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Volatile Organic Compound Emissions From Soil Following Wetting Events

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Key Points:
- We observed a rapid increase in the emissions of both CO_2 and volatile organic compounds (VOCs) upon the wetting of five dry soils
- CO_2 and VOC dynamics were qualitatively similar, but the spike in VOC emissions was of shorter duration than the spike in CO_2 emissions
- Carbon released as VOCs accounted for 5.0 ± 2.0% of carbon emitted as CO_2 from soils in the 48 hours following the event

Supporting Information:
- Supporting Information S1
- Data Set S1
- Data Set S2
- Data Set S3

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Abstract Dynamics of carbon dioxide (CO_2) emissions following the wetting of dry soil have been widely studied in field and laboratory settings. Nonmethane volatile organic compounds (VOCs) are also emitted from soil following a rain event and are evident from the characteristic smell of wet soil. Few studies have documented VOC emissions before and after soil rewetting. Soil emissions were studied using a dynamic flux chamber system purged with VOC-free air, with identification and quantification of emissions performed by gas chromatography/mass spectrometry. All soils exhibited a rewetting-induced pulse of VOC emissions, with VOC emissions 14 times higher (on average) in the few hours after rewetting compared to moist soils 2 days after rewetting. This VOC rewetting pulse mirrored the CO_2 rewetting pulse (the so-called "Birch Effect") but was shorter in duration. Average VOC emissions were 5.0 ± 2.0% of CO_2 emissions (molar C equivalent) and increased with increasing soil organic matter content ($\rho = 0.40$, $\rho = 0.99$ with one soil excluded). The amounts and types of VOCs varied with time since rewetting and across the five studied soil types, though acetone and small hydrocarbons were the dominant compounds emitted from all soils. Some of the VOCs emitted are likely important mediators of microbial activities and relevant to atmospheric chemical dynamics. Soil VOC emissions, similar to CO_2 emissions, are strongly affected by rewetting events, and it is important to consider these rewetting dynamics when modeling soil and ecosystem VOC emissions and understand their relevance to terrestrial ecosystem functioning and atmospheric processes.

1. Introduction

A rapid increase in microbial CO_2 production is widely observed when a dry soil is rewet (Birch, 1958; Bloem et al., 1992; Cui & Caldwell, 1997; Fierer & Schimel, 2002; Franzluebbers et al., 2000). This phenomenon, termed the "Birch effect," has been documented both in the field (e.g., Cui & Caldwell, 1997) and in the laboratory (e.g., Franzluebbers et al., 2000). The magnitude and duration of the Birch effect vary depending on soil type (Huxman et al., 2004; Waring & Powers, 2016), temperature (Borken et al., 2003), and moisture conditions (Lado-Monserrat et al., 2014; Sponseller, 2007; Xiang et al., 2008). The rewetting pulse in microbial CO_2 emissions has been attributed to a rewetting-induced release of labile soil organic carbon pools, rapid catabolism of microbial osmoregulants by intact cells, or microbial cell lysis resulting from osmotic shock (Adu & Oades, 1978; Appel, 1998; Bottner, 1985; Jenerette & Chatterjee, 2012; Lundquist et al., 1999; Moyano et al., 2013; Unger et al., 2010; Vangestel et al., 1992). These rewetting-associated pulses of CO_2 can be important to consider when quantifying and predicting soil CO_2 emissions, particularly in areas subject to frequent drying and rewetting events (Huxman et al., 2004; Schimel et al., 1999). CO_2 emissions typically peak within 24–48 hr after a rewetting event, with CO_2 emissions subsequently declining by 50–95% even if soil moisture levels remain elevated (Schimel et al., 2007; Wang et al., 2015; Waring & Powers, 2016). For example, integrated CO_2 emissions following precipitation events in the Sonoran Desert ranged from 2.5 to 19.3-g carbon-CO_2 (C_{CO2}) m^{-2} depending on the amount and frequency of the rain. Emissions returned to background rates (0.03–0.13 g C_{CO2} m^{-2} hr^{-1}) 48 hr after the event (Sponseller, 2007). Likewise, in a laboratory-based incubation, soil CO_2 emissions 24 hr after rewetting were 3 times higher than emission rates 72 hr after the rewetting event, even though soil moisture levels remained elevated (Fierer & Schimel, 2003).

CO_2 is not the only gaseous form of carbon (C) emitted by soil microbes, as microbes can also generate a chemically diverse range of volatile organic compounds (VOCs). These soil VOC emissions can have important impacts on soil nutrient cycling, soil microbial activities, and atmospheric chemistry. For example, VOCs mediate bacterial-fungal, bacterial-bacterial, and fungal-fungal interactions in soil, often through effects on

quorum sensing and gene expression (Wheatley, 2002). These soil VOCs can also influence the growth, colonization, and metabolic activity of soil microorganisms (Schmidt et al., 2015). Likewise, VOCs can influence rates of specific microbial processes in soil, including nitrogen (N)-cycling (e.g., nitrification and N mineralization rates; Bending & Lincoln, 2000; Paavolainen et al., 1998; White, 1988). VOCs can also stimulate or inhibit growth of certain microbial species or act as signaling molecules for interspecies and intraspecies communication (Baldwin & Preston, 1999; Effmert et al., 2012; Falik et al., 2011; Frost et al., 2007; Kai et al., 2009; Pichersky & Gershenzon, 2002; Wenke et al., 2010). The ecosystem-level consequences of soil VOC emissions extend beyond microbial processes, as some soil-derived VOCs are highly reactive compounds that modulate key chemical reactions in the atmosphere, including ozone and secondary organic aerosol production (Bowman & Seinfeld, 1994).

While these low molecular weight organic compounds (typically $<$250 AMU) can be produced by abiotic processes, such as hydrolysis, oxidation, and photochemistry (Bruggemann et al., 2017; Gray et al., 2010), microbial processes are likely responsible for the majority of soil VOC emissions (Leff & Fierer, 2008; Monson & Holland, 2001). Compounds that have been reported in emissions from microbial metabolism include alcohols, aldehydes, alkenes, esters, hydrocarbons, ketones, and terpenoids, with distinct soils typically emitting distinct VOC profiles (Isidorov & Jdanova, 2002; Jelen & Wasowicz, 1998; Larsen & Frisvad, 1995; Leff & Fierer, 2008; Smolander et al., 2006; Stahl & Parkin, 1996; Wilkins & Larsen, 1995).

Few studies have characterized soil VOC emissions and their dynamics upon rewetting of soil. There is evidence that certain VOCs, including methanol, acetone, formaldehyde, acetaldehyde, and terpenes, are released upon soil rewetting (Asensio et al., 2007; Schade & Goldstein, 2001; Veres et al., 2014). The amounts and types of VOCs emitted from soil can also vary as a function of soil moisture dynamics, soil temperature, solar irradiance, and carbon availability (Asensio et al., 2007; Bachy et al., 2018; Schade & Custer, 2004; Waring & Powers, 2016). While plants are generally the main sources of nonmethane VOC emissions in most terrestrial ecosystems (Fehsenfeld et al., 1992; Fuentes et al., 2000; Penuelas et al., 2014), soil VOC emissions can represent 10–50% of the net forest canopy VOC flux depending on the ecosystem type and environmental conditions (Aaltonen et al., 2013; Janson, 1993; Schade & Goldstein, 2001). In other words, microbial VOC emissions from soil could be relevant to atmospheric chemistry given that soil and litter emissions of specific VOCs can be similar in magnitude those from aboveground vegetation (Potard et al., 2017; Schade & Goldstein, 2001).

In this study, we investigated the chemical diversity and temporal dynamics of soil VOCs across distinct soil types following a rewetting event, information that is critical for understanding soil VOC emissions in ecosystems that experience frequent drying-rewetting (Fierer & Schimel, 2002; Leff & Fierer, 2008). Specifically, we asked if VOC emissions parallel the burst in CO_2 following rewetting as characterized by the Birch effect. In addition, we asked if the types of VOCs emitted from soil vary before and after a rewetting event and how these emissions differ across distinct soil types. To address these questions, we designed a laboratory-based soil microcosm experiment to simulate a precipitation event that rapidly increased moisture levels in air-dried soils. We simultaneously measured CO_2 and speciated VOC emissions before and after the rewetting event, tracking these emissions over time to determine if VOC emissions follow the canonical Birch effect observed for CO_2 emissions.

2. Materials and Methods

2.1. Sample Collection and Characterization

Five soils (S1–S5) were collected in early May 2017 from sites across Boulder County, Colorado, USA. Soils were chosen to represent a range of edaphic characteristics, with samples collected from tilled agricultural soils (S1 and S2), a semiarid grassland (S3), and subalpine forest soils (S4 and S5; Table 1). At each sampling location, the litter layer was removed and surface soil (0–6 cm depth) was collected. Soils were sieved to 2.0 mm and stored field moist at 4°C for $<$2 months prior to the start of the experiment.

Field gravimetric water content was determined from sieved soil before and after drying at 80°C for 48 hr. Soils were saturated with deionized water and allowed to drain for 1 hr to determine maximum water holding capacity (WHC). Physical and chemical soil characteristics (Table 1) were measured at the Colorado State University's Soil, Water, and Plant Testing Laboratory (Fort Collins, CO, USA) using standard methods.

Table 1
Source and Physical Properties for Soils Studied

Soil	Site	pH	OM %	NO_3 (N) (ppm)	EC (mmhos/cm)	P (ppm)	K (ppm)	Texture
S1	Tilled agricultural	7.2	6.4	21.9	0.7	124	698	Sandy loam
S2	Tilled agricultural	7.6	6.8	7.8	0.6	169	864	Sandy loam
S3	Semiarid grassland	7.6	3.6	11.9	0.4	4.60	236	Sandy clay loam
S4	Subalpine, north facing	4.7	21.2	85.0	0.8	58.5	244	Sandy loam
S5	Subalpine, south facing	6.3	15.6	80.9	0.7	19.4	203	Sandy loam

Note. Soils are referred to by their number (i.e., S1–S5). Abbreviated column headings are organic matter (OM), nitrate content (NO_3 [N]), electrical conductivity (EC), phosphorus content (P), and potassium content (K).

2.2. Wetting Experiments, Flux Chamber Design, Custom Inlet System, and Instrument

Experiments were conducted using a dynamic flux chamber system. Soil subsamples of approximately 30 cm^3 were allocated into 100-ml uncovered glass jars that were then placed inside a 475-ml glass jar with a steel lid, plastisol liner, and silicone rubber seal containing approximately 50 ml of water to maintain soil moisture throughout the experiment (Figure S1 in the supporting information). A custom sampling manifold and inlet system was built to manipulate soils and to sample the purge airflow through the dynamic flux chambers containing the soil sample (plumbing diagram of the dynamic flux chamber system is available in Figure S2, and plumbing diagram of sampling inlet system is available in S3). All tubing and fittings used in the system were stainless steel. The combination of the standing water and humidified zero airflow (140 ml/min, residence time 3.5 min) maintained 25–29 parts per thousand H_2O in the jars at a temperature of 23°C. The zero airflow was humidified with a stone bubbler in a water-filled polycarbonate tube with a polypropylene cap. To generate zero air, ambient air was compressed and flowed through a custom zero air generator that catalytically oxidized hydrocarbons present in the air to CO_2. To determine baseline ambient CO_2 levels, air from the room was analyzed for 24 hr leading up to soil experiments. The median of CO_2 measurements taken each minute during that period was used as the baseline CO_2 level. The sampling manifold, inlet system, and instrument were setup in a laboratory kept at 23°C. Room lights other than the emergency light were kept off during most of the experiment. Further, jars had opaque lids and sat in a wooden housing that blocked most light from reaching the soil samples (Figure S1).

Jars, and the samples contained within them, were subject to a 140-ml/min purge flow of zero air throughout the experiment. Removing VOCs from the air to which the soil is exposed does not allow the possibility of flux into the soil and forces VOCs from the soil. This setup does not necessarily mimic natural conditions but allowed us to study emissions from a variety of soil types under controlled conditions. Purge air was split and analyzed on a LI-COR LI-840a (LI-COR Environmental, Lincoln, NE, USA) to measure CO_2 and water vapor, with the instrument calibrated with dry zero air, humidified air, and CO_2 standards (Airgas, Radnor, PA, USA, calibrated against 423.0 ± 0.1 ppm CO_2 AmeriFlux standard, Berkeley, CA, USA) directed through a LI-COR LI-7000.

For the VOC sampling, a fraction of the purge flow from the jar was collected at a rate of 50 ml min^{-1} for 40 min, which resulted in a 2-L sample. Sampling flow from individual flux chambers was selected using an automated Valco gas switching valve (Valco Instruments Co. Inc., Part# EUTA-2SD10MWE, Houston, TX, USA). This setup allowed for the continuous and sequential sampling of up to 10 chambers, plus an empty chamber that served as a blank reference. Samples were drawn through a Peltier-cooled (−45°C) water trap for removal of water vapor and then collected on a microadsorbent trap cooled to −30°C that contained 25 mg of Carboxen 1016 and 220-mg Carboxen 1000 (Sigma Aldrich, St. Louis, MO, USA, Part # 11052-U and 11021-U Supleco; Tanner et al., 2006). The adsorbent trap was rapidly heated to 290°C to inject samples onto the gas chromatography column (details below). Following sampling, carrier gas (helium) was purged through the trap as it was heated to 325°C to clean and condition the trap for the next sample (bakeout). The water trap was also cleaned and conditioned following sampling by heating and pulling zero air through it. The saturation vapor saturation pressures of the VOC of interest at −45°C correspond to mixing ratios in the ppm range. Given that VOC mixing ratios in the sample air were several orders of magnitude lower, they are not expected to condense, respectively freeze out in the water trap.

Table 2
Table of Retention Times (RTs) and Identifications for Compounds in Soil Samples

Compound	RT (min)	Soil	Standard	MS	Elution ref.	Tentative
Ethylene oxide	19.5	1–5		x		x
2-Butene	19.9	1–5	x			
Acetone	22.1	1–5	x		x	
Isopropyl alcohol	22.4	4		x		x
Pentane	23.1	1–5	x		x	
Dimethyl sulfide	23.4	1–5		x	x	
Methylene chloride	23.7	4 and 5		x	x	
Nitromethane	24.1	1–5		x		x
Carbon disulfide	24.2	1–5		x	x	
Trimethylsilanol	25.0	1–5		x		x
2-Butanone	25.7	1–5		x	x	
2-Methyl-1-pentene	26.1	2–5		x		x
2-Methyl-3-buten-2-ol	26.4	4 and 5		x	x	
2-Azido-2,3,3-trimethyl-butane	26.5	1–5		x		x
Tetrahydrofuran	27.1	1–5		x	x	
2-Methyl-3-pentanol	27.5	1,3, and 4		x		x
3-Methyl-2-butanone	28.0	2–5		x	x	
3,3-Dimethyl-2-butanone	29.7	1, 2, 3, and 5		x		x
Hexanal	32.3	1–5		x	x	
1,3-Octadiene	33.4	4 and 5		x		x
2,2,4,6,6-Pentamethyl-3-heptene	38.5	1–5		x		x

Note. The right four columns indicate how the compound was identified and the confidence in the identification. Compounds with an "X" in the "standard" column were present in one of the multicomponent standards. "X" in the MS (mass spectrometer) and elution ref. (elution order reference) indicates that the compound was identified by its mass spectra and a reference for the elution order of that compound are available. "X" in the tentative column indicates that a compound was identified solely by the mass spectrometer and NIST spectral library and is therefore a tentative identification. See Table ST2 for mass spectra and library match identification. Elution order references are available in Table ST3 and compared to our elution order in Figure S4.

A Hewlett Packard 5890 Gas Chromatograph/Flame Ionization Detector (FID)/Agilent 5971 Mass Spectrometer instrument (Agilent Technologies, Santa Clara, CA, USA) with a 60-m DB-624 (Agilent Technologies, Santa Clara, CA, USA, Part # 123–1364) column was used to separate compounds, the FID to quantify VOCs, and the MS for compound identification. It should be noted that the applied analytical method has limitations for detecting multifunctional and highly polar compounds.

2.3. VOC Identification and Quantification

Volatile organic compounds were identified based on comparison of peak retention time and mass spectra with components in four multicomponent standards and with reference data. Table 2 characterizes compounds based on their identification. The standards used were an oxygenated VOC standard, and a multicomponent reference standard, both obtained from Apel-Riemer Environmental, Inc. (Broomfield, CO, USA), a National Physical Laboratory (London, UK) primary reference gas mixture, and a National Institute of Standards and Technology (NIST; Gaithersburg, MD, USA) certified monoterpene standard. Standard compositions and analyte mole fractions are available in Table ST1 in the supporting information. Emitted compounds that were not present in the standards were identified by comparing their spectra to the NIST Spectral Library. Chromatograms and spectra were analyzed using the Agilent Chemstation F.01.03.2357 software. Mass spectra were found by averaging 3–5 scans at the peak maximum, subtracting background signals, and searching for matching spectra using the NIST mass spectral search program (version 2.2, 10 June 2014). These mass spectra, and the top three matches from the NIST mass spectral search program, are available in Table ST2. Elution orders were compared against other records that utilized the DB-624 column, that is, the Agilent elution order reference (Agilent, 2014); the elution order from the Nitrogen, Aerosol Composition, and Halogens on a Tall Tower campaign (Brown et al., 2013); and an instrument calibrated to measure air toxics (Apel et al., 1998). Figure S4 shows the correlations between reference elution orders and the identifications proposed by this work. Correlations were fit with a second-order polynomial, and all R^2 values were >0.95. Table ST3 lists identified compounds supported by elution order data. Identified compounds not supported by reference elution order should be regarded as tentative because they were

selected solely based on the best available library match. Quantitation proceeded under the assumption that these identifications were correct, but we have limited confidence in these tentative identifications.

To mimic sampling conditions, standard mixtures were purged through the dynamic flux chamber system and collected by the sampling system. Compared with direct sampling from the tank, instrument response was within 10%. A dynamic dilution system consisting of zero air regulated by a mass flow controller (Tylan Coastal Instruments, INC. Burgaw, NC, USA) and an additional mass flow controller to meter the standard flow was used to calibrate the instrument response in the 1–5 ppb range.

Blank samples were collected between soil samples by capturing a fraction of the purge airflow through an empty jar with 50 ml of water. Dichlorodifluoromethane, styrene, toluene, and ethylbenzene were present in blank samples. These peaks were occasionally present in soil samples but, because of their presence in blank samples, were not reported as soil emissions.

The FID was used to quantify VOC mixing ratios. Total C emitted as VOC (C_{VOC}) flux was calculated by summing all chromatogram peaks minus peaks present in blank runs. C fluxes were determined for identified compounds present in one of the standards (Table ST1) by integrating their peak areas in the chromatogram and converting peak areas to mixing ratios using response factors calculated from standards. Response factors for individual components of the standard were also used to develop a calibration curve to estimate response factors for compounds not present in standards, based on their retention times. A second-order polynomial was fit to response factors of standard components, and the resulting formula was used to calculate response factors for compounds not present in standards. The standard components used to build the calibration curve are listed in Table ST4. The calibration curve is shown in Figure S5. Response factors were calculated per ppb C using effective carbon numbers as described in Scanion and Willis (1985). All standard components with peaks that could be separated and integrated were included initially. After fitting with a second-order polynomial, compounds with residuals greater than 3 standard deviations from the curve were excluded and the curve was recalculated. This curve was used to determine the response factor for compounds based on their retention time. All compounds considered and the final response factor curve are shown in Figure S5. This factor was multiplied by the theoretical effective carbon number of each identified compound to convert FID response to the mixing ratio (in ppb) of the compound and the mixing ratio of carbon by dividing through the number of carbon atoms in the molecule (ppb C). FID responses of unidentified compounds were converted to ppb C using the response factor curve (Figure S5) based on the peak retention time. Purge flow rates through the jars were used to convert mixing ratios to VOC masses emitted from the soil. Masses of dry soils and sampling time were used to calculate soil VOC fluxes. For unknown compounds, a C mass calibration curve (as a function of retention time, Figure S6) was used to convert mixing ratios to VOC fluxes. This curve is a second-order polynomial fit of the C mass present in standard components versus their retention times. Fluxes of unknown VOCs were summed. The proportional contributions of individual VOCs to total VOC emissions were calculated by dividing the compound's flux by the total VOC flux. Flux rates of both VOCs and CO_2 were integrated over the sampling time to determine the total mass of C emitted per unit soil throughout the incubation period.

2.4. Rewetting Experiment

Three samples of each soil type were evaluated. For each soil sample, approximately 30 cm^3 of field moist soil from the refrigerator was air-dried at room temperature in open glass jars for 5–10 days. Samples were not subject to purge airflows while drying. Samples were then placed in a sampling jar on the manifold and subjected to purge airflow for ~20 min before sampling began. Two data points from the purge airflowed over air-dried soils were collected prior to the rewetting event (T_0). To simulate a moderate precipitation event, soils were brought to 50% of their maximum WHC with deionized water. Ten minutes after rewetting, 2-L air from the purge airflow was collected (40-min purge air collection per air sample). Sample collections continued once every ~2 hr for a total of 48 hr after the rewetting event. After the initial rewetting at T_0, additional water (never more than 2.2 ml) was added to each soil sample as needed approximately every 12 hr to maintain the soils at 50% of maximum WHC. This was done by removing the small jars containing the soil from the dynamic flux chamber, weighing the small jar and soil, and adding enough water to bring the soil back to 50% WHC. Emission experiments from three samples of each soil type were conducted. Emission experiments were discrete and sequential; the 52 hr emission collection process was completed for each sample before analyzing the next sample.

2.5. Statistical Analyses

We used nonparametric multivariate statistics to determine if VOC profiles changed temporally over the experiment and if VOC profiles were different across soil samples. For this, the experiment was divided into three temporal segments based on sampling time. "Prepulse" refers to the two purge air samples collected prior to the T_0 rewetting event. "Pulse" refers to the 5 hr window immediately following the T_0 rewetting event, and "postpulse" refers to all sampling points post 5 hr through the end of the 48 hr incubation. The permutational multivariate analysis of variance (PERMANOVA; Anderson, 2001) was used to test the null hypothesis that the arithmetic mean (centroid) and the variability (statistical dispersion) of VOC speciation and relative abundances are equivalent among these temporal segments. For each soil replicate (i.e., triplicates of S1–S5), C_{VOC} flux was averaged for each unique VOC across all sample points within each temporal segment. We used the R package "vegan" (Oksanen et al., 2017) to perform PERMANOVA on Bray-Curtis dissimilarities of VOC profiles, and statistical significance was evaluated from 999 permutations. Further, we constructed a Nonmetric multidimensional scaling ordination plot to illustrate the dissimilarities of VOC speciation and relative abundances.

3. Results

3.1. Total CO_2 and VOC Emissions

We observed a pulse in CO_2 emissions immediately after rewetting. Within an hour of the rewetting event, CO_2 emissions were on average 20 times higher than emissions from the dry soil. Emission rates of CO_2 dropped exponentially over the next 3–6 hr postrewetting, and on average 48 hr after the rewetting event (with soils maintained at 50% WHC for the entire 48 hr period) were 3 times greater than the CO_2 emission rates from the dry soils (Figure 1).

Soils were only exposed to the airflow present in the sampling manifold for 20 min prior to the prerewetting samples. A "dry" experiment was conducted to examine the effect of the initial exposure to airflow on emissions from the dried soils. Dried garden soils (S1 soil) were put on the sampling manifold under normal flow conditions and sampled repeatedly. Total VOC emissions from the dry soils decreased to 70% of initial emissions after being exposed to manifold flow conditions for 7 hr (Figure S7) and decreased to ~20% of the initial response after 72 hr. Emissions remained constant over the next 28 hr, for a total of 100 hr of exposure to purge airflow.

Table 3 shows mean CO_2 and VOC emissions integrated across the 48 hr sampling period for each soil type, averaged across replicate samples. Table 3 also shows the standard deviation across samples as a measure of the repeatability and/or variability of emissions within soil type. The relative standard deviations of the CO_2 emissions within soil samples of each soil type were $\leq$10% for S1, S2, and S5; 12% for S4; and 36% for S3. Relative standard deviations of total VOC emissions between samples within soil types were $<$10% of for S1 and S2, 20% for S3, and 69 and 84% for S4 and S5, respectively (Table 3).

Total VOC emissions immediately after rewetting were an average of 6 times greater than from dry soil before the rewetting event and an average of 14 times greater than VOC emissions from moist soils 2 days after rewetting. Assuming the results of the dried soil purge air experiment described above are representative of all soils, had emissions from dried soils been allowed to equilibrate, total VOC emissions immediately after rewetting would have been an average of 30 times greater than emissions from dried soils. The pulse in total VOC emissions typically lasted for 1–5 hr (Figure 1). Peak total VOC flux rates, averaged across samples within a soil type, varied from 25 ng C g_{soil}^{-1} hr^{-1} in S3 to 190 ng C g_{soil}^{-1} hr^{-1}in S5 during the pulse event.

Across all soils, CO_2 was the dominant form of C emitted. Normalized to carbon (C), total carbon from VOC, C_{VOC}, was 5.03 ± 2.01% (mean ± SD) of the total carbon from CO_2 (C_{CO2}) emissions (Figure 1). This mean was calculated by averaging the ratio of C_{VOC} to C_{CO2} for each replicate of each soil type (available in Table 3) and then averaging across soil types. C_{VOC} emissions correlated with C_{CO2} emissions (Figure 2, linear regression results from all soil experiments combined were slope = 0.0256, ρ = 0.83, $P < 0.001$) across soil samples integrated over the first 12 hr of the experiment. The other 12 hr segments of the sampling period did not have statistically significant correlations (Figure 2, $\rho < 0.50$, $P > 0.05$), but there was a correlation over the entire 48 hr experiment (Figure S8, ρ = 0.59, P = 0.03). When we compare total C_{CO2} and C_{VOC} emissions

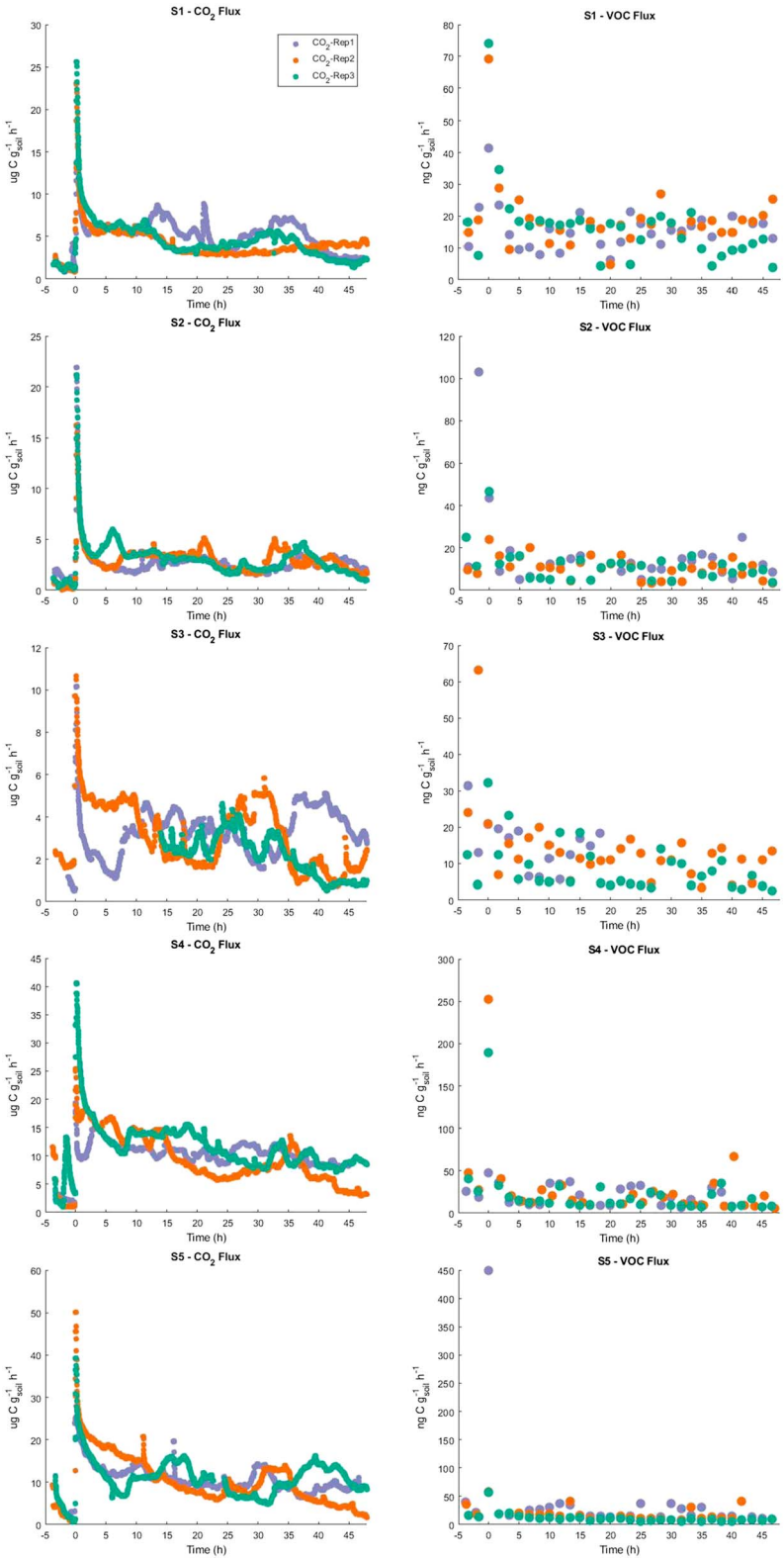

Figure 1. C_{VOC} and C_{CO2} flux rates over the duration of the 48 hr experiment. The *y* axis shows the C_{CO2} (left column of graphs) or C_{VOC} (right column of graphs) flux rates. Note the difference in units between CO_2 and VOC fluxes. Soils were rewet at time zero to 50% maximum water holding capacity. (a–e) Soils S1–S5. Triplicate samples are shown for each soil. The legend in (a) shows the color assigned to each replicate, which is consistent throughout all panels. Median ambient CO_2 levels between sampling periods were subtracted from CO_2 measurements collected during sampling.

Table 3
Volatile Organic Compound (VOC) and CO_2 Emissions Integrated Over the 48 hr Sampling Period and Averaged Across Three Replicate Samples of Each Soil Type

Soil	C_{VOC} emissions (ng g_{soil}^{-1})	C_{VOC} STD	C_{CO2} emissions (ng g_{soil}^{-1})	C_{CO2} STD	C_{VOC}/ C_{CO2} (%)	C_{VOC}/ C_{CO2} STD
1	771	67	13,600	1,400	5.75	1.03
2	520	46	8,590	604	6.10	1.00
3	462	92	7,650	2,780	7.40	2.14
4	700	480	30,000	3,530	3.16	0.72
5	636	533	31,700	2,300	2.73	1.39

Note. Standard deviations are included as a measure of the repeatability of the experiment. One S3 VOC sample was excluded due to lost chromatogram runs.

for the entire incubation period to each soil's organic matter content (Figure S9), C_{CO2} emissions were higher in soils with higher soil organic matter concentrations (Spearman's ρ = 0.93 for total C_{CO2} emissions, P = 0.13). C_{VOC} emissions also tended to be higher in soils with higher soil organic matter concentrations (Spearman's ρ = 0.40 for total C_{VOC} emissions, P = 0.52). Though the correlation is not statistically significant in either case, the correlation between C_{VOC} emissions and soil organic matter concentrations was stronger when S1 (residual = 3.6σ) was removed (ρ = 0.99, P = 0.08; Figure S9).

3.2. VOC Profiles by Soil Type

While rewetting drives most of the variation in the chemical diversity and quantities of VOCs across the entire experiment, VOCs varied by soil type, with 4.9% of the variation in VOC profiles being due to the soil type (PERMANOVA; R^2 = 0.049, P = 0.035; Figure 3). Compound identifications, by elution order and characterization method, are shown in Table 2. Table 3 contains compounds identified by mass spectra not present in the multicomponent standard, as well as their top five mass fragments, library match percentage, and other possible matches. 2,2,4,6,6-Pentamethyl-3-heptene (PMH), dimethyl sulfide (DMS), acetone, ethylene oxide, 2-butanone, hexanal, nitromethane, and 2-butene were present in postpulse emissions of all soils, but their relative abundances varied. The identifications of PMH, ethylene oxide, nitromethane, and 2-butene should be regarded as tentative because they are not supported by reference elution order data, nor were they present in standards. DMS made up 3.6% of C_{VOC} emissions in S1 but <2% of S2, S4, and S5 emissions. Following T_0, 0.3 to 1.1% of C_{VOC} emitted was in the form of tetrahydrofuran. Acetone made up 4.6% of S5 C_{VOC} emissions but <2% of S1 C_{VOC} emissions. Trimethylsilanol made 0.5% of S1 pulse C_{VOC} emissions but less than 0.1% of S3–S5 pulse emissions. 1,3-Octadiene was responsible for 0.8% of pulse C_{VOC} emissions in S4 but was not present in S2 and S3.

3.3. Temporal Variation in VOC Profiles

The types and amounts of VOCs emitted varied temporally across the experiment as well as between soil types (Figure 3). More of this variation (28%) was driven by the rewetting event than by soil type. VOC emission profiles from dry soils prior to rewetting ("prepulse"), moist soils immediately following the rewetting ("pulse," 1–5 hr), and moist soils during late stages of the experiment ("postpulse," 5–48 hr) were significantly distinct (PERMANOVA; R^2 = 0.28, P = 0.001; see section 2; Figure 3).

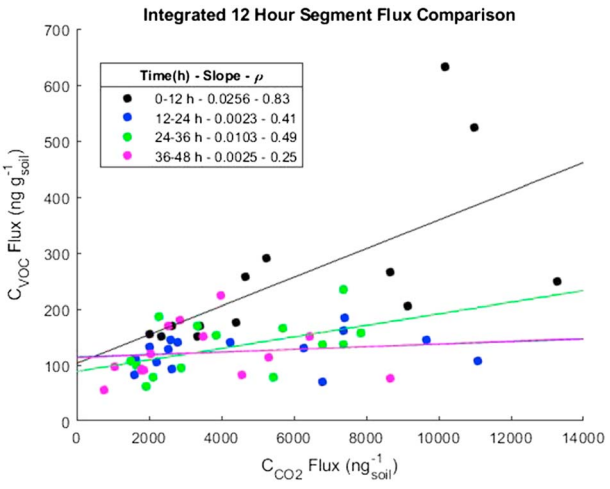

Figure 2. Integrated normalized C_{VOC} emissions (y axis) versus integrated C_{CO2} emissions (x axis) divided into 12 hr segments. Time segments with interruptions in sampling were excluded. Linear regressions show the correlation between CO_2 and volatile organic compound emissions, and Spearman's ρ values and regression line slopes are reported in the legend. The colors correspond to different sampling times (see legend). P values are <0.001 for all time segments except 36–48 hr, where P = 0.02

Figure 4 highlights the temporal changes in emissions of the most abundant VOCs detected in all soil types. A maximum number of compounds was observed in the first sample after rewetting for all soils; these chromatograms featured 40–70 peaks, while 20 or fewer peaks were observed at T_{48}. The most abundant VOCs included ethylene oxide, acetone, DMS, 2-butanone, 2-methyl-1-pentene, tetrahydrofuran, and PMH. Ethylene oxide and acetone made up 6.5–34% of prepulse C_{VOC} emissions for all soils. The most abundant VOCs represented 17–35% of the total VOCs emitted from the moist soils approximately 10 hr after the wetting event through the end of the 48 hr experiment. However, during the rewetting pulse (T_0–5 hr), these VOCs accounted for a slightly lower portion (i.e., 13–22% of the total VOC flux). Further, acetone, DMS, and PMH were responsible for 8.6–18% of C_{VOC} emissions from all soils from 0 to 5 hr and for 15–30% of emissions from all soils from 10 to 48 hr. 2-Butanone was responsible for 0.6–1% of the postpulse C_{VOC} emissions from all soils. Emissions from S5 immediately after rewetting were dominated by unidentifiable compounds (67%) and the chemical diversity of VOCs emitted peaked at this time (Figure 4).

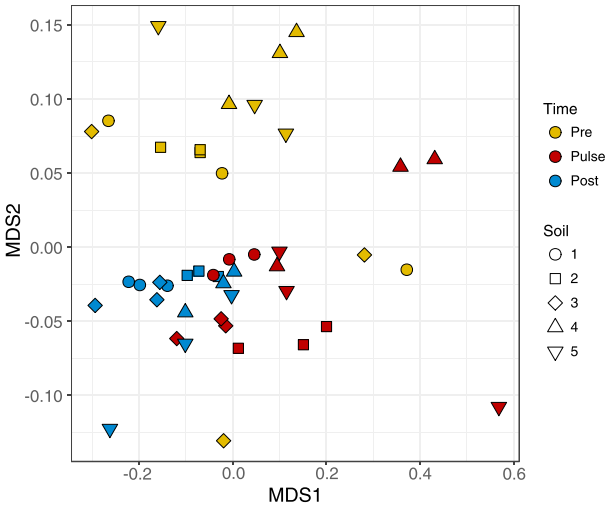

Figure 3. Nonmetric multidimensional scaling ordination plot. Each point represents the volatile organic compound (VOC) speciation and relative abundances from soils S1 to S5 (different shapes) averaged across various time sections of the rewetting experiment (colors). "Prepulse" reflects dry soils sampled prior to wetting. "Pulse" represents VOCs identified during the first 5 hr following rewetting soils to 50% water holding capacity. "Postpulse" represents VOCs identified during the remainder of the experiment between 5 and 48 hr following rewetting. VOC profiles vary across time segments (permutational multivariate analysis of variance [PERMANOVA]; $R^2 = 0.28$, $P = 0.001$) as well as across soil types (PERMANOVA; $R^2 = 0.049$, $P = 0.035$).

4. Discussion

4.1. Temporal Dynamics

In all soils, the magnitude and duration of the rewetting CO_2 pulse was equivalent to what has been observed in previous laboratory-based soil rewetting experiments (Fierer & Schimel, 2003; Franzluebbers et al., 2000). The temporal dynamics of total VOC emissions upon rewetting were qualitatively similar to those observed for the soil CO_2 emissions (Figure 1). VOC emissions peaked in the first sample taken after rewetting (sample air collection began 10 min after rewetting and continued for 40 min) and remained elevated for approximately 5 hr compared to dried soil emissions. If the soil had been given more time to come to equilibrium with the purge flow prior to the wetting (Figure S7), lower emission rates would have been expected before the wetting, which probably then would have resulted in a longer period of elevated VOC emissions (Figure S7). Our observed pulse in total VOC emissions immediately following rewetting was similar to that described in Veres et al. (2014), where in a laboratory experiment including agricultural and rainforest soils, it was also observed that the majority of gaseous organic carbon was released within the first 2 hr following a rewetting event. Likewise, a pulse in VOC emissions was detected above a ponderosa pine plantation following a rain event, and acetone fluxes were 3–4 times higher the morning after a rain event than during dry periods with similar soil temperatures (Schade & Goldstein, 2001).

Besides rewetting triggering CO_2 and VOC fluxes, it is also well established that emissions of NO_x from soil are elevated following a wetting event (Hudman et al., 2012; Yienger & Levy, 1995) and are mostly due to microbial community activity in the soil (Conrad, 1996). NO fluxes following the rewetting of dried soil increased by up to 5 orders of magnitude with an average of ~1,000% in the field and ~2,000% in the lab (Kim et al., 2012).

4.2. Comparison of CO_2 and VOC Emissions

The ratio of VOC to CO_2 production in this experiment averaged 5.0 ± 2.0% across all samples included in this study. This ratio is lower than the ratio of C_{VOC} to C_{CO2} emitted by leaf litter, where microbial activity was also recognized as the primary driver of emissions (Gray et al., 2010). Leaf litter C_{VOC} emissions from *Eucalyptus* sp. and *Populus tremuloides* made up 88 and 80%, respectively, of C_{CO2} emissions (Gray, 2014). Though the VOC emissions were smaller than CO_2 emissions from the soils studied here, VOCs are important mediators of microbial interactions as they can play vital roles in bacterial quorum sensing, motility, gene expression, and antibiotic resistance (Schmidt et al., 2015). For example, lactones, a class of volatile cyclic esters, prevented quorum sensing among a variety of Gram-positive and Gram-negative bacteria (Schulz et al., 2010). As another example, certain bacteria can produce caryophyllene, a sesquiterpene, which inhibits virulence gene expression in the pathogenic fungi *Fusarium oxysporum* (Minerdi et al., 2008).

Total C_{CO2} and C_{VOC} emissions were generally higher for those soils with higher soil organic matter concentrations (Figure S9). This was expected given that soil organic matter levels often correspond to overall enhanced microbial activity (Barton et al., 2016; Schimel et al., 1994; Seewald et al., 2010).

4.3. VOC Emission Profiles

Our findings are in line with previous work showing that different soils have distinct VOC emission profiles (Mancuso et al., 2015; Veres et al., 2014). Some specific compounds identified in both Veres et al. (2014) and this study are acetone, DMS, and 2-butanone. Hexanal emissions from soil were observed by Mancuso et al. (2015). Studies have also reported that methanol emissions from soil can be high (Gray et al., 2010; Stacheter et al., 2013). However, we were unable to measure methanol and other highly polar compounds with the analytical methods used here. Several compounds observed in this study are commonly found in soil, such as acetone and 2-butanone. Other observed compounds are found in materials that are introduced into soil from other sources. Still other compounds observed here have been shown to be products of microbial metabolism. Acetone is produced by a variety of bacteria including *Escherichia coli* and *Clostridium*

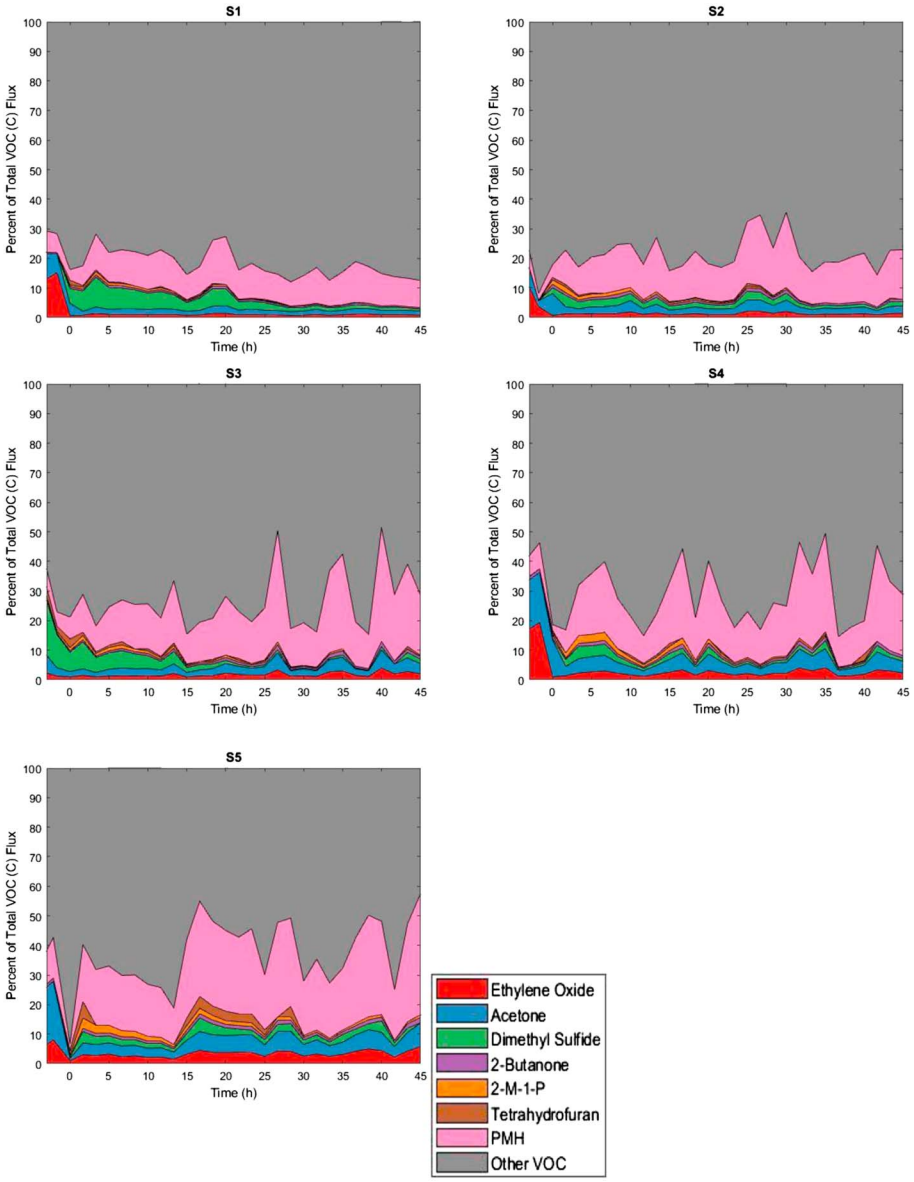

Figure 4. Individual C_{VOC} flux relative to total C_{VOC} flux (averaged across three replicates) of the dominant volatile organic compound (VOC) for soils S1–S5. Rewetting of soil to 50% water holding capacity occurred at time zero. The colors correspond to VOC identity (see legend), with "other VOC" consisting of the sum of all less abundant and unidentified VOCs. 2-M-1 P is 2-methyl-1-pentene. 2,2,4,6,6-Pentamethyl-3-heptene is 2,2,4,6,6-pentamethyl-3-heptene.

acetobutylicum (Maddula et al., 2009). Bacterial catabolism can produce DMS from dimethyl sulfide propionate (Todd et al., 2007). This is most common in marine bacteria, but DMS has been shown to be produced by soil bacteria reducing DMSO (Omori et al., 1995). Carbon disulfide is a product of metabolism of microbial soil communities, and as much as 80% of emissions are from natural sources (Canada, 1999).

Some of the VOCs emitted from the soils can also be relevant to atmospheric chemistry. For example, hydrocarbon and DMS oxidation by OH leads to atmospheric aerosol formation (Ayers & Cainey, 2007; Bowman & Seinfeld, 1994). Acetone is oxidized by OH as well, but the majority of acetone is degraded through photolysis, which can lead to the production of PAN (Singh et al., 1994) that can transport nitrogen oxides great distances and lead to formation of tropospheric ozone far down wind (Singh & Hanst, 1981).

Volatile organic compound profiles varied as a result of the time with respect to rewetting (Figure 3). Bunge et al. (2008) found that emitted VOCs changed with respect to the growth stage of a microbial consortium.

This is a likely explanation for the observed temporal diversity in VOC profiles. From the PERMANOVA analysis, we also found a significant dependence of VOC emission profiles on soil type, though the variation in emission profiles across soil types was less than the temporal variation. Another study found varying VOC profiles from different soil types (Mancuso et al., 2015). The distinct VOC profiles emitted from the different soil types may be a product of differences in soil microbial communities, the amounts and types of carbon metabolized, and soil nutrient levels (Larsen & Frisvad, 1995; Stahl & Parkin, 1996; Stotzky & Schenck, 1976; Wheatley et al., 1997).

We cannot confirm the fraction of emissions that result from abiotic or microbial processes. Abiotic processes can be important contributors to VOC emissions (de Gouw et al., 1999; Warneke et al., 1999). However, previous research suggests that biotic emissions of VOCs from soil or litter are 5–10 times higher than abiotic VOC emissions (Gray et al., 2010; Leff & Fierer, 2008). Thus, given the observed temporal dynamics in VOC emissions (Figure 1) and their correlation to CO_2 emissions (Figures 2 and S2), we predict that microbial activities are responsible for the majority of the VOC emissions measured here. Together, these results highlight that a short-lived pulse in total VOC emissions occurs following the rewetting of dry soils, and most of these VOCs are likely a product of microbial metabolism.

4.4. Relevance of Soil VOC Emissions to Atmospheric Chemistry

Our results demonstrate that soil VOC emission rates can change rapidly in response to rewetting events, with VOC emission dynamics being similar to those observed for CO_2 emissions. While the flux rates measured here are likely to differ from those measured in the field, the general phenomenon characterized in these experiments may have implications for modeling terrestrial sources of atmospheric VOCs.

Soil emissions of nitrogen oxide (NO), and their increase from soil wetting, have long been recognized and included in models. Over the African Sahel NO emission pulses after rain events contribute 21–44% of soil NO_x emissions (Zörner et al., 2016). Soil NO_x emissions following the wetting of dry soil have been shown to contribute up to 22% of annual emissions in a Venezuelan savanna (Davidson, 1992). Therefore, NO emissions from soil, including their increases during and after precipitation events, have been included in atmospheric chemistry and transport models, such as the Community Land Model version 4 and the Goddard Earth Observing System Model version 5 that factor in weather conditions such as temperature and precipitation to correctly forecast soil NO_x emissions (Lawrence et al., 2011; Lin, 2012).

Atmospheric models include components that consider biogenic VOC emission from terrestrial sources; vegetative and oceanic emissions are the dominant components (Guenther et al., 1995; Guenther et al., 2012; Lamarque et al., 2012). Soil VOC emissions have been included in models in varying forms. The Goddard Chemistry Climate Model includes isoprene and other VOC emissions from soil that are adjusted according to meteorological conditions; the ECHAM/MESSy Atmospheric Chemistry model has fixed VOC soil emissions scaled to meet annual net emissions (Jockel et al., 2006; Lamarque et al., 2013). As we have shown, soils can emit an abundance of VOCs, this behavior was consistent among five types of soils, and emissions were elevated after soil wetting. Based on the degree to which emissions were elevated following wetting, soil moisture and changes in soil moisture levels should be considered when incorporating soil VOC emissions into models. While our experimental approach did not allow extrapolation of the laboratory results to environmental surface fluxes, these observations nonetheless argue for further research, and that consideration of soil fluxes and their parameterization in models may improve regional to global estimates of VOC fluxes and their role in atmospheric chemistry.

Abbreviations

VOCs	volatile organic compounds
GC/MS	gas chromatography/mass spectrometry

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