1	Vapor pressure deficit helps explain biogenic volatile organic compound fluxes from the
2	forest floor and canopy of a temperate deciduous forest
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25 Abstract

26 Biogenic volatile organic compounds (BVOCs) play critical roles in ecological and earth-system processes. 27 Ecosystem BVOC models rarely include soil and litter fluxes and their accuracy is often challenged by 28 BVOC dynamics during periods of rapid ecosystem change. We measured BVOC concentrations within a 29 mixed deciduous forest and used a hybrid Lagrangian/Eulerian canopy transport model to estimate BVOC 30 flux from the forest floor, canopy, and whole ecosystem during spring leaf-out. Canopy flux measurements 31 were dominated by a large methanol source and small isoprene source during the leaf-out period, consistent 32 with past measurements and theory, and indicative of a BVOC flux situation rarely used in emissions model 33 testing. Measurements also revealed that the contribution of the forest floor to whole-ecosystem BVOC 34 flux is conditional on the compound of interest and often non-trivial. We then created linear models of 35 forest floor, canopy, and whole-ecosystem flux for each study compound and used information criteria-36 based model selection to find the simplest model with the best fit. Vapor pressure deficit (VPD) was 37 included in the best canopy, forest floor, and whole-ecosystem BVOC flux model more than any other study 38 variable, but most published BVOC flux models do not include VPD. Future studies should investigate how 39 VPD contributes to BVOC flux through biophysical mechanisms like evaporative demand, leaf temperature 40 and stomatal function.

41

42 Introduction

43 Ecosystems are dynamic sources and sinks of biogenic volatile organic compounds (BVOCs), which play 44 important roles in plant defense (Yuan et al. 2009; Junker and Tholl 2013), ecological signaling (Schiestl 45 2010; Holopainen and Blande 2012), and atmospheric chemistry and physics (Fuentes et al. 2000, 2016; 46 Kulmala et al. 2013; Faiola et al. 2014). BVOCs are also important in ecosystem and global carbon budgets. Their total global emission is on the order of 0.76 Pg C yr⁻¹ (Sindelarova et al. 2014), nearly a quarter of 47 48 the size of the net land carbon sink (Friedlingstein et al. 2019), and BVOC flux can comprise up to 10% of 49 photosynthetic carbon uptake at the ecosystem scale (Peñuelas and Llusià 2003). These emissions, however, 50 are dynamic and respond to continued shifts in land use, climate, and atmospheric chemistry (Peñuelas and

51 Staudt 2010; Calfapietra et al. 2013; Unger 2014; Hantson et al. 2017). It is thus critical to identify primary 52 drivers contributing to ecosystem BVOC fluxes to better understand BVOC dynamics in a changing world. 53 Most ecosystem BVOC emissions arise from plant foliage (Figure 1) (Guenther 1997), particularly 54 via plant stomata (Fall and Monson 1992), with important additional sources from leaf litter (Leff and Fierer 55 2008; Gray et al. 2010, 2014; Aaltonen et al. 2011). Dynamic source/sink behavior is also observed within 56 the soil itself (Cleveland and Yavitt 1997; Insam and Seewald 2010; Tang et al. 2019; Rinnan and Albers 57 2020). For example, in forests, soil BVOC flux results from belowground dynamics including the 58 functioning of roots (Kreuzwieser and Rennenberg 2013; Gray et al. 2014) and their mycorrhizal 59 associations (Trowbridge et al. 2020), and can subsequently alter the composition of the microbial 60 communities that give rise to BVOCs (McBride et al. 2020), resulting in complex feedbacks. It is unclear 61 if soils and litter make a meaningful contribution to total ecosystem BVOC flux to warrant inclusion in 62 ecosystem models (Asensio et al. 2007), though emerging evidence indicates that they likely do (e.g. Mäki 63 et al. 2019). Aboveground BVOC sinks include reactions with oxidative species within the plant canopy 64 (Carter 1994; Fuentes et al. 2007), dry deposition (Guenther 2015) and, critically, uptake by plant stomata 65 such that stomatal BVOC exchange should be treated as bi-directional (Niinemets et al. 2014) (Figure 1). 66 Despite our recognition of complex interactions among BVOC emissions drivers, ecosystem models tend 67 to focus on emissions from just the plant canopy, rather than including soils and leaf litter (Baldocchi et al. 68 1999; Niinemets et al. 2013; Guenther 2015), and they are seldom challenged with observations from a 69 broad set of ecosystem components. Not only are ecosystem BVOC emission models limited in the 70 variables and projections that are made, but we do not even know if further development, with inclusion of 71 more variables, is worth the time of further investigation. In other words, we are in a very non-informed 72 state with regard to the performance of the current generation of model projections and the most promising 73 opportunities for improvement. This study was aimed at enhancing our understanding of ecosystem BVOC 74 emission modeling with regard to soil and litter processes, and model inputs.

Models of ecosystem BVOC exchange are also challenged by plant phenology and seasonality
(Holzinger et al. 2005). These include emission bursts during periods of new foliage growth (Aalto et al.

77 2014, 2015) that may be due to the direct exposure of plant resin to the atmosphere (Eller et al. 2013), other 78 aspects of plant-water relations like xylem refilling (Vanhatalo et al. 2015), or the production or methanol 79 and acetone during leaf ontogeny (Macdonald and Fall 1993; Nemecek-Marshall et al. 1995). These plant-80 associated fluxes are controlled by a complex interplay among environmental and biological variables, 81 including intrinsic cellular processes as well as extrinsic factors such as air temperature, solar radiation, and 82 soil moisture (Monson et al. 1995; Guenther et al. 2012). Our knowledge about the interactions among plant 83 processes and the environment, however, is continually increasing and has progressed immensely since the 84 creation of the current generation of ecosystem BVOC emission models.

85 Model development typically lags behind empirical discovery, making it likely that there are 86 additional intrinsic and extrinsic variables that need to be added to existing models. These variables might 87 include the vapor pressure deficit (VPD) which represents atmospheric demand for water and is critical for 88 plant canopy conductance (Novick et al. 2016), wind speed and canopy roughness, which influence canopy 89 aerodynamic conductance and canopy air-space venting (Bohrer et al. 2009), the diffuse fraction of solar 90 radiation, which can penetrate the plant canopy more efficiently than the direct beam to impact the radiative 91 environment of the subcanopy (Oliphant and Stoy 2018; Moon et al. 2020), and the surface (skin) 92 temperature, which may provide a more accurate description of the temperature at which biological 93 processes are occurring compared to air temperature (Still et al. 2014; Pau et al. 2018). As in the case for 94 our current state of ignorance concerning the importance of soil and litter processes to accurately predict 95 ecosystem BVOC fluxes, there is a need for studies that take a step back from the current form of emissions 96 models and offer a fresh perspective at the relationships among model logic and existing knowledge of 97 canopy and plant ecophysiological processes.

98 To study the dynamics of BVOC flux during the leaf-out period and investigate model inputs 99 necessary to explain their dynamics, we measured BVOC concentrations within a mixed deciduous canopy 100 and estimated source and sink areas and fluxes using a hybrid Lagrangian/Eulerian canopy transport model. 101 The transport model incorporated BVOC concentration measurements from a unique logarithmic canopy 102 profiling system with a higher density of observations from lower in the canopy airspace, compared to past

103 studies, both of which allowed us to isolate the contribution of the forest floor to ecosystem-scale BVOC 104 exchange. The biotic diversity of species and traits in mixed forests creates additional challenges to 105 understanding controls over sources and sinks of BVOCs (Kaharabata et al. 1999) and we included analyses 106 of wind direction to understand if flux source area was important to describe efflux in the study forest. 107 Finally, models of BVOC flux are increasingly cognizant of compounds that make a minor contribution to 108 mass flux (Guenther et al. 2012) but may play disproportionate roles in ecological interactions and 109 atmospheric chemistry (Goldstein and Galbally 2007; Clavijo McCormick et al. 2014). We took care to not 110 exclude an analysis of these minor compounds by searching for associations with compounds that are better 111 understood for a more complete chemical description of ecosystem-scale BVOC flux.

112

113 Methods

114 Morgan Monroe State Forest

115 Measurements were made in the Morgan-Monroe State Forest in south-central Indiana, USA, at 39° 190' 116 N, 86° 250' W on and around a long-running Ameriflux eddy covariance tower (site code US-MMS, 117 Schmid 2000). The mean annual temperature is 10.9 °C and the mean annual precipitation is 1030 mm. The 118 study site is an approximately 80 year old mixed hardwood forest with trees that associate with ECM fungi 119 including shagbark and pignut hickory (Carya ovata and C. glabra), red and white oak (Quercus rubra and 120 Q. alba), and American beech (Fagus grandifolia), and those that associate with AM fungi including tulip 121 poplar (Liriodendron tulipifera), sugar maple (Acer saccharum), and sassafras (Sassafras albidum). 122 Seedlings and the isoprene-emitting spicebush (Lindera benzoin) are found in the understory. The mean 123 canopy height in the vicinity of the tower was 27 m when measurements were made. Please see (Brzostek 124 et al. 2015) for additional site details.

125 Micrometeorological measurements

126 The US-MMS eddy covariance tower includes a full suite of micrometeorological measurements including:

127 eddy covariance systems comprising CSAT3 (Campbell Scientific, Logan, UT) sonic anemometers and LI-

128 7000 closed path infrared gas analyzers (LICOR, Inc., Lincoln, NE) at 46 m, 34 m, and 2 m above the forest 129 floor; HMP35C air temperature/relative humidity measurements (Vaisala, Vantaa, Finland) at the same 130 heights; a CNR-1 four-component radiometer (Kipp and Zonen, Delft, The Netherlands) at 46 m; and 131 CS615/6 (Campbell Scientific) soil moisture sensors and soil temperature measurements at 10 cm depths 132 to bedrock. We use direct and diffuse photosynthetically active photon flux density (PPFD), measured by 133 a BF3 sunshine sensor (Delta-T Devices, Cambridge, UK) to describe BVOC responses to the light 134 environment.

135 Proton transfer reaction-mass spectroscopy

136 BVOC measurements were made using a proton transfer reaction-mass spectrometer (PTR-MS; Ionicon 137 Analytic, Innsbruck, Austria) housed in an air-conditioned research building adjacent to the US-MMS 138 tower. We selectively analyzed 49 different mass/charge (m/z) ratios following previous work on 139 compounds identified in ambient air (Gouw et al. 2007; Blake et al. 2009; Ellis and Mayhew 2013) (Table 140 S1). We focus on key compounds for which we have calibration standards, namely formaldehyde, 141 methanol, acetonitrole, acetaldehyde, acetone, dimethyl sulfide (DMS), isoprene, methyl vinyl ketone 142 (MVK), methacrolein, methyl ethyl ketone (MEK), benzene, toluene, C8 aromatics, C9 aromatics, and 143 monoterpenes (Table S1). Concentrations of the fragments of isoprene and monoterpene (m/z 41 and m/z144 81) were calculated using a theoretical transmission curve created for the PTR-MS instrument. The 145 concentrations of the fragments were then added to the concentration measurements of the compounds 146 calculated using calibration. Calibrations were performed prior to each measurement campaign using a 147 multi-component calibration mix (\pm 5% confirmed by the manufacturer using GC-MS) stored in nitrogen 148 gas (Apel-Riemer Environmental, Inc.). We studied the time series of the normalized mass-to-charge (m/z)149 ratios of compounds for which calibration standards were not available to see if they follow similar patterns 150 to compounds with calibration standards.

151 The PTR-MS drift tube pressure (*p*) was set at 2.1 mbar and temperature (*T*) to 333.15 K with a 152 drift field of 600 V. The parent ion signal was set to $\sim 8 \times 10^6$ counts per second. The protonated oxygen 153 to primary ion count (O₂⁺:H₃O⁺) ratio was < 3.5%. The volume mixing ratio (VMR, ppbv) of calibrated compounds was calculated by dividing its m/z by its calibration coefficient calculated using a linear fit. To
calculate concentrations using the transmission factor approach, the volume mixing ratio VMR of each
compound was calculated following (Ellis and Mayhew 2013):

157
$$VMR = \frac{i(MH^+) \times 10^9}{i(H_3 0^+) k t N_d}$$
(1)

where $i(MH^+)$ is the protonated compound of interest divided by its transmission factor, $i(H_3O^+)$ is the primary ion count divided by its transmission factor and multiplied by 500, *k* is the rate coefficient, *t* is reaction time, and the total number density of the gas in the drift tube, N_d , is:

$$N_d = \frac{pA_N}{RT} \tag{2}$$

162 where p is in Pa, A_N is Avogadro's number, and R is the ideal gas law constant (8.3145 m³ Pa mol⁻¹ K⁻¹).

163 *Canopy profile measurements*

The canopy BVOC profile measurement campaign took place from May 8 to May 25, 2015 with a 77minute missing measurement period during maintenance on May 12. During sampling, the inlet of the PTR-MS was attached to the canopy profiling system with measurements at 0.25 m, 0.5 m, 1 m, 2 m, 4 m, 8 m, 16 m, and 32 m (i.e. 2⁻² to 2⁵ m). Measurements were made every 10.45 seconds. The first three and last PTR-MS measurements at each level were discarded to ensure that the lines were flushed with fresh air. The remaining observations at each level were then used to calculate a mean concentration of each of the study compounds.

171 *Canopy flux estimation*

Estimating the net flux of a scalar (here, BVOCs) from canopy profile observations requires a model that can compute spatially-distributed scalar sources from time-distributed concentration measurements, known as the 'inverse problem' (Raupach 1989a). The challenge is to infer the source and sink (*S*) dynamics of a scalar as a function of height (*z*) from measurements of the scalar concentration (*c*) at different heights in the canopy across time (*t*) which are coupled by the principle of continuity and the scalar concentration budget equation (see Monson and Baldocchi 2014). The time- and horizontally-averaged, steady-state scalar conservation equation for planar homogeneous high Reynolds and Peclet numbers flow (i.e.
neglecting molecular diffusion, (Finnigan 1985; Raupach 1988) is given by:

180
$$\frac{\partial \langle \bar{c} \rangle}{\partial t} = 0 = -\frac{\partial \langle \overline{w} \bar{c} \bar{c} \rangle}{\partial z} + S$$
(3)

181 where *w* is vertical velocity, primes are fluctuations from time averages (represented by overbars), and the 182 angle bracket denotes horizontal averaging as discussed in (Raupach and Shaw 1982), such that $\langle \overline{w'c'} \rangle$ 183 represents the turbulent vertical flux of a scalar.

184 Early approaches used 'K-theory', which assumes that scalar fluxes, and, consequently, S (Eq. 3), 185 are related to scalar gradients through an eddy diffusivity coefficient within the plant canopy, which can 186 vary with height. However, the dynamics of turbulence within plant canopies, including counter-gradient 187 fluxes, often result in a situation where K-theory becomes unreliable (Denmead and Bradley 1985). 188 Whereas some approaches have improved models for eddy diffusivity to account for these shortcomings 189 (Freire et al. 2017), here we adopt the 'hybrid' approach of (Siqueira et al. 2000) that combines the two 190 dominant approaches designed to overcome the limitations of K-theory: inverse Lagrangian localized near-191 field (LNF) theory (Raupach 1989a, b) and high-order Eulerian closure models (Katul and Albertson 1999). 192 In brief, the hybrid approach acknowledges that LNF theory assumes normally-distributed vertical 193 velocity statistics, but also recognizes that non-Gaussian ejection-sweep cycles frequently drive mass 194 transport within tall plant canopies (Figure 1), and that pure Eulerian formulations are sensitive to 195 uncertainties in the measurement of c due to a limited scope for replication in the inversion of S from c196 (Sigueira et al. 2000). To overcome these limitations, Sigueira et al. (2000) proposed a model that retains

197 the concept of the inverse Lagrangian approach, which grants the model the desired robustness to 198 measurement errors, but using the Eulerian frame of reference to estimate the elements of the dispersion 199 matrix, thus mechanistically accounting for vertical-velocity skewness effects in scalar transport.

The procedure consists of dividing the canopy into multiple layers (Figure 1). The task then becomes to find the combination of the canopy layer source and sink strengths (i.e. *S*) that best recover the measured mean scalar concentration profile. In an inverse sense, the dispersion matrix is constructed by dividing the canopy into layers of unit source strength, and then calculating the expected mean concentration profiles from each layer individually using the scalar-flux budget equation (Eq. 3), which is re-arranged to provide a differential equation for scalar concentration (see Supplimental Material. Neglecting buoyancy, scalar drag and waving source terms, the time and horizontally averaged steady-state equation can be written as a second-order ordinary differential equation (ODE) for scalar concentration as a function of height (Siqueira et al. 2000):

209
$$M_1(z) \ \frac{\partial^2 \langle \bar{c} \rangle}{\partial z^2} + M_2(z) \ \frac{\partial \langle \bar{c} \rangle}{\partial z} = M_3(z)$$
(4)

where *c* is the scalar concentration function of height. The coefficients $M_{1,2,3}$ are functions of scalar flux and turbulent velocity statistics. The profiles of velocity statistics, when normalized by friction velocity (u*) at a reference height, becomes a function only of leaf-area-density vertical distribution (LAD), provided for MMSF by (Oliphant et al. 2006) (Figure 1) and can be obtained by a second-order closure model for turbulent flow. Here, we used the model described in (Siqueira et al. 2012), who explicitly solved an equation for turbulent-kinetic-energy dissipation, required for the *M*-coefficients.

Equation (4) is not closed because it requires the scalar fluxes, which can be obtained by Eq (3) given source distribution is known. With a prescribed source, as is the case for dispersion-matrix construction, the scalar budget equation (Eq. 3) can be integrated to provide the flux used in the *M*coefficients. Furthermore, with proper boundary condition, Eq. (4) can be numerically solved (here we used a finite-volume technique) to give the vertical profile of $\langle \bar{c} \rangle$.

221 Next, the dispersion matrix is computed from

$$222 D_{ij} = \frac{\langle \bar{c} \rangle_i - \bar{C}_R}{s \Delta z_j} (5)$$

where, $\langle \bar{c} \rangle_i$ represents the concentration at the measurement height *i* (*i*=1,2,...,*n*) resulting from the source layer *j* (*j*=1,2,...,*m*), calculated using Eq. (3) and (4), and \bar{C}_R is the concentration at a reference height. We adopted the last measurement height (32 m) as the reference, which was used as the boundary condition for Eq. (4). D_{ij} are the elements of the (*n* by *m*) dispersion matrix; *s* is an assumed unitary source strength and Δz_j is the source layer thickness. Once the dispersion matrix is determined, the source strengths S_i can be readily computed if *m*=*n*:

229
$$\bar{C}_{i,m} - \bar{C}_R = \sum_{j=1}^m D_{ij} S_j \Delta z_j \tag{6}$$

where $\bar{C}_{i,m}$, contrary to (5), are the time-averaged concentrations at height *i*. However, this would make estimated source sensitive to measurement errors (Raupach, 1989). To avoid such instability, redundant concentration measurements are necessary (i.e. n > m), such that the system becomes over-determined. As shown by (Raupach 1989a), such redundancy reduces (6) to a regression problem with the source strengths calculated by a least-squares approach:

235
$$\sum_{k=1}^{m} A_{jk} S_k = B_j \quad (j=1,..,m)$$
 (7)

where:

$$237 A_{jk} = \sum_{i=1}^{n} D_{ij} \Delta z_j D_{ik} \Delta z_k (8)$$

238 and

$$B_j = \sum_{i=1}^n (C_i - C_R) D_{ij} \Delta z_j \tag{9}$$

The above regression procedure addresses the limited-sampling problem inherent in pure Eulerian frameworks. However, such an approach, when applied to a limited sample size, retains high variance among redundant source estimates. To improve assessment of retrieved source values and their associated variances, an additional smoothness constraint was imposed on (7) and (8) using the Weighted Measuresof Length procedure (Menke, 2018; Siqueira et al. 2000).

245 *Modeling analysis*

246 We created linear models of the forest floor, canopy, and ecosystem flux of each studied BVOC compound 247 (Table 1) as a function of multiple micrometeorological variables and the surface-atmosphere flux of 248 carbon, water, and heat, fit using maximum likelihood. We discriminate amongst the models by calculating 249 the Akaike's Information Criterion for each with the assistance of the *dredge* function in the MuMIn 250 package (Bartoń, 2020) using R version 4.0.0 (R Core Team, 2020) and selecting the model with the lowest 251 AIC as the most parsimonious. The goal of the modeling analysis is to determine which variables should 252 not be excluded for understanding micrometeorological and canopy controls over BVOC flux rather than 253 creating models of the flux of 14 compounds from three sources during the leaf-out period of a mixed 254 deciduous forest. The micrometeorological variables used to create the models - in addition to those listed 255 above - include below canopy and diffuse photosynthetically active radiation (as a surrogate for incident 256 solar radiation), soil temperature and moisture, vapor pressure deficit, wind speed and direction as a 257 surrogate for source area within the diverse forest canopy, and canopy and forest floor surface (skin) 258 temperature calculated from outgoing longwave radiation measurements using the Stefan-Boltzmann Law 259 and assuming a canopy and forest floor emissivity of 0.98 (Jin and Liang 2006).

260

261 Results

262 *Meteorology*

The May 8 – 26, 2015 measurement period was characterized by alternating (relatively) warm and cool air
temperatures (Figure 2A). Most precipitation events occurring during the first half of the measurement
period (Figure 2A) and variability in PPFD resulted in warm/mostly sunny (May 8-11, 15, 23-25),
warm/cloudy (May 16-18, 26), cool/mostly sunny (May 12-14, 19, 22) and cool/cloudy (May 20-21)
periods (Figure 2A and 2B). Vapor pressure deficit was relatively high (> 20 hPa) on May 8 when

measurements began and during the latter measurement period (May 24-25, Figure 2C). Prevailing winds
arrived largely from the SSW (Figure 2C, S1A & S1B) with a peak distribution at 190 degrees at 46 m and
200 degrees at 34 m. Subcanopy wind speed was dominated by flows from the SW with little contribution
from the SE (Figure 2C & S1C). Plant area index increased throughout the May, 2015 measurement period
from 3.4 m² m⁻² to 4.7 m² m⁻² (Figure 3).

273 *BVOC concentrations within the canopy*

274 Methanol had the highest mean (\pm s.d.) concentration across all measurement heights at 12.7 \pm 6.5 ppbv 275 (Table 1). Within-canopy mean BVOC concentrations of the key compounds methanol, isoprene, and 276 monoterpenes were relatively high during the earlier part of the measurement period (Figure 4), then 277 declined and increased again on May 15 during a warm period after a small rain event. Canopy BVOC 278 concentrations rose again during the warm and sunny period of May 23-25. Notably, methanol, isoprene, 279 and monoterpene concentrations were often higher in the overstory at 16 m during May 8-9 and May 13 280 and isoprene and monoterpene concentrations were often higher near the soil surface and subcanopy at 281 0.25 m and 0.5 m from May 15-25 (Figure 4), implying different sinks and sources within the canopy 282 volume.

283 The time series for most key compounds exhibited characteristic concentration profiles as a 284 function of time of day and canopy height with elevated concentrations in the afternoon within the canopy 285 and near the forest floor (Figure 5) with the exception of methanol, which had an early morning peak 286 throughout the canopy volume, on average, and formaldehyde which had a peak in the lower forest canopy 287 in the afternoon. The mass-to-charge ratios of most of the 49 compounds studied also exhibited a 288 characteristic pattern with higher values within and above the canopy and in the afternoon (Figure S2) 289 noting that many compounds were close to the signal-to-noise ratios as evidenced by the striping pattern in 290 the time / height concentration plots. Some compounds exhibited time / height concentration dynamics that 291 were unique compared to other profiles (e.g. m/z 32, Figure S2).

292 Modeled BVOC fluxes, sources, and sinks

Models of the second and third moments of the vertical velocity normalized by u^{*} matched observations well on average (Figure S3). Modeled BVOC concentrations likewise tended to match measurements well with the exception of the lower canopy where modeled values were frequently lower than measurements (Figure 6) due likely in part to challenges in modeling turbulence near surfaces (the boundary layer effect) and challenges in redistributing parcels toward the surface in Lagrangian approaches. Forest floor BVOC source strength may be underestimated and/or sink strength overestimated as a consequence, and results are subject to this uncertainty.

300 Most BVOC compounds exhibited a relatively large net efflux to the atmosphere from the plant 301 canopy from the beginning of the measurement period starting at mid-day on May 8 until mid-day on May 302 9 (Figure 7) that resulted from (relatively) high BVOC concentrations in the overstory at 16 m during the 303 first day of measurements (e.g. Figure 4). There was a subsequent net uptake of most study BVOC 304 compounds from mid-day on May 9 until mid-day on May 12 during a cooling trend with cloudier 305 conditions (Figure 2 & 7). This was followed by another net efflux of most BVOC compounds from mid-306 day on May 12 until mid-day on May 13 during a sunnier period (Figure 2 & 7). Afterward, net BVOC flux 307 from the overstory tended to be minor for some compounds (e.g. methanol) or exhibit net uptake for others 308 (e.g. isoprene). The forest floor was a net cumulative sink of BVOCs across most of the measurement 309 period, which tended to buffer net canopy fluxes such that the net ecosystem source was smaller than net 310 canopy source alone (Figure 7), keeping in mind that the forest floor sink strength is likely underestimated 311 (Figure 6). There was an increase in forest floor BVOC efflux during the last two days of measurements 312 from mid-day on May 23 until mid-day on May 25 (Figure 7) during a warmer period (Figure 2A) when 313 subcanopy and above-canopy wind direction was decoupled (Figure 2D) as the forest canopy approached 314 closure (Figure 3). As a result of this similar behavior across time, the ecosystem flux of all study 315 compounds was significantly related to each other and the flux of one compound explained up to 81% of 316 the variability of other compounds (Figures S4 and S5). The canopy overstory was a net source of BVOCs 317 and the canopy air space below it was on average a net sink with the exception of the understory vegetation

which was a notable source of BVOCs, especially toward the latter part of the measurement period asdemonstrated for the key compounds methanol, isoprene, and monoterpenes (Figure 8).

320 *Ecosystem models*

Leaf area index and vapor pressure deficit entered the most parsimonious ecosystem, canopy, and forest floor BVOC flux model on 39 of 42 and 40 of 42 instances, respectively (Table 2). Air and canopy temperature both entered the most parsimonious model on 32 of 42 instances and soil temperature and the diffuse fraction of photosynthetically active radiation entered the most parsimonious model for forest floor flux on 12 of 14 instances. Below-canopy radiation was never an important input but wind speed and direction often were, suggesting that the source area of air masses in the diverse study forest played an important role in BVOC flux models.

328

329 Discussion

330 *Ecosystem BVOC efflux*

331 We observed a relatively large BVOC efflux from the canopy during the early part of the May measurement 332 period (May 8-9), especially at 16 m (Figures 4 and 8). This height roughly aligns with the canopy layer of 333 maximum leaf-area density located vertically near the middle of the foliated portion of the canopy (Figure 334 1). The observation of this early-spring efflux occurs during the period of rapid leaf expansion, in this case 335 during the time that leaves expanded from approximately 70% to 95% of full expansion area (Figure 3). 336 Methanol fluxes were at least an order of magnitude higher than all other BVOC emissions, including 337 isoprene, which normally dominates emissions in eastern US deciduous forests (Guenther et al. 1994; 338 Isebrands et al. 1999). It is likely that the high methanol fluxes that we observed, and the fact that isoprene 339 emission rates were much lower, are associated with the physiological maturation of leaves. Methanol is 340 known to be formed at high rates during leaf expansion as a product of pectin demethylation during cell-341 wall loosening (Levy and Staehelin 1992; MacDonald and Fall 1993; Galbally and Kirstine 2002). High 342 methanol emissions have been observed during the early spring leaf-out period from other mixed forests in 343 the north-central US (Karl et al. 2003; McKinney et al. 2011) and from other global forests (Aalto et al.

344 2014; Schallhart et al. 2018). At the same time, isoprene is known to be emitted at low to negligible rates 345 early during leaf expansion and is only fully activated as leaves near full expansion (Grinspoon et al. 1991), 346 or after treatment by relatively high accumulated temperature (Monson et al. 1994). Fluxes and atmospheric 347 concentrations of monoterpenes were relatively low (Table 1, Figure 7) likely due to the lack of coniferous 348 species in the forest canopy. The combination of relatively high methanol fluxes and relatively low 349 terpenoid fluxes represents a chemical-flux landscape seldom studied with regard to model testing, and 350 provided us with an opportunity to challenge the coupling between modeled emissions and climatic drivers 351 in a novel ecosystem context (also see Aalto et al. 2014).

352 The estimated rate of canopy isoprene emissions at its peak in early May was approximately 10% of 353 the rate previously measured in eastern US forests (Goldstein et al. 1998; Baldocchi et al. 1999). Of course, 354 comparisons of isoprene emissions rates among sites will depend on the fraction of trees at each site that 355 emit isoprene, and at high rates. However, the Morgan-Monroe forest has a relatively high representation 356 of oaks, which are high isoprene emitters, and there is no reason to suspect that such low isoprene emission 357 rates, compared to other sites, are due to forest species composition. Rather, it is more consistent with 358 suppressed emission rates due to leaf ontogenetic effects, as described above. Even with low basal emission 359 capacities, however, isoprene emissions showed some response to changes in seasonal weather conditions. 360 Isoprene emissions reached relatively high rates during the warm, cloudless period of May 8-12, consistent 361 with its high sensitivity to PAR and leaf temperature, but the cold, cloudy periods between May 12-16 and 362 again between May 19-22, appear to have caused a persistent decrease, consistent with past studies that 363 have shown a close coupling of isoprene emissions to prevailing weather periods and photosynthesis, and 364 a lag in recovery to high emission rates following short periods of cool, cloudy weather (Sharkey et al. 365 1999). On May 12, during a period of relatively high solar radiation, the prevailing wind direction switched 366 from its normal SSW flow to become progressively more northerly, causing the profiling system to measure 367 different area of the forest (Figure 2B & 2D). This shift may have contributed to the noticeable dip in 368 emissions of all BVOCs, but especially for isoprene and methanol, on May 12. Overall, BVOC sources 369 dominated the observed total canopy flux, as forest floor sinks were small during this part of the growing

370 season (Figure 11). Overall, the emission profile for this springtime campaign is skewed toward high 371 methanol emissions, but still responsive to climate variation, especially temperature, with regard to 372 terpenoid emissions. This creates a novel set of data for testing emissions models because there is evidence 373 of clear responses to the conventional climate drivers of temperature and PPFD, but with the added early-374 season condition of high methanol emissions due to phenological drivers.

375

376 Forest floor BVOC efflux

377 The forest floor was a net sink of most study BVOCs during most of the measurement period (Figure 7) in 378 agreement with the results of soil BVOC flux measurements from MMSF during the early growing season 379 of the previous year (Trowbridge et al. 2020) and noting again that the forest floor sink strength from profile 380 measurements should be interpreted as an underestimate of the true flux (Figure 6). These observations 381 align with numerous recent studies demonstrating that soils are often net sinks for BVOCs (Rinnan and 382 Albers 2020; Trowbridge et al., 2020). Importantly, the role of the forest floor as a BVOC sink in the 383 absence of fresh litter inputs during the leaf-out period buffered canopy BVOC flux during most of the 384 measurement period such that whole-ecosystem BVOC flux was lower than canopy BVOC flux (Figure 7), 385 but this effect varied by compound. Monoterpene flux from the forest floor was trivial (a fraction of a mmol 386 m^{-2} over the study period) such that canopy and ecosystem effluxes were nearly identical (Figure 7) but the 387 forest floor and canopy flux of compounds like acetonitrile were of similar orders of magnitude such that 388 including forest floor flux is necessary to describe whole-ecosystem flux even if the magnitudes of the flux 389 of these compounds are relatively small (Figure 7). These results suggest that the inclusion of the forest 390 floor to whole-ecosystem BVOC flux is conditional on the compound of interest. Notably, many minor 391 compounds tended to be highly correlated to two of the calibrated compounds, DMS (Whelan and Rhew 392 2016) and acetaldehyde (Karl et al. 2002) (Table S1), that had non-trivial contributions of forest floor 393 BVOC flux to ecosystem BVOC flux across most of the measurement period (Figure 7) suggesting that 394 forest floor fluxes of minor compounds may likewise be non-trivial.

397 Air temperature and PPFD (as a surrogate of shortwave radiation) frequently entered the most parsimonious 398 model of BVOC fluxes as anticipated (Table 2) and there was little evidence that alternate measurements 399 of temperature or PPFD (e.g., skin temperature or diffuse fraction) represented an improvement (Table 1): 400 air and radiometric canopy temperatures entered the most parsimonious ecosystem, canopy, and forest floor 401 models on the same number of instances but the latter is a more difficult measurement to make. These 402 observations suggest - at least for the study ecosystem and measurement period - that the variability in 403 canopy and forest floor temperature as well as below-canopy and diffuse radiation provide little new 404 information to canopy and ecosystem BVOC models than simple air temperature and incident radiation at 405 or near the top of the canopy (Guenther et al. 2006; Arneth et al. 2011). Likewise, radiometric forest floor 406 temperature did not represent an improvement over soil temperature for forest floor BVOC flux modeling.

407 Atmospheric VPD, on the other hand, consistently entered the linear model with the lowest AIC 408 score for canopy, forest floor, and whole-ecosystem BVOC flux models, and entered these models more 409 than any other variable, including air temperature and PPFD (Table 2). This is perhaps an unexpected result 410 given that nearly all flux modeling for isoprene and monoterpenes, the dominant compounds emitted from 411 most forested ecosystems, over the past three decades, has been founded on temperature and light as the 412 dominant driving variables, and with good physiological justification (Monson et al. 2012). It is possible 413 that the importance of VPD arises because of the diversity of BVOCs that we analyzed and the fact that 414 several of them have low Henry's Law volatility coefficients that renders their flux susceptible to stomatal 415 control. For the case of methanol, the BVOC emitted at highest rates during the spring campaign, it has 416 long been known that leaf emission rates are determined by stomatal conductance dynamics (Nemecek-417 Marshall et al. 1995), or a combination of stomatal conductance and leaf temperature (Harley et al. 2007). 418 The tendency for a BVOC compound to be controlled, or not, by stomatal conductance dynamics was 419 explained using chemical theory by Niinemets and Reichstein (2003). Oxygenated BVOCs, such as 420 methanol, acetone, acetaldehyde, MVK, formaldehyde and acetonitrile preferentially partition into the 421 liquid phase of the leaf and are emitted in a pattern similar to that of water molecules, with significant

422 modification by stomatal control. Hydrocarbon compounds, such as the terpenoids, partition preferentially 423 into the gas phase of the leaf, and are not susceptible to stomatal control during steady-state emissions (also 424 see Fall and Monson 1992). It is also worth noting that the canopy flux of oxygenated compounds, like 425 methanol, are also highly susceptible to uptake into moisture films on canopy surfaces (Laffineur et al. 426 2012). This can cause the canopy to be a sink for these compounds, especially during the early morning 427 and after rain events, when VPD would also be high. Between stomatal control over emissions at high VPD 428 and uptake to the canopy at low VPD, a correlation between net emission rates and VPD dynamics in the 429 modeling is likely explained. Thus, the tendency for VPD to control canopy BVOC emissions during the 430 spring might result from it falling into the model for many of the oxygenated compounds that were 431 observed.

432 It is surprising, however, that VPD emerged as a significant control in the modeling of nearly all 433 compounds from all sources (Table 2). This means that it also influenced significant control over dynamics 434 in several of the relatively hydrophobic terpenoids. It is not clear at this time as to how such control occurs. 435 It could be due to the fact that there is a high degree of correlation between VPD and air temperature, and 436 air temperature exerts such strong control over hydrocarbon emissions (due to their low boiling points). It 437 is possible that the cross-correlation between VPD and temperature is causing VPD to appear as important 438 in the Akaike's Information Criterion analysis. Ecosystem BVOC models use soil moisture to simulate 439 plant water stress (Guenther et al. 2012) and SWC entered many of the most parsimonious BVOC flux 440 models even though it was not lower than 33% during the measurement period and therefore not likely to 441 be limiting (Rodriguez-Iturbe et al. 2001), but did not enter models as frequently as VPD. Our results 442 suggest that VPD is a logical variable to add to BVOC flux models and we recommend additional 443 experiments to explore its role in BVOC flux at the ecosystem scale.

It is also important to note that wind speed and direction consistently entered models with the lowest AIC values, implying that the source area of the sampled air mass in the diverse study forest is important for describing BVOC flux (Table 2), as anticipated given the importance of source area for BVOC flux measurements (Guenther et al., 1996). LAI was also an important variable modeling BVOC flux as 448 anticipated given its critical role in existing flux models (Guenther et al. 2006). It also entered all models 449 of forest floor BVOC flux suggesting that it may be an effective surrogate of whole-ecosystem BVOC 450 dynamics due to simultaneous belowground autotrophic activity. It is also important to note that $PPFD_{DIF}$ 451 entered the most parsimonious forest floor flux model in most instances, but below-canopy radiation itself 452 did not. These results are consistent with the notion that BVOC flux associated with photodegradation -453 known to be important to litter decomposition (Austin and Vivanco 2006) – played little role in forest floor 454 BVOC flux but that the light environment below the canopy itself did (Moon et al. 2020). The flux of study 455 compounds was often highly correlated with each other, as has been found in multiple other studies (Schade 456 and Goldstein 2001), further lending confidence to the notion that BVOCs can be modeled categorically 457 (Guenther et al. 2012). As a whole our modeling results point to the importance of the canopy light 458 environment and evaporative demand for controlling BVOC flux in addition to the key variables included 459 in models.

460 *Conclusions*

461 We coupled BVOC flux estimates from canopy profile observations and a canopy transport model. Modeled 462 BVOC concentration tended to fit observations well with the exception of the lower canopy layers, 463 suggesting that the modeled forest floor BVOC sink may be underestimated. Observations demonstrate that 464 the addition of VPD may be a logical approach for further improving BVOC model fit and that the 465 contribution of the forest floor to whole ecosystem BVOC flux was either trivial or non-trivial depending 466 on the compound of interest. The fluxes and concentration time series of many compounds were highly 467 correlated, further lending strength to the idea that they can be modeled categorically. Future research 468 should further explore the mechanisms by which VPD controls ecosystem BVOC flux and how the forest 469 floor and canopy combine to create whole-ecosystem BVOC fluxes.

470

471 Data Availability

472 Eddy covariance and micrometeorological data are available at <u>https://doi.org/10.17190/AMF/1246080</u>

473 (Novick and Phillips (1999-). BVOC observations from the profiling system are available at

- 474 https://figshare.com/articles/dataset/Biogenic volatile organic compound concentrations from a vertic
- 475 <u>al profiling system in a mixed deciduous forest in Indiana USA/12746273</u>. BVOC fluxes are
- 476 available at
- 477 https://figshare.com/articles/dataset/Biogenic volatile organic compound fluxes from the forest floor
- 478 <u>canopy and whole ecosystem in a mixed deciduous forest in Indiana USA/12746384</u>.
- 479

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- 716

717 Tables

- 718 Table 1: The mean and standard deviation of study BVOC compound concentrations across all
- 719 measurement heights (Figure 1) during the May, 2015 study period.

Compound	Concentration (ppbv)
Formaldehyde	1.56 ± 0.60
Methanol	12.7 ± 6.5
Acetonitrile	0.23 ± 0.10
Acetaldehyde	2.30 ± 1.07
Acetone	2.97 ± 1.67
DMS	0.25 ± 0.18
Isoprene	1.32 ± 0.75
MVK	0.39 ± 0.28
MEK	0.52 ± 0.32
Benzene	0.12 ± 0.10
Toluene	0.48 ± 0.22
C8 aromatics	0.24 ± 0.15
C9 aromatics	0.69 ± 0.50
Monoterpenes	0.97 ± 0.64

Table 2: The number of times that biological and micrometeorological variables entered the linear model with the lowest AIC for models of the flux of each study BVOC compound (Table 1). FC: eddy covariancemeasured carbon dioxide flux, H: Sensible heat flux, LAI: leaf area index, PPFD: photosynthetically active photon flux density, PPFD_{BC}: below-canopy PPFD, PPFD_{DIF}: diffuse PPFD, SWC: soil water content, T_A : air temperature, T_{CAN} : radiometric canopy temperature, T_{FF} : radiometric forest floor temperature, T_S : soil temperature, VPD: vapor pressure deficit, WD: wind direction, WS: wind speed.

Variable	Ecosystem (of 14)	Canopy (of 14)	Forest Floor (of 14)	Total (of 42)
FC	4	4	10	18
Н	13	11	8	32
LAI	12	13	14	39
LE	12	10	5	27
PPFD	12	13	10	35
PPFD _{BC}	0	0	0	0
PPFD _{DIF}	7	9	12	28
SWC	7	8	12	27
T _A	12	12	7	31
T _{CAN}	12	12	6	30
T _{FF}	10	8	5	23
Ts	1	2	12	15
VPD	14	13	14	41
WD	11	11	12	34
WS	11	11	11	33

728 Figure Legends

Figure 1: Biological and physical sources, sinks, and transport of biogenic volatile organic compounds
(BVOCs) in an idealized plant canopy with leaf area density (LAD) measurements following (Oliphant et
al. 2006) and canopy profile measurement heights from the study ecosystem: a mixed deciduous forest in
the Morgan Monroe State Forest, Indiana, USA.

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Figure 2: Micrometeorological conditions during the May, 2015 biogenic volatile organic compound canopy profile measurement campaign at the Morgan Monroe State Forest (Indiana, USA) measurement tower (US-MMS). A: Air temperature measured at 46 m (T_a), soil temperature measured at 10 cm depth (T_s) and above-canopy precipitation (P). B: Photosynthetically active photon flux density (PPFD). C: Vapor pressure deficit (VPD). D: Wind direction (WD) measured above and within the plant canopy.

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Figure 3: The seasonal course of plant area index (PAI) measured using a LAI-2000 at the Morgan Monroe State Forest, Indiana, USA, in the vicinity of the eddy covariance tower US-MMS for 2001 - 2018 with linear interpolation between measurement points. The study year 2015 is indicated as a black line with black dots indicating measurements. The vertical grey bars show the times of the two experimental campaigns in May and October/November.

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Figure 4: Time series of methanol (A), isoprene (B), and monoterpenes (C) concentration as a function ofcanopy height at Morgan Monroe State Forest (US-MMS) during the May, 2015 sampling period.

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Figure 5: Average diurnal concentrations of key BVOC compounds for which calibration coefficients were
available (Table S1) as a function of height in the canopy during the May, 2015 sampling period at the
Morgan Monroe State Forest eddy covariance tower (US-MMS).

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753 Figure 6: Modeled isoprene concentrations *versus* measurements at the eight different measurement heights.

- Figure 7: The cumulative sum of fluxes from the ecosystem (black), plant canopy (green) and forest floor
- (blue) for each of the 15 study compounds during the May, 2015 study period.
- 756
- 757 Figure 8: The cumulative sum of sources and sinks of the key compounds methanol (A), isoprene (B), and
- 758 monoterpenes (C) at different levels of the mixed hardwood forest canopy air space as estimated by the
- 759 hybrid Lagrangian/Eulerian canopy modeling approach for the May, 2015 study period.
- 760

761 Figures



762

763 Figure 1





765 Figure 2



766767 Figure 3



Figure 4



771 Figure 5



773 Figure 6



775 Figure 7





Electronic Supplemental Material

Derivation of M -coefficients (Equation 4)

Applying time and horizontal averaging, the steady state scalar-flux conservation equation for planar homogeneous high Reynolds and Peclet numbers flow (neglecting molecular diffusion) can be written as:

$$\frac{\partial \langle \overline{w'c'} \rangle}{\partial t} = 0 = -\langle \overline{w'^2} \rangle \frac{\partial \langle \overline{c} \rangle}{\partial z} - \frac{\partial \langle \overline{w'w'c'} \rangle}{\partial z} - \left\langle \overline{c'\frac{\partial p'}{\partial z}} \right\rangle$$
(A1)

as before, c and w are scalar concentration is vertical velocity component, p is pressure and primes are fluctuations from time averages, overbars represent time average and the angle bracket denotes horizontal averaging as discussed in (Raupach and Shaw 1982).

The last two terms on the right-hand side of (A1) are unknowns requiring closure approximations. In this study, we adopt the transport term derived by Meyers and Paw U (1987) and the dissipation term modeled after Finnigan [1985]. These approximations are:

$$<\overline{w'w'c'}>=\frac{\tau}{C_8}\left[-<\overline{w'w'w'}>\frac{\partial<\overline{c}>}{\partial z}-<\overline{w'c'}>\frac{\partial<\overline{w'w'}>}{\partial z}-2<\overline{w'w'}>\frac{\partial<\overline{w'c'}>}{\partial z}\right]$$
(A2)

$$\left\langle \overline{c'\frac{\partial p'}{\partial z}} \right\rangle = C_4 \frac{\langle \overline{w'c'} \rangle}{\tau}$$
(A3)

In (3) and (4), C4 and C8 are closure constants and τ is an Eulerian relaxation time scale given by:

$$\tau = \frac{q^2}{\langle \varepsilon \rangle} \tag{A4}$$

where $q \ (= \sqrt{\langle \overline{u'_i u'_i} \rangle})$ is a characteristic turbulent velocity, ε is the mean rate of viscous dissipation, and are the velocity components in the x_1 (or x), x_2 (or y), and x_3 (or z) directions, respectively, with x_1 aligned along the mean wind direction so that $\overline{u_2} = 0$. Upon combining (A1), (A2) and (A3), a second order ordinary differential equation (ODE) can be derived for the scalar concentration:

$$M_{1}(z)\frac{\partial^{2}\langle \bar{c} \rangle}{\partial z^{2}} + M_{2}(z)\frac{\partial \langle \bar{c} \rangle}{\partial z} = M_{3}(z)$$
(A5)

where coefficients $M_{I,2,3}$ are given by:

$$M_1(z) = \frac{\tau}{C_8} \left\langle \overline{w'w'w'} \right\rangle \tag{A6}$$

$$M_{2}(z) = -\left\langle \overline{w'w'} \right\rangle + \frac{\mathrm{d}}{\mathrm{d}z} \left(\frac{\tau}{C_{8}} \left\langle \overline{w'w'w'} \right\rangle \right) \tag{A7}$$

$$M_{3}(z) = -\frac{\mathrm{d}}{\mathrm{d}z} \left[\frac{\tau}{C_{8}} \left(\left\langle \overline{w'c'} \right\rangle \frac{\mathrm{d}\left\langle \overline{w'w'} \right\rangle}{\mathrm{d}z} + 2\left\langle \overline{w'w'} \right\rangle \frac{\mathrm{d}\left\langle \overline{w'c'} \right\rangle}{\mathrm{d}z} \right) \right] + C_{4} \frac{\left\langle \overline{w'c'} \right\rangle}{\tau}$$
(A8)

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Table S1: Biogenic volatile organic compound (BVOC) mass to charge (m/z) ratios with nominal identifications following (Ellis and Mayhew 2013). Compounds with calibration coefficients are listed. The calibrated compound most similar to uncalibrated m/z ratios, as determined by correlation, are listed. *A fragment that is joined with its parent ion for analyses. [#]Compounds with available calibration coefficients.

m/z	Nominal identification	Most similar calibrated compound (correlation)
25		DMS (0.47)
30		DMS (0.64)
31#	Formaldehyde (CH ₂ O)	-
32		Monoterpenes (0.40)
33#	Methanol (CH4O)	-
37		DMS (0.70)
41	Isoprene fragment	-
42#	Acetonitrile (C ₂ H ₃ N)	-
43		Isoprene (0.87)
45#	Acetaldehyde (C ₂ H ₄ O)	-
47		DMS (0.80)
54		C9 aromatics (0.46)
56		Monoterpenes (0.40)
57		Acetone (0.89)
59#	Acetone (C ₃ H ₆ O)	-
61		Acetaldehyde (0.80)
63#	Dimethyl sulfide (C ₂ H ₆ S)	
68		DMS (0.34)
69 [#] +41	Isoprene (C ₅ H ₈) + fragment	-
71#	Methyl vinyl ketone, methacrolein (C ₄ H ₆ O)	-
73#	Methyl ethyl ketone (C ₄ H ₈ O)	-
75		Isoprene (0.75)
77		Acetaldehyde (0.30)

79#	Benzene (C ₆ H ₆), Ethylbenzene (C ₆ H ₅ CH ₂ CH ₃)	-
81	Monoterpene fragment (C ₆ H ₉ +)	-
83		Acetaldehyde (0.83)
85		Acetaldehyde (0.73)
87		Acetaldehyde (0.81)
89		Acetaldehyde (0.54)
93 [#]	Toluene (C ₇ H ₈)	-
95		DMS (0.64)
97		Acetaldehyde (0.70)
99		DMS (0.66)
101		Acetaldehyde (0.75)
103		DMS (0.47)
107#	C8 aromatics (C ₈ H ₁₀)	-
109		DMS (0.67)
115		Acetaldehyde (0.72)
121#	C9 aromatics (C9H12)	-
129		Acetaldehyde (0.58)
135		C9 aromatics (0.52)
137#+81	Monoterpenes (C ₁₀ H ₁₆) + fragment	
139		DMS (0.46)
143		DMS (0.51)
149		Monoterpenes (0.36)
153		DMS (0.41)
163		DMS (0.30)
167		DMS (0.32)
205		DMS (0.29)



Figure S1: Wind roses for the 46 m (A), 34 m (B), and 2 m (C) measurement levels at the Morgan Monroe State Forest eddy covariance tower (US-MMS) during the May, 2015 sampling period following Peirera (2020).



Figure S2: Mean normalized mass-to-charge ratios (m/z) (Table S1) as a function of canopy height and hour of day.



Figure S3: The modeled (red) and measured (blue) second moment of the vertical wind velocity (ww) divided by the squared friction velocity (u^{*2}) (left), and the modeled (red) and measured (blue) third moment of the vertical wind velocity (www) divided by u^{*3} (right).



Figure S4: The correlation between the modeled ecosystem fluxes of study compounds during the May, 2015 study period at the Morgan Monroe State Forest study ecosystem.



Figure S5: The correlation between the canopy profile time series of all m/z ratios.