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Contribution of leaf and needle litter to whole ecosystem BVOC fluxes

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HIGHLIGHTS

- Litter BVOC fluxes were measured by gradient flux and enclosure techniques.
- Emissions were shown to have exponential dependence on temperature and moisture.
- A litter BVOC emissions model was developed which successfully reproduced the emission measurements.
- Litter BVOC emissions make only a small contribution to the whole ecosystem flux of the BVOCs measured.

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ABSTRACT

Biogenic volatile organic compound (BVOC) emissions come from a variety of sources, including living above-ground foliar biomass and microbial decomposition of dead organic matter at the soil surface (litter and soil organic matter). There are, however, few reports that quantify the contributions of each component. Measurements of emission fluxes are now made above the vegetation canopy, but these include contributions from all sources. BVOC emission models currently include detailed parameterization of the emissions from foliar biomass but do not have an equally descriptive treatment of emissions from litter or other sources. We present here results of laboratory and field experiments to characterize the major parameters that control emissions from litter.

Litter emissions are exponentially dependent on temperature. The moisture content of the litter plays a minor role, except during and immediately following rain events. The percentage of carbon readily available for microbial and other decomposition processes decreases with litter age. These 3 variables are combined in a model to explain over 50% of the variance of individual BVOC emission fluxes measured. The modeled results of litter emissions were compared with above-canopy fluxes. Litter emissions constituted less than 1% of above-canopy emissions for all BVOCs measured. A comparison of terpene oil pools in litter and live needles with above-canopy fluxes suggests that there may be another canopy terpene source in addition to needle storage or that some terpene emissions may be light-dependent.

Ground enclosure measurements indicated that compensation point concentrations of BVOCs (equilibrium between BVOC emission and deposition) were usually higher than ambient air concentrations at the temperature of the measurements.

1. Introduction

Biogenic volatile organic compound (BVOC) emission fluxes have been reported in recent years from towers erected above forests, grasslands, and croplands (e.g., Guenther and Hills, 1998; Greenberg et al., 2003; Karl et al., 2002; Schade et al., 2000). In many landscapes, emissions of isoprene and monoterpenes have been estimated from leaf-level emissions of live foliar biomass (e.g., Guenther et al., 1995). However, a significant pool of dead biomass, particularly dead foliar biomass (leaf litter), is also present and may be a source of additional BVOC emissions. In order to more accurately predict BVOC emissions from landscapes, it is necessary to evaluate the importance of emissions from this litter, in addition to emissions from living vegetation.

Soil microorganisms (fungi, bacteria, and yeast) act in aerobic and anaerobic environments to decompose litter. As a consequence, various organic compounds are produced and some may be emitted into the atmosphere. These BVOCs include oxygenated VOCs, such as methanol, ethanol, acetone, acetaldehyde and other alcohol and carbonyl compounds (Isidorov and Jdanova, 2002; Gray et al., 2010; Leff and Feier, 2008; Wilczak et al., 2001).

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Derendorf et al. (2011) also reported C_2–C_5 hydrocarbons and methyl chloride emissions from litter. Other microorganisms may also consume some of these products (Fall, 2003). Production and consumption occur simultaneously, since both BVOC consuming and producing microorganisms are generally present. The rates of production and consumption of the organic material have been shown to be largely a function of temperature and moisture content, as well as organic carbon availability, the BVOC mixing ratio above the litter, and other relatively minor influences (Schade and Goldstein, 2001).

Many of the same BVOCs may also be produced abiotically by non-enzymatic thermo-chemical reactions. In these reactions, even at temperatures experienced by litter, decaying organic matter produces oxidized VOCs (alcohols, aldehydes, ketones), whose production is also strongly dependent on temperature (Warneke et al., 1999). Gray et al. (2010), however, determined that biotic emissions (the result of microbial activity) were significantly greater than abiotic emissions. Actual litter emissions may consist of a combination of the two processes.

Warneke et al. (1999) also noted that the rate of production of oxidized BVOCs from dry litter was not the same as their rates of release to the air. They speculated that some fraction of the BVOCs initially produced remained on the litter, which, when wetted, was partitioned into an aqueous phase from which the BVOCs were subsequently evaporated. The major abiotic emissions observed in their experiments with decaying beech leaves were methanol, acetone, ethanol and acetaldehyde. Isidorov et al. (2010) reported pine and spruce needle litter also emit monoterpene hydrocarbons into the gas phase at rates comparable to emissions from live needles and speculated that the forest floor may be an important source of terpenes. Aaltonen et al. (2011) also reported significant emissions of terpenes from litter as a function of temperature and litter age.

Modeling studies of regional and global BVOC emissions have focused on vegetation foliage, the dominant global source, even though other ecosystem components, such as leaf litter, may contribute to the above-canopy VOC flux. Most BVOC emission models simply neglect non-foliar VOC emissions and do not include any contributions from soil litter. The Model of Emissions of Gases and Aerosols from Nature (MEGAN, Guenther et al., 2006) estimates whole ecosystem fluxes of biogenic trace gases including all ecosystem components: soil, roots, litter, trunks, foliage, flowers, etc. This is accomplished by assigning an emission factor, representative of standard environmental conditions, based on above-canopy flux measurements, if available. For ecosystems and compounds for which there are no reported above-canopy measurements, a whole ecosystem flux is estimated based on scaling up emissions from individual vegetation species and their distribution in the landscape, an approach that therefore excludes soil and litter emissions.

In this manuscript the results of experiments to determine litter emissions and their dependence on temperature, moisture content, and available carbon are presented. A model is constructed to fit the observations to the emissions of individual BVOCs. The emissions measured are compared with above-canopy BVOC emission fluxes to assess the importance of litter emissions.

2. Methods

2.1. Laboratory experiments

Several experiments were performed in the laboratory to examine the dependence of BVOC emissions on temperature, moisture content and available carbon.

2.1.1. Labile organic matter

A distillation method (Greenberg et al., 2006) was used to differentiate the lignocellulose (non-labile or recalcitrant carbon) from the non-lignocellulose (labile carbon) fraction of litter. These authors observed that, at temperatures below 200 °C, water, methanol, acetaldehyde, acetone, terpenes and other VOCs were distilled from their stores in liquid pools or lost as volatile emissions generated by Maillard reactions (Warneke et al., 1999) or endothermic pyrolysis.

Leaf litter from ponderosa pine (*Pinus ponderosa*) was collected in February 2010 in a ponderosa pine plantation (see below). Moisture content of fresh litter was calculated after oven drying for 48 h at 60 °C. Litter samples (~1 g fresh weight) were placed at the bottom of a 15 ml Pyrex pressure tube (Ace Glass, Inc., Vineland, NJ). Nitrogen (at approximately 150 sccm) was introduced through a central tube (reaching to the bottom of vessel) and flow exited through a side tube. The apparatus sat within an oven controlled at 200 °C for 24 h. After the heating period, litter residue in the vessel was weighed. Litter mass loss was calculated, including an adjustment for the initial water content of the fresh litter. The percentage of litter mass remaining after the distillation process was assumed to be the more recalcitrant carbon fraction in litter (lignocellulose), while the percentage of mass lost was assumed to be the labile carbon fraction in litter, i.e. the carbon readily available for VOC production by biotic and abiotic processes.

2.1.2. Litter moisture content

Since it was undesirable to remove litter from the experimental setup during emission measurements, a method was devised to change the litter moisture content by adjusting the relative humidity (RH) of air entering the experimental litter chamber. Ten grams of litter were placed in a sealed glass chamber fitted with inlet and outlet ports. Gas flow into the chamber was controlled by two mass flow controllers, which adjusted a dry and wet air mixture ratio to achieve the desired relative humidity. Air for the wet air line passed through a humidifier downstream of the flow controller. Downstream of the humidifier, dry and wet lines were connected. RH and temperature sensors monitored humidity and temperature in the air mixture before and after the chamber. Total gas flow through the chamber was kept constant during all the experiments (~0.25 L min^{-1}). Periodically, a subsample of litter treated at constant RH was removed and used to determine the water content.

2.1.3. BVOC concentrations

BVOCs were detected and quantitated by proton transfer reaction mass spectrometer (PTR-MS, based on the design of Hanson et al., 2003). Oxygenated and unsaturated BVOC emissions, including methanol, acetaldehyde, acetone, isoprene, terpenes, and several other compounds are reported here. Details of the principles and applications of this instrument are given in De Gouw and Warneke (2007). The drift tube pressure was approximately 6.5 torr and the collision energy was set at 100 townsends. Calibration for individual BVOCs was made by analyzing gas mixtures obtained from continuous injection of a BVOC standard (approximately 0.3 mM BVOC in cyclohexane) delivered at approximately 2 μL per minute by a syringe pump (Harvard Apparatus, model 975, Holliston, MA, USA) into approximately 1 L per minute of dry nitrogen. Alternatively, calibrations were made from dynamic dilution of compressed gas standards containing ppm levels of BVOCs of interest.

2.1.4. Litter and live needle terpene concentrations

Litter samples were collected in April 2010; live needles from current year, 1- and 2-year old were collected from ponderosa pines

in the summer of 2011 at the field experiment location (see below) for the determination of the terpene composition and concentrations. Litter-fall primarily occurs in the autumn, so the newest litter had been deposited some 8 months earlier. Litter from previous years was also present and included in integrated litter samples. The litter or green needle sample was ground to a powder while frozen in liquid nitrogen; about 500 mg of the ground material was collected in a glass vial to which was added 5 ml of cyclohexane for extraction of terpenes. The extracts were analyzed (after approximately 7 days to allow for complete oil extraction) by gas chromatography with mass spectrometric and flame ionization detectors (Hewlett Packard model 5890 GC, model 5972 Mass Selective Detector, Palo Alto, CA, USA), according to the method of Lerdau et al. (1995).

2.1.5. Dependence of BVOC emissions on temperature and moisture content

Laboratory experiments examining the temperature and humidity dependence of litter BVOC emissions were conducted by placing a measured quantity of fresh litter into a sealed one-liter glass jar with inlet and outlet ports. Zero air (<0.1 ppm total VOC), with controlled humidity, flowed at a constant rate through the jar. A fraction of the outlet flow was connected to the PTR-MS for continuous measurements. Litter temperature during experiments was controlled by a water bath in which the glass jar containing the litter was submerged. The temperature of the bath was varied from 5 to 37 °C during the experiments. The litter temperature was monitored by thermocouples during experiments and was within 1 °C of bath temperature. The moisture content of the litter was controlled by the procedure described previously and kept constant during the experiments on the temperature dependence of litter BVOC emissions (approximately 4 h for each moisture level studied). It was assumed that the litter moisture content did not change significantly during the experiments.

2.2. Field experiments

Field experiments were conducted from 24 June to 30 July 2010 at the Manitou Experimental Forest (latitude 39° 6′ 0″ north, longitude 150° 5′ 30″ west), which is a ponderosa pine plantation located in the Central Rocky Mountains approximately 20 km north of Woodland Park, Colorado. The site is climatologically representative of the semi-arid western USA and is characterized by seasonal, transient snow cover in the winter, periods of cool rain in the spring and fall and highly episodic and localized intense thunderstorms in the summer. The relatively dry climate also permits large diurnal temperature and relative humidity changes, particularly in the summertime. The canopy is open, an average of approximately 17 m in height and of varying density, with mixed-age ponderosa pine up to 100 years old and a sparse vegetation surface cover of grasses, sage, forbs and exposed cryptogrammic soils. The above-ground woody biomass is almost exclusively ponderosa pine; the foliar biomass of species other than ponderosa pine is insignificant with respect to the litter and foliar emissions.

Measurements were made with static enclosures, to determine the direction of individual BVOC fluxes and by a gradient flux technique to quantify diurnal and areal emission fluxes. Rainfall events greater than 0.25 mm were measured at 2 locations at the site (atop a 30-m tower and at another ground site, approximately 100 m from the tower, and both within 100 m from the litter flux experiments). Measured rainfall was averaged over 5 min periods for both sites. At times of scattered showers these measurements may not have coincided exactly in terms of occurrences or amounts at the gradient and enclosure locations. Soil temperature and moisture were measured within the experimental plot at depths of 5, 20, 35, 80 and 150 cm. Similar measurements were made in an adjacent plot, where surface temperature was also measured with a wide angle infrared sensor (model SI-111 Infrared skin temperature sensor, Campbell Scientific, Logan, UT, USA).

2.2.1. Static enclosure experiments

BVOCs from automated static enclosures were measured from 19 to 24 June, 2010, in order to directly identify BVOC emissions and to determine the concentrations at which atmospheric concentrations may affect emission or deposition rates. Five polyvinyl chloride plastic cylinders, 45 cm diameter and 30 cm tall, with automated, transparent lids, were inserted 10 cm into the forest floor. The enclosure lid sealed against the cylinders with a polystyrene foam gasket. The enclosures remained open except during sampling. Enclosures were sampled in turn continuously, with each enclosure closed 30 min during its sampling. Consequently, one cycle of the five enclosures was completed every 2.5 h and individual enclosures were re-measured throughout the day, with the times of day changing on successive days. Concentrations at the beginning of the enclosure time were equated with ambient concentrations levels. Air was withdrawn from enclosures at a rate of approximately 50 sccm (1.5 L over the enclosure time) and measured by PTR-MS. The seal was not completely air tight and it was assumed that some leakage (equivalent to a small percentage of approximately 30 L above-soil chamber volume) came through the soil or gasket. No air was actively added to the enclosures to replace air withdrawn.

Before the commencement of measurements, all green vegetation and litter was removed from enclosures. Litter was gathered from adjacent areas and loaded into individual enclosures. Enclosures #1 and #2 had approximately 200 g litter (1250 g m^{-2}), #3 and #4 double that average amount; enclosure #5 had all litter removed to expose bare soil.

2.2.2. Gradient experiments

Gradient fluxes were measured between 25 June and 30 July at a location approximately 10 m from the enclosure experiment in order to observe the diurnal pattern and magnitude of emissions under undisturbed conditions. The fetch of gradient measurement was a treeless area, approximately 15 m in radius. Litter distribution (g m^{-2}) was not measured in the footprint, but was measured in a nearby transect (see below). The experimental system was located on a tripod at the center of this area and consisted of a sonic anemometer (Applied Technology, model SATI/3K, Longmont, CO, USA) at 1.0 m above-ground level, and two sample inlets at 0.5 and 1.5 m above ground. Sample air was drawn through a Teflon-lined stainless steel tube (2 mm inside diameter) at a constant rate of approximately 250 sccm from the inlets alternately for a 5-min period each and a fraction of this stream was analyzed continuously by online PTR-MS. Sonic anemometer wind and temperature data, collected continuously at 10 Hz, were analyzed for each 1/2 hour period to estimate eddy diffusivity. BVOC concentrations were averaged for the upper and lower sample levels for the same 1/2 hour periods.

Gradient fluxes of BVOCs from litter were determined from the relation:

$$\text{Flux} = \text{eddy diffusivity}^{*}\left([\text{BVOC}]_{\text{upper}} - [\text{BVOC}]_{\text{lower}}\right) \Big/ (z_2 - z_1)$$

The eddy diffusivity at the average height of the two inlets was calculated from the basic flux equation:

$$F = -K_c\frac{\Delta C}{\Delta z} = \frac{ku^*(C_2 - C_1)}{\ln(z_2/z_1) - \Psi_2 + \Psi_1}$$

where F is the flux, K_c is the eddy diffusivity, $z_1 = 1.5$ m (top inlet), $z_2 = 0.5$ m (bottom inlet), $\Delta z = z_1 - z_2$, C_1 = concentration at z_1, C_2 = concentration at z_2, $\Delta C = C_2 - C_1$, Ψ_1 = integrated stability function at z_1, Ψ_2 = integrated stability function at z_2, $k = 0.4$ (von Karman's constant), and u^* = friction velocity (determined from sonic anemometer measurements). The stability functions, Ψ, were computed for neutral, stable, and unstable conditions, following Edwards et al. (2005), and Businger et al. (1971).

BVOC concentrations were also measured by PTR-MS using a gradient system with sampling lines mounted at 1, 3.5, 7, 10, 15.5 and 23 m, respectively, on a 30-m tower approximately 100 m from the gradient litter flux experiment. The gradients were used to compute above-canopy flux of BVOCs. This experiment will be reported in a subsequent manuscript. The detailed setup for gradient measurements has been described elsewhere (Karl et al., 2004).

3. Results

3.1. Results of laboratory experiments

3.1.1. Relationship between relative humidity and litter moisture content

The relationship between RH in air and litter moisture content was studied for ponderosa pine litter. RH in the air entering the litter chamber was fixed at several RH levels (from 5% to 100%) during separate moisture determinations. It was observed that approximately 3 days were required for equilibration of moisture content to the RH of air entering vessel. A linear relationship was found between the relative humidity of air used to condition the litter and the equilibrium moisture content (g H_2O g-dw^{-1}) of the litter (slope = 0.2046 with $r^2 = 0.95$). This relationship was then used to adjust litter to different moisture contents for the study of the dependence of litter BVOC emissions on moisture content.

3.1.2. Lignin-cellulose index

The percent lignin content of litter was determined from the distillation process as the residue divided by the initial dry weight of the litter. This measure of refractory carbon is the commonly used lignin-cellulose index (LCI). The LCI found for pine litter (average age > 2 years after dropping to the ground) determined by this method was 0.79, which agrees with the lignocellulose index (LCI) measured in a pine plantation (LCI = 0.72) by Mellilo et al. (1989). These authors observed LCI values approaching 0.7 as litter reached a late stage of decay. Consequently, the fraction of carbon readily available for microbial or abiotic conversion to BVOC emissions decreases to approximately 0.3 in the late stages of decay.

3.1.3. Dependence of emissions on temperature and moisture content

Laboratory emissions experiments indicate an exponential dependence on temperature (T) and percent moisture content ($\%m$) of the form:

$$E(T) = A^*\exp(a^*T)$$

$$E(\%m) = B^*\exp(b^*\%m)$$

The exponential coefficients a and b for the temperature and % moisture dependence of emissions are listed in Table 1. The coefficients are reported for a standard temperature of 30 °C and moisture content of 6% (these coefficients change when other standard conditions are used).

Table 1
The coefficients of the exponential dependence of litter BVOC emissions on temperature and %moisture were determined in laboratory experiments for ponderosa pine at the standard conditions of 30 °C and 6% moisture content.

Emission	a (r^2)	b (r^2)
Methanol	0.074 (0.65)	0.035 (0.99)
Acetaldehyde	0.071 (0.88)	0.022 (0.92)
Acetone	0.112 (0.93)	0.031 (0.94)
Terpene	0.056 (0.80)	0.036 (0.82)

a: From $\gamma_{\%m} = \text{exponent}(a^*(\%m - \%m_s))$, $\%m_s = 6\%$.
b: From $\gamma_{\text{temperature}} = \text{exponent}(b^*(T - T_s))$, $T_s = 30$ °C.

3.1.4. Litter terpenoid concentrations

Analysis of cyclohexane extracts from live needles and needle litter of ponderosa pine were made for the determination of terpenes stored in the tissue. These were useful in describing the relative contributions of litter and live foliar terpene pools to the above-canopy flux. The LCI of litter samples was not determined but was assumed to give an average for the ages of the litter present at the time of collection. Concentrations (mg g^{-1} dry weight needles) are listed in Table 2; α- and β-pinene were the most abundant terpenes in the extracts.

3.2. Results of field experiments

3.2.1. Automated enclosure system

Several ions (mass–charge ratio: m/z) were monitored continuously by PTR-MS and corresponded to significant emissions of methanol (m/z 33), acetaldehyde (m/z 45), acetone and propanal (m/z 59), and acetic acid (m/z 61). Smaller emissions of terpenes (m/z 81 and 137) and sesquiterpenes (m/z 205) were also observed. Emissions of methanol and acetaldehyde (μg BVOC m^{-2} h^{-1}) were generally the highest, but were occasionally exceeded by acetone. VOCs compounds with m/z 69 and 87 were also observed to have small fluxes from the litter.

The lids of the enclosures were transparent. In the daytime, when soil and litter temperatures were hotter, especially when enclosures were exposed to direct solar radiation, chamber temperatures increased; consequently, emissions of methanol, acetone and acetaldehyde increased significantly. At night, when enclosure temperatures were near constant, BVOC concentrations increased initially for several minutes and then the increase slowed until their concentrations in the enclosure were relatively constant for the remainder (~20 min) of the enclosure period (Fig. 1).

3.2.2. Gradient flux

Fluxes of methanol, acetaldehyde, acetone, terpenes, ions with m/z 69 and 87 and several other VOCs were measured by the gradient system. These emissions showed very similar patterns throughout the experimental period, with higher emissions during warmer daytime periods (Fig. 2). Emissions also increased significantly for approximately 1 h after rainfall (Fig. 3). Litter moisture

Table 2
Terpene concentrations in live needles and litter (median and interquartile range, mg g^{-1} dw). New needles (1st year) were collected after the needles emerged to approximately mature length. Second and third year needles were sampled three times (approximately monthly) between May and August.

Age (yr)	α-Pinene	Camphene	β-Pinene	3-Carene	β-Phellandrene
1st	0.14 (0.14–0.18)	0.05 (0.04–0.16)	0.25 (0.18–0.28)	0.10 (0.07–0.12)	0.05 (0–0.07)
2nd	0.24 (0.16–0.26)	0.06 (0.05–0.09)	0.44 (0.30–0.58)	0.06 (0.04–0.11)	0.08 (0.05–0.10)
3rd	0.23 (0.20–0.27)	0.07 (0.06–0.08)	0.42 (0.31–0.62)	0.08 (0.05–0.12)	0.08 (0.05–0.10)
Litter	0.10	0.02	0.27	0.02	0.05

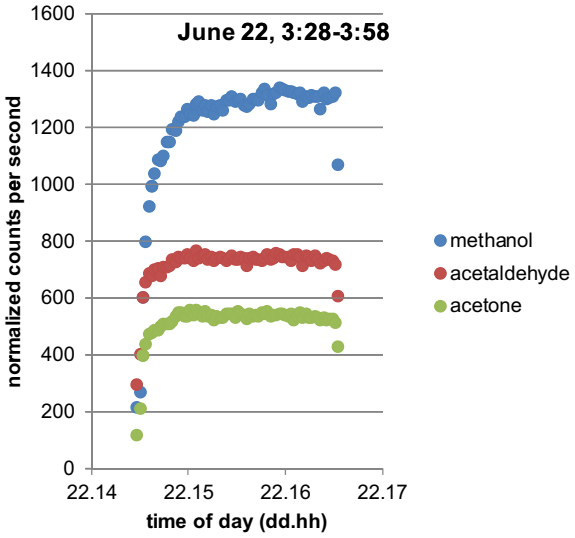

Fig. 1. Night time enclosure measurements (at relatively constant temperature) indicate that an equilibrium concentration, or compensation point concentration, is reached after several minutes.

content, measured periodically, was approximately 2% on the mostly hot and dry days of the experimental period.

Several short pulses (<30 min) of unusually high fluxes were measured occasionally around midday on several days. These were not associated with friction velocity (u^*), high temperature or rain. There was some correlation with winds coming from the north, where the trailers housing other experiments were located. It was assumed that the emission pulses were caused by incidental site activities; consequently, these data were not included in the model calculation of emissions versus independent variables.

3.2.3. Litter distribution

An average of 316 ± 50 g-dw m^{-2} was measured in 20 0.5 m^2 plots 5 m apart in a 100 m transect through the forest.

4. Models

A model was developed in which emissions were dependent on the major influences of temperature, moisture content, and labile carbon content of the litter. The emissions observed in field experiments had an exponential dependence on temperature and moisture content also observed in the laboratory experiments. Soil surface (skin) temperature was used as a surrogate for litter temperature. The percentage moisture of the litter was estimated. The dependence of emissions on temperature and moisture was

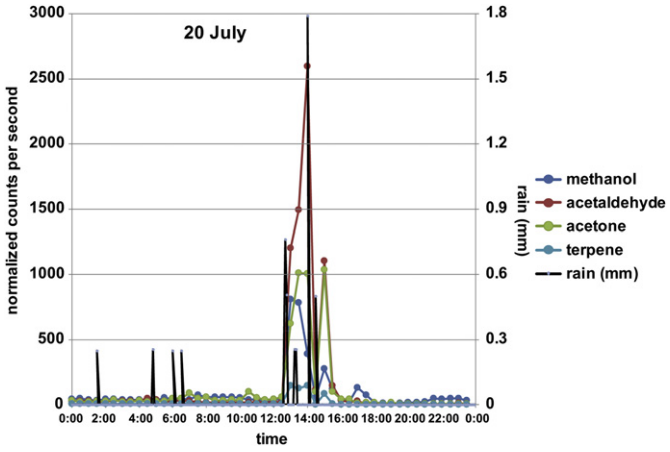

Fig. 3. Emissions of BVOCs increased significantly during and immediately after rain events.

normalized for these experiments to a litter temperature of 30 °C and moisture content of approximately 6%, consistent with the format of the MEGAN landscape emission model (Guenther et al., 2006). The percentage of labile carbon, whose effect on emissions was not quantified in laboratory experiments, was also included. This simple model is described by the expression:

$$\mathrm{Flux}_{\mathrm{BVOC_i}} = E_i{}^*\gamma_C{}^*\gamma_{\%\mathrm{moisture}}{}^*\gamma_{\mathrm{Temp}}, \text{ where}$$

E_i = emission capacity of $\mathrm{BVOC_i}$ at standard temperature and moisture (determined empirically to match gradient flux observations)

$\gamma_{\%\mathrm{moisture}} = \exp(a^*(\%m - \%m_0))$, where $\%m$ is the moisture content in percent

$\gamma_{\mathrm{Temp}} = \exp(b^*(T - T_0))$, where T is the skin temperature

$\gamma_C = \exp(-c^*(T - T_0))$, where available carbon decreases with time

Constants a and b were determined experimentally for each BVOC in the gradient experiments; constant c was chosen to reduce the available carbon fraction from 0.5 to 0.3 (0.5 was an estimate of the available carbon at the beginning of gradient measurements) for the experimental period. The γ factors were computed for each time step.

5. Discussion

5.1. Factors controlling emissions

The decay of litter may be divided into two distinct phases: (1) an initial period (several months) of monotonic mass loss,

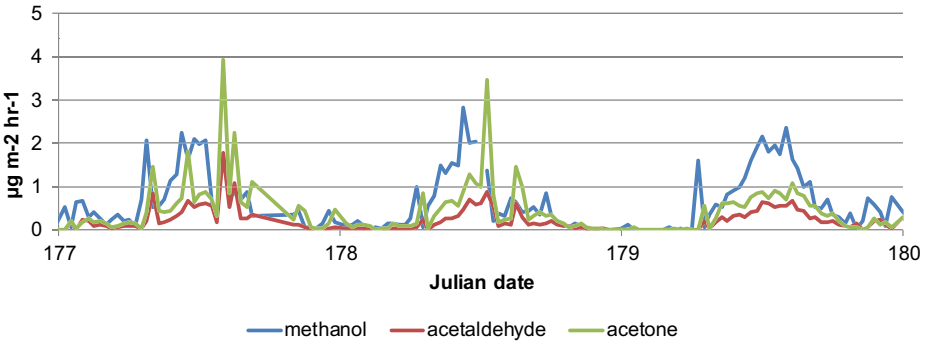

Fig. 2. The diurnal patterns of methanol, acetaldehyde and acetone emissions are similar.

corresponding to the evaporation of stored pools and microbial activity on other easily metabolized organic substrates (cellulose) and (2) a period of very slow or negligible mass loss (several years) dominated by degradation of lignin and hemicellulose (Mellilo et al., 1989).

The emissions of methanol, acetaldehyde, acetone (and propanal), and terpenes, measured in the field, were highly correlated (Table 3). Terpene and sesquiterpene emissions from litter are not the product of microbial activity. They are derived from stored pools of terpenes resident in the needles at the time of their deposition. Terpene concentrations in the needles increase during needle expansion and are highest in mature (1- and 2-year old) needles (Table 2). No new terpenes or sesquiterpenes are thought to be produced in needles after they fall. Thus, the quantity of these terpenes in the pine litter should decrease with time, either by direct emission or by microbial consumption of stored terpenes, resulting in declining terpene emissions. The needle terpene identities and concentrations listed in Table 2 are very similar to those previously reported for ponderosa pine needles (Zavarin et al., 1971; Latta et al., 2000).

Needle litter is deposited in the fall; newly deposited litter was not included in the litter samples analyzed and was not determined separately. The litter terpenes listed in Table 2 were from needles deposited the previous year or earlier. It is expected that terpene emissions from litter will be higher in the fall, after newer needles are deposited from trees. Higher terpene emissions from litter in autumn associated with the onset of litterfall have been reported by Aaltonen et al. (2011).

Deposition to the surface of 2-methyl 3-buten 2-ol (MBO, which produces the ions with m/z 69 and 87 in the PTR-MS technique) from the pine needles was assumed to be small, since enclosure measurements almost always showed positive fluxes for the corresponding ions. These masses, however, were not associated with isoprene (m/z 69) or MBO (m/z 69 and 87); MBO is a daytime (light-dependent) emission from ponderosa pine needles (Harley et al., 1998) and no significant isoprene emitting vegetation was present at the experimental site. They were more likely emissions of pentanal (m/z 69) or pentanal isomers (m/z 87) from litter decomposition (Karl et al., 2005). These fluxes were negligible compared to above-canopy fluxes of BVOCs with these masses. However, the net emissions of VOCs having these 2 masses are likely a combination of emissions from live foliar vegetation (P. ponderosa needles) and litter decomposition.

In the enclosure experiment, concentrations of emissions reached a maximum in the chambers after approximately 10 min and then leveled off. Beyond this time it was assumed there is equilibrium between the flux of the BVOCs out of the litter and deposition to the litter and underlying soil; that is, a compensation point concentration is maintained by these opposing fluxes. Since concentrations of the BVOCs observed increased from ambient levels after enclosure, the compensation point concentrations were higher at the measurement temperatures. The direction of fluxes for all BVOCs was, therefore, out of the litter and into the atmosphere. The compensation point phenomenon may indicate an active consumption of VOCs by soil microorganisms and, therefore, may be temperature dependent. Several soil microorganisms can use VOCs as a carbon source (reviewed by Insam and Seewald, 2010). Ramirez et al. (2009) observed that soils exposed to litter VOCs may absorb 80% of the VOCs emitted by litter, increasing soil respiration rates by 15% under controlled laboratory conditions. However, the significance of the potential microbial sink activity of soils in natural conditions was not determined in this experiment.

Temperature and moisture strongly affect soil microbial activity and, consequently, will affect microbial production and consumption of VOCs. The significant increase in litter BVOC emissions observed after rain events (Fig. 3) may be a rapid soil microbial response to moisture availability, resulting in increased microbial decomposition processes, which are the dominant source of BVOC emissions from decaying organic material (Gray et al., 2010). Alcohols, ketones, aldehydes, aromatics, terpenes and other microbially-produced VOCs have been measured in aerobically and anaerobically incubated soil and microbial cultures (Wheatley et al., 1996; Stahl and Parkin, 1996). Some studies indicate that the temporal evolution of VOCs emissions during microbial growth can be an indicator of soil microbial activity (Bunge et al., 2008; McNeal and Herbert, 2009). In addition to biotic VOC emissions, a pulse of abiotic VOCs after wetting dry leaf litter as described by Warneke et al. (1999) could have contributed to the significant increase in BVOC emissions.

Emission pulses often immediately followed rain events, but these pulses persisted less than 30 min after rainfall (Fig. 3). In the case of extended rainy periods, there were no continuous high emissions after the initial pulse. On days on which it rained, the percentage of emissions occurring in the hour immediately after the rain event accounted for as much as 8% of the daily emission of that BVOC (Table 4). Although laboratory experiments with *P. ponderosa* litter showed that emissions of BVOCs increased with moisture content, direct wetting (rain simulation) experiments were not performed. Some of the BVOC released during heavy rain events may be washed into soil and not released immediately into the atmosphere; this has not been included in the model.

5.2. Contribution of litter emissions to above-canopy BVOC fluxes

The model is compared with experimental results in Fig. 4. Skin temperature and rain are also plotted. The emissions clearly follow the trend in temperature. The dependence of litter moisture is of lesser importance. Although emissions increased for a short period after rain events, litter dried quickly under the hot daytime conditions. The correlation between the modeled and measured emissions gave a correlation (r^2) of approximately 0.5 for the BVOCs (Table 5). Adjusting the parameterization for estimating litter moisture did not significantly improve the correlation, nor did exclusion of fluxes above an arbitrary value, wind direction, low friction velocity, or other measured variables. The emission capacity (the emission rate at 30 °C and 6% moisture content, μg BVOC m^{-2} h^{-1}) for each of the BVOCs was determined from

Table 3
Correlations among BVOCs. Individual BVOC emissions were highly correlated. The ions m/z 69, 81 and 87 may represent several BVOCs.

	Methanol	Acetaldehyde	Acetone	m/z 69	m/z 81
Acetaldehyde	0.79				
Acetone	0.71	0.81			
m/z 69	0.73	0.78	0.85		
m/z 81	0.76	0.71	0.72	0.76	
m/z 87	0.47	0.65	0.66	0.60	0.58

Table 4
Percent of daily emission in period 1 h during and after rain event.

BVOC	Median%
Methanol	3.0
Acetaldehyde	3.4
Acetone	3.6
Terpene	7.6

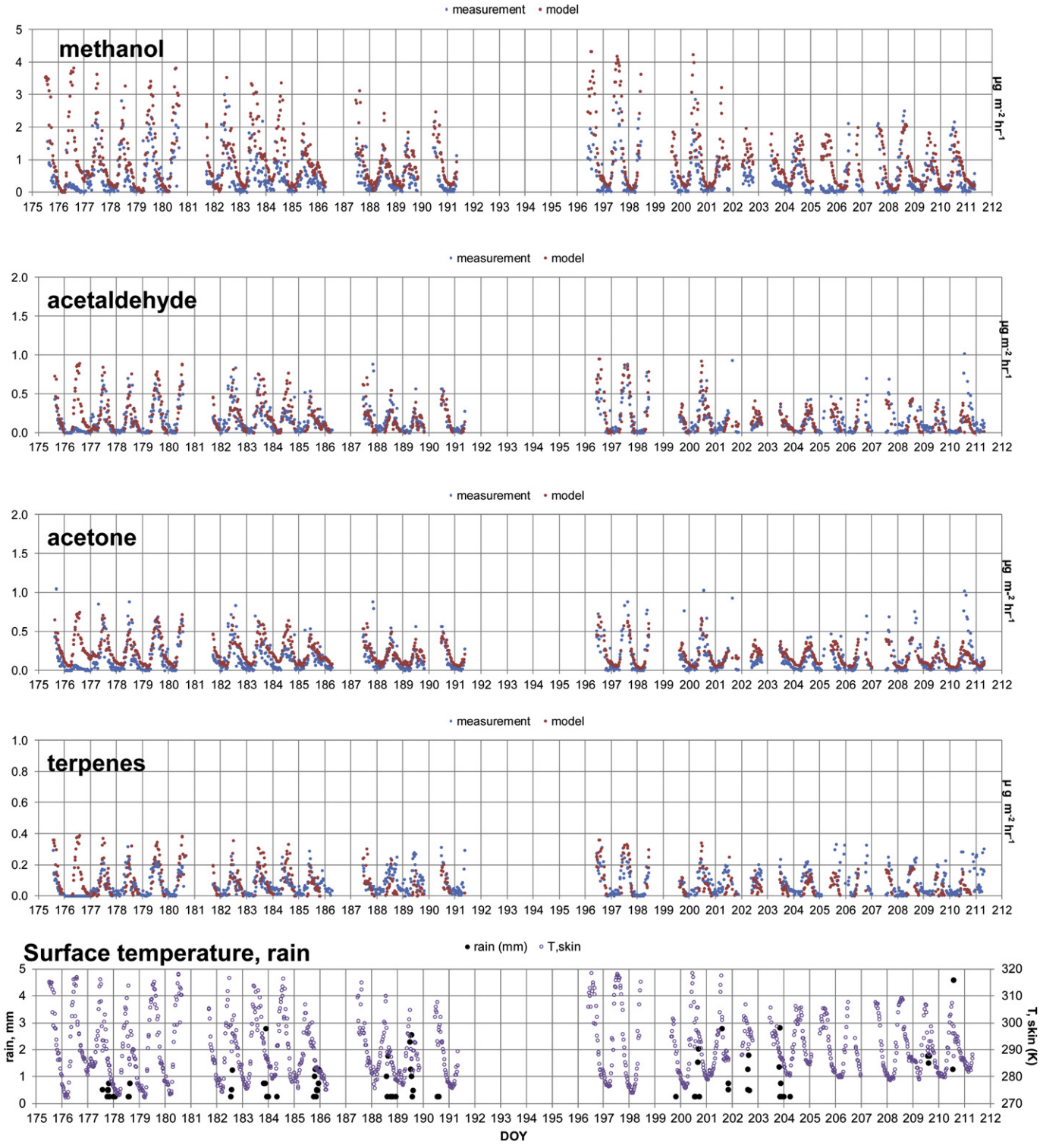

Fig. 4. Comparison of model (red) estimation of litter flux to the gradient system flux measurements (blue). The model explains approximately 50% of the variance in the measurements of BVOCs. The last panel shows surface temperature (violet) and rain, mm (black).

scaling the model emission rate to the observations. The parameters determined by the model fit to the measurements are listed in Table 5.

Above-canopy fluxes were calculated by using an inverse Lagrangian transport (ILT) model (Karl et al., 2004). BVOC concentrations were measured by PTR-MS using a gradient system with sampling lines mounted at 1, 3.5, 7, 10, 15.5, and 23 m, respectively, on the 30-m tower. BVOC fluxes were computed using the ILT model using the relationship

$$\vec{C} - C_{\mathrm{ref}} = \vec{\vec{D}} \cdot \vec{S}$$

where C is the VOC concentration ($\mu g\ m^{-3}$) vector for each of the six levels, C_{ref} is the VOC concentration ($\mu g\ m^{-3}$) at reference height

Table 5
Temperature and moisture exponential dependences and emission capacity for fluxes measured in the gradient experiment. Also shown is the correlation (r^2) between the model and the measurements for individual BVOCs.

m/z	Temperature exponent, a[a]	Moisture exponent, b[b]	Correlation (r^2)	Emission capacity[c]
Methanol	0.035	0.014	0.54	2.9
Acetaldehyde	0.028	0.010	0.46	1.0
Acetone	0.018	0.004	0.55	1.0
Terpene	0.025	0.003	0.46	0.5

[a] $\gamma_{temperature} = \text{exponent}(a^*(T - T_s))$.
[b] $\gamma_{\%m} = \text{exponent}(b^*(\%m - \%m_s))$.
[c] $\mu g\ m^{-1}\ hr^{-1}$.

(e.g. 23 m), D (m) represents a dispersion matrix and S (mg m^{-2} h^{-1} m^{-1}) the resulting VOC source/sink vector. D is expressed as a function of the Lagrangian timescale (Tl) and profiles are the standard deviation of the vertical wind speed (σ_w) divided by the friction velocity (u^*). The calculation was performed by interpolating concentration data to 10 equally spaced levels, based on which 6 source/sink levels were calculated. This resulted in a 10 × 6 dispersion matrix. Integration over all source and sink terms (S) yielded the canopy scale VOC flux (mg m^{-2} h^{-1}). Fluxes were calculated for 30 min intervals. The parameterization of D was based on turbulence measurements inside and above the canopy (σ_w/u^*, where σ_w is the standard deviation of vertical wind speed and u^* is the friction velocity) and calculated using the far- and near-field approach described by Raupach (1986). The Lagrangian timescale Tl (s) was parameterized according to Raupach (1986). Above-canopy fluxes for methanol, acetaldehyde, acetone and the sum of monoterpenes were 0.3 ± 0.1, 0.2 ± 0.1, 0.6 ± 0.2 and 0.3 ± 0.1 mg m^{-2} h^{-1} respectively. The average daytime air temperature for these days was 22.1 ± 2.4 °C, approximately the same as during the litter gradient flux experiment. The monoterpene flux has been measured in the same temperature range previously at approximately 0.3 mg m^{-2} h^{-1} at another ponderosa pine plantation (Lee et al., 2005). Methanol, acetaldehyde and acetone fluxes on the same order were also reported for this plantation by Schade and Goldstein (2001).

Canopy scale fluxes computed using this technique represent daytime fluxes averaged between 10 and 17 local time during the period of DOY 220–260 in 2010 (8 August–17 September). Average daytime BVOC fluxes from litter were compared to above-canopy estimates. Average surface (litter and soil) fluxes of methanol, acetaldehyde, acetone and monoterpenes represent less than 1% of the above-canopy scale fluxes (Table 6). Although litter BVOC fluxes were enhanced after rain, these emissions remained a small percentage of the measured above-canopy flux.

Average litter needle oil concentrations for individual terpenes are approximately 25–50% of those for live foliage. Litter needle biomass has been estimated at 20% of the live foliar biomass in another ponderosa pine forest (Klemmedson et al., 1990). A litter flux of 5–10% of the foliar terpene flux would therefore be expected, much higher than the less than 1% observed. This suggests that there is another source of terpenes in the canopy, such as in woody plant tissue (Miller et al., 2005), or that some terpenes have light-dependent emissions, independent of storage pools. Foliar emissions of α-pinene, β-pinene, and 3-carene, the major components of needle oil, are not primarily light-dependent; however, there is significant light-dependent emission of linalool, a terpene alcohol, from ponderosa pine (Bouvier-Brown et al., 2009). Linalool is detected as the same ions, m/z 81 and 137, as other terpenes, and is included in the above-canopy flux measurements. No measurements of emissions from woody tissues were made. Additionally, it was not determined if the emission of terpenes from pools in live or litter needles had the same temperature and moisture dependence.

Table 6
Comparison of average midday (11:00–17:00) above canopy and litter fluxes ($\mu g\ m^{-2}\ hr^{-1}$). Litter fluxes made only a minor contribution to the above-canopy flux for the BVOCs measured.

	Methanol	Acetaldehyde	Acetone	Monoterpenes
Litter	1.3	0.3	0.3	0.1
Above canopy	300	200	600	300
% flux[a]	0.4%	0.2%	0.1%	0.3%

[a] (Litter flux/above-canopy flux)%.

The flux-gradient method has been one of the most commonly used micrometeorological flux techniques over short vegetation for a variety of trace gas species (Businger, 1986; Lenschow, 1995), including VOCs, where eddy covariance and gradient experiments have produced excellent agreement (Karl et al., 2001). Since the location of the litter gradient experiment was within a clearing in the forest, the normal logarithmic vertical wind profile through the canopy required by the flux-gradient method was likely perturbed. However, wind speed measurements nearby in the forest show a maximum near the ground between 2 and 4 m. The inlet heights of 0.5 and 1.5 m should also be well above the roughness layer generated by the soil/litter surface, which, due to the lack of vegetation, had an estimated displacement height of less than 10 cm. Since the wind speed should approach zero at the ground surface, we assume that vertical profiles of wind speed (and, thus, of scalars and temperature) can be approximated by a logarithmic expression in the lowest 2 m, where the gradient inlets were located.

Litter was not uniformly distributed within the fetch of our experiment but was similar to that observed in the litter distribution transect. The litter distribution was not expected to differ significantly with wind direction.

Litter temperature was difficult to determine. The surface temperature was determined at a site approximately 100 m away from the gradient experiment, although similarly covered with litter. The surface temperature is the average for the surface area viewed by the infrared sensor. The area was probably unevenly heated, especially during times of direct sunlight (some areas were shaded at times by nearby trees or other litter cover). Since emissions were exponentially dependent on temperature, this probably had a significant effect on the areal emissions. A more adequate expression of litter temperature was not made experimentally or in the model. When the 1-m temperature from the sonic anemometer or the soil temperature at 5-cm depth was used instead, the agreement between observed and modeled fluxes was poorer.

The field exponential factors for the temperature dependence of litter emissions are similar to those measured in the laboratory experiments. The exponential factors for the moisture dependence, however, differ significantly from the laboratory determined values (Table 1). This was assumed to be partly a consequence of the difficulty in the estimation of litter moisture content in the field experiment. While continuous measurement of moisture content may be possible, this variable had only minor influence, except during and following rain events. Increased emissions due to rain were not treated in the model. Also, the microbial populations were not monitored either in the field or in the laboratory; the relative populations of BVOC consuming and producing microbes may have been significantly different, resulting in the different laboratory and field exponential factors. The temperature exponential factors determined from the model fit to field fluxes indicate similar values for individual BVOCs compared to those recorded by Schade and Goldstein (2001) in a California ponderosa pine plantation.

The pine litter tested in the laboratory emitted methanol, acetaldehyde and acetone, likely the result of microbial and other processes. Terpenes were also emitted; pines have terpenes stored in their needles that are released by evaporation (not microbial activity). Gray et al. (2010) showed the same dominant BVOC emissions from biotic and abiotic processes in 12 diverse plant species. We assume that the emissions of these BVOCs from the litter of other species arise from microbiological or other processes that have similar exponential dependences on temperature and moisture. Therefore, the BVOC emissions may be modeled in a similar fashion.

6. Conclusions

Needle litter biomass appears to contribute a small percentage (<1%) of the above-canopy emissions of the measured BVOC, including methanol, acetaldehyde, acetone, and terpenes. A numerical model of emissions, depending on litter temperature, moisture and litter needle age, was successful in describing approximately 50% of the variance in measured BVOC fluxes. Emissions of these BVOCs from litter were higher immediately after rainfall. The increase in emissions immediately after rainfall was not parameterized or included in the model. The application of these results or this model to other landscapes may include somewhat different scaling of the temperature or moisture dependence. The seasonal pattern of litterfall and carbon turnover time should also be included, since this may produce periodically higher emission.

A comparison of terpene needle oil composition in litter and live needle foliage, suggested the presence of another significant source of terpenes (possibly woody tissue pools or a light-dependent emission from foliage).

Laboratory and field experiments on litter both indicated an exponential dependence of emissions on temperature and moisture; the coefficient of the temperature term was nearly the same as for laboratory and field experiments. The exponential terms for the moisture dependence differed significantly. However, the dependence of emissions of temperature was much more important in the modeling of the litter gradient results, than the dependence on moisture. Dynamically changing populations of consuming and producing microbes may contribute to these differences. As a consequence, the extrapolation of the model framework to other landscapes may require some attention to microbial ecology.

The landscape emission model, MEGAN, simulates emission variations based on the current understanding of the processes controlling emissions. For example, nitric oxide emissions are estimated using algorithms that represent the known processes controlling soil emissions including soil temperature, moisture and nitrogen availability. For whole ecosystem VOC emissions, MEGAN assumes that there is only a small contribution from soil and litter and so uses algorithms developed to represent foliar emissions to simulate variations in BVOC emissions. This study may represent a reasonable approximation for the modeling of litter BVOC emissions in the MEGAN framework.

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References

Aaltonen, H., Pumpanen, J., Pihlatie, M., Hakola, H., Hellen, H., Kulmala, L., Vesala, T., Back, J., 2011. Boreal pine forest floor biogenic volatile organic compound emission peak in early summer and autumn. Agr. For. Met. 15, 682–691.

Bouvier-Brown, N.C., Goldestein, A.H., Gilman, J.B., Kuster, W.C., de Gouw, J.A., 2009. In-situ ambient quantification of monoterpenes, sesquiterpenes, and related oxygenated compounds during BEARPEX 2007 – implications for gas- and particle-phase chemistry. Atmos. Chem. Phys. 9, 10235–10269.

Bunge, M., Araghipour, N., Mikoviny, T., Dunkl, J., Schnitzhofer, R., Hansel, A., Schinner, F., Wisthaler, A., Margesin, R., Mark, T.D., 2008. On-line monitoring of microbial volatile metabolites by proton transfer reaction-mass spectrometry. Appl. Environ. Microbiol. 74, 2179–2186.

Businger, J.A., Wyngaard, J.C., Izumi, Y., Bradley, W.F., 1971. Flux-profile relationships in the atmospheric surface layer. J. Atmos. Chem. 28, 181–189.

Businger, J.A., 1986. Evaluation of the accuracy with which dry deposition can be measured with current micrometeorological techniques. J. Clim. Appl. Meteorol. 25, 1100–1124.

De Gouw, J., Warneke, C., 2007. Measurements of volatile organic compounds in the earth's atmosphere using proton-transfer-reaction mass spectrometry. Mass Spec. Rev. 26 (26), 223–257.

Derendorf, L., Holzinger, R., Wishkerman, A., Roekmann, T., 2011. Methyl chloride and C_2–C_5 hydrocarbon emissions from dry leaf litter and their dependence on temperature. Atmos. Environ. 45, 3212–3219.

Edwards, G.C., Rasmussen, P.E., Schroeder, W.H., Wallace, D.M., Halfpenny-Mitchell, L., Dias, G.A., Kemp, R.J., Ausma, S., 2005. Development and evaluation of a sampling system to determine gaseous mercury fluxes using an aerodynamic micrometeorological gradient method. J. Geophys. Res. 110, D10306.

Fall, R., 2003. Abundant oxygenates in the atmosphere: a biochemical perspective. Chem. Rev., 4941–4952.

Gray, C.M., Monson, R.K., Feier, N., 2010. Emissions of volatile organic compounds during the decomposition of plant litter. J. Geophys. Res. 115, G03015.

Greenberg, J.P., Guenther, A., Harley, P., Otter, L., Veenendaal, E.M., Hewitt, C.N., James, A.E., Owen, S.M., 2003. Eddy flux and leaf-level measurements of biogenic VOC emissions from mopane woodland of Botswana. J. Geophys. Res.-Atmos. 108, 8466. doi:10.1029/2002JD002317.

Greenberg, J.P., Friedli, H., Guenther, A.B., Hanson, D., Harley, P., Karl, T., 2006. Volatile organic emissions from the distillation and pyrolysis of vegetation. Atmos. Chem. Phys. 6 (1), 81–91.

Guenther, A.B., Hills, A.J., 1998. Eddy covariance measurement of isoprene fluxes. J. Geophys. Res. 103, 13.

Guenther, A., Hewitt, C.N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W.A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamaraju, R., Taylor, J., Zimmerman, P., 1995. A global model of natural volatile organic compound emissions. J. Geophys. Res. 100 (D5), 8873–8892.

Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P., Geron, C., 2006. Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). Atmos. Chem. Phys. 6, 3181–3210.

Hanson, D.R., Greenberg, J., Henry, B.E., Kosciuch, E., 2003. Proton transfer reaction mass spectrometry at high drift tube pressure. Int. J. Mass Spec. 223-224, 507–518.

Harley, P., Fridd-Stroud, V., Greenberg, J., Guenther, A., Vasconcellos, P., 1998. Emissions of 2-methyl-3-buten-2-ol from pines: a potentially large natural source of reactive hydrocarbon to the atmosphere. J. Geophys. Res. 103 (D19), 25,479–25,486.

Insam, H., Seewald, M., 2010. Volatile organic compounds (VOCs) in soils. Biol. Fertil. Soils 46, 199–213.

Isidorov, V., Jdanova, M., 2002. Volatile organic compounds from leaves litter. Chemosphere 48, 975–979.

Isidorov, V., Smolewska, M., Purzynska-Pugacewicz, A., Tyszkiewicz, Z., 2010. Chemical composition of volatile and extractive compounds of pine and spruce litter in the initial stages of decomposition. Biogeosciences 7, 2785–2794.

Karl, T., Guenther, A., Lindinger, C., Jordan, A., Fall, R., Lindinger, W., 2001. Eddy covariance measurements of oxygenated volatile organic compound fluxes from crop harvesting using a redesigned proton-transfer-reaction mass spectrometer. J. Geophys. Res. 106 (D20), 24,157–24,167.

Karl, T.G., Spirig, C., Rinne, J., Stroud, C., Prevost, P., Greenberg, J., Fall, R., Guenther, A., 2002. Virtual disjunct eddy covariance measurements of organic compound fluxes from a subalpine forest using proton transfer reaction mass spectrometry. Atmos. Chem. Phys. 2, 279–291.

Karl, T., Potosnak, M., Guenther, A., Clark, D., Walker, J., Herrick, J.D., Geron, C., 2004. Exchange processes of volatile organic compounds above a tropical rainforest: implications for modeling tropospheric chemistry above dense vegetation. J. Geophys. Res. 109, D18306. doi:10.1029/2004JD004738.

Karl, T., Harren, F., Warneke, C., de Gouw, J., Grayless, C., Fall, R., 2005. Senescing grass crops as regional sources of reactive volatile organic compounds. J. Geophys. Res. 110, D15302.

Klemmedson, J.O., Miller, C.E., Campbell, R.E., 1990. Litter fall transfers of dry matter and nutrients in ponderosa pine stands. Can. J. For. Res. 20, 1105–1115.

Latta, R.G., Linhart, Y.B., Lundquist, L., Snyder, M., 2000. Patterns of monoterpenes variation within individual trees in ponderosa pine. J. Chem. Ecol. 26 (6)

Lee, A., Schade, G.W., Holzinger, R., Goldstein, A.H., 2005. A comparison of new measurements of total monoterpene flux with improved measurements of speciated monoterpenes flux. Atmos. Chem. Phys. 5, 505–513.

Leff, J.W., Feier, N., 2008. Volatile organic compound (VOC) emissions from soil and litter samples. Soil Biol. Biochem. 40, 1629–1636.

Lenschow, D.H., 1995. Micrometeorological techniques for measuring atmosphere–biosphere trace gas exchange. In: Matson, P.A., Harriss, R.C. (Eds.), Biogenic Trace Gases: Measuring Emissions From Soil and Water. Blackwell Science, Oxford.

Lerdau, M., Dilts, S.B., Westberg, H., Lamb, B.K., Allwine, E.J., 1995. Monoterpene emission from ponderosa pine. J. Geophys. Res. 99 (D8), 16,609–16,615.
McNeal, K.S., Herbert, B.E., 2009. Volatile organic metabolites as indicators of soil microbial activity and community composition shifts. Soil Sci. Soc. Am. J. 73, 579–588.
Mellilo, J., Aber, J.D., Linkins, A.E., Ricca, A., Fry, B., Nadelhoffer, K.J., 1989. Carbon and nitrogen dynamics along the decay continuum: plant litter to soil organic matter. Plant Soil 115, 189–198.
Miller, B., Madilao, L.L., Ralph, S., Bohlmann, J., January 2005. Insect-induced conifer defense. white pine weevil and methyl jasmonate traumatic resinosis, de novo formed volatile Emissions, and Accumulation of Terpenoid Synthase and Putative octadecanoid pathway transcripts in Sitka Spruce. Plant Phyiology 137, 369–382.
Ramirez, K.S., Lauber, C.L., Fierer, N., 2009. Microbial consumption and production of volatile organic compounds at the soil-litter interface. Biogeochemistry 99, 97–107.
Raupach, M.R., 1986. Applying Lagrangian fluid mechanics to infer scalar source distributions from concentration profiles in plant canopies. Agric. For. Meteorol. 47, 85.
Schade, G.W., Goldstein, A.H., 2001. Fluxes of oxygenated volatile organic compounds from a ponderosa pine plantation. J. Geophys. Res. 106 (D3), 3111–3123.
Schade, G.W., Goldstein, A.H., Gray, D.W., Lerdau, M.T., 2000. Canopy and leaf level 2-methyl-3-buten-2-ol fluxes from a ponderosa pine plantation. Atmos. Environ. 34, 3535–3544.
Stahl, P.D., Parkin, T.B., 1996. Volatile organic compounds and microorganisms. Soil Sci. Soc. Am. J. 60, 821–828.
Warneke, C., Kark, T., Judmaier, H., Hansel, A., Jordan, A., Lindinger, W., Crutzen, P.J., 1999. Acetone, methanol, and other partially oxidized volatile organic emissions from dead plant matter by abiological processes: significance for atmospheric HO_x chemistry. Glob. Biogeochem. Cycles 13 (1), 9–17.
Wheatley, R.E., Millar, S.E., Griffiths, D.W., 1996. The production of volatile organic compounds during nitrogen transformations in soils. Plant Soil 181, 163–167.
Wilczak, J.M., Oncley, S.P., Stage, S.A., 2001. Sonic anemometer tilt correction algorithms. Boundary-Layer Meteorol. 99, 127–150.
Zavarin, E., Cobb Jr., F.W., Bergot, J., Barber, H.W., 1971. Variation of the *Pinus ponderosa* needle oil with season and needle age. Phytochemistry 10, 3107–3114.