Investigation of the nighttime decay of isoprene

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Abstract. A rapid nighttime decay of isoprene (2-methyl-1,3-butadiene) has been observed at several forest sites. Data from the Program for Research on Oxidants: PHotochemistry, Emissions, and Transport (PROPHET) have been carefully examined with respect to this phenomenon. Essentially every evening (at PROPHET), isoprene concentrations fall from several ppb to levels below 100 ppt, with an average lifetime of 2.7 hours. Since this decay rate exceeds that expected from established nighttime chemistry, other possible mechanisms are suggested and discussed. Reaction with ozone will not occur at a rate consistent with the observed decay. Calculations of nitrate radical concentrations reveal that this oxidant only becomes an important sink for isoprene after the majority of the isoprene decay has taken place. The isoprene flux data were not consistent with dry deposition playing a significant role in nighttime forest loss. On the basis of ambient measurements of OH radical concentrations at the PROPHET site, calculated isoprene decay rates were compared with observations. For some nights the observed decay can be fit strictly by OH consumption; however, the reported OH data overpredict the isoprene loss rate on most nights. We estimate that vertical mixing with isoprene-depleted air probably contributes to the fast isoprene decay observed; however, the measurements needed to support this suggestion have yet to be made.

1. Introduction

Biogenic hydrocarbons have received increasing attention in recent years due to recognition of their contribution to tropospheric ozone production [*Trainer et al*, 1987] Numerous studies have been conducted to investigate the importance and reactivity of the molecule isoprene (2-methyl-1,3-butadiene), a natural emission of many deciduous trees and the dominant reactive volatile organic compound (VOC) in most forest-impacted environments. Isoprene concentrations generally follow a pattern of steady increase throughout the morning, responding to radiation and temperature [*Fehsenfeld*, 1992],

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followed by a peak concentration near midafternoon, with slow decay throughout the afternoon as emission rates drop and isoprene is consumed by OH radicals. Established nighttime chemistry predicts a nighttime isoprene lifetime on the order of 20 hours, based on best estimates of radical and ozone concentrations. However, several investigators [*Yokouchi et al*, 1994; *Goldan et al*, 1995, *Starn et al*, 1998; *Banta et al*. 1997, *Biesenthal et al*, 1998] have observed surface isoprene decay at rates 5-10 times faster than this. Other possible nighttime chemical sinks include nitrate radicals and hydroxyl radicals.

In this paper we present representative isoprene data for a number of North American continental measurement sites and discuss the probable mechanisms that can explain the interesting behavior of isoprene at night. We will focus on data obtained from the Program for Research on Oxidants: Photochemistry, Emissions, and Transport (PROPHET) site in northern Michigan using data from summer 1997 and 1998 field studies.

2. Case Studies

To demonstrate the generality of this phenomenon, several examples are discussed here. Various forest sites were chosen on the basis of the observance of rapid isoprene decay at night and absence of significant anthropogenic influences. The individual measurement campaign locations are indicated in Figure 1. The sites include a boreal forest site in Saskatchewan, the PROPHET site in northern Michigan, the Harvard Forest site in central Massachusetts, Kejimkujik National Park in Nova Scotia, and the Scotia site in central Pennsylvania. With the exception of PROPHET (and to some extent, Kejimkujik), none of the sites was typically within short-range transport distance from a major body of water, given the prevailing wind directions. In Figure 2 we plot the diurnal average isoprene concentration data for

Figure 1. Map of field campaign locations. Included are inland sites, such as BOREAS, Scotia, and Harvard Forest, in addition to sites upwind of -lakes or oceans, such as Kejimkujik and PROPHET.

several forest sites, as well as the diurnal average of UV radiation from PROPHET 1998. All of the data were plotted on local solar time. The general pattern depicted in this figure is a qualitative measure of the isoprene decay that took place regularly at each location. Specifically, it is important to note that a substantial part of the decay occurs after sunset. when atmospheric chemistry models generally predict very low [OH].

Martin et al [1991] discuss the isoprene behavior at Scotia, a deciduous forested region in central Pennsylvania (40°48'N, 77°54'W). where a regular evening loss of isoprene was observed (see Figure 2) during the summer of 1988 Applying pseudo-first-order kinetics to the Scotia isoprene data, we calculate that a concentration of approximately 1×10^6 molecules cm^{-3} OH (or 15 ppt NO_3 radicals) would be required to produce this rate of isoprene decay. No measurements of either species were made during the Scotia study. Additionally, Pierce et al. [1998] compared modeled and measured diurnal profiles of isoprene, using RADM/BEIS2 and measurements from the Scotia site. The observed evening decay of isoprene was significantly steeper than could be predicted by the model, underscoring the need for a better understanding of nighttime chemistry and boundary layer dynamics.

Advection from a marine or lacustrine environment was ruled out by Martin et al [1991], as no major bodies of water are located within short-range transport distance from the site Further, the authors suggested depositional loss as the only viable explanation for the isoprene decay phenomenon.

Kejimkujik National Park, a remote wilderness area in Nova Scotia (44°36'N 65°12'W) was chosen for a portion of the

NARSTO-CE 1996 study during the summer of 1996 Nighttime isoprene lifetimes at this location ranged from 1 to 3 hours [Biesenthal et al, 1998]. Each night the isoprene loss rate exhibited first-order decay. Zero-dimensional computer simulations were conducted to investigate this occurrence. It was found by Biesenthal et al. [1998] that the observed decay could only be simulated by adding a 1 cm/s dry deposition velocity for isoprene, or a large concentration of OH ($>1 \times 10^6$ molecules cm^{-3}).

At the Harvard Forest site (42°32'N, 72°10'W), which is a mixed hardwood and conifer forest, a typical nighttime decay of isoprene took place with a lifetime of 1.5 hours, as shown in Figure 2. The data presented were collected during the 1995 summer campaign and are discussed by Goldstein et al. [1998] with respect to seasonal emission patterns The Boreal Ecosystem Atmosphere Study (BOREAS), which took place in August and September 1994, involved measurements in regions dominated by black spruce, jack pine, and aspen (53°12'N, 105°48'W). Young et al. (unpublished data, 1994) estimated that the isoprene decay rates at the jack pine and spruce sites were approximately 20 hours (based on the observed data and assuming pseudo-first-order kinetics), but at the aspen site, the decay was much faster, with a typical isoprene lifetime of approximately 4 hours. The corresponding OH radical concentration required to cause this observed decay is 8×10^5 molecules cm^{-3}.

The findings from these unrelated sites indicate that the causes of the isoprene decay phenomenon are probably general to surface-forested sites, whether polluted or unpolluted, near water
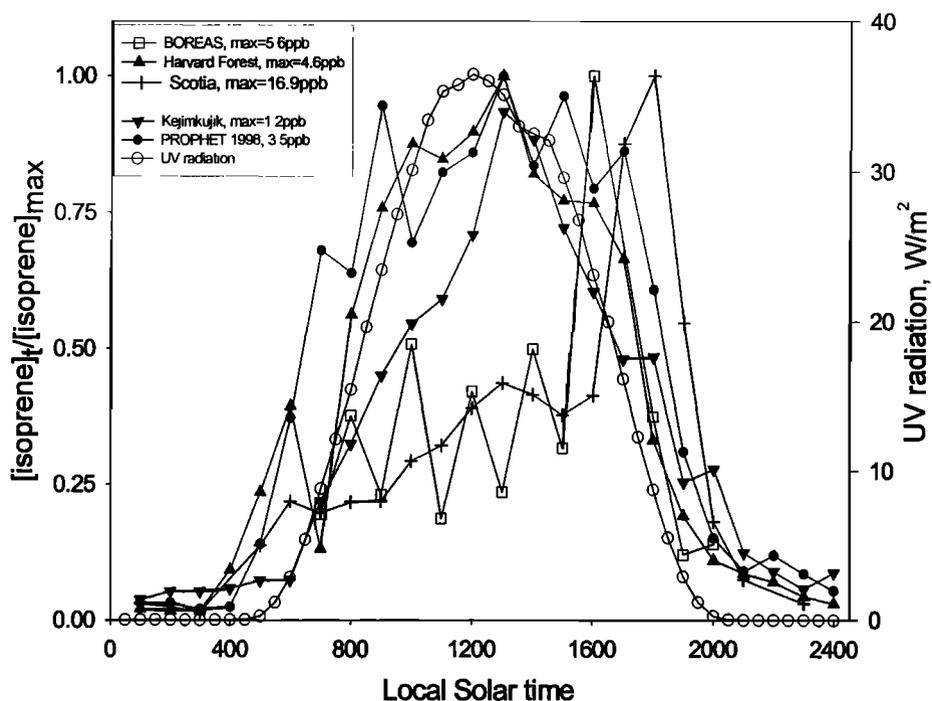
Figure 2. Diel average of isoprene concentration versus local solar time for various sites, scaled to their respective maximum concentrations, and UV radiation for the PROPHET site (1998).

or inland, but may show dependence on arboreal speciation. As shown in Figure 2, isoprene is typically observed to decay to levels < 100 ppt in the early morning hours. These observations suggest that our current understanding of nighttime chemistry may be incomplete.

2.1. PROPHET Intensives

To investigate the phenomenon thoroughly, we conducted measurements of isoprene and a suite of isoprene oxidation products and free radicals during the summers of 1997 and 1998 as part of the Program for Research on Oxidants: PHotochemistry, Emissions, and Transport (PROPHET). This program's goals include improving the quantitative understanding of atmospheric species that contribute to the production of tropospheric ozone and particulate matter and to investigate how atmospheric species interact with the forest ecosystem [*Carroll et al.*, this issue].

The University of Michigan Biological Station (UMBS) site, where the measurements were made, is a mixed deciduous/coniferous forest and has sparse local NO_x and anthropogenic VOC sources. The 1997 campaign included measurements of isoprene and its oxidation products and was followed by careful examination of the nighttime behavior of isoprene at this site. The 1998 campaign included measurements of isoprene and isoprene fluxes, O_3, CO, peroxyacetyl nitrate (PAN), peroxypropionyl nitrate (PPN), peroxymethacryloyl nitrate (MPAN), NO_x, NO_y, volatile organic compounds (VOCs), organic nitrates, peroxides, and aerosol physical properties and chemical composition, along with meteorological parameters [*Carroll et al.*, this issue; *Thornberry et al.*, this issue; *Pippin et al.*, this issue; *Barket et al.*, this issue; *Ostling et al.*, this issue; *Grossenbacher et al*, this issue; *Sumner et al.*,this issue; *Westberg et al.*, this issue; *Cooper et al.*, this issue]. In contrast to previous studies the PROPHET 1998 data set also features HO_x (OH and HO_2) measurements, which provide a unique

opportunity to test hypotheses regarding the operative isoprene chemical reaction mechanisms [*Tan et al*, this issue; *Faloona et. al*, this issue].

3. Experimental Methods

Sampling at the PROPHET site (45°30′N, 84°51′W) occurred from a 31 m walk-up tower, which sits in a mixed deciduous forest with an undergrowth of white pine (*Pinus strobus*) The top platform of the tower is at 31 m, approximately 10 m above the forest canopy. A glass sampling manifold is attached to the north side, reaching 35 m. Several investigators at PROPHET 1998 measured isoprene concentrations and fluxes, and a description of those systems, as well as a method intercomparison and discussion of data quality for isoprene is found in the work of *Barket et al.* [this issue]. For this paper we focus on tower isoprene data produced in 1997 and 1998 using the Tenax preconcentration GC/MS method described by *Starn et al.* [1998], as well as the isoprene flux data described by *Westberg et al.* [this issue].

Samples at Scotia were drawn through a stainless steel manifold into a cryogenic loop, then injected into a GC with flame ionization detection (FID), as described by *Martin et al* [1991]. An automated direct-sampling GC-FID system with cryogenic preconcentration was used to collect the isoprene data at Harvard Forest. Further detail is provided by *Goldstein et al.* [1998]. At Kejimkujik, samples were obtained via automated adsorbent trapping, followed by gas chromatography-mass-spectrometry (GC/MS) analysis, as described by *Biesenthal et al.* [1998]. Canister samples from BOREAS were shipped to Toronto and subjected to GC-FID with cryofocusing. During PROPHET 1998, aircraft samples were collected during several flights from a Piper Dakota 235. Air samples were drawn in through the pilot-side window, via a ¼ inch stainless steel tube, and compressed into stainless steel canisters using a metal
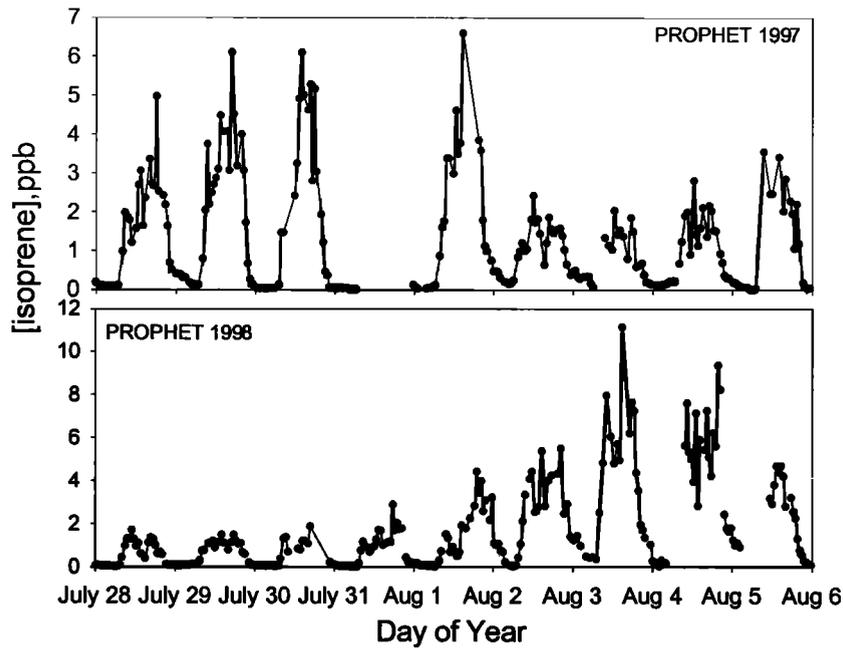
Figure 3. PROPHET 1997 and 1998 isoprene profiles.

bellows pump. The canister samples were then analyzed within 1-2 days in the PROPHET lab using the WSU GC/FID system [*Westberg et al*, this issue]. The OH/HO$_2$ data discussed here were obtained using a laser-induced fluorescence (LIF) system mounted at the tower inlet height, as discussed by *Faloona et al.* [this issue].

4. Results and Discussion

Figure 3 shows a set of isoprene concentration data obtained during PROPHET 1997 and PROPHET 1998. During both studies, isoprene peaked during midafternoon, with a sharp falloff

essentially every evening, occurring in the 1900-2200 (EDT) time frame. Decay rate constants were calculated for each evening (July 12 to August 16, 1998) from the average slope of ln(isoprene) versus time, typically starting after 1900 EDT; the resulting values correspond to isoprene lifetimes ranging from 2 to 5 hours, with an average of ~2.7 hours. Although for most cases the decay was essentially a single first-order exponential, for approximately 20% of the evenings analyzed, the data appear to exhibit two decay periods, the second occurring 2-3 hours later, as is illustrated in Figure 4 (discussed further below).

The change in concentration of any scalar may be found from the sum of the production and loss processes. For isoprene this
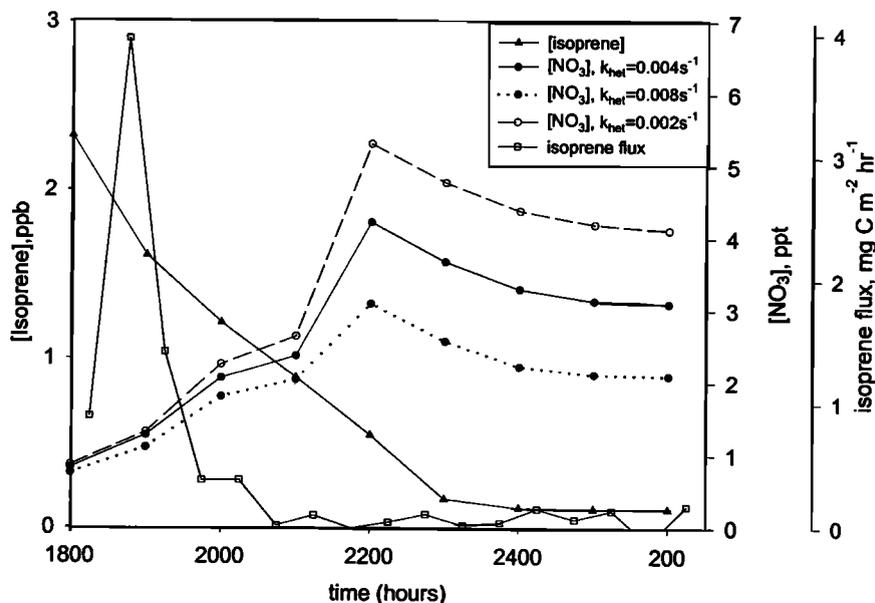
Figure 4. Isoprene concentration, isoprene flux, and simulated [NO$_3$] versus time for August 7, 1998. Nitrate radical concentrations were simulated from the average midnight values of O$_3$, NO, NO$_2$, HCHO, CH$_3$CHO, α-pinene, and β-pinene.

may be represented as indicated in equation (1):

$$\frac{-\delta[\text{isoprene}]}{\delta t} = (\Sigma k_i[\text{isoprene}] [\text{oxidant}_i])$$

$$+ \frac{U\delta[\text{isoprene}]}{\delta x} + \frac{V\delta[\text{isoprene}]}{\delta y}$$

$$- \frac{K_z\delta^2[\text{isoprene}]}{\delta z^2} + \frac{V_D[\text{isoprene}]}{h}$$

$$- \text{emission},\qquad\qquad (1)$$

where oxidant = O_3, NO_3, and OH, k_i is the reaction rate constant of isoprene with each oxidant, U and V are mean wind vectors, h is the height of the nighttime boundary layer (assumed to be 150 m, in part based on sodar data), and V_D is the isoprene deposition velocity. The horizontal flux terms and the mean vertical wind term are assumed to be negligible in the stable nighttime boundary layer To represent vertical flux divergence. a first-order (K theory) closure is used [Sorbjan, 1989] to give $K_z\delta^2(\text{isoprene})/\delta z^2$. where K_z is the eddy diffusion coefficient Using this expression as a guide, we may examine the different loss processes that contribute to the isoprene decay.

4.1. Ozone

The most abundant nighttime oxidant species is ozone. It reacts with isoprene by adding across a double bond, followed by decomposition of the ozonide, to form a Criegee biradical, with a room temperature rate constant of 1.22×10^{-17} cm^3 $molecule^{-1}$ s^{-1} [Greene and Atkinson, 1992] Although ozone concentrations are greater during the day, its relative contribution to oxidative chemistry is expected to be larger at night, when [OH] is lower than in the daytime However, even at daytime levels, its slow reaction rate coefficient makes its impact on isoprene decay rather modest at best. Specifically, isoprene will have a lifetime, $\tau = (k_{Ozone}\cdot[O_3])^{-1} = 15$ to 30 hours for an O_3 concentration of 30 to 60 ppb [Cooper et al., this issue; Thornberry et al., this issue]. At the PROPHET site at night the isoprene ozonolysis lifetime is generally near the high end of this range. Thus it is clear that O_3 reaction does not contribute significantly to the observed decay.

4.2. Nitrate Radical

Another potentially important oxidant is the nitrate radical, which is produced as follows:

$$NO_2 + O_3 \rightarrow NO_3 + O_2. \qquad (2)$$

The nitrate radical can reach significant concentrations only at night and in the absence of large NO emissions, because of the importance of reactions (3) and (4) below.

$$NO_3 + NO \rightarrow 2NO_2 \qquad (3)$$
$$NO_3 + h\upsilon \rightarrow NO_2 + O(^3P) \qquad (4a)$$
$$\rightarrow NO + O_2. \qquad (4b)$$

At rural sites such as PROPHET, NO concentrations become very low at night, because of reaction 5

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (5)$$

and limited local scale emissions. NO_3 reacts with isoprene as in reaction 6. Given $k_5 = 6.33 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}

$$NO_3 + C_5H_8 (+ O_2) \rightarrow O_2NOC_5H_8OO \qquad (6)$$
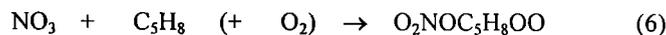
at 285K [Wayne et al., 1991], a typical evening temperature, if $[NO_3] = 7$ ppt, $\tau_{isoprene}$ would be 2.5 hours.

During the day the nitrate radical is not likely to be a major isoprene sink, since it is rapidly removed by photolysis ($\tau_{NO3} = 5$ s at noon). In the absence of radiation, NO_3 becomes more important as a sink for isoprene, as discussed by Wayne et al [1991] and Starn et al. [1998]. These investigators suggest that in NO_x-impacted forested areas, the dominant fate of the nitrate radical is reaction with isoprene to produce organic nitrates. To cause the isoprene decay observed at PROPHET, 5-10 ppt of NO_3 would be required. However, at the PROPHET site during the summer 1998 measurement period, NO_x concentrations were quite low [Thornberry et al., this issue]. With a mean daytime concentration of 750 ppt and ozone typically at 30-60 ppb, NO_3 concentrations are not expected to be large enough to cause the isoprene decay. To test this, a simple box model of NO_3 production and loss was constructed, as shown in Table 1. In Figure 4 we use hourly measurement data for the NO_3 sinks (isoprene, NO_x, HCHO, and terpenes (initial concentrations are given in Table 1)), and calculated photolysis rate coefficients [Tan et al., this issue] to obtain values of NO_3 for the evening

Table 1. Nighttime NO_3 Chemistry

Reaction	Rate Coefficient[a]
$O_3 + NO_2 \rightarrow NO_3 + O_2$	3.23×10^{-17}, (a)
$NO_3 + NO_2 \rightarrow N_2O_5$	1.20×10^{-12}, (b)
$N_2O_5 \rightarrow NO_2 + NO_3$	4.7×10^{-2}, (b)
$NO_3 \rightarrow NO_2 + O$	variable, (c)
$NO_3 \rightarrow NO + O_2$	variable, (c)
$NO_3 \rightarrow$ surface	4.01×10^{-3}, (c)
$N_2O_5 \rightarrow$ surface	9.26×10^{-4}, (c)
$NO_3 +$ isoprene $\rightarrow$ products	6.20×10^{-13}, (b)
$NO_3 +$ HCHO $\rightarrow$ $HNO_3 + NO_2$	5.80×10^{-16}, (b)
$NO_3 + CH_3CHO \rightarrow$ products	2.7×10^{-15}, (b)
$NO + NO_3 \rightarrow NO_2 + NO_2$	2.6×10^{-11}, (d)
$NO + O_3 \rightarrow NO_2 + O_2$	1.85×10^{-14}, (e)
$NO_3 + \alpha$-pinene $\rightarrow$ products	6.16×10^{-12}, (b)
$NO_3 + \beta$-pinene $\rightarrow$ products	2.30×10^{-12}, (b)

Initial Concentations, molecules/cm^3

O_3	1.38×10^{12}
Isoprene	5.99×10^{10}
CH_3CHO	2.32×10^{11}
NO	1.24×10^9
α-pinene	1.03×10^9
HCHO	5.9×10^{10}
NO_2	2.75×10^{10}
β-pinene	1.48×10^9

Average nighttime concentrations of all VOC's, NO_x, and O_3 were used.
a) zero order in molecules cm^{-3} sec^{-1}; first order in sec^{-1}; second order in cm^3 $molecule^{-1}$ sec^{-1}.
b) De More et al. [1994].
c) Wayne et al., [1991].
d) see text.
e) Finlayson-Pitts et al.
f) Wu et al. [1975].

period (1800-0200 EDT) on August 7, 1998. This particular evening was chosen in part because it represented the most complete data coverage for all species required for the model. Although NO₃ reaches steady state in less than 1 min, we are limited by the time resolution of the VOC measurement data to compute [NO₃] once per hour. As discussed by *Li et al.* [1993], an important removal mechanism for NO₃ is reactive uptake on atmospheric particulate matter. Rate constants for heterogeneous loss of NO₃, k_{het1} = 4.0 x 10⁻³ s⁻¹, and N₂O₅, k_{het2} = 9.3 x 10⁻⁴ s⁻¹ were calculated using the method of *Schwartz* [1986]. The values obtained are very similar to the estimated rate constants reported by *Li et al.* [1993] for Egbert, Ontario. The remaining rate constants were calculated for a temperature of 285K according to published Arrhenius expressions. For this evening at 2000 the NO₃ loss term via reaction with isoprene (k_5·[isoprene] = 0.027 s⁻¹) is 1.5 times larger than the heterogeneous loss rate for NO₃.

As shown in Figure 4, during the initial decay period, [NO₃] is approximately 1 ppt. As the evening progresses, a buildup of nitrate radicals is apparent, reaching a maximum of ~4.3 ppt at 2200 (EDT) and then decreasing to ~3 ppt by 0200. The increase is due in part to the decrease of J_{NO3} but is mostly attributed to the decrease in the isoprene reaction sink. The decrease after 2200 is simply a function of the product of [O₃]·[NO₂], which falls by approximately a factor of 1.5 during the 2300-0200 EDT time frame. Since the particle data do not allow us to explicitly calculate the heterogeneous loss rate constants as a function of time, the sensitivity of NO₃ production with respect to the heterogeneous loss rate was examined by varying k_{het1} values between the upper and lower limits of our estimated uncertainty of k_{het1}. The range of

heterogeneous loss rate constants resulted in maximum values of 2-6 ppt of NO₃, as shown in Figure 4. These maximum NO₃ concentrations correspond to lifetimes for isoprene of approximately 3-9 hours, but these values are achieved only after most of the decay has already occurred.

As an extreme case, the model was run with conditions representing the evening with the largest [O₃]·[NO₂] product, August 3, 1998. Measured values of ozone, NO₂, NO, HCHO, terpenes, and isoprene at time 2000 EDT were used to represent conditions at the start of the decay. The calculated heterogeneous loss constant (k_{het1}) discussed previously was used for all time steps. The model simulates an NO₃ concentration of 1.7 ppt for NO₂ and O₃ concentrations of 1.0 and 77.1 ppb, respectively. This results in an isoprene first-order decay constant of 2.8 x 10⁻⁵ s⁻¹, corresponding to a lifetime of approximately 10 hours. A low initial NO₃ concentration is mostly attributed to loss via reaction with isoprene and terpenes; however, later in the evening, when isoprene decays to lower levels, NO₃ could build up to concentrations that lead to a considerably shorter isoprene lifetime and, ultimately, lower isoprene concentrations. By 0000 EDT, NO₃ increases to approximately 5 ppt, to give an isoprene lifetime of 3.5 hours due to reaction with NO₃; however, by this time, the isoprene concentration is only 0.2 ppb. This makes it clear that NO₃ reaction alone cannot account for the rapid decay in the1800-2200 (EDT) time frame; however, after isoprene has decayed to concentrations less than 0.2 ppb, NO₃ increases to levels that could lead to a shorter lifetime for isoprene. Thus it seems that NO₃ reaction could result in a slower but still significant decay of isoprene after 2200 (EDT).
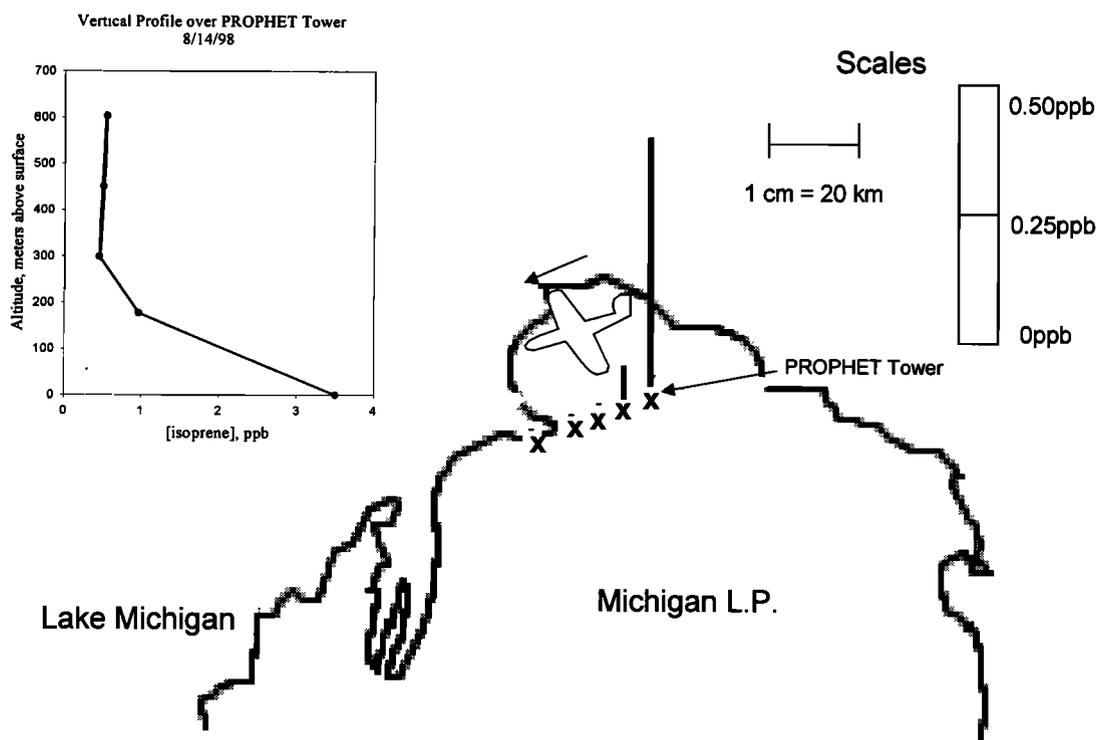
Figure 5. Isoprene Flight Data; vertical and horizontal profiles (450 m agl) for August 14, 1998, 1600 EDT. The flight began at the PROPHET tower and proceeded into the wind (WSW 3.2 m/s) out over Lake Michigan. Each sample collection point is indicated with a cross and the height of the bar over the cross represents the isoprene concentration in the sample.

4.3. Dry Deposition

A possibility that should be considered is dry deposition, e.g., uptake into the waxy cuticular surfaces of leaves. *Cleveland and Yavitt* [1997] indicated that ~5% of the global isoprene budget may involve uptake by soil. From the average observed isoprene decay rate, the dry deposition value required to account for the evening decay may be estimated. If we assume that isoprene is lost strictly by dry deposition, the data from 1997 and 1998 result in V_D values in the 1.5 - 2.0 cm s^{-1} range, with a nocturnal boundary layer (NBL) height of 150 m estimated from sodar data. These values are consistent with what would be expected for polar/adsorptive compounds such as H_2O_2 or HCHO [*Sumner et. al*, this issue]. Since isoprene is a nonpolar species, this makes dry deposition an unlikely candidate for the isoprene sink.

The most convincing evidence against dry deposition is the measured isoprene flux. In Figure 4 we show the isoprene concentration and the measured isoprene flux, for August 7, 1998. As shown, after 2000 EDT the measured isoprene flux drops to near zero, while the isoprene concentrations continue to decrease. If dry deposition were occurring, the measured isoprene flux at the tower height would most likely be negative, which is not observed.

4.4. Advection

Another conceivable mechanism is that advection of isoprene-poor air masses to the site may be responsible for the observed decrease in isoprene at night. Figure 5 depicts the isoprene data collected at 450 m altitude (above ground level) during a horizontal transect flight. On this evening (August 14, 1998) we obtained a vertical profile of isoprene concentrations over the tower, shown in the insert in Figure 5. We then flew directly into the wind (WSW) at a constant altitude of 450 m and collected samples from the tower to the farthest point west, which was over Lake Michigan. As shown in the figure, isoprene concentrations were relatively high near the PROPHET tower, i.e., consistent with the isoprene emission data discussed by *Westberg et al.* [this issue]. In contrast, air masses over the Great Lakes contain insignificant amounts of isoprene. After being transported to the site, this air aloft could mix down and result in an observed decrease in isoprene (S. Sillman et al., unpublished data, 2001; hereinafter referred to as S2001). This "lake theory" implies that we would observe directional dependence to the isoprene decay rates. The results shown in Figure 6 indicate that the decay rate is independent of flow direction, e.g., there are westerly flows that exhibit slow decays and southerly flows during which rapid isoprene decay occurs. If transport and mixing of air masses from over the lakes produced the rapid decay of isoprene, then we would see evidence of faster or more prevalent isoprene decay with westerly or easterly flow. Additionally, if advection from isoprene-poor regions was causing the decay process, an oscillation of isoprene concentration would be seen throughout the night as wind direction fluctuates. Alternating air masses of isoprene-poor and isoprene-rich air would sometimes pass though the sampling area, causing isoprene to occasionally increase in concentration as well as decrease. We find (see Figure 3) that isoprene essentially never increases once it reaches low (<0.1 ppb) levels. If the lake theory satisfactorily explained the decay, then a change in flow direction from
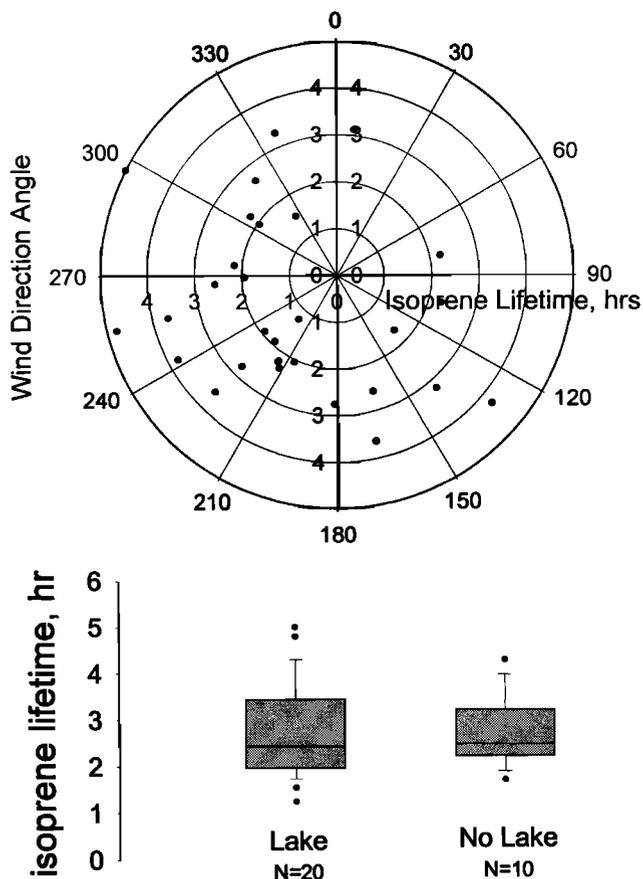
Figure 6. (top) Isoprene lifetime versus wind direction mode (bottom) Isoprene lifetimes plotted as a function of lake influence. Boxes represent 25th and 75th percentiles, error bars represent 5th and 95th percentiles, and individual points are outliers.

westerly to flow from the south and southeast would be accompanied by increases in isoprene concentration, which has never been observed at PROPHET. Finally, strong evidence to counter the lake theory is found in the occurrence of rapid isoprene decay at several independent sites. Specifically, at Harvard Forest, Scotia, and the BOREAS sites, isoprene exhibits regular rapid nighttime decay, with no bodies of water located within short-range transport distance.

Although wind at ground level frequently becomes lighter or calm at night within the NBL, winds aloft may accelerate to supergeostrophic speeds to produce the nocturnal jet. The statically stable air in the NBL tends to suppress turbulence, while the nocturnal jet enhances wind shears that may generate turbulence. As a result, turbulence sometimes occurs in relatively short bursts that can cause mixing throughout the NBL [*Stull*, 1988]. Since this phenomenon is intermittent, sporadically varying concentrations of isoprene and other species would be evident if the nocturnal jet influenced the decay process, which is not the case.

4.5. Consumption by OH

The dominant removal mechanism for isoprene during daylight hours is reaction with OH radicals. The production of HO_x radicals is believed to occur largely via photolysis of
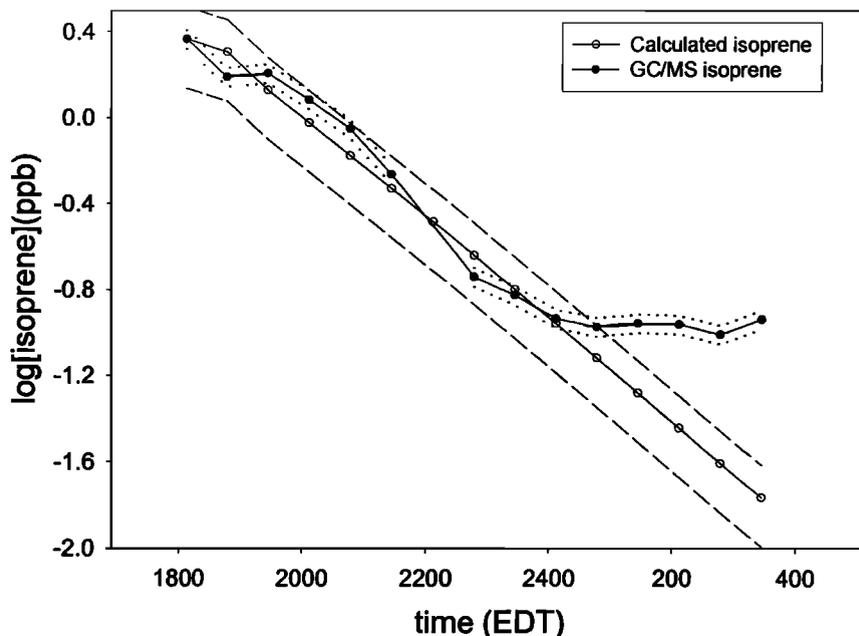
Figure 7. Calculated and observed isoprene for August 7, 1998.

ozone followed by reaction of the product $O(^1D)$ with water molecules and by HCHO photolysis [*Tan et al.*, this issue]. The O_3 photolysis source is more important in the lower portion of the troposphere, as there is more water vapor present. The diurnal pattern of OH has been studied by several groups [*Eisele et al.*, 1996; *Dorn et al.*, 1996; *Mount*, 1992]. Maximum concentrations are seen at noon, following the radiation profile, and levels of OH decline with decreasing radiation during the latter part of the day. Typical late afternoon/early evening values are of the order of 1×10^5 molecules cm^{-3}, as indicated by both measurement and modeling studies [*Mount*, 1992; *Bey et al.*, 1997]. Although photolytic production of the OH radical does not occur at night, we should not a priori rule out the possibility of other formation mechanisms [*Atkinson and Aschmann* 1997; *Paulson and Orlando*, 1996]. In fact, the observed nighttime OH levels at the PROPHET site are surprisingly high. Given the median PROPHET 1998 nighttime (2100-600 EDT) values for OH, O_3, and NO_3 of 0.043 ppt, 40 ppb, and 3 ppt (the latter based on model estimates, as described previously), respectively, the OH removal pathway should dominate, based on kinetics (i.e., effective first-order loss constants of 1.08, 0.12, and 0.47x 10^{-4} s^{-1}, respectively). Discussion of the instrumentation and data quality for OH measurements is found in the work of *Faloona et al.* [this issue]. The implications for the isoprene decay may be explored in several ways. A plot of the observed decay rates versus average OH concentration for each night gives rise to a slope that agrees well with the second-order rate constant for isoprene reaction with OH [*Faloona et al.*, this issue]. To demonstrate the fit of the data to the observed OH, we examined the decay for individual nights and plotted calculated isoprene concentrations based on the first-order decay of isoprene, interpolating between measured OH points, using equation (7):

$$[\text{isoprene}]_t = [\text{isoprene}]_0 \cdot e^{-k[OH]\Delta t} \tag{7}$$

The results of this calculation for August 7 are plotted with the

observed isoprene data in Figure 7, starting with the observed isoprene concentrations at 1800 (EDT). As shown, the observed decay for this day is fit by the calculation based on OH consumption rather well in the 1800-2400 period. In fact, the reported OH concentrations predict well, or slightly overpredict the loss rate of isoprene on most nights. We note that it is often the case, as shown in Figure 7, that there is a significant amount of residual isoprene late at night/early morning, in spite of the fact that the OH concentration data predict continued decay to very low levels. This persistence of isoprene in the early morning hours could be explained if some previously uninvestigated small isoprene source exists at that time. It has been hypothesized that there could be a nonenzymatic plant source amounting to 1-10 μg m^{-2} hr^{-1} [*Guenther*, 1999]. To estimate the size of this source at PROPHET, equation (8) below may be used.

$$E/H = k_{OH}[\text{OH}][\text{isoprene}] \tag{8}$$

We performed this calculation using the average midnight concentrations of OH and isoprene, and where k_{OH} is the rate constant for isoprene + OH [*Stevens et al.*, 1999], and H is an estimated NBL height of 150 m, based on sodar data. The E term is the emission flux that would exist under these conditions, and for the average midnight hour condition, we find $E = 40$ μg C m^{-2} hr^{-1}, which is ~5-10 times greater than the range of estimated values.

Given the remarkable nature of the observed nighttime [OH], it is essential to speculate as to the potential production mechanisms. A thorough discussion of this topic is presented by *Faloona et al.* [this issue].

4.6. Vertical Mixing

Physical processes such as mixing have also been suggested as mechanisms to explain the observed decay [*Goldstein et al.*, 1998; S2001]. One possibility is mixing with isoprene-depleted air from aloft after emissions have stopped. Isoprene
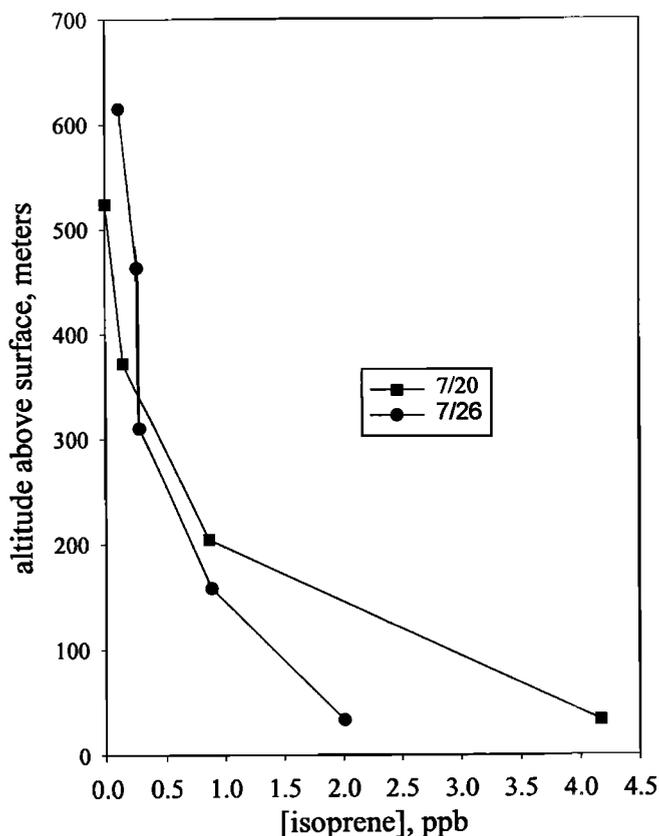
Figure 8. Evening (~1800 EDT) vertical profiles for Pellston, Michigan, July 1998.

exhibits a strong exponential decay from the surface to very low levels a few hundred meters aloft, resulting from its rapid reaction with OH radicals upon emission [*Trainer et al.*, 1987]. In Figure 8 we show the results of two separate aircraft vertical profile measurements, conducted at ~1800 (EDT) in the evening. If some of this isoprene-depleted air aloft were to mix downward, the observed isoprene mixing ratios at the surface would decrease. The rate at which this occurs can be described by the magnitude of the eddy diffusivity K_z. Several reports of nighttime boundary layer K_z values may be found in the literature, and they cover a broad range, from 0.1 to 5m² s⁻¹ [*Hanna et al.*, 1982; *Johansson and Janson*, 1993; *Plummer et al.*, 1996, *Seinfeld and Pandis*, 1998; *Stull*, 1988; *Zhang et al.*, 1982]. Values of K_z required to produce the isoprene decay observed at PROPHET 1997 have been modeled using CALGRID [*Yamartino et al.*, 1992]; these values have been used in the modeling study of S2001. According to the model, K_z after sunset steadily increases from <1 m² s⁻¹ at the tower height to 4m² s⁻¹ at 120 m altitude, reaches 5m² s⁻¹ at 240 m, and then remains constant with altitude. Note that this model does not include the effects of chemistry. We assume here that the timescale to diffuse to H_t, the scale height for isoprene, is the approximate timescale for vertical-mixing-derived dilution of this species. Using the average profile of d[isoprene]/dz and the average surface isoprene concentration from the data in Figure 8, a scale height of 175m is obtained. As defined by Einstein's equation, $\tau_{mix} = H^2/2K_z$ [*Jacob*, 1999]. Using an average value for K_z within the NBL over this scale of 2 m²s⁻¹ (from the CALGRID model), the timescale for isoprene to mix

over the vertical scale H_t would be 2.1 hours. It is clear, however, that this rate is highly uncertain. Using the extreme K_z values found in the literature, this time scale could fall anywhere from 0.85 to 42 hours. From this information we can conclude that vertical mixing most likely contributes significantly to dilution of the surface isoprene at night; however, using the lower limit K_z value (0.1m² s⁻¹), its effect could also be negligible. To approach this problem more quantitatively, vertical profile measurements of both K_z and isoprene should be made during future field campaigns.

Modeling of concentrations for isoprene oxidation products such as methyl vinyl ketone (MVK) and methacrolein (MACR) gives us additional criteria with which to test chemical explanations for the observed isoprene decay, since OH consumption will produce these species. A simple zero-dimensional model was constructed to explore this issue. The OH concentration was kept constant during each run and chosen on the basis of the fit to the first-order decay of isoprene for the specific evening modeled. If consumption by OH was the only mechanism for isoprene decay, then net production of MVK and MACR should be evident during the initial portion of the decay, as indicated by the model. As model isoprene concentrations reach very low levels, MVK and MACR concentrations then begin to decrease, as their consumption by OH becomes faster than their production from isoprene reaction with OH; however, the typical observation is that the measured MVK and MACR concentrations (T. Couch, unpublished data, (1998), and A. Apel, unpublished data, (1998)) decrease slightly during the initial isoprene decay period and remain relatively constant for the remainder of the evening.

It is likely the case that, as for isoprene, OH chemistry is not the only process controlling the nighttime behavior of MVK and MACR. Specifically, vertical mixing (and advection) may also contributes to the observed temporal behavior of the concentration of these species; therefore a realistic model simulation of the MVK and MACR behavior would need to include a vertical mixing component. Although we have limited vertical profile data for isoprene, nighttime vertical profiles of MVK and MACR were not obtained at any of the sites. Because these species are longer-lived than isoprene, we expect their vertical profiles to be less steep, leading to slower apparent decay rates at the tower height due to vertical mixing. A comparison of the decay rates of isoprene and its oxidation products will require information regarding the vertical profiles to enable quantification of the relative dilution rates of these species.

4.7. Quantifying Isoprene Loss

Using equation (1), we can calculate the sum of all of the loss processes for isoprene. Several sets of input values may be used to solve this equation. Since the decay typically initiates between 1900 and 2200 (EDT), the average 2000 (EDT) concentrations of all species may be used to represent concentrations during the decay period. An eddy diffusivity value of 2 m² s⁻¹ was used to estimate the contribution to isoprene loss from vertical mixing. This leads to an overall first-order loss rate coefficient for mixing, assuming isoprene only needs to be transported vertically to 175 m, of 1.3 x 10⁻⁴ s⁻¹. The calculated average (or best estimate in the case of vertical mixing) first-order decay rate for isoprene resulting
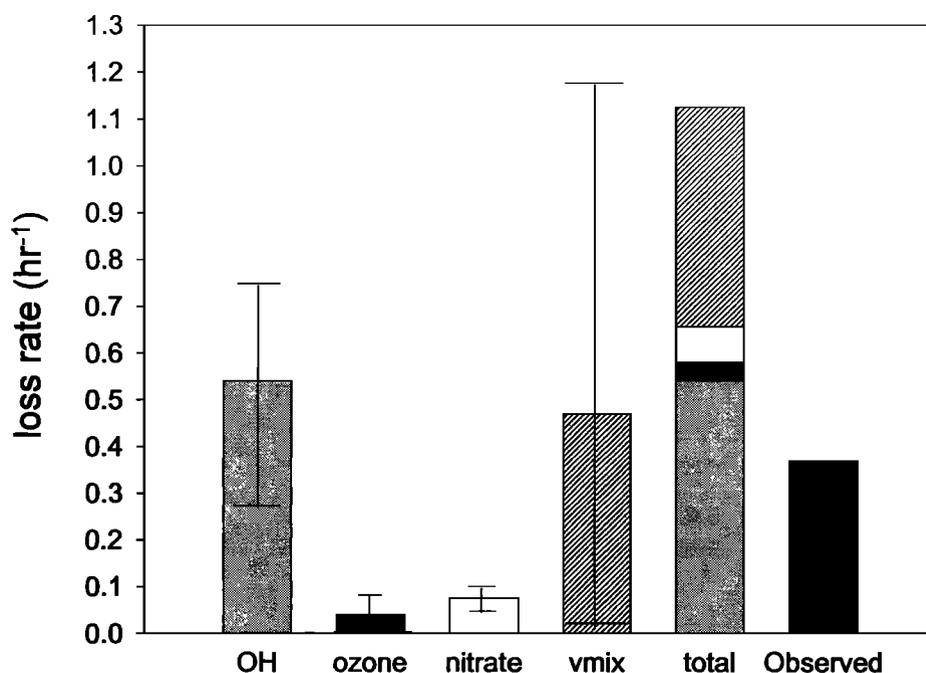
Figure 9. Contributions to isoprene loss rate. Error bars represent the calculated or estimated uncertainties for each stack.

from all terms in equation (1) (excluding dry deposition) is 1.1hour^{-1} during the decay period, as illustrated in Figure 9. For these average conditions, 48% of the decay rate found for all removal terms is calculated to arise from OH reaction, and 42% from vertical mixing, using the CALGRID estimates for the K_z profile. In contrast, the average observed lifetime is 2.7 hours. In Figure 9 we include error estimates for the individual decay terms. The uncertainties for the O_3 and OH loss terms are derived from propagation of the measurement uncertainties and the published rate constant uncertainties. To obtain an uncertainty value for the nitrate radical estimate, a standard propagation of error calculation was performed, using the steady state expression for nitrate radicals. Since eddy diffusivites were not measured, the most uncertain component is vertical mixing. To estimate this uncertainty, we plotted the range of published values as an error bar for the vertical mixing term in Figure 9.

Although the observed isoprene loss rate is markedly less, on average, than the calculated loss rate from the sum of all terms, the difference falls within the limits of uncertainty. With respect to the prognostic equation (1), this overprediction may result from a residual source of isoprene or an error in the sink terms. Since the decay occurs between 1900 and 2200 hours, some daytime emission is likely to persist during the initial period of the decay. If we add to this the small residual nighttime emission that has been hypothesized to occur within the developing relatively stable boundary layer, as discussed above, it seems likely that a significant contributor to the overprediction of the decay is nonzero isoprene emissions at this time. The bars in Figure 9 indicate that either the OH measurements or the vertical mixing estimates alone are sufficient to explain the observed decay rates. An improved quantitation of this phenomenon will require confirmation and understanding of the source of the nighttime OH and better

information regarding the impact of nighttime turbulence and advection in the mixed layer at night. Given the unexpected nature of the data involved, measurements of all critical species should be repeated for this and other sites. The general nature of the observations implies that it is possible that OH near the surface is also elevated at sites such as Harvard Forest and Scotia, and this should certainly be explored.

5. Conclusions

At several forest sites, isoprene exhibits a rapid nighttime decay rate. Loss by reaction with ozone or by dry deposition does not occur on a timescale that is consistent with the observed loss of isoprene. Model simulations of NO_3 concentrations indicate that this oxidant only becomes an important sink for isoprene after the majority of the decay has taken place. The decay process occurs independently of wind direction or site location. This fact argues against the possibility that lake-influenced air is the exclusive cause of the decay. Additionally, comparison of isoprene profiles from several unrelated sites reveals that nearby marine or lacustrine influences are not required to produce the rapid decrease in concentration. Harvard Forest, Scotia, and BOREAS show similar evening behavior for isoprene, with no possibility of transport from lake- or marine-influenced air.

This phenomenon currently can only be explained by chemistry if the discovery of high evening OH radicals is confirmed and understood. Observed decay rates show good overall agreement with the second-order isoprene + OH rate constant. Additionally, the isoprene decay can, for several evenings, be simulated using measured OH. Our best estimate of the rate of dilution by isoprene-poor air from aloft via vertical mixing can also simulate the observed decay, but no direct measurement data exist for vertical mixing rates in

forested environments to better support this estimate. Altitude profiles of K_z and isoprene should be obtained in future field campaigns in order to more quantitatively investigate this phenomenon. The sum of the loss rate terms in the prognostic equation (1) significantly overpredicts the observed isoprene decay rate. This result may be attributed at least in part to neglect of residual isoprene emissions during the initial decay period or later in the evening when the NBL is well established. Additionally, an overestimation of the removal mechanisms must be considered. To improve understanding of the chemical loss components of the isoprene decay, further investigations of nighttime isoprene chemistry should be pursued via laboratory and field studies.

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