Soil Biogenic Volatile Organic Compound Flux in a Mixed Hardwood Forest: Net Uptake at Warmer Temperatures and the Importance of Mycorrhizal Associations

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Abstract Biogenic volatile organic compounds (bVOCs) play important roles in ecological interactions and Earth system processes, yet the biological and physical processes that drive soil bVOC exchanges remain poorly understood. In temperate forests, nearly all tree species associate with arbuscular mycorrhizal (AM) or ectomycorrhizal (ECM) fungi. Given well-established differences in soil biogeochemistry between AM-dominated and ECM-dominated stands, we hypothesized that bVOC exchanges with the atmosphere would differ between soils from the two stand types. We measured bVOC fluxes at the soil-atmosphere interface in plots dominated by AM- and ECM-associated trees in a deciduous forest in south-central Indiana, USA during the early and late vegetative growing season. Soils in both AM- and ECM-dominated plots were a net bVOC sink following leaf-out and were a greater bVOC sink or smaller source at warmer soil temperatures ($T_s$). The flux of different bVOCs from ECM plots was often related to soil water content in addition to $T_s$. Methanol dominated total bVOC fluxes, and ECM soils demonstrated greater uptake relative to AM-dominated plots, on the order of 170 nmol m$^{-2}$ hr$^{-1}$ during the early growing season. Our results demonstrate the importance of soil dynamics characterized by mycorrhizal associations to bVOC dynamics in forested ecosystems and emphasize the need to study bidirectional soil bVOC uptake and emission processes.

Plain Language Summary Plants and soils emit and absorb complex carbon-containing molecules in ways that remain poorly understood. These molecules—called “biogenic volatile organic compounds,” or bVOCs—mediate ecological interactions, including plant defense, and also impact atmospheric chemistry, including aerosol formation. We are becoming more aware of the importance of “mycorrhizal associations” as indicators of biogeochemical variation in forests. Tree species that associate with arbuscular mycorrhizal fungi typically have fast-decaying leaf litters and faster nutrient cycling relative to tree species that associate with ectomycorrhizal (ECM) fungi, which generally have slow-decaying leaf litters and slower nutrient cycling. As such, we hypothesized that forest plots dominated arbuscular mycorrhizal- versus ECM-associated trees would differ in their bVOC emissions. We measured soil bVOC flux in a deciduous forest in Indiana, USA, and noted that soils that were dominated by ECM fungi had greater bVOC uptake, especially when soils were warmer. bVOC uptake in soils dominated by ECM fungi was also sensitive to soil moisture. With this new knowledge, we can create improved models of bVOC fluxes at the ecosystem scale to gain a richer understanding of how soil characteristics impact ecosystem processes and atmospheric chemistry.

1. Introduction

Biogenic volatile organic compounds (bVOCs) affect the Earth’s radiation balance, precipitation regimes, and air quality through their role in ozone, aerosol, and cloud condensation nucleus dynamics (Chameides et al., 1988; Fehsenfeld et al., 1992; Kulmala, 2003; Lelieveld et al., 2008; Müller et al., 2017). As such, understanding controls over bVOC fluxes to and from ecosystems is a critical research priority in the wake of human-accelerated environmental change. To date, much of what is known about ecosystem bVOC flux comes from investigations of plant ecophysiology and plant-insect interactions in forests. However, emerging evidence suggests that forest soils may be important sources of and sinks for bVOCs...
Soil-derived bVOCs impact tropospheric chemistry and also play important roles in plant-microbe signaling and microbe-microbe signaling, with consequences for plant productivity and ecosystem functioning (Carslaw et al., 2010; Laathwornkitkul et al., 2009; Pinto et al., 2007). Soil bVOCs are synthesized and emitted by plant roots and soil microorganisms involved in the breakdown of soil organic matter (Albers et al., 2018; Isidorov & Jdanova, 2002; Leff & Fierer, 2008; Rasmann & Agrawal, 2008; Steeghs et al., 2004; Tsuruta et al., 2018). For example, rhizosphere-derived bVOCs can serve as chemoattractants for rhizobacteria, which can in turn promote plant growth and increase resistance to stress (for reviews see Massalha et al. (2017), Peñuelas et al. (2014), and Wenke et al. (2010)). Rhizosphere-derived bVOCs can also alter the composition and function of the soil microbial community (Insam & Seewald, 2010), which in turn can inhibit plant pathogens (Van Agtmaal et al., 2018) and alter biogeochemical cycling (Asensio et al., 2012; Smolander et al., 2006). These biotic controls interact with abiotic factors in multiple ways that emphasize the importance of understanding their interactions for a comprehensive understanding of bVOC fluxes.

Prevailing climatic conditions and soil properties (e.g., porosity) interact with the biotic community to control the strength and directionality of soil bVOC fluxes (Asensio et al., 2007; Bradford, 1976; Kai et al., 2009). Soil bVOC fluxes are often positively correlated with air and soil temperature (Aaltonen et al., 2011; Asensio et al., 2008; Greenberg et al., 2012), and both temperature and moisture are strong controls over soil methanol and terpene flux (Gray et al., 2010; Schade & Custer, 2004). However, Gray et al. (2014) failed to find a relationship between temperature and bVOC fluxes in a girdled forest comparison, suggesting that roots and root-associated microbes may be primarily responsible for the bVOC flux. In agricultural soils, methanol emissions are highly correlated with sensible heat flux and solar irradiance, but not with soil temperature ($T_s$), suggesting that methanol flux is the result of physical desorption from heated soil surfaces (Schade & Custer, 2004). Thus, the combined biotic and abiotic nature of soil bVOC flux—including the composition of the microbial community, root activity, the timing and type of litter inputs, and the current microclimate—may ultimately determine whether bVOCs are consumed by or emitted from soil (Greenberg et al., 2012; Schade & Goldstein, 2001). While much work has focused on net bVOC emissions from soil, the complex biological and physiochemical environment of soil can also result in net bVOC sinks (Albers et al., 2018; De Deyn et al., 2008; Peñuelas et al., 2014), which can dampen bVOC release (Kramshøj et al., 2018). For example, the uptake of methanol by methylotrophic bacteria and fungi can be appreciable in some soils (Kolb, 2009; Yavitt et al., 1990), emphasizing the importance of studying the bidirectional soil bVOC flux in forests and other ecosystems.

Most tree species associate with either arbuscular mycorrhizal (AM) fungi or ectomycorrhizal (ECM) fungi. Trees within a mycorrhizal group tend to possess similar nutrient use traits (Comas & Eissenstat, 2009; Keller & Phillips, 2019; See et al., 2019; Zhang et al., 2018) that influence carbon (C) and nitrogen (N) cycling (Jo et al., 2019; Lin et al., 2017; Mushinski et al., 2019; Phillips et al., 2013). Given the different effects these mycorrhizal associations can have on belowground processes, it is likely that AM- and ECM-dominant stands differ in their production and consumption of soil bVOCs. ECM trees have leaf and root litters that decay more slowly than AM litters (Keller & Phillips, 2019; See et al., 2019), resulting in greater soil organic matter stocks near the soil surface (Craig et al., 2018) and more fungal-dominated microbial communities (Cheeke et al., 2017; Mushinski et al., 2019). Moreover, ECM fungi (but not AM fungi) have the capability of decomposing soil organic matter directly (Zak et al., 2019) and ECM-colonized roots can release more C to soil than AM roots, resulting in higher levels of microbial activity (Brzostek et al., 2015; Phillips & Fahey, 2005; Sulman et al., 2017; Yin et al., 2014). Thus, in ECM-dominated stands, a direct conduit may exist to channel recent photosynthate into soil bVOCs, whereas the majority of emitted bVOCs in AM stands may be from breakdown products of organic matter oxidation. Despite major advances in understanding the factors that determine bVOC fluxes at the soil-atmosphere interface and our growing understanding of the role of tree species and mycorrhizal associations on forest biogeochemistry, the importance of soil dynamics broadly categorized by mycorrhizal associations to soil bVOC emissions has yet to be measured.

It is critical to determine the primary drivers of soil bVOC emissions and uptake to better understand how ongoing changes to climate will impact the ecosystem feedback and multitrophic interactions that are
mediated by soil bVOCs. Given the multiple effects that mycorrhizal associations have on belowground processes, we hypothesized that bVOC exchange—the quantity and chemical composition of bVOCs emitted and rates of uptake by the surrounding soil environment—would differ between AM- and ECM-dominated stands. Specifically, we predicted higher bVOC emissions from plots dominated by ECM-associated trees due to inputs of both root- and litter-derived C substrates to soil in these stands, recognizing that mycorrhizal associations affect multiple parts of the belowground ecosystem. Thus, we tested our hypothesis within an ECM and AM framework, using these descriptors to represent complex processes and heterogeneity present within those systems. To do so we collected gas samples in situ using a dynamic headspace system from a deciduous hardwood forest in south-central Indiana, USA, and analyzed the compounds emitted and consumed using proton transfer reaction–mass spectroscopy (PTR-MS). Our approach allowed us to examine the interactive effects of soil temperature ($T_s$), soil water content (SWC), seasonality, and soil dynamics broadly categorized by mycorrhizal associations on the soil efflux and uptake of individual compounds as well as the strength of the soil as a net source or sink of bVOCs.

### 2. Materials and Methods

#### 2.1. Site Description

Our study site was located within the Morgan-Monroe State Forest at 39°19′0″N, 86°25′0″W in south-central Indiana, USA. This ~80-year-old hardwood forest contains tree species that associate primarily with AM or ECM fungi. ECM-associated trees include red oak (*Quercus rubra*), white oak (*Quercus alba*), American beech (*Fagus grandifolia*), shagbark hickory (*Carya ovata*), and pignut hickory (*Carya glabra*). AM-associated trees include sugar maple (*Acer saccharum*), tulip poplar (*Liriodendron tulipifera*), and sassafras (*Sassafras albidum; Table S1*). The understory contains tree seedlings and patches of spicebush (*Lindera benzoin*), which associates with AM fungi. The climate is humid continental, with a mean annual temperature of 11.6 °C and mean annual precipitation of 1,200 mm. Soils are thin, unglaciated inceptisols, derived from siltstone, shale, and limestone. Additional site details can be found in Brzostek et al. (2015) and Table S2.

Eight 15 × 10-m experimental plots were set up in the spring of 2014 from an experimental setup established in 2011. Plots were characterized as either AM- or ECM-dominated, whereby 85% of the basal area of the plot was comprised of tree species associated with the respective mycorrhizal type ($n = 4$ for each mycorrhizal type). We subsequently refer to these as “AM plots” and “ECM plots,” and note that our measurements incorporate all of the different soil and belowground plant processes that the different mycorrhizal associations mediate in addition to any potential differences in bVOC fluxes from the mycorrhizae themselves, which we do not measure directly. For in situ bVOC measurements, three open-top stainless-steel collars (973 cm$^2$) were placed in each of the eight plots in October 2013. Each collar was inserted 2 cm into the soil, with ~1.5 L of headspace air, approximately 3 m from the tree with the largest diameter at breast height within the plot in three randomly chosen cardinal directions (Table S1). It is important to note that methanol adsorbs to stainless steel and can impact concentration measurements in systems with small stainless steel tubes (Yokelson et al., 2003). Despite this we feel that its impacts on our measurements were negligible given that we observed similar results with PVC collars in separate measurement campaigns.

SWC (%) and $T_s$ were measured at 12-cm soil depth just outside each collar during bVOC sampling using a HydroSense II (Campbell Scientific Inc., Logan, UT) and a standard glass thermometer, respectively. We also analyzed 2-m air temperature ($T_a$) measurements (HMP-35D, Vaisala, Vantaa, Finland), measurements of $T_s$ using thermocouples at 10 cm belowground, and measurements of SWC at 3 cm below the surface (CS615, Campbell Scientific, Inc.) measured half hourly at the US-MMS AmeriFlux eddy covariance tower, located within 100 m of the study plots.

#### 2.2. Field bVOC Flux Measurements

To capture seasonal variation in net soil bVOC flux, we performed in situ dynamic headspace measurements during four separate campaigns during the 2014 growing season. Two campaigns were made at the beginning of the growing season, the first prior to leaf-out from 16 April through 2 May (hereafter period I) and after leaf-out between 20 May through 4 June (hereafter period II). Two measurement campaigns were
made at the end of the growing season, the first prior to leaf senescence from 24 September through 9 October (hereafter period III) and the last after leaf senescence from 21 through 30 October (hereafter period IV). We intended to measure throughout the entire growing season, but instrumentation repairs were necessary during the midsummer period. One plot from each AM and ECM site was randomly selected on each sampling date within the sampling periods. Leaf litter was removed prior to measurements then returned to the chambers until the next sampling date. Litter removal was necessary so we could address the main objective of the study, which was to assess the impact of ECM- and AM-dominated soils on soil-atmosphere flux. We recognize that removing the litter may have had indirect effects on microbial activity; however, by only removing litter for the short sampling time (~30 min), we assumed that the presence of litter during the rest of the season would allow microbial dynamics to proceed as usual.

To capture bVOC flux, two custom-made Teflon chamber lids were placed on top of the collars, equipped with a small diaphragm pump pushing 200 mL min$^{-1}$ of ambient air in through the chamber after passing through an ozone scrubber (Sep-Pak Potassium Iodide, Waters, Milford, MA, USA). Chambers were allowed to equilibrate for 20 min, triple the residence time as calculated using volume of the chamber and flow rate. Teflon tubing connected to the outlet was then attached to a Vac-U-Chamber (SKC, Eighty Four, PA, USA) equipped with a 10-L Tedlar bag (CEL Scientific, Cerritos, CA, USA) and small handheld pump (SKC) that pulled 150 mL min$^{-1}$. The Vac-U-Chamber was used because it is capable of directly filling the sample bag using negative pressure provided by the sample pump, avoiding any contamination that might occur from direct contact with a pumping system. Because we could only measure two chambers at a time, for each plot measured, two of the three collars were measured simultaneously followed by the third collar and a blank chamber, which was comprised of an empty collar placed on aluminum foil rather than soil. Measurements were taken from two plots each day from 10:00 to 14:00 local standard time to minimize diurnal variation in emissions. Samples were taken for 30 min to obtain approximately 4.5 L of air and each bag was cleaned with successive flushes of N$_2$ gas before the next collection. Following collection, the stainless-steel inlet of the bag was immediately closed and bags were stored in a cool dark shed before being transported back to Indiana University to be analyzed via PTR-MS on the same day.

### 2.3. Laboratory PTR-MS Measurements

Bags were connected directly to the PTR-MS and 42 compounds were selectively analyzed (Table 1) based on published work of compounds identified in ambient air (Blake et al., 2009; de Gouw & Warneke, 2007; Ellis & Mayhew, 2014). The PTR-MS drift tube was operated at 2.1 mbar and 60 °C, with a drift field of 600 V. The parent ion signal was maintained at ~8 × 10$^6$ cps and the O$_2^+$/H$_3$O$^+$ ratio was <3.5%. The scan was allowed to run until the bag was nearly empty, and the stable points were averaged for each collar. We solved for the volume mixing ratio (VMR; ppbv) of each compound following Ellis and Mayhew (2014):

$$\text{VMR} = \frac{i(MH^+)}{i(H_3O^+)} 10^9 \text{kt} N_d$$

(1)

where $MH^+$ is the protonated compound of interest divided by its transmission factor, H$_3$O$^+$ is the primary ion count divided by its transmission factor and multiplied by 500, $k$ is the rate coefficient, $t$ is the reaction time, and $N_d$ is the total number density of the gas in the drift tube calculated as

$$N_d = \frac{p N_A}{RT}$$

(2)

where $p$ is the pressure in the drift tube (Pa), $N_A$ is the Avogadro’s number, $R$ is the ideal gas law constant of 8.3145 L kPa mol$^{-1}$ K$^{-1}$, and $T$ is the temperature in the drift tube (K). Mixing ratios were converted to flux rates (F; nmol m$^{-2}$ hr$^{-1}$) following Gray et al. (2014):

$$F = \frac{\text{VMR}_{ch} - \text{VMR}_{bl}}{R \times A \times T_a} \times Q \times P$$

(3)

where $\text{VMR}_{ch}$ is the measured chamber bVOC concentration (converted to mole fraction; nmol mol$^{-1}$), $\text{VMR}_{bl}$ is the measured blank chamber concentration in mole fraction (nmol mol$^{-1}$), $Q$ is the flow rate through the chamber in L hr$^{-1}$, $P$ is the barometric pressure in kPa, $A$ is the area of the chambers in m$^2$, and $T_a$ is the temperature in the drift tube (K).
Table 1
Nominal Identifications of Biogenic Volatile Organic Compounds (bVOCs)
From Mass to Charge (m/z) Ratios Following Ellis and Mayhew (2014)
With the Driving Variable of the Best Fit Linear Model Identified Using
Akaïke's Information Criterion

| m/z | Nominal identification                  | AM | ECM | Total |
|-----|----------------------------------------|----|-----|-------|
| 31  | Formaldehyde (CH$_2$O)                 | S  | T   | *     |
| 33  | Methanol (CH$_3$O)                     | B  | B   |       |
| 41  | Isoprene fragment (see m/z 69)         | a  | a   | a     |
| 42  | Acetonitrile (C$_2$H$_3$N)             | T  | T   | T     |
| 43  | Acetaldehyde (C$_2$H$_4$O)             | T  | B   | T     |
| 47  | T                                        | B   | T   |       |
| 54  |                                        | T   | T   | T     |
| 56  |                                        | *   | T   | T     |
| 57  |                                        | *   | S   | T     |
| 59  | Acetone (C$_3$H$_6$O)                  | T  | B   | T     |
| 61  |                                        | B   | B   |       |
| 63  | Dimethyl sulfide (C$_2$H$_4$S)         | *  | *   |       |
| 68  |                                        | *  | T   | T     |
| 69  | Isoprene (C$_5$H$_8$) + fragment       | T  | B   | B     |
| 71  | Methyl vinyl ketone, methacrolein (C$_4$H$_6$O) | T  | B   | T     |
| 73  | Methyl ethyl ketone (C$_4$H$_6$O)      | T  | B   | T     |
| 75  |                                        | T   | T   | T     |
| 77  |                                        | *  | *   | T     |
| 79  | Benzene (C$_6$H$_6$), ethylbenzene (C$_6$H$_5$CH$_2$CH$_3$) | *  | *   | *     |
| 81  | Monoterpane fragment (C$_5$H$_9$; see m/z 137) | a  | a   | a     |
| 83  |                                        | T   | S   | B     |
| 85  |                                        | T   | B   | T     |
| 87  |                                        | T   | T   |       |
| 89  |                                        | *   | *   | T     |
| 93  | Toluene (C$_7$H$_8$)                   | *   | B   | T     |
| 95  |                                        | *   | T   | *     |
| 97  |                                        | *   | B   | T     |
| 99  |                                        | B   | B   | T     |
| 101 |                                        | T   | S   | T     |
| 103 |                                        | *   | S   | T     |
| 105 |                                        | *   | T   | T     |
| 107 | C$_8$ aromatics (C$_9$H$_{10}$)        | *  | *   | *     |
| 109 |                                        | *  | T   | T     |
| 121 | C$_9$ aromatics (C$_9$H$_{12}$)        | *  | *   | *     |
| 129 |                                        | T  | B   | T     |
| 135 |                                        | *  | *   | T     |
| 137 | Monoterpenes (C$_{10}$H$_{16}$) + fragment | T  | T   | T     |
| 139 |                                        | T  | S   | T     |
| 143 |                                        | *  | B   | T     |
| 149 |                                        | *  | *   | *     |
| 153 |                                        | T  | T   | T     |
| 163 |                                        | *  | S   | *     |
| 205 |                                        | S   | *   | *     |

Note. T soil temperature, S soil water content, B both soil moisture and soil temperature. bVOC fluxes calculated using calibration for nominally identified compounds and the theoretical transmission curve for noncalibrated compounds are given in Table S1.

*Best fit models were not statistically significant at the p < 0.05 level. A fragment that is joined with its parent ion for analyses. bThe compounds for which calibration coefficients were available.

and $T_a$ is the ambient air temperature in K. Calibrations were performed prior to each set of monthly runs using a multicomponent calibration mix containing various known concentrations (<1,000 ppb, ±5% confirmed by the manufacturer using GC-MS) of formaldehyde, acetaldehyde, methanol, isoprene, acetone, DMS, acetonitrile, methacrolein, methyl vinyl ketone, methyl ethyl ketone, benzene toluene, p-xylene, a-pinene, and 1,2,4-trimethylbenzene stored in nitrogen gas (Apel-Riemer Environmental, Inc.). Prior to each set of runs, we created five-point calibration curves by diluting the multicomponent compressed gas with humidified zero air (Air Gas, Inc., humidity set within 5% of ambient) using a set of mass flow controllers (MKS, Inc.) and a water bubbler, calculating the resulting concentrations, and plotting the normalized counts per second as a function of concentration. It is prudent to note here the difficulty associated with precisely quantifying formaldehyde fluxes using this instrument. This challenge is due to the humidity-dependent sensitivity of the instrument and the similar proton affinity of formaldehyde in relation to water, which can lead to back reactions and inaccuracies in estimates (Vlasenko et al., 2010). Thus, we stress that our objective was not necessarily to improve on methods for quantifying formaldehyde but to determine whether or not relative fluxes varied between the plots. Without humidity-dependent calibration curves, our reported formaldehyde fluxes, therefore, should be considered a lower limit. The VMR of other compounds not found in the calibration tank were derived from a theoretical transmission curve calculated using calibration values. Results are presented in m/z except for compounds that are commonly identified as having particular m/z and for which calibration values were available as specified in Table 1. The common fragments for isoprene (m/z 41) and monoterpenes (m/z 81) were added to their parent compound for analysis.

3. Data
All data were analyzed using Matlab (Mathworks, Inc., Natick, MA, USA) and R (R Core Team, 2018). We tested the main effects of seasonality/time and mycorrhizal association on the total VOC flux with a linear mixed effect model using the “lmer” function in the lme4 package for R with individual soil collars set as the random effect. The function “r.squaredGLMM” was then used to evaluate the variance explained by the fixed and random effects. To test if $T_a$ and SWC were necessary to explain patterns in bVOC flux, linear models for the flux of each compound as a function of SWC, $T_a$, and SWC + $T_a$ were fit using maximum likelihood techniques and the model with the lowest value of Akaïke’s Information Criterion (AIC) chosen as the most parsimonious. We adopted this approach to ask if one of the measurements was unnecessary and $T_a$ + $T_s$ + SWC were necessary to explain the variance in bVOC fluxes and therefore if a simpler explanation of its variability was sufficient. All bVOC data are available at (MSU Scholarworks) and the US-MMS micrometeorological tower data are available at ameriflux.lbl.gov.

4. Results
4.1. Meteorological Conditions
$T_a$ measured at the US-MMS meteorological tower averaged 12.1 °C, 16.8 °C, 15.5 °C, and 12.6 °C during periods I–IV, respectively
Figure 1. (a) Observed air temperature ($T_a$), (b) 10-cm soil temperature ($T_s$), and (c) 3-cm soil water content (SWC) from the eddy covariance and meteorological tower at the Morgan Monroe State Forest, IN, USA. Roman numerals and grey shading represent the four periods during which biogenic volatile organic compounds (bVOCs) were measured.

4.2. Seasonal Patterns of and Environmental Controls Over bVOC Fluxes

The forest soil surface was a net bVOC sink of $-25.9 \pm 20.6$ nmol m$^{-2}$ hr$^{-1}$ (mean ± standard error) across the entire measurement period when combining both mycorrhizal treatments (see Figure 2 and Table S3). The net bVOC sink was $-58.8 \pm 33.6$ nmol m$^{-2}$ hr$^{-1}$ in the ECM-dominated plots and $-5.4 \pm 23.7$ nmol m$^{-2}$ hr$^{-1}$ in the AM-dominated plots ($p = 0.09$). Substantial seasonal variability was observed ($F_{3,60} = 4.04$, $p = 0.01$) and time had a significant interactive effect with mycorrhizal type ($F_{3,60} = 2.88$, $p = 0.04$) where fixed effects explained 20% of the variation and the fixed and random effects explained 25% of the variation. Total bVOC flux differed significantly between ECM and AM plots only during period II ($p < 0.05$; Figure 2).

As an example of the difference in the seasonal variability of ECM- and AM-dominated plots, the mean net bVOC uptake exceeded (was more negative than) $-45$ nmol m$^{-2}$ hr$^{-1}$ during measurement periods II (largely in May) and III (largely in September) in ECM-dominated plots, but only during period II in AM-dominated plots (Figure 2). These seasonal patterns in bVOC flux were driven largely by the seasonal pattern of methanol flux (Figure 3a), which was taken up by the soil during all measurement periods but especially during periods II and III in ECM-dominated plots. The seasonal flux of many compounds exhibited this pattern and fluxes were negatively correlated with $T_s$; higher $T_s$ was related to a less positive (i.e., more uptake) flux of many compounds (see Table 1 and Figures 5a and 6a).

Total bVOC flux was dominated by methanol uptake, which averaged $-53.6 \pm 5.4$ nmol m$^{-2}$ hr$^{-1}$ (Figure 3a). Methanol uptake was significantly greater in the ECM-dominated plots relative to the AM plots ($F_{2,48} = 6.41$, $p = 0.0001$). Nonmethanol bVOCs were net sources to the atmosphere of 25.3 ± 15.7 nmol m$^{-2}$ hr$^{-1}$, much of which was comprised of formaldehyde (Figure 3b) and acetaldehyde (Figure 3c). There was no difference in these fluxes, however, between ECM and AM plots over time. A number of other nominally identified compounds had mean fluxes that were significantly different from zero across the measurement campaign including acetic acid, isoprene, C9 aromatics, and monoterpenes (Figure 4). However, none of the compounds exhibited significantly different fluxes between ECM and AM plots over the course of the experiment, except for C9 aromatics ($p = 0.03$), where AM plots exhibited more uptake. The absolute value of the mean flux of each these compounds did not exceed 0.5 nmol m$^{-2}$ hr$^{-1}$.

When combining bVOC flux from both mycorrhizal treatments, the AIC analysis selected a model that included only $T_s$ for 28 of 42 m/z classes and a model that included both $T_s$ and SWC for 4 classes (Table 1). In the AM plots, the AIC analysis selected a model with only $T_s$ for 19 m/z classes, only SWC for 2 classes, and both $T_s$ and SWC for 2 classes. In the ECM plots, the AIC analysis selected only $T_s$ for 13 classes, only SWC for 6 classes, and both $T_s$ and SWC in 14 classes. In other words, SWC entered the model with the lowest AIC value for 20 classes of compounds in the ECM plots, but only 4 classes in the AM plots or when considering all mycorrhizal treatments in concert.

These dynamics can be demonstrated using two representative compounds. The relationship between acetaldehyde fluxes and SWC was positive in ECM plots but no such relationship existed in the AM plots.
Figure 2. Observed total biogenic volatile organic compound (bVOC) flux for the 42 measured m/z ratios for the four measurement periods described in Figure 1 (see also Table S1). AM refers to plots with tree species that are associated with arbuscular mycorrhizae and ECM refers to plots with tree species that are associated with ectomycorrhizal fungi. Positive values represent a flux from forest floor to atmosphere. The asterisk represents a significant difference in flux between AM and ECM plots ($p < 0.05$) during a particular sampling period.

5. Discussion

The primary goal of this study was to examine the interactive effects of micrometeorological variability (i.e., $T_s$ and SWC), seasonality, and soil dynamics broadly categorized by mycorrhizal associations on the net soil efflux and uptake of bVOCs in situ. We hypothesized that relatively high levels of root exudates and microbial activity characteristic of soils surrounding ECM-colonized roots would lead to higher microbial-derived bVOC emissions from soils. While we failed to observe greater bVOC efflux from ECM plots, our results show greater bVOC uptake by ECM soils when compared to AM plots, but only once the impacts of seasonality are considered. Our results also show that environmental factors including $T_s$ and (for ECM soils) SWC are critical controls over these fluxes (Table 1), in addition to the processes mediated by the dominant mycorrhizal association present within the stand. We discuss the implications of our findings in the context of individual bVOC compound dynamics, belowground sources and sinks, and ecosystem modeling.

5.1. ECM and AM-Dominated Soil Dynamics and bVOCs

The ECM soils exhibited higher NAGase and APase enzyme activities (Figure S1), indicating stronger N and P demand by soil microbes (Midgley & Phillips, 2019) as well as higher fine root biomass (Table S2). A notable difference between AM- and ECM-dominated plots was the variation in the magnitude and direction of bVOC fluxes during the growing season (Figure 2). ECM-dominated plots were bVOC sources on average prior to leaf out, then relatively strong sinks throughout the rest of the growing season. In contrast, AM-dominated plots were weak sinks and then weak sources over the growing season. In both cases, methanol was the dominant compound controlling the net flux (Figure 3), prompting the question of why methanol profiles differ by mycorrhizal type. A possible reason for this is the low-quality leaf litter produced by ECM trees (Keller & Phillips, 2019). The dominant ECM species in the region (e.g., oaks, hickories, and beech) typically produce leaf litters with lignin concentrations (defined as acid unhydrolyzable residue) that are nearly two-fold greater than litters of AM trees (Craig et al., 2018). Given that high lignin litters release methanol upon decomposition, and that increases in methanol fluxes can promote methylotrophic (i.e., methanol consuming) taxa (Fall & Benson, 1996), greater methanol consumption in ECM soils would be expected. Moreover, three microbial genera that have been shown to consume methanol—Beijerinckia, Afipia, and Mycobacterium (Kolb, 2009; Morawe et al., 2017)—were reported to be threefold to fourfold more abundant in ECM soils than AM soils in a nearby forest with similar tree species (R. Mushinski, personal communication). Thus, our observations are consistent with the notion that the differences in bVOC flux between AM- and ECM-dominated stands are related to variations in litter quality and their intending effects on the soil microbial communities. SWC was also necessary to explain the flux of most compounds.
in ECM soils, which is consistent with the notion that biological processes were responsible for the observed bVOC flux patterns. That being said, differences in bVOCs between AM and ECM plots only emerged during some sampling periods, specifically shortly after leaf-out when temperatures were warmer. This suggests that much of the time categorizing plots by dominant mycorrhizal associations is not necessary to explain soil bVOC flux, but proves to be a useful ecosystem-scale property for explaining fluxes when microbes are more active under favorable environmental conditions.

Leaf removal immediately prior to our measurements allowed us to separate litter emissions from those produced from soil; however, we cannot exclude the fact that roots—and their associated mycorrhizal fungi and microbes—can also synthesize and emit bVOCs into the rhizosphere (Kreuzwieser & Rennenberg, 2013) and these species-specific emission profiles may have directly and/or indirectly impacted the observed bVOC patterns. Plants have the potential to allocate a significant amount of recently assimilated carbon toward root bVOCs (e.g., Gray et al., 2014) that, depending on concentration, soil adsorption, and environmental factors, can potentially diffuse into the atmosphere. In our study, much of the efflux observed from soils was comprised of formaldehyde (Figure 3b) and acetaldehyde (Figure 3c). While Gray et al. (2014) observed significant soil uptake of formaldehyde in a subalpine forest, we observed formaldehyde production from SOC specifically during the beginning of the growing season. Mancuso et al. (2015) also observed formaldehyde efflux from soils and linked its production to methylotrophic metabolism, specifically demethylation reactions (Vorholt et al., 2000). The high methanol consumption in our plots is consistent with high methylotrophic activity as noted above, which may explain formaldehyde emissions more than plant roots as a primary source. The soils in our study also exhibited net acetaldehyde efflux for most...
of the growing season, specifically from AM plots. Acetaldehyde emissions could be due to microbial activity, the product of oxidation reactions in the soil, or root metabolism (Tang et al., 2019), but the latter has only been observed under anoxic conditions (Kreuzwieser et al., 1999; Holzinger et al., 2000). We have no evidence to suggest that soils in our study were under such stress, suggesting that microbes associated with AM plots may be dominant contributors to the observed flux.

Soil-derived bVOCs are transported across the soil matrix, influencing biotic processes and ecological interactions including root-microbe signaling that can stimulate or suppress microbial growth (Insam & Seewald, 2010). In particular, root VOCs can impact soil microbial communities by potentially serving as resources for organisms in carbon-limited soil environments (Kleinheinz et al., 1999; Owen et al., 2007). Arbuscular mycorrhizae have also been shown to alter bacterial communities where deposition of mycelium products can serve as substrates for bacterial growth (Marschner & Baumann, 2003). Specifically, the presence of roots has been shown to influence net bVOC uptake (Asensio et al., 2007) and is thought to be due to root exudate inputs serving as carbon sources for microbes, particularly stimulating those that consume bVOCs (Greenberg et al., 2012). The net uptake of many bVOCs observed in our study are in line with the mechanisms proposed above, and while we cannot say definitively that flux patterns at our site are due to differences in microbial communities or activity driven specifically by the presence of ECM or AM fungi, results are broadly consistent with an emerging understanding of bidirectional bVOC flux and the contribution of roots and mycorrhizae to the overall soil microbial community structure and activity (Zhao et al., 2010).

It is also possible that differences in net bVOC uptake among plots were due to physiochemical mechanisms. These include factors that may be influenced of fungal associations on soil characteristics, including soil particle affinity for specific bVOCs based on their polarity or ionic charges (Arocha et al., 1996; Morrissey & Grismer, 1999). Direct mycorrhizal hyphae contact and interactions with mycelium products can influence soil aggregation and stabilization mechanisms (Rillig & Mummey, 2006) that impact soil structure, its chemical properties (Diaz-Zorita et al., 2002; Six et al., 2004), and thus its adsorption-desorption capabilities. The net efflux of specific bVOCs in AM soils during different times during the growing season may be due to mycorrhizae-induced shifts in the soil properties, including the number of competitive binding sites and their chemical affinities. Mycorrhizal types and species may also affect NO3 and OH radicals, ozone, and hydrogen peroxide levels within soils (Insam & Seewald, 2010), dictating the oxidative capacity

Figure 6. (a) The relationship between methanol (m/z = 33) flux and soil temperature ($T_s$) and (b) soil water content including the best fit linear relationship for measurements within arbuscular mycorrhizae (AM)-dominated plots (solid lines) and ectomycorrhizae (ECM)-dominated plots (dashed lines).
within the soil matrix and net uptake or efflux of reactive compounds. For evidence that the oxidative environment within the soil air space differs among AM and ECM plots, note that isoprene was taken up by soils and one of its oxidation products, methyl ethyl ketone, was a net source to the atmosphere in ECM plots but not AM plots (Figure 4). Future work should therefore measure differences in oxidative compounds in the soil air space as a function of mycorrhizal types and species.

5.2. Temperature and Moisture Controls

Our results also suggest that a linear model is sufficient to explain bVOC flux (e.g., Figures 5 and 6), rather than the exponential relationship expected from temperature-sensitive biological and abiotic processes. The simple linear dependence with \( T_s \) may be due to competing uptake and efflux processes (Kramshøj et al., 2018) that are both temperature sensitive, and which must be isolated to identify the abiotic and biotic processes responsible for net flux to create functional relationships that can be used in bVOC flux models (e.g., MEGAN; Guenther et al., 2006). Underlying exponential relationships between bVOC flux and \( T_s \) may also have been obscured by the considerable scatter in the observations of some compounds. For example, univariate linear models of acetaldehyde flux as a function of temperature only explained on the order of 10–27% of its variability (Figure 5), but temperature alone explained 57% of the variability of methanol flux from ECM plots (Figure 6).

According to the physical adsorption and desorption mechanism (Laffineur et al., 2012), methanol uptake is most likely to occur when soil temperature is low and water content is high, which minimizes outgassing and encourages dissolution, respectively. Our results not only show net methanol uptake during the growing season, but in particular, consumption of methanol was greatest when soils were both warm and dry (Figure 6). Our results are in contrast with studies that observed net methanol emission, which occurred in only 10% of our observations. bVOC fluxes in our study plots were dominated by methanol uptake of similar magnitude to methanol efflux found by Gray et al. (2014) but in the opposite direction (Albers et al., 2018). In contrast to our study, Bachy et al. (2018) observed methanol efflux under warm and dry conditions; however, this efflux was from a bare agricultural soil and methanol emissions notably decreased when the vegetation developed under hot and dry conditions, suggesting a methanol sink most likely in the form of methylotrophic microorganisms in the rhizosphere. It is also important to note that we isolated soil bVOC efflux in our study by removing litter and that litter bVOC sources (Isidorov & Jdanova, 2002; Schade & Goldstein, 2001) may be dampened by net soil uptake (Ramirez et al., 2010). To understand process-based controls over forest floor bVOC uptake and emissions, soil and litter fluxes should be studied in situ across the seasonal cycle to understand how key events like the addition of fresh litter and its decomposition (Greenberg et al., 2012), microbial succession (Isidorov et al., 2016), and seasonal transitions like thaw events (Kramshøj et al., 2018) influence bVOC flux from the combined soil and litter matrix.

Soils were a net source of monoterpenes (Figure 4 and Table S1) similar to Gray et al. (2014). In both cases, these results suggest that soils contribute to the total ecosystem monoliterpenes budget. While studies conducted in coniferous forests suggest that litter monoliterpenes emissions constitute approximately 0.3% of above-canopy emissions (Greenberg et al., 2012), the relative contribution of the observed monoliterpenes flux from our study to the ecosystem level cannot be deduced and is likely to change in magnitude, and perhaps directionality (e.g., efflux versus uptake), when the litter layer is considered. Other compounds known to be emitted by the leaves of some plant species, including isoprene, exhibited net soil uptake such that the soil would dampen ecosystem-scale emissions of these compounds noting that the magnitude of this uptake for the case of isoprene was small and less than 0.5 nmol m\(^{-2}\) hr\(^{-1}\) on average. We also note that \( m/z \) 205 (commonly identified as sesquiterpenes), which are considered to be important biogenic secondary organic aerosol precursors in the atmosphere, demonstrated very small emissions (not different from zero in period III and \(-0.04\) nmol m\(^{-2}\) hr\(^{-1}\) during period IV) that are orders of magnitude smaller than efflux observed in tropical forests (Bourtsoukidis et al., 2018). Such observations demonstrate the wide variability of soil bVOC efflux and the need for a synthesis of soil bVOC flux across different global ecosystems. Furthermore, while soil biota is an important sesquiterpene emission source, the net flux is highly dependent on the presence and species of litter cover (Horváth et al., 2012). Considering the atmospheric and ecological importance of these more minor components, our results point to different bVOC uptake and efflux processes in AM- and ECM-associated soils, and highlight the need to isolate the mechanisms responsible for these processes. Moreover, our results indicate that additional studies that isolate the relative role of leaf litter and soil
processes should lead to an improved understanding of belowground and forest floor processes in diverse forest ecosystems.

6. Conclusions

Soils have the capacity to serve as both bVOC sources and sinks and the relative strength of each varies across ecosystems, litter and soil types, soil microbial communities, and in response to environmental factors. Understanding the interactive effects of the environmental and biotic factors that govern bVOC fluxes will improve global bVOC estimates and enhance our understanding of soil bVOCs in mediating ecological interactions. To this end, our study highlights the importance of considering mycorrhizal associations in determining bVOC soil source-sink dynamics. We observed net bVOC uptake to be greater in soils surrounding hardwood forest trees that are associated with ECM fungi. Furthermore, bVOC flux in these soils was often sensitive to soil moisture in addition to soil temperature, demonstrating the need to consider water limitation as a factor that impacts soil bVOC flux and other factors associated with seasonality. bVOC fluxes in our system were dominated by methanol, which is emitted in large quantities from soils of other ecosystems (Asensio et al., 2008; Schade & Goldstein, 2001). However, we observed a net uptake of methanol in this temperate hardwood forest, an observation that aligns with studies that have demonstrated greater biological activity in the soils surrounding ECM-associated trees. Whether the observed bVOC flux pattern is due to enhanced consumption by methylotrophic microbes, direct mineralization, indirect effects of mycorrhizae on the soil environment, or some combination remains unclear. Overall, our results suggest complex and competing bVOC uptake and emission processes in temperate mixed-forest soils, and this work provides a foundation for future studies and mechanistic analyses of these processes to construct effective models of net soil bVOC flux.

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