The referee comments are in bold and our response is given directly following the comment.

Referee #1

Specific Comments

The deposition analysis for MeONO₂ assumes a constant concentration with height in the NBL. But on these calm nights while MeONO₂ is depositing there must be a vertical gradient in concentration. How would this calculation depend on the measurement height?

We agree it is possible that a vertical gradient in MeONO₂ will develop as a result of nighttime surface depletion. However, we do not have any vertical profile information on the boundary layer height and structure for summers 2002 and 2004 at TF. Accordingly, we have to assume that the surface to the nocturnal inversion is uniformly mixed. In Section 3.2.1, we explicitly noted that our results will scale directly with the value chosen for the boundary layer height. We also stated we used an assumed constant boundary layer height in our calculations, but we have reworded the text to make this more clear. Several studies conducted in various continental environments have reported the nocturnal inversion to be approximately 75-125 m above ground level (e.g., Galbally, 1968; Garland and Derwent, 1979; Shepson et al., 1992; Hastie et al., 1993; Neu et al., 1994; Güsten et al., 1998). Based on these results, we chose a constant nocturnal inversion height of 125 m as a reasonable estimate for the TF site. Previous studies have used this same methodology to calculate emission and removal rates of various trace gases at TF (e.g., Talbot et al., 2005; Sive et al., 2007; Mao et al., 2008; White et al., 2008; Zhou et al., 2008). Our focus is not on the vertical profile of MeONO₂ but is to present evidence for its dry deposition. Based on our assumption that entrainment and horizontal advection are negligible on nights with strong NBLs and the near surface (15 m) height of the sample inlet, we do not expect the development of a vertical gradient over the several hours when the NBL is present to have a significant impact on our results. However, in the future, we plan on addressing this point with tethered balloon measurements.

Do you see similar behavior indicating dry deposition for the other ANs? Is there any reason to expect MeONO₂ to behave differently than these?

As noted in the first paragraph in Section 3.2, the C₂-C₅ alkyl nitrates did exhibit a similar diurnal variation as MeONO₂ with decreasing mixing ratios overnight and increasing mixing ratios throughout the morning. There were a few occasions throughout summers 2002 and 2004 when an alkyl nitrate other than MeONO₂ decreased on nights with strong NBLs. However, only MeONO₂ consistently exhibited decreasing mixing ratios on the nights with stable NBLs; thus we limited our discussion to MeONO₂. Text was added to Section 3.2.1 which discussed why we only focused on MeONO₂ and why we think it may exhibit different behavior than the other alkyl nitrates:

“It should be noted that our analysis is limited to MeONO₂ because the C₂-C₅ alkyl nitrates did not consistently exhibit nighttime depletion under the stable NBL. Methyl nitrate is more soluble (Henry’s Law constant ~2.0 M/atm) than the C₂-C₅ alkyl nitrates (0.34-1.6 M/atm)

(Kames and Schurath, 1992; Sander, 1999). Therefore, the greater solubility of MeONO₂ may explain the different behavior compared to the C₂-C₅ alkyl nitrates.”

How would these dry deposition losses affect your sequential reaction analysis (section 5)?

We did estimate deposition velocities for the C₂-C₅ alkyl nitrates using the observed nighttime decrease in their hourly average mixing ratios (not included in manuscript). We also performed analyses which included a dry deposition term in the sequential reaction scheme for the C₂-C₅ alkyl nitrates discussed in Section 5. Again, we did not include these results in the manuscript because we did not have sufficient evidence that the C₂-C₅ compounds consistently underwent deposition. Nonetheless, including a first order removal rate due to dry deposition ($k_D = V_d/H = 1/\tau_d$) in the alkyl nitrate removal rate constant term ($k_B = k_6[\text{OH}] + J_5 + k_D$) in Eq. (2) for each C₂-C₅ RONO₂/RH, caused the calculated ratios to quickly reach a constant value, and the curves did not extend beyond processing times of ~2 days on the pure photochemistry curves. Based on this preliminary analysis, including a k_D term in Eq. (2) did not improve agreement between the observations and the predicted RONO₂/RH trend.

Ocean source/sink analysis (section 4.2)

We have included a calculation of the saturation anomaly of the alkyl nitrates and added the following text:

*“The saturation anomalies ($[(\text{seawater concentration} - \text{air concentration})/\text{air concentration}] * 100\%$) of MeONO₂, 2-PrONO₂, and 2-BuONO₂ ranged between $\pm 150\%$. The similar range of positive and negative saturation anomalies suggests that the New England coastal seawater was neither a net source nor sink of alkyl nitrates.”*

Abstract is very wordy and I recommend shortening.

We have combined some sentences and removed text to streamline the abstract. It now reads:

“Seven C₁-C₅ alkyl nitrates were measured both on the mainland and off the coast of New Hampshire using gas chromatographic techniques. Five separate data sets are presented to characterize the seasonal and diurnal trends and the major sources and loss processes of these compounds. Based on in situ measurements conducted at the University of New Hampshire (UNH) Atmospheric Observing Station at Thompson Farm (TF) located in southeast NH during winter (January-February) 2002, summer (June-August) 2002, summer (July-August) 2004, and on daily canister samples collected at midday from January 2004-February 2008, the median total alkyl nitrate mixing ratio (ΣRONO_2) was 23-25 pptv in winter and 14-16 pptv in summer. During summers 2002 and 2004, MeONO₂ decreased overnight and reached minimum hourly average mixing ratios in the early morning. Comparison with wind speed and trace gas trends suggested that dry deposition contributed to the early morning MeONO₂ minimum which is a previously unaccounted for removal mechanism. The mean dry deposition rate and velocity of MeONO₂ was estimated to be $-0.5 \text{ nmol m}^{-2} \text{ hr}^{-1}$ and 0.13 cm s^{-1} , respectively. Results from ambient air and surface seawater measurements made onboard the NOAA R/V Ronald H. Brown in the Gulf of Maine during the 2002 New England Air Quality Study and from ambient canister samples collected throughout the Great Bay estuary in August 2003 are also presented. Comparisons between the alkyl nitrate trends with anthropogenic and marine tracers suggest that a marine source of alkyl nitrates is not significant in coastal New England. Given the

apparent prominence of a secondary source, comparisons between observed and predicted alkyl nitrate/parent hydrocarbon ratios were made which demonstrated that background mixing ratios have a continuous and prevalent influence on the alkyl nitrate distribution.”

Introduction. Somewhere please talk about how the compounds you’re measuring compare to total organic nitrates.

We have made sure to explicitly define our use of the phrase total alkyl nitrate (ΣRONO_2) as the sum of the seven individual C₁-C₅ alkyl nitrates in Section 2.1 and at the beginning of Section 3.1. We reorganized the introduction and added text specifying that our work is focused on alkyl nitrates, but that there are other types of organic nitrate compounds, and inserted ‘C₁-C₅’ before ‘alkyl nitrate’ in several places throughout the text. The text added to the introduction reads as follows:

“Alkyl nitrates are a component of total reactive nitrogen ($\text{NO}_y = \text{NO}_x + \text{HNO}_3 + \text{NO}_3 + \text{N}_2\text{O}_5 + \text{organic nitrates}$), and their relative contribution to NO_y varies with location. It should be noted that the term organic nitrate refers to several types of compounds, including monofunctional alkyl nitrates, peroxyacetyl nitrates, and other multifunctional organic nitrate compounds. Some recent studies (i.e., Day et al., 2003; Perring et al., 2009) have used the term total alkyl nitrates (ΣRONO_2) to refer to nonspeciated measurements of several organic nitrate classes including isoprene nitrates, hydroxyalkyl nitrates, multifunctional organic nitrates, and the monofunctional alkyl nitrate compounds included in this work. In continental regions, the monofunctional alkyl nitrates typically comprise less than 10% of NO_y because of the close proximity to primary NO_x emissions (e.g., Shepson et al., 1993; Flocke et al., 1998; Thornberry et al., 2001; Simpson et al., 2006). In contrast, they may constitute a much larger proportion of NO_y in remote regions, such as the equatorial marine boundary layer (20-80%) (Talbot et al., 2000; Blake et al., 2003a) or the Arctic (~10-20%) (Muthuramu et al., 1994).”

Sections 2.1-2.3- many experimental details are given here. In the interest of readability consider just putting the basics here and move the details to supplemental information for those who are interested.

We have removed some of the specific details regarding sample collection and analysis for the in situ TF GC (Section 2.1) and canister samples (Section 2.3).

Section 2.3.2- were tests done to verify compound stability in the canisters over this long storage time (1-3 months)?

Yes. We have conducted numerous canister and instrument intercomparison studies which have demonstrated that compounds remain stable in the canisters for several months (e.g., Sive et al., 2005; Zhou et al., 2008; Russo et al., 2010). In all cases, measurements made by in situ instruments and our canisters (which were analyzed within <1-3 months after collection) were in good agreement. Furthermore, we have conducted several measurement intercomparison experiments of both surface and aircraft canister samples with the University of California-Irvine (UCI). We have rephrased the last sentence in Section 2.3.2 to:

“Furthermore, we have conducted several instrument intercomparison studies to verify that the measurements from the in situ TF GC and canister samples made over multiple years are

comparable and to ensure the stability of VOCs within our canisters (see Sive et al., 2005; Zhou et al., 2008; Russo et al., 2010)."

Section 2.4- again, consider just stating the key finding (“good agreement”) and move details and figure to supplemental.

We have removed this section from the manuscript to streamline the readability of the experimental section.

Section 3.1 and elsewhere. Lists of numeric values in the text are tiresome.

We appreciate the reviewer’s comment and agree that long lists of numbers can be tiresome and hinder the readability of text. However, we do not feel that there were too many lists of numeric values in our manuscript. We think it is important to provide a balance of text with some quantitative information easily available within it because it can be a nuisance to need to flip back and forth between text and tables. Nonetheless, we combined the ΣRONO_2 winter and summer statistics for 2002 and 2004-2008 in order to reduce the amount of numbers listed and removed some ranges of mixing ratios from the second paragraph in Section 3.1.

p. 23381, L1. From Fig. 4, the MeONO_2 and EtONO_2 seasonality seems to become more pronounced in 2006-7. Is that the case and is it real?

Yes, it is real. The MeONO_2 and EtONO_2 seasonality appears more pronounced because the mid-to-late summer minimum mixing ratios were lower in 2006 and 2007 than in 2004-2005. We think this reflects natural interannual variability in the ambient mixing ratios of these compounds.

p. 23381, L3. I don’t think you’ve told us yet what the lifetimes are.

Thank you for pointing out that we hadn’t discussed the lifetimes yet. The sentence was deleted because the differences in alkyl nitrate lifetimes are discussed in the last paragraph of Section 3.1.

p. 23381, L20-end. Differing seasonal lags would be one way to look at causes of the seasonality. Do you see any lag between the different RONO_2 compounds reflecting differing photochemical lifetimes?

We rephrased the text in the first paragraph of Section 3.1 to make the difference in seasonal trends for the shorter and longer lived alkyl nitrates more clear:

“The nearly 60 % lower ΣRONO_2 mixing ratio in summer was driven by the reduced levels of $\text{C}_3\text{-C}_5$ alkyl nitrates which were typically highest in late winter-early spring (February-March) and exhibited a broad minimum from May-October (Figure 3, Table 2). In contrast, the monthly mean and median mixing ratios of the longer-lived MeONO_2 and EtONO_2 were more uniform all year, particularly in 2004-2005, and both compounds exhibited low day-to-day variability in late fall-winter (Fig. 3a). Methyl and ethyl nitrate mixing ratios were lowest in mid-to-late summer through the fall (July-October) (Table 2).”

p. 23383, L18. I believe ozone deposition occurs mainly via stomatal uptake (i.e. controlled by stomatal conductance), and possibly reaction with biogenic hydrocarbons, and not so

much by solubility-controlled deposition to surfaces. So this comparison seems inappropriate.

We have removed the Henry's Law constant comparison for MeONO₂ and O₃ to avoid confusion. However, our rationale for comparing MeONO₂ and O₃ in Section 3.2 is to illustrate that MeONO₂ tracks O₃ under the NBL which suggests that they are influenced by similar removal mechanisms. The nighttime removal of O₃ at TF is caused by both chemistry and deposition (Talbot et al., 2005). Chemical removal of MeONO₂ at night should be negligible suggesting that deposition is the likely cause of the decreasing MeONO₂ mixing ratios. Deposition of O₃ to surfaces is controlled by several factors, including stomatal conductance and surface wetness (e.g., Finkelstein et al., 2000; Wesely and Hicks, 2000). At night, which is the time period we are focused on, stomates are predominantly closed and stomatal uptake is likely to be minimal/negligible. At this time, we do not have enough information to determine the mechanism(s) responsible for MeONO₂ deposition at TF.

p. 23384. Comment on why the NO_y behavior is so different for the two highlighted nights in Fig. 6?

We think NO_y exhibits different behavior on the nights of 7-8 and 13-14 June 2002 because of different air mass source regions. The wind direction during the several hours preceding the development of the NBL and throughout both nights was different. We added the following text to the first paragraph of Section 3.2.1:

“The slightly different NO_y trend on both nights is likely a combination of deposition and different air mass source regions. On 7-8 June, the wind direction shifted from easterly to southwesterly, whereas the wind was from the south-southwest throughout the entire day on 13 June and continuing into 14 June.”

p. 23385. SE's in table 3 for V_d seem small. Are they the standard error for the regression? If so this generally underestimates the true uncertainty. Better to use a bootstrap or jackknife approach.

The standard errors for V_d in Table 3 were the standard deviation of the mean V_d (=standard deviation/sqrt(N)) of the N = 4 and 16 nights during 2002 and 2004, respectively. We agree that this underestimates the true uncertainty and have changed Table 3 to list the mean dry deposition flux ± standard deviation and the mean V_d ± standard deviation.

Table 4: I suggest presenting information in Table 4 in a more communication friendly plot form. Perhaps a wind-rose plot.

We appreciate the suggestion of providing the information in Table 4 in a wind rose plot. As part of our original analysis, we generated a whole series of wind rose plots; including them for each compound and season presents an unnecessarily large number of graphs. We feel that a table is a more reader-friendly and succinct way to provide the quantitative results.

p. 23388, L18-20. Also depends on differing amounts of the various NMHCs.

We changed this sentence in the second paragraph of Section 4.1. It now reads:

“This characteristic continental source signature reflects a balance between the increasing alkyl nitrate yield and the decreasing lifetimes of both the parent alkane and alkyl nitrate with

increasing carbon number (Atkinson et al., 1982; Flocke et al., 1991; 1998; Arey et al., 2001), as well as the distribution of parent hydrocarbons in a specific region.”

p. 23389, L10. What different sources? Please discuss somewhere the differing anthropogenic sources of the NMHC precursors for the nitrates you’re looking at.

We added text to Section 4.1 which included references (White et al. 2008; Russo et al., 2010) to papers that discuss the sources of the hydrocarbons observed at TF in detail. The specific text reads as follows:

First paragraph in Section 4.1

“The sources of the precursor hydrocarbons observed at TF include fuel evaporation, vehicle exhaust, and natural and liquefied petroleum gas usage and leakage (White et al., 2008; Russo et al., 2010).”

Last paragraph in Section 4.1

“In addition, the C₁-C₅ alkyl nitrates tracked each other extremely well (Figs. 2 and 3) reflecting their similar photochemical and/or collocated hydrocarbon precursor sources.”

p. 23391, L7. Assumes dominant fate of RO₂ is reaction with NO, i.e. high-NO_x conditions. Should be mentioned and stated why this is an appropriate assumption.

We added text to the first paragraph in Section 5 discussing why it is valid to assume that RO₂ + NO is dominant at TF. The specific text is:

“The production and loss reactions of alkyl nitrates summarized in Reactions (R1-R6) can be simplified as follows by assuming that Reaction (R1) between the parent hydrocarbon and OH is the rate-limiting step and that reaction with NO is the main reaction pathway for RO₂ radicals (R3 and R4) (i.e., no peroxy radical self reactions).....It is worth noting that the mean NO mixing ratios at TF were 2.5 and 0.35 ppbv in winter and summer 2002, respectively. These mixing ratios are sufficient (~0.04-0.1 ppbv) for reaction with NO to be the dominant reaction pathway for RO₂ radicals (e.g., Flocke et al., 1991; Roberts et al., 1998). Thus, we assume that the RO₂ + NO reaction is dominant at TF.”

p. 23394, L1. “significant amount” – give fraction

The actual amount is 70-90 %, and we added this to the text.

p. 23394, L18-end. This argument doesn’t seem to make sense and I recommend deleting the last 4 sentences of the section.

We rephrased the text in the last paragraph of Section 5 to now read:

“This result is likely because the C₅ compounds (n-pentane and pentyl nitrates) have shorter lifetimes and lower mean and background mixing ratios than for n-butane and 2-BuONO₂ (Tables 1, 2, 5).”

Other questions about the sequential reaction analysis:

Are the denominators (i.e. NMHC concentration) always above LOD? How well-defined are the RONO₂-OH rate constants?

Yes, the NMHCs were always well above the LOD. According to Atkinson et al. (2006), the alkyl nitrate + OH rate constants are known to within $\Delta \log k \sim \pm 0.3$. This reference is given in the text and in Table 5 for the reader to get additional information if necessary.

Technical Comments:

p. 23377, L25. “an EVACUATED two-liter...”

We inserted “evacuated” into the text.

p. 23387, L17. Which mixing ratios are you referring to? All alkyl nitrates?

We are referring to the total alkyl nitrate (ΣRONO_2) mixing ratio, and we clarified this in the text:

“In winter, the ΣRONO_2 mixing ratio was fairly uniform in the SW, NW, and NE sectors but was significantly higher ($p < 0.05$) in the SE sector, while in summer, the mean mixing ratio in both the SE and SW sectors was significantly higher ($p < 0.001$) than in the northern sectors (Table 4).”

p. 23388, L2-3. Rephase, it is not a new discovery that the industrialized NE is a source of NMHCs.

We rephrased this sentence in the first paragraph of Section 4.1 to now read:

“Furthermore, in both seasons, the highest and lowest mean parent hydrocarbon (ethane, propane, n-butane, n-pentane) mixing ratios were observed in the southern and northern transport sectors, respectively (not shown). The high levels observed are consistent with the location of major urban and industrial regions to the west-southwest of New England.”

p. 23388, L13. “their major source” – unclear whether “their” is referring to PrONO₂ and BuONO₂ or to ΣRONO_2 .

We were referring to 2-PrONO₂ and 2-BuONO₂. We changed the text to:

“The dominant and consistent contribution of 2-PrONO₂ and 2-BuONO₂ to ΣRONO_2 at TF over various years and time scales further corroborates that the major source of both alkyl nitrates was photochemical production from propane and n-butane, respectively (Tables 1 and 2). The C₃-C₄ alkanes are among the most abundant NMHCs at TF (Russo et al., 2010).”

p. 23388, L22. “to be undersaturated IN THE SURFACE OCEAN”

We rephrased the text to state that the light alkyl nitrates were supersaturated in the surface ocean in remote oceanic regions.

Please increase font size on Figures 3-10. Fig 10 symbols and labels are too small and hard to see.

We increased the font size for the figures. In the final publication, Figure 9 will be in portrait format, and we intend to have a full page for this figure which should make it easier to see and

read. (Note: Figure 10 in the discussion paper is now Figure 9 because we removed Section 2.4 and Figure 2 from the discussion paper.)

Fig 10 color schemes seem unnecessarily complicated and confusing. Why not have just three colored lines which are the same in every panel and for both the abscissa and ordinate.

We understand and appreciate the reviewer's comment of having three lines for $\text{RONO}_2/\text{RH} = 0$, seasonal mean, and seasonal background. However, we chose to plot the lines predicted using specific initial ratios for both aesthetic and quantitative reasons. For the green line, both the abscissa and ordinate are equal to the seasonal background. For the red line, we chose to have $[\text{2-BuONO}_2]_o/[\text{n-butane}]_o$ equal to the seasonal background and the ordinates equal to the seasonal mean because we think this best illustrates our point that the predicted RONO_2/RH lines using the seasonal mean and background initial ratio values of $\text{EtONO}_2/\text{ethane}$, $\text{2-PrONO}_2/\text{propane}$, and $\text{1-PrONO}_2/\text{propane}$ encompass the observations.

The pentyl nitrate/n-pentane ratios exhibit unique behavior because the observations fall below the $[\text{RONO}_2]_o/[\text{RH}]_o = 0$ curve (the black line). This same observation has been made in previous studies. In this case, we chose to have $[\text{2-BuONO}_2]_o/[\text{n-butane}]_o$ equal to the seasonal mean and $[\text{PenONO}_2]_o/[\text{n-pentane}]_o$ equal to the seasonal background because the predicted pentyl nitrate/n-pentane ratios match the observations under these conditions. This suggests that the different lifetimes of the C_4 and C_5 compounds is a potential explanation for why the observed pentyl nitrate/n-pentane ratios are lower than predicted.

Referee #2
Specific Comments

The authors should be careful with the use of “total alkyl nitrates” and ΣRONO_2 notation. It has been demonstrated that in many air masses, $\text{C}_1\text{-C}_5$ alkyl nitrates comprise only a small fraction of the true total alkyl nitrates due to the dominance of isoprene-derived nitrates. Most notably, line 5 on page 23395 needs to be reworded. I would also highly recommend a few short sentences in the introduction that reference the fraction of the total alkyl nitrate abundance that is in the form of a $\text{C}_1\text{-C}_5$ straight chain AN.

We changed the summary (line 5 page 23395) to clearly state that our results are based on $\text{C}_1\text{-C}_5$ alkyl nitrates:

“The total $\text{C}_1\text{-C}_5$ alkyl nitrate mixing ratio was generally $\sim 20\text{-}30$ pptv and constituted only a small component ($\leq 1\%$) of ambient NO_y at TF. This suggests that the $\text{C}_1\text{-C}_5$ alkyl nitrates are not likely to have a significant influence on the local O_3 or NO_y budget.”

We added text to the introduction specifying that our work is focused on alkyl nitrates, but that there are other types of organic nitrate compounds, and inserted ‘ $\text{C}_1\text{-C}_5$ ’ before ‘alkyl nitrate’ in several places throughout the text. The text added to the introduction reads as follows:

“Alkyl nitrates are a component of total reactive nitrogen ($\text{NO}_y = \text{NO}_x + \text{HNO}_3 + \text{NO}_3 + \text{N}_2\text{O}_5 + \text{organic nitrates}$), and their relative contribution to NO_y varies with location. It should be noted that the term organic nitrate refers to several types of compounds, including monofunctional alkyl nitrates, peroxyacetyl nitrates, and other multifunctional organic nitrate compounds. Some recent studies (i.e., Day et al., 2003; Perring et al., 2009) have used the term total alkyl nitrates (ΣRONO_2) to refer to nonspeciated measurements of several organic nitrate classes including isoprene nitrates, hydroxyalkyl nitrates, multifunctional organic nitrates, and the monofunctional alkyl nitrate compounds included in this work. In continental regions, the monofunctional alkyl nitrates typically comprise less than 10% of NO_y because of the close proximity to primary NO_x emissions (e.g., Shepson et al., 1993; Flocke et al., 1998; Thornberry et al., 2001; Simpson et al., 2006). In contrast, they may constitute a much larger proportion of NO_y in remote regions, such as the equatorial marine boundary layer (20-80%) (Talbot et al., 2000; Blake et al., 2003a) or the Arctic ($\sim 10\text{-}20\%$) (Muthuramu et al., 1994).”

What is the deposition rate of the other measured alkyl nitrates? This data should be included for comparison.

We did estimate deposition rates for the $\text{C}_2\text{-C}_5$ alkyl nitrates using the observed nighttime decrease in their hourly average mixing ratios. This preliminary analysis indicated that the deposition rates ranged from 0.4 to 1.8 $\text{nmol m}^{-2} \text{hr}^{-1}$. We are not including this data in the manuscript because we do not have consistent evidence that the $\text{C}_2\text{-C}_5$ alkyl nitrates undergo deposition.

If deposition is the major sink mechanism (at least for MeONO_2), why is it not included in the analysis in section 5? It should be an important contribution to equation 2? How does this alter these results and previous interpretations of RH/AN ratios using this methodology?

We did not intend to imply that dry deposition is the major sink mechanism for MeONO₂. The purpose of our analysis was to present evidence that deposition influences MeONO₂ under certain conditions. As noted in the previous comment, we did not include dry deposition results for the C₂-C₅ alkyl nitrates in Section 5 because we did not have sufficient evidence that these compounds consistently underwent dry deposition. Nonetheless, including a first order removal rate due to dry deposition ($k_D = V_d/H = 1/\tau_d$) in the alkyl nitrate removal rate constant term ($k_B = k_6[\text{OH}] + J_5 + k_D$) in Eq. (2) for each C₂-C₅ RONO₂/RH caused the calculated ratios to quickly reach a constant value, and the curves did not extend beyond processing times of ~2 days on the pure photochemistry curves. Based on this preliminary analysis, including a k_D term in Eq. (2) did not improve agreement between the observations and the predicted RONO₂/RH trend.

Technical Corrections:

p. 23380 line 18. The use of median and standard deviation together is a bit awkward.

We changed median (\pm standard deviation) to mean (\pm standard deviation).

p. 23381-23382. Shouldn't observations of CO provide some hint as to whether the summer minimum is due to transport or photochemistry.

We think that more than one factor contributes to the seasonal trends of VOCs at TF. The focus of this section was to discuss the most likely factors which contribute to the seasonal variation of alkyl nitrates. We reorganized the last paragraph in Section 3.1 to read as follows:

“Two possible explanations for the seasonal variation of alkyl nitrates at TF are (1) their different tropospheric lifetimes throughout the year and (2) different regional scale transport patterns. The alkyl nitrate lifetimes are shorter in summer than in winter because of higher OH concentrations and faster photolysis rates which may explain the lower C₃-C₅ alkyl nitrate mixing ratios (winter lifetimes ~1-3 weeks, summer lifetimes \leq ~1 week) (Atkinson, 1990; Atkinson et al., 2006; Clemitshaw et al., 1997; Talukdar et al., 1997). In addition, the longer lifetimes of MeONO₂ and EtONO₂ likely contribute to their more homogeneous distribution throughout the year (winter lifetimes ~1 month, summer lifetimes ~1 week) (Figs. 2 and 3; Tables 1 and 2). Additionally, previous research has documented that the chemical composition of air masses transported to New England strongly depends on both the season and source region. For example, north-northwesterly winds typically transport clean, Canadian air masses to New England that contain low O₃, CO, NO_y, and hydrocarbon mixing ratios and that are representative of background conditions (Munger et al., 1996; Moody et al., 1998; Shipham et al., 1998). This transport pattern is more frequent during the winter. In contrast, air masses containing enhanced levels of anthropogenic emissions are primarily observed during transport from the south and west. This air mass transport pathway occurs most frequently in summer (Moody et al., 1998; Fischer et al., 2004; Mao and Talbot, 2004b). Consequently, the seasonal variation in the dominant source region(s) of alkyl nitrates and their precursors may contribute to the seasonal trends in ambient alkyl nitrate mixing ratios observed at TF.”

p. 23384 line 17. Please provide an explanation of why the MeONO₂ concentration was constant for a few hours.

The original phrasing of this sentence was not entirely correct. For example, on 7-8 June 2002, MeONO₂ did decrease throughout the entire night as would be expected if deposition was

occurring under the NBL. On 13-14 June 2002, both MeONO₂ and O₃ decreased for several hours overnight but then remained constant for a couple hours. We rephrased the text in this paragraph to state that MeONO₂ tracked O₃ on both nights.

p. 23385 line 9. Given the slow vertical mixing conditions of the nocturnal boundary layer, wouldn't you expect a strong gradient in MeONO₂ concentration? How would this impact your analysis?

In Section 3.2.1, we explicitly noted that our results will scale directly with the value chosen for the boundary layer height and we indicated that we used a constant boundary layer height in our calculations. We have reworded the text to make our assumption of a constant boundary layer height more clear. We do not have any vertical profile information on the boundary layer height and structure for summers 2002 and 2004 at TF. Accordingly, we have to assume that the surface to the nocturnal inversion is uniformly mixed. Previous studies have used this same methodology to calculate emission and removal rates of various trace gases at TF (e.g., Talbot et al., 2005; Sive et al., 2007; Mao et al., 2008; White et al., 2008; Zhou et al., 2005). Several studies conducted in various continental environments have reported the nocturnal inversion to be approximately 75-125 m above ground level (e.g., Galbally, 1968; Garland and Derwent, 1979; Shepson et al., 1992; Hastie et al., 1993; Neu et al., 1994; Güsten et al., 1998). Based on these results, we chose a constant nocturnal inversion height of 125 m as a reasonable estimate for the TF site. We agree it is possible that a vertical gradient in MeONO₂ will develop as a result of nighttime surface depletion. Based on our assumption that entrainment and horizontal advection are negligible on nights with strong NBLs and the near surface (15 m) height of the sample inlet, we do not expect the development of a vertical gradient over the several hours when the NBL is present to have a significant impact on our results. We plan on doing vertical profiling with tethered balloon measurements in the future to specifically address this question and to examine the influence of the nocturnal inversion on the budgets of various trace gases at TF.

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