Investigation of isoprene dynamics during the day-to-night transition period

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1. Low turbulent mixing during clear and calm nights leads to accumulation of isoprene within the canopy

2. Turbulent mixing accounts for 80% of the observed nighttime isoprene loss rates

3. Isoprene flux measurements did not capture the majority of the removel of the accumulated isoprene

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Abstract

At the University of Michigan Biological Station during the 2016 AMOS field campaign, isoprene concentrations typically peak in the early afternoon (around 15:00 local time, LT) under well-mixed conditions. However, an end-of-day peak (around 21:00 LT) occurs on 23% of the campaign days, followed by a rapid removal (from 21:00 - 22:00 LT) at rate of 0.57 hr^{-1} during the day-to-night transition period. During the end-of-day peak, in-canopy isoprene concentrations increase by 77% (from 3.5 ppbv to 6.2 ppbv) on average. Stratification and weak winds (< 3.4 m s^{-1} at 46 m) significantly suppress turbulent exchanges between in- and above-canopy, leading to accumulation of isoprene emitted at dusk. A critical standard deviation of the vertical velocity (σ_w) of 0.14, 0.2, and 0.29 m s^{-1} is identified to detect the end-of-day peak for the height of 13, 21, and 34 m, respectively. In 85% of the end-of-day cases, the wind speed increases above 2.5 m s^{-1} after the peak along with a shift in wind direction, and turbulence is re-established. Therefore, the wind speed of 2.5 m s^{-1} is considered as the threshold point where turbulence switches from being independent of wind speed to dependent on wind speed. The reinstated turbulence accounts for 80% of the subsequent isoprene removal with the remaining 20% explained by chemical reactions with hydroxyl radicals, ozone, and nitrate radicals. Observed isoprene fluxes do not support the argument that the end-of-day peak is reduced by vertical turbulent mixing, and we hypothesize that horizontal advection may play a role.

1 Introduction

Isoprene accounts for almost half of the non-methane biogenic volatile organic compound (BVOCs) fluxes emitted to the atmosphere globally (Guenther et al., 2012). Isoprene substantially influences hydroxyl radical (OH) concentration in the atmosphere and thus atmospheric oxidative capacity and tropospheric chemistry (Taraborrelli et al., 2012; Fuchs et al., 2013). In addition, because of the large flux of isoprene into the atmosphere (Guenther et al. 2012), oxidation of isoprene is a significant source of secondary organic aerosols (SOA) with implication for air quality and climate (Claeys, 2004; Robinson et al., 2011). While daytime isoprene has been studied thoroughly, its day-to-night transition has received little attention. The near-zero emissions during the transition period allow us to better quantify processes responsible for isoprene loss, which is critical for accurate estimation of nighttime chemistry and SOA formation (especially nitrate SOA; Ng et al. 2008).

Daytime isoprene concentrations shows pronounced diurnal cycles with a peak in the early afternoon (around 15:00 local time) in response to sources (e.g. emission) and sinks (e.g. turbulent mixing and chemical reactions). Isoprene emission from plants is linked to photosynthesis and thus highly temperature- and light-dependent. As a result, isoprene emission peaks around noon and shuts down after sunset (Guenther et al., 1993). After being emitted into the atmosphere, isoprene is redistributed by turbulent mixing and at the same time chemically consumed by OH, ozone (O_3), and nitrate radicals (NO_3). Since the O_3 reaction is slow ($\tau = 30$ h at $[O_3] = 30$ ppbv) and NO_3 mainly exists at night, OH is considered to be the major chemical sink of isoprene during the daytime (Levy, 1971; Lelieveld et al., 2008). OH is photolytically produced and its concentrations drop significantly at sunset due to reduced radiation. Given that the loss of isoprene to OH diminishes towards the end of the day ($\tau = 11.5$ hours at $[OH] = 2.42 \times 10^5$ molecules cm^{-3}, 2016 AMOS campaign average for 19:00 local time), turbulent mixing of isoprene emitted close to dusk plays an important role in shaping the nocturnal isoprene mixing ratios.

An End-Of-Day (EOD) peak was frequently observed around 21:00 local time (LT) during the AMOS (Atmospheric Measurements of Oxidants in Summer) field campaign, followed by a precipitious decay in isoprene from 21:00 - 22:00 LT (Fig. 1a). In this study, we aim to (i) characterize the EOD peak and understand its origin and (ii) constrain the possible mechanisms responsible for the rapid decline in isoprene. As for the EOD peak, previous field studies have reported elevated surface isoprene concentrations during the early evening in various locations (Martin et al., 1991; Montzka et al., 1993; Goldan et al., 1995; Starn et al., 1998). Martin et al. (1991) observed that peak isoprene concentrations at Scotia, Pennsylvania, occurred at 20:00 local time, at levels 2-3 times those observed at noon. Starn et al. (1998) interpreted elevated isoprene concentrations as a result of

₇₁ advective transport to the measurement site. But little quantitative explanations for the
₇₂ EOD isoprene peak are provided by previous studies. As for the subsequent decay, rapid
₇₃ isoprene removal during the day-to-night transition period has been frequently observed in
₇₄ forested environments. Due to the lack of constraints from reliable measurements, the cause
₇₅ of this rapid decrease in isoprene has been attributed to chemical loss (Faloona et al., 2001)
₇₆ or dynamics (Sillman et al., 2002; Apel, 2002). Hurst et al. (2001) estimated that either OH
₇₇ or vertical mixing could be the reason for this phenomenon, but no direct measurements
₇₈ were available to differentiate the two processes. Faloona et al. (2001) observed abnormally
₇₉ high OH concentrations at night, suggesting OH was responsible for the rapid decay in
₈₀ isoprene, but interferences for this OH instrument were later reported (Feiner et al., 2016).
₈₁ Apel (2002) and Sillman et al. (2002) postulated vertical dilution or horizontal advection
₈₂ could explain the rapid removal, but no turbulence data existed to support the speculation.

₈₃ During the day-to-night transition period, organization of canopy flows in forested sites
₈₄ falls into two major categories: (i) well-mixed conditions where the turbulence is continuous
₈₅ down to the ground; (ii) more stable conditions as the canopy begins to cool, characterized
₈₆ by a temperature inversion and turbulence suppressed on all scales (Mahrt, 1999). Onclear
₈₇ and calm nights, thermal stratification and weak mechanical production of turbulence favor
₈₈ the generation of such stable conditions (B. Van de Wiel et al., 2012; Van de Wiel et al.,
₈₉ 2012) under which the above- and in-canopy air layer exchanges are significantly weakened
₉₀ (commonly known as decoupling). Early-evening decoupling has been observed frequently
₉₁ (at least 31% of the summer nighttime periods, Alekseychik et al. 2013) at various forested
₉₂ sites (Burns et al., 2010; van Gorsel et al., 2011; Alekseychik et al., 2013; Oliveira et al.,
₉₃ 2012). Smaller biogenic fluxes and larger gradients in temperature and scalar concentration
₉₄ between above- and in-canopy layers coincide with decoupling conditions due to reduced
₉₅ mixing (Alekseychik et al., 2013; Oliveira et al., 2012).

₉₆ However, overnight turbulence generation can lead to a breakdown of the decoupling
₉₇ state, allowing for re-coupling and mixing between the canopy interior and the air above
₉₈ it (Oliveira et al., 2012; Alekseychik et al., 2013). During the aforementioned decoupling
₉₉ period, nonstationary motions (such as density currents, drainage flow, and canopy waves)
₁₀₀ dominate (Mahrt et al., 2012; Sun et al., 2012) and turbulence is weak, intermittent and
₁₀₁ independent of the mean wind speed (Liang et al., 2014). However, evidence suggests
₁₀₂ that there is a "threshold" point at which stable-condition turbulence switches from being
₁₀₃ independent of wind speed to being dependent on wind speed (Mahrt et al., 2012; Sun et
₁₀₄ al., 2012; Liang et al., 2014). The resultant wind-induced turbulence significantly affects
₁₀₅ the nighttime vertical profile of scalars as well as scalar flux determination (Oliveira et al.,

106 2012). Therefore, wind speed and the resultant turbulence are then expected to influence
107 the vertical gradient of isoprene during the transition period.

108 The 2016 AMOS campaign at UMBS (University of Michigan Biological Station) pro-
109 vide detailed measurements of isoprene and its oxidants (i.e. OH, NO_3, O_3) as well as
110 meteorological and turbulence data, which allow us to fill in the gaps in our knowledge of
111 the chemical and physical processes governing isoprene dynamics during the day-to-night
112 transition period. In the present study, we compare two distinct isoprene patterns during
113 the transition period to show the characteristics and origin of the EOD isoprene peak. We
114 also discuss and constrain possible mechanisms for the subsequent isoprene removal to il-
115 luminate the relative importance of turbulence and chemistry on nocturnal distribution of
116 reactive gases in forested environment.

2 Methods

2.1 Study site

119 The 2016 AMOS (Atmospheric Measurements of Oxidants in Summer) field campaign
120 was conducted in the UMBS (University of Michigan Biological Station) site located near
121 the northern end of the lower peninsula of Michigan, US during the month of July. The
122 UMBS site is a mixed deciduous/coniferous forest and isoprene-dominated (Millet et al.,
123 2018). It is surrounded by the Great Lakes, with Lake Superior 21 km to the north, Lake
124 Michigan 35 km to the west, and Lake Huron 42 km to the east. In addition, there are
125 smaller lakes scattered within 3 km of the site. For example, Douglas lake is less than 200
126 meters to the north of the UMBS site and Burt Lake is about 2.5 km south of the site. There
127 was little indication of local anthropogenic pollution in the surrounding area during the field
128 campaign (NO<0.1 ppbv), although the region is frequently impacted by the transport of
129 NO_X from urban areas to the south and west (e.g., Milwaukee, Chicago, Detroit; Cooper
130 et al., 2001; VanReken et al., 2015) as well as long-range transport of smoke pollution from
131 Canada (Cooper et al., 2001; Gunsch et al., 2018). The 31 m PROPHET (Program for
132 Research on Oxidants: PHotochemistry, Emissions, and Transport) tower extends to 34 m
133 with a triangle tower on top. The canopy height surrounding the tower is about 22.5 m.

2.2 Measurements

135 Turbulence data (10 Hz) were collected at 5 heights on the PROPHET tower: 34 m
136 (CSAT 3B, Campbell Scientific Inc.), 29 m (81000, RM Young), 21 m (CSAT 3, Campbell
137 Scientific Inc.), 13m (CSAT 3, Campbell Scientific Inc.), and 5 m (CSAT 3, Campbell
138 Scientific Inc.). High-frequency data outside of 3.5-standard deviations were removed and

139 data then were separated into 30-minute windows to apply a tilt correction (Foken, 2009).
140 The 30-minute periods that experienced rain (as measured by the rain-gauge at the UMBS
141 AmeriFlux tower), weak winds (< 0.5 m s^{-1} at the top sonic anemometer), and wind
142 directed through the tower were excluded due to potential interference. Other meteorologial
143 measurements (at 46 m) used here include photosynthetic photon flux densities (PPFD)
144 measured at the US-UMB Ameriflux tower (about 130 m from the PROPHET tower) using
145 a BF5 Sunshine Sensor (Delta-T Devices Ltd.), air temperature measured with a Vaisala
146 HMP-60 in a 6-plate radiation shield at the top of the PROPHET tower, and wind speed
147 and direction.

148 Measurements of isoprene and other VOCs were performed by PTR-QiTOF (Ionicon
149 Analytik, GmbH) from 6 sampling heights on the PROPHET tower: 34, 21, 17, 13, 9,
150 and 5 m (Millet et al., 2018; Alwe et al., 2019). The measurement sequence cycled hourly
151 between these inlets using a custom-built automated sampling manifold, with 30 min per
152 hour spent sampling from the 34 m inlet and 5 min per hour from the remaining five inlets.
153 The remaining 5 min of each hour was used to perform a measurement blank. It is therefore
154 an approximation to treat the vertical gradient of isoprene as a complete gradient at a
155 single point in time, because it reflects sequential measurements. Thirty days of isoprene
156 data were obtained. We excluded the cloudy and rainy days, and identified 7 cases with
157 end-of-day peaks and 7 cases with early-afternoon peaks (hereafter referred to as standard
158 cases). Turbulence measurements performed at the 34 m isoprene sampling inlet were used
159 to compute hourly isoprene fluxes. Details of the isoprene measurements and calibration
160 can be found in Millet et al. (2018).

161 Other chemical measurements at the PROPHET tower implemented in this study in-
162 clude OH (hydroxyl radical) and O_3 (ozone) concentrations. O_3 were measured at 6 m using
163 a Model 205 (2B Technologies, Inc.) dual-beam UV absorption instrument. OH radicals
164 were measured at the top of the PROPHET tower at a height of 32 m using the Indiana
165 University Laser-Induced Fluorescence - Fluorescence Assay by Gas Expansion (LIF-FAGE)
166 instrument (Dusanter et al., 2009). To quantify potential interferences during ambient mea-
167 surements of OH, perfluoropropylene (C_3F_6) was added above the sampling nozzle using an
168 automated injector to chemically remove ambient OH radicals (Griffith et al., 2016; Rickly
169 & Stevens, 2018). Any signal measured during C_3F_6 addition thus provided a quantification
170 of instrumental interferences. During PROPHET-AMOS, no unknown interferences were
171 detected during the campaign using this method.

172 ### 2.3 Data analysis

173 #### *2.3.1 Virtual potential temperature*

174 Virtual potential temperature (θ_v) was calculated using the equation below:

$$\theta_v = \mathrm{T}_v (\frac{p_0}{p})^{\kappa} \tag{1}$$

175 where T_v is the virtual temperature, p_0 is the standard pressure at sea level (1013.25 hPa),
176 p is the air pressure at the height of T_v, and κ is the Poisson constant (0.2854). In the
177 present study, we used the sonic temperature (T_s) from the sonic anemometers as the
178 virtual temperature (T_v) because they are almost equal (Rebmann et al., 2011). Two levels
179 of pressure data (6m and 34 m) are available. The 6 m pressure data was used for the
180 calculations of θ_v within the canopy (at 5 m, 13 m, and 21 m), and the 34 m pressure data
181 for the above-canopy (at 29 m and 36 m) calculations.

182 #### *2.3.2 Turbulent mixing timescale*

183 A mass balance approach was employed to calculate the turbulent mixing timescale for
184 isoprene. Assuming horizontal homogeneity, the mass balance for the isoprene mixing ratio
185 can be expressed as (Freire et al., 2017):

$$\frac{\partial[\mathrm{ISOP}]}{\partial \mathrm{t}} = -\frac{\partial \mathrm{w}'[\mathrm{ISOP}]'}{\partial \mathrm{z}} + S(z) \tag{2}$$

186 where S(z) is the source/sink term. An eddy diffusivity (K) model ($\mathrm{w}'[\mathrm{ISOP}]' = -\mathrm{K}\frac{\partial[\mathrm{ISOP}]}{\partial \mathrm{z}}$)
187 is employed in equation (2) and the term of vertical gradients in eddy diffusivity ($\frac{\partial K}{\partial z}$) is
188 neglected for simplicity and analytical tractability. The assumption of $\frac{\partial K}{\partial z} = 0$ is imposed
189 to the domain h < z < z_0 (h is the canopy height, and z_0 is the top of the stable boundary
190 layer). Then equation (2) reduces to:

$$\frac{\partial[\mathrm{ISOP}]}{\partial \mathrm{t}} = -\mathrm{K}\frac{\partial^2[\mathrm{ISOP}]}{\partial \mathrm{z}^2} + S(z) \tag{3}$$

191 The homogeneous solution (S = 0) to equation (3) represents the time evolution of the
192 isoprene mixing ratio due to turbulent mixing in the domain h < z < z_0. A solution subject
193 to the initial condition [ISOP](z, t = 0) = 0, the lower boundary condition [ISOP](z = h,
194 t) = [ISOP]$_h$, and the upper boundary condition of a zero isoprene flux at z = z_0 is sought.
195 In this case, the transient solution for the isoprene mixing ratio above the canopy can be
196 expressed as Liu (2008):

$$\frac{[\text{ISOP}](z, t)}{[\text{ISOP}]_h} = 1 - \sum_{n=0}^{\infty} \frac{4}{(2n+1)\pi} \exp\left\{-\left(\frac{(2n+1)\pi}{2}\right)^2 \frac{K(z)t}{(z_0 - h)^2}\right\} \sin\left[\frac{(2n+1)\pi}{2} \frac{z - h}{z_0 - h}\right] \quad (4)$$

197 A height-dependent turbulent mixing time scale can be obtained from equation (4) by finding
198 the time required for the isoprene mixing ratio to reach a certain fraction of the imposed
199 value at the top of the canopy. In the present study, the turbulent mixing time scale is
200 defined as the time required for $\frac{[ISOP](z)}{[ISOP]_h} = 0.95$. This value of 0.95 was obtained using
201 the vertical gradients of isoprene observed in the standard (STD) case (see section 2.2) to
202 represent well-mixed conditions. The inverse of the turbulent mixing timescale is then used
203 as the isoprene loss rate associated with turbulent mixing.

3 Results

3.1 End-of-day peak in isoprene

3.1.1 Case studies

207 Here we define two classes of diurnal isoprene profiles: (i) the end-of-day (EOD) case
208 where isoprene increased at dusk (1 of the 7 identified cases displayed in Fig. 1a) and (ii)
209 a standard (STD) diurnal cycle (1 of the 7 identified cases displayed in Fig. 1a). In the
210 STD case, isoprene has a pronounced diurnal cycle with a peak in the early afternoon and a
211 minimum just before sunrise (Fig. 1a). This diurnal pattern of isoprene has been observed
212 in many forests ranging from deciduous to tropical under clear and well-mixed conditions
213 (Apel, 2002; Wei et al., 2018), and is well-captured by models of different scales (de Arellano
214 et al., 2011; Ashworth et al., 2015). During the 2016 AMOS field campaign at UMBS, an
215 end-of-day peak in isoprene was observed during clear and calm days. The peak occurs
216 around 21:00 local time (LT) when the emissions are near-zero (sunset is around 21:30 LT).
217 Isoprene increases by over 3 ppbv from 19:00 LT to 21:00 LT followed by a precipitous
218 decline in the next two hours (Fig. 1a).

219 During the daytime, air temperature in the EOD case is on average 8 °C lower than
220 that in the STD case (Fig. 1d), indicating less surface heating and thus weaker mixing in
221 the EOD case, demonstrated by the decrease in the mid-day standard deviation of vertical
222 velocity (σ_w) by a factor of 2 (Fig. 1c). During the day-to-night transition period, both
223 case studies show clear (cloudless) conditions (Fig. 1b) that favor the radiative cooling
224 of the canopy and thus the development of a more stable boundary layer. In a stable
225 boundary layer, thermal stratification leads to the destruction of turbulence and therefore
226 turbulence production depends on wind shear (Van de Wiel et al., 2012). Van de Wiel et
227 al. (2012) predict that the minimum wind at the crossing level (where the wind is relatively
228 stationary compared to lower and higher levels, typically some decameters above the surface)

for sustainable turbulence at the surface is 5-7 m s^{-1} during the day-to-night transition period. The STD case shows wind speed of 5 m s^{-1} at 46 m that appears to be adequate to sustain turbulent mixing as demonstrated by the relatively high σ_w value of 0.7 m s^{-1} throughout the evening (Fig. 1c, f). In this case, the sustained mixing dominates over the decreasing emission at dusk, leading to decreases in isoprene mixing ratios during the day-to-night transition period.

In the EOD case, however, wind speed is low (around 2 m s^{-1}) and drops to almost zero at 21:00 LT when the end-of-day peak occurs (Fig. 1f), indicating little mechanical production of turbulence at the time. Consequently, the σ_w decreases to less than 0.1 m s^{-1} around 21:00 LT (Fig. 1c). Therefore, we hypothesize that during clear and calm nights, stratification and weak wind suppress turbulent exchanges between the canopy and the air above (also referred to as decoupling), leading to the accumulation of isoprene emitted at dusk in the canopy. In addition to the increase in wind speed, a shift in wind direction from north to south occurs at the same time as the peak, likely influencing the rapid decline of isoprene (Fig. 1f; see section 3.3.1).

3.1.2 Relationship between isoprene mixing ratio and σ_w

To demonstrate the generality of this phenomenon, seven (seven) out of thirty days are identified as EOD (STD) case. The isoprene mixing ratio and σ_w are averaged over all events to show their diurnal evolution (Fig. 2). For the EOD case, in-canopy isoprene begins to increase two hours before the peak that appears at 21:00 LT (Fig. 2a). Due to the time sequencing of the gradient measurements, the actual peak time could be somewhere between 20:35 - 21:00 LT (see section 2.2). Within the two hours, the average in-canopy isoprene increases 77 % (from 3.5 ppbv to 6.2 ppbv) and the in-canopy σ_w decreases below 0.2 m s^{-1}, indicating that the mixing rate becomes inadequate to transport the isoprene emitted out of the canopy. Within one hour of the peak, the above-canopy isoprene (1.5z/h) starts to decrease while the in-canopy isoprene (0.9z/h) keeps increasing in response to the fact that less and less isoprene is transported out of the canopy, resulting in a significant gradient between the two layers (4 ppbv) at the time of the in-canopy EOD peak (21:00 LT; Fig. 2a). This gradient, along with the low σ_w, suggests the decoupling of the canopy layer from the air above and thus the accumulation of isoprene in the canopy. Note that because of the 25 minute lag time in the measurement of 1.5z/h and 0.9z/h (see section 2.2), as well as the opposite trends in isoprene concentrations of the two layers, the 4 ppbv represents the upper bound of the actual gradient. In the STD case, however, no substantial gradients (< 1 ppbv) between the above- and in-canopy isoprene is observed at the time of the EOD

peak (21:00 LT), and σ_w above the canopy and in the upper canopy is generally greater than 0.4 m s^{-1}, indicating stronger vertical mixing than the EOD case.

Isoprene is well-mixed throughout the entire canopy during the day-to-night transition period for both EOD and STD cases (Fig. 2a, b). The large differences in σ_w between the two cases (Fig. 2c, d) suggest the well-mixed conditions are driven by different processes. For the STD case, no significant decrease in σ_w was observed even after the sunset, indicating that turbulence is continuous through the day-to-night transition, leading to a well-mixed canopy. This result also supports the assertion that turbulent mixing accounts for the isoprene removal during the transition period in the STD case. The continuous turbulence in the STD case is likely sustained by the large-scale forcing (i.e. the relatively high wind speed above the canopy; Fig. 3d, h). Unlike the STD case, weak turbulence in the EOD case ($\sigma_w <$ 0.2 m s^{-1}) under decoupled conditions is likely generated by local shear instability associated with nonstationary disturbances, such as density currents, drainage flow, and canopy waves (Acevedo & Fitzjarrald, 2003; Cava et al., 2004; Alekseychik et al., 2013). Isoprene emissions at all heights combined with the weak vertical mixing during the decoupling period may contribute to minimal in-canopy gradients in the EOD case.

We use the correlation between the changes in isoprene relative to the peak isoprene concentration with time ($\partial[\frac{\text{ISOP}}{\text{ISOP}_\text{peak}}]/\partial t$) and the standard deviation of the vertical velocity (σ_w) to define a critical threshold for σ_w that could inhibit vertical mixing. This threshold indicates when the emissions dominate over mixing in the late afternoon, and the isoprene mixing ratio starts to increase. The time period (∂t) used here is the two hours before the EOD peak for both cases, where isoprene increases in the EOD case and decreases in the STD case. The peak isoprene concentration (ISOP$_\text{peak}$) is the EOD peak concentration for the EOD case and the highest isoprene concentration for the STD case (i.e. the concentration at the begining of this two-hour period). A critical σ_w of 0.14, 0.2, and 0.29 m s^{-1} is identified for heights of 0.6 z/h (13 m), 0.9 z/h (21 m), and 1.5 z/h (34 m), respectively (Fig. 2e). In the EOD case, σ_w drop below the critical values and isoprene peaks occur, while in the STD case σ_w remain above the critical values in the upper canopy (Fig. 2c, d). In the EOD case, the rate of increase of isoprene shows little correlation with the magnitude of σ_w, indicating a negligible contribution of mixing on isoprene mixing ratios. For the STD case, the rate of change of isoprene is relatively small and becomes less negative with σ_w above and within the canopy, indicating the varying source strength and/or other sinks (such as chemical losses) associated with different weather conditions. The results here suggest that a critical σ_w can be identified to detect the EOD peak in gases with similar or longer chemical lifetimes as isoprene, and the magnitudes of the critical σ_w depend on the source strength of the gases such as the daily emission cycle.

299 ### 3.2 Static stability and wind shear

300 In section 3.1.2, we show a strong relation between low mixing and EOD peak and in
301 section 3.1.1 we hypothesize that clear and calm nights could drive low mixing. Here, we
302 examine the evolution of the stratification and wind shear during the day-to-night transition
303 period (Fig. 3) to provide a mechanistic explanation for the low mixing responsible for the
304 EOD peak and subsequent isoprene removal.

305 Overall, the virtual potential temperature (θ_v) in the STD case is higher than that in
306 the EOD case. In the STD case, the θ_v at the floor of the canopy is 1 Kelvin (K) lower
307 than the canopy top throughout the day-to-night transition period (Fig. 3b), suggesting
308 a weakly stable canopy layer. A weakly stable boundary layer is defined as the regime in
309 which turbulence is continuous and thus the dominant transport process, distinguishable
310 from a very stable boundary layer where turbulence is relatively weak compared to other
311 (sub)mesoscale motions such as waves (Nieuwstadt, 1984; Mahrt, 1999; Steeneveld, 2012).
312 The θ_v at the canopy top is 3 K higher than aloft, suggesting a weakly unstable layer above
313 the canopy (Fig. 3b). This is likely caused by the heat storage of the canopy based on the
314 large temperature difference between the STD and the EOD cases. Overall, the averaged
315 temperature gradients are small (< 3K). The day-to-day variations in θ_v (as shown by the
316 error bars in figure 3a-b) are generally larger than the vertical gradients. However, we note
317 that only two levels of pressure data (36 m and 6 m) are available for the calculation of
318 the θ_v (see section 2.3.1) and as a result, we may be underestimating the θ_v gradient. To
319 complement the θ_v data set, we also examine the dimensionless stability parameter (z/L)
320 that expresses the relative roles of shear and buoyancy in the production of turbulence.
321 Values greater than zero indicate stable conditions while values less than zero indicate un-
322 stable conditions. Mahrt (1998) divide the stable boundary layer into three stability regimes
323 as a function of z/L: (i) weakly stable regime (0<z/L< $O(0.1)$); (ii) intermediate regime
324 ($O(0.1)$<z/L< $O(1)$) where the strength of turbulence decreases rapidly with increasing sta-
325 bility; (iii) very stable regime (z/L> $O(1)$). In the STD case, the boundary layer becomes
326 stable after 19:00 LT as z/L became positive (Fig. 3f). The z/L is generally less than 0.1,
327 indicating a weakly stable boundary layer. This is in agreement with the results from the
328 θ_v profiles described above. In a weakly stable boundary layer, continuous turbulence in the
329 evening can only be sustained by wind shear. The wind speed above the canopy (>2 m s^{-1}
330 at 36 m and >4 m s^{-1} at 46 m) is relatively high (Fig. 3d, h) and appears to sustain the
331 continuous turbulence as shown in Figure 2d, suggesting the wind speed here is above the
332 minimum wind speed for sustainable turbulence proposed by (Van de Wiel et al., 2012). In
333 summary, the high wind speed (>4 m s^{-1} at 46 m) is able to sustain the turbulence in the
334 stable boundary layer during the day-to-night transition period.

For the EOD case, a stable boundary layer evolves early in the evening and becomes less stable later at night (Fig. 3a, e). Two hours before the EOD peak, even though the canopy layer is already stable, the θ_v at the canopy top is 2 K higher than in the overlying air, suggesting a weakly unstable air layer between z/h = 1 and z/h = 1.5. As the radiative cooling continues, a very stable layer is established over the EOD period (19:30 - 21:30 LT), demonstrated by the z/L values reaching 4. This large z/L is likely forced by the near-zero winds (Fig. 3g) that cause a very small L. Turbulence production then depends on wind shear in the stable boundary layer. Wind speed above the canopy is low (<1.5 m s^{-1}; Fig. 3c), suggesting little wind shear production. Even though the wind speed above the canopy (46 m) continues to increase during this period (Fig. 3g), the turbulence is still weak as shown in section 3.1.2. These results indicate, unlike the STD case, the wind speed above the canopy (< 3.4 m s^{-1} at 46 m and <1.5 m s^{-1} at 36 m) is inadequate to sustain the turbulence. Therefore, the combination of stratification and weak wind lead to the reduction of turbulence during the EOD period (19:30 - 21:30 LT).

As the wind increases progressively after the EOD peak (Fig. 3g), the z/L values drop to less than 1 (Fig. 3e), indicating the transition from a very stable canopy layer to a less stable canopy layer. Previous studies (Mahrt et al., 2012; Sun et al., 2012; Russell et al., 2016) show that there is a threshold point at which stable condition turbulence switches from being independent of wind speed to being dependent on wind speed. During the EOD period (19:30 - 21:30 LT), the turbulence does not respond to the increase in wind speed. However, after the wind speed becomes greater than a certain value (> 3.4 m s^{-1} at 46 m; Fig. 3g), the stability is reduced (Fig. 3e) and σ_w above the canopy increases (Fig. 2c).

The dependence of σ_w on the mean wind speed is explored to identify the threshold wind speed and thus to illustrate the recovery of turbulence in the EOD case (Fig. 4). A clear relation between the σ_w and the wind speed exits when the wind speed (u) is greater than 2.4 m s^{-1} (Fig. 4). Sun et al. (2012) define a threshold wind speed, after which turbulence intensity increases rapidly using the correlation of the turbulence intensity with the mean wind speed. According to Sun et al. (2012), the value of 2.4 m s^{-1} can be identified as the threshold wind speed using Figure 4. In addition, the data suggest a two-term exponential form ($\sigma_w = 0.18e^{-0.17u} + 0.02e^{0.75u}$, R^2=0.98) with the second term accounting for the rapid increase of σ_w at higher wind speeds and both terms explaining the slow increase of σ_w at lower wind speeds. We define the wind speed where the second term becomes dominant over the sum of the two terms (i.e. $\frac{\text{term2}}{\text{term1}+\text{term2}} > 50\%$) as the threshold value. This gives a threshold wind speed of 2.5 m s^{-1} that is in agreement with the value (2.4 m s^{-1}) identified using Figure 4 as well as previous studies on the stable boundary layer in forested environments (e.g. Russell et al. 2016).

Turbulence in the stable boundary layer has been categorized into various regimes based on different governing variables or threshold values (Mahrt, 1999; de Wiel et al., 2003; Sun et al., 2012). For example, Sun et al. (2012) uses the threshold wind speed to define turbulent regimes, including (i) regime 1 ($u < 2.5$ m s^{-1}), a weak turbulence regime where the σ_w shows little dependence on the mean wind speed u; (ii) regime 2 ($u > 2.5$ m s^{-1}), a strong turbulence regime when the σ_w increases rapidly with u. The σ_w in regime 1 is predominately from two hours before and at the EOD peaks. These σ_w at the EOD peak (red symbols in Fig. 4) increase as the wind speed exceeding the threshold value after the EOD peaks (cyan symbols in Figure 4), suggesting the re-enhancement of turbulence. The σ_w of regime 2 are predominantly from the STD case and the post-peak with two exceptions (Jul 20 and Jul 28 2016). However, the increases in the σ_w after the EOD peaks in these two cases still suggest the reinstate of the turbulence by the winds as other EOD cases. Some of the post-peak σ_w are still below the critical σ_w (0.29 m s^{-1}, Fig. 2e), however, the critical σ_w is based on changes in isoprene before the peak occurs when emissions are still occurring. In the post-peak period (21:00-22:00 LT), emissions have likely ceased and lower σ_w is required to reduce isoprene concentrations. In summary, the wind speed of 2.5 m s^{-1} can be considered as the threshold wind speed where turbulence becomes dependent on the mean wind speed in this study. For the EOD case, turbulence is reduced due to stratification and weak wind during the clear and calm nights, leading to the EOD peak (i.e. accumulation of isoprene in the canopy). However, the wind speed above the canopy increases to the threshold value after the EOD peak, and turbulence is then reinstated. The recovery of turbulence produced by wind shear plays an importance role in the rapid isoprene removal (see section 3.3.1).

3.3 Nighttime removal of isoprene

3.3.1 Contributions of chemistry and vertical mixing to the nighttime removal

The observed isoprene loss rates from 21:00 LT - 22:00 LT are 0.57 hr^{-1} and 0.55 hr^{-1} on average for the EOD and STD case, respectively (Fig. 5). The similar magnitude of the two loss rates suggests that the processes responsible for this rapid decline are similar. Previous studies also report similar loss rates of isoprene at this study site (Hurst et al., 2001) as well as in other forested sites (Doughty et al., 2013). Assuming horizontal homogeneity at the study site, the possible nighttime sinks for isoprene are vertical mixing and chemical reactions with OH, ozone (O$_3$), and nitrate radicals (NO$_3$). No significant dry deposition of isoprene has been observed to date, probably due to its nonpolar structure (Hurst et

al., 2001) and the high surface resistance (Wesely, 2000). In this section, we constrain the possible loss rates noted above using available observations.

Because the in-canopy rapid decay typically initiates between 21:00 PM and 22:00 PM (refered to as "the decay period" hereinafter), the average concentrations of the oxidants (OH, O_3, and NO_3) over this period are used to calculate the chemical loss rates. The AMOS 2016 campaign-average OH is 6.19×10^4 cm^{-3} for the decay period, resulting in an average loss rate of 0.02 hr^{-1} (Fig. 5). The standard deviation (1σ) of the measured OH is 8.86×10^5 cm^{-3} and represents the daily variations as well as the precision of the measurements from the top of the tower. The uncertainty associated with the calibration of the OH instrument is approximately 18% (Dusanter et al., 2008). The PROPHET 1998 (Program for Research on Oxidants: PHotochemistry, Emissions, and Transport) and the CABINEX 2009 (Community Atmosphere-Biosphere INteractions EXperiment) campaigns at this study site reported an average nighttime OH concentrations of 1.1×10^6 cm^{-3} measured by the Penn State laser-induced fluorescence (LIF) instrument (Faloona et al., 2001) and 3.75×10^5 cm^{-3} measured by the Indiana University Fluorescence Assay by Gas Expansion (IU-FAGE) instrument (Griffith et al., 2013), respectively. These concentrations are approximately 18 and 6 times higher than that measured during AMOS 2016. Recent studies have noted that unknown interferences may contribute to the reported OH concentrations in LIF measurements that only used a wavelength modulation technique without a chemical removal system (Feiner et al., 2016). This is one possible explanation for the higher nighttime OH concentrations obtained during the PROPHET 1998 and CABINEX 2009 campaigns. Measurements of potential interferences associated with the IU-FAGE instrument during CABINEX 2009 suggest that an unknown interference potentially accounts for 50-100 % of the nighttime OH concentrations (Griffith et al., 2013). However, as discussed above, the chemical removal system used during AMOS 2016 did not reveal any significant interference, suggesting that the measured concentration during the in-canopy decay period accurately reflect the ambient OH concentration above the canopy. Given the low radiation and high isoprene concentrations in the canopy in the early evening, the OH concentration in the canopy may be even lower than that above the canopy. Therefore, the observed OH concentrations are inadequate to account for the observed isoprene loss rates at night at the study site, yet more precise and accurate measurements are needed to reduce the uncertainties.

Reaction of O_3 with isoprene is much slower than with OH. The average O_3 mixing ratios during the decay period are 28($\pm$11) ppbv and 20($\pm$9) ppbv for the STD and EOD case, respectively. O_3 measurements were made in the trunk space (6 m) where O_3 concentrations are generally lower than those in upper canopy and above canopy especially when

⁴⁴¹ vertical mixing is low (Freire et al., 2017). Therefore, the lower O_3 concentrations in the
⁴⁴² EOD case provide additional support to the likelihood of low vertical mixing driving the
⁴⁴³ EOD isoprene peak. Given that the mixing remains relatively high in the STD case, O_3 is
⁴⁴⁴ assumed to be well-mixed and represent the concentrations in the upper canopy. Therefore,
⁴⁴⁵ the O_3 concentrations in the STD case (28 ± 11 ppbv) were used to calculate the isoprene
⁴⁴⁶ loss rate, leading to $5(\pm2)$ % of the observed isoprene loss rate for both cases. Note that
⁴⁴⁷ this loss rate acts as an upper bound for the EOD case, as the lower mixing would also
⁴⁴⁸ reduce O_3 transport into the canopy.

⁴⁴⁹ NO_3 has been shown to be the main factor for nighttime isoprene decay in high-NO_X
⁴⁵⁰ regions (Brown et al., 2009; Doughty et al., 2013; Millet et al., 2016). An average NO_X
⁴⁵¹ level of $0.77(\pm0.73)$ ppbv and $0.70(\pm0.62)$ ppbv were observed during the decay period for
⁴⁵² the EOD and STD case respectively, indicating clean conditions at the study site. The
⁴⁵³ combination of low NO_X and aforementioned low O_3 levels results in NO_3 mixing ratios
⁴⁵⁴ that are always below the limit of detection of the instrument (LOD=1.4 pptv) during the
⁴⁵⁵ decay period for both cases. In fact, 93 % of the NO_3 measured during the entire campaign
⁴⁵⁶ are below LOD with a maximum of 3.9 pptv. Measurements at other clean forest sites
⁴⁵⁷ also show that NO_3 mixing ratios in the canopy are nearly always below a LOD of $1.3-1.4$
⁴⁵⁸ pptv (Liebmann et al., 2018). If all isoprene loss were attributed to reaction with NO_3, the
⁴⁵⁹ observed isoprene loss rates would require a NO_3 of 10 pptv on average, which would be
⁴⁶⁰ an order of magnitude larger than observed. Therefore, NO_3 is not expected to be large
⁴⁶¹ enough to cause the observed isoprene removal at the study site. Because all measurements
⁴⁶² are below the LOD, we use the Forest Canopy Atmosphere Transfer model (Ashworth et al.,
⁴⁶³ 2015), as constrained by isoprene, O_3, NO_X measurements, to estimate NO_3. An estimate
⁴⁶⁴ of $1.1(\pm0.05)$ pptv was obtained, accounting for only $11(\pm0.5)$ % of the observed isoprene
⁴⁶⁵ loss rates for both cases (Fig. 5). Hurst et al. (2001) estimate an maximum NO_3 of 1.7 pptv
⁴⁶⁶ for an NO_2 and O_3 of 1.0 ppbv and 77.1 ppbv during the decay period for the same study
⁴⁶⁷ site. Our estimate of NO_3 is slightly lower due to the lower NO_2 and O_3 concentrations
⁴⁶⁸ observed.

⁴⁶⁹ In summary, the chemical losses in total can account for 20 % of the observed isoprene
⁴⁷⁰ loss rates for both EOD and STD cases. The largest uncertainty in the chemical loss
⁴⁷¹ estimation described above lies in the dusk-to-nighttime OH concentrations. For example,
⁴⁷² if the true OH conctrations during the decay period were higher than the reported values
⁴⁷³ by an average of 1σ, OH removal could explain up to 60 % of the observed isoprene loss
⁴⁷⁴ (Fig. 5).

⁴⁷⁵ To estimate the isoprene loss rate due to turbulent mixing, we use a residual method.
⁴⁷⁶ The residual (LR_mix_res) between the observed and the total chemical losses are then con-

⁴⁷⁷ sidered as the contribution by mixing, accounting for 80 % of the observed loss rates for
⁴⁷⁸ both EOD and STD case on average. The estimated loss rate in response to vertical mixing
⁴⁷⁹ (LR_mix_est) is calculated from the sonic anemometer data using equation 4. This estimate
⁴⁸⁰ is similar to the residual for the EOD case (LR_mix_est = 0.45 ± 0.21 hr^{-1}; LR_mix_res =
⁴⁸¹ 0.45 hr^{-1}) and 30 % higher than the residual for the STD case (LR_mix_est = 0.57 ± 0.15
⁴⁸² hr^{-1}; LR_mix_res = 0.44 hr^{-1}). Discrepancies between the two estimates (LR_mix_res and
⁴⁸³ LR_mix_est) may be attributed to (i) uncertainties in the estimation of LR_mix_est associ-
⁴⁸⁴ ated with the choice of stable boundary height and the value of $[ISOP]_{above}/[ISOP]_{in-canopy}$
⁴⁸⁵ (Section 2.3); (ii) and/or the lack of interactions between physical and chemical processes in
⁴⁸⁶ LR_mix_res which could be important under stable/nighttime conditions (Freire et al., 2017).
⁴⁸⁷ For example, incomplete mixing could cause segregation between isoprene and OH and thus
⁴⁸⁸ reduction in the reaction rates (Kim et al., 2016), which would lead to a lower chemical loss
⁴⁸⁹ rate and then a higher residual loss rate due to mixing. Overall, the LR_mix_est agree with
⁴⁹⁰ LR_mix_res. Note that the similarity of the loss rates between the EOD and STD cases
⁴⁹¹ (Fig. 5) suggests that the main process responsible for this rapid decline are similar (i.e.
⁴⁹² turbulent mixing). This is supported by the sustained turbulence by the continuously high
⁴⁹³ wind speeds in the STD case, and by the reintroduction of turbulent mixing by increased
⁴⁹⁴ winds above the canopy in the EOD case.

⁴⁹⁵ Further evidence of turbulent mixing accounting for the observed isoprene loss rates
⁴⁹⁶ could be supported by positive isoprene fluxes above the canopy during the decay period.
⁴⁹⁷ However, the isoprene flux data are not valid because of low turbulence (the friction velocity
⁴⁹⁸ $u_* < 0.2$ m s^{-1}) during the decay period for the EOD case. For the STD case, the average
⁴⁹⁹ isoprene flux (F_{OBS}) during the decay period is $0.01(\pm 0.01)$ ppbv m s^{-1}. To establish a
⁵⁰⁰ metric to explain and assess the magnitude of the observed flux, a flux-gradient method
⁵⁰¹ (i.e. $F_{Cal} = -K\frac{\Delta C}{\Delta z}$) was used to estimate the isoprene fluxes. The calculation suggests
⁵⁰² an average of 0.18 ppbv m s^{-1} and 0.03 ppbv m s^{-1} for F_{Cal} for the EOD and STD case,
⁵⁰³ respectively. The estimated and measured isoprene fluxes are in the same order of magnitude
⁵⁰⁴ for the STD case, serving as a verification of the fidelity of the flux-gradient method for the
⁵⁰⁵ decay period. From flux-gradient theory, it is reasonable to suppose a higher isoprene flux in
⁵⁰⁶ the EOD case given the greater concentration gradient (ΔC_{EOD}=-3.84 ppbv, ΔC_{STD}=-0.42
⁵⁰⁷ ppbv) but similar eddy diffusivity (K_{EOD}=0.62 m^{2}s^{-1}, K_{STD}=0.89 m^{2}s^{-1}). However, the
⁵⁰⁸ observations did not capture the fluxes corresponding to the removal of the accumulated
⁵⁰⁹ isoprene for the EOD case. There are several possible reasons for this discrepancy. First,
⁵¹⁰ the majority of the isoprene fluxes associated with the EOD peak might not be captured
⁵¹¹ by the flux measurements measured 30 minutes later due to the time differences between
⁵¹² the gradient and flux observations (see Section 2.3). Second, eddies associated with the
⁵¹³ weak turbulence transporting isoprene out of the canopy during the decay period in the

514 EOD case might be too small to be captured by the eddy covariance system placed at 10 m
515 above the canopy. The calculation-observation discrepancy also raises a possibility that the
516 assumption of horizontal homogeneity used here is invalid for the EOD case at the study
517 site (see discussion in Section 3.3.2).

518 ### 3.3.2 *Influences of advection on the nighttime removal*

519 Section 3.2 described the observed increased wind speed to a critical value and its effect
520 of increasing the turbulent mixing in the EOD case, indicating that synoptic forcing becomes
521 important in the stable boundary layer. In this study, a wind direction shift from the north
522 to the south was observed along with the increase in wind speed for 85 % of the EOD peak
523 events (e.g. Fig. 1f). Because this wind direction shift occurs after the isoprene peak,
524 we hypothesize that horizontal advection is an important driver of the nighttime isoprene
525 decline. This shift in wind direction resembles lake breeze that has been observed in the
526 Great Lake regions (Moroz, 1967). The lake breeze is most frequently observed in July and
527 August due to the minimal daytime cloudiness and the low wind speeds that maximize the
528 land-lake temperature differences in the Great Lake regions (Ryznar & Touma, 1981). Note
529 that the clear and calm conditions during which the EOD peak developed also favor the
530 lake breezes by enhancing the land-lake temperature differences.

531 The lake breeze phenomenon would introduce another uncertainty (i.e. advection) in
532 the investigation of nighttime isoprene removal. Assuming horizontal homogeneity (i.e. no
533 advection) for simplicity and analytical tractability, we show the rapid removal of isoprene
534 could be driven by vertical mixing for the EOD case (Section 3.3.1). However, Sun et al.
535 (1998) showed that a lake breeze could generate a significant advection for CO_2. If this is the
536 case for isoprene, the small fluxes measured above the canopy as well as the rapid isoprene
537 removal could be due to the significant advection dominating over the vertical mixing. This
538 hypothesis of advection is supported by the increased wind and the wind direction shift
539 (Fig. 1e, f and Fig. 3c, g). The advection can be estimated by vertical flux divergence
540 measurements made on very tall towers (Lee & Hu, 2002), yet these measurements do not
541 exist at the site. More data are required to validate the occurrence of lake breeze and
542 quantify the contribution of advection in the nighttime isoprene removal.

543 ## 4 Summary and Conclusions

544 Seven days (23 % of the measurement period) during the 2016 AMOS field campaign
545 are identified as having an end-of-day peak in isoprene mixing ratio. The peak occurs around
546 sunset (21:30 local time) and the in-canopy isoprene increases by 77 % (from 3.5 ppbv to
547 6.2 ppbv) on average. Stratification and weak wind (< 3.4 m s^{-1} at 46 m) during clear

and calm nights significantly suppress turbulent exchanges between in- and above-canopy, leading to the accumulation of isoprene emitted at dusk in the canopy, observed as the EOD peak. A critical σ_w of 0.14, 0.2, and 0.29 m s^{-1} is identified to detect the EOD peak for the height of 13, 21, and 34 m, respectively. As wind speeds increases, mixing recovers to reduce isoprene mixing ratios. Observed shifts in wind direction suggests that the increased wind speed could be attributed to the lake breezes. When the wind speed increased above 2.5 m s^{-1}, turbulence is enhanced again. Therefore, a wind speed of 2.5 m s^{-1} is considered as the threshold point where turbulence switches from being independent of wind speed to dependent on wind speed. However, in the standard case where wind speed is greater than the threshold point throughout the evening hours, turbulence is sustained ($\sigma_w > 0.4$ m s^{-1}) by wind shear and no EOD peak is observed.

The observed isoprene exhibit similar loss rates for the EOD and standard cases of 0.57 hr^{-1} and 0.55 hr^{-1} on average, respectively. Measured OH, O$_3$, and NO$_3$ suggest that chemical losses in total accounts for 20% of the observed loss rate for both cases. The largest uncertainty in the chemical loss estimation is associated with the OH instrument. Estimated turbulent mixing timescales suggest that turbulent mixing accounts for the remaining 80% of the observed loss rates. Observations did not capture the fluxes corresponding to the turbulent removal of the accumulated isoprene in the canopy, and this may be due to the sampling intervals used to quantify both fluxes and concentration gradients or challenges in micrometeorological methods under stable conditions. Another possible reason is that advection induced by the lake-breeze-like motion dominates over the vertical mixing, indicating the assumption of horizontal homogeneity may not be valid under calm and clear nighttime conditions at the study site. However, measurements do not exist at the site to test this hypothesis.

In summary, stagnant days characterized with clear and calm conditions promote the cooling of the canopy and thus low mixing conditions that lead to the EOD peak. These stagnant conditions are unable to sustain the isoprene peak for more than 2 hours due to enhanced wind speed generated by the developments of a lake-breeze-like motion in the atmosphere. This interesting behavior of isoprene has been reported in many forested regions, but none of previous work provided a clear explanation that accounts for both physical and chemical processes. This study presents representative atmospheric dynamics and chemistry data for temperate forest sites and discuss the possible mechanisms, providing a frame of reference for understanding in-canopy behaviors of reactive gases in forested environments. In addition, these results highlight unique features about reactive in-canopy chemistry. Models are known to have difficulties capturing transitions in the boundary layer

583 from dawn to dusk, and this study illuminates the processes of isoprene in the canopy and

584 its transfer to the free troposphere.

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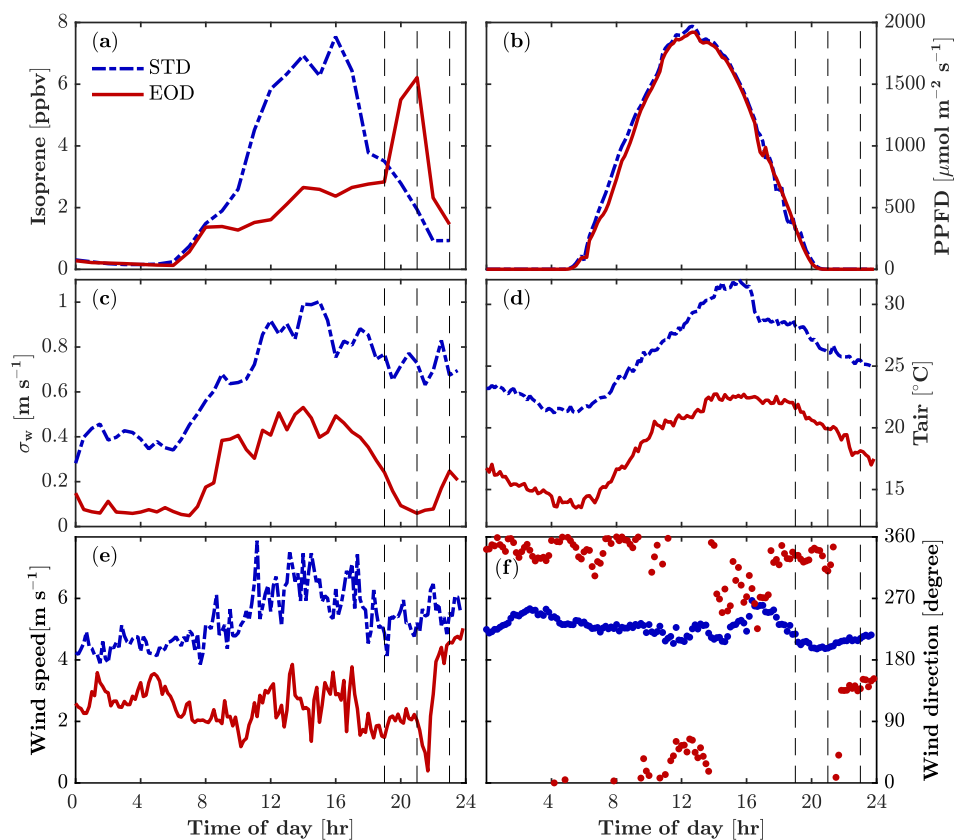
Figure 1. Examples of the End-Of-Day peak case (EOD; July 19 2016) and the standard case (STD; July 13 2016). (**a**) Diurnal variations of hourly isoprene mixing ratios [ppbv] at 21 m. (**b**) Diurnal variations of 10-min Photosynthetic Phototon Flux Density (PPFD) at 46 m. (**c**) Diurnal variations in half hourly standard deviation of vertical velocity (σ_w) at 21 m. (**d**) Diurnal variations in 10-min air temperature at 46 m. (**e**) Diurnal variations in hourly isoprene flux at 34 m. (**f**) Diurnal variations in 10-min wind speed (line) and wind direction (dot) at 46 m. (**g, h**) Diurnal variations in 5-min NO_X and O_3 mixing ratios at 6 m, respectively. The canopy height is about 22.5 m.
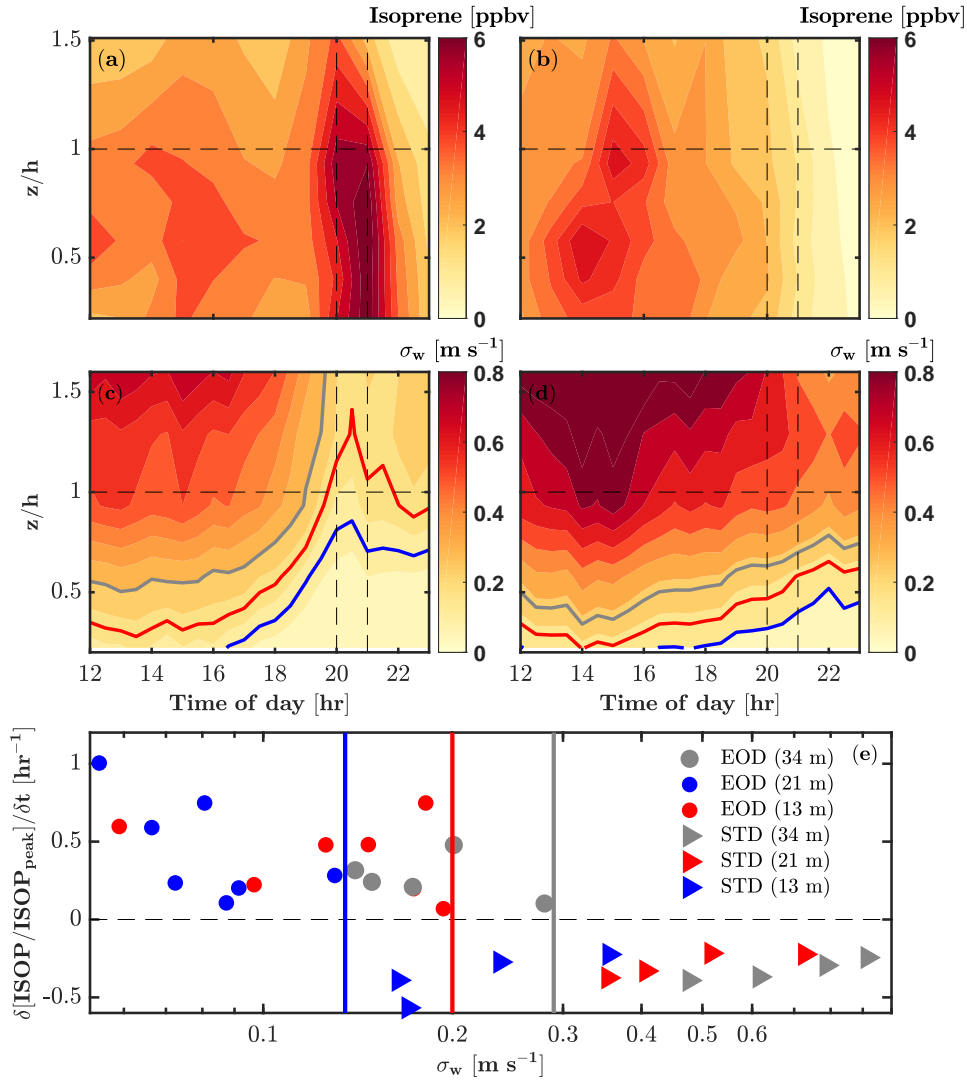
Figure 2. In-canopy profiles of isoprene and σ_w averaged over all EOD (**a, c**) and STD (**b, d**) cases. Isoprene mixing ratios as a function of local time and height for the EOD case (**a**) and STD case (**b**). Averaged σ_w as a function of local time and height for the EOD case (**c**) and STD case (**d**). The vertical dashed lines in panels a-d denote the period within 1 hour before the peak (20:00-21:00 local time). The correlation between the changes in isoprene relative to the peak isoprene concentration with time ($\partial[\frac{\text{ISOP}}{\text{ISOP}_{\text{peak}}}]/\partial t$) and σ_w at heights above the canopy (34 m: **grey** markers) and in the canopy (21 m: **red** markers; 13 m: **blue** markers)(**e**). Data shown in (e) are prior-peak data only. Critical σ_w values are noted with vertical lines for the 3 heights for the EOD

cases (**circles**) and the STD cases (**triangles**). The contour lines for the critical σ_w values are
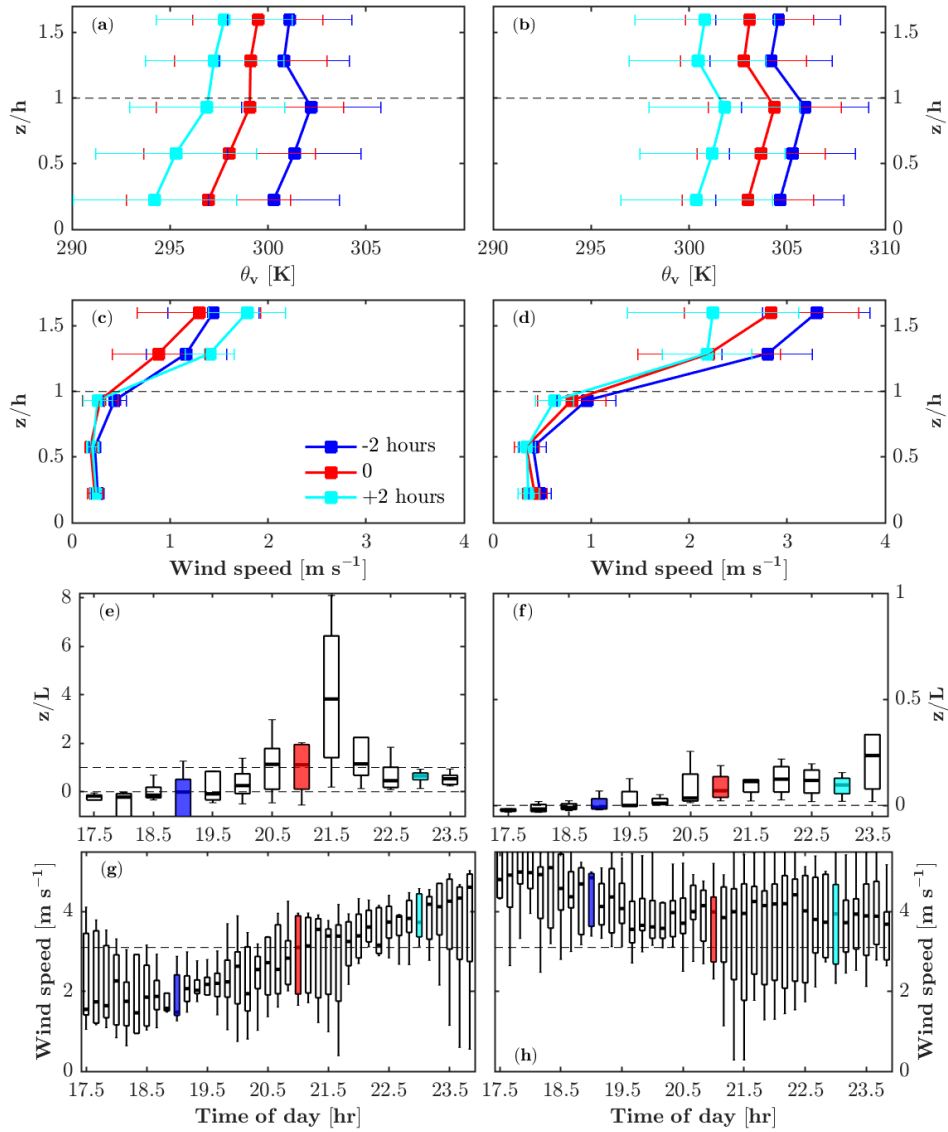
Figure 3. Averaged profiles of virtual potential temperature (θ_v) for the EOD case (**a**) and STD case (**b**) for these periods: 2 hours before the peak (**blue**), the average peak time 21:00 LT (**red**), and 2 hours after the peak (**cyan**). Averaged profiles of wind speed from sonic anemometers for the EOD case (**c**) and STD case (**d**). The evolution of dimensionless stability parameter z/L for the EOD case (**e**) and STD case (**f**) (note different y-axis scales for e and f; a dashed line on e compares the maximum for f). The evolution of wind speed at 46 m for the EOD case (**g**) and STD case (**h**).
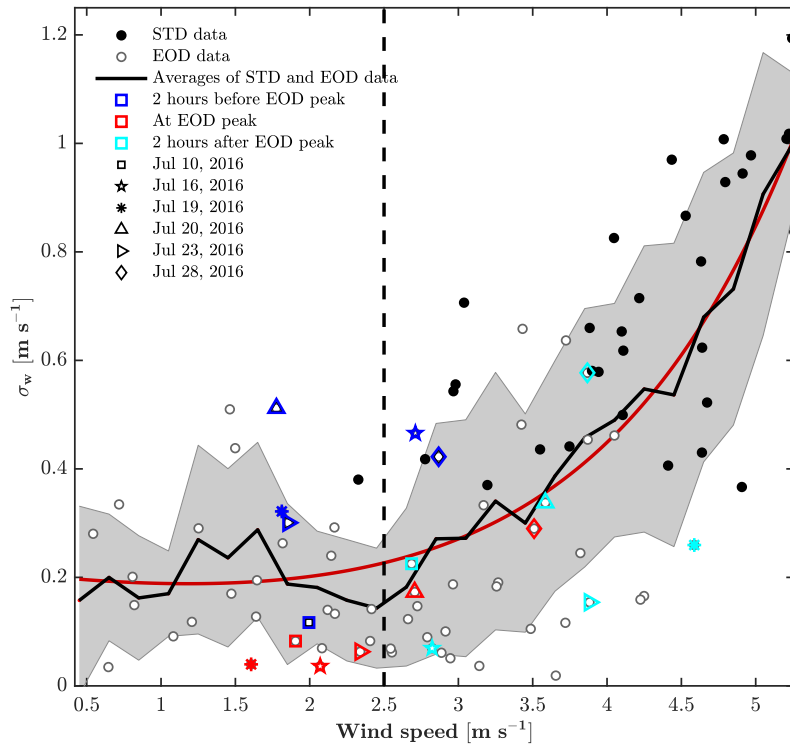
Figure 4. Dependence of σ_w on wind speed. Markers denote observations for the STD case (**solid black circles**) and the EOD case (**open black circles**). The data points of 2 hours before (**blue**), at (**red**), and 2 hours after the EOD peaks (**cyan**) are color coded with different symbols denoting different EOD-peak days (the turbulence data for Jul 4 2016 are missing). The bin-averaged (bin width is 0.25 m s^{-2}) data (**black line and the shaded area**) and the fitting curve (**red line**) are also shown. The σ_w data measured at 34 m and wind speed data at 46 m are used in this figure.
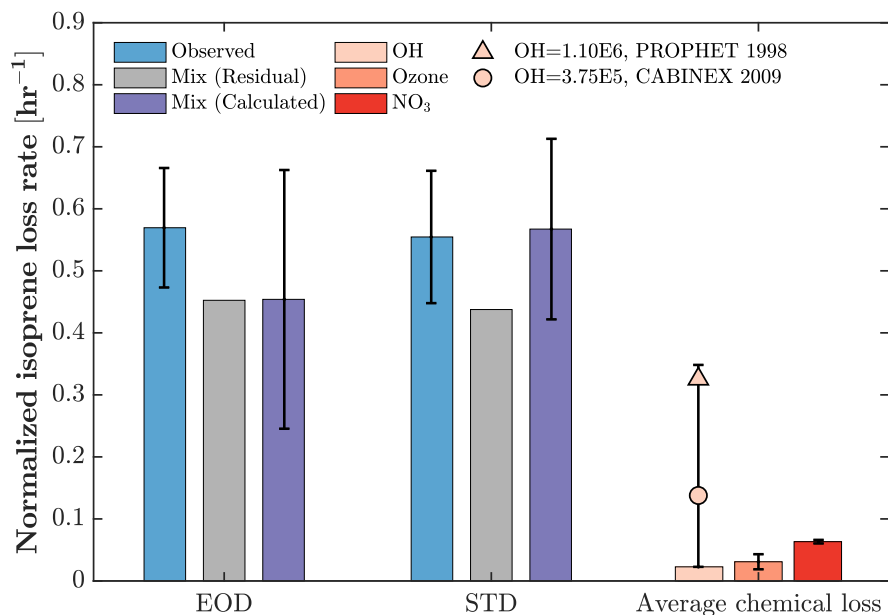
Figure 5. The loss rates of isoprene from 21:00 LT - 22:00 LT. Isoprene loss rate calculated from the observed isoprene mixing ratios (**blue**). Chemical loss with respect to hydroxyl radicals OH (**pink**), ozone (**orange**), and nitrate radicals NO_3 (**red**). Estimated isoprene loss rate due to vertical mixing (**grey**) as the differences between the observed (blue) and the chemical losses (pink, orange, and red). Estimated isoprene loss rate due to vertical mixing using the sonic anemometer data (Equation 4; **purple**). Isoprene chemical loss rates with respect to OH from previous campaigns at the same site (Faloona et al., 2001; Griffith et al., 2013) (**triangle and circle**). Error bars represent day-to-day variations. The error bar for OH also includes measurement uncertainty.
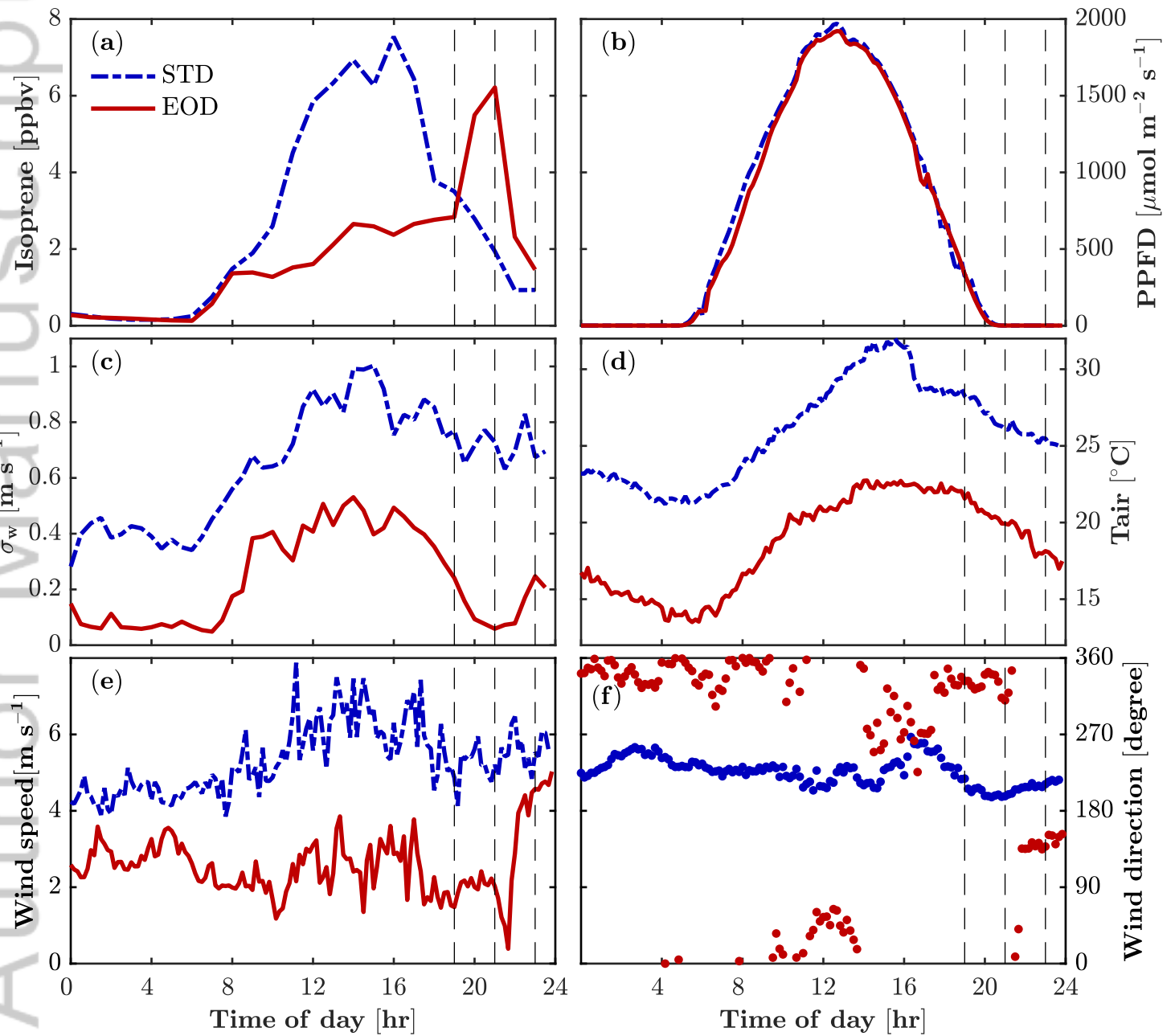
Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.