

# Loss of isoprene and sources of nighttime OH radicals at a rural site in the United States: Results from photochemical models

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[1] A one-dimensional Lagrangian model for atmospheric transport and photochemistry has been developed and used to interpret measurements made at Pellston, Michigan, during the summer of 1998. The model represents a moving vertical column of air with vertical resolution of 25 m near the ground. Calculations have been performed for a series of trajectories, with representation of emissions, vertical mixing, and photochemistry for a 3-day period ending with the arrival of the air column at Pellston. Results have been used to identify causes of the observed decrease in isoprene at night, to investigate causes of high nighttime OH. Significant OH can be generated at night by terpenes if it is assumed that some fast-reacting monoterpenes are emitted at rates comparable to inventory emissions for terpenes. However, this nighttime OH is confined to a shallow surface layer (0–25 m) and has little impact on nighttime chemistry. The observed decrease in isoprene at night can be reproduced in models with low OH, and is attributed primarily to vertical dilution. There is also evidence that transport from Lake Michigan contributes to low nighttime isoprene at Pellston. Model results compare well with measured isoprene, NO<sub>x</sub>, and with isoprene vertical profiles. Significant model-measurement discrepancies are found for OH, HO<sub>2</sub>, methylvinylketone, and formaldehyde. *INDEX TERMS:* 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305)

## 1. Introduction

[2] The series of field measurements at Pellston, Michigan, during summers 1997 and 1998 [Carroll *et al.*, 2001] generated evidence of significant nighttime chemistry. Isoprene concentrations were found to decrease rapidly after sunset, suggesting the possibility of an unknown photochemical loss mechanism at night [Hurst *et al.*, 2001]. Unusually high concentrations of the OH radical were also observed at night [Faloona *et al.*, 2001]. Faloona *et al.* [2001] have suggested that terpene chemistry might provide a source of nighttime OH. Both Faloona *et al.* [2001] and Hurst *et al.* [2001] suggested that the observed nighttime OH might be a major factor in explaining the observed decrease in isoprene at night.

[3] Although nighttime chemistry might be the cause of the observed decrease in isoprene, there are alternative explanations

that are not dependent on chemistry. One possibility is loss of isoprene through vertical diffusion. During the daytime, isoprene concentrations often decrease sharply with altitude [Andronache *et al.*, 1994; Guenther *et al.*, 1996a, 1996b], especially over forests that directly emit isoprene. After sunset, when isoprene emissions cease, near-surface isoprene concentrations may decrease as surface isoprene is dispersed vertically. Makar *et al.* [1999] found that vertical diffusion can cause a significant decrease in isoprene during the early evening. Another possibility is advection of low-isoprene air from Lake Michigan. The Pellston site is located 25 km from the lakeshore, and the lake is 150 km wide in an east-west direction opposite Pellston (see Figure 1). Air over Lake Michigan during the daytime is expected to have very low isoprene, since the travel time across Lake Michigan is much longer than the photochemical lifetime of isoprene during the daytime (1 hour). This lake air should have little influence on isoprene at Pellston during the daytime, since it must travel over forested land for an hour or more before arriving at Pellston. However, if air from Lake Michigan arrives at the Michigan shore after sunset, it can travel to Pellston without receiving freshly emitted isoprene. Thus advection from Lake Michigan at nighttime has the potential to cause a significant decrease in isoprene at Pellston.

[4] The possibility that dynamical factors rather than chemistry cause the observed loss of isoprene is especially important because the hypothesized nighttime sink for isoprene is very uncertain. The observed high nighttime OH at Pellston [Faloona *et al.*, 2001] provided the first evidence for active nighttime radical chemistry. The source of this OH is uncertain. Faloona *et al.* [2001] proposed that OH was generated by terpene chemistry, but

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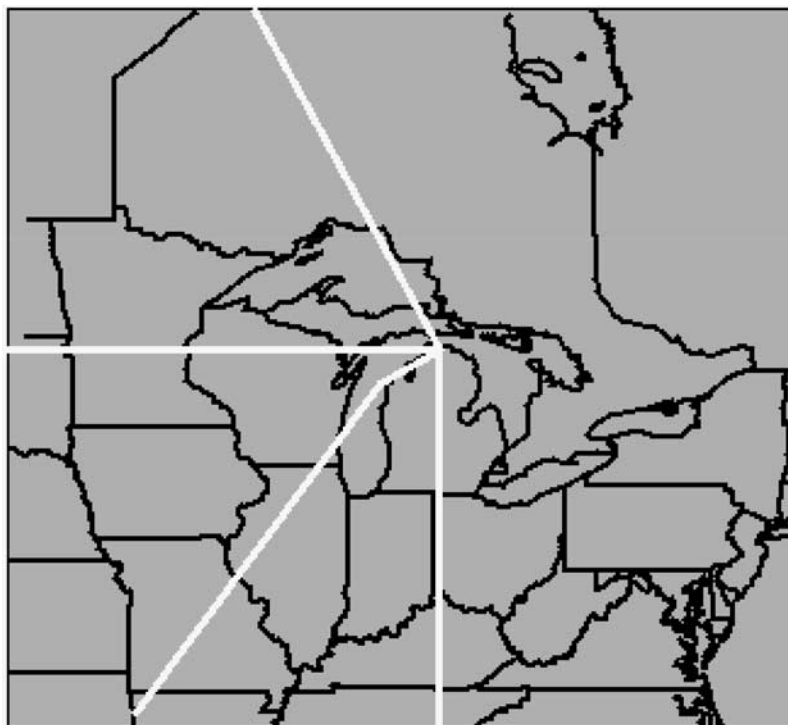
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**Figure 1.** Map of the north-central United States showing the location of Pellston and the four 72-hour back trajectories for air arriving at Pellston used in the model.

it is unclear whether OH generated in this manner would provide a significant sink for isoprene. It is also unclear whether the Pellston measurements would provide evidence in favor of a nighttime chemical sink for isoprene. If dynamical factors were included, the observed nighttime decay may not provide clear evidence for nighttime chemistry, and may even provide evidence against the proposed nighttime chemical sink.

[5] This paper describes a series of one-dimensional (1-D) model calculations designed to evaluate the relative impact of chemistry, vertical diffusion, and advection from Lake Michigan on nighttime isoprene at Pellston. The distinctive feature of this model is the use of much sharper vertical resolution (down to 25 m) than is usually provided in three-dimensional (3-D) regional-scale models. The model is exercised in Lagrangian mode to represent the variations in emissions and vertical dynamics as air travels across Lake Michigan to arrive at the Pellston site. A similar two-dimensional (2-D) Lagrangian model was presented by *Sillman* [2000] and used to represent the evolution of plumes from large power plants. This type of model is especially suitable for a rural site like Pellston, where upwind emissions are spatially homogeneous (except for Lake Michigan) and where issues of vertical diffusion are important.

[6] The model will be used to identify the impact of vertical mixing on isoprene concentrations at Pellston and to evaluate the possible impact of nighttime OH in calculations that include dynamics as well as chemistry. Model scenarios will be developed with high and low nighttime OH in order to identify possible impacts of nighttime OH on isoprene. Model scenarios will also be developed with and without transport from Lake Michigan, and differences between scenarios will be used to identify possible measurement-based signals for the impact of lake transport at the site. Lastly, model-measurement comparisons will be shown for a range of measured species at Pellston. The analysis presented here complements analyses of measured isoprene, OH and HO<sub>2</sub>, HCHO, and NO<sub>x</sub> presented elsewhere [*Hurst et al.*, 2001; *Faloona*

*et al.*, 2001; *Tan et al.*, 2001; *Sumner et al.*, 2001; *Thornberry et al.*, 2001].

## 2. Simulation Methods

[7] The 1-D Lagrangian model used here represents species concentrations in a moving vertical column of air extending from the surface to 2300 m. The vertical resolution and mixing are similar to the 2-D model for power plant plumes described by *Sillman* [2000] but with the horizontal dimension eliminated. There have been minor changes in the calculation of vertical mixing and in the chemical mechanism, and also some modifications based on conditions specific to Pellston.

[8] The model includes 16 vertical layers and has vertical resolution of 25 m for 0–100 m above ground, 50 m for 100–300 m above ground, and resolution at higher elevations successively decrease from 100 to 300 m. The column is assumed to move along a specific trajectory from upwind for a 3-day period and is compared with measurements at the time of its arrival at Pellston. Calculations have been performed for separate trajectories arriving at Pellston at 1-hour time intervals.

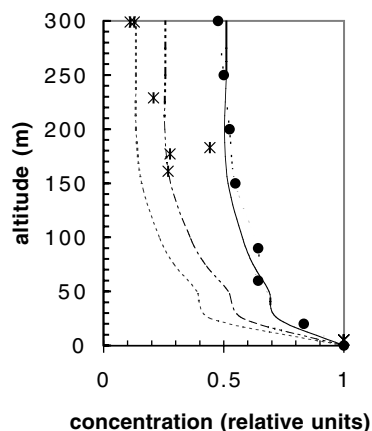
[9] Emission rates along an upwind trajectory provide some uncertainty because transported air is subject to significant horizontal diffusion as it travels. There is also significant vertical wind shear, which contributes to effective horizontal diffusion through vertical mixing. In order to represent this we have introduced emissions along trajectories based on inventory emissions over an area extending about the trajectory center. This emissions area is equal to the area covered by a Gaussian plume, initialized as a point at Pellston and traveling backward in time along the upwind trajectory, including 1s widths to either side of the plume center. Thus, as the trajectory approaches Pellston, emissions are based on inventory values in the immediate vicinity of the center of the trajectory, but at distant upwind locations, emissions are based on the inventory

average for a wide area about the trajectory center, representing the larger horizontal diffusion and/or uncertainty associated with the back trajectory for transport from distant locations. Horizontal spreading of this “emissions plume” is calculated on the basis of estimates from Gifford [1982] for horizontal widths of Gaussian plumes as they move downwind. Emission rates are based on the Environmental Protection Agency (EPA) [1993] and biogenic emissions inventory system 2 (BEIS2) [Geron et al., 1994] inventories, except as noted in section 3.

[10] The above approach effectively represents emissions from distant sources along the upwind trajectory as regional area-averaged emissions. This approach is subject to the same types of limitations as are 3-D Eulerian models with coarse grid resolution [e.g., Sillman et al., 1990; Jacob et al., 1993]. For emission sources 500 km upwind this resolution of emissions is equivalent to a horizontal Eulerian model with  $100 \times 100$  km horizontal resolution. Obviously, resolution of emissions improves for sources closer to Pellston.

[11] The vertical column is assumed to travel along the upwind trajectory without accounting for vertical wind shear. Wind shear is included indirectly to the extent that wind shear in combination with vertical mixing contributes to horizontal diffusion of emissions from different sources. This representation is probably adequate during the daytime, when air is rapidly mixed throughout a convective layer of 1000 m or more. However, at night, there is typically a sharp vertical gradient in wind speed and direction close to the ground, with much lower wind speeds in the lower 100 m [e.g., Stull, 1988]. This gradient in wind speed is likely to affect the rate of transport from Lake Michigan to Pellston at night. In order to approximate this vertical wind gradient, we have added a model representation of a separate column of air from 0 to 100 m above the ground (with 25 m resolution), which remains in the vicinity of Pellston. These nighttime layers are initialized at sunset each evening, on the basis of species concentrations in the lower 100 m of the main model for the trajectory arriving at Pellston at sunset. The nighttime layers then receive emissions based on inventory emission rates near Pellston and undergo chemical transformations and vertical mixing through the night. Mixing to these layers from above 100 m is calculated on the basis of species concentrations above 100 m in the trajectories arriving at Pellston at each hour of the night in the main model. In effect, this allows the contents of transported air from above 100 m to diffuse down into the relatively still near-surface layers at night.

[12] Vertical mixing within the convective mixed layer is adapted from Pleim and Chang [1992] with one significant modification. Pleim and Chang represented convective mixing by assuming direct upward transport from the lower model layer to all higher layers contained within the region of convective mixing and mass-conserving downward transport from each layer to the next lower layer. This mimics the transport associated with rising thermals in the convective mixed layer and represents a significant improvement over normal eddy diffusion. In the original formulation, the rate of transport from the lowest model layer to higher elevations was uniform with height throughout the convective layer. This method typically produces a very sharp decrease in concentration between the lowest model layer and the next higher layer for a species that is emitted directly into the lowest layer. As reported by Pleim and Chang, calculations with large eddy simulations show a more gradual decrease from 0 to 200 m elevation than calculations with their method. Near-surface vertical gradients are especially important for isoprene, since the measured above-canopy concentrations are often critically dependent on rates of vertical mixing and are often compared with measured vertical profiles. In order to correct for this small deficiency, we have modified the initial assumption that vertical transport from the first model layer is uniform with height. Instead, transport from the first model layer



**Figure 2.** Isoprene (relative units) versus altitude above the forest canopy (meters) measured at Rose, Alabama, compared with model values. Measured values (dashed line with solid circles) represent median daytime vertical profiles reported by Andronache et al. [1994]. Model values are shown for (1) a “generic” scenario with no spatial variation in isoprene emissions and no transport from Lake Michigan at 1400 LT (Eastern Standard Time) (solid line); (2) the standard scenario at Pellston, with isoprene emissions higher at Pellston than in the surrounding region by a factor of four, also at 1400 LT (dashed-dotted line); and (3) the standard scenario at Pellston at 1900 LT (dashed line). The asterisks represent individual measurements at the Pellston site.

is assumed to be distributed as follows: 40% from 25 to 100 m, 8% from 100 to 150 m, 4% from 150 to 200 m, and the remaining 48% distributed uniformly with height throughout the rest of the convective mixed layer. When used with this modification, the Pleim-Chang algorithm generates vertical profiles for isoprene that compare well with measured vertical profiles reported by Andronache et al. [1994] and Guenther [1996a, 1996b]. As shown in Figure 2, when calculations are performed with spatially uniform emissions of isoprene, they result in an isoprene decay rate with altitude that is comparable to the average measured decay rate, and with a similar pattern with height.

[13] At nighttime and above the mixed layer, vertical transport is represented using standard vertical eddy diffusion coefficients. Diffusion coefficients were derived from similarity theory [e.g., Brost and Wyngaard, 1978] using typical measured values during the intensive period. Obukhov lengths were derived from measured friction velocities and heat fluxes reported by Westberg et al. [2001]. The diffusion coefficients for 2200 to 0400 LT (Eastern Standard Time) were derived based on a typical Obukhov length of 50 m and a friction velocity of  $0.3 \text{ m s}^{-1}$ . This resulted in a maximum value of  $0.8 \text{ m}^2 \text{ s}^{-1}$  at 30 m above the model surface, decreasing to  $0.1 \text{ m}^2 \text{ s}^{-1}$  at 100 m and  $0.05 \text{ m}^2 \text{ s}^{-1}$  at higher elevations. We assumed more rapid mixing during the early evening (1900–2200 LT) with maximum diffusion at  $3 \text{ m}^2 \text{ s}^{-1}$  and relatively high values extending to 200 m. These values were based on the higher Obukhov lengths (150 m) measured during those hours. Stable conditions are assumed to begin near the ground at 1900 LT, shortly before sunset. The onset of convective mixing in the morning begins at 0600 LT. However, stable mixing is assumed for air as it passes over the Great Lakes, even during the daytime [see Sillman et al., 1993].

[14] Chemistry and dry deposition rates are the same as in previous models [Sillman et al., 1998; Sillman, 2000]. A brief summary will be presented here. We use a photochemical mechanism based on that of Lurmann et al. [1986] with numerous updates, including updated reaction rates [DeMore et al., 1997] and

chemistry of isoprene and related species based on those of *Paulson and Seinfeld* [1992]. The isoprene reaction mechanism has been updated on the basis of product yields reported by *Carter and Atkinson* [1995]. The model also includes updated RO<sub>2</sub>-HO<sub>2</sub> reaction rates and additional RO<sub>2</sub>-RO<sub>2</sub> reactions recommended by *Kirchner and Stockwell* [1996]. The reaction rates for organic peroxides with OH were updated on the basis of recommendations from *Stockwell et al.* [1997]. However, the rate for the reaction of RO<sub>2</sub> radicals with NO ( $8.9e-12 \text{ cm}^3 \text{ s}^{-1}$ ) was taken from *Atkinson* [1994], which was consistent with *Paulson and Seinfeld* [1992] and *Carter and Atkinson* [1995]. *Kirchner and Stockwell* [1996] recommend a lower value ( $4e-12 \text{ cm}^3 \text{ s}^{-1}$ ). Reactions for  $\alpha$ -pinene and limonene from *Stockwell et al.* [1997] have also been added. The resulting mechanism has many features that are similar to *Stockwell et al.*, but it includes more detailed speciation of many secondary organic species (aldehydes, organic nitrates, and peroxides) and representation of all radicals as individual species rather than as counters. It also includes additional reactions that are important in the remote troposphere (OH + HO<sub>2</sub>, PAN + OH, and others reported by *Lurmann et al.* [1986]).

[15] As discussed in section 5, *Faloona et al.* [2001] have hypothesized that nighttime chemistry may be influenced by fast-reacting monoterpenes (e.g.,  $\alpha$ -Terpinene) which react rapidly with O<sub>3</sub> to form OH. We have represented these species in some model scenarios by adding a species that undergoes the same reactions as  $\alpha$ -pinene with the same product yields, but which has a much faster reaction rate with O<sub>3</sub> ( $2e14 \text{ cm}^3 \text{ s}^{-1}$  molecule<sup>-1</sup>).

[16] Dry deposition velocities during the daytime are SO<sub>2</sub>, O<sub>3</sub>, and NO<sub>2</sub>,  $0.6 \text{ cm s}^{-1}$ ; NO,  $0.1 \text{ cm s}^{-1}$ ; PAN,  $0.25 \text{ cm s}^{-1}$ ; H<sub>2</sub>O<sub>2</sub> and HNO<sub>3</sub>,  $5 \text{ cm s}^{-1}$ ; and organic peroxides,  $1.2 \text{ cm s}^{-1}$ . Deposition velocities at nighttime are equal to half these values. The high deposition velocity for H<sub>2</sub>O<sub>2</sub> and HNO<sub>3</sub> is based on results from *Sillman et al.* [1998] and *Hall and Claiborn* [1997]. Deposition rates over Lake Michigan and Lake Superior are  $0.05 \text{ cm s}^{-1}$  for all species that are subject to dry deposition, on the basis of the assumption that the lake surface is stable [*Sillman et al.*, 1993; *Walcek*, 1987; *Voldner et al.*, 1986]. Dry deposition of formaldehyde has not been included, although there is evidence that significant dry deposition occurs for this species [*Sumner et al.*, 2001].

[17] The model is initialized with species concentrations typical for remote continental locations: 40 ppb O<sub>3</sub>, 0.15 ppb NO<sub>x</sub>, 0.1 ppb PAN, 1 ppb H<sub>2</sub>O<sub>2</sub>, 200 ppb CO, 1700 ppb CH<sub>4</sub>, and 4 ppb C volatile organics.

[18] A similar 1-D Lagrangian model approach was used by *Bergin et al.* [1999] and *Bergin and Milford* [2000] to represent conditions in Los Angeles. *Bergin et al.* [1999] estimated that model uncertainties (resulting from uncertain trajectories, emission rates, and photochemistry) were 25–60% for O<sub>3</sub> and HCHO, 37–64% for HNO<sub>3</sub>, 45–82% for PAN, and 30–40% for NO<sub>y</sub>. Because the spatial variation in emissions is more complex in the vicinity of Los Angeles, uncertainties associated with trajectories are likely to be no larger for Pellston.

### 3. Model Application for Pellston

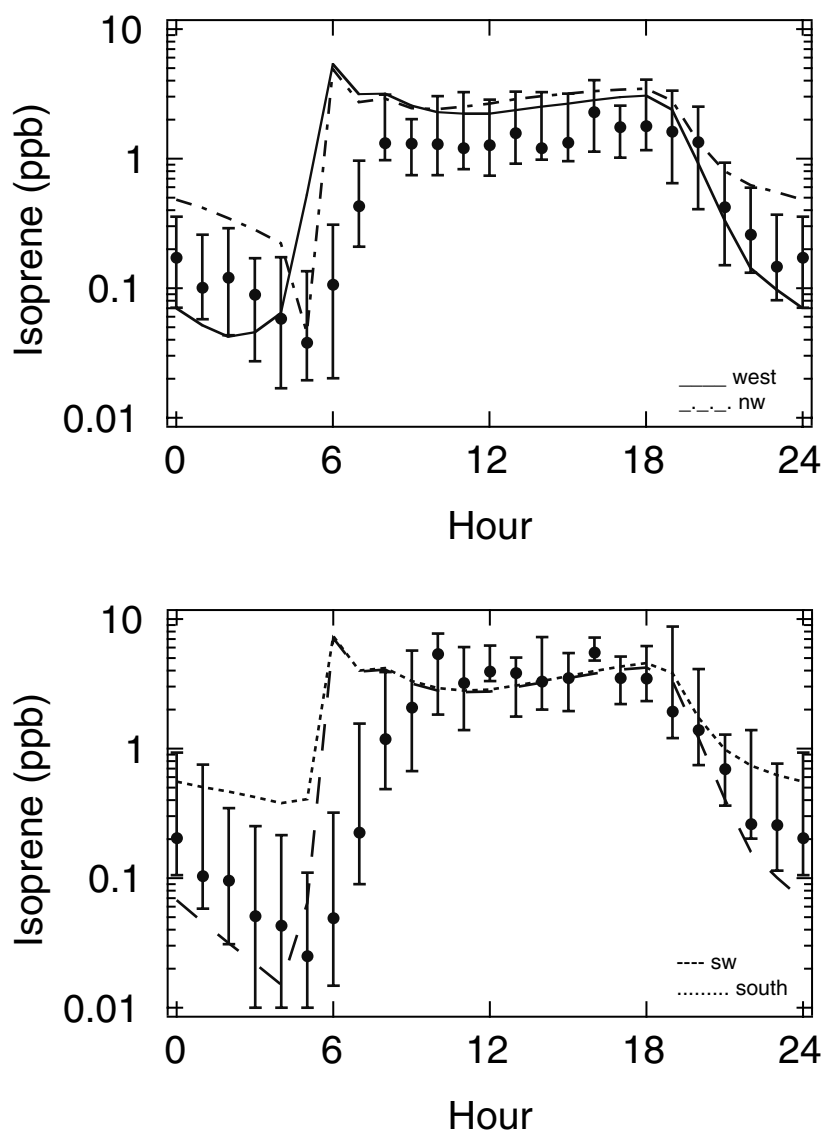
[19] Results will be presented for a series of trajectories arriving at Pellston, representing the major source regions for air at Pellston (see *Cooper and Moody* [2001] for a more detailed description) and also the distinction between trajectories that have crossed Lake Michigan and trajectories that have traveled mainly over land. Four trajectories will be shown (see Figure 1): (1) a trajectory from due west, representing source regions in Wisconsin and Minnesota and arrival at Pellston following a 5-hour traverse of Lake Michigan; (2) a trajectory from the north-northwest (NNW), representing primarily remote source regions in northern Canada and the upper

peninsula of Michigan, with a brief (3-hour) traverse of Lake Michigan and a longer traverse of Lake Superior (farther upwind); (3) a trajectory from the south-southwest (SSW), with source regions in Illinois and Missouri and including higher emission associated with the Chicago area and other urban regions and a long (8-hour) traverse of Lake Michigan; and (4) a trajectory from the south, with urban source regions in Ohio and southern Michigan and no traversal over any of the Great Lakes. The SW, SSW, and south trajectories are simulated with relatively warm temperatures (diurnal peak 30°C at the surface), while the west and NNW trajectories represent somewhat cooler conditions (diurnal peak 27°C), both of which were common at Pellston during the time of measurements. The temperature follows a standard diurnal cycle. It is assumed that no diabatic heating occurs as air traverses Lake Michigan, so that as air passes over Lake Michigan during the daytime it retains the same temperature it had at the time it began the traversal. Relative humidity was assumed to be 50% during the afternoon, comparable to median observed values. The simulations all represent clear-sky conditions. For each of the five trajectories, 24 separate calculations are performed representing air arriving at Pellston at hourly intervals throughout the day. These calculations represent the diurnal cycle for air arriving at Pellston along each trajectory.

[20] *Cooper and Moody* [2001] found that back trajectories of air arriving at Pellston during the experiment can be divided into three flow regimes: transport from the north, representing 44% of the duration of the experiment; transport from the southwest (16%); and transport from the southeast (8%). The remainder of the experiment (33%) represented either periods of light and variable winds or periods of transition between the three regimes. *Cooper et al.* distinguish between trajectories that included transport from Lake Michigan and trajectories that represented transport over land. Their results [*Cooper and Moody*, 2001, Figure 1] suggest that roughly half of the northern trajectories came predominantly from the west-northwest, across Lake Michigan and northern Wisconsin. Others had come from the north and northeast, including only a brief traverse of the northern end of Lake Michigan, and sometimes a traverse over more distant lakes (Huron or Superior). The southwest flow regime described by *Cooper et al.* include a mix of air arriving from rural Wisconsin and air arriving from regions with larger emissions to the south (Illinois, Indiana). Some of these trajectories included a long traverse of Lake Michigan. *Cooper and Moody* reported that the southwest and southeast regimes included a wide range of measured conditions, with daytime O<sub>3</sub> between 40 and 80 ppb and total reactive nitrogen (NO<sub>y</sub>) from 1 to 4 ppb. The more numerous northerly trajectories generally had daytime O<sub>3</sub> below 40 ppb and NO<sub>y</sub> below 1 ppb.

[21] In the model application the west and NNW trajectories are intended to represent conditions during the most common flow regime at Pellston. The two trajectories differ in that the west trajectory includes direct transport from Lake Michigan, and somewhat higher upwind emissions (northern Wisconsin and Minnesota, as opposed to the remote regions of Canada). The SSW and south trajectories are intended to represent the most polluted conditions at Pellston, with transport over Lake Michigan and over land, respectively.

[22] An additional adjustment was applied to the model emissions to represent conditions specific to the measurement site. Emission rates along the trajectories are based on the *EPA* [1993] and BEIS2 [*Geron et al.*, 1994] inventories, which provide emission rates on a 20 × 20 km spatial scale based on county averages. However, it is likely that emissions in the immediate vicinity of the measurement site differ significantly from inventory estimates for the 20 × 20 km<sup>2</sup> area about the site. The site is located in a dense forest, whereas the larger regions include forests, agricultural fields, small lakes, and towns. *Westberg et al.* [2001] measured isoprene fluxes at the site and found that they were comparable to emission rates derived from BEIS2 for the on-site



**Figure 3.** Isoprene (ppb) versus time of day (hours, LT) measured at Pellston during summer 1998, compared with model values. Measured values represent the hourly median (solid circles) and upper and lower 67th percentiles (vertical bars). Results are (top) measurements for the north trajectory category, model west trajectory (solid line), and model northwest (dashed-dotted line); and (bottom) measurements for southwest and southeast trajectory categories, model southwest trajectory (dashed line), and model south trajectory (dotted line).

forest (equivalent to a rate of  $2.5e12$  molecules  $\text{cm}^{-2} \text{s}^{-1}$  at  $30^\circ\text{C}$  and full sunlight). The BEIS2 inventory value for the area around Pellston is significantly lower ( $0.6e12$  molecules  $\text{cm}^{-2} \text{s}^{-1}$ ). This difference between on-site emissions and emissions in the surrounding area has a significant impact on model results for isoprene and other directly emitted species. In order to represent on-site emissions, we have changed the emission rates for the last half hour of each trajectory simulation (representing the time of arrival at the site). The isoprene emission rate for this final half hour is set equal to the rate derived by Westberg et al. for the forest at the site. Emission rates for other biogenic species were increased by the same proportion relative to area-wide inventory values. Emission rates for anthropogenic species during the last half hour of the simulation were reduced to 20% of the area-wide inventory value. The latter adjustment has a significant impact on NO at night but has little effect on other species.

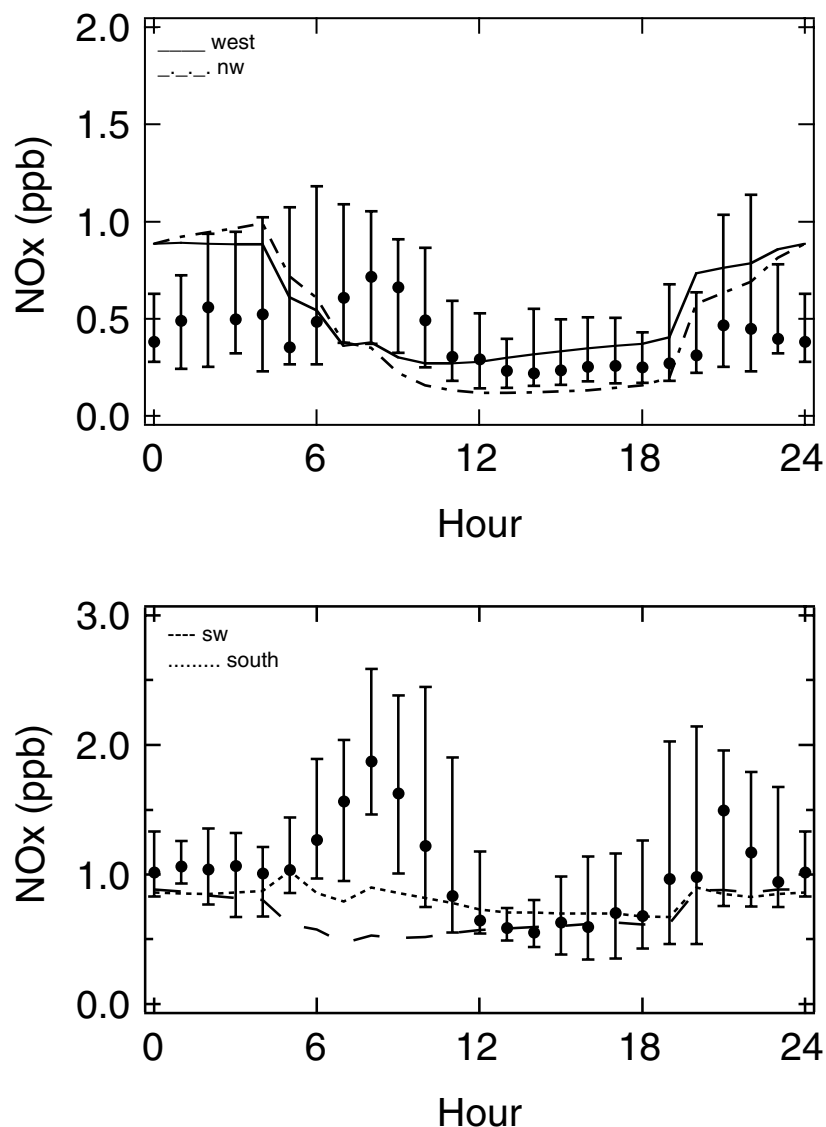
[23] The assumed higher isoprene emissions at the Pellston site have an impact on the predicted vertical distribution of isoprene

during the daytime. Concentrations are predicted to decrease more rapidly with height when emissions are increased during the last half hour of the simulation (see Figure 2).

#### 4. Measurements

[24] The measurements reported here are all described in separate publications. A brief summary will be presented here.

[25] Measurements of isoprene and its first-generation oxidation products, methacrolein and methylvinylketone, were made by both the Purdue [Hurst et al., 2001] and National Center for Atmospheric Research groups (E. C. Apel et al., Measurement and interpretation of isoprene fluxes and isoprene, methacrolein and methyl vinyl ketone mixing ratios at the PROPHET site during the 1998 intensive, submitted to *Journal of Geophysical Research*, 2001) using gas chromatographic separation followed by mass spectrometric identification (GC/MS). The limit of detection for



**Figure 4.**  $\text{NO}_x$  (ppb) versus time of day (hours, LT) measured at Pellston during summer 1998, compared with model values. Measured values represent the hourly median (solid circles) and upper and lower 67th percentiles (vertical bars). Results are (top) measurements for the north trajectory category, model west trajectory (solid line), and model northwest (dashed-dotted line); and (bottom) measurements for southwest and southeast trajectory categories, model southwest trajectory (dashed line), and model south trajectory (dotted line).

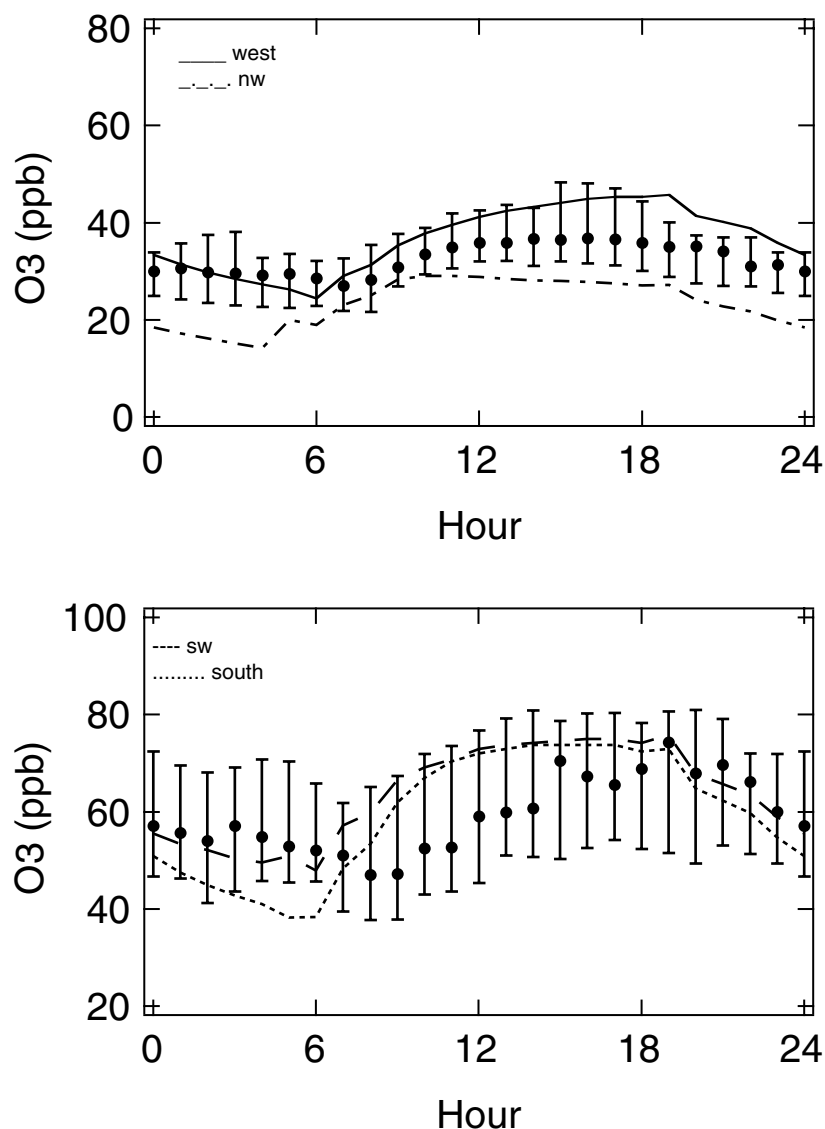
this instrument is estimated at 1 part per trillion by volume (pptv) with an absolute accuracy based on propagation of errors through the calibration process of 6%. The instrument has a precision of 1% and an uncertainty of 10%. Results shown here for isoprene, methylvinylketone, and methacrolein are from the Purdue group [Hurst *et al.*, 2001].

[26] Ambient measurements of formaldehyde were conducted at the PROPHET tower site from 11 July to 20 August 1998 using an automated continuous-flow injection analysis system [Fan and Dasgupta, 1994; Sumner and Shepson, 1999] that uses a Nafion membrane diffusion scrubber to extract gas-phase HCHO into water. The estimated accuracy, due to uncertainties in the calibration standard concentration, is  $\pm 15\%$ . For a complete description, see Sumner *et al.* [2001].

[27] NO and  $\text{NO}_2$  were measured using a custom-built  $\text{NO}-\text{O}_3$  chemiluminescence instrument. The sample flow passed through a Pyrex flow cell that was periodically illuminated by opening a shutter to photolyze  $\text{NO}_2$  to NO. NO was measured when the

shutter was closed and the increase in signal with the cell illuminated was used to determine  $\text{NO}_2$ . The  $2\sigma$  detection limit in 1 min was 1.3 pptv for NO, and 2–12 pptv for  $\text{NO}_2$ . The estimated uncertainty was  $\pm(19\% + 2 \text{ pptv})$  for NO and  $\pm(21\% + 14 \text{ pptv})$  for  $\text{NO}_2$  ( $2\sigma$ , 1-min averages) [Thornberry *et al.*, 2001].  $\text{NO}_y$  was measured by catalytic conversion to NO followed by detection of the NO by  $\text{NO}-\text{O}_3$  chemiluminescence. The converters used were 24-karat gold tubes operated at  $300^\circ\text{C}$  with 0.3% CO in the sample flow as a reductant. The detection limit of the  $\text{NO}_y$  measurement was 1.9 pptv ( $2\sigma$ , 1 min) and the total uncertainty of the measurement was estimated to be  $\pm(30\% + 45 \text{ pptv})$  [Thornberry *et al.*, 2001].

[28] The OH and  $\text{HO}_2$  radical measurements were made with the Penn State ground-based tropospheric hydrogen oxides sensor instrument, which is based on laser-induced fluorescence (LIF) of the OH molecule. The same instrument in a slightly different configuration (airborne tropospheric hydrogen oxides sensor) has been deployed in three aircraft experiments aboard NASA's DC-8



**Figure 5.** O<sub>3</sub> (ppb) versus time of day (hours, LT) measured at Pellston during summer 1998 compared with model values. Measured values represent the hourly median (solid circles) and upper and lower 67th percentiles (vertical bars). Results are (top) measurements for the north trajectory category, model west trajectory (solid line), and model northwest (dashed-dotted line); and (bottom) measurements for southwest and southeast trajectory categories, model southwest trajectory (dashed line), and model south trajectory (dotted line).

airborne laboratory [Brune *et al.*, 1998]. The estimated uncertainty of these measurements is  $\pm 40\%$  [Faloona *et al.*, 2001; Tan *et al.*, 2001].

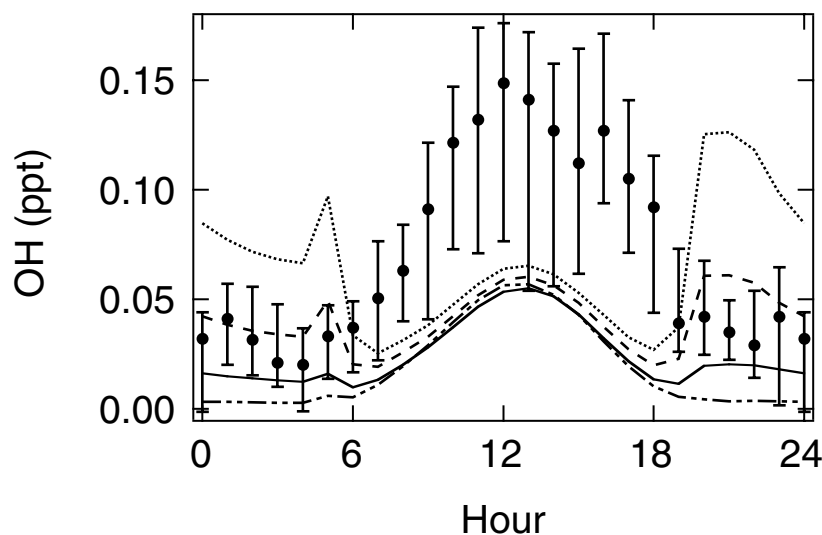
[29] Radicals were measured using a radical detector based on the principle of chemical amplification, similar to that described by Arias and Hastie [1996]. This detector is not specific to a particular type of radical but rather measures the sum of all radicals and the measured quantity is usually called RO<sub>x</sub> (= HO<sub>2</sub> + RO<sub>2</sub> + OH + RO). However, since the peroxy radicals (RO<sub>2</sub> and HO<sub>2</sub>) are the dominant radical species, they also dominate the detector response and this instrument is often called a peroxy radical detector.

[30] Calibration was performed using a radical source based on the photolysis of water vapor in air [Schultz *et al.*, 1995]. Recent laboratory work [Mihele and Hastie, 1998] has shown that the response of the radical detector is sensitive to ambient water vapor. Therefore the calibrations from this calibration source, which

produces radicals in relatively dry conditions (<200 ppmv), were corrected for ambient water concentrations. The correction for relative humidities less than 80 introduces a small additional error to the measurements, so the estimated uncertainty is 30%, although any systematic variation between the wall conditions in the laboratory and field systems cannot be estimated. At higher humidities, there are no laboratory data, and an extrapolation was used to estimate the correction. The error in this procedure is unknown and all the data obtained under these conditions must be regarded as lower limits.

## 5. Model-Measurement Comparisons

[31] Figures 3, 4, and 5 show the diurnal cycle of isoprene, NO<sub>3</sub>, and O<sub>3</sub>, respectively. Measurements are shown separately for the main trajectory categories identified by Cooper and Moody



**Figure 6.** OH (ppt) versus time of day (hours, LT) measured at Pellston during summer 1998 compared with model values. Measured values represent the hourly median (solid circles), and upper and lower 67th percentiles (vertical bars) for north trajectory events. Model values represent the west trajectory standard scenario (solid line), scenario in which half the emitted terpenes are represented by fast-reacting species (dashed line), scenario in which all the emitted terpenes are represented by fast-reaction species (dotted line), and scenario with zero terpenes (dashed-dotted line).

[2001]: the north trajectory and the combined southwest and southeast trajectories (which were associated with similar species concentrations). The measured values represent the median and the upper and lower 67th percentiles, and are compared with model values for trajectories corresponding to the trajectory category of the subset of measurements.

[32] The model successfully reproduces many features of the observed isoprene,  $\text{NO}_x$ , and  $\text{O}_3$ . With few exceptions, model values fall within the upper and lower 67th percentile of measurements for the appropriate trajectory category. Most model values are also within 50% of the measured median isoprene and  $\text{NO}_x$  (except for the very low nighttime isoprene) and within 20% of median  $\text{O}_3$ . Model results and measurements both show relatively high isoprene during the afternoon followed by a rapid decrease after sunset. Model results and measurements also show relatively high  $\text{NO}_x$  at night and lower  $\text{NO}_x$  during the afternoon. The model and measurements both show much higher  $\text{NO}_x$  and  $\text{O}_3$  for events with transport from the south. The main differences between model results and measurements concern morning  $\text{NO}_x$  and isoprene. Measured  $\text{NO}_x$  peaks sharply at 0800–0900 LT, a feature not reproduced by the model. The model also erroneously predicts high isoprene immediately after sunrise.

[33] By contrast, there are large differences between measured and model values for daytime OH (Figure 6). Model values are lower than measurements by a factor of 2 or more. The model also overestimates daytime  $\text{HO}_2$  by  $\sim 30\%$  in comparison with measurements (Figure 7), and sharply underestimates the OH/ $\text{HO}_2$  ratio. This result is consistent with the analysis by Tan *et al.* [2001]. Tan *et al.* used a zero-dimensional calculation driven by measured concentrations of long-lived species (isoprene,  $\text{O}_3$ , etc.). The resulting OH was much lower than measured values. The model shown here reproduces these results. Calculations with correct values for the species that determine the major sources and sinks of OH cannot generate OH that is consistent with observed daytime values during the Pellston experiment.

[34] The difference between model and measured daytime OH is worrisome because erroneous OH is likely to affect the model results for other species (e.g., isoprene). This level of divergence between model and measurements is typical for OH experiments, but it is more common for model OH to be higher than measured values [Poppe *et al.*, 1994; Eisele *et al.*, 1996; McKeen *et al.*, 1997;

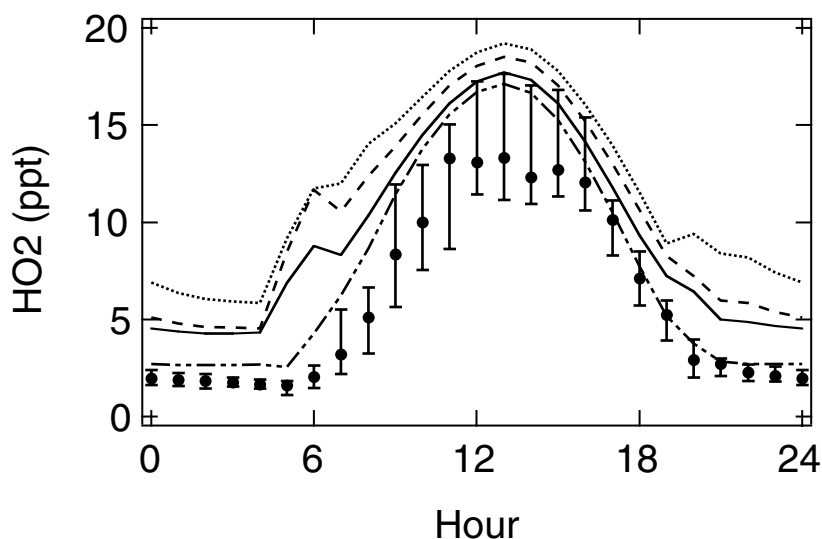
George *et al.*, 1999; Frost *et al.*, 1999; Carslaw *et al.*, 1999]. Volz-Thomas and Kolahgar [2000] also reported a case where measured OH was higher than modeled.

[35] Results for other secondary species during the daytime are summarized in Table 1. The model tends to overestimate methylvinylketone and methacrolein in comparison with measurements and underestimates HCHO. Each of these species is generated mainly from biogenic precursors (usually isoprene) in the model for Pellston, although HCHO is also generated from anthropogenic sources (see discussion of HCHO by Sumner *et al.* [2001]). Methylvinylketone and methacrolein are both removed primarily by reaction with OH, while HCHO is removed largely by photolysis (although it also reacts with OH). Thus the model overestimate for methylvinylketone and methacrolein could plausibly be the result of underestimated OH.

[36] The major features of the nighttime measurements [Faloona *et al.*, 2001] were surprisingly high OH (0.04 ppt median) combined with low  $\text{HO}_2$  (2 ppt). Summed  $\text{HO}_2 + \text{RO}_2$ , measured in 1997, was also low at night (3–6 ppt). Model calculations using standard emission of monoterpenes (represented as  $\alpha$ -pinene and limonene) generate significant nighttime OH (0.02 ppt), although still lower than observed. Faloona *et al.* [2001] reported that high nighttime OH could be explained by fast-reacting terpenes (e.g.,  $\alpha$ -Terpinene), which react rapidly with  $\text{O}_3$  to form OH. In order to test this hypothesis we have repeated the initial model scenarios with the assumption that the emitted monoterpenes consist primarily of these fast-reacting species rather than  $\alpha$ -pinene and limonene. As shown in Figure 6, the model scenarios with fast-reacting terpene have nighttime OH as high or higher than measurements. However, these scenarios have nighttime  $\text{HO}_2$  twice as high as measured values and underestimate the ratio OH/ $\text{HO}_2$ . In addition, the scenarios with fast-reacting terpenes generate extremely high  $\text{RO}_2$  (see Figure 7). No such high  $\text{RO}_2$  was observed. Model scenarios with zero monoterpenes generate nighttime  $\text{HO}_2$  and  $\text{RO}_2$  in agreement with measured values but with very low OH (0.003 ppt).

[37] A final feature of nighttime chemistry concerns the difference between model scenarios with transport over Lake Michigan and scenarios in which air arrives at Pellston following transport primarily over land. As shown in Figure 3, the scenarios with lake transport have low nighttime isoprene, typically 10 times lower





**Figure 7.** HO<sub>2</sub> (ppt) versus time of day (hours, LT) measured at Pellston during summer 1998 compared with model values. Measured values represent the hourly median (solid circles), and upper and lower 67th percentiles (vertical bars) for north trajectory events. Model values represent the west trajectory standard scenario (solid line), scenario in which half the emitted terpenes are represented by fast-reacting species (dashed line), scenario in which all the emitted terpenes are represented by fast-reaction species (dotted line), and scenario with zero terpenes (dashed-dotted line).

than in the scenarios with transport over land. Nighttime isoprene will be discussed in detail in section 6.

## 6. Loss of Isoprene at Night

[38] Two results of the Pellston experiment are especially worthy of attention: the sharp decrease in measured isoprene after sunset and the unexpectedly high nighttime OH. *Hurst et al.* [2001] and *Faloona et al.* [2001] have both suggested that reaction with OH might account for a significant part of the observed decrease in isoprene at night. As shown in section 5, the observed decrease of isoprene also appeared in model calculations. Here, model results are used to analyze possible causes of the loss of isoprene.

[39] Three factors are likely to contribute to the loss of isoprene at night: (1) chemical removal, largely through reaction of isoprene with OH; (2) vertical dispersion, as high surface isoprene in the early evening mixes with lower isoprene aloft; and (3) advection of low-isoprene air from Lake Michigan. There is significant evidence in support of each of these possibilities. Other possibilities include chemical removal of isoprene through reaction with O<sub>3</sub> and with NO<sub>3</sub>, but these are not likely to be important at Pellston (see discussion by *Hurst et al.* [2001]). The process of isoprene removal through NO<sub>3</sub> should properly be seen as a two-reaction sequence, initiated by the rate-limiting reaction NO<sub>2</sub> + O<sub>3</sub> → NO<sub>3</sub>, and followed by reaction of NO<sub>3</sub> with isoprene. Conversion of NO<sub>3</sub> to NO<sub>2</sub> occurs on a timescale of 10 hours. Since isoprene and NO<sub>2</sub> in the early evening have similar concentrations (1 ppb), the lifetime of isoprene with respect to NO<sub>3</sub> must be longer than 10 hours. Model

results show a removal rate for isoprene through NO<sub>3</sub> equal to 0.05 hr<sup>-1</sup> if no terpenes are present, and much slower if terpenes are present. The rate of reaction of isoprene with O<sub>3</sub> implies a lifetime of 25 hours for typical nighttime levels of O<sub>3</sub> (40 ppb). Neither of these can account for the observed rapid decrease of isoprene at Pellston.

[40] The hypothesis that reaction with OH represents the dominant loss mechanism for isoprene at night is supported by two features: (1) observed isoprene at night shows a pattern of apparent exponential decay, and (2) observed OH at night implies a chemical loss rate that is comparable to the observed rate of decay. The measured isoprene between 1900 and 0400 LT (see Figures 3 and 10) can be fitted to a log linear pattern in time ( $\ln c = a_0 + a_1 t$ , for concentration  $c$ , time  $t$ , and regression coefficients  $a_0$  and  $a_1$ ). The resulting least squares estimate for the decay rate ( $a_1$ ) is 0.42 hr<sup>-1</sup>. The loss rate for isoprene from reaction with OH, based on median measured OH for this time period (0.04 ppt), is similar to this observed decay rate. The observed exponential decay of isoprene and inferred loss through reaction with OH is discussed in more detail by *Hurst et al.* [2001] and *Faloona et al.* [2001]. The major weakness of this hypothesis concerns the need to identify a source of nighttime OH that would not be confined to a shallow surface layer. Model calculations can generate OH comparable to observed levels, but the high nighttime OH only appears in the model within 25 m of the forest canopy. If chemical removal of isoprene were limited to this region, then the lost isoprene would be replaced by mixing from aloft. Vertical mixing on a spatial scale of 25 m occurs on a timescale shorter than 1 hour.

[41] If vertical mixing were the dominant loss mechanism for isoprene, then the observed loss rate would be fastest in the early

**Table 1.** Comparison Between Measurements and Model Results for Secondary Species<sup>a</sup>

	Measurements		Model			
	North	SW/SE	NNW	West	SW	South
Methylvinylketone, ppb	.13	.41	.41	.41	.37	.65
Methacrolein, ppb	.15	.45	.33	.26	.30	.46
HCHO, ppb	2.3	3.9	0.8	1.4	2.2	3.0

<sup>a</sup> Measurements represent median values at 1300 LT (Eastern Standard Time) for the north trajectory category and the combined southwest and southeast categories; model results are shown for all four trajectories.

**Table 2.** Pseudo-First-Order Isoprene Loss Rates From Measurements and Model Scenarios<sup>a</sup>

	Hour Interval, LT <sup>b</sup>			OH, ppt <sup>c</sup>
	1900–2300	2300–0300	1900–0300	
Measurements	.61	.24	.42	.044
Model <sup>d</sup>				
Zero terpenes	.38	.15	.27	.003
Standard scenario	.41	.17	.29	.010
Half fast-reacting terpenes	.48	.19	.33	.036
All fast-reacting terpenes	.58	.26	.42	.080
Constrained high OH	.84	.50	.67	.042

<sup>a</sup> Loss rate is determined by least squares fit of measured data and/or model results to the log linear equation,  $\ln c = a_0 + a_1 t$  for concentration  $c$  and time  $t$  over the given time interval. The regression coefficient  $a_1$  represents the pseudo-first-order decay rate.

<sup>b</sup> Units are in  $\text{hr}^{-1}$ .

<sup>c</sup> OH values for the measurements were measured between 1900 and 0300, and model OH values are at 0–25 m elevation in each model scenario.

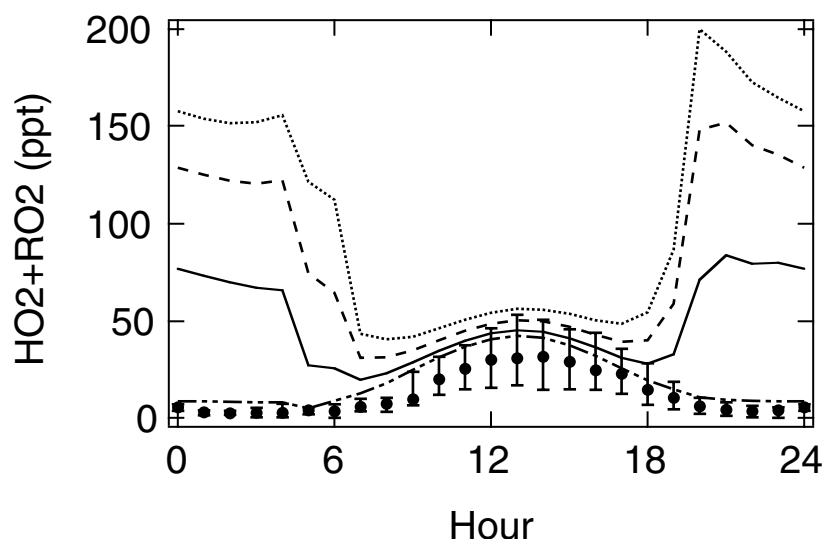
<sup>d</sup> Model results are for the NNW trajectory.

evening and slower during the later hours. The observed isoprene provides some evidence that this is the case. The loss rate for isoprene between 1900 and 2300 LT (using a least squares fit to a log linear pattern) is  $0.62 \text{ hr}^{-1}$ , while the loss rate between 2300 and 0300 LT is  $0.24 \text{ hr}^{-1}$  (see Table 2). The slower loss rate of isoprene after 2300 LT is also visible in Figure 3 (see also Figure 10) and in results reported by *Hurst et al.* [2001] (Figure 8). There is no comparable decrease in measured OH between these time periods. When compared with the chemical loss rate of isoprene relative to OH ( $0.36 \text{ hr}^{-1}$ ), these loss rates would imply that an additional process was acting to increase the loss rate of isoprene during the early evening and compensate for chemically removed isoprene in the later evening. This behavior would be consistent with vertical mixing. Model results, discussed below, also provide evidence for vertical mixing.

[42] The major weakness of vertical mixing as a sink for isoprene concerns the inability to explain the very low measured isoprene concentrations ( $<0.1 \text{ ppb}$ ). Vertical dispersion at nighttime can lead to near-surface isoprene concentrations that are comparable to the concentrations at 100–300 m altitude. Measured vertical

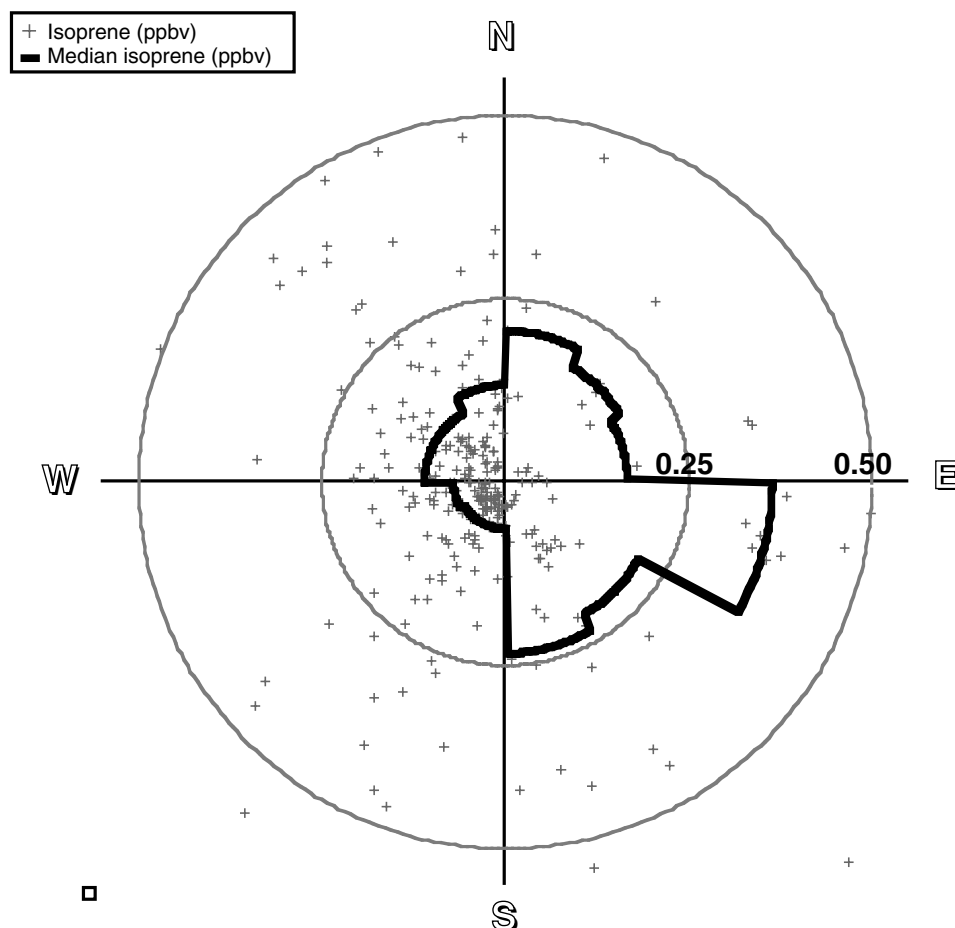
profiles [*Andronache et al.*, 1994; *Guenther et al.*, 1996a, 1996b] show that isoprene at 100–300 m is typically lower than isoprene just above the forest canopy during the daytime but only by a factor of 2. The current modeling exercise predicts a sharper vertical gradient of isoprene at Pellston, largely because in situ emissions at the Pellston site are much higher than in the surrounding region (see Figure 2). The model also predicts a sharper vertical gradient toward sunset, because vertical mixing is much slower and surface emission of isoprene persists (see Figure 2). However, isoprene in the model remains at 0.3–0.5 ppb in the early evening if there is no transport from Lake Michigan (see Figures 2 and 3). If there were no other sinks for isoprene, then isoprene would remain at this level throughout the evening.

[43] There is evidence from observations that isoprene does decrease rapidly with height at Pellston. As reported by *Hurst et al.* [2001] and *Westberg et al.* [2001], isoprene aloft was measured at Pellston during summer 1998 on four occasions (at 1230, 1500, 1730 and 1830 LT on 14 August, 16 August, 26 July, and 20 July, respectively). Ratios of isoprene aloft to surface isoprene from these four sets of measurements are shown in



**Figure 8.**  $\text{HO}_2 + \text{RO}_2$  (ppt) versus time of day (hours, LT) measured at Pellston during summer 1997 compared with model values. Measured values represent the hourly median (solid circles), and upper and lower 67th percentiles (vertical bars). Model values represent the west trajectory standard scenario (solid line), scenario in which half the emitted terpenes are represented by fast-reacting species (dashed line), scenario in which all the emitted terpenes are represented by fast-reaction species (dotted line), and scenario with zero terpenes (dashed-dotted line).

## Isoprene (2300-0500 LT) vs Local Wind Direction



**Figure 9.** Wind rose showing measured isoprene during the hours 2300 to 0500 LT versus wind direction. The points (plus signs) show individual measurements. The bold solid line represents the median of measured values for each  $30^\circ$  interval in wind direction.

comparison with previously measured vertical profiles and with model values in Figure 2. Although this data set is limited, it appears that isoprene decreases more rapidly with height at Pellston than was found in the more extensive measurements at Rose, as reported by *Andronache et al.* [1994] and in similar measurements by *Guenther et al.* [1996a, 1996b]. The measurements at Pellston are also consistent with the decrease of isoprene with height in the model.

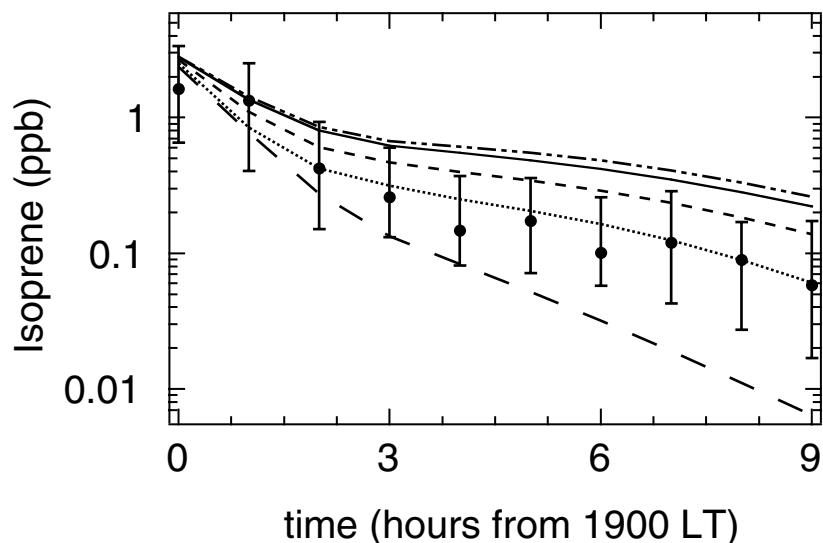
[44] The possibility that nighttime isoprene at Pellston is influenced by advection from Lake Michigan is supported by the measured correlation between isoprene and wind direction. Model results (Figure 3) predict that isoprene during the early evening should have similar concentrations and show a similar decrease with time regardless of wind direction. In the later evening, very low isoprene concentrations are predicted in association with transport from Lake Michigan, while isoprene would remain higher (0.3–0.5 ppb) in the absence of such transport. Measurements (Figure 9) show that during the hours of 2300 to 0500 LT, isoprene is strongly correlated with wind direction. Median isoprene between 2300 and 0500 LT is 0.06 ppb when winds are from the southwest quadrant, 0.13 ppb when winds are from the northwest, and 0.2–0.3 ppb when winds are from the southeast or northeast. Measured isoprene below 0.1 ppb are associated primarily, but not exclusively, with winds from the west and southwest. This varia-

tion in measured isoprene with wind speed is broadly consistent with model predictions for nighttime isoprene in the model west and NNW trajectories (0.05 ppb, west; 0.4 ppb, NNW).

[45] Advection from upwind source regions other than Lake Michigan can also make minor contributions to the observed nighttime decrease in isoprene at Pellston. Isoprene emission rates within 50 km of Pellston (excluding the Great Lakes) are generally twice as high as emission rates in the boreal forest ecosystem farther north, or in the less forested regions of southern Michigan. Advection from these regions has a modest impact ( $0.1 \text{ hr}^{-1}$  in models), but it may explain some of the observed decrease in isoprene during the late evening.

[46] The major difficulty with hypothesized lake transport as a cause of low isoprene is that it cannot explain measured low isoprene concentrations at times when winds are not coming from Lake Michigan. In addition, isoprene has been observed to decrease at night at several other sites in addition to Pellston (see summary by *Hurst et al.* [2001]). These include some locations (e.g., Harvard, Massachusetts) that are unlikely to be influenced by transport from the ocean or Great Lakes. Model results show that the impact of lake or ocean transport on nighttime isoprene is unlikely to extend more than 100 km inland.

[47] In order to evaluate this further, we will compare results of model scenarios with varying levels of nighttime OH. These



**Figure 10.** Isoprene at night versus time (hours after 1900 LT) measured at Pellston during summer 1998 compared with model values. Measured values represent the hourly median (solid circles) and upper and lower 67th percentiles (vertical bars) for north trajectory events. Model values represent the west trajectory standard scenario (solid line), scenario in which half the emitted terpenes are represented by fast-reacting species (short-dashed line), scenario in which all the emitted terpenes are represented by fast-reacting species (dotted line), scenario with zero terpenes (dashed-dotted line), and scenario with nighttime OH constrained to be 0.04 ppt (long-dashed line).

include a scenario with zero terpenes and negligibly small OH, the standard scenario (0.01 ppt nighttime OH in the lowest model layer), scenarios with varying amounts of fast-reacting terpenes (0.04 and 0.09 ppt OH), and a scenario with nighttime OH constrained to be 0.04 ppt (the observed median value at Pellston) throughout the model domain. Nighttime OH is effectively much higher in the scenario with constrained OH, because in the other scenarios high nighttime OH only occurs in the lowest model layer (0–25 m.). Results (Figure 10) are for the NNW trajectory, which has minimal impact from lake transport.

[48] Results suggest that production of OH at night from terpenes can have some impact on isoprene, but it is not the major cause of the observed nighttime decrease. In the model scenario with zero terpenes and low OH, isoprene decreases by a factor of 5 between 1900 and 1200 LT (from 2.8 to 0.6 ppb). In the scenarios with fast-reacting terpenes, isoprene is decreased to 0.3 ppb (with 0.04 ppt OH) or to 0.2 ppb (with 0.08 ppt OH). The scenario with constant 0.04 ppt nighttime OH has isoprene decreased to a much lower level (0.05 ppb). Measured isoprene show best agreement with results from the model scenario with fast-reacting terpenes, but the scenarios with low nighttime OH also shows reasonable agreement with measurements. The scenarios with low OH have higher nighttime isoprene than the measured median, but the lowest nighttime isoprene is generally associated with lake transport (see Figure 9).

[49] The results in Figure 10 can be expressed more quantitatively by deriving a pseudo-first-order decay rate for isoprene, based on measurements and model results for each time interval. This is done by performing a least squares fit to the log linear equation,  $\ln c = a_0 + a_1 t$ , for concentration  $c$  and time  $t$ . The regression coefficient  $a_1$  represents the pseudo-first-order decay rate for the given time interval. Results are shown in Table 2 for the time intervals 1900–2300, 2300–0300, and 0700–0300 LT for each model scenario and for measured values. The measured decay rate from 1900 to 0300 LT ( $.42 \text{ hr}^{-1}$ ) is comparable to the decay rate in the model scenario with all fast-reacting terpenes ( $.42 \text{ hr}^{-1}$ ) and somewhat higher than the decay rate in the scenario with zero terpenes ( $.27 \text{ hr}^{-1}$ ). The model scenario with constrained 0.04 ppt OH has a higher decay rate ( $.64 \text{ hr}^{-1}$ ). Decay rates are much faster for the early evening (1900–2300 LT) than for the late evening

(2300–0300 LT) in all model scenarios. Measurements also show a faster decay rate for the early evening.

[50] The rate of removal of isoprene associated with OH chemistry is a critical issue for evaluating the impact of OH. *Hurst et al.* [2001] and *Faloona et al.* [2001] both argued that the impact of OH is equal to the pseudo-first-order rate of the isoprene-OH reaction for the measured OH concentration ( $.36 \text{ hr}^{-1}$ ). Here model calculations suggest that the impact of nighttime OH on isoprene is actually much smaller. The removal rate associated with OH chemistry in model scenarios is equal to the difference between the isoprene decay rate in each scenario and the decay rate in the scenario with very low nighttime OH (zero terpene scenario). Referring to the 1900–0300 LT time interval in Table 2, the isoprene removal attributed to OH is  $0.40 \text{ hr}^{-1}$  for the scenario with constrained 0.04 ppt OH. This rate is comparable to the pseudo-first-order rate of the isoprene-OH reaction for the given OH concentration ( $.36 \text{ hr}^{-1}$ ). By contrast, the isoprene removal attributed to OH in the scenarios with fast-reacting terpenes are  $0.06 \text{ hr}^{-1}$  (with 0.04 ppt near-surface OH) and  $0.15 \text{ hr}^{-1}$  (with 0.08 ppt OH). These removal rates are 5 times lower than the pseudo-first-order rate constants based on near-surface OH concentrations.

[51] Nighttime OH has a limited impact on isoprene in the model scenarios with OH generated by terpene chemistry, because OH in these scenarios is limited to a shallow surface layer (0–25 m above the forest canopy). The impact of this OH is limited by dilution over the effective height of mixing at night. Assuming a vertical eddy diffusion coefficient of  $0.6 \text{ m}^2 \text{ s}^{-1}$  and a 5-hour time period, the effective mixing height is 104 m. Thus the impact of OH would be diluted by roughly a factor of 4 relative to its near-surface value.

[52] Results of this modeling exercise suggest that the observed decrease in isoprene at night is due primarily to vertical diffusion rather than OH chemistry, although OH can be a contributing factor. This interpretation is consistent with many features of the Pellston measurements. The measured rate of decrease in isoprene at night and the faster rate of decrease in the early evening are both consistent with results from models with near-zero OH and few other chemical sinks of isoprene. These findings are consistent with the previous analysis by *Makar et al.* [1999]. Makar et al. performed a similar model-based analysis of ambient isoprene at a

site in Ontario, using more detailed vertical resolution. They also found that OH radicals can be generated at night, but that the observed decrease in isoprene during the early evening was due to vertical diffusion rather than chemical removal. These results are likely to be relevant to patterns of nighttime isoprene reported elsewhere [Biesenthal *et al.*, 1998; Starn *et al.*, 1998].

[53] Because nighttime OH has limited impact on isoprene, it is difficult to derive evidence about nighttime OH from the observed isoprene decay rate. The difference in the isoprene decay rate between model scenarios with near-zero OH and with OH close to observed levels is too small ( $.27 \text{ hr}^{-1}$  versus  $33 \text{ hr}^{-1}$ ) to provide evidence about the presence or absence of OH. However, results from model scenario with prescribed nighttime OH might be interpreted as evidence that the OH measured by Faloona *et al.* [2001] does not persist throughout the nocturnal boundary layer. The combined impact of dynamics and elevated OH in this scenario generate an isoprene removal rate that is significantly faster than observed.

[54] Faloona *et al.* [2001] and Hurst *et al.* [2001] have both suggested that the impact on nighttime OH on isoprene may be larger than shown here. Hurst *et al.* found that the combined impact of vertical diffusion and OH chemistry (assuming that OH is constant throughout the nocturnal boundary layer) would result in a removal rate for isoprene that is faster than observed but suggested that the difference might be due to nighttime emission of isoprene. Faloona *et al.* [2001] found that day-to-day variations in the isoprene decay rate could not be correlated with nighttime Obukhov lengths. In the current modeling exercise the loss of isoprene attributed to vertical diffusion is dependent on the assumed diffusion rates, especially during the early evening.

[55] The uncertainty concerning nighttime isoprene might be resolved by measuring isoprene vertical profiles during the evening hours and comparing measured values with model predictions. The current model scenarios generate the following predictions concerning isoprene vertical profiles: (1) Isoprene decreases sharply with height from 0 to 200 m above the forest canopy during the early evening. (2) This vertical gradient in isoprene largely disappears by midnight in model scenarios with and without nighttime OH, so long as there is no transport from Lake Michigan. (3) In scenarios with transport from Lake Michigan a sharp vertical gradient in isoprene persists until midnight or later. (4) Isoprene at 100 m decreases by a factor of 2 between 1900 and 0000 LT in scenarios without transport from Lake Michigan. Isoprene at 100 m decreases by a factor of 5 or more between 1900 and 0000 LT only in scenarios with transport from Lake Michigan. (5) Isoprene increases with height in the late evening only if there is chemical removal associated with surface emissions. This occurs in model scenarios with OH generated from terpenes, but it also occurs in the model south trajectory even with zero OH (due to the isoprene- $\text{NO}_3$  reaction).

[56] The above predictions provide a test for the model and also identify possible evidence for the impact of nighttime chemistry. A measured increase in isoprene with height would provide evidence for chemical removal of isoprene near the surface. The rate of decrease of isoprene at 100 m would provide evidence for the wider impact of nighttime chemistry. The results shown here suggest that chemical removal of isoprene is limited to a shallow surface layer and, consequently, has limited impact. This claim would be refuted only if it were found that isoprene at 100 m also decreases rapidly during the evening hours in events without transport from Lake Michigan.

## 7. Conclusions

[57] The 1-D Lagrangian model described here was used primarily to investigate conditions associated with the observed decrease in isoprene at night and the possible impact of nighttime OH at Pellston. A series of scenarios was developed in order to

represent the most important features of dynamics and photochemistry at Pellston: local and regional emissions, vertical mixing, and transport from Lake Michigan. Comparison with measurements show that the model is able to reproduce many important features relating to isoprene chemistry, including the isoprene daytime concentrations, evening decrease, and vertical profiles. Model results also show reasonable agreement in comparison with measured  $\text{NO}_x$  and  $\text{O}_3$ . Model OH concentrations and the OH/ $\text{HO}_2$  ratio were both lower than measured values by a factor of 2 or more, a result consistent with the previous investigation of OH at Pellston by Tan *et al.* [2001]. The model also fails to provide a satisfactory explanation for the observed high nighttime OH at Pellston.

[58] Nighttime loss of isoprene is attributed to three factors: chemical reaction with OH, vertical diffusion, and advection from Lake Michigan. Model results suggest that the observed loss of isoprene can be explained primarily by vertical diffusion. Nighttime OH has a smaller impact on isoprene than would be inferred from its measured concentration because high nighttime OH is likely to be confined to a shallow surface layer. Model results show that OH generated by nighttime terpene chemistry (the source of nighttime OH hypothesized by Faloona *et al.* [2001]) would only be present near the surface. The removal rate of isoprene attributed to this OH would be 5 times lower than the rate implied by pseudo-first-order chemical rate constants derived from surface OH concentrations. Alternatively, if OH as high as the measured concentrations persisted throughout the nocturnal boundary layer, then the predicted removal rate for isoprene would be much higher than the observed rate. These results suggest that the high nighttime OH observed at Pellston is linked to nighttime emissions or other surface processes, and is unlikely to persist at higher elevations.

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