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2

## 3 **Profiles of volatile organic compound emissions from soils**

### 4 **amended with organic waste products**

5 Letizia Abis <sup>1,2</sup>, Benjamin Loubet<sup>2</sup>, Raluca Ciuraru <sup>2</sup>, Florence Lafouge <sup>2</sup>, Samuel Dequiedt <sup>3</sup>, Sabine Houot<sup>2</sup>,  
6 Pierre Alain Maron<sup>3</sup>, Sophie Bourgeteau-Sadet <sup>3</sup>

7 <sup>1</sup>INRA UMR ECOSYS, INRA, AgroParisTech, Université Paris-Saclay, F-78850 Thiverval-Grignon, France,  
8 Sorbonne Université, UPMC

9 <sup>2</sup>INRA, UMR ECOSYS, INRA, AgroParisTech, Université Paris-Saclay, 78850, Thiverval-Grignon, France

10 <sup>3</sup>INRA, UMR AgroEcologie, AgroSup Dijon, BP 87999, 21079 Dijon cedex, France

11 Corresponding author: [letizia.abis@inra.fr](mailto:letizia.abis@inra.fr)

#### 12 **Abstract**

13 This study investigates the Volatile Organic Compounds (VOCs) emitted from soil amended with four different  
14 organic waste products (OWP) every two years since 1998 and until now at a rate of ~4 tC ha<sup>-1</sup>: municipal solid  
15 waste compost (MSW), green waste and sludge co-compost (GWS), bio-waste compost (BIOW) and farmyard  
16 manure (FYM). Soil samples were collected two years after the last application of OWP. The aim of this study  
17 was to detect different VOCs emissions from soils amended with OWP in order to establish a VOCs signature of  
18 the OWP and to understand if the total VOCs flux depends on the type of OWP in soil. They were compared to a  
19 soil which received no organic inputs (CN). The emissions were detected using a PTR-ToF-MS (Proton Transfer  
20 Reaction-Time of Flight-Mass Spectrometry). OWP in soil were detected using a laboratory system made of two  
21 pyrex chambers, one with samples and the second one empty. The on-line detection has been made measuring in  
22 first place the empty chamber in order to have a blank; secondly, a measure of the emissions in the chamber with  
23 the soil has been performed. Our results confirmed that VOCs emissions were affected by the type of organic  
24 amendment to soil. Overall, the most emitted compounds were acetone, butanone and acetaldehyde in all  
25 treatments. We found some compounds which had statistically different emissions between the treatments. For  
26 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

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

29

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

## 31 **1 Introduction**

32 The family of volatile organic compounds (VOCs) is composed of a large range of molecules with different  
33 functional groups and different chemical and physical properties. The common traits between VOCs are the high  
34 vapour pressure under ambient conditions and low boiling points which explain their presence in the atmosphere.  
35 Volatile organic compounds sources have been extensively studied because of their contribution to global warming  
36 and pollution (Kesselmeier and Staudt, 1999). It has been demonstrated that VOCs are involved in many chemical  
37 reactions in the atmosphere among which the production cycle of tropospheric ozone (O<sub>3</sub>) in combination with the  
38 NO<sub>x</sub> cycle (Seinfeld and Pandis, 2016). Another important chemical processes in the atmosphere that involves  
39 VOCs are the photolysis of formaldehyde and other carbonyls in presence of NO which are responsible of hydroxyl  
40 (OH) formation (Atkinson, 2000). Additionally, VOCs are precursors of secondary organic aerosol (SOA) (Singh  
41 et al., 1995) and are involved in the production of nitrates in the troposphere (Monson and Holland, 2001). For  
42 these reasons VOCs alter the air quality and thus they have indirectly consequences on human and ecosystems  
43 health.

44 Several studies demonstrate that biogenic VOCs contribute to 90% of the total VOCs emissions (Atkinson, 2000),  
45 while anthropogenic sources such as industries, solvents, transportations etc. contribute only for the 10% of the  
46 total VOCs emissions. Among the most important biogenic sources of VOCs are living plants, with a global  
47 emission of 1Pg C y<sup>-1</sup>, mainly monoterpenes from broadleaves forests (Guenther et al., 1995; Zemankova and  
48 Brechler, 2010; Harrison et al., 2013). Furthermore, it has been shown that the soil and litter can release around  
49 12 to 136 % of monoterpenes compared to canopy emissions in spring and fall (Faiola et al., 2014).

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

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

58 From another perspective, intensive agriculture may lead to the decrease of soil organic matter contents (Chan et  
59 al., 2002) and Europe is encouraging the use of organic waste products (OWPs) in crops (European Commission,  
60 2010) to favour carbon storage in soils (Peltre et al., 2012). The recycling of OWPs in soils also represents an  
61 alternative to waste management by landfilling or incineration. The application of OWPs also provides nutrients  
62 such as nitrogen (N) and phosphorous (P) which make possible the substitution of mineral fertilizer, improves soil  
63 biodiversity and has positive impacts on soil physical properties such as aggregate stability (Annabi et al., 2007;  
64 Diacono and Montemurro, 2010). The negative impacts are not negligible though; for instance OWP release  
65 contaminants that can be transferred to plants, water or to the atmosphere (Belon et al., 2012). Organic wastes also  
66 affect soil pH, and pH is one of the chemical properties that impact on VOCs emissions (Brinton, 1998). Positive  
67 and negative impacts in soil vary with the applied organic waste product (Obriot et al., 2016). For example Seewald  
68 et al. (2010) studied VOCs production by adding glucose to soils regularly amended by different composts. There  
69 was no impact on the VOCs emissions compared to control sample with one of the composts, while for another  
70 one and mineral fertilization they observed different VOCs emissions. Moreover, Potard et al. (2017) showed that  
71 different soil organic fertilizers such as pig slurry and methanized pig slurry impact in a different way soil VOCs  
72 emissions: pig slurry releases double quantities of VOCs while methanized pig slurry emits even less than the  
73 unamended samples. Contrasting type of VOCs emissions from soil have been reported from several studies. For  
74 instance, in Mediterranean soils the most emitted compound was methanol (Asensio et al., 2007a) while in soil  
75 amended with straw it was acetone (Zhao et al., 2016). In fact, emissions of VOCs are strongly related to the  
76 substrate quality and it is important to note that even small variations in nutrient composition may change the type  
77 and the amount of individual VOCs produced (Wheatley, 2002).

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

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

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

## 103 **2 Methods**

### 104 **2.1 Site description**

105 Samples were collected in the QualiAgro site, a field station taking part of the SOERE-PRO-network  
106 ([https://www6.inra.fr/qualiagro\\_eng/Nos-partenaires/The-SOERE-PRO-network](https://www6.inra.fr/qualiagro_eng/Nos-partenaires/The-SOERE-PRO-network)). The QualiAgro site is located  
107 at Feucherolles in northwestern France (35 km west of Paris; 48°52'N, 1°57'E, alt 150 m), on a silt loam textured  
108 soil. The soil of QualiAgro site of Feucherolles is classified as a hortic glossic Luvisol (IUSS Working Group  
109 WRB, 2014), representative of the Parisian Basin. The main characteristics of these soils are represented by the  
110 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)  
111 and good drainage. Moreover, the Qualiagro field experiment is in a cropland dominated region, which lead to a  
112 low organic carbon and low organic matter concentrations (initial content of 1.1%) (Meersmans et al., 2012). On

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

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

## 127 **2.2 Experimental setup**

### 128 **2.2.1 Soil analysis**

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

### 135 **2.2.2 Soil sample preparation for PTR-TOF-MS analysis**

136 Samples of the same plot were mixed and homogenized by passing through a 2 mm sieve to remove aboveground  
137 plant materials, roots and stones, then dried up at room temperature ( $\sim 23^\circ\text{C}$ ) for 2 weeks.

### 138 **2.2.3 Laboratory flux chambers**

139 In order to measure VOC emissions, soil samples were first moisturised to the field capacity by adding ultrapure  
140 water (resistivity  $18.2 \text{ M}\Omega$ ). The amount of water necessary was determined on a sub-sample and used for all

141 samples (15 mL of water for each sample). Soil samples were then inserted, one at a time, in a pyrex chamber  
 142 having a volume of 106 cm<sup>3</sup>. The quantity of soil inserted in the chamber ( $m_{dry\ soil}$ ) was 60 g (dry mass) for each  
 143 measurement. Soil was homogeneously spread on the chamber surface (132 cm<sup>2</sup>). An empty chamber was used as  
 144 a reference for zero emissions. **Figure 1** represents the design of the measurement scheme. An air flow ( $Q_{air}$ ) of  
 145 0.2 L min<sup>-1</sup> (equivalent volumetric flow at 0°C and 1 atm) of dry synthetic air (Alphagaz 1 Air: 80% nitrogen, 20%  
 146 oxygen, 99.9999%, Air Liquide®) was passed through a hydrocarbons and humidity filter (Filter for fuel gas, final  
 147 purity=99.999%, Restek®) and a Hydrocarbon Trap (Supelco, Supelpure® HC) prior to injection in the chambers.  
 148 A mass flowmeter (Bronkhorst® model F-201CV, accuracy: standard 0.5% Rd plus 0.1% FS, range: 0.2 L min<sup>-1</sup>  
 149 to 5 L min<sup>-1</sup> air) was used to control the synthetic air flow rate. Air was sampled at the chamber outlet into a PTR-  
 150 ToF-MS with a 0.05 L min<sup>-1</sup> flow rate with a 2 m long, 1 mm internal diameter PEEK tube, heated at 80 °C. A  
 151 measurement cycle consisted in measuring the VOC mixing ratio at the outlet of the chamber containing the soil  
 152 ( $x_{VOC\ soil}$  in ppb) for 180 s. Then air was sampled for 120 s on the empty chamber to determine  $x_{VOC\ empty}$  (ppb).  
 153 We sampled the empty chamber less than the chamber with soil because the signal was stable after only ~10 s.  
 154 Only the last 60 s of each measurement were kept to calculate averaged mixing ratios in order to ensure a stable  
 155 VOCs mixing ratio. The VOC emission ( $E_{VOC}$  in nmol g<sup>-1</sup> s<sup>-1</sup> dry soil) was calculated as:

$$156 \quad E_{VOC} = \frac{Q_{air} \times (x_{VOC\ soil} - x_{VOC\ empty})}{V_{mol}^{air} \times m_{dry\ soil}} \quad (1)$$

157 Where  $V_{mol}^{air}$  is the air molar volume at standard temperature and pressure (22.4 L mol<sup>-1</sup> at 0°C and 1 atm). In total  
 158 15 samples were measured: 3 replicates for each of the 5 treatments. Each measurement was further repeated 3  
 159 times to compute the mean and standard deviation of the measurement. This led to 45 measurements in total. After  
 160 each measurement, the chamber was cleaned with diluted sodium hydroxide in order to destroy any organic  
 161 compound that could affect the next measurements, and then rinsed with ultrapure water (resistivity 18.2 MΩ).

162

### 163 **2.3 VOC analysis with the proton transfer reaction time of flight mass spectrometer (PTR-TOF-MS)**

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

169 digital converter (Burle Industries Inc., Lancaster, PA, USA). In this study, ionisation was carried out with  $\text{H}_3\text{O}^+$   
170 as proton donor. The transfer reaction was effective for VOCs with a proton affinity higher than  $691.7\text{kJ mol}^{-1}$ ,  
171 which is the proton affinity of the water. In the drift tube, the pressure was tuned to 4 mbar, the temperature to  
172  $80^\circ\text{C}$ , and the drift voltage to 1000 V, while the extraction voltage at the end of the tube (UDx) was 44 V. The E/N  
173 ratio (Electric field/density of natural particles) was 132 Td where 1 Td is  $10\text{ V m}^2$ . These parameters were  
174 controlled in order to maintain constant ionization conditions within the drift tube. The setup of the time of flight  
175 timing was: TOF extraction period 40000 ns, pulse width 2000 ns, trigger delay 100 ns. The number of channels  
176 was 240.000. This gave a mass spectrum measurement up to 510 m/z. The measurement period was set to 1 s,  
177 which means that each sample corresponded to 60 acquisitions of 25000 individual spectra. Raw PTR-ToF-MS  
178 data were recorded by TofDaq software (Tofwerk AG, Switzerland).

### 179 **2.3.1 Peak detection of the mass spectra and mass calibration**

180 We used the PTR viewer 3.1.0.29 software (Ionicon, Analytik GmbH) to detect mass peaks in each spectrum. The  
181 mass calibration was performed using the oxygen isotope of the ion source  $\text{H}_3^{18}\text{O}^+$  (21.022 m/z) and acetone,  
182  $\text{C}_3\text{H}_7\text{O}^+$ , (59.0449 m/z). These two were chosen as they were present in all samples. Mass calibration was made  
183 over the entire dataset allowing for a change of 0.1 m/z around the peak maximum between consecutive samples  
184 and using a moving average of 50 successive samples for better stability. Overall the instrument resolution was  
185 around 4000. In order to create a peak table including the largest number of peaks, we used the automatic research  
186 feature of the software selecting as search mode “multiple peaks” with a threshold of 5 counts per second.  
187 Following this step, a manual check of each peak was performed in order to correct for any software miss-fits.  
188 Each peak was manually readjusted. The modes used to auto-select and manually adjust the peak areas that are  
189 used for mixing ratio calculation were the Gaussian or the multi-peak modes. The Gaussian peak mode was used  
190 for the analysis of isolated peaks; while for a better fit of multiple peaks we used the multi-peak mode. The range  
191 of the mass detection was limited between 31 and 400 m/z. Finally, masses deriving from the water cluster such  
192 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.

### 193 **2.3.2 Isotopes and fragments identification**

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



197 coefficient larger than 0.99 were considered either fragments or isotopes depending on the m/z difference. In total  
198 16 isotopes and 2 likely fragments were identified (Table S1).

### 199 2.3.3 PTR-TOF-MS mixing ratio calibration

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

$$203 \chi_{i \text{ standard transmission}} = 1.657 e^{-11 \frac{U_{\text{drift}} T_{\text{act}}^2 [\text{K}]}{k p_{\text{act}}^2 [\text{lbar}]}} \frac{R^+}{\text{H}_3\text{O}^+} \frac{\text{TR}_{\text{H}_3\text{O}^+}}{\text{TR}_{\text{R}^+}} \quad (2)$$

204 Where  $\chi_{i \text{ standard transmission}}$  is the mixing ratio of the compound in ppb,  $U_{\text{drift}}$  is the voltage of the drift (V),  $T_{\text{act}}$   
205 is the drift-tube temperature in Kelvin,  $R^+$  is the signal of the product ion in count per second (cps),  $k$  is the  
206 protonation reaction rate constant ( $2 \cdot 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ ) assumed equal for all compounds,  $\text{TR}_{\text{H}_3\text{O}^+}$  is the transmission  
207 factor for mass of primary ion,  $\text{TR}_{\text{R}^+}$  is the transmission factor for mass of product,  $p_{\text{act}}$  is the pressure of the drift,  
208 ion  $\text{H}_3\text{O}^+$  is the primary ions signal in cps. The standard transmission curve from supplier was used to compute  
209  $\text{TR}_{\text{H}_3\text{O}^+}/\text{TR}_{\text{R}^+}$  (see Table S2 in supplementary material).

210 We used the following primary ions mass: 21.02 m/z ( $\text{H}_3^{18}\text{O}^+$ , multiplier factor 487.56), 38.03 m/z (water cluster  
211  $\text{H}_2^{18}\text{O} \cdot \text{H}_3^{18}\text{O}^+$  with two  $^{18}\text{O}$  isotopes, multiplier factor 819.51) and mass 55.03 m/z ( $\text{H}_2\text{O} \cdot \text{H}_3\text{O}^+ \cdot \text{H}_3\text{O}^+$  multiplier  
212 factor 1.0008).

213 In order to account for the normal loss of sensitivity of the PTR-TOF-MS, due to the MCP degradation over time,  
214 the change of  $\text{H}_3^{18}\text{O}^+$  produced in the source, or other factors, we used a calibration procedure to account for the  
215 actual sensitivity of the analyser. We used benzene, toluene and ethylbenzene as reference compounds for this  
216 calibration. The mixing ratio of these compounds was modulated using a dilution system with a standard cylinder  
217 containing 102 ppb of benzene, 104 ppb of toluene, 130 ppb of ethylbenzene and 336 ppb of xylene (Btex,  
218 Messer®). We used the same synthetic air for the dilution system as the one described for the chamber set up. The  
219 sensitivity  $S^{\text{norm}}$  was calculated as the slope of the regression between measured mixing ratio with the standard  
220 transmission provided by Ionicon and mixing ratio calculated with equation (2), and forcing a zero intercept. The  
221 calibrated mixing ratio of all compounds was then calculated as:

$$222 \chi_i = \left[ \chi_{i \text{ standard transmission}} - \chi_{i(0)} \right] \times S^{\text{norm}} \quad (3)$$

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

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

#### 229 **2.3.4 VOC identification**

230 We first identified the molecular formula with the Spectra Analyser within the PTR viewer 3.1.0.29 software  
231 (Ionicon, Analytik GmbH). The spectra analyser is a tool that allows the manual selection of the peaks chosen for  
232 the identification. The identification of the compounds corresponding to each mass peak was performed by  
233 searching the possible combinations of elements that led to the closest molecular weight. The following elements  
234 were selected for all peaks: C, N, O and H. Other compounds were selected on purpose for masses higher than 70  
235 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  
236 maximum number of atoms per molecule was set to 50, while the error on the molecular weight was fixed to  $\pm 0.01$   
237 m/z. Subsequently, a list of possible compounds was produced. The compounds listed represent the best matches  
238 for the selected exact m/z. Finally, a match of the isotopes of each compound was evaluated. Once the molecular  
239 formula was determined, we tried to identify the potential compounds with the use of the literature reviews. We  
240 have to stress that this method does not provide an undoubtable identification of the compounds as several  
241 compounds could have the same molecular mass but not the same chemical structure. Moreover, even with this  
242 procedure, some compounds could not be identified at all.

#### 243 **2.4 Statistical analysis**

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

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

## 254 **3 RESULTS**

### 255 **3.1 Soil characteristics of each treatment**

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

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

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

280

### 281 3.2 VOCs Emissions

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

### 289 3.3 Differentiating VOCs for each treatment

290 In order to determine if OWP amended soils affect the profile of VOCs emissions, we performed a Between  
291 Component Analysis (BCA). The first two components of the BCA explained 40.2% and 33.8% of the total dataset  
292 variability. In **Figure 4** we observe that GWS and BIOW treatments are isolated from the other OWP (FYM, MSW  
293 and CN), which means that they have a VOC profile which is different from the other OWP. The VOCs that most  
294 explained the variance in the two first components of the BCA were selected as those having a coordinate larger  
295 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  
296 **Figure 4**. The tentative identification of the compound listed above is shown in **Table S4**.

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

## 306 DISCUSSION

### 307 3.4 Identification and quantification of VOCs emitted

#### 308 3.4.1 Most emitted VOCs: acetone, butanone, acetaldehyde, methanol, isoprene and ethanol

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

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

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

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

337 The third most emitted compound from soil was acetaldehyde which was detected by Asensio et al. (2007a) as the  
338 second most emitted compound from their Mediterranean soil samples. Schade and Goldstein (2001) detected a  
339 flux of acetaldehyde of  $100 \mu\text{g m}^{-2} \text{h}^{-1}$  at  $24^\circ\text{C}$  quite similar to what we found  $\sim 280 \mu\text{g m}^{-2} \text{h}^{-1}$ . Similar to this study,  
340 though smaller, Peñuelas et al., (2014) reported between 2 and  $100 \mu\text{g m}^{-2} \text{h}^{-1}$  emissions of acetaldehyde for  
341 different type of soil, such as: forest soil, ponderosa pine plantation and shrubland soil. Gray et al., (2014) reported  
342 much smaller emissions ( $0.2 \mu\text{g m}^{-2} \text{h}^{-1}$ ), but demonstrated that acetaldehyde emissions were largely coming from  
343 the roots system which was partly removed from our measurements by sieving at 2 mm. Mancuso et al. (2015)  
344 also detected acetaldehyde as the most emitted compound. It is noticeable that acetaldehyde is an oxidation product  
345 of ethanol. We should also stress that measurements of acetaldehyde with PTR-MS (not TOF ones) may catch  
346 some  $\text{CO}_2\text{H}^+$  and hence include some soil respiration. Indeed, although  $\text{CO}_2$  has a proton-affinity lower than the  
347 one of water, we found that  $\text{CO}_2$  was protonated in our TOF at  $m/z = 44.997$  (Loubet, personal communication).

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

363 stress that methanol, as a soluble compound is adsorbed and desorbed from water films (Laffineur et al., 2012).  
364 This mechanism may have boosted emissions due to water evaporation in the chamber exposed to dry air.  
365 Isoprene was reported as a compound emitted by agricultural soils amended with straw at only 0.1% of the total  
366 emissions by Zhao et al. (2016). Our results showed that around 6% of the total VOCs emissions were represented  
367 by isoprene emissions. Mancuso et al. (2015) measured isoprene emissions from agricultural and forest soil  
368 samples. Isoprene is a metabolite directly related to the presence of microorganisms in soil even if the role of this  
369 compound in microorganisms cell has not been clarified yet (Hess et al., 2013).  
370 Ethanol is one of the compounds emitted during the sugar degradation as showed by Seewald et al. (2010). Schade  
371 and Goldstein (2001) reported emission of ethanol from bare soil between 300 and 500  $\mu\text{g m}^{-2} \text{h}^{-1}$  while we found  
372 lower emissions around 100  $\mu\text{g m}^{-2} \text{h}^{-1}$ .

#### 373 **3.4.2 Other compounds detected**

374 Several aromatic compounds have been observed as emitted from our soil samples. Microorganisms and plants  
375 release aromatic compounds through the shikimate pathway or by the degradation of phenylalanine or tyrosine.  
376 Aromatic compounds are known to be emitted by plants under stress conditions (Misztal et al., 2015) and absorbed  
377 by humic substances in soil (Lu and Pignatello, 2004). Toluene is one of the aromatic compounds most emitted by  
378 our samples, but in a similar amount between treatments which was also reported by Asensio et al. (2007b).  
379 Toluene is rather a compound linked to oil, either natural (crude oil) or from derivatives, such as solvents, gasoline  
380 or other fuels as well as in the production process of coke from coal. The flux of this compound from soil is always  
381 very low but due to the several impacts that this compound might have on the health is important to quantify and  
382 characterize the emissions. It is interesting to notice that we also detected monoterpenes and p-cymene, which is  
383 an aromatic compound formed by the oxidation of monoterpenes (Gratien et al., 2011). We found around 0.018  
384  $\text{nmol m}^{-2} \text{s}^{-1}$  which is higher than the range of monoterpenes emissions detected by Asensio et al. (2007a) (between  
385  $-0.004 \text{ nmol m}^{-2} \text{s}^{-1}$  and  $0.004 \text{ nmol m}^{-2} \text{s}^{-1}$ ). Hayward et al. (2001) reported that emissions of monoterpenes from  
386 soil of Sitka spruce forest were  $0.026 \text{ nmol m}^{-2} \text{s}^{-1}$ , and were strongly related to soil temperature (Raza et al., 2017).  
387 It is also known that monoterpene emissions from forests exceed those from agriculture (Guenther, 1997;  
388 Kesselmeier and Staudt, 1999). Assuming soil emissions are linked to plant residues degradation in the soil this  
389 might explain the higher emissions from forest's soils compared to what we find here.

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

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

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

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

406 It is important to bear in mind in the previous discussion that our measurement set up was giving potential  
407 emissions since zero air was supplied at the chamber inlets. This may have led to marked differences when  
408 compared to other in-situ measurements that captured the bi-directionality of some fluxes (e.i. Mozaffar et al.,  
409 2018). Moreover, we should also stress that evaluations of percentage of total VOC emissions are sensitive to the  
410 number of peaks identified. We could hence expect larger percentages by studies using PTR-MS with small  
411 number of peaks or GC-MS focussed on certain masses compared to PTR-TOF that screens all peaks.

### 412 **3.5 Effects of organic waste product applications on VOCs emission rates by soils**

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



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

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

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

440 Furthermore, it has been shown by Seewald et al. (2010) that anaerobic conditions lead to increased  
441 amount and diversity of VOCs emitted as opposed to aerobic conditions that leads to CO<sub>2</sub> as the end product of  
442 microbial decomposition. The increase of soil organic matter in treatments receiving OWP is known to improve  
443 soil structure and aggregate stability (Annabi et al., 2007; Diacono and Montemurro, 2010). Gupta and Larson,  
444 (1979) have shown that OM content increases water soil retention which may promote anaerobic conditions in  
445 microsites and hence modify VOC emission diversity and amounts. OM content may also modify the porosity and  
446 hence gas diffusivity which can affect the emission and storage processes of VOCs in soil system (Penuelas et al.,  
447 2014). One should however keep in mind that the soils used in our study were sieved before VOCs analysis, which  
448 would suppress any effects of OM on soil porosity above 2 mm.

449 According to the BCA and ANOVA analysis, GWS and BLOW have different VOC emission spectra: 21  
450 compounds were found to have statistically different emissions between the treatments. BLOW released more  
451 acetone, more 74.06 m/z (unidentified compound), and C<sub>3</sub>H<sub>8</sub>O<sub>2</sub> (77.05 m/z). At this stage we are not able to say  
452 why the BLOW samples released these three compounds in higher quantities than the other samples. What we can  
453 conclude is that the compounds cited above can be used as marker compounds for the bio-waste treatment. The  
454 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  
455 and 113.01 m/z. Benzamide is an intermediate compound produced by microorganisms during the degradation of  
456 2,6-dichlorobenzonitrile which is a persistent herbicide in soil (Holtze et al., 2006). The last herbicide application  
457 was two years before the sampling period. The content of Benzamide could be related also to the herbicide present  
458 in the green wastes used for the GWS compost. Similarly, CN can be differentiated from the other treatments with  
459 high emissions of 136.02 m/z and 221.15 m/z. For the FYM and MSW no distinctive compound was found.

#### 460 **4 Conclusions**

461 Our results confirmed that VOCs emissions were affected by the type of organic waste product in soil. Overall,  
462 the most emitted compounds were acetone, butanone and acetaldehyde in all treatments. We further found that 21  
463 compounds had statistically different emissions between the treatments. We hence suggest that a certain number  
464 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  
465 (benzamide), 111.07 m/z and 113.01 m/z than the other OWPs. These differences can be explained by abiotic  
466 factors among which pH and temperature, and biotic factors, such as the presence of certain microorganisms in  
467 soil. We also observed that organic matter content and pH jointly influenced total VOC emissions, with larger  
468 emissions for higher pH and OM content. Our results also suggest that the VOC emissions profiles are linked to  
469 C/N ratio of the small fraction of particulate organic matter which is an indicator of OM degradability. It is difficult  
470 to draw conclusions concerning the biological pathway (i.e. degradation of sugar, mineralisation of the organic  
471 matter ;..) leading to VOCs emissions observed. Other analysis of microorganisms' activity and diversity are  
472 necessary to unveil these aspects.

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