AGU PUBLICATIONS

JGR

Journal of Geophysical Research: Biogeosciences

RESEARCH ARTICLE
10.1002/2013JG002575

Key Points:
- Emission rates from the soil were highest for methanol and monoterpenes
- Uptake rates into the soil were highest for isoprene and formaldehyde
- Root presence and temperature correlated with BVOC flux rates

Supporting Information:
- Readme
- Figure S1

Correspondence to:
C. M. Gray,
chris.gray@colorado.edu

Citation:
Gray, C. M., R. K. Monson, and N. Fierer (2014), Biotic and abiotic controls on biogenic volatile organic compound fluxes from a subalpine forest floor, *J. Geophys. Res. Biogeosci.*, *119*, 547–556, doi:10.1002/2013JG002575.

Received 20 NOV 2013
Accepted 15 MAR 2014
Accepted article online 27 MAR 2014
Published online 21 APR 2014

Biotic and abiotic controls on biogenic volatile organic compound fluxes from a subalpine forest floor

Christopher M. Gray[1], Russell K. Monson[2], and Noah Fierer[1,3]

[1]Department of Ecology and Evolutionary Biology, University of Colorado Boulder, Boulder, Colorado, USA, [2]School of Natural Resources and Environment, University of Arizona, Tucson, Arizona, USA, [3]Cooperative Institute for Research in Environmental Sciences, University of Colorado Boulder, Boulder, Colorado, USA

Abstract Nonmethane biogenic volatile organic compounds (BVOCs) play key roles in the atmosphere, where they can influence a wide range of chemical processes, and in soils, where they can alter the rates of biogeochemical cycles and impact the growth of plants and soil organisms. However, the diversity and quantities of BVOCs released from or taken up by soils remain poorly characterized as do the biotic and abiotic controls on these fluxes. Here we used proton transfer reaction mass spectrometry to quantify BVOC flux rates from soils with and without active root systems in a subalpine coniferous forest. The total measured BVOC flux averaged 102 nmol $m^{-2} h^{-1}$ (an estimated 2.0 μg-C $m^{-2} h^{-1}$). The individual BVOCs with the highest net emissions from soil included monoterpenes and methanol (averaging 646 and 641 ng-C $m^{-2} h^{-1}$, respectively) while soil represented a net sink of isoprene (−98 ng-C $m^{-2} h^{-1}$) and formaldehyde (−37 ng-C $m^{-2} h^{-1}$). Tree roots, directly or indirectly, contributed an average of 53% of the total carbon emitted from the soil as BVOCs, with methanol and acetaldehyde among those BVOCs most strongly associated with active root presence. The fluxes of most of the dominant BVOCs emitted from soil, including methanol, increased linearly with increasing temperature. Together the fluxes of certain BVOCs into or out of the forest floor (particularly methanol, isoprene, and monoterpenes) are likely relevant to ecosystem-level processes and belowground ecology, but these fluxes are highly variable and are strongly controlled by both root presence and soil abiotic conditions.

1. Introduction

Nonmethane biogenic volatile organic compounds (BVOCs) are low molecular weight carbon (C) compounds that are produced primarily by plants and microbes in terrestrial systems. These compounds can have wide-ranging impacts on atmospheric chemistry, terrestrial nutrient cycles, and soil ecology [*Atkinson and Arey*, 2003; *Insam and Seewald*, 2010]. In the atmosphere, the oxidation of BVOCs results in the formation of tropospheric ozone and the formation of secondary organic aerosol particles, which lead to increased cloud albedo and altered precipitation dynamics [*Atkinson*, 2000; *Kesselmeier and Staudt*, 1999]. Within terrestrial systems, BVOCs can alter the rates of specific microbial processes associated with the C and nitrogen (N) cycles. For example, monoterpenes, a well-studied class of BVOCs, inhibit the oxidation of methane in soils [*Amaral and Knowles*, 1998; *Maurer et al.*, 2008] and inhibit several N cycling processes, including nitrification and N mineralization [*Paavolainen et al.*, 1998; *Smolander et al.*, 2006; *Uusitalo et al.*, 2008; *White*, 1994]. In soils, various BVOCs have been shown to alter the growth and activity of plants [*Farag et al.*, 2006], fungi [*Bruce et al.*, 2004], nematodes [*Gu et al.*, 2007], and bacteria [*Wheatley*, 2002]. Several interspecies interactions within the soil also appear to be mediated by BVOCs, including the formation of nodules in legumes [*Horiuchi et al.*, 2005] and the antagonistic interactions between bacteria and fungi [*Bruce et al.*, 2004; *Mackie and Wheatley*, 1999].

BVOCs clearly have the potential to alter the structure and functioning of terrestrial systems in a myriad of ways [*Insam and Seewald*, 2010], but research into BVOC fluxes has historically concentrated on plant foliar emissions, with soil sources and sinks of BVOCs largely ignored. For example, a widely used model to calculate BVOC flux rates from a system (MEGAN: Model of Emissions of Gases and Aerosols from Nature) primarily considers the dynamics of foliar emissions and uses a single variable to account for any uptake by the canopy or soil [*Guenther et al.*, 2012]. However, several studies comparing canopy-level fluxes to forest floor fluxes suggest that the forest floor (ground vegetation and soil) can be an important source and sink of

certain BVOCs to the atmosphere [*Aaltonen et al.*, 2011; *Cleveland and Yavitt*, 1997; *Hellen et al.*, 2006], yet the rates and controls on soil BVOC fluxes remain poorly characterized. The work that has been done suggests that BVOC fluxes can vary considerably across soil and litter types. For example, previous work on BVOC emissions from decomposing litter has shown that the types and quantities BVOCs will vary depending on the plant litter type in question with most of these BVOCs produced by microbial processes [*Gray et al.*, 2010]. Under laboratory conditions, these BVOC fluxes can reach as high as 63 μmol g-litter^{-1} h^{-1} and the amount of carbon (C) emitted as BVOCs can be equivalent to the amount of C emitted from decomposing litter as CO_2 [*Gray and Fierer*, 2012]. There is also evidence that biotic processes within mineral soil can lead to the net consumption of specific BVOCs [*Asensio et al.*, 2007; *Ramirez et al.*, 2010; *Scheutz et al.*, 2004] and that the presence of active roots in soil can increase uptake of certain BVOCs and increase net emission of others [*Asensio et al.*, 2007; *Back et al.*, 2010; *Chen et al.*, 2004; *Steeghs et al.*, 2004]. However, only a few studies have examined BVOC fluxes in the field and the biotic or abiotic controls on these fluxes [*Asensio et al.*, 2007; *Asensio et al.*, 2008; *Greenberg et al.*, 2012]. In particular, consumption (i.e., uptake) of BVOCs into soil is poorly studied as most previous studies have used air free of BVOCs, rather than ambient air, to flush soil chambers before quantification of flux rates. This method cannot capture consumption rates and alters the natural concentration gradients between soil and the sampled air, artificially increasing diffusion into the sampled air and thus leading to overestimation of net emission rates. Also, much of the previous work on soil or litter emissions of BVOCs have used analytical techniques that do not measure methanol, one of the dominant BVOCs emitted from soils and decomposing litter [*Asensio et al.*, 2008; *Gray and Fierer*, 2012; *Greenberg et al.*, 2012].

To address some of these gaps in our current understanding of BVOC fluxes from soils and the controls on these fluxes, we designed a study to answer the following questions. (1) What are the types and amounts of BVOCs emitted or consumed (soil uptake) from undisturbed soils in situ from a subalpine forest floor during the growing season? (2) How much does the presence of active roots and root rhizodeposition contribute to BVOC fluxes from soil? (3) How do temperature and soil moisture relate to the temporal variability in soil BVOC flux rates? To answer these questions, we utilized a high-sensitivity proton transfer reaction mass spectrometer (PTR-MS) to measure BVOC fluxes in soil chambers receiving ambient air from intact plots and from plots on which trees had been girdled, removing the potential for shoot-to-root rhizodeposition, in a subalpine forest in Colorado, USA.

2. Methods

2.1. Site Description

Our study site was located near the Niwot Ridge AmeriFlux tower in northern Colorado, USA (40°1′58″N, 105°32′47″W; elevation 3050 m). This subalpine system is dominated by *Abies lasiocarpa* (subalpine fir), *Picea engelmannii* (Engelmann spruce), and *Pinus contorta* (lodgepole pine) with interspersed groves of *Populus tremuloides* (quaking aspen). The understory is sparse, containing tree seedlings and patches of *Vaccinium myrtillus* (whortleberry). Soils are sandy and derived from granitic moraine with a distinct, thin (<6 cm) organic horizon. Additional site details can be found in *Scott-Denton et al.* [2006] and *Monson et al.* [2010].

The trees in three plots (~50 m^2) dominated by *P. contorta* were girdled, and the soil around the plots was trenched in the spring of 2009, 3 months before we began soil BVOC measurements. The timing of the girdling and trenching was chosen to reduce the unintended effects of the disturbances on soils within the plots [*Scott-Denton et al.*, 2006; *Weintraub et al.*, 2007]. Trees were girdled by scraping away a 15–20 cm swath of bark and phloem at breast height. Thus, only the outer layer of xylem (wood) was exposed in the girdled area. The girdling of trees severs the phloem connection between shoots and roots and effectively blocks photosynthate from reaching the roots or rhizosphere. Girdling, combined with trenching to 20 cm depth around the perimeter of the plots to remove invading shallow roots, removed active roots and shoot-to-root rhizodeposition (both herein referred to as an "active root system") and has been shown previously to effectively eliminate approximately 50% of the soil respiration rate in non-girdled plots [*Scott-Denton et al.*, 2006; *Weintraub et al.*, 2007]. Three similar plots were selected as control plots where neither girdling nor trenching was implemented. The number of trees in each plot ranged from 3 to 7. Throughout the experiment, aboveground cover was clipped to ground level at weekly intervals in the girdled and trenched plots (herein referred to as the "girdled plots") and control plots to exclude BVOC emissions that might originate from understory vegetation. Chambers were placed near the center of the plots in undisturbed areas and located so they did not cover the clipped but sparse herbaceous ground cover.

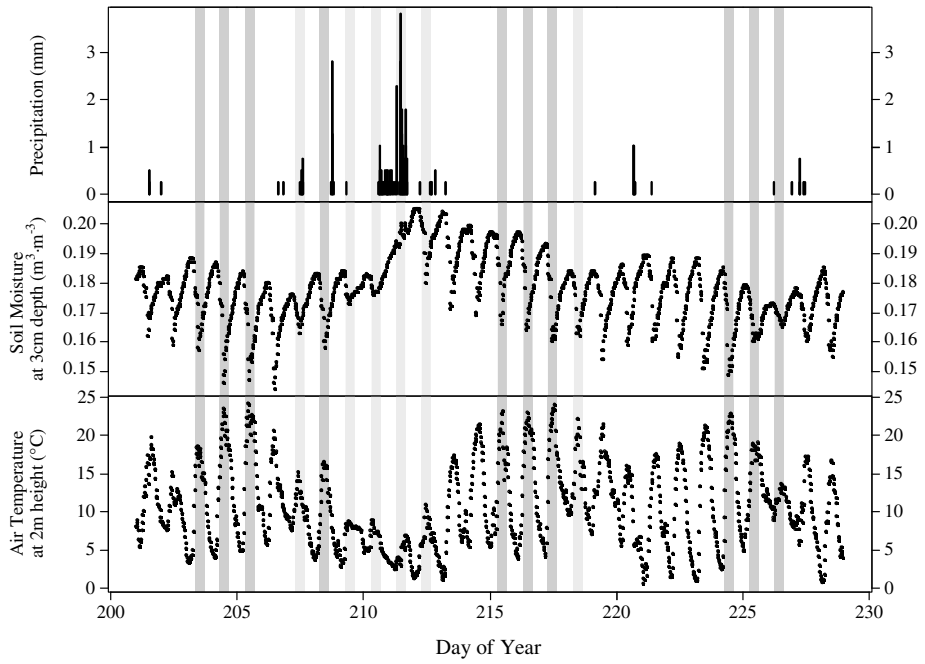

Figure 1. Recorded precipitation, soil moisture (at 3 cm), and air temperature (at 2 m) taken from the Niwot Ridge Ameriflux site, Colorado. Dark gray bars indicate measurement time periods without a visibly wet litter layer or rain, and light gray bars indicate measurement time periods with visibly wet soil or rainfall.

Environmental data were taken from sensors at the Niwot Ridge AmeriFlux tower site, which was located within 300 m of the study plots. Measurements used in this study included air temperature at 2 m (Vaisala HMP-35D), barometric pressure at 12 m (Vaisala PTB-101B), volumetric soil moisture 3 cm below the surface (Campbell Scientific Instruments CS615), and a precipitation gauge (Met One Model 385). Data are recorded from these instruments every 30 min and made publicly available as part of the AmeriFlux Network (http://public.ornl.gov/ameriflux/index.html). Values for soil moisture are not meant to represent the actual moisture at our plots but rather represent the relative changes throughout the experiment in response to precipitation events. Figure 1 provides the precipitation, soil moisture, and air temperature data during the experiment and information on when BVOC flux rates were measured from the plots.

2.2. BVOC Flux Measurements

A stainless steel collar with an area of 0.132 m^2 was placed in each of three girdled and three control plots 1 month before BVOC measurements began (Figure 2). Each collar was inserted 2–5 cm into the soil with the exact depth dependent on the presence or absence of rocks beneath the surface and an approximate 10 L headspace volume. Two equal lengths of Dekoron tubing (3/8″ O.D. Type 1300; effects determined minimal relative to chamber emissions) were positioned between each plot and the centrally located proton transfer reaction mass spectrometer (PTR-MS). One Dekoron line was connected to a stainless steel lid that was placed on top of the collars while sampling, and the other was placed at the inlet of the stainless steel lid to capture BVOC concentrations in ambient air (Figure 2). We sampled on 16 days within a 4 week period during the 2009 growing season. Days not included were either due to limited access to the site or when methodological issues made it impossible to take measurements. On each day of sampling (Figure 1), one plot from each of the control and girdled replicate plots was selected at random for sampling. Chamber lids were placed on top of the collars, and ambient air was pulled through chambers and lines for 1 h prior to and during sampling with a diaphragm pump at ~400 mL min^{-1} with ~100 mL min^{-1} of the flow diverted to the PTR-MS for analysis. Temperature and humidity within the chambers were not measured but are assumed to have changed little as all chambers were shaded by the canopy. Description and operation of the PTR-MS has been previously described in detail [*Lindinger et al.*, 1998]. The specific PTR-MS techniques and settings used for this study follow those described previously [*Gray and Fierer*, 2012; *Gray et al.*, 2010]. Since the PTR-MS only characterizes compounds, or fractions of compounds, by their molecular weight, the identities of the BVOCs measured are

Figure 2. (top) Trenched experimental plot with girdled trees and stainless steel collar placed into the soil. (bottom) Soil chamber during the measurement of BVOCs with an ambient line to quantify ambient BVOCs and a chamber line to quantify soil BVOCs.

considered putative. On each day of sampling, selected BVOC masses (Table 1) were measured 4 times: once every 50 min over a 3.5 h period. Each line measurement contained the average of three PTR-MS cycles taken over a span of 3 min. All measurements were taken between 10:30 and 15:30 local time to capture midday fluxes. Masses 49, 53, 67, 77, 105, 119, 131, 147, and 149 were measured but excluded from all calculations as they were determined to be indistinguishable from the background levels of the PTR-MS system.

Data from the PTR-MS (in ppbv) were converted to soil BVOC flux rates using the following equation:

$$F_{BVOC} = \frac{(C_{Ch} - C_{Am}) \times Q \times P}{R \times A \times T}$$

where F_{BVOC} is the flux rate in nmol $m^{-2} h^{-1}$, C_{Ch} is the measured chamber BVOC concentration converted to mole fraction (nmol mol^{-1}), C_{Am} is the measured ambient BVOC concentration in mole fraction (nmol mol^{-1}), Q is the flow rate through the chamber in L h^{-1}, P is the barometric pressure in kPa, R is the gas law constant of 8.3145 L kPa $mol^{-1} K^{-1}$, A is the footprint area of the soil chambers in m^2, and T is ambient air temperature in K. Because many BVOCs vary in their molar C concentrations and to facilitate comparisons to fluxes measured in other studies, molar BVOC fluxes were also converted to an estimated C mass flux using the equation:

$$F_C = F_{BVOC} \times r \times G_C$$

where F_C is the C flux rate in ng-C $m^{-2} h^{-1}$, F_{BVOC} is the flux rate as nmol $m^{-2} h^{-1}$, r is the conservatively estimated molar ratio of C to the measured protonated mass (Table 1), and G_C is the molar mass of C in ng-C $nmol^{-1}$.

2.3. Data Analysis

All analyses were run using R statistical software (R Foundation for Statistical Computing, Vienna, Austria). Two sampling days from the girdled plots (days 205 and 217) were removed from all analyses due to debris that had infiltrated the Dekoron lines. Only data from sampling days without visibly wet litter were used to compare flux rates of individual protonated masses, summed BVOC flux rates (flux rates for each individual protonated mass summed for each measurement point), and the effects of active roots on BVOC emissions (Figure 2). We excluded days with wet litter from these analyses to get a baseline estimate of BVOC fluxes under conditions that are more typical for this site. For each individual protonated mass measured, Welch's t tests were used to compare flux rates from the control plots to the rates from the girdled plots. Due to the large number of individual tests (48 masses and the summed rate), a Bonferroni adjusted α of 0.001 was used for the determination of significance.

To measure the effects of temperature and soil moisture on BVOC emissions, all sampling days, including those with visibly wet and dry litter, were included in the analyses to maximize the range in temperature and soil moisture conditions across which BVOC emissions were measured. Using multiple linear regressions, air temperature and soil moisture were fit to individual protonated mass flux rates as well as the summed BVOC flux rates.

Table 1. BVOC Flux Rates From an Alpine Soil[a]

Protonated Mass (*m/z*)	Putative ID	Conservative Molar Ratio	BVOC flux (nmol $m^{-2} h^{-1}$)		C flux (ng-C $m^{-2} h^{-1}$)	
			Control	Girdled	Control	Girdled
Protonated Masses With Highest Average Emission Rates						
33 + 51*	methanol	1	53.35 ± 31.84	11.22 ± 11.73	640.8 ± 382.4	134.7 ± 140.8
43	propanol/ acetic acid	2	5.12 ± 4.32	3.06 ± 3.16	123.1 ± 103.7	73.4 ± 76.0
45*	ethanal/ acetaldehyde	2	9.12 ± 5.55	1.92 ± 2.77	219.1 ± 133.3	46.2 ± 66.5
47*	formic acid/ ethanol	1	6.92 ± 6.38	−1.07 ± 2.59	83.1 ± 76.6	−12.9 ± 31.2
59	propanal/ acetone	3	6.03 ± 7.14	−0.09 ± 2.84	217.4 ± 257.3	−3.1 ± 102.2
61	acetic acid	2	4.35 ± 6.04	0.72 ± 4.99	104.5 ± 145.1	17.2 ± 119.9
73	methyl ethyl ketone	4	3.64 ± 8.60	4.60 ± 13.82	174.9 ± 413.1	221.2 ± 664.1
81 + 137	monoterpene	10	5.38 ± 4.22	5.34 ± 3.25	646.5 ± 507.4	640.8 ± 389.8
Protonated Masses With Highest Average Uptake Rates						
31	formaldehyde	1	−3.09 ± 1.01	−3.39 ± 1.11	−37.1 ± 12.1	−40.7 ± 13.3
69	isoprene/ furan	4	−2.03 ± 1.32	−1.86 ± 0.76	−97.7 ± 63.3	−89.2 ± 36.5
75	methyl acetate/ propionic acid	3	−2.46 ± 2.75	−2.09 ± 1.57	−88.5 ± 99.0	−75.2 ± 56.7
91		1	−1.12 ± 0.40	−0.87 ± 0.41	−13.4 ± 4.8	−10.5 ± 4.9
Sum Flux Rate of All Other Measured Masses						
All others[b]		1	6.21 ± 13.88	4.41 ± 8.34	74.6 ± 166.7	53.0 ± 100.2

[a]The nine protonated masses with highest average emissions (soil emissions), the four masses that exhibited the highest rates of soil uptake, and the sum of other measured masses along with putative compound identifications, a conservative carbon molar ratio for the given protonated mass(es), average fluxes (molar BVOC flux and grams of carbon flux), and standard error from control and girdled/trenched plots. "*" indicate significant differences between treatments after Bonferroni correction ($\alpha < 0.001$).

[b]Other protonated masses measured included: 41, 42, 57, 63*, 65*, 71, 79, 83, 85, 87, 89, 93, 95, 97, 99, 101, 103, 107, 109*, 111, 113, 115, 117, 121, 123, 125, 127, 129, 133, 135, 139, 141, 143, 145.

3. Results and Discussion

3.1. General Characteristics of BVOC Fluxes

From the control plots, individual BVOC fluxes summed at each measurement point averaged 2.0 μg-C $m^{-2} h^{-1}$ and ranged from −1.8 to 7.2 μg-C $m^{-2} h^{-1}$ with Figure 3 showing the mean flux of each protonated mass along with the sum of all positive and negative fluxes (net emission and soil uptake, respectively) from control and girdled plots. The summed BVOC fluxes from this study were comparable to C fluxes from BVOCs measured from a boreal forest floor where BVOC fluxes varied between 0.6 and 9.8 μg-C $m^{-2} h^{-1}$ [*Aaltonen et al.*, 2011]. Our measured BVOC emissions are lower than what would be estimated from the results of a laboratory study (~6 mg-C $m^{-2} h^{-1}$) that measured emissions during the decomposition of fresh *P. contorta* litter [*Gray and Fierer*, 2012]. The discrepancies between this study and the laboratory study could be due to BVOC uptake within the mineral soil [*Ramirez et al.*, 2010] that should decrease net rates measured in the field, or the discrepancies could be related to the laboratory study having incubated fresh litter under nearly optimal moisture and temperature conditions, thus maximizing net BVOC fluxes. In addition, we found that the estimated net C emissions as BVOCs (i.e., the summed BVOC C flux) were 5 orders of magnitude lower than C fluxes in the form of CO_2 previously measured at this site [*Scott-Denton et al.*, 2006]. Compared to CO_2 emissions, BVOC emissions do not represent a major pathway by which belowground C is transported to the atmosphere. However, this may not necessarily be true in other systems [*Gray and Fierer*, 2012] or during other times of the year [*Aaltonen et al.*, 2013]. Furthermore, gross BVOC flux rates within the soil could be much higher than net rates would indicate and even low concentrations of BVOCs within soils could have important effects on belowground processes and community dynamics [*Insam and Seewald*, 2010].

The range of summed BVOC fluxes observed here, with individual BVOCs showing either net positive efflux out of soil or net uptake into soil, are likely the outcome of many independent biotic and abiotic processes. Although we cannot separate abiotic from biotic sources with these results, previous work has suggested that the abiotic contribution is likely minimal [*Gray et al.*, 2010]. Table 1 provides detailed mean flux rates for the nine masses with the highest mean emission rates and the four masses with the highest mean uptake rates. Methanol (33^+ and 51^+) had the largest mean molar emission rate of 53.35 nmol $m^{-2} h^{-1}$ and a maximum measured rate of 189.08 nmol $m^{-2} h^{-1}$. This is in agreement with other studies showing that methanol was the dominant BVOC emitted from soils [*Asensio et al.*, 2008; *Greenberg et al.*, 2012]. According to above-canopy

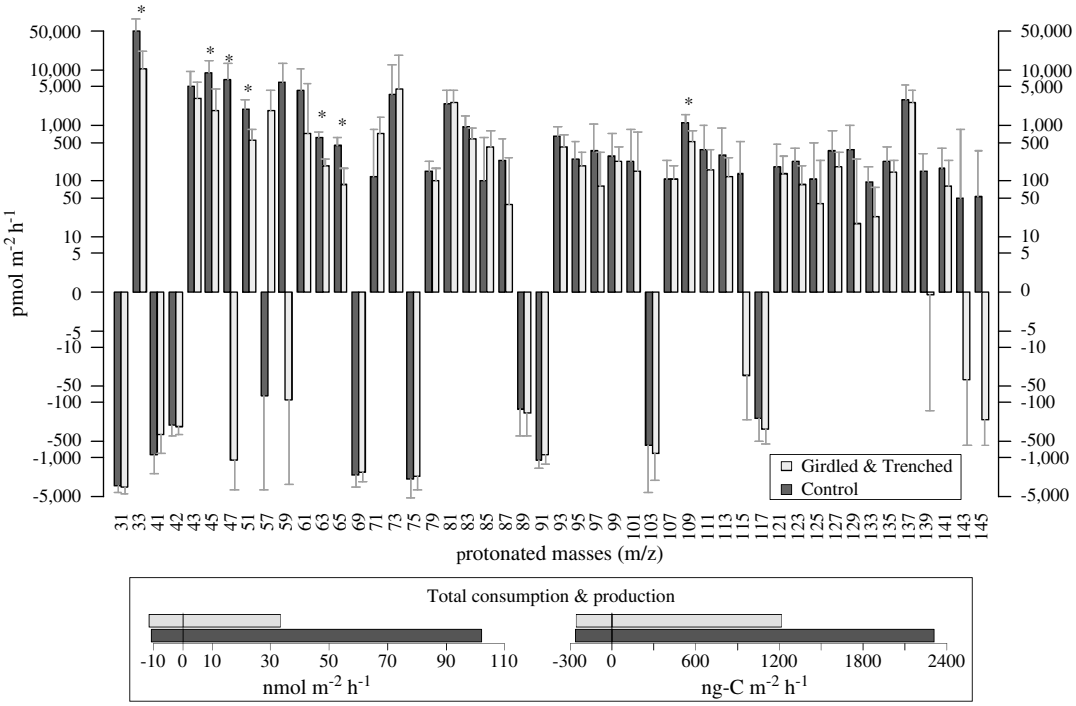

Figure 3. Soil fluxes of measured BVOCs from a field site primarily consisting of lodgepole pines (*Pinus contorta*) at Niwot Ridge, Colorado. Fluxes of protonated masses are from undisturbed control plots (dark) and from recently trenched plots with surrounding trees girdled (light). One S.E.M. is indicated by vertical error bars. Significance after Bonferroni correction ($\alpha^* = 0.001$) for multiple *t* tests is indicated with asterisk. Inset figure gives the summed fluxes for all measured masses that were produced on average (right of 0) and for all those that were consumed on average (left of 0). Molar fluxes and C fluxes from control and girdled and trenched plots are given.

measurements of methanol fluxes at this site, which are estimated to be ~30 μmol m^{-2} h^{-1}, our emissions represent roughly 0.2% of the above-canopy flux [*Baker et al.*, 2001; *Karl et al.*, 2002]. This is in agreement with *Greenberg et al.* [2012] who found that methanol emissions from soil comprised only 0.4% of the above-canopy flux from a *Pinus ponderosa* forest. Although the contribution of soil and litter to total ecosystem methanol emissions is low, other systems, including deciduous forests, are likely to have far higher fluxes of methanol given that the decomposition of deciduous litter types can represent large sources of methanol [*Gray and Fierer*, 2012]. Nevertheless, methanol emissions at this site could still be important to soil processes (e.g., C dynamics within the soil) as methanol is readily consumed by the broad diversity of C1-oxidizing bacteria and fungi found in soil [*Kolb*, 2009].

Monoterpenes (137^+ and 81^+), a class of BVOCs with a C number of 10, had the largest mean estimated C emission rate (as opposed to molar emission rate) of 646.5 ng-C m^{-2} h^{-1} (Table 1) and a maximum rate of 3827 ng-C m^{-2} h^{-1}. These rates are similar to those reported previously from coniferous forests [*Aaltonen et al.*, 2011; *Greenberg et al.*, 2012; *Hayward et al.*, 2001; *Hellen et al.*, 2006]. At our study site, *Rinne et al.* [2000] found that the above-canopy flux of α-pinene (a major monoterpene emitted from this ecosystem) was roughly 15,800 ng-C m^{-2} h^{-1}. This puts an estimated soil contribution to the above-canopy fluxes at 4% with the maximum contribution reaching 24%. Our estimated contribution falls in the range of forest floor contribution estimates by *Aaltonen et al.* [2011] and *Hellen et al.* [2006] at ~10% and ~60%, respectively, but was larger than the 0.3% found by *Greenberg et al.* [2012]. We could be overestimating the contribution of soil to above-canopy monoterpene emissions because monoterpenes, as measured by the PTR-MS, comprise many different compounds, only one of which is α-pinene. However, it does suggest that forest floor monoterpene emissions could reach levels high enough to be important for local BVOC inventories and models of local atmospheric chemistry. Alternatively, if α-pinene is only a small fraction of the soil emissions, then the soil emissions during this time of the year would likely more closely resemble the results from *Greenberg et al.* [2012]. Further studies are required to determine under what circumstances monoterpenes

from the forest floor might be contributing significantly to canopy-level emissions. Beyond their potential effects on atmospheric chemistry, we note that the monoterpene fluxes observed here could have important effects on belowground processes given that even low concentrations of monoterpenes are capable of inhibiting N mineralization [*Smolander et al.*, 2006], net nitrification [*Uusitalo et al.*, 2008], denitrification, and methane oxidation rates [*Amaral et al.*, 1998].

Although methanol and monoterpenes were typically observed to have net positive emission rates from these soils, all compounds displayed net soil uptake at some point during the experiment. Unlike other studies that flush their chambers with air scrubbed of all BVOCs and thus are unable to detect net uptake rates, our measurement method allowed us to quantify net consumption of ambient atmospheric VOCs in soil. Formaldehyde (31^+) had the largest mean molar uptake rate of 3.09 nmol m^{-2} h^{-1}, while isoprene/furan (69^+) had the largest estimated C uptake rate of 97.7 ng-C m^{-2} h^{-1}. A portion of the measured uptake into the soil could be due to abiotic mechanisms within the soil, such as adsorption onto soil particles or dissolution into soil water. However, several past studies have suggested that microorganisms living in mineral soil can catabolize BVOCs emitted from the litter layer or the surrounding canopy [*Asensio et al.*, 2007; *Asensio et al.*, 2008; *Ramirez et al.*, 2010]. Likewise, *Cleveland and Yavitt* [1997] observed microbial consumption of isoprene in the soil and suggested that the rates could be relevant to ecosystem flux rates and the global isoprene budget. As isoprene consumption is likely enzymatically driven [*Cleveland and Yavitt*, 1998], increases in ambient concentrations of isoprene would be expected to increase uptake rates. If this is the case, further studies should be done to determine the significance of soil uptake rates at different ambient concentrations, including uptake rates in forested systems where ambient levels of isoprene have been measured at 35 ppbv [*Wiedinmyer et al.*, 2005], over 10 times higher than levels measured during our experiment.

3.2. Effect of Root Presence on BVOC Fluxes

The presence of an active root system increased the summed molar BVOC flux by 76% and the BVOC C flux by 53%, on average (Figure 3). In terms of the fractional contribution of an active root system to net soil fluxes, an active root system contributed to the C flux from BVOCs at the same ratio as that for CO_2. At this site, using similar girdling and trenching techniques, the root system was found to be responsible for 44% of the CO_2 emitted from the soil [*Scott-Denton et al.*, 2006], and a review of 37 studies from forested sites found that the mean root system contribution was 48.6% [*Hanson et al.*, 2000]. These results suggest that the effect of an active root system on net C emissions from soil is similar regardless of whether C emissions are measured as emissions of CO_2 or BVOCs. In other words, the contribution of roots to belowground BVOC and CO_2 emissions appears to be similar at around 50%. We do not know if this similarity is merely coincidental or if there are shared mechanisms (i.e., a direct links between respiration and the processes leading to BVOC emissions) that drive this apparent similarity in root contributions to C emission from soil.

The effect of root presence on BVOC emissions was not equivalent across all measured masses. Several individual protonated masses showed significant changes in flux rates between the control and girdled plots (Figure 3). For example, methanol (33^+ and 51^+) fluxes from girdled plots were on average 21% of those from control plots, a finding in agreement with research suggesting that methanol is a product of root metabolism in some tree species [*Folkers et al.*, 2008]. However, as we were unable to separate root from rhizosphere flux and given that BVOC emissions have been detected from roots, rhizosphere, and associated fungi [*Back et al.*, 2010; *Chen et al.*, 2004; *Lin et al.*, 2007], we do not know if the methanol is coming directly from the roots themselves. In addition, emissions of mass 47^+ (likely formic acid and/or ethanol) significantly changed from net positive emissions (6.9 nmol m^{-2} h^{-1}) in control plots to net uptake (average rate of -1.1 nmol m^{-2} h^{-1}) in plots where active roots were removed. This pattern highlights the likely role of the root system as a source of mass 47^+ and the ability of soil processes (likely microbial catabolism) to consume this BVOC. Monoterpenes, likely the most frequently studied of the nonmethane BVOCs emitted from soils, showed no change in flux rates between control and girdled plots. This suggests that monoterpene fluxes originated from either the needle litter or the mineral soil itself, a finding in agreement with results reported previously [*Hayward et al.*, 2001; *Hellen et al.*, 2006].

3.3. Effects of Temperature and Moisture

At this site, air temperature and soil moisture were strongly correlated (Figure 4; $p \ll 0.001$, $R^2 = 0.59$); the cooler days generally coincided with higher soil moisture levels (Figure 2). For this reason, we were unable to

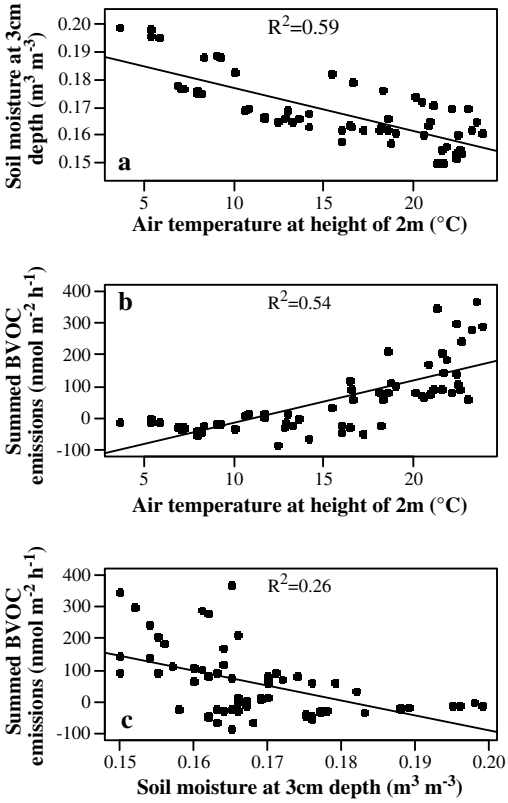

Figure 4. (a) Soil moisture was correlated with air temperature at the study site. (b, c) Summed BVOC flux from all measured masses correlated with air temperature and soil moisture.

quantify the independent effects of temperature and moisture variability on BVOC fluxes. However, multiple linear regressions testing the effects of air temperature and soil moisture on the summed BVOC flux from all measured masses showed that air temperature is the only independent variable significantly correlated with BVOC flux ($p \ll 0.001$, $R^2 = 0.54$) and including soil moisture in the statistical model led to only marginal increases in the predictive strength ($p \ll 0.001$, $R^2 = 0.65$). Our finding that BVOC emissions increased with increasing temperatures could be a result of both biotic (e.g., plant and microbial metabolisms) and abiotic processes (e.g., increased evaporation of soluble compounds and physical degradation of labile carbon). Other studies have also found that BVOC flux rates from soil generally increase with increasing temperature [*Aaltonen et al.*, 2011; *Asensio et al.*, 2008; *Greenberg et al.*, 2012]. Neither air temperature nor soil moisture correlated with the summed BVOC flux from the girdled plots, suggesting that these variables are more strongly linked to BVOC fluxes from the roots or associated rhizosphere rather than to fluxes from litter or mineral soil alone.

This correlation between net BVOC emissions and temperature was largely driven by the dominant compounds described in Table 1, with the emissions of individual compounds, including methanol, acetaldehyde, and acetone/propionaldehyde exhibiting significant, positive correlations with air temperature (Figure S1 in the supporting information). Alternatively, compounds that were detected at 91^+ (several possibilities including diethyl sulfide 2,3-butanediol and thioacetic acid methyl ester) showed increases in net uptake rates with increasing temperature (Figure S1). Although the flux rates of these BVOCs are assumed to be primarily biotic in origin, the relationships with temperature were not exponential, as would be expected of an enzymatically driven process. This could be due to the interactions between temperature and moisture effects, the limited range of temperatures observed at the study site, or because we measured net flux rates instead of gross rates. More controlled, experimental work is needed to isolate the effects of temperature and moisture on BVOC emissions from soil and to identify how these environmental factors directly influence the gross consumption and production of these compounds.

4. Conclusion

There was appreciable net production and consumption of many BVOCs during the growing season in the subalpine soils examined here. The dominant compounds emitted from the soils were methanol and monoterpenes, with monoterpene emission rates approaching estimated above-canopy flux rates. Formaldehyde and isoprene were the dominant compounds taken up by the soil. Future research on soil flux rates should utilize techniques that permit the quantification of consumption rates as we clearly show that consumption of BVOCs does occur in situ. The activity from roots and associated rhizosphere in this system contributed to over 50% of the C emitted from the system as BVOCs. Although we observed a correlation between air temperature at the site and BVOC flux rates, more experimental work needs to be conducted under controlled conditions to better understand how temperature and soil moisture independently affect flux rates. Also, methods should be developed to independently measure gross production and consumption within intact soils as the specific controls on these processes are likely distinct.

Acknowledgments
The data for this paper are available upon request to the corresponding author: chris.gray@colorado.edu. Funding for this work was provided by the Cooperative Institute for Research in Environmental Sciences (CIRES) Innovative Research Program and a grant awarded to N.F. from the National Science Foundation (DEB 0953331).

References

Aaltonen, H., J. Pumpanen, M. Pihlatie, H. Hakola, H. Hellen, L. Kulmala, T. Vesala, and J. Back (2011), Boreal pine forest floor biogenic volatile organic compound emissions peak in early summer and autumn, *Agric. For. Meteorol.*, *151*(6), 682–691, doi:10.1016/j.agrformet.2010.12.010.

Aaltonen, H., J. Aalto, P. Kolari, M. Pihlatie, J. Pumpanen, M. Kulmala, E. Nikinmaa, T. Vesala, and J. Back (2013), Continuous VOC flux measurements on boreal forest floor, *Plant Soil*, *369*(1–2), 241–256, doi:10.1007/s11104-012-1553-4.

Amaral, J. A., and R. Knowles (1998), Inhibition of methane consumption in forest soils by monoterpenes, *J. Chem. Ecol.*, *24*(4), 723–734, doi:10.1023/a:1022398404448.

Amaral, J. A., A. Ekins, S. R. Richards, and R. Knowles (1998), Effect of selected monoterpenes on methane oxidation, denitrification, and aerobic metabolism by bacteria in pure culture, *Appl. Environ. Microbiol.*, *64*(2), 520–525.

Asensio, D., J. Penuelas, I. Filella, and J. Llusia (2007), On-line screening of soil VOCs exchange responses to moisture, temperature and root presence, *Plant Soil*, *291*(1–2), 249–261, doi:10.1007/s11104-006-9190-4.

Asensio, D., J. Penuelas, P. Prieto, M. Estiarte, I. Filella, and J. Llusia (2008), Interannual and seasonal changes in the soil exchange rates of monoterpenes and other VOCs in a Mediterranean shrubland, *Eur. J. Soil Sci.*, *59*(5), 878–891, doi:10.1111/j.1365-2389.2008.01057.x.

Atkinson, R. (2000), Atmospheric chemistry of VOCs and NO_x, *Atmos. Environ.*, *34*(12–14), 2063–2101.

Atkinson, R., and J. Arey (2003), Gas-phase tropospheric chemistry of biogenic volatile organic compounds: A review, *Atmos. Environ.*, *37*, doi:10.1016/s1352-2310(03)00391-1.

Back, J., H. Aaltonen, H. Hellen, M. K. Kajos, J. Patokoski, R. Taipale, J. Pumpanen, and J. Heinonsalo (2010), Variable emissions of microbial volatile organic compounds (MVOCs) from root-associated fungi isolated from Scots pine, *Atmos. Environ.*, *44*(30), 3651–3659, doi:10.1016/j.atmosenv.2010.06.042.

Baker, B., A. Guenther, J. Greenberg, and R. Fall (2001), Canopy level fluxes of 2-methyl-3-buten-2-ol, acetone, and methanol by a portable relaxed eddy accumulation system, *Environ. Sci. Technol.*, *35*(9), 1701–1708, doi:10.1021/es001007j.

Bruce, A., S. Verrall, C. A. Hackett, and R. E. Wheatley (2004), Identification of volatile organic compounds (VOCs) from bacteria and yeast causing growth inhibition of sapstain fungi, *Holzforschung*, *58*(2), 193–198.

Chen, F., D. K. Ro, J. Petri, J. Gershenzon, J. Bohlmann, E. Pichersky, and D. Tholl (2004), Characterization of a root-specific Arabidopsis terpene synthase responsible for the formation of the volatile monoterpene 1,8-cineole, *Plant Physiol.*, *135*(4), 1956–1966, doi:10.1104/pp.104.044388.

Cleveland, C. C., and J. B. Yavitt (1997), Consumption of atmospheric isoprene in soil, *Geophys. Res. Lett.*, *24*(19), 2379–2382.

Cleveland, C. C., and J. B. Yavitt (1998), Microbial consumption of atmospheric isoprene in a temperate forest soil, *Appl. Environ. Microbiol.*, *64*(1), 172–177.

Farag, M. A., C. M. Ryu, L. W. Sumner, and P. W. Pare (2006), GC-MS SPME profiling of rhizobacterial volatiles reveals prospective inducers of growth promotion and induced systemic resistance in plants, *Phytochemistry*, *67*(20), 2262–2268, doi:10.1016/j.phytochem.2006.07.021.

Folkers, A., K. Huve, C. Ammann, T. Dindorf, J. Kesselmeier, E. Kleist, U. Kuhn, R. Uerlings, and J. Wildt (2008), Methanol emissions from deciduous tree species: Dependence on temperature and light intensity, *Plant Biol.*, *10*(1), 65–75, doi:10.1111/j.1438-8677.2007.00012.x.

Gray, C. M., and N. Fierer (2012), Impacts of nitrogen fertilization on volatile organic compound emissions from decomposing plant litter, *Global Change Biol.*, *18*(2), 739–748, doi:10.1111/j.1365-2486.2011.02569.x.

Gray, C. M., R. K. Monson, and N. Fierer (2010), Emissions of volatile organic compounds during the decomposition of plant litter, *J. Geophys. Res.*, *115*, G03015, doi:10.1029/2010JG001291.

Greenberg, J. P., D. Asensio, A. Turnipseed, A. B. Guenther, T. Karl, and D. Gochis (2012), Contribution of leaf and needle litter to whole ecosystem BVOC fluxes, *Atmos. Environ.*, *59*, 302–311, doi:10.1016/j.atmosenv.2012.04.038.

Gu, Y. Q., M. H. Mo, J. P. Zhou, C. S. Zou, and K. Q. Zhang (2007), Evaluation and identification of potential organic nematicidal volatiles from soil bacteria, *Soil Biol. Biochem.*, *39*(10), 2567–2575, doi:10.1016/j.soilbio.2007.05.011.

Guenther, A. B., X. Jiang, C. L. Heald, T. Sakulyanontvittaya, T. Duhl, L. K. Emmons, and X. Wang (2012), The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): An extended and updated framework for modeling biogenic emissions, *Geosci. Model Dev.*, *5*(6), 1471–1492, doi:10.5194/gmd-5-1471-2012.

Hanson, P. J., N. T. Edwards, C. T. Garten, and J. A. Andrews (2000), Separating root and soil microbial contributions to soil respiration: A review of methods and observations, *Biogeochemistry*, *48*(1), 115–146, doi:10.1023/a:1006244819642.

Hayward, S., R. J. Muncey, A. E. James, C. J. Halsall, and C. N. Hewitt (2001), Monoterpene emissions from soil in a Sitka spruce forest, *Atmos. Environ.*, *35*(24), 4081–4087, doi:10.1016/s1352-2310(01)00213-8.

Hellen, H., H. Hakola, K. H. Pystynen, J. Rinne, and S. Haapanala (2006), C-2-C-10 hydrocarbon emissions from a boreal wetland and forest floor, *Biogeosciences*, *3*(2), 167–174.

Horiuchi, J., B. Prithiviraj, H. P. Bais, B. A. Kimball, and J. M. Vivanco (2005), Soil nematodes mediate positive interactions between legume plants and rhizobium bacteria, *Planta*, *222*(5), 848–857, doi:10.1007/s00425-005-0025-y.

Insam, H., and M. S. A. Seewald (2010), Volatile organic compounds (VOCs) in soils, *Biol. Fertil. Soils*, *46*(3), 199–213, doi:10.1007/s00374-010-0442-3.

Karl, T. G., C. Spirig, J. Rinne, C. Stroud, P. Prevost, J. Greenberg, R. Fall, and A. Guenther (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.

Kesselmeier, J., and M. Staudt (1999), Biogenic volatile organic compounds (VOC): An overview on emission, physiology and ecology, *J. Atmos. Chem.*, *33*(1), 23–88.

Kolb, S. (2009), Aerobic methanol-oxidizing Bacteria in soil, *FEMS Microbiol. Lett.*, *300*(1), 1–10, doi:10.1111/j.1574-6968.2009.01681.x.

Lin, C., S. M. Owen, and J. Penuelas (2007), Volatile organic compounds in the roots and rhizosphere of *Pinus* spp, *Soil Biol. Biochem.*, *39*(4), 951–960, doi:10.1016/j.soilbio.2006.11.007.

Lindinger, W., A. Hansel, and A. Jordan (1998), On-line monitoring of volatile organic compounds at pptv levels by means of proton-transfer-reaction mass spectrometry (PTR-MS)—Medical applications, food control and environmental research, *Int. J. Mass Spectrom.*, *173*(3), 191–241.

Mackie, A. E., and R. E. Wheatley (1999), Effects and incidence of volatile organic compound interactions between soil bacterial and fungal isolates, *Soil Biol. Biochem.*, *31*(3), 375–385.

Maurer, D., S. Kolb, L. Haumaier, and W. Borken (2008), Inhibition of atmospheric methane oxidation by monoterpenes in Norway spruce and European beech soils, *Soil Biol. Biochem.*, *40*(12), 3014–3020, doi:10.1016/j.soilbio.2008.08.023.

Monson, R. K., M. R. Prater, J. Hu, S. P. Burns, J. P. Sparks, K. L. Sparks, and L. E. Scott-Denton (2010), Tree species effects on ecosystem water-use efficiency in a high-elevation, subalpine forest, *Oecologia*, *162*(2), 491–504, doi:10.1007/s00442-009-1465-z.

Paavolainen, L., V. Kitunen, and A. Smolander (1998), Inhibition of nitrification in forest soil by monoterpenes, *Plant Soil*, *205*(2), 147–154, doi:10.1023/a:1004335419358.

Ramirez, K. S., C. L. Lauber, and N. Fierer (2010), Microbial consumption and production of volatile organic compounds at the soil-litter interface, *Biogeochemistry*, *99*(1–3), 97–107, doi:10.1007/s10533-009-9393-x.

Rinne, H. J. I., A. C. Delany, J. P. Greenberg, and A. B. Guenther (2000), A true eddy accumulation system for trace gas fluxes using disjunct eddy sampling method, *J. Geophys. Res.*, *105*(D20), 24,791–24,798, doi:10.1029/2000JD900315.

Scheutz, C., H. Mosbaek, and P. Kjeldsen (2004), Attenuation of methane and volatile organic compounds in landfill soil covers, *J. Environ. Qual.*, *33*(1), 61–71.

Scott-Denton, L. E., T. N. Rosenstiel, and R. K. Monson (2006), Differential controls by climate and substrate over the heterotrophic and rhizospheric components of soil respiration, *Global Change Biol.*, *12*(2), 205–216, doi:10.1111/j.1365-2486.2005.01064.x.

Smolander, A., R. A. Ketola, T. Kotiaho, S. Kanerva, K. Suominen, and V. Kitunen (2006), Volatile monoterpenes in soil atmosphere under birch and conifers: Effects on soil N transformations, *Soil Biol. Biochem.*, *38*(12), 3436–3442, doi:10.1016/j.soilbio.2006.05.019.

Steeghs, M., H. P. Bais, J. de Gouw, P. Goldan, W. Kuster, M. Northway, R. Fall, and J. M. Vivanco (2004), Proton-transfer-reaction mass spectrometry as a new tool for real time analysis of root-secreted volatile organic compounds in arabidopsis, *Plant Physiol.*, *135*(1), 47–58, doi:10.1104/pp.104.038703.

Uusitalo, M., V. Kitunen, and A. Smolander (2008), Response of C and N transformations in birch soil to coniferous resin volatiles, *Soil Biol. Biochem.*, *40*(10), 2643–2649, doi:10.1016/j.soilbio.2008.07.009.

Weintraub, M. N., L. E. Scott-Denton, S. K. Schmidt, and R. K. Monson (2007), The effects of tree rhizodeposition on soil exoenzyme activity, dissolved organic carbon, and nutrient availability in a subalpine forest ecosystem, *Oecologia*, *154*(2), 327–338, doi:10.1007/s00442-007-0804-1.

Wheatley, R. E. (2002), The consequences of volatile organic compound mediated bacterial and fungal interactions, *Antonie Van Leeuwenhoek*, *81*(1–4), 357–364.

White, C. S. (1994), Monoterpenes: Their effects on ecosystem nutrient cycling, *J. Chem. Ecol.*, *20*(6), 1381–1406, doi:10.1007/bf02059813.

Wiedinmyer, C., et al. (2005), Ozarks Isoprene Experiment (OZIE): Measurements and modeling of the "isoprene volcano", *J. Geophys. Res.*, *110*, D18307, doi:10.1029/2005JD005800.