Minor contributions of daytime monoterpenes are major contributors to atmospheric reactivity

Deborah F. McGlynn[1], Graham Frazier[1], Laura E.R. Barry[2], Manuel T. Lerdau[2,3], Sally E. Pusede[2], and Gabriel Isaacman-VanWertz[1]

[1]Department of Civil and Environmental Engineering, Virginia Tech, Blacksburg, VA, 24061, USA
[2]Department of Environmental Sciences, University of Virginia, Charlottesville, VA, 22904, USA
[3]Department of Biology, University of Virginia, Charlottesville, VA, 22904, USA

Correspondence: Gabriel Isaacman-VanWertz (ivw@vt.edu)

1 Abstract

Emissions from natural sources are driven by various external stimuli such as sunlight, temperature, and soil moisture. Once biogenic volatile organic compounds (BVOCs) are emitted into the atmosphere, they rapidly react with atmospheric oxidants, which has significant impacts on ozone and aerosol budgets. However, diurnal, seasonal, and interannual variability of these species are poorly captured in emissions models due to a lack of long-term, chemically speciated measurements. Therefore, increasing the monitoring of these emissions will improve the modeling of ozone and secondary organic aerosol concentrations. Using two years of speciated hourly BVOC data collected at the Virginia Forest Lab (VFL), in Fluvanna County, Virginia, USA, we examine how minor changes in the composition of monoterpenes between seasons are found to have profound impacts on ozone and OH reactivity. The concentrations of a range of BVOCs in the summer were found to have two different diurnal profiles, which we demonstrate appear to be driven by light-dependent versus -independent emissions. Factor analysis was used to separate the two observed diurnal profiles and determine the contribution from each emission type. Highly reactive BVOCs were found to have a large influence on atmospheric reactivity in the summer, particularly during the daytime. These findings reveal the need to monitor species with high atmospheric reactivity, even though they have low concentrations, to more accurately capture their emission trends in models.

2 Introduction

Biogenic volatile organic compounds (BVOCs) are important chemical sinks for atmospheric oxidants and precursors for secondary organic aerosol (SOA) and ozone formation (Atkinson and Arey, 2003a; Guenther et al., 1995, 2000; Kroll and Seinfeld, 2008). Their emissions are primarily driven by the species of plants present and by changes in temperature and light, with secondary effects from other factors such as meteorology and deposition. Light dependent or *de novo* biosynthesis emissions are produced within the leaves of plants and emitted shortly after formation through plant stomata (Niinemets and Monson, 2013). These emissions tend to increase with temperature (Guenther et al., 2006; Guenther, 1997) but are also linked

to photosynthesis and therefore require photosynthetically active radiation (PAR). The dominant *de novo* BVOC emitted is isoprene, though some monoterpenes can be emitted in this manner (Staudt and Seufert, 1995; Tingey et al., 1979; Ghirardo et al., 2010; Taipale et al., 2011). In contrast, other emissions occur independently of light and are driven by temperature from a wide variety of vegetation, and therefore occur year-round. (Niinemets and Monson, 2013; Ghirardo et al., 2010; Guenther et al., 1991). Monoterpenes, sesquiterpenes, and diterpenes are largely emitted in a temperature dependent manner through volatilization from storage pools or resin ducts from within the plant (Zimmerman, 1979; Lerdau et al., 1997; Lerdau and Gray, 2003). The rate of volatilization is determined by the compound's vapor pressure.

The diurnal concentration profile of individual species (i.e., the observed average variability within a 24-hour period) is a function of the drivers of emissions, the concentrations of atmospheric oxidants, and meteorology. For isoprene, which is emitted from plants in a light-dependent manner, the diurnal profile is well established and relatively consistent across environments (Rinne et al., 2002; Guenther et al., 2000; Delwiche and Sharkey, 1993; Niinemets and Monson, 2013; Guenther et al., 1991; Bouvier-Brown et al., 2009). Due to strong daytime emissions, concentrations peak around midday to late afternoon, when incoming solar radiation and temperatures are greatest. Nighttime emissions of *de novo* emitted BVOCs drop to near zero due to the lack of photosynthetically active radiation (Niinemets and Monson, 2013; Ghirardo et al., 2010; Panopoulou et al., 2020; Guenther et al., 1996; Rinne et al., 2002). Concentrations of *de novo* emitted species concomitantly drop as suspended gases are depleted by atmospheric oxidation, deposited to surfaces, and diluted through dispersion.

The diurnal variation of monoterpenes is substantially more variable and complex. Because their emissions are predominantly temperature dependent, emissions peak in the afternoon but continue throughout the night. Consequently, monoterpene concentrations are often greatest during the nighttime hours, when oxidation by photochemically formed hydroxyl radicals is minimal and boundary height is reduced, decreasing dilution through atmospheric mixing (Bouvier-Brown et al., 2009; Haapanala et al., 2007; Panopoulou et al., 2020; Hakola et al., 2012). However, some plants do produce and emit monoterpenes in a light-dependent manner (Staudt et al., 1999; Staudt and Seufert, 1995; Harley et al., 2014; Yu et al., 2017; Taipale et al., 2011; Guenther et al., 2012). Despite these findings, light dependent monoterpene emissions have largely been deemed to contribute minimally to total monoterpene emissions. (Bouvier-Brown et al., 2009; Lerdau and Gray, 2003). Some studies suggest that this lack of contribution to total flux occurs because they are emitted from only a handful of plant taxa and the emission rates themselves have not been shown to be significant (Staudt et al., 1999; Loreto et al., 1998; Staudt and Seufert, 1995). However, a few studies find that many trees emit low levels of monoterpenes in a light dependent manner, and that these emissions are seasonal and change with phenological patterns (Fischbach et al., 2002; Ghirardo et al., 2010; Taipale et al., 2011; Steinbrecher et al., 1999). Overall, understanding of the scale and seasonality of *de novo* monoterpene emissions is limited and highly variable in the literature. A major goal of the present work is to understand the potential role that the minor contribution of light dependent emissions and/or individual compounds with differing temporal variability may play in the atmosphere. Certain monoterpenes that are often emitted at low levels and/or in a light dependent manner have extremely high reactivities, raising the question of whether or not chemical impact may be disproportionate to flux magnitude.

A lack of understanding of how individual compounds are emitted from vegetative sources makes emission modeling difficult and more uncertain. This is largely due to the impact the structure of a BVOC has on its aerosol formation potential and its

reaction rates with atmospheric oxidants, particularly for reactions involving ozone. For example, endocyclic monoterpenes (e.g., limonene and 3-carene) and sesquiterpenes (e.g., α-humulene and β-caryophyllene) have a greater aerosol formation potential and tend to react faster than compounds with exocyclic double bonds (e.g. α-pinene, α-cedrene). Consequently, long-term measurements of speciated BVOCs can assist in modeling BVOC emissions and in understanding their contribution to ozone modulation and SOA formation (Porter et al., 2017). These impacts extend further to the importance of individual fast-reacting isomers, which can represent substantial fractions of total reactivity even at low concentrations (Yee et al., 2018). In this context, a detailed understanding of the different drivers of isomer emissions and the temporal variability of composition is critical for interpreting such data.

Using two years of chemically resolved concentration measurements of in-canopy, biogenic volatile organic compound (BVOC) concentration data, we examine the contribution of individual monoterpene compounds to ozone and OH reactivity on diurnal, seasonal, and interannual timescales. We elucidate the impact of temporal variability on ozone and OH reactivity on scales from hours to years by identifying two varying components in the data, which we identify as arising from light dependent and independent emissions and quantifying their chemical impacts on each timescale. Factor analysis is used to quantitatively separate these observed profiles and their contributions to total monoterpene concentration and ozone and OH reactivity. Our findings highlight the need to better understand the drivers of emissions with isomer-level chemical resolution and improve their representation in emissions models as they have significant atmospheric impact.

3 Methods

3.1 Data collection and preparation

We measured in-canopy BVOC concentrations at the Virginia Forest Lab (VFL, 37.9229 °N, 78.2739 °W) in Fluvanna County, Virginia. The VFL sits on the east side of the Blue Ridge Mountains and is about 25 km east-southeast of Charlottesville, VA, USA. The forest is largely composed of oak, maple, and pine trees; oak predominantly emits isoprene while pine is a major source of monoterpenes and sesquiterpenes. Additional information pertaining to the measurement site can be found in McGlynn et al., 2021 and information on the forest can be found in Chan et al., 2011. The site houses a 40-meter meteorological tower, with a climate-controlled, internet-connected lab at the bottom that is supplied by line power. The BVOC concentrations were measured using a gas chromatograph with flame ionization detection (GC-FID) adapted for automated collection and analysis of air samples from mid-canopy ($\sim$20 m) of the VFL. In brief, air is pulled from mid-canopy ($\sim$20 m above ground level) through an insulated and heated Teflon tube. Ozone is removed from the sample using a sodium thiosulfate infused quartz fiber filter (Pollmann et al., 2005) at the front of the inlet. Samples were collected mid-canopy in order to more closely represent the in-canopy environment for co-located studies seeking to understand ozone loss processes. A subsample of air is concentrated onto a multibed adsorbent trap, the details of which can be found in McGlynn et al., 2021. A custom LabVIEW program (National Instruments) operates the instrument for hourly automated sample collection and analysis. Following sample collection, the trap is thermally desorbed to transfer the sample to the head of the GC column; details pertaining to GC run methods, column, and gas flow rates can be found in McGlynn et al., 2021.

The instrument is calibrated using a multi-component calibrant (Apel-Riemer Environmental Inc.) optionally mixed at one of four different flows to generate four different mixing ratios. A calibration sample occurs once every seven hours, rotating between zero air only, a calibrant at a fixed "tracking" mixing ratio, and a calibrant at one of three other mixing ratios. Details pertaining to calibrant composition, concentrations, peak integration, and data uncertainty can be found in McGlynn et al., 2021.

To identify analytes in the samples, a mass spectrometer (MS, Agilent 5977) was deployed in October 2019, September 2020, and June 2021 in parallel with the FID. Retention times of analytes detected by the two detectors were aligned using the retention time of known analytes. Analytes were identified by mass spectral matching with the 2011 NIST MS Library and reported retention indices (Mass Spectrometry Data Center, NIST, 2022). The chromatographic data were analysed using the freely-available TERN software package by Isaacman-VanWertz et al., 2017 within the Igor Pro 8 programming environment (Wavemetrics, Inc.). The measurement period included in this work extends from September 15, 2019, to September 14, 2021. This work presents all isoprene and monoterpene data collected during the measurement period but focuses largely on the monoterpenes between May and September (2020 primarily shown in the main text, with 2021 provided in the Supplementary Information).

3.2 Positive Matrix Factorization

Positive matrix factorization (PMF) has been widely used for source apportionment problems (Norris et al., 2014; Ulbrich et al., 2009; Kuang et al., 2015). A large number of variables can be reduced by the PMF algorithm to the main sources or factors that drive the observed variability (Norris et al., 2014). Application of PMF to multi-variable data generates two matrices, the factor contributions and factor profiles (Norris et al., 2014), which for environmental data represent a timeseries as a set of covarying variables (e.g. chemical species).

This work employed the United States Environmental Protection Agency's (US EPA) PMF 5.0 program to support the identification in the observational data of two apparent sources or drivers of BVOC concentration variability. Specifically, a two-factor PMF solution was examined to better understand and quantify the profiles and temporal variability of each observed factor. The two years of monoterpene data were run separately ("2020": September 15th, 2019-September 14th, 2020, and "2021": September 15th, 2020- September 14th, 2021), with uncertainty, u, in the data calculated using the equation provided by Norris et al., 2014:

$$u = \sqrt{(0.15 \times concentration)^2 + (0.5 \times MDL)^2} \quad (1)$$

The method detection limit, MDL, is 2.2 ppt for monoterpenes (McGlynn et al., 2021). Values below the method detection limit were substituted with MDL/2 in both the concentration and uncertainty file. Missing data are excluded from the data processing. The uncertainty value of 0.15 is recommended by Norris et al., 2014 as an estimate of overall uncertainty in the data. It reasonably represents the uncertainty of this instrument as well based on uncertainties in calibration slopes, and inherent

uncertainty in integration of chromatographic peaks, which has been shown to be on the order of 10-15% (Isaacman-VanWertz et al., 2017). Further information on the PMF output can be found in Norris., 2014.

3.3 Reactivity calculations

Reactivity of an individual BVOC with ozone (O3R) and OH (OHR) is calculated as the sum of the products of the concentration and oxidation reaction rate constant of each $BVOC_i$:

$$OxR_{tot}(s^{-1}) = \sum (k_{O_x+BVOC_i}\,[BVOC_i]) \tag{2}$$

All rate constants (units: cm^3 $molec^{-1}$ s^{-1}) used in this work are listed in Table S1 (Atkinson et al., 2006, 1990a; Pinto et al., 2007; Atkinson and Arey, 2003b; Shu and Atkinson, 1994; Pratt et al., 2012; Atkinson et al., 1990b). A temperature of 298K is assumed for all rate constants, representing the approximate midpoint between day and night temperatures in the summer at this site, which vary by roughly 10°C (McGlynn et al., 2021). Taking the temperature dependence of rate constants into account would increase daytime OH reactivity by 5-8%, and decrease nighttime OH reactivity by approximately the same amount. These differences suggest the true difference between the light dependent (daytime) and light independent (nighttime) mixtures is ∼10-16% higher than calculated, but this effect is not included quantitatively because temperature dependence is not known for many monoterpene reaction rates. Additionally, some rate constants such as thujene were calculated from structure activity relationships and previous work has found that calculated rate constants add significant uncertainty to calculated ozone reactivity (Frazier et al., 2022). However, compounds that contribute the most to atmospheric reactivity, such as α-pinene, limonene, and sabinene have measured rate constants, therefore, we do not expect significant uncertainty in our calculations.

4 Results and discussion

At the VFL, concentrations of a wide range of species, including anthropogenic and other VOCs, are measured hourly. The BVOCs measured include isoprene, methyl vinyl ketone, methacrolein, 11 monoterpenes, and 2 sesquiterpenes. This work focuses primarily on monoterpenes, which contribute the largest fraction of speciated ozone and OH reactivity from BVOCs at the research site throughout the year (McGlynn et al., 2021). While the measurement method captures two sesquiterpenes, they are not included in the analysis because these and related measurements have found they do not contribute significantly to most oxidant reactivity (Frazier et al., 2022; McGlynn et al., 2021).

4.1 Monoterpene seasonality

To understand the drivers of monoterpene variability, we first examine diurnal and seasonal patterns in two monoterpenes found at the site, α-pinene and limonene, that exhibit features of two different concentration profiles. Seasonal averages are defined as: December, January, and February (Winter); March, April, May (Spring); June, July, August (Summer); and September, October, November (Fall). Diurnal trends in these species demonstrate some clear differences in their concentration patterns (Fig.

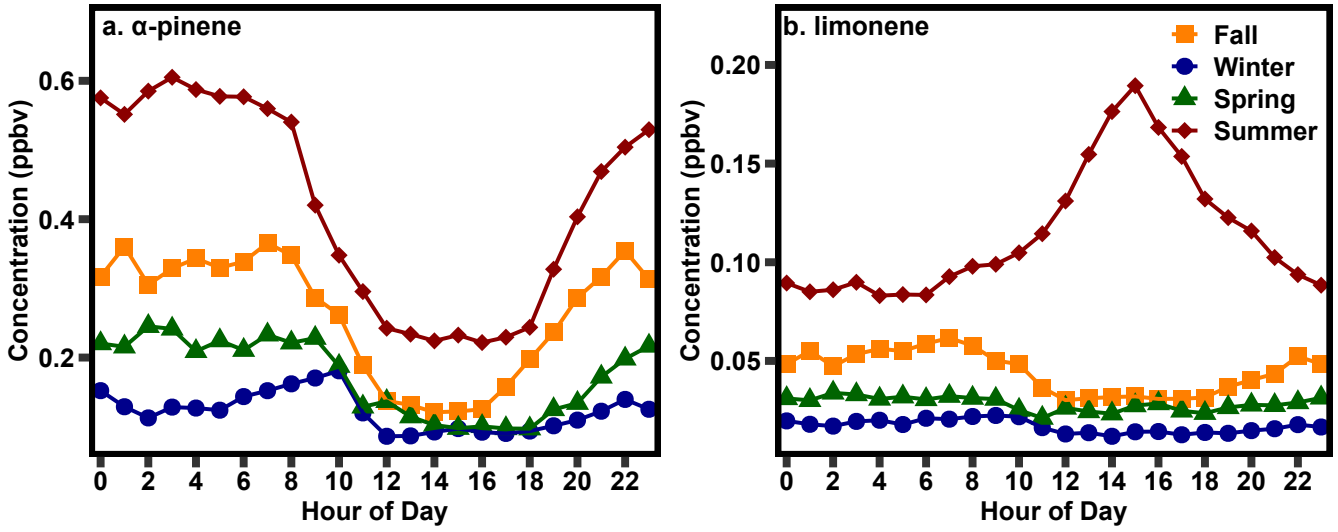

Figure 1. The mean (a) α-pinene and (b) limonene concentration in the four seasons of the northern hemisphere between September 2019 and September 2021.

1). α-pinene concentrations were lowest in the daytime winter hours at about 0.05 ppb and highest in the nighttime summer hours, at 0.60 ppb. In all seasons, α-pinene concentrations were highest at night and decreased in the morning hours, following "typical" patterns of light-independent emitted monoterpene concentrations which are largely modulated by variability in the planetary boundary layer (Bouvier-Brown et al., 2009). Concentrations were lowest in the middle of the day, between 10:00 and 17:00 and highest between 20:00 and 8:00 (Fig. 1a). Concentration transitions between these periods vary somewhat by season in accordance with the changing temperature and daylight hours of a subtropical climate zone.

In contrast, while limonene concentrations were similarly lowest in the daytime winter hours, at 0.01 ppb, they were highest during the daytime summer hours, at 0.2 ppb. In fall, winter, and spring, limonene exhibited the same seasonality as α-pinene with daytime minima and nighttime maxima, though with weaker diurnal variability (Fig. 1b). In summer, however, diurnal trends in limonene concentrations are very different, with a peak in the mid to late afternoon and evening concentrations higher than at other times of the year. To reach daytime peaks in concentration, daytime emissions of limonene must be high during the day, particularly given that the reaction rates of limonene with the OH radical and ozone are, respectively, 3 and 2.3 times faster than those of α-pinene.

The seasonal rise and fall in the observed daytime peak of limonene, in contrast to the relative stability of α-pinene, is apparent in a spring/summertime comparison of daytime (7AM - 7PM) and nighttime (7PM - 7AM) average concentrations (Fig. 2). The full two-year time series of this plot can be found in the supplemental document (Fig. S1). As observed in the diurnal profiles, α-pinene nighttime concentrations are higher than daytime concentrations throughout the year; while concentrations increase in the summer, this increase is observed in both daytime and nighttime concentrations (Fig. 2a). In contrast, while concentrations of limonene are highest at night throughout the early spring, concentrations begin to peak in the

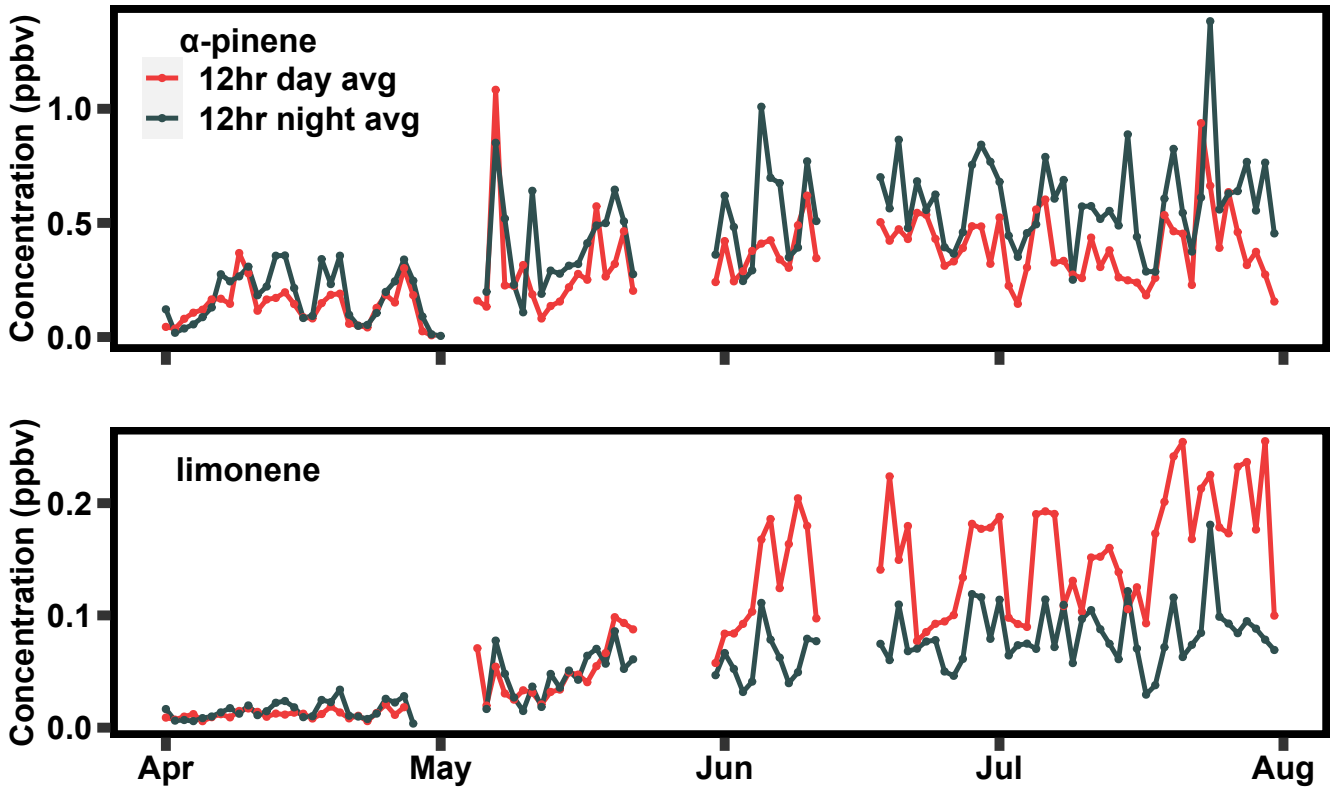

Figure 2. The 12-hour average of α-pinene and limonene between April 2021 and August 2021. The averaging period for each compound was between 7 AM and 7 PM.

daytime in late-May (Fig. 2b). From late-May through mid-September, concentrations are highest during the day, suggesting a strong daytime source of limonene specifically in the summer, which may be co-emitted with other monoterpenes but is not a strong feature for α-pinene. The daytime peak in limonene is unique to summer and occurs in both years (Fig. 1, 2, and S1). Interestingly, while the daytime peak in summer is relatively consistent across years, nighttime concentrations of limonene in the summer are substantially lower in 2021 compared to 2020 (Fig. S1), suggesting sources for daytime and nighttime limonene that differ in their interannual variation. However, additional years of data are likely necessary to better understand the drivers of this interannual variability. We demonstrate below that the timing of the rise and fall of the strong daytime source of limonene correlates with concentrations of isoprene, a known *de novo* emitted BVOCs, and appears to be a component of a set of light-dependent monoterpene emissions.

4.2 Light dependent and light independent monoterpene concentration

To better characterize the observed light-dependent monoterpenes and quantify their impacts, the patterns in monoterpenes were deconvolved as two factors using PMF. The determined factors demonstrate a clear separation between a set of monoterpenes that exhibit only nighttime peaks in concentration, and a set of compounds that exhibit a tendency toward daytime maxima. Quantitative assessment of the uncertainty of the two-factor solution is performed using bootstrapping, in which 100 runs are performed using arbitrary subsets of data; 95% of bootstrap runs reproduce both factors (Table S2) with no unmapped base factors. An unmapped base factor indicates that one or more bootstrap runs did not correlate with a determined factor from the base model run (Norris et al., 2014). The Pearson correlation coefficient threshold used for this analysis was the EPA PMF default value of 0.6 (Norris et al., 2014).

A "light dependent" factor is present primarily during the summer, characterized by daytime peaks that roughly coincide with the seasonality and variability of isoprene (Fig. 3, results from 2020 shown, Table S3 contains the percent contribution of each species in each factor in 2020, results from 2021 in Fig. S1). This factor even mirrors transient decreases in concentrations observed in isoprene, such as those observed in June 2020, July 2020, and September 2020, denoted with black arrows in Fig. 3a. The largest contributor to the light dependent factor is limonene (roughly one-third), followed by cymene, sabinene, and a relatively small contribution from α-pinene, denoted by the pie charts above each factor time series. A table indicating the percent contribution for the species in each factor can be found in Table S2. A more dominant factor contains most of the α- and β-pinene and exhibits a diurnal pattern and seasonality more in line with what is typical for temperature-driven monoterpenes; this factor is referred to as "light independent" to distinguish it and because the dominant biogenic emission model (MEGAN) distinguishes between emission pathways as light dependent (i.e., *de novo*) vs. independent (i.e., temperature-driven volatilization from storage pools) (Guenther et al., 2012). Interpretation of factors is further supported by their diurnal trends, a representative sample of which is shown in Fig. 4 with a sampling from Summer 2021 shown in Fig. S4. The light dependent factor peaks mid-day, following a similar temporal pattern as isoprene. We infer these monoterpenes to be emitted through similar processes as isoprene and attribute them to *de novo* emissions. Additionally, isoprene concentrations correlates reasonably well with light dependent monoterpenes during summer (r^2=0.57, Fig. S3a) and does not correlate with light independent monoterpenes (r^2=0.01, Fig. S3b). In contrast, the higher-concentration monoterpene factor peaks in the nighttime to early morning hours, following more typical monoterpene diurnal patterns. We attribute these monoterpene concentrations to temperature-driven light independent emissions of monoterpenes. It is important to note that most monoterpenes are split between the two factors and vary within the year, likely because of changing phenological patterns. While some compounds such as α- and β-pinene are almost wholly found in the light independent factor, most of the compounds in the light dependent factor, such as limonene, still exhibit a strong light independent component.

Overall, the light dependent factor accounts for $\sim$25% of summertime monoterpene concentration, but at times the light dependent factor may contribute significantly or even dominate concentrations due to their differing diurnal variability in emissions. Interestingly, greater than 85% of the most dominant monoterpenes, including α-pinene, β-pinene, tricyclene, fenchene, and camphene are found almost entirely in the light independent factor (Table 1). Conversely, greater than 85% of cymene,

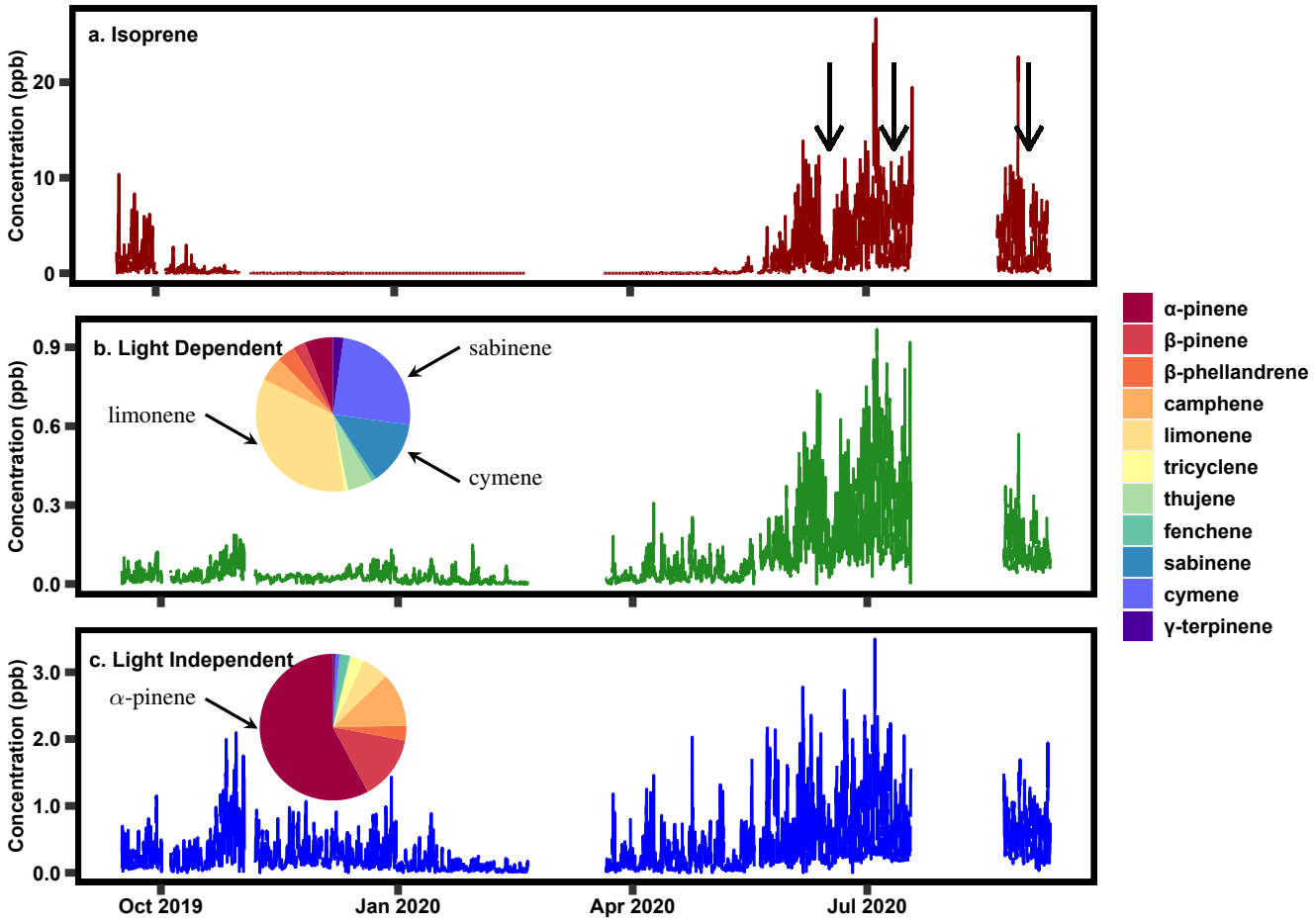

Figure 3. Time series of isoprene concentration and the two positive matrix factorization factors between September 2019 and September 2020 and the breakdown of the monoterpene species that contribute to each factor. The black arrows in fig. 3a denote the transient periods that are apparent in both the isoprene data (3a) and the light dependent factor (3b).

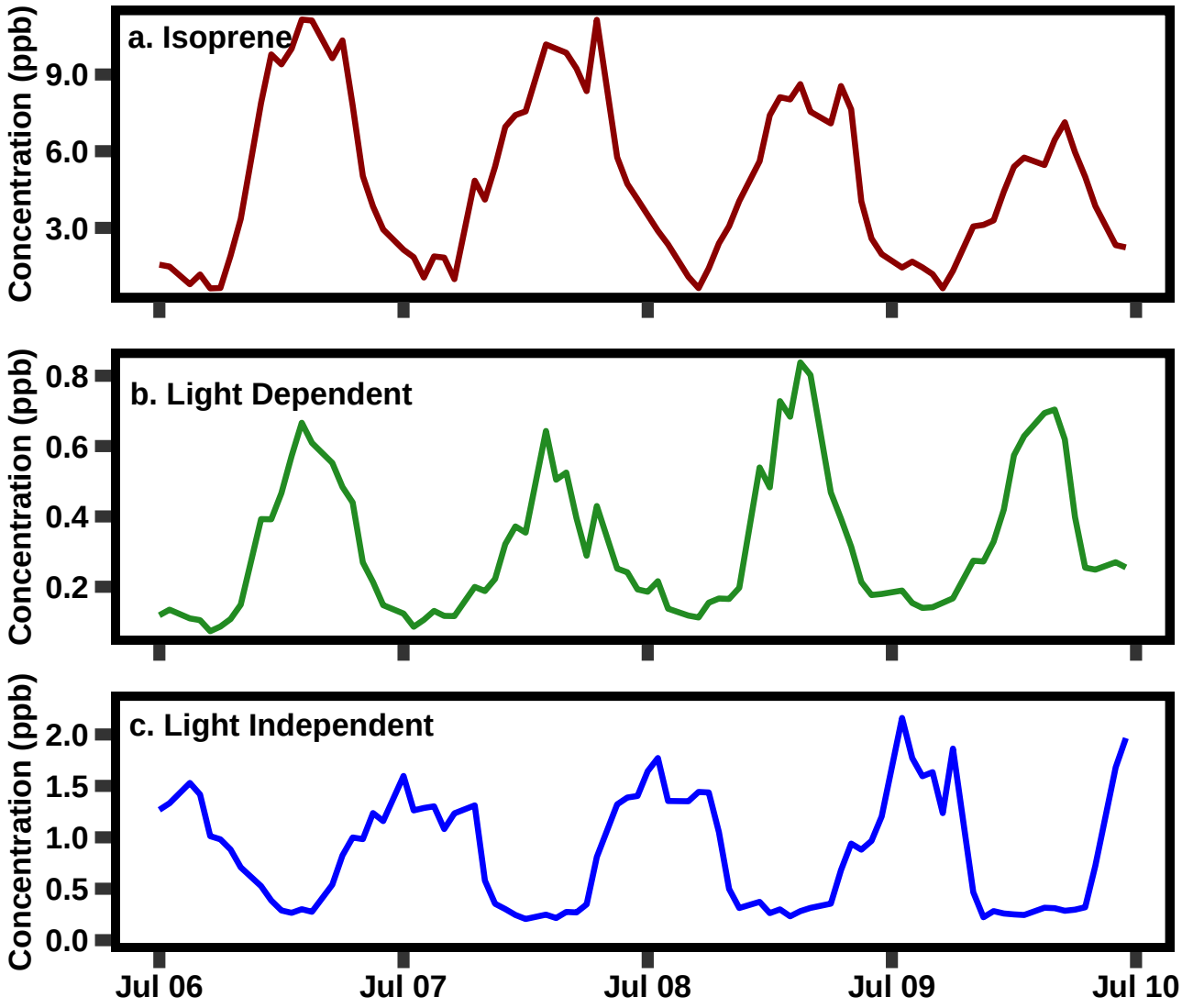

Figure 4. A four-day period in July 2020 of isoprene, and the two PMF factors (Light Dependent and Light Independent).

sabinene, and thujene are found in the light dependent factor (Table 1). A small number of species are more evenly split, with larger percentages of their concentrations attributed to light dependent emissions than light independent emission in the summer months. These species include, β-phellandrene, limonene, and γ-terpinene (Table 1).

4.3 Ozone and OH reactivity

Despite the low contribution of the light dependent factor to total monoterpene concentration, this factor has a large impact on ozone and OH reactivity. Comparing the stacked diurnal concentration profile (Fig. 5a) to the stacked ozone and OH

Table 1. Percent of concentrations attributed to light independent (LIF) and light dependent (LDF) emissions between September 2019 - September 2020 and in summer 2020 (June, July, August)

	Annual		Summer	
compound	% LIF	% LDF	% LIF	% LDF
α-pinene	97.7	2.3	96.6	3.4
β-pinene	96.1	3.9	94.2	5.8
tricyclene	94.3	5.7	91.8	8.2
fenchene	92.1	7.9	88.6	11.4
camphene	91.0	9.0	87.2	12.8
β-phellandrene	78.9	21.1	71.5	28.5
γ-terpinene	48.5	51.5	38.6	61.4
limonene	43.0	57.0	33.5	66.5
thujene	14.6	85.4	10.2	89.8
cymene	14.0	86.0	9.8	90.2
sabinene	0.0	100.0	0.0	100.0

reactivity diurnal profile (Fig. 5b, c) in summer, limonene and α-pinene prevail as the major contributors to both ozone and OH reactivity. While the concentration profile shows that the majority of species peak at night, there is a slight increase in the middle of the day, owing to the contribution from light dependent emissions. When this profile is multiplied by respective reaction rate constant for each species and oxidant, there is a clear mid-day peak that is a significant contributor to ozone and OH reactivity in the summer. Further, the largest contributor to total ozone and OH reactivity is limonene despite its relatively low contribution to total concentration due to its high reaction rate with each atmospheric oxidant. PMF results from 2020-2021 are generally very similar to the results shown here in terms of diurnality and composition (Fig. S5).

A majority of the highly reactive isomer limonene is associated with light dependent monoterpenes (57%), while the more dominant α-pinene concentrations are almost entirely attributed to pool emissions (98%, Table 1). Sabinene is also a notable contributor to the light dependent mixture, contributing approximately 30% to concentration, 25% to ozone reactivity, and 33% to OH reactivity; it is not found in the light independent mixture. The major contribution of limonene and sabinene to the light dependent monoterpene mixture makes light driven emissions particularly reactive, with a reaction rate roughly 1.5 times that of the light independent mixture for both ozone and OH reactivity. This daytime peak has an significant impact on daytime ozone and OH reactivity (Fig. 5e, f), such that calculated summertime ozone and OH reactivity consequently have a less pronounced diurnal pattern and is roughly uniform throughout the day (average: 1.4-2.4 $\times$ 10^{-6} s^{-1} for ozone reactivity and 1-2 s^{-1} for OH reactivity) during the summer months. Even in the summer, when concentrations of light dependent monoterpenes are highest, the diurnal profile of the total monoterpene chemical class roughly follows that of α-pinene (Fig. 5a) with only moderate daytime concentrations. However, this average profile is a combination of a nighttime peak dominated by light independent compounds (Fig. 5g) and a daytime peak dominated by light dependent compounds (Fig. 5d) that has a greater contribution

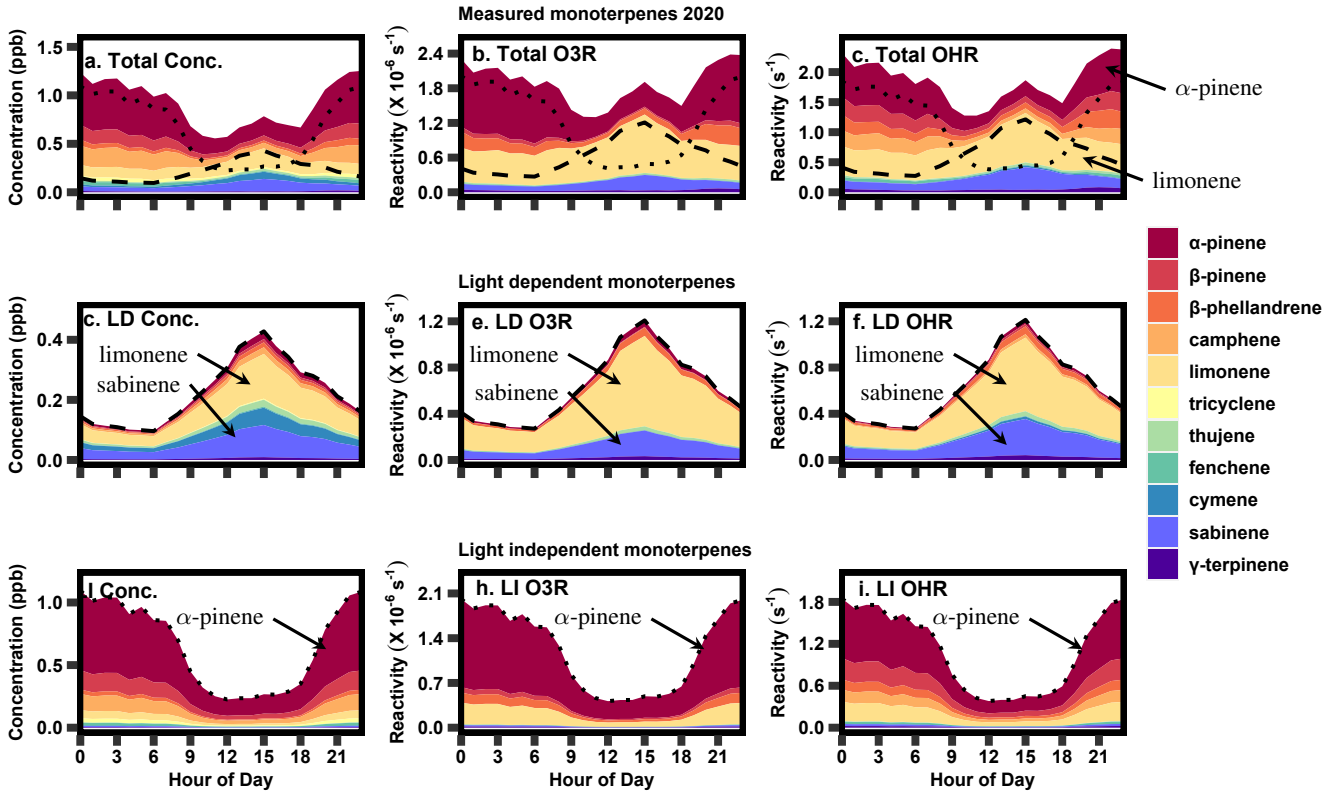

Figure 5. The 2020 summer diurnal profile of (a) measured monoterpene concentration, (b) calculated monoterpene ozone reactivity and (c) calculated OH reactivity, as well as light dependent (LD) (d) concentrations, (e) ozone reactivity, and (f) OH reactivity, and light independent (LI) (g) concentration, (h) ozone reactivity, (i) OH reactivity. The dashed lines in a, b, and c represent the contribution from LD monoterpenes (d, e, and f) while the dotted lines represent the contribution from LI monoterpenes (g, h, and i).

to daytime reactivity. Consequently, understanding light dependent monoterpenes is critical, not only to better characterize the carbon cycle and predict long-term trends, but also because it has immediate and substantial impacts on the atmospheric oxidant budget in the summer that would be overlooked when considering monoterpenes as a bulk compound class.

5 Conclusions

Using two years of hourly speciated BVOC concentrations collected at a meteorological tower in central Virginia, we identify and quantify diurnal and seasonal variability of chemically speciated monoterpenes. Though a majority of monoterpene concentrations exhibit temporal behaviour expected from pool emissions whose flux rates are independent of light, we identify a minor (in mass terms) contribution from monoterpenes with seasonality and diurnal variability that show a strong light dependence and resemble *de novo* emissions. These light dependent monoterpene emissions are strongest in the summer, where

they contribute ∼25% to total monoterpene concentrations, with smaller contributions in other seasons. However, the minor contribution to total monoterpene mass obscures their major impact on ozone and OH reactivity. Due to differences in the temporal variability of the two monoterpene classes and the significantly higher reaction rates of the light dependent mixture, we observe high ozone and OH reactivity in the summer daytime that is not well captured by bulk monoterpene concentration. This reactivity is dominated by limonene, which contributes ∼80% and ∼65%to light dependent sourced ozone and OH reactivity and roughly ∼20% to light independent sourced ozone and OH reactivity. In a changing climate, these BVOC emission sources may vary. For example, drought may decrease vegetative growth which could increase per-unit-leaf-area in emissions for stored (i.e., light independent) monoterpenes, even as canopy leaf area declines (Lewinsohn et al., 1993; Funk et al., 2004). But increased precipitation can decrease photosynthesis, causing a decrease in *de novo* (i.e., light dependent) emissions (Lewinsohn et al., 1993; Funk et al., 2004). These findings highlight the need for speciated long-term monitoring studies with a focus on capturing low concentration but highly reactive species.

A significant implication of this work is that the unique drivers of each monoterpene isomer challenge our ability to view this class monolithically or simplify its variability. Measurement studies focused on total BVOC classes may be sufficient to gain an understanding of total BVOC concentrations but demonstrate a need for isomer-resolved understanding of oxidant reactivity. For example, while this work supports the general conclusion that light dependent monoterpenes are a minor component (reflected in current emission models (Guenther et al., 2012) and supported by measurement studies (Bouvier-Brown et al., 2009; Kesselmeier and Staudt, 1999; Niinemets et al., 2002; Tingey et al., 1979; Davison et al., 2009; Taipale et al., 2011; Rinne et al., 2002), the composition and temporal variability of light dependent monoterpenes, as well as their high per-molecule reactivity, drive strong atmospheric impacts. It is clear that drivers of limonene and sabinene emissions are particularly critical for understanding this ecosystem (see also (McGlynn et al., 2021). Capturing the detail of this or any monoterpene in emissions models is difficult, as the light dependent fraction depends on plant species and other ecological variables. However, it is clear there is some disconnect between the results here and dominant models that, for example, estimate α-pinene as more strongly light dependent than limonene (Guenther et al., 2012) and do not tend to vary light dependent fraction by plant function type. These small gaps in our understanding of what drives monoterpene emissions may lead to significant uncertainty in models or outcomes with respect to oxidation and oxidant chemical loss. Furthermore, oxidation of these compounds ultimately leads to SOA formation, but the impacts on this process of the different long- and short-term temporal trends of each isomer is difficult to assess. It is clear from existing literature that SOA yields vary significantly by isomer and are dependent on structure (Lee et al., 2006; Faiola et al., 2018; Friedman and Farmer, 2018; Lim and Ziemann, 2009). Consequently, we anticipate that light dependent and independent monoterpenes vary in their average SOA yields, and the seasonal and interannual variability observed in this work has significant regional impacts on aerosol loadings. Unfortunately, these differences are difficult to quantify, with previous studies even disagreeing on whether α-pinene or limonene has a higher SOA yield (Faiola et al., 2018; Friedman and Farmer, 2018). Enhanced monitoring of BVOC concentrations and emissions needs to be supplemented by improved chemically-resolved measurements of SOA concentrations and formation processes in order to enhance our understanding of the contribution of these emissions to SOA mass loadings.

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Data availability. The data set can be found at: https://data.mendeley.com/datasets/jx3vn5xxcn/2

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