A comparison of isoprene nitrate concentrations at two forest-impacted sites

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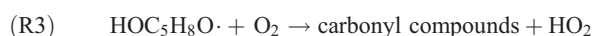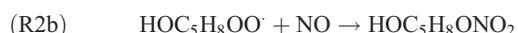
[1] We report measurements of isoprene nitrates as part of the Southern Oxidants Study during the summer of 1999 at a rural/forest site in Tennessee. Average midday concentrations of the isoprene nitrates were ∼115 ppt. This is ∼10 times greater than the previously reported concentrations during the Program for Research on Oxidants: Photochemistry, Emissions, and Transport (PROPHET) study in 1998 at Pellston, Michigan, representing as much as 5% of NO_y. Here we investigate the possible factors for the large difference in concentrations. To investigate the role of the NO_x concentration on the isoprene nitrate production chemistry at the two sites, [OH] was calculated using a simple steady state model. The results of this calculation help explain the difference in magnitude of the isoprene nitrate concentrations between the two field sites in terms of the [NO_x]-dependent behavior of the OH-initiated oxidation of isoprene and the subsequent isoprene peroxy radical reactions with NO_x. However, it is also clear that the large apparent differences in the photochemical ages of the air masses sampled at the two sites significantly impacted the observed concentrations.   *INDEX TERMS:* 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; *KEYWORDS:* isoprene nitrates, nitrogen oxides, isoprene

1. Introduction

[2] In forested areas, isoprene (2-methyl-1,3-butadiene) can be the dominant reactive hydrocarbon in the lower troposphere. It is well known that isoprene chemistry can play an important role in the production of ozone in the boundary layer [*Trainer et al.*, 1987; *Chameides et al.*, 1988, 1992; *Biesenthal et al.*, 1997]. The following reactions show the overall features of isoprene oxidation by OH in the presence of NO_x:

(R1) $C_5H_8 + \cdot OH (+O_2) \rightarrow HOC_5H_8OO\cdot$

(R2a) $HOC_5H_8OO\cdot + NO \rightarrow HOC_5H_8O\cdot + NO_2$

(R2b) $HOC_5H_8OO\cdot + NO \rightarrow HOC_5H_8ONO_2$

(R3) $HOC_5H_8O\cdot + O_2 \rightarrow carbonyl\ compounds + HO_2$

In the presence of NO_x, OH-initiated oxidation can lead to the production of organic nitrates, i.e., isoprene nitrates [*Tuazon and Atkinson*, 1990; *Werner et al.*, 1999], as shown in reaction (R2b). The production of isoprene nitrates removes radicals and NO_x, and thus decreases the radical chain length in the process of ozone production [*Carter and Atkinson*, 1996]. When NO_2 is produced from peroxy radical oxidation of NO (as in reaction (R2a)), ozone is formed in the following reactions:

(R4) $NO_2 + h\nu \rightarrow NO + O(^3P)$

(R5) $O(^3P) + O_2 \rightarrow O_3$

Since organic nitrates remove NO_x, they also limit the amount of ozone that can be produced in isoprene-impacted environments [*Carter and Atkinson*, 1996; *Horowitz et al.*, 1998; *Chen et al.*, 1998]. The isoprene nitrates are reactive, multifunctional compounds that undergo rapid oxidation themselves, and thus the ultimate form of nitrogen removal from the atmosphere is a complex issue, as discussed by *Shepson et al.* [1996], *Grossenbacher et al.* [2001], and

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P. K. Giacopelli et al. (A comparison of the measured and simulated isoprene nitrate distributions above a forest canopy, submitted to *Journal of Geophysical Research*, 2003) (hereinafter referred to as Giacopelli et al., submitted manuscript, 2003).

[3] To observe the role of NO_x in the oxidation of isoprene, and the role of isoprene in impacting the fate of NO_x, isoprene nitrate concentrations were measured during two field studies: PROPHET 1998 [*Carroll et al.*, 2001] and the Southern Oxidants Study (SOS) 1999. To more accurately understand and simulate tropospheric ozone, especially in forested areas, it is critical to understand the chemistry of the isoprene nitrates. The results of the PROPHET study are described by *Grossenbacher et al.* [2001]. In that study, the mean daytime isoprene nitrate concentrations were ~10 ppt. Here we report isoprene nitrate concentration measurements at the Dickson, Tennessee, site during SOS99. The observed isoprene nitrate concentrations at the SOS99 Dickson site were significantly (~5−10 times) greater than those seen during PROPHET98. In this paper we discuss the factors that may influence the relative isoprene nitrate concentrations at the PROPHET and Dickson sites. Specifically, the differences can be caused by a combination of the NO_x dependence of OH and isoprene peroxy radical chemistry, and the impact of the site characteristics on the average photochemical age of the sampled air.

2. Experiment

[4] Measurements of gas-phase isoprene nitrate concentrations were made in the summer of 1998 at the Program for Research on Oxidants: Photochemistry, Emissions, and Transport (PROPHET) laboratory in Pellston, Michigan, and during the summer of 1999 at the Dickson site in rural Tennessee as part of the 1999 Southern Oxidants Study (SOS). A map showing the locations of the field studies is shown in Figure 1. The PROPHET site is a mixed deciduous/coniferous forest site in northern Lower Michigan [*Carroll et al.*, 2001], while the field site at Dickson is in rural central Tennessee. The isoprene nitrate measurements as part of the PROPHET study are described in detail by *Grossenbacher et al.* [2001]. The Dickson site is a rural site 50 km WNW of Nashville, Tennessee (36.2°N, 87.4°W). This site was situated in an open pasture in a predominantly agricultural area surrounded by significant areas of patchy forest. The town of Dickson, population ~12,000, lies ~15 km to the south. Large coal-fired power plants were located in Cumberland (2600 MW capacity, ~25 km to the WNW) and Johnsonville (1485 MW capacity, ~50 km to the SW). The proximity of the Dickson site to these power plants and the predominance of westerly airflow led to higher and more variable NO_x levels, on average, than those observed at the PROPHET site.

[5] The measurements at Dickson were conducted using an instrument and method only slightly modified from that used at PROPHET as described by *Grossenbacher et al.* [2001]. Sampling was conducted from a 12 m Pyrex glass manifold. A 4 m PFA-Teflon inlet line was maintained at 100°C to minimize adsorptive losses of the analytes during sample transport from the manifold to the instrument. An additional two-position solenoid valve was placed just
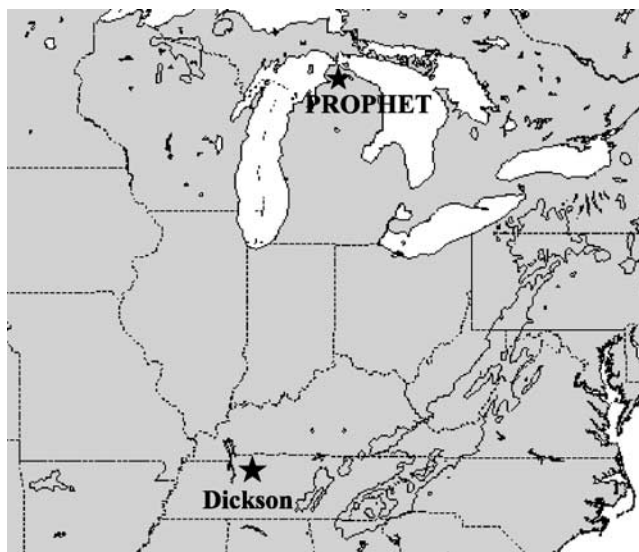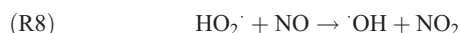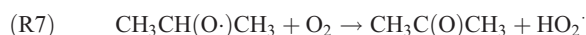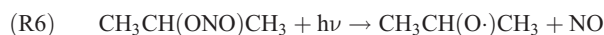

Figure 1. Map of field study locations.

upstream of the air pump in the sampling train to allow for rapid flushing of the inlet line during the instrument's analysis step. The instrument was automated using National Instruments LabVIEW 5.0 for computer control and data acquisition. This enabled automated, round-the-clock, hourly sampling during the SOS field study, which was an improvement over the previous measurements made during the PROPHET study.

[6] The instrument was calibrated through the heated inlet using gas-phase standards of isobutyl nitrate as described by *Grossenbacher et al.* [2001]. In addition to these standards, gas-phase standards of isoprene nitrates were employed. These standards were prepared by irradiation of mixtures of isoprene (1.3 ppm), NO (13.2 ppm), and isopropyl nitrite (1 ppm $CH_3CH(ONO)CH_3$) in zero air in a 200 L Teflon bag for under 1 min. Irradiations were performed so that ~20−25% of the isoprene was consumed, thus reducing the likelihood of generation of secondary products and/or exhaustion of NO. The reaction mechanism for production of isoprene nitrates via this mechanism is shown below, followed by reactions (R1) and (R2b).

(R6) $CH_3CH(ONO)CH_3 + h\nu \rightarrow CH_3CH(O\cdot)CH_3 + NO$

(R7) $CH_3CH(O\cdot)CH_3 + O_2 \rightarrow CH_3C(O)CH_3 + HO_2^{\cdot}$

(R8) $HO_2^{\cdot} + NO \rightarrow \, ^{\cdot}OH + NO_2$

The initial [NO]/[isoprene] ratio was ~10 to ensure that the isoprene peroxy radicals reacted exclusively with NO. The concentration of isoprene nitrates was calculated on the basis of the amount of isoprene consumed during the irradiation and the isoprene nitrate production yield of 4.4 ± 0.8% [*Chen et al.*, 1998]. This is equivalent to the method used for generation of the PROPHET data set, so the two data sets are directly comparable. The isoprene concentrations in the bag were measured before and after irradiation
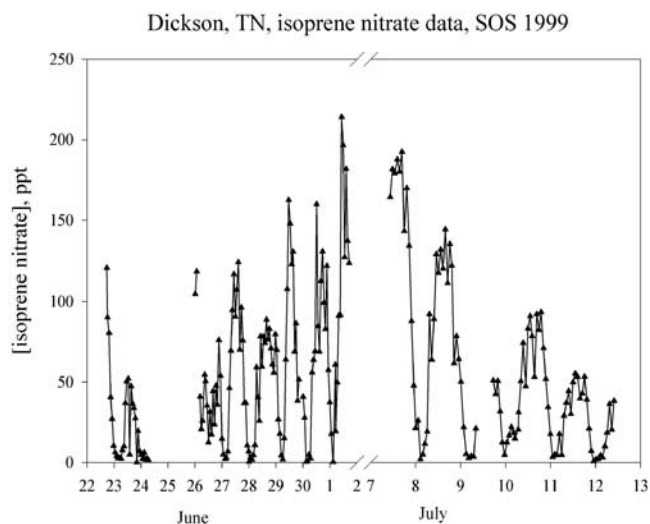
Figure 2. Isoprene nitrate concentration time series data for SOS99 at Dickson, Tennessee.

using the Purdue University GC-MS autosampler, which is described by *Barket et al.* [2004].

[7] As a result of the propagation of uncertainties in the method, including calibration and line losses, the estimated uncertainty in the isoprene nitrate determinations during the PROPHET study is +(50% + 0.5 ppt)/−(35% + 0.5 ppt) for concentrations above the detection limit of 0.5 ppt. This asymmetric uncertainty estimate reflects the contribution of potential sampling losses, which would lead to significantly lower concentrations. For the SOS field study the instrument was calibrated through the heated inlet with the surrogate compound isobutyl nitrate and the isoprene nitrates themselves. At Dickson, the overall measurement uncertainty was estimated at ±(35% + 1.2 ppt) for concentrations above the detection limit of 1.2 ppt.

3. Results

[8] As we do not have individual isoprene nitrate isomer standards for the eight different isomers [*Chen et al.*, 1998], but use an instrument that responds identically to each of them, we discuss here the concentration of the sum of the isoprene nitrate isomers (i.e., [INs]). As discussed by Giacopelli et al. (submitted manuscript, 2003), we believe that the dominant isoprene nitrates are the 1,2- and the 4,3-hydroxy nitrates (in that order of importance; i.e., $HOCH_2C(CH_3)(ONO_2)CH=CH_2$, and $CH_2=C(CH_3)CH(ONO_2)CH_2OH$), as the 1,4- and 4,1-hydroxy nitrates are expected to react rapidly with O_3. Figure 2 shows the total isoprene nitrate concentrations observed between 22 June and 13 July, during SOS99. The concentrations ranged between nighttime minima of 5–10 ppt and afternoon maxima of ∼100–150 ppt. At the afternoon maximum, the isoprene nitrates represent typically ∼5% of NO_y. This is consistent with model results from *Liang et al.* [1998]; however, ambient concentrations can be lower than model predictions unless ozonolysis is considered (Giacopelli et al., submitted manuscript, 2003). On average, the Dickson isoprene nitrate concentrations were ∼5–10 times greater than those observed during

PROPHET98 [*Grossenbacher et al.*, 2001], even though isoprene concentrations at the two sites were quite similar. In Figure 3 we present a comparison of the diel average total isoprene nitrate concentrations measured at both field sites. The error bars represent one standard deviation about the hourly means, i.e., the daily variability within the hourly bins, not the measurement uncertainty. The isoprene nitrate concentrations follow a diel pattern consistent with their daytime photochemical production and losses at night as the isoprene oxidation rate becomes smaller. However, the difference in the magnitudes of the isoprene nitrate concentrations at the two sites is striking. The isoprene levels at the two field sites are comparable, with average midday concentrations of ∼2 ppb [*Barket et al.*, 2004; *Hurst et al.*, 2001], but there is, on average, at least twice as much NO_x observed at the Dickson site. Data from the PROPHET98 study are presented by *Thornberry et al.* [2001]. It is known that [OH], and thus VOC oxidation rates, are nonlinearly dependent on [NO_x] [*Lin et al.*, 1988]. To rationalize the data, we first examine the isoprene nitrate concentrations as a function of NO_x through the use of a steady state calculation of [OH], which is discussed in detail by *Barket et al.* [2004]. It is also the case that the sample manifold inlets are quite different in the two cases; while at Dickson the inlet is in a clearing at a height of ∼10 m, at PROPHET it is ∼12 m above the forest canopy. Thus we also consider the impact of this on the effective isoprene photochemical age.

[9] The instantaneous rate of isoprene nitrate production depends on two factors: one, the rate of isoprene peroxy radical production (k_1[OH][isoprene]), and two, the fraction of isoprene peroxy radicals that react with NO, rather than with HO_2 or RO_2, as shown in reactions (R9) and (R10).

(R9) $HOC_5H_8O_2\cdot + HO_2 \rightarrow HOC_5H_8OOH + O_2$

(R10) $HOC_5H_8O_2\cdot + RO_2 \rightarrow HOC_5H_8O\cdot + RO + O_2$

We note that for both sites, the dominant RO_2 radicals are expected to be $HOC_5H_8O_2\cdot$ [*Sumner et al.*, 2001; *Hurst et al.*, 2003]. It is well known that OH concentrations are a
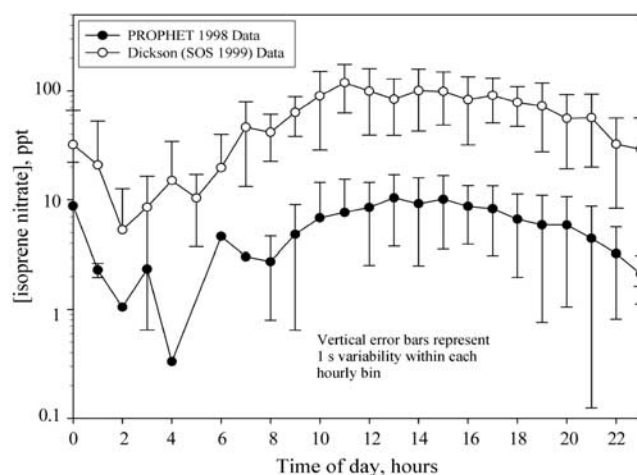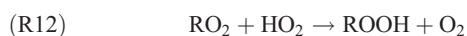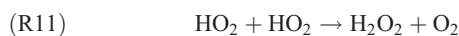

Figure 3. Calculated diel average isoprene nitrate concentrations at the PROPHET and Dickson field sites.
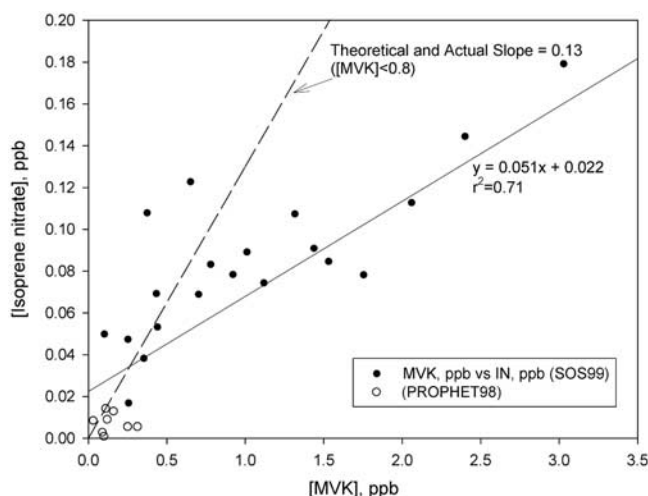
Figure 4. Observed [IN] versus observed [MVK] during PROPHET98 and SOS99.

strong function of $[NO_x]$, because of the competition between reaction (R8) above, and those that terminate HO_x, e.g., reactions (R11)–(R13) below. Thus as described by *Lin et al.* [1988], [OH]

$$(R11) \qquad HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

$$(R12) \qquad RO_2 + HO_2 \rightarrow ROOH + O_2$$

$$(R13) \qquad OH + NO_2 \rightarrow HNO_3$$

tends to maximize at $\sim$1–3 ppb $[NO_x]$, when these reactions are less effective at competing with HO_x recycling via reactions such as reaction (R1) (and OH reaction with CO, HCHO, and other VOCs) and reaction (R8). We thus would predict an optimum condition for isoprene nitrate production, where the isoprene nitrate production rate (P[INs]) is as shown in equation (1), where α is the isoprene

$$P[INs] = k_1 \cdot [OH][isoprene] \cdot \alpha \cdot \gamma \qquad (1)$$

nitrate production yield when all isoprene peroxy radicals react with NO (i.e., $k_{2b}/(k_{2a} + k_{2b}) = 0.044$; *Chen et al.* [1998]), and γ is the fraction of isoprene peroxy radicals that react with NO. Although there is considerable uncertainty with respect to α [*Tuazon and Atkinson*, 1990; *Chen et al.*, 1998; *O'Brien et al.*, 1998; *Sprengnether et al.*, 2002], it is a constant. The key atmospheric variables in equation (1) are [isoprene], [OH], and γ.

[10] We note that for typical conditions in eastern North America, P[INs] is a significant sink for NO_x, in comparison to HNO_3 production. For example, for the average daytime condition at Dickson of [isoprene] = 1.7 ppb, NO_2 = 1.5 ppb, and $\gamma = 0.9$, the rate of HNO_3 production via reaction (R13) is $0.338 \ s^{-1} \cdot [OH]$, while the rate of isoprene nitrate production (from equation (1)) is $0.206 \ s^{-1} \cdot [OH]$.

[11] To make use of equation (1) in examining the NO_x dependence of isoprene nitrate production, we must know [OH], as well as an estimate for γ, for all isoprene nitrate

measurement conditions. OH radical concentrations were measured during PROPHET98 [*Tan et al.*, 2001]. However, there are no corresponding data for the Dickson site. Thus it was necessary for us to independently estimate [OH] for both sites, as discussed and reported by *Barket et al.* [2004].

4. Discussion

[12] To assess the overall quality of the isoprene nitrate data set we compare it to the parallel more dominant oxidation product of isoprene, methyl vinyl ketone (MVK). Figure 4 shows a plot of observed [INs] versus [MVK], for daytime data from both the PROPHET98 data, and the SOS99 Dickson site. The plot shows data for which INs and MVK were determined within 15 min of each other, and only for time of day between 1000 and 1600. The plot is reasonably linear, although the slope of the regression is not as steep as expected. The expected slope should relate to the relative formation rates, i.e., as shown in equation (2),

$$P[INs]/P[MVK] = \alpha_{IN}/\{\alpha_{MVK} + ((\beta/\gamma) - \beta))\} \qquad (2)$$

where α_{IN} and α_{MVK} are the formation yields of isoprene nitrates and MVK in the presence of NO_x (0.044 [*Chen et al.*, 1998] and 0.32 [*Tuazon and Atkinson*, 1990], respectively), β is the formation yield of MVK in the absence of NO_x, 0.17 [*Miyoshi et al.*, 1994], and γ is the fraction of time that RO_2 radicals derived from isoprene react with NO versus HO_2 and RO_2. Using an average value for γ of 0.94 at SOS99 [*Barket et al.*, 2004], the slope should be 0.13. The observed slope may be less than this calculated value because of the contribution of MVK transported to the measurement site in addition to the MVK that is produced locally. We assume, on the basis of relative atmospheric lifetimes, that the isoprene nitrates are produced locally. The slope may also show curvature, because, as discussed by Giacopelli et al. (submitted manuscript, 2003), the isoprene nitrates are considerably shorter lived than is MVK. For large extents of reaction, there is considerable isoprene nitrate consumption, and so the ratio [INs]/[MVK] will decrease as the air mass becomes more processed. For example, for the 1,4- and 4,1-nitrates, the atmospheric lifetime resulting from OH and O_3 reaction is calculated to be $\sim$29 min, using [OH] = 2 × 10^6 molecules/cm^3, and $[O_3]$ = 40 ppb (photolysis is an insignificant removal process for these olefinic nitrates). In contrast, the MVK lifetime is $\sim$8 times longer. As shown in Figure 4, the observed slope for [MVK] $\leq$ 0.8 ppb is actually equal to the theoretical slope of 0.13 for γ = 0.94, providing confidence in the IN measurements. Furthermore, the relative PROPHET and Dickson MVK data provide confidence in the fact that there is a significant difference in the extent of isoprene oxidation at the two sites, as discussed in detail below. We discuss further the atmospheric removal processes of the isoprene nitrates below.

[13] A complete analysis of the $[NO_x]$ dependence of isoprene nitrate formation involves using the calculated [OH] and γ to compare the expected behavior of the isoprene nitrate chemistry with measurement data. In Figure 5 we present the calculated isoprene nitrate production rate (equation (1)) versus $[NO_x]$ for the Dickson and PROPHET data. The isoprene nitrate production rate data
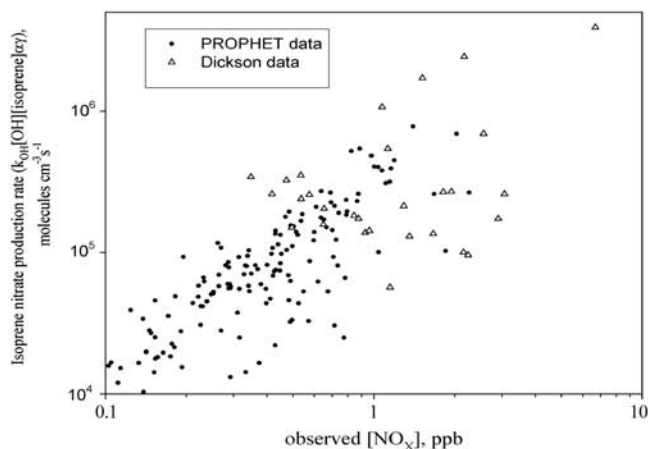
Figure 5. [NO_x] dependence of P[INs].

were generated with equation (1) using calculated values for [OH] and γ [*Barket et al.*, 2004], $\alpha = 0.044$ (the organic nitrate yield from isoprene oxidation [*Chen et al.*, 1998]), the rate constant for the reaction of OH with isoprene, $k_{OH} = 1.1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} [*Stevens et al.*, 1999] and measured [isoprene], for all times when isoprene nitrates were measured, between 1000 and 1600 at Dickson and PROPHET. Although the data set was obtained from the Dickson and PROPHET sites where [NO_x] was almost always below 10 ppb, the plot reflects the shape of [OH] versus [NO_x] presented by *Barket et al.* [2004]. There is a significant overlap between the data points from each site, however, the Dickson data extends to higher values of [NO_x] (as much as 7 ppb), with corresponding maximum calculated isoprene nitrate production rates that are ~5 times greater than the maximum for the PROPHET data.

[14] From equation (1) we can derive equation (3), below. Since the magnitude of both [OH]

$$P[INs]/[isoprene] = k_1 \cdot \alpha \cdot [OH] \cdot \gamma \quad (3)$$

and γ are determined by [NO_x], we would expect to see a [NO_x] dependence for observed [INs]/[isoprene], assuming
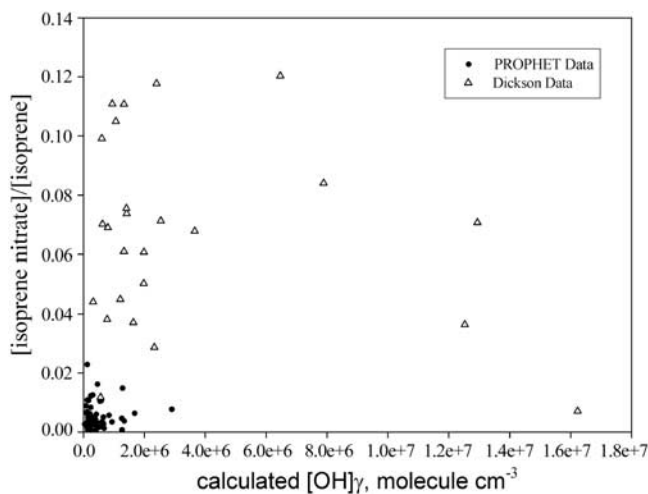
that [INs]/[isoprene] is directly proportional to P[INs]/[isoprene]. Figure 6 shows a plot of observed [INs]/[isoprene] versus calculated [OH]γ, for the 1000−1600 time frame. Although there is a weak correlation between [INs]/[isoprene] and [OH]γ, there is considerable scatter. This may reflect in part the uncertainty in the calculated [OH], but more likely reflects the fact that the observed concentrations are a function of both reactive losses, and the effective extent of isoprene oxidation, as discussed below. When observed [isoprene nitrate]/[isoprene] is plotted versus [NO_x] in Figure 7, the relationship better mimics that for [OH] versus [NO_x]; however, unfortunately there is not a wide enough range in NO_x for either site alone to unambiguously isolate the [NO_x] variable.

[15] Despite the limited data sets used in producing Figure 7, it appears that the [INs]/[isoprene] values increase to a maximum at ~2 ppb [NO_x], similar to that for [OH] versus [NO_x]. However, the relationship is quite weak, and it appears from the plot in Figure 7 that the Dickson and PROPHET data sets have quite distinct character. An alternative explanation for this fact is the nature of the sampling sites. While the tower at Dickson is in a clearing, with surrounding patchy forest, the PROPHET tower at University of Michigan Biological Station is 12 m above a reasonably dense deciduous forest canopy. Thus as discussed by *Apel et al.* [2002], the effective isoprene reaction time t is on the order of 360 s. Similar to the analysis presented by *Apel et al.* [2002], the ratio [INs]/[isoprene] can be expressed as shown in equation (4), where k_1 and k_{14} refer to the rate

$$[INs]/[isoprene] = 0.044 \cdot k_1 \left(1 - e^{(k1-k14)[OH]t}\right)/(k_{14} - k_1) \quad (4)$$

constants for reactions (R1) and (R14), 0.044 is the isoprene nitrate production yield at high-NO_x

(R14) $HOC_5H_8ONO_2 + OH \rightarrow$ products

conditions, and t is the reaction time. The value 0.044 holds for conditions when all peroxy radicals react with NO, which, as discussed by *Barket et al.* [2004], is a good
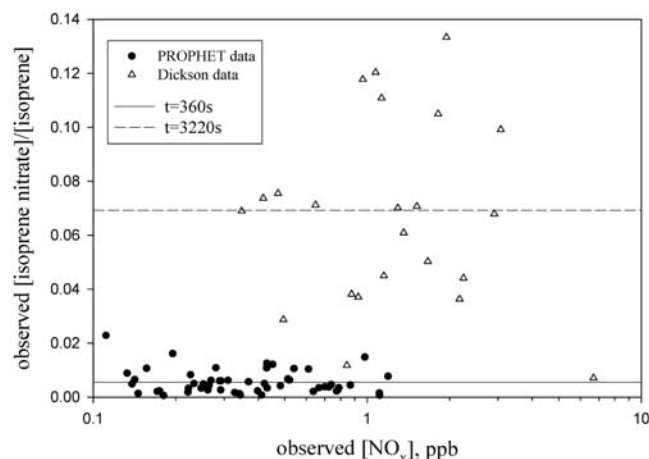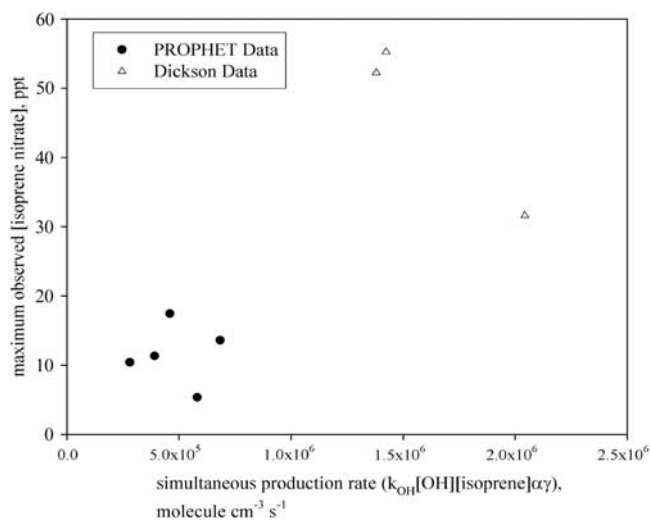

Figure 6. Observed [isoprene nitrate]/[isoprene] versus calculated [OH] · γ. Read 2.0e + 6 as 2.0×10^6.

Figure 7. [NO_x] dependence of [isoprene nitrate]/[isoprene].

Figure 8. Observed daily maximum [isoprene nitrate] versus simultaneous calculated production rate (k_1[OH][isoprene]$\gamma\alpha$).

approximation. Reaction (R14) is relatively rapid, since isoprene nitrates are olefinic. If we use the average daytime [OH] value for the PROPHET site used by *Apel et al.* [2002] of 3.35×10^6 molecules/cm^3, the k_{14} value calculated for the predicted dominant nitrate (1-hydroxy-2-nitrooxy-2-methyl-3-butene) of 3.4×10^{-11} cm^3 molecule^{-1} s^{-1} (Giacopelli et al., submitted manuscript, 2003), and the value t = 360 s, as found from the methyl vinyl ketone PROPHET data of *Apel et al.* [2002], we obtain a calculated average [INs]/[isoprene] = 0.0055, for the PROPHET site. Although we expect that isoprene nitrates react fairly rapidly with O$_3$ (Giacopelli et al., submitted manuscript, 2003), this value is probably a good approximation, since the reaction time is so short, and k_1 is large. In Figure 7, we show the value 0.0055 as a line, for the PROPHET data. The average observed daytime ratio for the PROPHET data set shown in Figure 7 is 0.0040. The isoprene nitrate data are thus remarkably consistent with the effective isoprene reaction time found from the MVK measurements of *Apel et al.* [2002]. Again the fact that both INs and MVK are relatively low at PROPHET is reflected in the [INs] versus [MVK] regression for the two sites shown in Figure 4. The average measured [INs]/[isoprene] ratio for the Dickson site is 0.0692, or 17 times larger than at PROPHET; this value is shown as the dashed line in Figure 7. This corresponds to an effective reaction time of 54 min, quite similar to the value of 40 min derived by *Stroud et al.* [2001], for the urban/suburban clearing site in Nashville at the time of the Dickson study. It thus seems clear that the PROPHET and Dickson site data express distinctly different degrees of photochemical processing.

[16] While much of the difference in the two data sets appears to be related to the extent of processing, there appears from Figures 5–7 to be a NO$_x$ dependence to that processing, based largely on the NO$_x$ dependence of [OH], as discussed by *Barket et al.* [2004]. To examine that further, we present in Figure 8 a plot of the daily maximum observed [isoprene nitrate] versus the simultaneous isoprene nitrate production rate calculated using equation (1). We

calculated the corresponding P(INs) for each daily maximum [IN] for which OH could be calculated within a 40 min window. However, because of the paucity of time-matched data for the daily maximum [INs] and the data from which [OH] is calculated, there are only 8 points in Figure 8. However, from Figure 8 it is appears that at Dickson, where the calculated isoprene nitrate production rates (at the daily maximum [IN]) were consistently greater than at PROPHET, there were correspondingly higher daily maximum isoprene nitrate concentrations. However, the actual concentrations depend on the removal rates, which are difficult to calculate, since some of the removal rate depends on dry deposition and some is "lost" via ventilation. For example, for a 1000 m mixing height, a dry deposition velocity of 2 cm/s, and an OH rate constant of 3.4×10^{-11} cm^3 molecule^{-1} s^{-1} for the INs, the first-order loss frequencies for dry deposition and OH radical reaction would be (for [OH] = 2×10^6 molecules/cm^3) 2×10^{-5} s^{-1} and 6.8×10^{-5} s^{-1}, respectively. Additionally, as described by Giacopelli et al. (submitted manuscript, 2003), isoprene nitrate removal via reaction with ozone is also very important. However, the rates of removal at the two sites should be comparable since the ozone levels are similar, on average. It thus appears that the difference in isoprene nitrate concentrations at the two sites is impacted by both the difference in NO$_x$ levels, and thus [OH], between the two sites, as well as the effective reaction time. The SOS99 data make it clear, however, that for well processed isoprene-impacted boundary layer conditions, isoprene nitrates can be a significant component of reactive nitrogen.

5. Conclusions

[17] The isoprene nitrate concentrations reported for Dickson are much more in line with what has been predicted for summertime regional-scale continental boundary layer environments [*Liang et al.*, 1998]. The relationship between INs and MVK provides us with confidence in the two IN data sets. While there appears to be some impact of [NO$_x$] on the INs, the ratio [INs]/[isoprene] is likely more impacted for these data sets by the effective reaction time. It thus would be useful to measure [INs] at the PROPHET site as a function of altitude, over the lowest 200 m, corresponding to the altitude over which isoprene decays by approximately x10. Interestingly, [NO$_x$] plays a key role in determining the rates of conversion of atmospheric NO$_x$ into isoprene nitrates, through control of the levels of OH, and to a much smaller extent, the chemical fate of the peroxy radicals derived from isoprene. Thus the forest is much more efficient in sequestering NO$_x$ in the form of isoprene nitrates when [NO$_x$] is relatively large. It is important that isoprene nitrates be quantified as part of future atmospheric field studies, along with other biogenic nitrates, to assess biogenic organic nitrates relative role in sequestering atmospheric NO$_x$, and the extent to which the biogenic organic nitrates represent a significant fraction of the "ANs" detected by *Day et al.* [2002]. This is particularly important in light of suggestions that atmospheric deposition of nitrogen may be an important source of nitrogen to nitrogen-limited forests [*Sievering et al.*, 2000; *Ollinger et al.*, 2002], and that gas-phase nitrogen compounds can undergo direct uptake by leaves, thus potentially

impacting the carbon cycle [*Sparks et al.*, 2001, 2003; *Lockwood et al.*, 2003].

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