

Emissions of volatile organic compounds during the decomposition of plant litter

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[1] Volatile organic compounds (VOCs) are emitted during plant litter decomposition, and such VOCs can have wide-ranging impacts on atmospheric chemistry, terrestrial biogeochemistry, and soil ecology. However, we currently have a limited understanding of the relative importance of biotic versus abiotic sources of these VOCs and whether distinct types of litter emit different types and quantities of VOCs during decomposition. We analyzed VOCs emitted by microbes or by abiotic mechanisms during the decomposition of litter from 12 plant species in a laboratory experiment using proton transfer reaction mass spectrometry (PTR-MS). Net emissions from litter with active microbial populations (non-sterile litters) were between 0 and 11 times higher than emissions from sterile controls over a 20-d incubation period, suggesting that abiotic sources of VOCs are generally less important than biotic sources. In all cases, the sterile and non-sterile litter treatments emitted different types of VOCs, with methanol being the dominant VOC emitted from litters during microbial decomposition, accounting for 78 to 99% of the net emissions. We also found that the types of VOCs released during biotic decomposition differed in a predictable manner among litter types with VOC profiles also changing as decomposition progressed over time. These results show the importance of incorporating both the biotic decomposition of litter and the species-dependent differences in terrestrial vegetation into global VOC emission models.

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1. Introduction

[2] Biogenic volatile organic compound (VOC) emissions from terrestrial ecosystems can have important effects on atmospheric chemistry and ecosystem-level processes. In the atmosphere, biogenic VOCs are initially degraded by hydroxyl radicals, a photochemically produced compound in the atmosphere that is responsible for the oxidation of several types of greenhouse gases, including methane. Because biogenic VOCs, along with greenhouse gases, can be competitive reactants for available hydroxyl radicals, many regional and global atmospheric chemistry models explicitly consider biogenic VOC emissions when predicting the tropospheric lifetime of greenhouse gases [Haughustaine *et al.*, 1998; Lelieveld *et al.*, 1998; Poisson *et al.*, 2000]. Additionally, the products of biogenic VOC oxidation can serve as cloud condensation nuclei affecting local cloud albedo and precipitation dynamics [Spracklen *et al.*, 2008] or they can react with tropospheric NO_x, affecting nitrogen transport [Harley *et al.*, 1999; Monson and Holland, 2001]. As all VOCs are

comprised of a carbon skeleton, their emissions from the biosphere are also a component of local and global carbon cycling [Guenther, 2002; Kesselmeier *et al.*, 2002]. There is also evidence that VOCs can influence biogeochemical processes within soils, altering rates of carbon cycling by serving as substrates for microbial metabolism [Shennan, 2006], inhibiting microbial processes associated with the nitrogen cycle [Amaral *et al.*, 1998; Bending and Lincoln, 2000; Smolander *et al.*, 2006], and either stimulating or inhibiting the growth of specific microbial taxa [Bruce *et al.*, 2004; Wheatley, 2002].

[3] The emissions of VOCs from living plants have been studied for decades and, although key knowledge gaps remain, we have a reasonably good understanding of the biotic and abiotic controls over plant VOC emissions [Kreuzwieser *et al.*, 1999]. In contrast, VOC emissions from soil and litter have received far less attention even though recent studies suggest that they may represent important sources of VOCs in terrestrial systems [Asensio *et al.*, 2007; Leff and Fierer, 2008]. There have been some recent efforts to incorporate soil and litter sources into VOC models [Jacob *et al.*, 2005], but such models are often constrained by the paucity of relevant data. For example, Warneke *et al.* [1999] used abiotic emissions from leaf litter of a single plant species (*Fagus sp.*), to estimate global VOC emissions from soil, assuming that biotic sources of VOCs from the litter are

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Table 1. Characteristics of the Litter From 12 Plant Species Included in This Study

Species	Family	Litter location	N (%)	C:N	Litter C Fractions (%)			
					Cell soluble	Hemi-cellulose	Cellulose	Lignin
<i>Centaurea maculosa</i>	Asteraceae	Missoula, MT	1.15	39.14	32.33	20.42	37.83	9.42
<i>Rhododendron maximum</i>	Ericaceae	Otto, NC	0.41	122.46	59.23	7.45	18.02	15.30
<i>Quercus macrocarpa</i>	Fagaceae	CU Boulder, CO	0.77	64.78	58.32	12.96	14.85	13.87
<i>Quercus rubra</i>	Fagaceae	CU Boulder, CO	1.27	37.09	60.02	15.63	11.45	12.90
<i>Eucalyptus sp.</i>	Myrtaceae	Arroyo Grande, CA	0.70	75.47	63.60	8.28	13.32	14.80
<i>Fraxinus pennsylvanica</i>	Oleaceae	CU Boulder, CO	1.21	36.11	66.43	11.95	12.25	9.36
<i>Pinus contorta</i>	Pinaceae	Niwot Ridge, CO	0.69	76.53	36.25	13.89	19.73	30.13
<i>Pinus ponderosa</i>	Pinaceae	Boulder Canyon, CO	0.64	86.31	48.86	13.62	18.94	18.58
<i>Miscanthus sp.</i>	Poaceae	Superior, CO	0.72	61.33	39.19	27.52	24.61	8.68
<i>Thinopyrum intermedium</i>	Poaceae	Boulder Canyon, CO	0.58	77.66	28.87	32.39	34.18	4.56
<i>Populus deltoides</i>	Salicaceae	CU Boulder, CO	0.46	97.57	71.50	11.49	12.23	4.78
<i>Populus tremuloides</i>	Salicaceae	Niwot Ridge, CO	0.52	95.75	74.58	8.06	6.99	10.37

insignificant and that litter from different species emit similar types and quantities of VOCs.

[4] Recent research on VOC emissions from soil and decomposing litter suggest that microbes may be important sources of VOCs and that such emissions are highly variable across litter types. *Isidorov and Jdanova* [2002] found differences between essential oils extracted from leaf litter and the VOCs that were emitted, suggesting that microbial enzymes were breaking down these oils into volatiles. Likewise, *Leff and Fierer* [2008] sampled VOC emissions from litter and soil and found a high correlation between respiration, microbial biomass and VOC emission levels, suggesting that microbial decomposition processes are the dominant source of VOC emissions. They also found that the litter produced a greater diversity and quantity of VOCs compared to soil. However, we still do not know the relative importance of biotic versus abiotic sources of VOC emissions during litter decomposition and how VOC emissions vary among types of decomposing litter from different plant species. We would expect the types and quantities of VOCs emitted to vary across litter types due to differences in litter chemistry and/or differences in decomposer communities. Both microbial community composition [*Bunge et al.*, 2008; *Lechner et al.*, 2005] and substrate-type [*Van Lancker et al.*, 2008] have been shown to influence VOC production by microorganisms.

[5] We measured VOC emissions from both sterile and non-sterile litter from 12 plant species over a 20-d laboratory incubation, using proton transfer reaction mass spectrometry (PTR-MS) to quantify the concentration of specific VOCs above the litter and facilitate calculation of compound-specific emission rates. The study was designed to address the following questions that currently represent gaps in our understanding of terrestrial VOC emissions. First, what is the relative importance of abiotic versus biotic processes to VOC emissions from litter? If biotic controls on global emission models are important, current models that assume strictly abiotic emissions will have to be revised. Second, does the decomposition of litter from different plant species yield different types and quantities of emitted VOCs? And if so, can these differences in VOC emissions among litter types be predicted from either plant taxonomy and/or litter chemical characteristics? Addressing these questions will help improve our estimates of VOC emissions from decomposing litter in the field and improve our predictions of how VOC emissions

from terrestrial ecosystems may be altered over time and space with shifts in vegetation type.

2. Methods

2.1. Sample Collection

[6] Leaf litter was collected from 12 plant species in September and October of 2008 from California, Colorado, Montana and North Carolina (Table 1). Litter samples from deciduous species were collected within 5 days of leaf fall. For evergreen species, litter was collected from the ground, selecting litter that appeared newly dropped. Dead grass leaves were clipped from tillers that had gone dormant at the end of the growing season. All samples were oven-dried at 60°C then stored at 4°C prior to the start of the experiment.

2.2. Sample Characterization

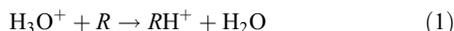
[7] Subsamples of each litter type were ground to a fine and coarse powder with a Wiley mill (60 and 20 mesh respectively). The percentage of carbon (%C) and nitrogen (%N) in the litter was measured using the fine powder and a CHN 4010 Elemental Combustion System (Costech Analytical Technologies, Valencia, CA) (Table 1). The coarse powder was analyzed using a plant fiber analyzer (Ankom Technology, Macedon, New York, USA) to determine litter solubility and quantities of various C fractions [*Hobbie and Gough*, 2004]. Briefly, the coarse powder was sealed in filter bags and digested at 100°C in a dilute neutral detergent to determine the cell soluble fraction lost. What remained was then digested in a weak acid detergent to quantify the hemi-celluloses fraction lost. Finally, the remaining filter bags were digested using sulfuric acid and the mass lost was contributed to the cellulose in the leaf. The mass remaining was considered an estimate of the lignin fraction of the litter.

2.3. Lab Incubation and VOC Measurements

[8] Each litter sample was cut into pieces of approximately 40 mm² and thoroughly homogenized. The samples were then divided into eight 125 mL glass jars, each with 1.6 g dry weight (± 0.06 g) of cut homogenized litter. Six jars without litter were added for experimental “blanks” and were used as background measurements of VOC concentrations in the ambient air, for a total of 102 jars (8 jars per litter type and 6 “blanks”). Each 125 mL glass jar was placed into a 500 mL

glass jar, which was then closed with a gas-tight Teflon sealed cap. Two holes were drilled into each cap and fitted with brass Swagelok connectors and Whatman 0.2 μm polyVENT filters to exclude contamination from airborne microbes. All jars were sterilized by autoclaving at 121°C for 45 min. Autoclaving most likely released VOCs from the litter samples and may have altered litter chemistry to some degree. Thus, autoclaving may have either increased measured VOC emissions (by accelerating litter breakdown) or decreased measured emissions (by driving off VOCs prior to the start of the incubation). However, our goal was to compare VOC emissions between litter types and treatments, not necessarily to quantify VOC emissions as they may occur from decomposing litter in the field. Autoclaving was determined to be the most effective means of sterilization and, regardless of our choice of sterilization method, VOC emissions would have likely been altered to some degree. Four jars of each litter type were kept sterile as abiotic controls for a total of 48 abiotic samples (4 per litter type). All jars were stored in the dark at room temperature ($\sim 22^\circ\text{C}$) for the duration of the experiment. Autoclaved deionized water was added through the filters to bring the sterilized litter sample to 80% of water holding capacity (WHC). Water was also added through the filters into the outer 500 mL glass jar to keep humidity levels constant during the incubation period. The other four autoclaved jars of each litter type were inoculated with non-sterile soil and used as biotic controls. Homogenized soil slurry was created by mixing 20 g of soil (a mixture of 3 local soil types) in 800 mL of autoclaved deionized water. To inoculate each litter type, 1 mL of the soil slurry was added directly to the litter. Autoclaved deionized water was then added to bring the litter to 80% WHC. As with the sterile samples, water was added to the outer 500 mL jar to keep air humidity levels constant. Blank jars received autoclaved deionized water in both the 125 mL jar and 500 mL jar but no litter or inoculum was added.

[9] All jars were incubated in the dark at room temperature ($\sim 22^\circ\text{C}$) throughout the 20-d incubation period. The filters were left unsealed in order to allow for diffusive gas exchange in between VOC measurement periods. Sterility of the litter in the abiotic jars was confirmed throughout the experiment both visually and by monitoring CO_2 fluxes (or lack thereof) using a LI-COR 6400 (LI-COR Biosciences, Lincoln, Nebraska, USA). Measurements of headspace VOC concentrations started three days after setup and continued on regular intervals for 20 days. VOC concentration measurements were taken using PTR-MS (Ionicon GmbH, Innsbruck, Austria) as described by *Lindinger et al.* [1998]. Briefly, headspace air containing VOCs is drawn through a drift tube containing hydronium (H_3O^+) ions. The H_3O^+ reacts with the VOC (R), transferring a proton, which increases the mass by 1 amu and gives the VOC a positive charge (equation (1)).



A quadrupole detector in the PTR-MS selects for compounds with characteristic masses at a resolution of 1 amu. A secondary electron multiplier quantifies the amount of each selected mass. The PTR-MS was operated at 125 Townsends (Td; 1 Td = 10^{-17} V cm^2 molecule $^{-1}$) to keep fragmentation of the target compounds low and the clustering of water and

H_3O^+ ions low. The concentration of the measured VOC were calculated with the following equation

$$[\text{RH}^+] = [\text{H}_3\text{O}^+]_0 (1 - e^{-k[R]t}) \approx [\text{H}_3\text{O}^+]_0 k[R]t, \quad (2)$$

where t is the time of flight of H_3O^+ through the drift tube and k is the rate coefficient for the proton-transfer reaction. Ambient air concentrations were concurrently determined using VOC measurements taken from the blank jars. These were then averaged at each time point and subtracted from the experimental jar measurements. Emission rates (E) were calculated using the equation:

$$E = ([C]F)/aW. \quad (3)$$

In equation (3), $[C]$ is the concentration of the measured VOC in micromol per mol, F is the flow rate through the headspace in liters per hour, W is the dry weight of the sample in grams and a is the standard molar volume of 22.414 L \cdot mol $^{-1}$. Emission rates are reported as micromoles of VOC per gram dry litter per hour. Identification of VOCs was based solely on molecular mass and comparison to VOCs described in other studies. Thus, the identity of individual compounds has not been confirmed and any identifications are considered to be putative.

2.4. Data Analysis

[10] All analyses were run using the R statistical software (R Foundation for Statistical Computing, Vienna, Austria). Total VOC emissions (for the entire incubation period) were calculated by integrating compound emission rates over time, and the resulting total emissions were compared between treatments using Welch's two-sample t-test (Figure 1). Total emissions among litter types were compared with analysis of variance (ANOVA). An analysis of similarity (ANOSIM) was performed on the individual percentages of emitted VOCs to determine the similarity in VOC emission profiles between the abiotic and biotic treatments and between litter types. Finally, the percentages of VOCs emitted from each litter type (VOC profiles) were compared to the measured litter characteristics using Mantel tests [*Mantel*, 1967].

3. Results

3.1. Abiotic Versus Biotic Emissions

[11] For the non-sterile ('biotic') litters, net VOC emissions over the 20-d experiment ranged from 29 to 4816 $\mu\text{mol} \cdot \text{g-litter}^{-1}$ while the net emissions from the sterile ('abiotic') litters ranged from 50 to 344 $\mu\text{mol} \cdot \text{g-litter}^{-1}$ (Figure 1 and Table 2). On average, net biotic emissions were 946 $\mu\text{mol} \cdot \text{g-litter}^{-1}$ (611%) greater than abiotic emissions. *Fraxinus pennsylvanica*, the *Eucalyptus sp.*, and *Populus deltoides* had the largest disparity between biotic and abiotic emissions, with biotic emissions exceeding abiotic emissions by an average of 1042%, 1044% and 2229% respectively. Seven of the 12 litter types showed significantly ($P < 0.05$) higher net VOCs emissions from the biotic treatments. However, those litter types that were not significantly higher during the 20-d experiment still had a larger variation of individual emission rates when compared to the abiotic emission rates (mean standard deviation of 0.70 among biotic treatments and 0.04 among abiotic treatments of these five litter types). AN-

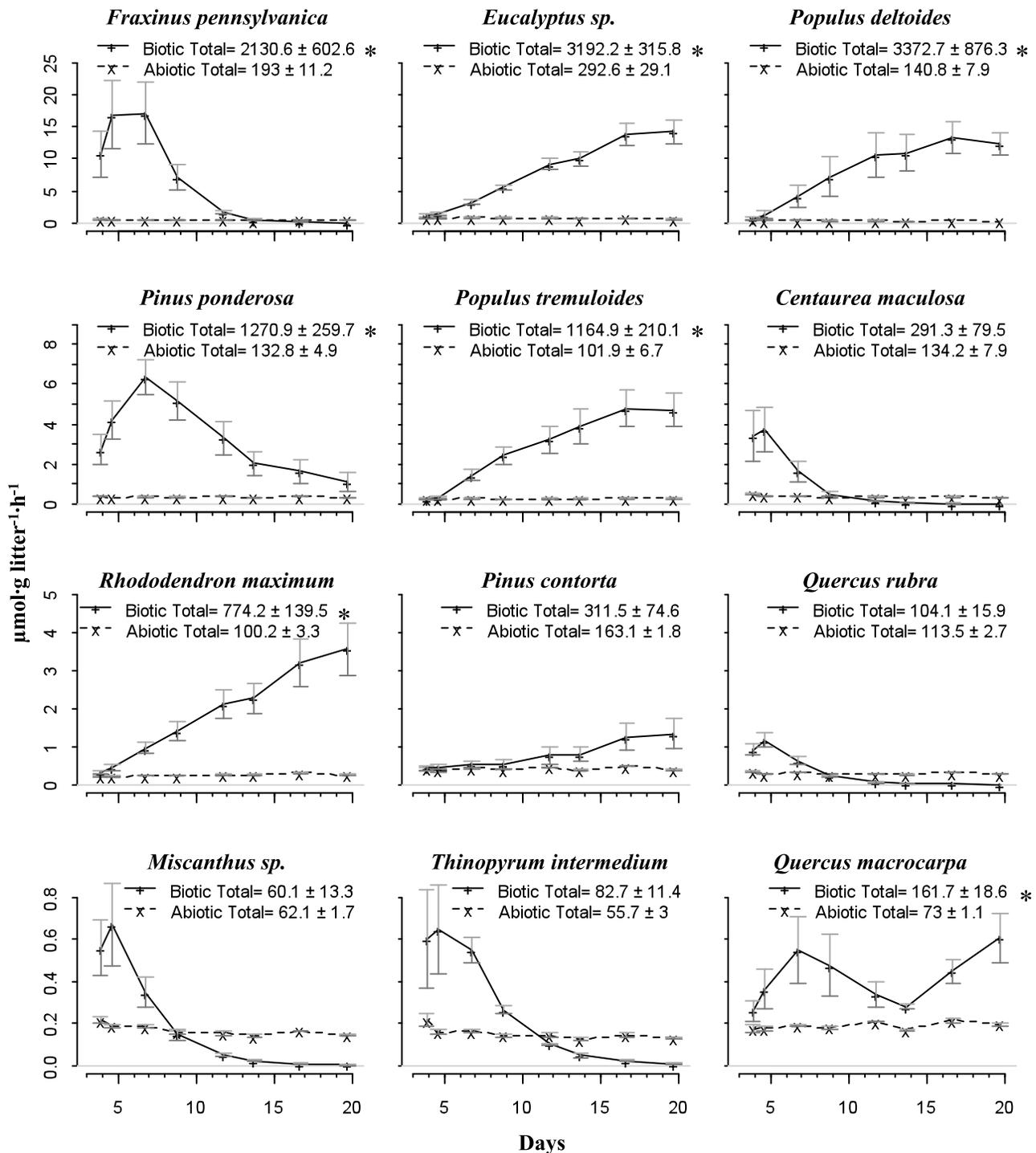


Figure 1. Net emissions from 21 measured VOC masses over a 20 day period. Biotic emissions (solid line) peak at levels higher than the emissions from non-sterile samples (dashed line) in all litter types. The y axis values are in μmol of total VOCs emitted per gram of dry litter per hour ($\mu\text{mol g litter}^{-1} \text{h}^{-1}$). Inset values are total VOCs emitted over the measure time with standard error. Asterisk indicates a statistical difference ($P < 0.05$) between the total VOCs emitted over the measured time.

OSIM statistics comparing the proportional representation of the types of VOCs emitted from biotic and abiotic treatments showed that the VOC profiles were also significantly different (Global $R = 0.83$, $P < 0.001$) (Figures 2 and 3a). VOC emis-

sions from the abiotic litters were dominated by protonated masses 33, 45 and 59 (suspected to be methanol, acetaldehyde, and a combination of propanal and acetone respectively) with average percentages of total VOCs emitted of 56%, 23%, and

Table 2. Net VOC Emissions From the Decomposing Litter of 12 Plant Species^a

Mass (m/z)	Suspected Compound(s)	<i>Centaurea maculosa</i>		<i>Rhododendron maximum</i>		<i>Quercus macrocarpa</i>		<i>Quercus rubra</i>	
		Biotic	Abiotic	Biotic	Abiotic	Biotic	Abiotic	Biotic	Abiotic
33+51	methanol	285.654(79.071)	70.058(5.616)	763.284(139.307)	76.709(3.209)	150.059(18.877)	47.328(1.457)	94.591(15.604)	48.910(3.372)
43	n-propano/acetate acid	0.943(0.134)	3.143(0.283)	1.385(0.066)	2.055(0.090)	1.511(0.185)	3.227(0.586)	1.426(0.092)	6.431(0.411)
45	acetaldehyde	0.110(0.081)	44.637(1.315)	0.056(0.018)	13.051(0.329)	0.101(0.014)	14.856(0.721)	0.265(0.022)	41.388(0.692)
47	formic acid ethanol	0.369(0.201)	0.163(0.025)	0.301(0.072)	0.184(0.069)	0.154(0.069)	0.190(0.047)	0.389(0.033)	0.423(0.118)
57	butanol	0.370(0.091)	0.845(0.078)	0.348(0.058)	0.098(0.019)	1.106(0.098)	0.162(0.040)	1.448(0.086)	0.225(0.015)
59	propanal/acetone	2.345(0.640)	6.667(0.934)	7.041(0.403)	4.163(0.118)	6.080(1.225)	2.699(0.064)	2.620(0.151)	5.698(0.158)
61	acetic acid	0.518(0.144)	1.735(0.229)	0.436(0.099)	1.572(0.068)	0.404(0.063)	2.864(0.640)	0.434(0.076)	5.387(0.437)
69	isoprene	0.076(0.017)	2.682(0.244)	0.197(0.031)	0.177(0.015)	0.206(0.027)	0.270(0.015)	0.263(0.006)	0.535(0.027)
73	methyl ethyl ketone (MEK)	0.405(0.167)	2.763(0.111)	0.474(0.212)	0.317(0.013)	0.949(0.299)	0.608(0.031)	1.324(0.133)	3.299(0.195)
93	toluene	0.013(0.004)	0.016(0.000)	0.022(0.006)	0.016(0.009)	0.019(0.005)	0.014(0.002)	0.023(0.008)	0.022(0.006)
135	unknown	0.002(0.001)	0.007(0.004)	0.005(0.002)	0.007(0.002)	0.017(0.004)	0.004(0.002)	0.021(0.005)	0.006(0.002)
81+137	monoterpenes	0.006(0.004)	0.107(0.004)	0.053(0.015)	0.014(0.011)	0.123(0.025)	0.167(0.027)	0.074(0.011)	0.275(0.029)

Mass (m/z)	Suspected Compound(s)	<i>Fraxinus pennsylvanica</i>		<i>Pinus contorta</i>		<i>Pinus ponderosa</i>	
		Biotic	Abiotic	Biotic	Abiotic	Biotic	Abiotic
33+51		2817.840(355.878)	2113.636(601.559)	140.538(12.054)	293.634(74.937)	86.136(2.017)	1217.715(256.632)
43		12.051(1.948)	1.799(0.121)	4.192(0.408)	2.390(0.698)	7.148(0.471)	3.422(0.255)
45		0.538(0.056)	0.608(0.299)	34.556(1.482)	0.076(0.007)	38.310(2.055)	1.070(0.164)
47		1.160(0.183)	0.492(0.046)	0.239(0.021)	0.268(0.095)	1.208(0.114)	1.337(0.188)
57		3.473(0.531)	1.864(0.224)	0.647(0.035)	0.533(0.082)	0.614(0.038)	2.242(0.225)
59		120.279(38.289)	10.812(0.159)	3.938(0.391)	3.814(0.516)	9.542(0.100)	21.989(2.361)
61		0.962(0.144)	3.656(0.319)	0.678(0.062)	1.416(0.957)	6.016(0.444)	0.690(0.101)
69		3.052(0.202)	1.433(0.090)	1.908(0.061)	0.240(0.038)	1.517(0.114)	1.442(0.082)
73		7.941(4.261)	1.804(0.598)	2.591(0.151)	0.038(0.017)	2.436(0.184)	2.448(0.454)
93		4.256(0.846)	0.007(0.003)	0.017(0.005)	0.506(0.047)	0.481(0.038)	1.012(0.122)
135		8.602(2.066)	0.006(0.002)	0.006(0.002)	0.216(0.029)	0.173(0.022)	1.180(0.097)
81+137		205.058(40.930)	0.067(0.020)	0.158(0.024)	7.848(1.348)	8.085(0.715)	14.388(2.358)

Mass (m/z)	Suspected Compound(s)	<i>Thinopyrum intermedia</i>		<i>Populus deltoides</i>		<i>Populus tremuloides</i>	
		Biotic	Abiotic	Biotic	Abiotic	Biotic	Abiotic
33+51		54.603(12.353)	77.131(11.635)	30.294(1.485)	3340.120(867.458)	94.567(5.718)	1150.668(208.908)
43		0.937(0.218)	0.901(0.072)	2.034(0.198)	3.102(0.520)	3.683(0.261)	2.036(0.081)
45		0.040(0.013)	0.041(0.017)	15.682(0.782)	3.679(2.062)	31.354(2.467)	0.710(0.313)
47		0.173(0.047)	0.126(0.025)	0.150(0.026)	6.148(3.173)	0.244(0.047)	0.818(0.288)
57		0.360(0.080)	0.432(0.041)	0.489(0.095)	2.619(1.044)	0.520(0.020)	0.858(0.183)
59		1.922(0.572)	5.804(0.385)	3.487(0.249)	11.248(1.381)	5.316(0.840)	6.404(0.336)
61		0.461(0.182)	3.239(0.727)	1.400(0.162)	0.804(0.131)	2.756(0.322)	0.674(0.169)
69		0.182(0.014)	0.408(0.010)	0.082(0.031)	0.631(0.106)	0.487(0.022)	0.354(0.019)
73		0.729(0.196)	0.695(0.048)	0.601(0.065)	2.378(1.212)	0.691(0.045)	1.193(0.521)
93		0.007(0.001)	0.010(0.002)	0.015(0.002)	0.033(0.007)	0.009(0.004)	0.030(0.005)
135		0.006(0.003)	0.001(0.000)	0.001(0.000)	0.042(0.018)	0.019(0.010)	0.004(0.001)
81+137		0.006(0.006)	0.060(0.008)	0.093(0.054)	0.311(0.076)	0.148(0.031)	0.068(0.015)

^aThe top 12 compounds from the measured 21 masses are shown. Values are in $\mu\text{mol of VOC emitted per gram of dry litter } (\mu\text{mol g}^{-1})$ totalled over 20 days. Parentheses contain standard error. The identities of the suspected compounds have not been confirmed and are considered putative.

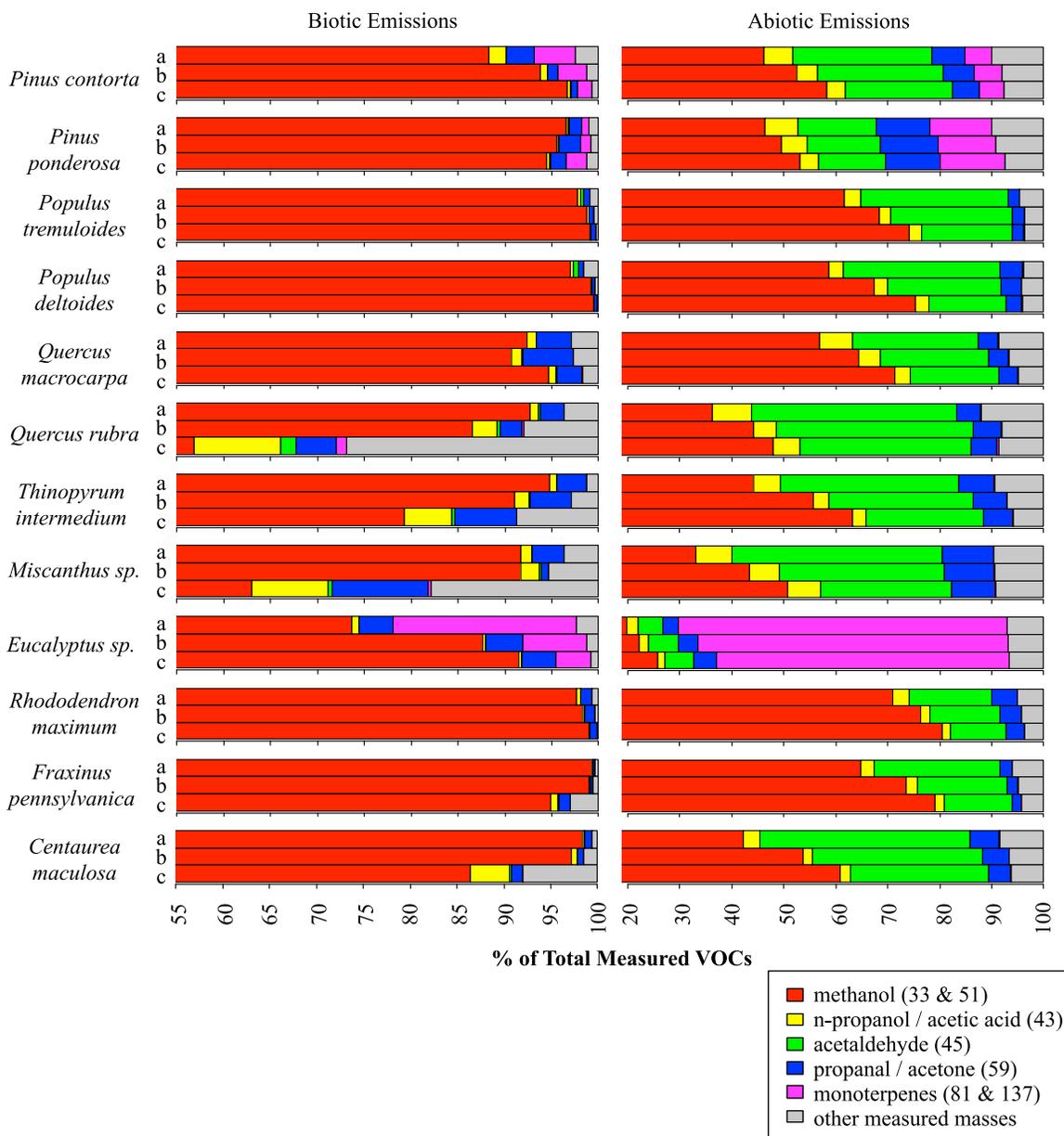


Figure 2. The proportional contribution of measured VOCs to the net emissions from the decomposing litter of 12 plant species during a 20 days incubation. In each row, the top bar (bar a) is the average emissions from hour 93 to hour 212. The middle bar (bar b) is the average emissions from hour 212 to hour 330. The bottom bar (bar c) is the average emissions from hour 330 to hour 473. Legend shows possible compound(s) with the measured protonated mass(es) in parentheses.

5%, respectively (Figure 2). In contrast, VOC emissions from the biotic litters were dominated by protonated masses 33, 59 and 43 with average percentages of 95%, 2%, and 1% respectively (Figure 2).

3.2. Differences in Biogenic VOC Emissions Between Litter Types

[12] Total VOC emissions were significantly affected by litter type ($P < 0.001$) with emission rates highest in litter from *Fraxinus pennsylvanica*, the *Eucalyptus* sp., and *Populus deltoides* (Figure 1). The types of VOCs emitted were also significantly different between litter type (Global $R = 0.64$, $P < 0.001$) (Figure 3b). Although protonated mass 33 (meth-

anol) was the dominant VOC in all cases (representing 78–99% of total VOC emitted), the relative proportions of VOCs varied across litter types with far more variability between plant species than between replicate litter samples from the same species (Figure 3b). In particular, decomposing *Eucalyptus* sp. emitted relatively high levels of protonated mass 137 (suspected to be monoterpene) throughout the 20-d incubation with emission levels reaching 20% of total VOC emissions within the first 8 days (Figure 2). *Quercus rubra* and *Miscanthus* sp. emitted less of protonated mass 33 during the last 6 days of the incubation, reaching 57% and 63% of the total VOC emission respectively.

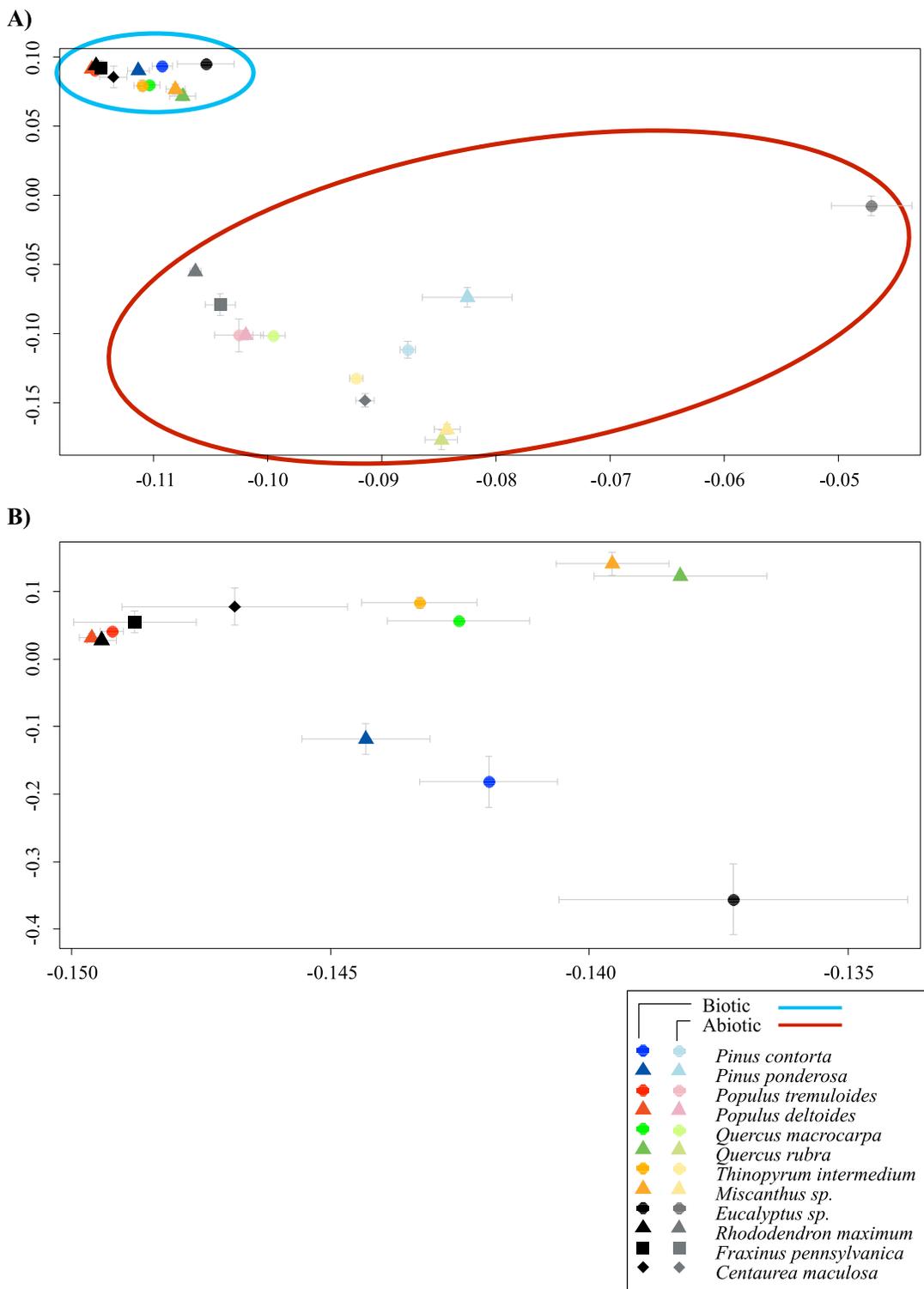


Figure 3. PCA plots transforming the differences between measured plant species litter VOC emissions into two dimensions. Plant species detritus with similar VOC emissions during decomposition are closer in the PCA plot. (a) Biotic and abiotic emissions. (b) Biotic emissions. The blue circle indicates the grouping of the non-sterile samples, and the red circle indicates sterile samples.

3.3. Predictability of Biogenic VOC Emissions

[13] There was a significant relationship between the types of VOCs emitted and plant family (Global $R = 0.097$, $P = 0.006$), a pattern also evident in Figure 3b which shows that

VOC profiles from litter of related plant species were often similar. However, VOC emissions were not highly predictable from the measured litter chemical characteristics. There were some weak but statistically significant correlations

between total net emissions and soluble cell mass, hemicellulose and to a lesser degree cellulose ($r = 0.57, -0.49$ and -0.44 respectively with all $P < 0.002$). The remaining litter characteristics (and combinations thereof) had no significant relationships with the total VOCs emitted from the non-sterile samples ($r < 0.05$ and $P > 0.13$ in all cases). Likewise, Mantel tests showed no significant correlation between these litter chemical characteristics, or combinations thereof, and the percentages of VOCs emitted (VOC profiles) from the biotic treatments (Mantel $r < 0.593$, $P > 0.01$ in all cases).

4. Discussion

[14] In nearly all cases, biotic VOC emission rates exceeded those from the abiotic controls throughout most of the incubation period (Figure 1). However, in only seven of the 12 litter types did the total biotic VOC emissions statistically differ from abiotic emissions during the 20-d experiment. The lack of statistical difference was either due to slow increases in biotic emissions (*Pinus contorta*) or an initial increase in emissions above the control followed by a marked decrease in emissions (to below the control) over the course of the incubation (*Centaurea maculosa*, *Quercus rubra*, *Miscanthus sp.* and *Thinopyrum intermedium*). From this experimental design, we were unable to ascertain whether the decrease in VOC emissions to values below the controls is caused by a decrease in VOC production or an increase in VOC consumption [see *Shennan*, 2006]. Nevertheless, the dynamic differences in net biotic emissions over 20 days of decomposition suggest that field emissions should be measured in order to include the biotic component in regional and global VOC emission models. Using abiotic emissions alone for models [e.g., *Warneke et al.*, 1999] not only underestimates the net VOC flux but also leads to incorrect assumptions about the specific types of VOCs emitted during litter decomposition (Figures 2 and 3a).

[15] Litter from all of the species included here differed with respect to the quantities and types of VOCs emitted as they were being actively decomposed. This finding was similar to studies by *Leff and Fierer* [2008] and *Isidorov and Jdanova* [2002] that also found differences in VOCs emissions between different litter types. Although litter chemistry itself was not a great predictor of VOC emissions, the decomposition of litter from closely related species in the same family (e.g., Pinaceae and Salicaceae) often yielded similar VOC emission profiles (Figure 3b). The types and quantities of VOCs emitted during litter decomposition are likely to be regulated by the characteristics of the decomposer communities, the specific litter components being consumed, or some combination thereof. Many microorganisms have been found to produce different VOCs depending on the substrates catabolized. For example, indoor fungal molds will produce different VOCs depending on the nature of the substrate being consumed [*Van Lancker et al.*, 2008]. Likewise, each litter type likely harbored different microbial decomposer communities [*Moorhead and Sinsabaugh*, 2006; *Strickland et al.*, 2009] and this could contribute to the observed differences in VOC profiles. *Lechner et al.* [2005] and *Bunge et al.* [2008] found that different bacteria produced different VOC profiles when grown on the same media. Future work determining the specific factors regulating the types and quantities of VOCs emitted from micro-

organisms during litter decomposition is necessary in order to gain a more predictive understanding of VOC emissions from litter.

[16] In all biotic cases, protonated mass 33 (methanol) was the dominant VOC emitted accounting for 78 to 99% of the emitted VOCs (Figure 2). Methanol emissions have been shown to be emitted from flowering plants [*Macdonald and Fall*, 1993] with rates related to pectin levels within the primary cell walls of the plant tissue [*Galbally and Kirstine*, 2002]. However, since we did not measure the pectin levels of the plant litter, we do not know if the same patterns exist for litter decomposition. A comparable study utilizing PTR-MS [*Asensio et al.*, 2008] also found that methanol was the primary VOC emitted from the combined litter and soil in a Mediterranean shrubland. However, studies using GC-MS to examine soil or litter VOCs [*Isidorov and Jdanova*, 2002; *Leff and Fierer*, 2008] have not reported methanol emissions because the GC-MS analyses did not permit the detection of such low molecular weight compounds. The contributions from other compounds varied across litter types and families, with the largest average from protonated masses 59 and 43. However, as incubations continued over the 20-d experiment, the VOC profiles often changed (Figure 2), demonstrating that the types of VOCs emitted can be influenced by the progression of decomposition. Studies using longer-term incubations will allow for a greater understanding of how VOC emission profiles change throughout the decomposition process, particularly if such studies include GC-MS, proton transfer reaction time of flight mass spectrometry (PTR-TOF-MS) or other such techniques to better confirm the identity of the compounds emitted.

[17] Although the results from this lab-based study, with litter incubated under nearly optimal temperature and moisture conditions, cannot necessarily be used to predict the specific rates of VOC emissions in the field, these results do point at the potential importance of VOC emissions from decomposing litter. In particular, this work highlights the relatively high emissions of methanol from all litter types, an important observation given that methanol is an important component of the OH and ozone global budgets and is also a significant atmospheric source of formaldehyde and carbon monoxide [*Jacob et al.*, 2005]. Recent attempts to model global methanol do not take soil emissions from biotic decomposition into consideration [*Galbally and Kirstine*, 2002; *Jacob et al.*, 2005]. This study suggests that including methanol emissions from the biotic decomposition of plant litter might improve the accuracy of global methanol modeling efforts. However, we note that net methanol emissions will not necessarily be positive in all cases as under certain scenarios we might expect methanol consumption to exceed methanol production rates. Also, the differences in VOC emissions from the different plant species' litter suggests that changes in vegetation type can have an important influence on microbially derived VOC emissions when considered at local, regional, and global scales.

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