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Profiles of volatile organic compound emissions from soils amended with organic waste products

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Abstract

This study investigates the Volatile Organic Compounds (VOCs) emitted from soil amended with four different organic waste products (OWP) every two years since 1998 and until now at a rate of ~4 tC ha^{-1}: municipal solid waste compost (MSW), green waste and sludge co-compost (GWS), bio-waste compost (BIOW) and farmyard manure (FYM). Soil samples were collected two years after the last application of OWP. The aim of this study was to detect different VOCs emissions from soils amended with OWP in order to establish a VOCs signature of the OWP and to understand if the total VOCs flux depends on the type of OWP in soil. They were compared to a soil which received no organic inputs (CN). The emissions were detected using a PTR-ToF-MS (Proton Transfer Reaction-Time of Flight-Mass Spectrometry). OWP in soil were detected using a laboratory system made of two pyrex chambers, one with samples and the second one empty. The on-line detection has been made measuring in first place the empty chamber in order to have a blank; secondly, a measure of the emissions in the chamber with the soil has been performed. Our results confirmed that VOCs emissions were affected by the type of organic amendment to soil. Overall, the most emitted compounds were acetone, butanone and acetaldehyde in all treatments. We found some compounds which had statistically different emissions between the treatments. For instance, GWS released more 94.03 m/z, 95.02 m/z, 110.06 m/z (benzamide), 111.07 m/z and 113.01 m/z than the

other OWPs. Our results suggest that organic matter and pH jointly influenced total VOC emissions. Other factors explaining the diversity of VOC emitted and the influence of treatments are discussed.

Keywords: VOC, soil, organic waste products, PTR-TOF-MS

1 Introduction

The family of volatile organic compounds (VOCs) is composed of a large range of molecules with different functional groups and different chemical and physical properties. The common traits between VOCs are the high vapour pressure under ambient conditions and low boiling points which explain their presence in the atmosphere. Volatile organic compounds sources have been extensively studied because of their contribution to global warming and pollution (Kesselmeier and Staudt, 1999). It has been demonstrated that VOCs are involved in many chemical reactions in the atmosphere among which the production cycle of tropospheric ozone (O_3) in combination with the NO_x cycle (Seinfeld and Pandis, 2016). Another important chemical processes in the atmosphere that involves VOCs are the photolysis of formaldehyde and other carbonyls in presence of NO which are responsible of hydroxyl (OH) formation (Atkinson, 2000). Additionally, VOCs are precursors of secondary organic aerosol (SOA) (Singh et al., 1995) and are involved in the production of nitrates in the troposphere (Monson and Holland, 2001). For these reasons VOCs alter the air quality and thus they have indirectly consequences on human and ecosystems health.

Several studies demonstrate that biogenic VOCs contribute to 90% of the total VOCs emissions (Atkinson, 2000), while anthropogenic sources such as industries, solvents, transportations etc. contribute only for the 10% of the total VOCs emissions. Among the most important biogenic sources of VOCs are living plants, with a global emission of 1Pg C y^{-1}, mainly monoterpenes from broadleaves forests (Guenther et al., 1995; Zemankova and Brechler, 2010; Harrison et al., 2013). Furthermore, it has been shown that the soil and litter can release around 12 to 136 % of monoterpenes compared to canopy emissions in spring and fall (Faiola et al., 2014).

Another source of biogenic VOCs is the interaction between soil and microorganisms. Soils VOCs emissions are up to three times lower than the VOCs release from the canopy. Nevertheless, it has been demonstrated that under certain temperatures and soil water contents, and for specific ecosystems, VOCs emissions from soil could reach the same magnitude as canopy emissions (Peñuelas et al., 2014). Additionally, little is known about the emissions from agricultural fields, although they are recognised as large contributors of methanol and acetone to the

atmosphere (Bachy et al., 2018; Mozaffar et al., 2018; Goldan et al., 1995). It however appears from recent measurements that soils may contribute to a large extent to the overall balance of VOC fluxes in crop rotations (Bachy et al., 2016)

From another perspective, intensive agriculture may lead to the decrease of soil organic matter contents (Chan et al., 2002) and Europe is encouraging the use of organic waste products (OWPs) in crops (European Commision, 2010) to favour carbon storage in soils (Peltre et al., 2012). The recycling of OWPs in soils also represents an alternative to waste management by landfilling or incineration. The application of OWPs also provides nutrients such as nitrogen (N) and phosphorous (P) which make possible the substitution of mineral fertilizer, improves soil biodiversity and has positive impacts on soil physical properties such as aggregate stability (Annabi et al., 2007; Diacono and Montemurro, 2010). The negative impacts are not negligible though; for instance OWP release contaminants that can be transferred to plants, water or to the atmosphere (Belon et al., 2012). Organic wastes also affect soil pH, and pH is one of the chemical properties that impact on VOCs emissions (Brinton, 1998). Positive and negative impacts in soil vary with the applied organic waste product (Obriot et al., 2016). For example Seewald et al. (2010) studied VOCs production by adding glucose to soils regularly amended by different composts. There was no impact on the VOCs emissions compared to control sample with one of the composts, while for another one and mineral fertilization they observed different VOCs emissions. Moreover, Potard et al. (2017) showed that different soil organic fertilizers such as pig slurry and methanized pig slurry impact in a different way soil VOCs emissions: pig slurry releases double quantities of VOCs while methanized pig slurry emits even less than the unamended samples. Contrasting type of VOCs emissions from soil have been reported from several studies. For instance, in Mediterranean soils the most emitted compound was methanol (Asensio et al., 2007a) while in soil amended with straw it was acetone (Zhao et al., 2016). In fact, emissions of VOCs are strongly related to the substrate quality and it is important to note that even small variations in nutrient composition may change the type and the amount of individual VOCs produced (Wheatley, 2002).

Significant emissions of the VOCs released by soil are produced by microorganisms (Isidorov and Jdanova, 2002; Stahl and Parkin, 1996). It has been reported that the composition and amount of VOCs emitted are linked to the microbial community living in the soil (Asensio et al., 2007b; Schade and Custer, 2004; Seewald et al., 2010). Microorganisms produce VOCs as a result of the degradation of sugar, alcoholic fermentation, amino acid and fatty acid degradation, terpenoid biosynthesis and sulphur reduction. For instance, acetaldehyde, which is one of the compounds most emitted from soil, is formed during the alcoholic fermentation that produces ethanol (Castaldelli et al., 2003; Karl et al., 2003). Previous studies have reported that microorganisms degrade sugar

following three major pathways: (1) Embden-Meyerof pathway, (2) Heterolactic/homolactic pathway and (3) Entner-Douoroff pathway. In these processes, intermediate compounds are produced such as pyruvate, glyceraldehyde-3-phosphate, lactate and acetate which are precursors for the biosynthesis of several VOCs (Peñuelas et al., 2014). VOCs are also released as molecules resulting from the secondary metabolisms of micro-organisms (Werner et al., 2016). Secondary metabolites might be produced under certain circumstances or development stages; hence they might be used as indicator of the cellular state (Patti et al., 2012). Furthermore, it has been demonstrated that the nature of the substrate can affect microorganisms' community and thus change VOCs emissions (Peñuelas et al., 2014). Moreover, the application of OWP in soil stimulate its diversity, the abundance and the activities of microorganisms in soil compared to soils that only received mineral fertilizers. This is a consequence of the addition of microorganisms previously present in the OWP (Ros et al., 2006).

The aim of this study was to determine whether soil regularly amended with different organic waste products for a long period have a differentiated volatile organic compound signature. Four soils amended for 20 years with organic wastes products were considered: bio-waste compost (BIOW), green waste and sludge compost (GWS), municipal solid waste compost (MSW) and farmyard manure (FYM). All these soils were compared with a control sample that had never received any OWP. We measured VOCs fluxes under standardised laboratory conditions with a proton transfer reaction – time of flight- mass spectrometer (PTR-TOF-MS). The VOCs released were identified and quantified and the relationship between VOCs emissions and soil chemical characteristics (pH, organic matter, I_{roc}…) was studied.

2 Methods

2.1 Site description

Samples were collected in the QuagliAgro site, a field station taking part of the SOERE-PRO-network (https://www6.inra.fr/qualiagro_eng/Nos-partenaires/The-SOERE-PRO-network). The QualiAgro site is located at Feucherolles in northwestern France (35 km west of Paris; 48◦52'N, 1◦57'E, alt 150 m), on a silt loam textured soil. The soil of QualiAgro site of Feucherolles is classified as a hortic glossic Luvisol (IUSS Working Group WRB, 2014), representative of the Parisian Basin. The main characteristics of these soils are represented by the lack of clay, a silt-loam texture (15.0% clay, 78.3% slit) nad an initial pH of 6.9 in the surface horizon (0-30 cm) and good drainage. Moreover, the Qualiagro field experiment is in a cropland dominated region, which lead to a low organic carbon and low organic matter concentrations (initial content of 1.1%) (Meersmans et al., 2012). On

the other hand, observing QualiAgro site on a smaller scale, differences in the organic carbon content, total nitrogen or pH between samples are due to the different applications of OWP.

The experiment was a randomized block design with 4 replicates comparing 4 organic waste products: BIOW (bio-waste compost derived from the co-composting of green wastes and source-separated organic fractions of municipal solid wastes), GWS (compost derived from the co-composting of green wastes with sewage sludge), FYM (farmyard manure) and MSW (municipal solid waste compost derived from the composting of residual solid wastes after removing dry and clean packaging); plus a control without organic input (CN). Moreover, the 20 field blocks studied were additionally amended with mineral N to reach optimal N application. The field was cropped with a winter wheat – maize rotation. The wheat crop residues were exported, whereas the maize residues were returned to the soil. Since 1998, the organic waste products (OWP) have been applied at a rate of ~4 tC ha^{-1} every two years on the wheat stubbles in September, after harvesting. In each plot, 5 soil cores were randomly sampled at 0-30 cm depth using a core drill and stored in a cold chamber at 4°C prior to analysis. The sampling was performed in early September 2015, two years after the last amendment of OWP. Each type of amended soil was sampled as described by Noirot-Cosson et al. (2016).

2.2 Experimental setup

2.2.1 Soil analysis

Soil pH was determined following the standard NF ISO 10390 protocol, where a glass electrode was used in a 1:5 (volume ratio) suspension of soil in water. Total carbon in soil was measured by dry combustion and organic carbon calculated after correction of the carbonate content (ISO 10694). Total N was determined also by dry combustion (ISO 13878). Finally, organic matter in soil was calculated by multiplying C organic x 1.72, while organic matter for composts was determined by loss on ignition at 550°C. The soil cation exchange capacity was determined with cobaltihexamine following NF X 31-130 (AFNOR 1999)

2.2.2 Soil sample preparation for PTR-TOF-MS analysis

Samples of the same plot were mixed and homogenized by passing through a 2 mm sieve to remove aboveground plant materials, roots and stones, then dried up at room temperature (~23°C) for 2 weeks.

2.2.3 Laboratory flux chambers

In order to measure VOC emissions, soil samples were first moisturised to the field capacity by adding ultrapure water (resistivity 18.2 MΩ). The amount of water necessary was determined on a sub-sample and used for all

samples (15 mL of water for each sample). Soil samples were then inserted, one at a time, in a pyrex chamber having a volume of 106 cm^3. The quantity of soil inserted in the chamber ($m_{dry\ soil}$) was 60 g (dry mass) for each measurement. Soil was homogeneously spread on the chamber surface (132 cm^2). An empty chamber was used as a reference for zero emissions. **Figure 1** represents the design of the measurement scheme. An air flow (Q_{air}) of 0.2 L min^{-1} (equivalent volumetric flow at 0°C and 1 atm) of dry synthetic air (Alphagaz 1 Air: 80% nitrogen, 20% oxygen, 99.9999%, Air Liquide®) was passed through a hydrocarbons and humidity filter (Filter for fuel gas, final purity=99.999%, Restek®) and a Hydrocarbon Trap (Supelco, Supelpure® HC) prior to injection in the chambers. A mass flowmeter (Bronkhorst® model F-201CV, accuracy: standard 0.5% Rd plus 0.1% FS, range: 0.2 L min^{-1} to 5 L min^{-1} air) was used to control the synthetic air flow rate. Air was sampled at the chamber outlet into a PTR-ToF-MS with a 0.05 L min^{-1} flow rate with a 2 m long, 1 mm internal diameter PEEK tube, heated at 80 °C. A measurement cycle consisted in measuring the VOC mixing ratio at the outlet of the chamber containing the soil ($x_{VOC\ soil}$ in ppb) for 180 s. Then air was sampled for 120 s on the empty chamber to determine $x_{VOC\ empty}$ (ppb). We sampled the empty chamber less than the chamber with soil because the signal was stable after only ~10 s. Only the last 60 s of each measurement were kept to calculate averaged mixing ratios in order to ensure a stable VOCs mixing ratio. The VOC emission (E_{VOC} in nmol g^{-1} s^{-1} dry soil) was calculated as:

$$\boldsymbol{E_{VOC}} = \frac{\boldsymbol{Q_{air}} \times (\boldsymbol{x_{VOC\ soil}} - \boldsymbol{x_{VOC\ empty}})}{\boldsymbol{V_{mol}^{air}} \times \boldsymbol{m_{dry\ soil}}} \quad (1)$$

Where V_{mol}^{air} is the air molar volume at standard temperature and pressure (22.4 L mol^{-1} at 0°C and 1 atm). In total 15 samples were measured: 3 replicates for each of the 5 treatments. Each measurement was further repeated 3 times to compute the mean and standard deviation of the measurement. This led to 45 measurements in total. After each measurement, the chamber was cleaned with diluted sodium hydroxide in order to destroy any organic compound that could affect the next measurements, and then rinsed with ultrapure water (resistivity 18.2 MΩ).

2.3 VOC analysis with the proton transfer reaction time of flight mass spectrometer (PTR-TOF-MS)

The VOCs were analysed with a PTR-TOF-MS (PTR-Quadrupole Ion guide-TOF, Ionicon, Analytik GmbH, AU). The analyser is described in details by Sulzer et al., 2014. It consists in a drift tube where VOCs are ionised and accelerated prior to be injected into a quadrupole ion guide and electromagnetic lenses. The electromagnetic lenses focus the ions in a time of flight mass spectrometer detector (TOF, TofWerk, Switzerland) which separates the ions by inertia prior to detection. The detection is made with a multi-channel-plate (MCP) detector and a time-to-

digital converter (Burle Industries Inc., Lancaster, PA, USA). In this study, ionisation was carried out with H_3O^+ as proton donor. The transfer reaction was effective for VOCs with a proton affinity higher than 691.7kJ mol^{-1}, which is the proton affinity of the water. In the drift tube, the pressure was tuned to 4 mbar, the temperature to 80°C, and the drift voltage to 1000 V, while the extraction voltage at the end of the tube (UDx) was 44 V. The E/N ratio (Electric field/density of natural particles) was 132 Td where 1 Td is 10 V m^2. These parameters were controlled in order to maintain constant ionization conditions within the drift tube. The setup of the time of flight timing was: TOF extraction period 40000 ns, pulse width 2000 ns, trigger delay 100 ns. The number of channels was 240.000. This gave a mass spectrum measurement up to 510 m/z. The measurement period was set to 1 s, which means that each sample corresponded to 60 acquisitions of 25000 individual spectra. Raw PTR-ToF-MS data were recorded by TofDaq software (Tofwerk AG, Switzerland).

2.3.1 Peak detection of the mass spectra and mass calibration

We used the PTR viewer 3.1.0.29 software (Ionicon, Analytik GmbH) to detect mass peaks in each spectrum. The mass calibration was performed using the oxygen isotope of the ion source $H_3{}^{18}O^+$ (21.022 m/z) and acetone, $C_3H_7O^+$, (59.0449 m/z). These two were chosen as they were present in all samples. Mass calibration was made over the entire dataset allowing for a change of 0.1 m/z around the peak maximum between consecutive samples and using a moving average of 50 successive samples for better stability. Overall the instrument resolution was around 4000. In order to create a peak table including the largest number of peaks, we used the automatic research feature of the software selecting as search mode “multiple peaks” with a threshold of 5 counts per second. Following this step, a manual check of each peak was performed in order to correct for any software miss-fits. Each peak was manually readjusted. The modes used to auto-select and manually adjust the peak areas that are used for mixing ratio calculation were the Gaussian or the multi-peak modes. The Gaussian peak mode was used for the analysis of isolated peaks; while for a better fit of multiple peaks we used the multi-peak mode. The range of the mass detection was limited between 31 and 400 m/z. Finally, masses deriving from the water cluster such as 37.03 m/z, 38.03 m/z, 39.03 m/z, and 55.03 m/z were not taken into account during the analysis of the dataset.

2.3.2 Isotopes and fragments identification

In order to make sure that a compound was not twice counted, we identified likely isotopes and fragments by performing a correlation analysis on the mass spectra. The Pearson’s correlation coefficient was computed between each m/z based on all measured mixing ratios during the experiment (N=45). The m/z having a correlation

coefficient larger than 0.99 were considered either fragments or isotopes depending on the m/z difference. In total 16 isotopes and 2 likely fragments were identified (Table S1).

2.3.3 PTR-TOF-MS mixing ratio calibration

The MCP provides the counts per seconds of detected ions after the TOF. In order to calculate the mixing ratio of gases in ppb that enter the PTR, a series of calculations was performed. The mixing ratio was calculated using the PTR-viewer software, which uses the following equation:

$$\chi_{i\ \mathrm{standard\ transmission}} = 1.657e^{-11}\ \frac{U_{drift}\ T_{act}^{2}[K]}{k\ p_{act}^{2}[mbar]}\ \frac{R^{+}}{H_3O^{+}}\ \frac{TR_{H_3O^{+}}}{TR_{R^{+}}} \qquad (2)$$

Where $\chi_{i\ standard\ transmission}$ is the mixing ratio of the compound in ppb, U_{drift} is the voltage of the drift (V), T_{act} is the drift-tube temperature in Kelvin, R^{+} is the signal of the product ion in count per second (cps), k is the protonation reaction rate constant (2 10^{-9} cm^3 s^{-1}) assumed equal for all compounds, $TR_{H_3O^{+}}$ is the transmission factor for mass of primary ion, $TR_{R^{+}}$ is the transmission factor for mass of product, p_{act} is the pressure of the drift, ion H_3O^{+} is the primary ions signal in cps. The standard transmission curve from supplier was used to compute $TR_{H_3O^{+}}/TR_{R^{+}}$ **(see Table S2 in supplementary material).**

We used the following primary ions mass: 21.02 m/z ($H_3{}^{18}O^{+}$, multiplier factor 487.56), 38.03 m/z (water cluster $H_2{}^{18}O{\bullet}H_3{}^{18}O^{+}$ with two ^{18}O isotopes, multiplier factor 819.51) and mass 55.03 m/z ($H_2O{\bullet}H_3O^{+}$ $\bullet H_3O^{+}$ multiplier factor 1.0008).

In order to account for the normal loss of sensitivity of the PTR-TOF-MS, due to the MCP degradation over time, the change of $H_3{}^{18}O^{+}$ produced in the source, or other factors, we used a calibration procedure to account for the actual sensitivity of the analyser. We used benzene, toluene and ethylbenzene as reference compounds for this calibration. The mixing ratio of these compounds was modulated using a dilution system with a standard cylinder containing 102 ppb of benzene, 104 ppb of toluene, 130 ppb of ethylbenzene and 336 ppb of xylene (Btex, Messer®). We used the same synthetic air for the dilution system as the one described for the chamber set up. The sensitivity S^{norm} was calculated as the slope of the regression between measured mixing ratio with the standard transmission provided by Ionicon and mixing ratio calculated with equation (2**)**, and forcing a zero intercept. The calibrated mixing ratio of all compounds was then calculated as:

$$\chi_i = \left[\chi_{i\ standard\ transmission} - \chi_{i_{(0)}}\right] \times S^{norm} \qquad (3)$$

Where χ_i is the mixing ratio of the compound in ppb, $\chi_{i\ standard\ transmission}$ is the mixing ratio calculated using the standard transmission as in equation (2), $\chi_{i_{(0)}}$ is the mixing ratio of the compound measured for dry synthetic air.

The procedure was applied for the three compounds cited above for the calibration. We found that the sensitivity was 3.11±0.15. A single sensitivity value of 3 was applied for all masses, since the protonation reaction constant was assumed equal for all masses. In total we selected 754 peaks in the mass spectra used for these analyses.

2.3.4 VOC identification

We first identified the molecular formula with the Spectra Analyser within the PTR viewer 3.1.0.29 software (Ionicon, Analytik GmbH). The spectra analyser is a tool that allows the manual selection of the peaks chosen for the identification. The identification of the compounds corresponding to each mass peak was performed by searching the possible combinations of elements that led to the closest molecular weight. The following elements were selected for all peaks: C, N, O and H. Other compounds were selected on purpose for masses higher than 70 m/z like S, Si, Cl, Ca and K, when C, N, O and H did not lead to a good agreement with the peak mass. The maximum number of atoms per molecule was set to 50, while the error on the molecular weight was fixed to ± 0.01 m/z. Subsequently, a list of possible compounds was produced. The compounds listed represent the best matches for the selected exact m/z. Finally, a match of the isotopes of each compound was evaluated. Once the molecular formula was determined, we tried to identify the potential compounds with the use of the literature reviews. We have to stress that this method does not provide an undoubtable identification of the compounds as several compounds could have the same molecular mass but not the same chemical structure. Moreover, even with this procedure, some compounds could not be identified at all.

2.4 Statistical analysis

Several statistics test were performed on the VOCs emissions calculated for each treatment in order to identify the VOCs that mark the differences between the OWP treatments. All statistical analysis were performed using R software (Version 1.0.153 – © 2009-2017 RStudio). First, a normality test (Shapiro-Wilk test, W> 0.9) has been applied to verify that the mean mixing ratios were normally distributed for each VOC. Secondly, the homogeneity of the variances was verified for each treatment using the Levene test. Once the normality and the homogeneity of de variances were validated, the ANOVA test followed by Tukey post hoc test were performed. Finally, the Between Class Analysis (BCA, Package *Ade4* Version 1.0.153 – © 2009-2017 R Studio) was performed. The

ANOVA and BCA were specifically used to identify the VOCs that differentiate between each OWP treatment. The Between-Class analysis is a particular case of a Principal Component analysis, it calculates the axes maximizing the covariance between the different treatments analysed.

3 RESULTS

3.1 Soil characteristics of each treatment

The **Figure 2** summarizes soils characteristics as a function of OWP. The carbon content is in the range 10-18 g kg^{-1} DM which spans from typical to high carbon content for a silt-loam. Organic matter was mainly found in the clay fraction of the soil (60%) and in the smaller fraction of the particulate organic matter, mainly in the form of O-alkyls, Alkyls and Aryls (Paetsch et al., 2016).

The CN samples showed the lowest cation exchange capacity, organic matter content, total nitrogen content, pH and organic carbon while its C/N ratio was not different from BIOW and GWS treatments (Figure 2). The treatment with the highest cation exchange capacity was BIOW while we found the highest C/N ratio in the FYM. Furthermore, the total N, organic carbon and organic matter were higher for the BIOW and the GWS treatments. Concerning the pH, BIOW and MSW had the highest values, while CN and GWS had the lowest values.

These results show that the repeated application of OWP has significantly increased soil organic carbon content (OC in **Figure 2**) in all organic treatments compared to the CN, but not in the same amount. Although all OWP are applied based on the same input of organic C, their different characteristics can explain their varying efficiencies at increasing soil organic carbon (Peltre et al., 2012). Indeed, the index of residual organic carbon (I_{roc}) that represents the portion of organic carbon potentially incorporated into soil organic carbon after the organic waste application (Lashermes et al., 2009) was similar to OC: I_{roc} was the lowest for the MSW samples (I_{roc}=49% Org C), and was the highest for BIOW and GWS (I_{roc}=77% and 75 % Org C, respectively) (Obriot et al., 2016). Total organic nitrogen (Ntot) was also greater in the organic treatments compared to CN and was ordered similarly as soil organic carbon. The C/N ratio is in the same order of magnitude for all the samples. The soil CEC was increased in treatments receiving OWP, which in line with previous finding, that CEC increased with organic matter in soils (Kaiser et al., 2008). Finally, the BIOW and MSW treatments increased soil pH mainly because of their contents in carbonates. FYM only slightly increased pH compared to control while GWS had no effect on soil pH. Paetsch et al., (2016) further showed that the C/N ratio of the fine fraction of particulate organic matter rather represented the crops residues than organic waste inputs. They deduced lower degradability of organic matter in BIOW and GWS although they show the highest OM content.

3.2 VOCs Emissions

In order to verify whether the treatments affected the bulk production of VOCs, the fluxes of all compounds detected with the PTR-TOF-MS were summed up. They ranged between 36 ± 8 10^{-4} nmol s^{-1} g^{-1} and 52 ± 12 10^{-4} nmol s^{-1} g^{-1} (Figure 3a and Supplementary material Table S2). The treatment with the highest total flux rate is the BIOW and the treatment with the lowest total flux rate is the MSW while the other three treatments have non-significantly different total VOC emissions (ANOVA and a post hoc Tukey test with p value < 0.05). Moreover, the Shannon diversity indexes are similar in all treatments, though slightly smaller in BIOW indicating that BIOW less compounds contribute to the overall VOC flux.

3.3 Differentiating VOCs for each treatment

In order to determine if OWP amended soils affect the profile of VOCs emissions, we performed a Between Component Analysis (BCA). The first two components of the BCA explained 40.2% and 33.8% of the total dataset variability. In **Figure 4** we observe that GWS and BIOW treatments are isolated from the other OWP (FYM, MSW and CN), which means that they have a VOC profile which is different from the other OWP. The VOCs that most explained the variance in the two first components of the BCA were selected as those having a coordinate larger than 0.9 on the first component and 0.5 on the second one (in absolute value). The m/z of these VOCs is shown in **Figure 4**. The tentative identification of the compound listed above is shown in **Table S4**.

Furthermore, an ANOVA analysis was performed in order to determine the VOCs that significantly differentiated the treatments. A Tukey test was performed on those compounds to detect significance in means differences. The emission rates of the 21 compounds statistically different are plotted in **Figure 5**. **Table S4** summarises the most emitted VOCs and those highlighted by the BCA and the ANOVA analysis. These 49 compounds listed in **Table S4** contribute between 70% and 91% of the total emission rate. For all treatments includes the control we found that acetone, butanone and acetaldehyde were the most emitted compounds always as first, second and third. In **Table S4** we added a tentative identification of the compounds and the corresponding chemical class. BIOW generally showed larger emissions than other treatments for small weighed compounds while GWS showed clearly higher emissions than other treatments for compounds in the mass range 80-130.

DISCUSSION

3.4 Identification and quantification of VOCs emitted

3.4.1 Most emitted VOCs: acetone, butanone, acetaldehyde, methanol, isoprene and ethanol

This study was focused on VOCs emissions from soils regularly amended with 4 different organic waste products compared to unamended soil. However, the soils were sampled two years after the last OWP application. Thus the differences in VOCs emitted could be associated to long-lasting effects of the OWP applications and to changes in soil organic matter characteristics due to these repeated OWP applications. We first notice that in all treatments including the control, the 3 most emitted compounds were acetone, 2-butanone and acetaldehyde regardless of amendments.

This study showed acetone emissions of 1000 ± 240 µg m^{-2} h^{-1}. Smaller acetone emissions are usually reported from laboratory experiments such as those by Asensio et al. (2007a) for a Mediterranean soil who found 10 times smaller fluxes than what we measured here. On the contrary, Schade and Goldstein (2001) reported acetone emissions in the same range as our study using a field chamber and a dual GC-FID system on a ponderosa pine plantation; they indeed found peak emissions of 800 µg m^{-2} h^{-1} following rain but smaller emissions 260 µg m^{-2} h^{-1} on average. Peñuelas et al. (2014), in their review, reported emissions ranging from 4 to 800 µg m^{-2} h^{-1}. Acetone is often observed in rural areas (Goldan et al., 1995; Lamanna and Goldstein, 1999; Riemer et al., 1998). Acetone emissions seem to be mainly driven by biogenic sources such as litter decomposition (Gray et al., 2010), microorganisms in soils (Bunge et al., 2008; Schöller et al., 2002 Schöller et al., 2006; Penuelas et al., 2014) but also functioning leaves (Karl et al., 2009; Mozaffar et al., 2018). However, acetone was also found to be produced from abiotic degradation of plant material in the soil at a rate of 100 µg g^{-1}DM by Warneke et al., (1999). Emissions of acetone from soils depend on moisture, temperature and on the technique used to detect the fluxes which could explain the differences between the fluxes reported in the studies cited previously (Peñuelas et al., 2014). Organic matter seem to enhance acetone emissions as reported by Zhao et al. (2016) who found that acetone was the most emitted compound from soil amended with straw contributing to 50 ± 9% of the total VOCs emissions. For comparison, in our study acetone contributed to around 30% of the total mass of VOC emissions (**Table S4**).

Butanone was the second most emitted compound from our samples contributing up to 20% of the total VOCs emissions. Zhao et al. (2016) also reported butanone emissions with a contribution of 9 ± 2% to the total VOCs emissions. McNeal and Herbert (2009) also detected butanone production by soil microcosm, while Larsen and Frisvad (1995a; 1995b) showed that butanone was one of the VOCs emitted from fungi. Apart from these

references butanone was not detected in other studies, at least not as one of the major compound emitted such as we found here.

The third most emitted compound from soil was acetaldehyde which was detected by Asensio et al. (2007a) as the second most emitted compound from their Mediterranean soil samples. Schade and Goldstein (2001) detected a flux of acetaldehyde of 100 µg m^{-2} h^{-1} at 24°C quite similar to what we found ~280 µg m^{-2} h^{-1}. Similar to this study, though smaller, Peñuelas et al., (2014) reported between 2 and 100 µg m^{-2} h^{-1} emissions of acetaldehyde for different type of soil, such as: forest soil, ponderosa pine plantation and shrubland soil. Gray et al., (2014) reported much smaller emissions (0.2 µg m^{-2} h^{-1}), but demonstrated that acetaldehyde emissions were largely coming from the roots system which was partly removed from our measurements by sieving at 2 mm. Mancuso et al. (2015) also detected acetaldehyde as the most emitted compound. It is noticeable that acetaldehyde is an oxidation product of ethanol. We should also stress that measurements of acetaldehyde with PTR-MS (not TOF ones) may catch some $CO_2.H^+$ and hence include some soil respiration. Indeed, although CO_2 has a proton-affinity lower than the one of water, we found that CO_2 was protonated in our TOF at m/z = 44.997 (Loubet, personal communication).

Methanol, isoprene and ethanol were also detected with a significant emission rate in this study (**Table S4**). Methanol has already been reported by Mancuso et al. (2015), Seewald et al. (2010) and was the compound most emitted as reported by Asensio et al. (2007) and Ramirez et al. (2010). Peñuelas et al., (2014) reported emissions in field conditions ranging from 4 to 530 µg m^{-2} h^{-1}, while Bachy et al., (2018) found a range from -50 to 200 µg m^{-2} h^{-1}, which agreed with Schade and Custer, (2004) measuring the emissions from a bare soil. Our results (~66 µg m^{-2} h^{-1}) are in good agreement with the cited studies. Ramirez et al. (2010) showed that methanol contributed to 89% of the total VOCs emissions by a forest soil while in our study methanol emissions contributed around 2% of the total mass VOCs emissions only. Methanol was also reported by Potard et al. (2017) as one of the most emitted compounds by soil. In fact it contributed between 20% to 40% of the total VOCs emissions in the control treatment and between 20% and 90% in soil amended with methanized pig slurry (Potard et al., 2017). Several studies showed different methanol sources from soil, i.e. abiotic production through SOM degradation (Schade and Custer, 2004), (a)biotic production from the litter (Gray et al., 2010; Ramirez et al., 2010; Bachy et al., 2018). Methanol might be produced via the microbial breakdown of plant pectin (Jayani et al., 2005; Schink and G. Zeikus, 1980). The small amount of plant residues in our samples may explain the lower contribution of methanol to VOCs emissions compared to Potard et al., (2017) and Ramirez et al., (2010). It is also important to

stress that methanol, as a soluble compound is adsorbed and desorbed from water films (Laffineur et al., 2012). This mechanism may have boosted emissions due to water evaporation in the chamber exposed to dry air.

Isoprene was reported as a compound emitted by agricultural soils amended with straw at only 0.1% of the total emissions by Zhao et al. (2016). Our results showed that around 6% of the total VOCs emissions were represented by isoprene emissions. Mancuso et al. (2015) measured isoprene emissions from agricultural and forest soil samples. Isoprene is a metabolite directly related to the presence of microorganisms in soil even if the role of this compound in microorganisms cell has not been clarified yet (Hess et al., 2013).

Ethanol is one of the compounds emitted during the sugar degradation as showed by Seewald et al. (2010). Schade and Goldstein (2001) reported emission of ethanol from bare soil between 300 and 500 µg m^{-2} h^{-1} while we found lower emissions around 100 µg m^{-2} h^{-1}).

3.4.2 Other compounds detected

Several aromatic compounds have been observed as emitted from our soil samples. Microorganisms and plants release aromatic compounds through the shikimate pathway or by the degradation of phenylalanine or tyrosine. Aromatic compounds are known to be emitted by plants under stress conditions (Misztal et al., 2015) and absorbed by humic substances in soil (Lu and Pignatello, 2004). Toluene is one of the aromatic compounds most emitted by our samples, but in a similar amount between treatments which was also reported by Asensio et al. (2007b). Toluene is rather a compound linked to oil, either natural (crude oil) or from derivatives, such as solvents, gasoline or other fuels as well as in the production process of coke from coal. The flux of this compound from soil is always very low but due to the several impacts that this compound might have on the health is important to quantify and characterize the emissions. It is interesting to notice that we also detected monoterpenes and p-cymene, which is an aromatic compound formed by the oxidation of monoterpenes (Gratien et al., 2011). We found around 0.018 nmol m^{-2} s^{-1} which is higher than the range of monoterpenes emissions detected by Asensio et al. (2007a) (between -0.004 nmol m^{-2} s^{-1} and 0.004 nmol m^{-2} s^{-1}). Hayward et al. (2001) reported that emissions of monoterpenes from soil of Sitka spruce forest were 0.026 nmol m^{-2} s^{-1}, and were strongly related to soil temperature (Raza et al., 2017). It is also known that monoterpene emissions from forests exceed those from agriculture (Guenther, 1997; Kesselmeier and Staudt, 1999). Assuming soil emissions are linked to plant residues degradation in the soil this might explain the higher emissions from forest's soils compared to what we find here.

Other noticeable compounds detected are the organosulfur compounds such as dimethylsulfide, dimethethydisulfide and diethylsulfide. Other studies have reported emissions of these compounds from soils. For

instance, Potard et al. (2017), Veres et al. (2014), Zhao et al. (2016), Mayrhofer et al. (2006), and Raza et al. (2017) reported emissions of dimethylsulfide from soils. Dimethethydisulfide is a fungistatic produced by *Bacillus*, *Pseudomonas* and *Actinomicetes* (Schöller et al., 1997; Wilkins, 1996). It represents also a precursor of atmospheric aerosols which hence has impacts on climate and health (Ayers and Cainey, 2007).

Propene is also in our list of characteristic compound, and was reported by Zhao et al. (2016) from amended agricultural soil as one of the most emitted compound with a significantly positive correlation between this compound and bacterial communities in soil. In Zhao et al. (2016), propene contributed to 1.1% of the total emissions similar to what we found in this study (1.4%).

The VOCs emitted from the soil samples may derivate from the microbial activity in soil. In fact, different VOCs derive from several metabolic pathways. Fermentative pathways such as ethanol fermentation, with acetaldehyde as an intermediate product, and butyric acid, acetone and methanol fermentation take part of the microorganisms' primary metabolism (Castaldelli et al., 2003; Karl et al., 2003; Raza et al., 2017). On the other hand, more complex molecule with a higher molecular weight may derive from secondary metabolism pathways, such as production of signalling compounds or antibiotics (Mathivanan et al., 2008; Splivallo, 2008; Wheatley, 2002).

It is important to bear in mind in the previous discussion that our measurement set up was giving potential emissions since zero air was supplied at the chamber inlets. This may have led to marked differences when compared to other in-situ measurements that captured the bi-directionality of some fluxes (e.i. Mozaffar et al., 2018). Moreover, we should also stress that evaluations of percentage of total VOC emissions are sensitive to the number of peaks identified. We could hence expect larger percentages by studies using PTR-MS with small number of peaks or GC-MS focussed on certain masses compared to PTR-TOF that screens all peaks.

3.5 Effects of organic waste product applications on VOCs emission rates by soils

Total VOCs emissions were statistically higher in BIOW than in MSW (Figure 3). Despite the fact that the amount of carbon imported in these two treatments was the same over 17 years, The I_{roc} indicator which is the fraction of carbon stored in the soil to that applied was found to be lower in MSW (49% Org C) than in BIOW (77% Org C) (Lashermes et al., 2009). As a consequence, the organic matter (OM) content is higher in BIOW compared to MSW (Figure 2). This suggests that total VOC production is linked to OM content in the soil. However, the OM content is not the only driver of the total VOCs emissions, because otherwise GWS, which shows the largest OM content, would have had the highest VOCs emission which was not the case.

The BCA and ANOVA analysis show that the emitted compounds from BIOW and GWS were the most differentiated and were also differentiated from emissions by CN, MSW and FYM, which were grouped. It is noticeable that the same classification was also found in the C/N ratio of the small particle organic matter (POM) fraction reported by Paetsch et al., (2016) on the same site. Indeed, they found higher C/N ratios of these fractions in CN, MSW, FYM. Higher C/N ratios indicate higher organic matter degradability. This would mean that the VOC compounds that are mostly associated with CN, MSW and FYM treatments may be more representative of the degradation of the small fraction of POM.

Overall, BIOW emitted more alcohols and alkenes, N compounds and terpenes than the other treatments, while GWS mainly emitted more aromatic compound (**Figure S1**). Peñuelas et al., (2014) reported that bacterial VOCs emissions contain mostly alkenes, ketones, terpenes and pyrazines while fungi emit more aldehydes, benzenoids, nitriles and alkynes. We could hence argue that BIOW promote bacterial-mediated VOCs emissions as shown by the dominance of alkenes and terpenes, and also by the larger total VOC emissions (Figure 3a). Since, BIOW has also the lowest VOC diversity index; this suggests that BIOW may promote more specific VOC emission processes than other treatments.

A notable difference in the measured soil characteristics between BIOW and GWS treatments is the soil pH. Since soil pH affects nutrient availability and the physiological state of microorganisms, we could also expect that pH may affect VOCs emission profiles. Insam and Seewald, (2010) reported that VOC are largely adsorbed by the mineral and organic fraction of soil. This adsorption depends on soil pH, with higher adsorption in alkaline soils and lowers in acid soils. We tend to observe a complex dependency to pH which also interacts with organic matter. The total emission of VOC tends indeed to increase with the product of pH with organic matter (Figure S2).

Furthermore, it has been shown by Seewald et al. (2010) that anaerobic conditions lead to increased amount and diversity of VOCs emitted as opposed to aerobic conditions that leads to CO_2 as the end product of microbial decomposition. The increase of soil organic matter in treatments receiving OWP is known to improve soil structure and aggregate stability (Annabi et al., 2007; Diacono and Montemurro, 2010). Gupta and Larson, (1979) have shown that OM content increases water soil retention which may promote anaerobic conditions in microsites and hence modify VOC emission diversity and amounts. OM content may also modify the porosity and hence gas diffusivity which can affect the emission and storage processes of VOCs in soil system (Penuelas et al., 2014). One should however keep in mind that the soils used in our study were sieved before VOCs analysis, which would suppress any effects of OM on soil porosity above 2 mm.

According to the BCA and ANOVA analysis, GWS and BIOW have different VOC emission spectra: 21 compounds were found to have statistically different emissions between the treatments. BIOW released more acetone, more 74.06 m/z (unidentified compound), and $C_3H_8O_2$ (77.05 m/z). At this stage we are not able to say why the BIOW samples released these three compounds in higher quantities than the other samples. What we can conclude is that the compounds cited above can be used as marker compounds for the bio-waste treatment. The GWS treatment has other marker compounds such as: 94.03 m/z, 95.02 m/z, 110.06 m/z (benzamide), 111.07 m/z and 113.01 m/z. Benzamide is an intermediate compound produced by microorganisms during the degradation of 2,6-dichlorobenzonitrile which is a persistent herbicide in soil (Holtze et al., 2006). The last herbicide application was two years before the sampling period. The content of Benzamide could be related also to the herbicide present in the green wastes used for the GWS compost. Similarly, CN can be differentiated from the other treatments with high emissions of 136.02 m/z and 221.15 m/z. For the FYM and MSW no distinctive compound was found.

4 Conclusions

Our results confirmed that VOCs emissions were affected by the type of organic waste product in soil. Overall, the most emitted compounds were acetone, butanone and acetaldehyde in all treatments. We further found that 21 compounds had statistically different emissions between the treatments. We hence suggest that a certain number of VOCs could be used as marker of soils. For instance, GWS released more 94.03 m/z, 95.02 m/z, 110.06 m/z (benzamide), 111.07 m/z and 113.01 m/z than the other OWPs. These differences can be explained by abiotic factors among which pH and temperature, and biotic factors, such as the presence of certain microorganisms in soil. We also observed that organic matter content and pH jointly influenced total VOC emissions, with larger emissions for higher pH and OM content. Our results also suggest that the VOC emissions profiles are linked to C/N ratio of the small fraction of particulate organic matter which is an indicator of OM degradability. It is difficult to draw conclusions concerning the biological pathway (i.e. degradation of sugar, mineralisation of the organic matter ;..) leading to VOCs emissions observed. Other analysis of microorganisms' activity and diversity are necessary to unveil these aspects.

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