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Volatile Organic Compound emissions from soil: using Proton-Transfer-Reaction Time-of-Flight Mass Spectrometry (PTR-TOF-MS) for the real time observation of microbial processes

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Abstract

In this study we report on the emissions of volatile organic compounds (VOC) and nitric oxide (NO) from two contrasting soils (equatorial rainforest and arid cotton field) analyzed in a laboratory based dynamic chamber system. The effect of soil moisture and soil temperature on VOC and NO emission was examined in laboratory incubation experiments by measuring as a pre-saturated soil dried out. Our results suggest that real time monitoring of VOC emissions from soil using a proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS) instrument can be used to improve our understanding of the release mechanisms of trace gases (e.g. NO, N_2O) that are involved in the nitrogen cycle. Moreover, we report on the release rate of various VOC species, many of which exhibit a temperature dependent response indicative of biological production, namely a temperature amplification factor (Q_{10}) ~ 2–3. Contrary to the conventional modeling of NO emissions from soils, that the release of NO from the overall community across the range of soil water content can be modeled as an optimum function, we suggest that VOC measurements indicate there exist multiple distinct contributing microbial guilds releasing NO. These microbial guilds could likely be individually identified with the observed VOC profiles. Using a cotton field soil sample from a Sache oasis (Taklimakan desert, Xinijang, P. R. China), we identify five VOC emission groups with varying degrees of NO co-emission. An equatorial rainforest soil (Suriname) was shown to emit a variety of VOC including acetaldehyde, acetone, DMS, formaldehyde, and isoprene that vary strongly and individually as a function of temperature and soil moisture content. PTR-TOF-MS with high time resolution, sensitivity, and molecular specificity is an ideal tool for the real time analysis of VOC and NO emitting processes in soil systems. These experiments can be used as a template for future experiments to more completely and specifically identify the active microbial guilds in soils and to characterize the impact of soil VOC emissions on the atmosphere.

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1 Introduction

It is now well established that the microbiological processes of nitrification and denitrification in soil are responsible for both the production and consumption of NO within the first centimeters of topsoil (Conrad, 1995; Rudolph and Conrad, 1996). An overview of the different microbial groups and enzymes involved in these processes is given elsewhere (Braker and Conrad, 2011). There is evidence that the enzymes responsible for soil emissions of NO are unspecific and thereby can react with various volatile organic compounds (VOC) that might be (i) naturally produced by microbial or abiotic decomposition in soil (Arp and Stein, 2003; Hymann et al., 1988; Keener and Arp, 1994) or (ii) originate from abiotic decomposition in soil (Insam and Seewald, 2010). It seems reasonable that these processes are dependent on soil moisture and soil temperature as has been previously shown for the release of NO. Ambient trace gas concentration (NO and VOC), nutrient availability (C and N) and pH are also major factors driving the release of NO (Ludwig et al., 2001) and therefore most likely of VOC.

The relationship of these factors to the release rate of NO has been frequently studied in laboratory incubation experiments (Bargsten et al., 2010; Feig et al., 2008; Gelfand et al., 2009; Laville et al., 2009; van Dijk et al., 2002; Kirkman et al., 2001; Otter et al., 1999; Behrendt et al., 2014). It is typically assumed that the relationship of NO release rate and soil moisture follows an optimum function which is based on the microbial aerobic activity (Skopp et al., 1990). Furthermore, a recent study discovered a link between VOC and NO mediated inflammatory response suggesting that biogenic release mechanisms of these gases are closely linked (Inamdar and Bennett, 2014). Studies combining molecular analysis and release of trace gases, e.g. CO_2, identify multiple peaks in microbial activity (i.e. transcriptional activation as proxy for microbial activity) indicating the presence of various microbial groups throughout the incubation time (Placella et al., 2012; Placella and Firestone, 2013). Several studies have also observed a pulse of CO_2 and other trace gases (such as NO, N_2O) directly after re-wetting of dry soil (Ludwig et al., 2001; Yahdjian and Sala, 2010; Kim et al.,

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2012). It is still unclear what effect causes these water induced pulses, either (i) rapidly responding microbial activity (Placella et al., 2012), or (ii) abiotic processes such as efflux of intracellular solutes (Kleft et al., 1987), (iii) extracellular enzymes from dead microbes (Blagodatskava and Kuzyakov, 2013), or (iv) chemidesorption from the soil surface (Warneke et al., 1999). However, since abiotic and biotic processes should exhibit a different response to temperature, the Q_{10} value and activation energy are frequently used to experimentally separate these different processes (Winkler et al., 1996; Laville et al., 2009; Saad and Conrad, 1993).

Unfortunately, compared to soil emissions of NO, relatively little research is available on the contribution of soils to atmospheric VOC despite recent work identifying soils as potentially important sources in terrestrial systems (Asensio et al., 2007; Leff and Fierer, 2008; Insam and Seewald, 2010; Ramirez et al., 2010). Indeed global budgets of VOC rarely include a soil source (Warneck and Williams, 2012), with the main source assumed to be from terrestrial vegetation. The majority of available soil VOC studies focus on the characterization of different compounds that are released, not on high-resolution soil dry-out experiments to investigate responsible abiotic and biotic drivers of the emissions (Schulz and Dickschat, 2007), though recent research has become increasingly focused on this (Gray et al., 2010; Asensio et al., 2007). As VOC play an important role in the Earth's atmosphere by considerably influencing tropospheric chemistry (Atkinson, 2000; Williams, 2004) and the formation of secondary organic aerosols (Kanakidou et al., 2005), it seems prudent that the contribution of soils to atmospheric VOC budgets are quantified and parameterized in a manner conducive to inclusion into atmospheric models. Understanding the drivers, abiotic and microbial, for the release of VOC from soils is therefore necessary to gain a better understanding of this contribution.

Proton-transfer-reaction mass spectrometry (PTR-MS) has long been used to identify VOC released and consumed in soil ecosystems (Bunge et al., 2008). These studies have generally been limited in scope and instrumental capabilities, as historically measurements are often made under static or non-natural conditions with a focus on

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identification of emitted VOC. Since microbial activity strongly varies based on soil conditions, these studies likely have not identified the net potential of released VOC.

In this work, we present measurements targeting an improved understanding of VOC emissions during naturally occurring processes, e.g. drying out of a soil sample, using proton-transfer-reaction time-of-flight mass spectrometry (PTR-TOF-MS) and link them to NO measurements in order to better understand the microbial processes occurring with soil systems. The PTR-TOF-MS instrumentation offers significantly improved monitoring capabilities in comparison to both PTR-MS and gas chromatography methods, yielding increased time resolution and more comprehensive measurements of a larger range of organic compounds than previously available. We demonstrate and quantify VOC emissions from two very contrasting soils: a tropical equatorial rainforest, and an arid agricultural cotton field soil. Throughout these experiments tremendous increases in the release rate of VOC are observed after re-wetting of a dry soil up to field capacity at nearly constant soil moisture, with additional emission occurring at various lower ranges of soil moisture content. Our work attempts to both quantify VOC emissions from soil as well as relate the microbial production of NO to VOC over a wide range of soil moisture and temperature. This work presents a promising method for use in future experiments aimed at quantifying and identifying VOC emissions from biotic and abiotic processes in soil with the potential of improving our ability to identify active microbial guilds in soil systems.

2 Methods

Two contrasting soil samples are presented in this work (i) cotton field soil (SC) taken from Sache oasis, Taklimakan desert, Xinjiang Uygur Autonomous Region, P. R. China (38.3342° N, 77.4845° E), and (ii) rainforest (SR) soil sample, collected in Suriname (5.0763° N, −55.0029° W). We selected SR as a representative of an equatorial rainforest soil and SC to represent an arid ecosystem. These ecosystems are known for

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contrasting chemical and physical soil properties, e.g. pH, total carbon content, and texture (Behrendt et al., 2014).

In accordance with previously reported measurements of effective soil depth (Rudolph et al., 1996), samples were selectively collected in the field from the top layer of the soil surface, 0–0.05 m depth, which has been shown to be the active layer for NO release. While the field-moist SR sample was measured immediately upon receipt, the air-dried SC sample was stored at 4 °C until measurement. These conditions are necessary to prevent changes in microbial abundance (Stotzky et al., 1962).

A detailed description of the newly developed laboratory incubation system used in this study is presented elsewhere (Behrendt et al., 2014), therefore, only a brief description of the chamber system will be given. At the center of the dynamic soil chamber system are six ventilated Plexiglas chambers (0.009 m^3) into which soil samples can be placed. The sample chambers are flushed with dry "zero"-air (i.e. free of NO and VOC), in parallel, in a thermo-stated flow system shown schematically in Fig. 1. During each experiment one chamber is left empty to serve as a background for the 6 soil containing sample chambers. When actively sampling, a 4.2×10^{-5} m^3 s^{-1} (2.5 slpm) flow of dry zero-air is passed through the cell sweeping gaseous emissions to the analyzers. This flow rate is necessary to provide sufficient sample volume for the three gas analyzers used in this study, a PTR-TOF-MS (Ionicon, Austria), a NO_x analyzer (model 42i, Thermo Scientific, USA), and a LI-COR 840 analyzer (Biosciences Inc., USA). The H_2O signal of the latter is used to measure the water vapor in the headspace of the soil chamber, which is converted by a mass balance approach to gravimetric soil moisture and described in detail elsewhere (Behrendt et al., 2014).

When the chambers are not being actively sampled, the airflow through each chamber is reduced to 8.3×10^{-6} m^3 s^{-1} (0.5 slpm) to extend the drying out process. Typically, a single chamber is monitored for four minutes such that all chambers, including the empty blank, were analyzed once per 28 min. During a given experiment, the incubator, including the soil chambers, could be modulated between incubation temperatures (20 °C and 30 °C) in order to determine the relationship between soil tempera-

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ture and trace gas emissions. From this relationship a temperature amplification factor, Q_{10} value, can be directly calculated.

Prior to measurement, soil samples (0.06 kg) are homogenized by sieving through a 0.002 m mesh, wetted, and placed into the laboratory chamber system. Soil emission monitoring began immediately after rewetting of the soil sample to field capacity (~ 1.8 pF), a value that depends on the type of soil analyzed. Here we define field capacity as the soil water content observed in the field after two to three days of gravitational settling post rainfall or irrigation. Measurements of a given set of soils continued until all samples reach an approximate minimum in soil water content as determined by the calculated percent of water-holding capacity (%WHC).

VOC measurements were performed using a commercial proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS) instrument from Ionicon Analytik GmbH (Innsbruck, Austria). A detailed description of the measurement technique can be found elsewhere (Graus et al., 2010). Briefly, VOC with a proton affinity greater than water undergo proton transfer reactions with H_3O^+ ions, produced in the hollow cathode ion source, and are drawn through the air sample by means of a voltage gradient to produce positive ions that are detected with a time-of-flight mass spectrometer. As an example, acetone (C_3H_6O) will be detected at a mass-to-charge ratio (m/z) of 59.0491 ($C_3H_7O^+$). Key benefits of using PTR-TOF-MS for the measurement of VOCs, in comparison to previous techniques such as GC-MS or quadrupole PTR-MS, are the high duty cycle and the mass resolution of the instrument. Mass resolution, defined by the full width half maximum at m/z 21.0221, was determined to be $3700 m/\Delta m$ during these experiments. One example of the resolving power of the PTR-TOF-MS instrument is the ability to distinguish between carbon suboxide (C_3O_2, m/z 68.9982), Furan (C_4H_4O, m/z 69.0345), and Isoprene (C_5H_8, m/z 69.0699) all of which are measured at a nominal m/z of 69 by the equivalent quadrupole mass spectrometer and therefore inseparable using the latter technique. Full mass spectra were collected ranging from m/z 10–500 and averaged on a 10 s timescale.

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During laboratory experiments, PTR-TOF-MS sampled from the chamber manifold at a flow rate of 8.3×10^{-6} m^3 s^{-1} (0.5 slpm) through a 1 m long, 0.0016 m o.d. PEEK inlet heated to 50 °C. The instrument was operated with a drift voltage of 600 V and a drift pressure of 2.20 hPa (E/N 140 Td, 1.4×10^{-19} V m^{-2}). Internal mass calibration of the TOF was performed by standard addition of 1,3,5-trichlorobenzene permeated into the sampled flow. Post data acquisition analysis was performed according to procedures described elsewhere (Mueller et al., 2011, 2010; Titzmann et al., 2010). VOC mixing ratios are reported in parts-per-billion by volume (ppbv). Calibration standards for VOC were either purchased as pressurized gas bottle standards (Apel-Riemer Environmental) or dynamically produced using calibrated permeation sources (Veres et al., 2010). VOC concentrations, background corrected by the measurements in the empty chamber to account for any VOC entering the soil chambers, were converted to a VOC release rate (ng kg^{-1} s^{-1}) calculated using the following equation:

$$E = \frac{[C]F}{W} \quad (1)$$

where F is the gas flow through the cell (m^3 s^{-1}), $[C]$ the background corrected mixing ratio of the gas species (ng m^{-3}) according to the mass balance of the dynamic chamber (Behrendt et al., 2014; Breuninger et al., 2012), and W the dry soil sample weight (kg).

3 Results and discussion

Once a soil sample is wetted and throughout drying, both physical and biological processes within the soil cause trace gases to be released. Previous studies have long identified soils as globally significant sources of greenhouse gases (Warneck and Williams, 2012). The most highly studied of these gaseous emissions are well-known greenhouse gases (e.g. CH_4, CO_2, NO, and N_2O). Less well known is that soil systems

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can produce, as well as consume, VOC in the gas phase. In this study we use clean, zero air to flush the soil chambers thereby focusing solely on the emission of VOC.

Figure 2 shows an example of the type of data collected during a typical soil experiment, using the SC soil sample. The gravimetric soil moisture content is normalized to %WHC, indicated by the blue shaded region. The NO maximum at a %WHC of ~ 10 suggests a maximum release of NO caused by optimal diffusion and microbial activity at this soil moisture (Skopp et al., 1990). However, in this instance the acetone release rate is observed peaking immediately upon wetting of the soil and decaying throughout the drying out process, suggestive of multiple periods of elevated microbial activity.

Figure 2 also contains a larger subset of VOC from the SC sample. The data presented in Fig. 2 are limited to compounds for which the PTR-TOF-MS was calibrated to and therefore quantified emission rates are available. It is obvious from these results that the temporal emission of VOC as a function of %WHC are highly variable. While isoprene shows a clear maximum midway through the drying process, formaldehyde peaks only at the beginning of the drying process.

The emission types observed in this study can be described largely by two general mechanisms of VOC release from soil (i) microbial and (ii) abiotic production of VOC, including but not limited to the mechanisms described in the introduction. These two emission types will be examined and discussed in detail and evidence for each type of emission presented.

3.1 Pulsing of VOC and NO

In the soil types examined, by far the largest release rate of gaseous organic carbon occurs during the first hours (< 2) of the rewetting procedure. Examples of VOC exhibiting these high initial emissions, shown in Fig. 2, include acetone, acetaldehyde, xylene, and methanol. Nearly all observed VOC emissions show a measureable release rate during the initial wetting stage of the experiment, however, in many cases secondary maxima are also observed at a lower %WHC. This is obvious for acetaldehyde, Fig. 2, where a secondary maximum occurs at a %WHC of approximately 10 %.

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Abiotic chemidesorption has been described as one possible explanation for this type of rapid emission of VOC after wetting for decaying plant matter (Warneke et al., 1999). In these experiments, beech leaves were baked at 100 °C for several days followed by a rewetting which induced a large release rate of partially oxidized volatile organic compounds, more generally VOC. The VOC emissions in that study are attributed to solvation of organics from the leaf litter surface and subsequent partitioning, based on their Henry's law constant, to the gas phase. While this set of leaf litter experiments differs significantly from the soil based experiments presented here, this process is likely to occur to some extent in the soil samples studied here, and therefore is one possible explanation for the rapid production of VOC observed upon soil wetting.

In contrast to the Warneke et al. (1999) study, more recent work performed by Placella et al. (2012) suggest that CO_2 pulses observed as a result of soil wetting are indicative of sequential resuscitation of the microbial community within soil. They have classified microbial groups into three responses types: rapid responders (actinobacteria), intermediate responders (bacilli), and delayed responders (α-, β-, and γ-proteobacteria). The largest of the three communities, rapid responders, contributes a significant portion of observed CO_2 within 1 h of soil re-wetting. This source of CO_2 has been suggested to occur as a result of microbial cellular lysis or an active efflux of intracellular solutes to prevent lysis (Fierer and Schimel, 2003), a process that occurs following rapid changes in water potential (Kieft et al., 1987).

As mentioned previously, there is evidence that nonspecific enzymes, e.g. ammonium monooxygenase (AMO), can produce various VOC in soil (Arp and Stein, 2003; Keener and Arp, 1994; Hymann et al., 1988). A byproduct of this process is NO, which is then observed as gaseous emission from the soil. Maximum VOC release rates are observed at high soil moisture where low release rates of NO are observed. Therefore we present two possible interpretations of our results (i) unspecified enzymatic reactions within the soil leading to high emission rates of VOC or (ii) an inhibitory effect that suppresses the formation of NO as a result of high organic soil loadings. In the first interpretation, nonspecific enzymes will convert pre-cursor organics rather than

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NH_4^+ (Arp and Stein, 2003) to lighter weight VOC that will be released into the gas phase from the soil. NH_4^+ will therefore not be available for reaction with hydroxylamine thereby inhibiting the formation of NO. It is likely that in addition to AMO, there exist other enzymes that are also nonspecific resulting in further reduction of the release rate of NO. In the second interpretation, this inhibitory effect could be caused by high mass loading of organics as a result of extracellular enzymes or intracellular solutes. The latter interpretation more fully explains our observations of high VOC release rates upon wetting of the soil with NO emissions increasing at lower soil moisture contents and is consistent previous studies (Placella et al., 2012; Placella and Firestone, 2013; Davidson, 1992).

Based on the results observed in this experiment alone, however, the source of the initial VOC pulse cannot be unambiguously identified as (i) CO_2 was not routinely measured, (ii) molecular techniques were not applied, and (iii) sterilization of soil alters the physical and chemical properties of soil, especially the organic matter (Davidson, 1992). Additional experiments using a combination of the techniques from the two aforementioned studies and modern gas analyzers such as PTR-TOF-MS could be used to improve our understanding of this process. Future experiments targeting the atmospheric impact of soil emissions on global and regional scales should focus on the co-measurement of CO_2 and this initial VOC pulsing effect as it represents the largest release rate of organic carbon observed throughout the range of %WHC studied in the soils sampled.

3.2 Temperature dependent VOC emissions

The dynamic soil chamber system has the capability to modulate soil temperature between 20 °C and 30 °C during a single experiment in order to investigate the effect of soil temperature on VOC emission rates. Research has shown that the emission response to soil temperature can be used to distinguish between a biological response and a physiochemical process (Radmer and Kok, 1979; Saad and Conrad, 1993). Either the activation energy (Saad and Conrad, 1993) or the Q_{10} value, the magnitude of

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change in an emission as a result of 10 °C increase in temperature, are used to characterize different processes, such as nitrification, denitrification, etc. in soil (Winkler et al., 1996). For biological processes the value of Q_{10} is typically on the order of 2 to 3 (Mohr and Schopfer, 1995) and is expressed as follows:

$$Q_{10} = \left(\frac{E_{T2}}{E_{T1}}\right)^{10/(T_2-T_1)} = \left(\frac{[C]_{T_2}}{[C]_{T_1}}\right)^{10/(T_2-T_1)} \quad (2)$$

where $[C]_{T1}$ and $[C]_{T2}$ are the measured concentrations a temperatures of T1 and T2 respectively.

The SR soil sample was analyzed using the temperature modulation described above. Figure 3 presents mixing ratios of observed VOC for soil temperatures of 20 °C and 30 °C. For each of the compounds shown, Q_{10} values were determined during periods in which VOC measurements were above the instrumental detection limit, Table 1. In Fig. 3, Q_{10} values are displayed for different VOCs, black circles, along with an average for the entire measurement period, colored diamonds ± one standard deviation of the mean. Unfortunately due to instrument failure, data is unavailable for the time period between 30–50 h. As no data is available during this time period, we are unable to determine if additional emission maxima would occur and to what types of processes those would be attributable. However, we believe that this does not influence the interpretation of the available data for these experiments.

The average Q_{10} value over the entire drying process was found to be in the range of 2–3 for all of the compounds shown in Fig. 3. This result suggests that, for the SR soil type, all VOC emissions presented here occur as a result of microbial activity. Our results are indicative of microbial populations alternatively activating and becoming dormant at various stages of the drying out process (Placella et al., 2012; Placella and Firestone, 2013), with a variable dependence of enzymatic activity on temperature. During the period from 0–20 h, however, both 2-butanone and acetone show a Q_{10} value in the range of 1–2. The initial pulse of these two compounds combined with a relatively lower Q_{10} value is more indicative of an abiotic process such as (i)

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chemidesorption of VOC off of the soil surface (Warneke et al., 1999), (ii) an efflux of intracellular solutes (Kleft et al., 1987), (iii) extracellular enzymes from dead microbes (Blagodatskava and Kuzyakov, 2013), or (iv) any combination of (i) to (iii).

The extent to which these VOC emissions will reach the atmosphere will depend on concomitant uptake processes in the more complex soil ecosystems found in nature, and as such we suggest that these emission rates represent maximum values. While a detailed discussion of the atmospheric impacts and scale of VOC emissions from soil is beyond the scope of this paper, it is interesting to note that a microbial source of dimethyl sulfide (DMS) is observed that to our knowledge has not previously been quantified. The atmospheric impacts of DMS have been extensively studied and include the potential for climate relevant atmospheric aerosol formation (Ayers and Cainey, 2007).

Future experiments to determine the temperature optimum of VOC emissions and microbial community activity can be pursued as further evidence of biological production (Saad and Conrad, 1993; Radmer and Kok, 1979; Placella and Firestone, 2013; Asensio et al., 2007; Placella et al., 2012). Furthermore, similar measurements using pure cultures of the active microbiological constituents could help to identify and validate a biological source of soil VOC (Bunge et al., 2008).

3.3 Co-emission of VOC and NO

Many different VOC emission profiles as a function of soil water content are observed for each soil sampled, with the commonality that for a given soil, VOC can be grouped into several sets of emissions with similar temporal behavior and hence soil moisture dependency. For example, VOC observed in the SC soil experiment can largely be grouped into five different emission profiles. The first of these emission profiles, occurring within two hours of the wetting process, has previously been discussed in Sect. 3.1 and is illustrated by the VOC shown in the first panel of Fig. 2. The remaining four emission profiles occur later in the drying out process at lower %WHC and correspond to the lower four panels of Fig. 2.

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Previous work suggests that the relationship between NO emissions and soil moisture can be modeled as an optimum function (Meixner and Yang, 2006; Skopp et al., 1990), representative of production from a bulk microbial community with the maxima occurring at the period of highest microbial activity. However, in this work we choose an approach that assumes there exist several microbial guilds within the soil system responsible for the emission of various quantities of NO throughout the full range of gravimetric soil moisture studied. This concept is similar to that proposed from the molecular analysis used in Placella et al. (2012; 2013), which identifies different microbial guilds responsible for release of CO_2. Furthermore we assert that these guilds can be represented by the four VOC emission groups observed with a maximum in activity occurring at the VOC emission peak, shown as the vertical dotted lines in Fig. 2.

Figure 4 shows the results of fitting the measured NO emission profile from the SC soil, open black circles, with four theoretical Gaussian emission contributions, colored dashed lines, centered at the times of the four observed VOC maxima. It is clear from the goodness of the cumulative NO fit, dashed black line, that we are able to reconstruct the NO emission curve to a high degree using these four hypothetical VOC emission processes. We suggest that these curves represent four dominant microbial processes or guilds within the soil that individually contribute to the total observed NO. Figure 4 also includes a representative VOC from each of the four observed VOC emission groups, colored circles, by which the hypothetical NO emission sources were defined. The NO in each panel has been scaled by the factor reported in the legend to give an approximation of the NO : VOC ratio for each comparison. It is clear that the observed VOC groups correlate well with the four hypothetical NO concentration profiles which are the result of emitting guilds, where the ratio of NO to VOC varies for each guild. These results suggest that active monitoring of VOC can be used to better understand the origin of NO emissions from soil allowing for a more targeted approach to identification of the active microbial populations.

Future laboratory and field experiments should be designed to utilize the observed VOC emission groups to better understand the contribution of different microbial pro-

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cesses, such as denitrification, fermentation, and nitrification, to soil biogenic NO release. Sub-samples of soil during peak activity periods have to be subjected to molecular analysis in order to better attribute these microbial processes to the release of VOC. In the absence of such a detailed analysis, which is beyond the scope of this work, we submit a brief discussion, based on currently available literature linking the emission of VOC to microbial guilds, of the potential sources for the subset of observed VOC, identified in Fig. 4.

A net release of DMS and NO is observed at very high soil moisture content, e.g. the beginning of the experiment; therefore it seems likely that the process of denitrification is responsible for DMS production. From a study of available literature, a microbial release of DMS within the soil habitat seems likely to originate from the α-proteobacteria and γ-proteobacteria class (Schulz and Dickschat, 2007). The class of α-proteobacteria, sub class rhizobiales, contains the genera *Rhizobium*, *Bradyrhizobium* as well as *Nitrobacter*. The first two genera, *Rhizobium* and *Bradyrhizobium*, are known to be involved in the N-cycle as denitrifiers (Garciaplazaola et al., 1993; Bedmar et al., 2005), while the latter nitrite oxidizing bacteria (NOB) can release NO as an intermediate in nitrification (Aamand et al., 1996). Additionally, within the class of γ-proteobacteria, several strains of *pseudomonas* are involved in denitrification (Knowles, 1982).

Production of isoprene occurs in a large range of microbial species (Scholler et al., 2002; Kuzma et al., 1995; Schulz and Dickschat, 2007). However, as a co-emission with NO at a medium range of soil moisture it seems likely that isoprene might be a product of the metabolism of *Actinomycetes* (Scholler et al., 2002). Alternatively, *Streptomyces* could also be responsible for the co-release of isoprene and NO. *Streptomyces* are known to produce exospores and for growing on cell constituents of dead organisms, e.g. amino acids (Salton, 1955), which might be an advantage in dryland soils such as the SC sample. In earlier studies, *Streptomyces thioluteus* has been identified to denitrify (Shoun et al., 1998), while *Streptomyces nitrificans* is known to nitrify (Isenberg et al., 1954).

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Previous research has indicated that hexanol is released from a large range of bacteria and fungi (Dickschat et al., 2005; Blom et al., 2011; Beck et al., 2012). A co-release of hexanol and NO, however, could be attributable to the *Burkholderia* genus, which is capable of both nitrogen fixation (Estrada-De los Santos et al., 2001) and heterotrophic nitrification (Matsuzaka et al., 2003).

Release of 2,3-butanediol and 1,3-butadiene has previously been observed during the fermentation process from *Klebsiella*, *Enterobacter*, *Bacillus* and *Serratia* strains (Ji et al., 2011). Depending on the products of fermentation, two types of microbial groups can be defined: (i) organic acid producers and (ii) 1,3 butadiene producers. The latter microbes can be identified by a positive Voges-Proskauer reaction (Eddy, 1961). It is also known that *Klebsiella pneumonia* is involved in nitrification and denitrification (Padhi et al., 2013) and can thereby release NO as well.

While the release of DMS and hexanol occurs on a relatively short time scale, the release of isoprene and 1,3-butadiene is observed over a longer time period, i.e. range of soil moisture. This might be explained by emission by "specialists" that release DMS and hexanol while "generalists", capable of growing over a larger range of soil moisture content, are responsible for emissions of isoprene and 1,3-butadiene.

4 Conclusion

We have presented the results of PTR-TOF-MS measurement of VOC emitted from two very contrasting samples, (i) cotton field soil taken from Sache oasis, Taklimakan desert, Xinjinag Uygur Autonomous Region, P. R. China, and (ii) rainforest soil sample, collected in Suriname. A relatively large release rate of VOC from soils over a range of soil moisture and temperatures has been observed using a novel soil chamber system. By far the largest release rate of organic carbon occurred immediately after rewetting of the soil; however, emissions of many additional VOC continued throughout various stages of soil moisture.

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We suggest two mechanisms for the generation of VOC from soils: microbial or abiotic production. In the soil sample collected from the Suriname rainforest, nearly all observed VOC were determined to be associated with microbial processes, yielding a Q_{10} value in the range of 2–3. These emitted VOC can be grouped into several distinct temporal/soil moisture emission profiles, suggestive of various populations of microbes activating at different levels of soil moisture. Consequently, no single VOC was aligned with the emission of NO throughout the entire range of soil moisture. However, the observed NO emission profile can be reconstructed to a high degree by assuming that a variable amount of NO production is associated with each of the four VOC emission groups, excluding frequently observed pulsing of VOC upon soil wetting. It is therefore likely that the observed NO represents a sum of emissions from several microbial populations activating at varying soil moisture, not a product of a single population. As such, high time resolution measurements of VOC allows for a more complete understanding of the processes that control soil emission of NO.

While it is potentially useful, for global up-scaling of VOC emissions from soils, to express the amount of VOC emitted as a ratio to NO, our observation of 4 distinct NO emitting groups prohibits one from using NO as a scalar for use in any global atmospheric models (Vallero et al., 2009). Given the varying results of observed emissions for the two soils sampled in this study, at this time no promising metric has been determined to serve this purpose. Instead we recommend that VOC emissions be parameterized as a function of soil moisture. Given the above observations, we expect emission of VOC to be controlled by the activity of different microbial groups in soils and therefore exhibit a response as a function of soil moisture, that when normalized to %WHC may be comparable between different soil samples.

One of the more impactful conclusions of our research is the ability of this technique to be applied towards an improved understanding of the active microbial or fungal communities occurring within soils, especially the links/interactions between reactive trace gases involved in the carbon and nitrogen cycle. Observations of separate VOC emission groups associated with distinct processes, each co-emitted with various amounts

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of biologically produced NO can be used to focus future research. VOC groups observed in this study could serve as a molecular fingerprint, known as volatilomics, for the various processes occurring, allowing for a more targeted soil sampling approach during periods of maximum microbial activity identified by real time VOC measurements, using a technique such as PTR-TOF-MS. While molecular sampling is destructive and costly, our results suggest that it is possible to identify and monitor the activity of microbial guilds in soil via nondestructive measurement of VOC in the headspace. Future experiments using a combination of available molecular methods, such as functional marker genes, pyrosequencing, or TRFLP fingerprinting, in conjunction with the PTR-TOF-MS technology described here should be designed to attribute the release of VOC to specific microbial guilds.

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Table 1. Summary of PTR-TOF-MS detection limits for species reported.

Analyte	Detection Limit (3σ)	
	ppb	ng kg^{-1} s^{-1}
Acetone	0.16	0.30
Acetaldehyde	0.49	0.68
Trimethylbenzene (TMB)	0.53	1.96
Methanol	0.27	0.27
Xylenes	0.40	1.32
Acetonitrile	0.65	0.84
Formaldehyde (HCHO)	0.33	0.31
Dimethyl Sulfide (DMS)	0.35	0.68
Isoprene	0.15	0.27
Terpenes	0.93	3.96
1,3-Butadiene	0.82	1.39
2-butanone	0.14	0.31

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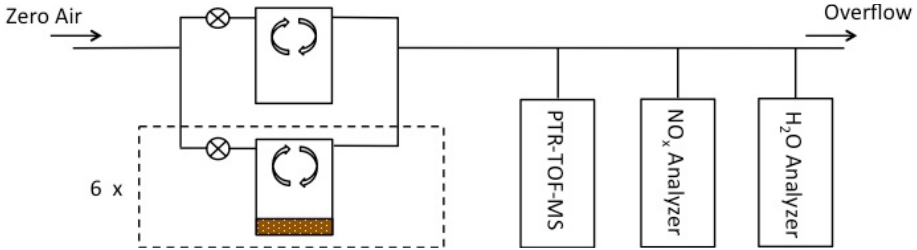

Figure 1. Simplified schematic of the soil sampling chamber system used in this study. A very detailed description of this system can be found in Behrendt et al. (2014).

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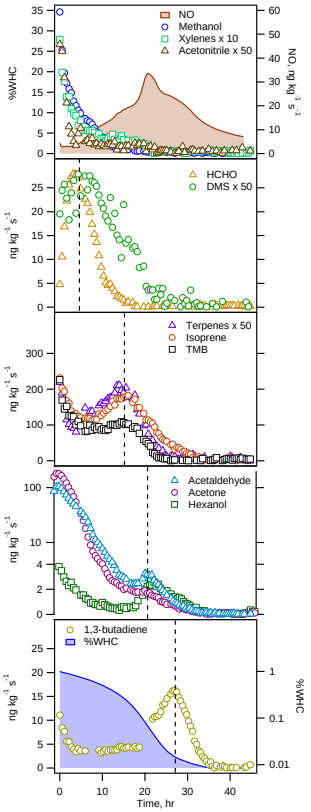

Figure 2. Displayed is a summary of various significant VOC release rates (ng kg^{-1} s^{-1}) from the arid cotton field soil (SC soil sample). Maxima occur at various degrees of water holding capacity (%WHC), with several VOC exhibiting multiple local maxima, indicated by the vertical dotted lines. Typically the largest release rates of organic carbon are observed immediately after soil wetting. Abbreviations are given in graph legends for trimethylbenzene (TMB), formaldehyde (HCHO) and dimethyl sulfide (DMS).

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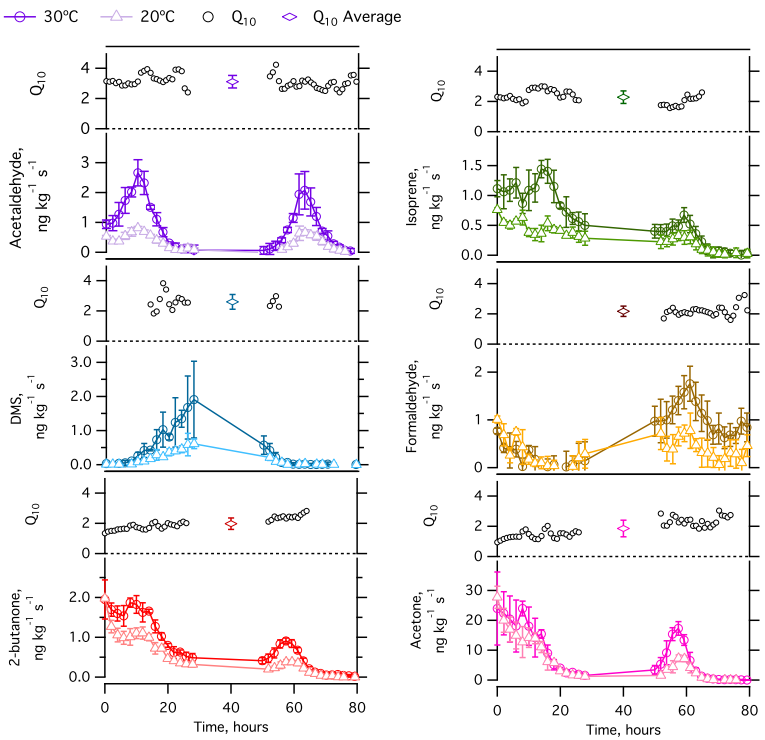

Figure 3. VOC emission observed from the Suriname rainforest (SR) soil sample. Soil temperature was modulated between 20 °C (colored triangles) and 30 °C (colored circles) to determine the temperature amplification factor, Q_{10} value (black markers), which can be used to separate microbial and abiotic processes driving the emission of VOC. The colored diamonds represent the average Q_{10} value for entire experiment ± one standard deviation.

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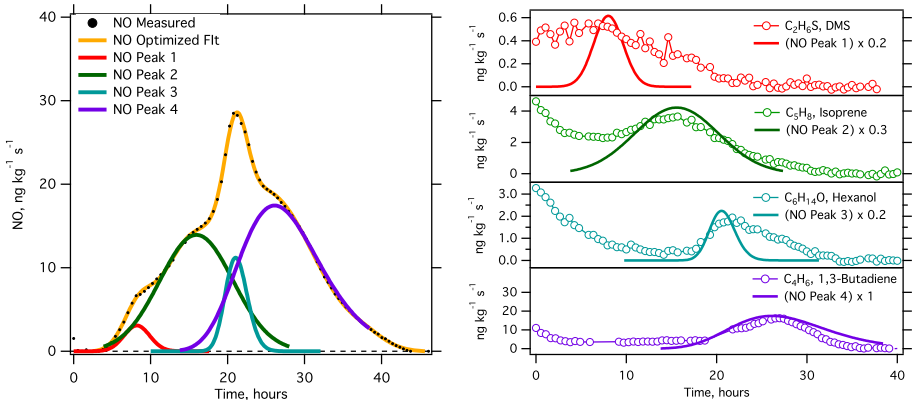

Figure 4. For the cotton field soil (SC) sample, four NO emitting processes, occurring with maxima corresponding to those identified in Fig. 2, were assumed and used to perform a multi-peak fit of the measured NO, left panel. Measured VOC representative of the four emission groups are shown in the right panel, colored circles, along with the resulting NO emission processes generated in the multi-peak Gaussian fit, solid color lines. The four hypothetical NO emitting processes are reasonably well captured by the measured VOC suggesting that VOC measurements can be used to probe the activity of individual microbial processes contributing to NO emission in soil systems.

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