

MINOR CONTRIBUTIONS OF DAYTIME MONOTERPENES DOMINATE OZONE REACTIVE LOSS

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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, 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 Research Lab, in Fluvanna County, Virginia, we examine how minor changes in the composition of monoterpenes between seasons are found to have profound impacts on ozone reactivity. The concentration of a range of BVOCs in the summer were found to have two different diurnal profiles, largely driven by temperature- versus light-dependent emissions. Factor analysis was used to separate the two observed diurnal profiles and determine the contribution from each driver. Highly reactive BVOCs were found to exert outsized influence on ozone reactivity in the summer, particularly during the daytime. These findings reveal a need to monitor species with high atmospheric reactivity but are low in concentration and to more accurately capture their emission trends in models.

Introduction

Biogenically emitted volatile organic compounds are important precursors for reactions with atmospheric oxidants and secondary organic aerosol (SOA) formation¹⁻⁴. Their emissions are primarily driven by the species of plants present and by changes in temperature and light, with secondary effects of other ecological factors. Light dependent or *de novo* biosynthesis emissions are produced within the leaves of plants and emitted shortly after formation through plant stomata⁵. These emissions tend to increase with temperature^{6,7} but also require light. The dominant *de novo* BVOC emitted is isoprene, though some monoterpenes can be emitted in this manner⁸⁻¹¹. In contrast, other emissions occur independently of light from a wide variety of vegetation and therefore occur year-round primarily with temperature dependence^{5,10,12}. Monoterpenes, sesquiterpenes, and diterpenes are largely emitted in a temperature dependent manner through volatilization from storage pools or resin ducts from within the plant^{5,13-15}. The rate of volatilization is determined by the compound's vapor pressure¹⁵.

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^{5,10,12,16}, the diurnal profile is well established and relatively consistent across environments^{5,17-19}. Due to strong daytime emissions, concentrations peak 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 light^{5,10,17,20,21}.

Concentrations of *de novo* emitted species concomitantly drop as suspended gases are depleted by atmospheric oxidation.

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 evening hours^{16,20,22}, when oxidation by photochemically formed hydroxyl radicals is minimal and boundary height is reduced, decreasing dilution through atmospheric mixing^{16,20,23}. However, some plants do produce and emit monoterpenes in a light-dependent manner^{3,8,11,24-26}. Despite these findings, light dependent monoterpene emission have largely been deemed to contribute minimally to total monoterpene emissions^{15,16}. 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 overwhelming^{8,24,27}. Interestingly, a few studies find that many trees emit low levels of monoterpenes in a light dependent manner, and these studies have found that this emission activity is seasonal and changes with phenological patterns^{10,28 10,11,29}. Despite representation of light dependent and independent monoterpene emissions, discrepancies exist between this representation and the literature^{3,8-11,16,17,24,28,29}.

The explanation for these discrepancies among studies appears to lie in the fact that for some plant species, e.g., members of the genus *Pinus*, monoterpene emissions are largely not light-dependent, though this also tends to vary with season^{24,25,30}. While for other plants species, e.g., *Fagus* and the European live oaks (sub-genus *Cerris*), emissions are largely light-

dependent^{5,31}. The observed variability appears to be a function of both plant species and terpenes species^{8,10,29,30}. That is, the same terpenoid compound may be light-dependent in one species but light-independent in another. From the perspective of atmospheric processes though, the impacts of monoterpenes depend on their absolute fluxes, the timing and control over these fluxes, and their specific reactivities. A major goal of the present work is to understand the potential role that the minor contribution of highly reactive individual compounds with differing temporal variability may play in the atmosphere. Certain monoterpenes that are often emitted at low levels but have high reactivities raises 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 can have 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. β -pinene, β -cedrene). Consequently, long-term measurements of speciated BVOCs can assist in modeling BVOC emissions and in understanding their contribution to ozone modulation and SOA formation³². This extends further to the importance of individual fast-reacting isomers, which can represent substantial fractions of total reactivity even at low concentrations³³. 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 reactivity on diurnal, seasonal, and interannual timescales. We elucidate the impact of temporal variability on ozone reactivity on scales from hours to years by identifying two varying components in the data, which are identified as coming 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 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.

Methods

Data collection and preparation

We measured in-canopy BVOC concentrations at the Virginia Forest Research Lab (VFRL) (37.9229 °N, 78.2739 °W) in Fluvanna County, Virginia. The VFRL sits on the east side of the Blue Ridge Mountains and is about 25 km east-southeast of Charlottesville, VA. 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 chromatography flame ionization detector (GC-FID) adapted for automated collection and analysis of air samples from mid-canopy (~20 m) of the VFRL. Additional details pertaining to the measurement location, instrument operation, and data analyses can be seen in McGlynn et al.³⁴. 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 indices³⁵. The chromatographic data were analysed using the freely-available TERN software packaged³⁶ 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 the months of May-September. BVOC concentrations measured during the first year are published as doi: <https://doi.org/10.17632/jx3vn5xxcn.1>.

Positive matrix factorization (PMF)

Positive matrix factorization (PMF) has been widely used for source apportionment problems³⁷⁻³⁹. A large number of variables can be reduced by the PMF algorithm to the main sources or factors that drive the observed variability³⁷. Application of PMF to multi-variable data generates two matrices, the factor contributions and factor profiles³⁷, which for environmental data represent timeseries as a set of covarying variables (e.g., chemical species).

This work employed EPA's 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.³⁷:

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

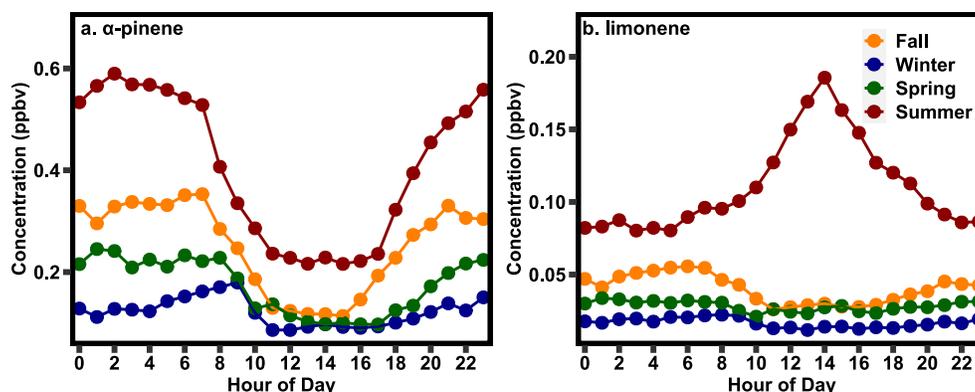


Figure 1. The mean (a) α -pinene and (b) limonene concentration averaged in the four seasons of the northern hemisphere between September 2019 and September 2021.

The method detection limit, MDL, is 2.2 ppt for monoterpenes³⁴. 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 processing³⁷. Factor contributions are returned from the PMF program as normalized values, which are converted to concentration by multiplying returned values by the sum of the concentrations of species in the factor profiles.

Ozone reactivity calculations

Reactivity of an individual BVOC with ozone (O_3R) is calculated as the sum of the products of the concentration and oxidation reaction rate of each BVOC_i:

$$O_3R_{\text{tot}} (s^{-1}) = \sum(k_{O_3+BVOC_i} [BVOC_i]) \quad (2)$$

All rate constants (units: $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$) at 298 K used in this work are published in a range of literature⁴⁰⁻⁴⁵.

Results and Discussion

At the Virginia Forest Research Lab, 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 dominant fraction of speciated ozone reactivity from BVOCs³⁴ at the research site throughout the year.

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 (Figure 1). α -pinene concentrations were lowest in the daytime winter hours at about 0.05 ppb and highest in the evening 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 temperature-driven monoterpene concentrations¹⁶ due to the higher planetary boundary layer and increased concentrations of oxidants during the day. Concentrations were lowest in the middle of the day, between 10:00 and 17:00 and highest between 20:00 and 8:00 (Figure 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 lows and night-time highs, though with weaker diurnal variability (Figure 1b). In summer, however, diurnal trends in limonene concentrations are very different, with a peak in the mid to late afternoon. To reach daytime peaks in concentration, daytime emissions of limonene must be high, particularly given that the reaction rate of limonene with OH radical, ozone, and nitrate is 3, 2.3, and 1.3 times as fast, respectively, as 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 night-time (7PM - 7AM) average concentrations (Figure 2). As observed in the diurnal profiles, α -pinene evening concentrations are higher than daytime concentrations throughout the year; while concentrations increase in the summer, this

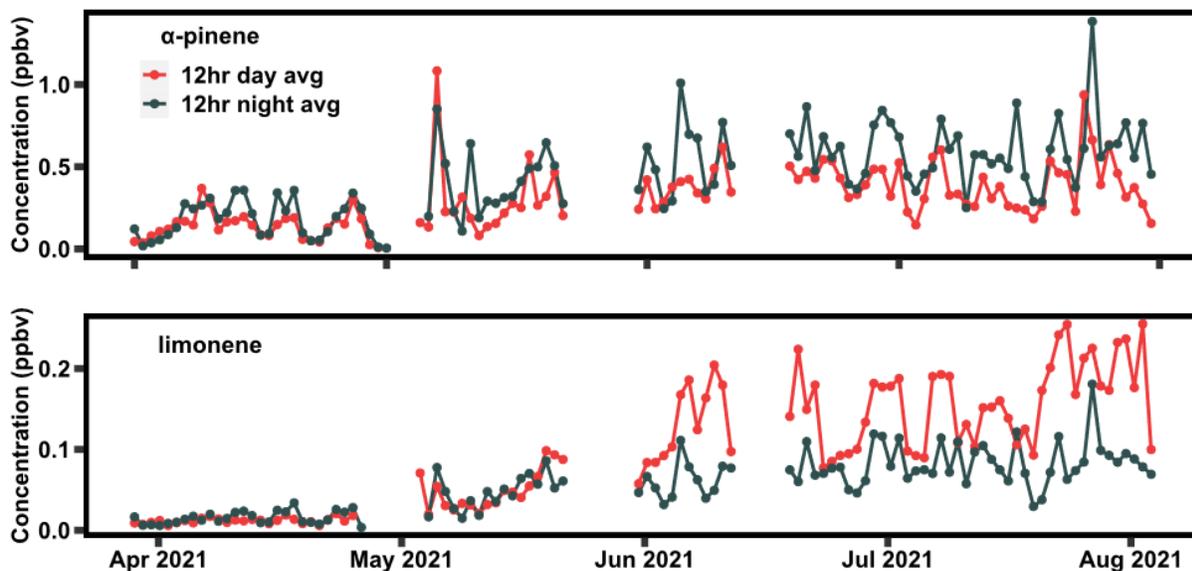


Figure 2. The 12-hour average of α -pinene and limonene between April 2021 and August 2021. The averaging period for each compound was between 7 AM and 7 PM.

increase is observed in both daytime and nighttime concentrations (Figure 2a). In contrast, while concentrations of limonene are highest at night throughout the early spring, concentrations begin to peak in the daytime in late-May (Figure 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 (Figures 1, 2). 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 BVOC species, and appears to be a component of a set of light-dependent monoterpene emissions.

Light dependent and light independent monoterpene concentration

To better characterize the observed light-dependent monoterpenes and quantify their impacts, the observed 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 to have high daytime concentrations. 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 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 run³⁷. The Pearson correlation

coefficient threshold used for this analysis was the EPA PMF default value of 0.6³⁷.

A “light dependent” factor is present primarily during the summer, characterized by daytime peaks that roughly coincide with the seasonality and variability of isoprene (Figure 3). 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 Figure 3a, b. 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 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 stored pools)³. Interpretation of factors is further supported by their diurnal trends, a representative sample of which is shown in Figure 4. 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. In contrast, the higher-concentration monoterpene factor peaks in the evening to early morning hours, following more typical monoterpene diurnal patterns. We attribute these monoterpene concentrations to temperature-driven light independent emissions of monoterpenes.

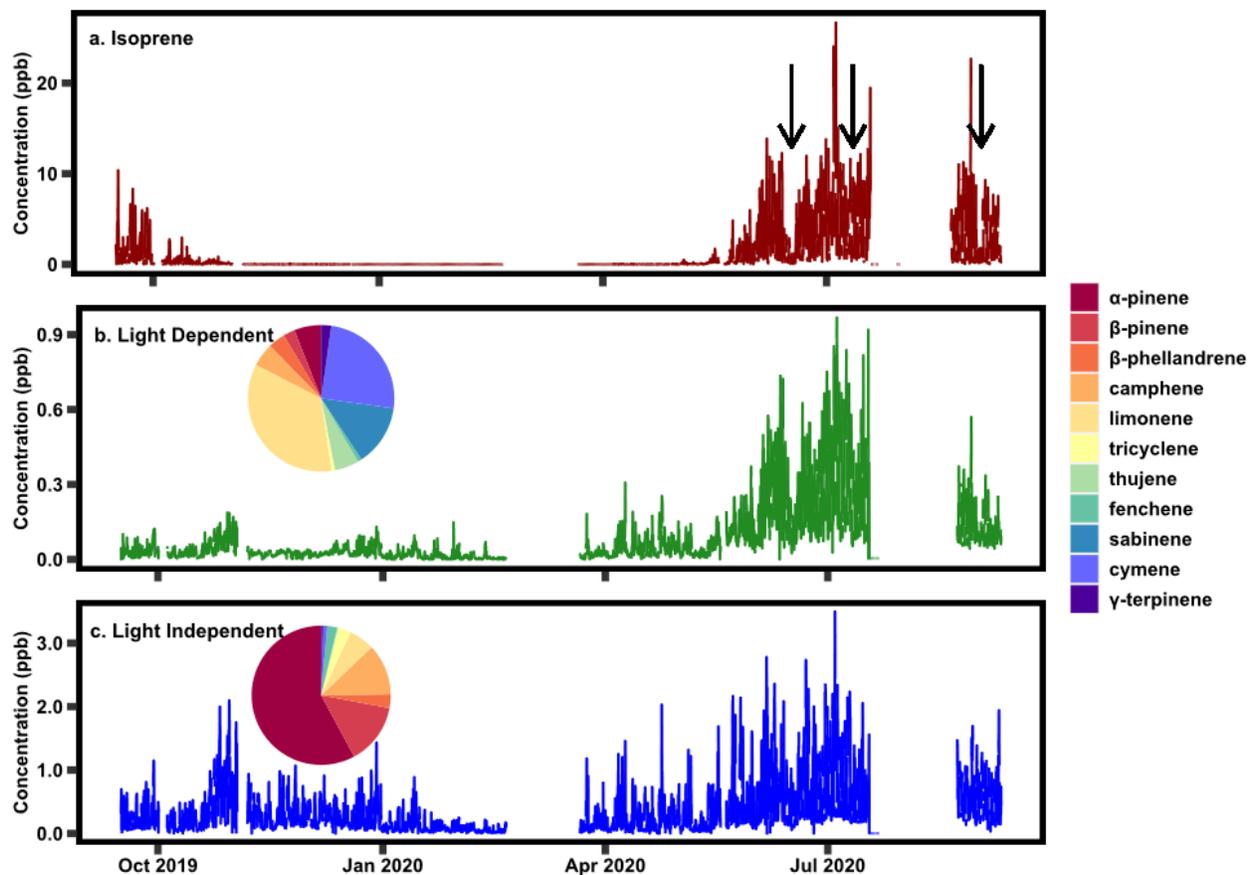


Figure 3. Time series of isoprene concentration, the two positive matrix factorization factors between September 2019 and September 2020 and the breakdown of the monoterpene species that contribute to each factor. The arrows on 3a indicate periods when both isoprene and the light dependent monoterpene factor decreased together.

Table 1. Percent of concentrations attributed to *de novo* and pool emissions by compound for 2019-2020

compound	Annual		Summer	
	% 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	9	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	57	33.5	66.5
thujene	14.6	85.4	10.2	89.8
cymene	14	86	9.8	90.2
sabinene	0	100	0	100

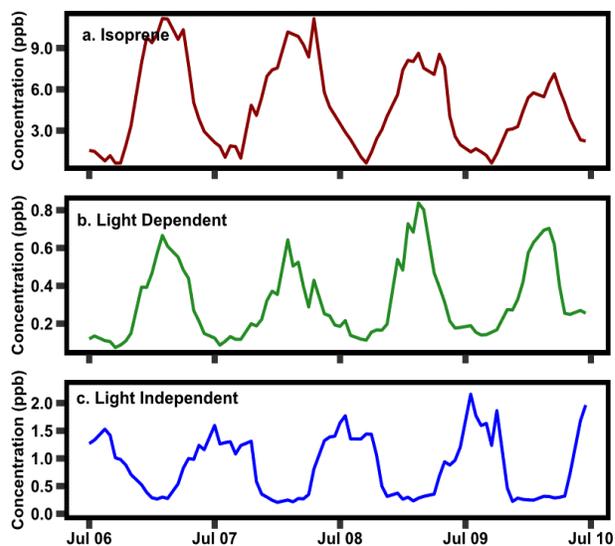


Figure 4. A four-day period in July 2020 of isoprene, and the two PMF factors (Light Dependent and Light Independent).

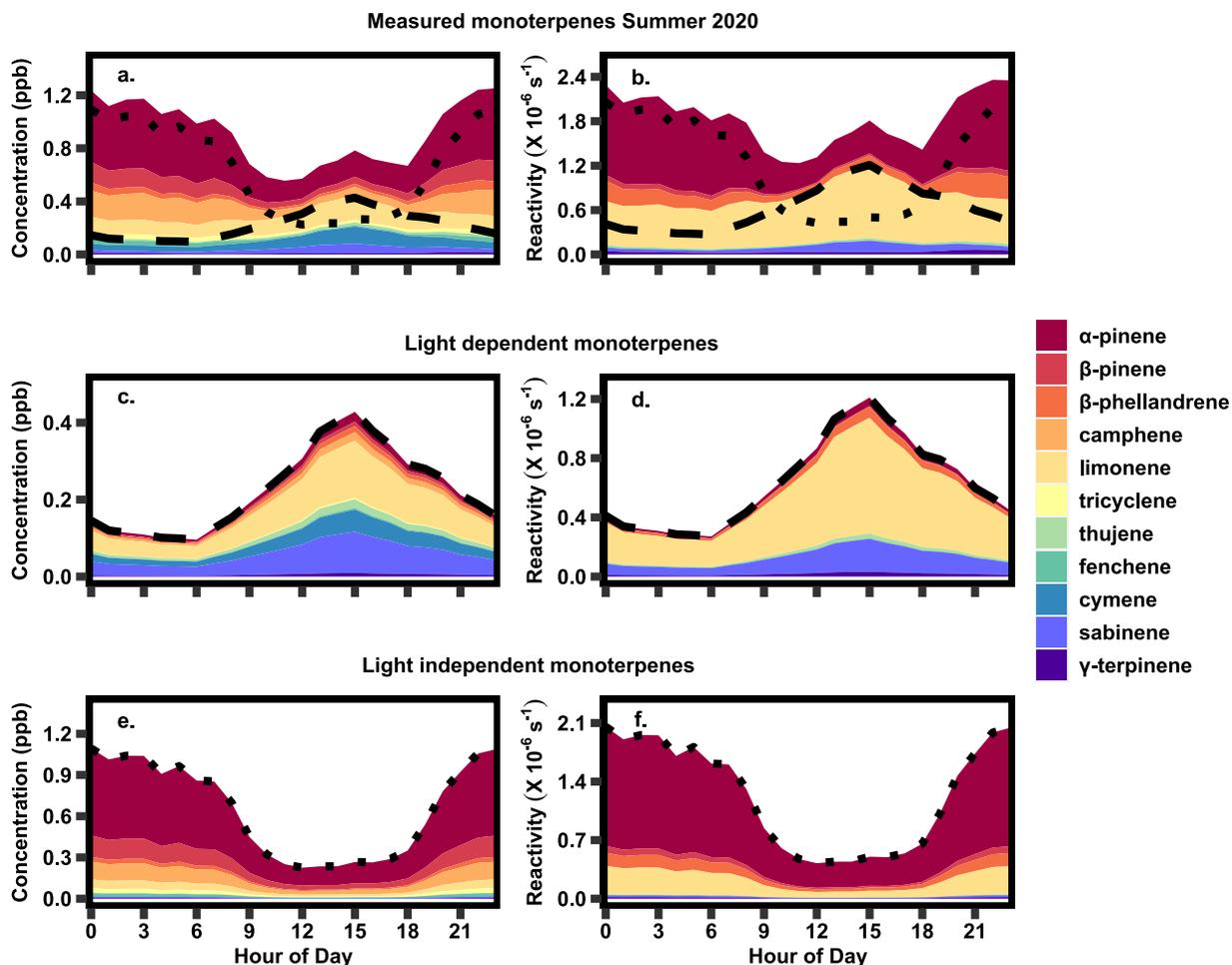


Figure 5. The diurnal profile of (a) measured monoterpene concentration and (b) ozone reactivity, (c) factor 1 monoterpene concentration and (d) ozone reactivity, and (e) factor 2 monoterpene concentration and (f) ozone reactivity for summer 2020.

Overall, the light dependent factor accounts for ~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 only in the light independent factor (Table 1). Conversely greater than 85% of cymene, sabinene, and thujene are found in the light dependent factor (Table 1). A small number of species are more 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).

Ozone reactivity

Despite the low contribution of the light dependent factor to total monoterpene concentration, this factor has a large impact on ozone reactivity. Comparing the

stacked diurnal concentration profile (Fig. 5a) to the stacked ozone reactivity diurnal profile (Fig. 5b) in summer illuminate's clear differences in their variability. 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 the ozone reaction rate constant for each species, there is a clear mid-day peak that contributes about as much as nighttime ozone reactivity in the summer. Further, the two largest contributors to total ozone reactivity are α -pinene and limonene despite limonene's lower contribution to total concentration due an ozone reaction rate that is 2.3 times greater than α -pinene.

A majority of the 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%). The major contribution of limonene to the light dependent monoterpene mixture makes light driven emissions

particularly reactive, with a reaction rate roughly 1.4 times that of the light independent mixture. 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. Even in the summer, when concentrations of light dependent monoterpenes are highest, the diurnal profile of the total chemical class (Figure 5a) roughly follows that of α -pinene (Figure 1a) with only moderate daytime concentrations. However, this average profile is a combination of a night-time peak dominated by light independent compounds (Figure 5e) and a daytime peak dominated by light dependent compounds (Figure 5c). This daytime peak has a large impact on daytime ozone reactivity (Fig. 5d, f), such that calculated summertime ozone reactivity consequently has little diurnal pattern and is roughly uniform throughout the day (average between 1.4 - $2.4 \times 10^{-6} \text{ s}^{-1}$) during the summer months.

Conclusion

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 monoterpenes and isoprene. 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 belies their impact on ozone reactivity. Due to differences in the temporal variability of the two monoterpene classes and the higher reaction rates of the light dependent mixture, we observe high ozone reactivity in the summer daytime that is not well captured by bulk monoterpene concentration. This reactivity is dominated by limonene, which contributes >80% to light dependent sourced ozone reactivity and ~25% to light independent sourced ozone reactivity (while α -pinene contributed the other half). These findings highlight the need for speciated 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 and for quantifying OH reactivity but demonstrate a need for isomer-resolved understanding of ozone reactivity. For example, while this work supports the general conclusion that light dependent monoterpenes are a minor component (reflected in current emission models³ and supported by measurement studies^{9,11,16,17,24,30,46}), 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 light dependent emissions are critical for understanding this ecosystem. 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, but 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 limonene³ and do not tend to vary light dependent fraction by plant function type. Small gaps such as these in our understanding of what drives monoterpene emissions may lead to significant uncertainty in models or outcomes.

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