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Effect of senescence on biogenic volatile organic compound fluxes in wheat plants

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Abstract. Exchanges of biogenic volatile organic compounds (BVOC) between plants and the 12 13 atmosphere are likely to vary, in amount and composition, between different plant species but 14 also for a single plant during its development. However, the effect of plant development stages, including senescence, on BVOC exchanges remains poorly investigated, especially in the case of 15 crop plants. We investigated the BVOC exchange patterns for wheat plants, the most grown crop 16 17 species worldwide, during seed maturation, senescence and after harvest. Fluxes were measured 18 online, in situ, at the plant scale by combining automated chambers and a Proton Transfer -19 Reaction - Quadrupole ion guide - Time of Flight - Mass Spectrometer (PTR-Qi-Tof-MS). The 20 high resolution and sensitivity of this method enabled the measurement of a large mass spectrum of compounds emitted at very small amounts, allowing a precise characterization of BVOC 21 22 exchanges. We found that the overall BVOC emissions increased twofold during the senescence 23 stage compared to the maturation stage. Methanol was found to be the most emitted compound (49 - 60%) of the overall flux on a molar basis) followed by acetone (7.5 - 8.2%) of the overall 24 25 flux on a molar basis) during each developmental stage investigated. Acetaldehyde was another 26 major emitted compound contributing mainly during late senescence to the overall flux (9.7%). 27 When normalized for temperature and light conditions, most BVOC emissions increased during 28 senescence, showing a clear effect of senescence on BVOC exchanges. Chamber emissions were 29 comparable to whole ecosystem fluxes measured at the same site by eddy covariance the previous 30 year. The OH reactivity of the emitted compounds was evaluated based on known reaction rate 31 constants and was the largest during the first senescence stage, peaking at 12 s⁻¹ in the chambers. 32 The results of this study show the need for considering plant phenology when computing BVOC 33 emissions from crops.

34 Keywords: BVOC, dynamic chamber, crop, development stage, PTR-Qi-Tof-MS.

35 1. Introduction

36 Plants synthesize and release an incredible diversity of volatile organic compounds (VOCs) into 37 the atmosphere; more than 1700 biogenic VOCs (BVOCs) have already been identified (Knudsen et al. 2006). BVOC emissions from terrestrial vegetation are estimated to be 760 Tg (C) yr⁻¹ 38 39 representing 90% of total emissions at global scale (Sindelarova et al., 2014). Besides the 40 importance of these compounds in the interaction between plants and their environment, BVOCs 41 are known to impact air quality, climate, human health and vegetation. Indeed BVOCs contribute 42 to the formation of tropospheric ozone (Fehsenfeld et al., 1992), of secondary organic aerosols 43 (SOA) (Ziemann and Atkinson, 2012) and increase the lifetime of methane in the atmosphere by 44 reducing the oxidative capacity of the atmosphere (Isaksen et al., 2009). These issues explain the 45 growing interest, over the last decades, in BVOC emissions into the atmosphere.

BVOC species are diverse and include several organic classes such as terpenes, fatty acid
derivatives, alcohols, alkanes, alkenes, esters and acids, among others (Pichersky and Gershenzon

48 2002; Peñuelas and Llusià 2001). Several factors influence - quantitatively and qualitatively -49 BVOC exchanges between plants and the atmosphere. First, the biosynthesis of VOCs by plants 50 is strongly linked to the genetic information of the plant (Degen et al. 2004; Delphia et al. 2009; 51 Splivallo et al. 2012). Thus, emissions of these compounds vary greatly from one species to 52 another and even within the same plant species (Gonzaga Gomez et al., 2019; Splivallo et al., 53 2012). Secondly, BVOC exchanges depend also on environmental factors, such as temperature, light, relative humidity, atmospheric CO₂ and O₃ concentrations, nutrient availability and soil 54 55 moisture (Gouinguené and Turlings, 2002; Laothawornkitkul et al., 2009; Staudt and Bertin, 56 1998). Finally, it has been shown that BVOC exchanges depend also on specific characteristics of 57 the plant, varying for example during plant development (Bachy, 2018; Bracho-Nunez et al., 58 2011; Mozaffar et al., 2018; Rottenberger et al., 2005).

59 BVOC exchanges during different developmental plant stages have so far been poorly 60 investigated. In addition, most of the existing studies have focused mainly on the developmental 61 effect on isoprenoids and methanol emissions. For example, it has been reported that methanol 62 emissions are strongly associated with plant growth (Bracho-Nunez et al., 2011). Indeed, this 63 compound is formed in plants from the demethylation of pectin, a mechanism occurring during 64 cell wall alteration (Fall and Benson, 1996). An increase in emissions of this compound has also 65 been observed during leaf senescence of maize plants (Mozaffar et al., 2018). It has also been 66 shown that isoprene emission is lower in young leaves than in mature leaves. This may be due to a higher respiration rate competing for pyruvate, a common substrate to isoprene biosynthesis 67 68 and respiratory processes (Loreto et al., 2007). Other examples are monoterpenes, sesquiterpenes 69 and acetone showing higher emission rates in young leaves and reduced or non-existent 70 emissions rates at leaf maturity (Bracho-Nunez et al., 2011).

71 It has been estimated that agricultural crops in Europe account for 27% of the overall BVOC 72 emissions (Karl et al., 2009), which represents a non-negligible contribution. Despite the species-73 specific dependence of BVOC emissions, as mentioned before, most studies have focused on 74 BVOC fluxes from trees and thus on isoprenoids. For this reason fluxes from agricultural plant 75 species, which appear to be dominated by oxygenated VOCs (Karl, 2009), remain poorly 76 understood. These estimates are in fact mostly based on measurements made on a few plant 77 species, over a short time period and with analytical constraints. Therefore, since these 78 measurements may not be representative of the variety of crops, and regions, the contribution of 79 these ecosystems to the overall BVOC emissions remains inaccurate.

80 The widely used MEGAN 2.1 model (Guenther et al., 2012) provides estimates of BVOC 81 emissions from terrestrial ecosystems. Despite the recent improvement of this model, the 82 estimated emission rates from crops remain inaccurate (Guenther et al., 2012). This is mainly due 83 to the assignment of emission factors by default to all crop species given the lack of emission rate 84 measurements on these species. Indeed in MEGAN 2.1 crop plant species are all grouped into 85 one "functional plant type" for which one emission factor value is attributed. Current knowledge, 86 however shows that BVOC emissions vary strongly (composition and amounts) between species 87 and even between varieties of the same species (Gonzaga Gomez et al., 2019). Thus, emission 88 factors should be better investigated on most grown crop species such as wheat, rice, maize or 89 oilseed rape. In addition, despite the dependence of VOC emissions on the plant's age, in the 90 MEGAN 2.1 model, the plant developmental stage is not taken into account when estimating 91 emissions for all oxygenated compounds, apart from methanol. In order to achieve a more 92 reliable estimate of these emissions, more accurate emission factors for individual crop plants are 93 needed, as well as a better understanding of how the different drivers (e.g. light, temperature,
94 age) influence BVOC exchanges.

95 Wheat is the most widely grown crop in the world and in Europe, representing more than 15 % 96 and 33 % (FAOSTATS 2017) of the total croplands cultivated surface, respectively. However, 97 the studies on BVOC emissions from wheat plants are quite limited and show a large divergence 98 between results (Bachy, 2018; Butter et al., 1985; Gallagher et al., 2000; König et al., 1995; 99 Morrison et al., 2016; Piesik et al., 2011; Winer et al., 1992). Recently, Bachy (2018) conducted 100 a study over a wheat field where BVOC exchanges were investigated during the whole growing 101 season at the ecosystem level. The authors found that, like for most crop species, methanol was 102 the most emitted compound and the emissions of this compound and acetaldehyde increased with 103 plant senescence. However, their study could not distinguish between emissions originating from 104 plants and from soil. In addition, flux measurements were limited to a small number of 105 compounds in order to maintain a high measurement frequency, which raises questions of other 106 VOCs that could have been overlooked.

107 In order to improve the understanding and the quantification of BVOC fluxes in wheat crops, this 108 study aims to - (a) characterize, quantitatively and qualitatively, BVOC exchanges of wheat at 109 the plant level during ripening, senescence and harvest, over a wide spectrum of compounds; (b) 110 propose physiological mechanisms explaining the variations of emissions during the investigated 111 developmental stages and discuss how climatic factors (humidity, temperature, and light) can 112 influence these emissions. To achieve these objectives a Proton Transfer - Reaction - Quadrupole 113 ion guide - Time of Flight - Mass Spectrometer (PTR-Qi-Tof-MS) was used in combination with 114 multiple dynamic automated chambers for online measurements of BVOC fluxes from wheat plants. The chamber fluxes were challenged against eddy covariance fluxes measured in a nearbyfield the year before to verify the general relevance of our results.

117 **2.** Materials and methods

118 **2.1. Site**

Flux measurements took place on a field belonging to the experimental farm of Grignon owned by AgroParisTech and located about 30 km west of Paris in France (48°51'N, 1°58'E). The site is a 2 ha field, with a crop rotation of wheat and maize since 2011, located next to the ICOS FR-Gri site on the south-east. The details about the ICOS site can be found in Loubet et al. (2011), Laufs et al. (2017) or Vuolo et al. (2017).

Wheat (*Triticum aestivum L*; Fructidor variety) was sown on October 21^{st} , 2016 and harvested on June 30^{th} , 2017. Certain agricultural practices such as fertilizer, fungicide and herbicide application are detailed in Appendix A. Indeed these practices are likely to impact the emissions of VOC by plants as well as the measurements of these compounds.

128 **2.2. Experimental campaign**

129 The measurement campaign covered the period from June 10th to July 04th, 2017. Measurements 130 were performed simultaneously on two wheat plant replicates using two automated dynamic 131 chambers, based on the original design of Pape et al. (2009), modified and detailed in Gonzaga 132 Gomez et al. (2019). The complete plant above ground was enclosed in the \approx 35 L chamber 133 placed outdoors in the field. In short, the chambers consisted of an acrylic glass (PMMA) 134 cylinder covered by a fully light-permeable FEP film (50 µm thick PTFE, MICEL). A motorized 135 lid also covered by FEP film was used to open the chambers between measurements intervals. A 136 quantum sensor (SOLEMS, PAR/CBE 80, Palaiseau, France) and a copper-constantan

137 thermocouple device ensured the continuous monitoring of air temperature and 138 Photosynthetically Active Radiation (PAR) inside the chambers. An axial fan (D341T-012GK-2, 139 MICRONEL) was used to purge ambient air into the cuvette at ≈ 14 L min⁻¹. Each chamber was 140 equipped with two twenty-meter-long PFA sampling tubes (1/8 inch internal diameter): one for 141 the inlet air (ambient air) and one for the outlet air (inside chamber air) sampling. Each of these 142 sample tubes was heated to 50°C to avoid condensation of the air until it reached the PTR-Qi-143 ToF-MS (Ionicon, Analytik GmbH, AU), which was used to measure BVOC concentration at 10 144 Hz. In the present work, the instrument was operated at drift tube pressure and temperature of 145 4 ± 0.0001 mbar and 80 ± 0.06 °C, respectively. The inlet flow rate was set to 150 ± 5.42 ml min⁻¹ 146 and the E/N value (where E is the electric field strength and N the gas density) to about 147 132 ± 0.03 Td (1 townsend = 10^{-17} V cm²). An infrared gas analyzer (Li-Cor 840 model, Li-Cor, 148 Lincoln, Nebraska, USA) was used to follow CO₂ and H₂O concentrations from the inlet and 149 outlet air sampling of each chamber. In order to determine the effect of chambers on VOC 150 measurements we previously measured on an empty chamber. We thus detected some heavy 151 compounds emitted by the chambers (m/z 118.063, 190.962 and 192.960) which were removed 152 from the analysis. Further details about the experimental device, including chambers and PTR-153 Qi-TOF-MS operation, can be found in Gonzaga Gomez et al. (2019).

154 **2.3. PTR-MS concentration**

The pre-processing steps provided averages and standard deviations of count rates (cps in counts per seconds) for the compounds (ion peaks) selected R_i. The mixing ratio of the compound χ_i (in ppbv) was calculated as in Abis et al., (2018) and Gonzaga Gomez et al. (2019):

$$158 \qquad \chi_{i} = 1.657 \ 10^{-11} \times \frac{U_{drift} T_{drift}^{2}}{k \ p_{drift}^{2}} \times \left(\frac{c p s_{R_{i}H^{+}}^{norm}}{c p s_{H_{3}O^{+}}^{norm} + c p s_{H_{2}O.H_{3}O^{+}}^{norm}} - \frac{c p s_{R_{i}H^{+}}^{norm}(z e roair)}{c p s_{H_{3}O^{+}}^{norm} + c p s_{H_{2}O.H_{3}O^{+}}^{norm}(z e roair)} \right) \times S_{i} \quad (1)$$

159
$$cps_{R_{i}H^{+}}^{norm} = \frac{TR_{H_{3}O^{+}}}{TR_{R_{i}H^{+}}} \times cps_{R_{i}H^{+}}$$

160 where U_{drift} is the voltage of the drift tube (V), T_{drift} is the drift tube temperature in Kelvin (K), $cps_{R_iH^+}$ is the count rate (cps) of the product ion, $cps_{H_3O^+}$ and cps_{H_2O,H_3O^+} are the count rates of 161 162 the source ion and the first water cluster, k is the protonation rate constant assumed identical for all compounds (2.5 10^{-9} cm³ molecule⁻¹ s⁻¹), norm stands for normalized, TR_{H₃O⁺} is the 163 transmission factor for H_3O^+ , $TR_{R_iH^+}$ is the mass-dependent transmission factor for the 164 protonated compound R_i , p_{drift} is the pressure in the drift tube, and S_i is the normalised sensitivity 165 166 of the analyzer. Here zeroair stands for the count rates measured for zero air under the same 167 conditions of pressure, temperature and voltage. The standard transmission curve from the supplier was used to compute the normalised counts per seconds $cps_{R_{i}H^{+}}^{norm}$ (Table B1, Appendix 168 B). The $cps_{H_3O^+}^{norm}$ was computed from ion m/z 21.022 (H₃¹⁸O⁺) by multiplying by the isotopic 169 170 factor 487.56, the first water cluster was taken as the ion peak m/z 37.028. The number 1.657 e^{-11} is a constant specific to the instrument, accounting for the reaction time in the drift 171 tube and detailed in Appendix B. 172

173 2.4. Mixing ratio calibration and uncertainties

 S_i was determined as explained in Gonzaga et al. (2019), section 2.9: a standard cylinder containing 102 ppbv of benzene, 104 ppbv of toluene, 130 ppbv of ethylbenzene and 336 ppbv of xylene (122 ppbv Ortho, 121 ppbv Meta, 123 ppbv Para; BTEX, Messer) was diluted with synthetic air. S_i was then computed as the slope between measured mixing ratios as computed by equation 1 when $S_i=1$, and the mixing ratio prescribed by the dilution system. Assuming that the protonation rate constant was similar for all compounds a single S_i was computed ($S_i = 2 \pm 0.15$) 180 for all compounds except methanol for which a comparison with another PTRMS itself calibrated 181 for methanol was used to determine $S_{\text{methanol}} = 15$. However, acknowledging that assuming an 182 identical protonation rate constant k, and hence a single S_i for all compounds may lead to 183 systematic errors, we evaluated this potential bias in the computed concentrations. To do so, we 184 computed the ratio S_i / S_{toluene}, using data from another experiment performed with the same 185 instrument the year before (data from Loubet et al. 2021), as well as the using data from the 186 literature (Koss et al. 2018), with an instrument similar to ours, though not exactly the same. This 187 exercise (Table B2) shows that for most compounds the systematic error made by assuming a 188 single k is limited to less than 40% error, which is the range expected from theoretical estimations 189 of k. However, for ethanol, formaldehyde, methanol and propene, the bias may be high (from ~ 3 190 to ~40), with a tendency to underestimate the actual mixing ratio. For methanol, a specific calibration was performed in this study against another PTRMS which was itself precisely 191 192 calibrated. For the ethanol, formaldehyde and propene the bias may have been be large, and 193 especially for ethanol. For monoterpenes there might also be large differences in S_{methanol}, but this 194 may be specific to the species composition at each site, since each monoterpene may fragment in 195 different patterns (Tani et al., 2003).

Since no specific calibration was performed, except for toluene and methanol during this study, we did not correct our data using the $S_i / S_{toluene}$ shown in table B2, but rather proposed alternative estimates in standard emission factors in the discussion section. Nevertheless, the calibration data from Koss et al. (2018 and Loubet et al. (2021) also provided some estimates of the overall uncertainty on the mixing ratio determination, which is also provided in Table B2 as a relative standard deviation. Assuming these relative uncertainties would be similar in different experiments, we estimated the uncertainties in mixing ratios would have been on average 15%and ranged from 1% to 100%.

204 **2.5.** Uncertainties in calculated concentrations due to humidity

205 It is well documented that PTR-MS sensitivity is strongly influenced by relative humidity (RH), 206 resulting in uncertainty in the calculated BVOC concentration (Baasandorj et al., 2015; Christian 207 et al., 2004; Feilberg et al., 2010; Kari et al., 2018; Thomas Karl et al., 2003; Pang, 2015; 208 Steinbacher, 2004). Such humidity influence can lead to either an overestimation or an 209 underestimation of the BVOC concentrations depending on the compounds considered and the 210 setting of other parameters of the PTR-MS, notably the E/N (ratio of electric field to gas density). 211 For example, several studies show a significant underestimation of formaldehyde concentrations, 212 ranging from a factor of 3 to 5, by PTR-MS with increasing humidity (Christian et al., 2004; 213 Thomas Karl et al., 2003; Steinbacher, 2004; Vlasenko et al., 2010). Baasandorj et al. (2015) 214 showed that the sensitivity of PTR-MS to acetic acid decreases with humidity when the collision 215 energy in the PTR-MS drift tube is high (E/N >125 Td). In contrast, when E/N is low, a clear 216 increase in the sensitivity of PTR-MS to acetic acid with humidity was observed by the authors. 217 Changing the water vapor pressure from 0.61 to 3 kPa at E/N 142 Td, resulted in a significant 218 decrease of 30% in the sensitivity of the PTR-MS to acetic acid (Baasandorj et al., 2015) due to 219 an increase of the fragmentation of this compound at high RH (Feilberg et al., 2010). Assuming 220 Baasandorj et al. (2015) results could be transposed to our setup, we evaluated that this effect 221 would lead to an underestimation of the deposition flux of acetic acid of 35% on average. 222 Regarding GLVs compounds, Pang et al. (2015) showed a linear increase in sensitivity with 223 increasing humidity. Sensitivities increased between 20% and 35% when the humidity increased 224 from 0 to 70%. In contrast, mono- and sesquiterpenes do not appear to show significant humidity

dependence. In general, a slight increase in sensitivity was reported for some terpenes ranging
from 1% to 4% over a wide range of relative humidity from 0% to 100% (Tani et al. 2004).

In order to minimize the effect of humidity on PTR-MS sensitivity, the chambers remained open during non-sampling periods to avoid overheating and plant over-transpiration. However, even with these precautions, changes in humidity in the sampled air may have introduced uncertainties in the calculated concentrations as discussed in this section.

231 **2.6. Leaf area and dry-weight estimations**

Wheat plants were no longer growing during the measurement period. Thus, the leaf area was considered constant throughout the experiment, since senescence did not induce large changes according to visual inspection. Leaf area was determined by plant harvesting at the end of the experiment and subsequent scanning and image analysis using IMAGEJ[®]. Dry weight (g) was obtained after placing the plant organs (leaves and fruits) for 48 hours in a stove at 80°C.

237 Table 1 Wheat dry weight (DW) and leaf area in each chamber at the end of the experimental period.

	Ear DW (g)	Leaf DW(g)	Biomass DW(g)	Leaf Area (m ²)
Wheat 1	21.2	3.3	24.5	0.06
Wheat 2	16.4	2.0	18.4	0.05

²³⁸

239 **2.7. BVOC fluxes**

As detailed in Niinemets et al. (2011), after chamber closure, the time necessary to reach the chamber steady-state can be estimated as 4 times the half-time of complete air replacement of the chamber. According to Niinemets et al. (2011) this time allows for 94% of full system response and it is a satisfactory approximation of the time required to reach a steady-state:

(2)

$$t_{ss} = 4 \frac{\ln(2) V}{Q_V}$$

where Q_V is the volumetric air flow rate (m^3, h^{-1}) into the chamber and V is the chamber volume 245 (m^3) . Our system parameters gave a stabilization time t_{ss} of about 7 minutes. We hence chose to 246 247 start measurements 10 minutes after chamber closure to ensure sufficient time for mixing and to 248 facilitate overall automation. PTR-Qi-TOF-MS measurements in each sampling line (inlet and 249 outlet air) took 1 minute, of which only the last 30 seconds were kept to allow signal 250 stabilization. Each chamber was opened again immediately after the end of measurements. 251 Measurements were taken every hour and so during a complete cycle each chamber remained 252 closed for 12 minutes of 1 hour.

The flux of each BVOC was calculated based on the concentration difference of the compound measured in the outlet and inlet air of the chambers:

255
$$\mathbf{F} = \frac{\left(C_{\text{out}}(VOC) - C_{\text{in}}(VOC)\right)Q_V}{DW}$$
(3)

where F is the BVOC flux expressed in $\mu g. g^{-1}$ (*biomass dry weight*). h^{-1} , C_{out}(VOC) and C_{in}(VOC) are the outlet and inlet BVOC concentrations in $\mu g m^{-3}$, DW is the dry biomass of plants in g (leaves and/or ear organs) inside the chamber, and Q_V is expressed in $m^3. h^{-1}$.

259 **2.8.** Net photosynthesis

260 Equation 3 (Von Caemmerer and Farquhar, 1981) was used to calculate the net photosynthesis:

261
$$Pn = \frac{\left(\chi_{\rm in}(CO_2) - \chi_{\rm out}(CO_2)\right)Q_m}{S} \tag{4}$$

12

where *Pn* is the net photosynthesis (μ mol CO₂ m⁻² s⁻¹), $\chi_{in}(CO_2)$ and $\chi_{out}(CO_2)$ are the CO₂ dry molar ratios from chamber inlet and outlet air, respectively (μ mol CO₂ mol⁻¹), *S* is the leaf area (m²), and $Q_m = V_{mol}(air) \times Q_V$ is the molar air flow rate (*mol.* s⁻¹).

265 2.9. Standard emission factors

266 As discussed in section 1, BVOC emissions are strongly affected by environmental factors and in 267 particular temperature and light, which are hence always used in models as drivers to simulate 268 BVOC emissions. However, individual BVOC species can respond differently to temperature and 269 light. Some compounds depend only on temperature, notably those originating from storage 270 pools, while others depend on light and temperature, in particular when linked with the 271 photosynthesis pathway, such as isoprene. In order to normalise measured emissions for 272 temperature and light, the standard emission factor was calculated by fitting the following 273 equation from Guenther et al. (1995):

$$F = E_S C_L C_T$$
(5)

Where E_S is the standard emission factor and F is the measured BVOC flux, both expressed in µg 276 g_{DW}^{-1} h⁻¹. C_T and C_L are coefficients describing respectively the temperature and light dependency 277 of the flux. For BVOC compounds depending on light and temperature (model TP), such as 278 isoprene, C_T and C_L were computed as:

279
$$C_{\rm T} = \frac{\exp\left[\frac{C_{T1}(T - T_{\rm S})}{R T_{\rm S} T}\right]}{1 + \exp\left[\frac{C_{T2}(T - T_{\rm M})}{R T_{\rm S} T}\right]}, \qquad C_{\rm L} = \frac{\alpha C_{L1} {\rm PAR}}{\sqrt{1 + \alpha^2 {\rm PAR}^2}}$$
(6)

with the empirical constants $C_{T1} = 95000 \text{ J} \text{ mol}^{-1}$, $C_{T2} = 230000 \text{ J} \text{ mol}^{-1}$, $T_M = 314 \text{ K}$, $\alpha = 0.0027$, $C_{L1} = 1.066$, and where T is the leaf experimental temperature (K), T_S is the leaf

temperature at standard conditions (303 K), *R* the gas law constant (8.314 1 J mol⁻¹ K⁻¹), and PAR the photosynthetically active radiation (PAR) flux (μ mol_{photon} m⁻² s⁻¹). For BVOC species depending only on temperature (like monoterpenes, model Tonly), $C_L = 1$ and C_T was computed as:

$$C_{\rm T} = \exp(\beta(T - T_{\rm S})) \tag{7}$$

287 with the empirical constant $\beta = 0.09K^{-1}$.

We fitted the measured flux for each individual BVOC with the two proposed dependency models (eq. 5 and 6) and selected the model with the highest R^2 coefficient to estimate the standard emission factors (SEF) at each developmental stage. We noticed that for the most exchanged BVOC species the temperature dependency model C_T showed most of the time the best R² (see Appendix C).

293 **2.10. BVOC** tentative identification

294 Identification was attempted with the software PTR-MS VIEWER 3 (Ionicon) coupled with the 295 NIST database. Exact identification of all ions presented in this study was not possible. Indeed 296 because of the principle of mass spectrometry, distinction of compounds having the same 297 molecular weight (isobaric) or the same chemical formula (isomeric) was not possible. Thus, 298 some compounds have been suggested for these masses based on the literature, and in 299 comparison with GC-MS measurements in a campaign conducted in 2018 at the same farm 300 (Kammer et al., 2019). The concentration of the m/z 43.018 compound strongly correlated (0.98 correction factor during ripening and senescence) with the m/z 61.029 (acetic acid), which 301 302 strongly suggest that the m/z 43.018 is a fragment of acetic acid. Based on the linear regression 303 slope between m/z 43.018 and m/z 61.029, a correction factor of 2.7 was worked out for acetic 304 acid concentrations. However, due to uncertainties in the evaluation of this correction factor, we

305 did not systematically apply this correction factor to the data, but rather proposed an alternative

306 evaluation of the acetic acid standard emission factor.

307Table 2. List of ions detected in this study for which a tentative identification is proposed. The measured308mass-to-charge ratio (m/z) of the ions, their potential compounds and/or chemical formula as well as the309measured m/z peak deviation from the theoretical m/z are presented. In bold compounds that are discussed in310this study due to their relevant contribution to the overall fluxes or commonly cited in literature.

		Peak	Tentative chemical formula		
Suggested compound	m/z	deviation			
Formaldehyde	31.018	0.0000	$(CH_2O)H^+$		
Methanol	33.034	0.0000	(CH ₄ O)H ⁺		
Isoprene (frag.); Propyne	41.038	0.0000	(C ₃ H ₅) ⁺ ; (C ₃ H ₄)H ⁺		
Acetonitrile	42.034	0.0000	$(C_2H_3N)H^+$		
Ketene; Acetic acid (frag.) ^a	43.018	0.0002	(C ₂ H ₂ O)H ⁺ ; (C ₂ H ₃ O) ⁺		
Propene	43.054	0.0010	$(C_{3}H_{6})H^{+}$		
Acetaldehyde	45.033	0.0010	$(C_2H_4O)H^+$		
Formic acid	47.014	0.0008	$(CH_2O_2)H^+$		
Ethanol	47.049	0.0011	$(C_2H_6O)H^+$		
Methanethiol	49.011	0.0000	$(CH_4S)H^+$		
Acrolein	57.034	0.0005	$(C_3H_4O)H^+$		
Hexenal (frag.); Butanol (frag.)	57.069	0.0009	$(C_4H_8)H^+$		
Acetone	59.048	0.0011	$(C_3H_6O)H^+$		
Acetic acid ^a	61.029	0.0004	$(C_2H_4O_2)H^+$		
Triazole ^b	69.032	0.0004	$(C_2H_2N_3)H^+$		
Isoprene ; Methyl butenol (frag.)	69.069	0.0001	$(C_{5}H_{8})H^{+}$		
Methyl vinyl ketone ; methacrolein	71.049	0.0011	$(C_4H_6O)H^+$		
Pentene	71.084	0.0015	$(C_5H_{10})H^+$		
Propenoic acid	73.028	0.0014	$(C_{3}H_{4}O_{2})H^{+}$		
Methyl ethyl ketone (MEK)	73.064	0.0018	$(C_4H_8O)H^+$		
Benzene	79.051	0.0012	$(C_6H_6)H^+$		
Hexene ; Monoterpenes (frag.); Hexenal (frag.)	81.070	0.0009	$(C_6H_8)H^+$		
Methylfuran	83.048	0.0001	$(C_5H_6O)H^+$		
Hexenol (frag.); Hexadiene	83.084	0.0015	$(C_6H_{10})H^+$		
Pentenone	85.062	0.0018	$(C_5H_8O)H^+$		
Pentenol; Pentanal; Pentanone; Methyl butenol	87.078	0.0034	$(C_5H_{10}O)H^+$		
Iron dihydroxide	90.946	0.0017	$(FeH_2O_2)H^+$		
-	91.053	0.0012	$(C_7H_6)H^+$; $(C_7H_7)H^+$		
Hexenal; Hexenone	99.079	0.0034	$(C_6H_{10}O)H^+$		
Heptene	99.114	0.0008	$(C_7H_{14})H^+$		
Pentenoic acid; ISOPOOH	101.058	0.0007	$(C_5H_8O_2)H^+$		
Hexenol	101.092	0.0041	$(C_6H_{12}O)H^+$		
Methacrylicperoxy acid	103.039	0.0010	$(C_4H_6O_3)H^+$		
Pentanoic acid	103.074	0.0024	$(C_5H_{10}O_2)H^+$		
Styrene	105.068	0.0010	$(C_8H_8)H^+$		
Benzaldehyde	107.047	0.0001	$(C_7H_6O)H^+$		
-	108.957	0.0003	NO ₄ P ^{+ b} ; CO ₄ S		
Octadiene	111.114	0.0028	$(C_8H_{14})H^+$		
Santene	123.114	0.0018	$(C_9H_{14})H^+$		
_ c	125.959	0.0003	$(NO_5P)H^+$		
Methylbenzoate	137.059	0.0017	$(C_8H_8O_2)H^+$		

8-Azaadenine		0.0010	$(C_4H_4N_6)H^+$
Monoterpenes	137.132	0.0015	$(C_{10}H_{16})H^+$
Isofraxidin; 3-(Acetyloxy) benzoic acetic	223.055	0.0009	$(C_{11}H_{10}O_5)H^+$
-	225.035	0.0006	$(C_{10}H_{18}O_6)H^+$

a. The m/z 43.018 fragment of acetic acid led to a correction factor of 2.7 of acetic acid concentrations and fluxes.
 This correction was not systematically applied but rather used to evaluate an alternative standard emission factor for acetic acid in the discussion section.

b. Triazoles are documented degradation products of "azole" fungicides which were used on the wheat during the

315 spring and are known to be persistent in the ecosystem for several months.

316 c. Isotopic pattern consistent at m/z + 1 and m/z + 2

317

318 **2.11.** Wheat plant developmental periods

319 The experiment started at the maturation of the seeds. The beginning of plant senescence was 320 identified by a gradual decrease in the rate of photosynthesis as discussed in Taiz et al. (2015) or 321 Mozaffar et al. (2018). Three developmental periods have been distinguished: (1) Ripening, 322 during which the plants have constant photosynthetic activity, (2) Senescence 1, when the 323 photosynthesis decreases gradually but plants remain green and (3) Senescence 2, characterized 324 by no photosynthetic activity and plants turning progressively yellow (chlorosis) (Figure 1). Chlorosis occurred from Jun 21st to 29th. Afterwards, the plants were cut at the base (about 20 cm 325 326 above the ground) simulating a harvest and measurements continued for 4 days.





330 2.12. Statistical analyses

Data analyses were performed with R (RStudio 1.1.463, R version 3.5.2). A Student's t-test was performed in order to evaluate whether the mean BVOC fluxes were significantly different from zero. The fluxes were first averaged per day for each ion before performing the t-test to limit temporal correlation. Similarly the mean fluxes and 95% confidence intervals for each ion were computed as follows. For each day, ion and plant, the daily mean emission was first computed. Then the averaged daily emission and the corresponding confidence interval were computed over all days and both plants.

2.13. Comparison with eddy covariance fluxes obtained in a nearby field the year before

339 Given the limited number of replicates of our experimental design with only two wheat plants, no 340 statistically significant differences could be assessed to determine if there is a real effect of plant 341 development stages on BVOC emissions. To overcome this difficulty, we used Eddy covariance 342 (EC) fluxes measured with the same instrument at the same site one year prior to the present 343 study. These measurements by EC were taken during the same developmental stages and on the 344 same soil. These data were compared with the emission factors reported here and their variations 345 with plant developmental stages. These data were reported by Loubet et al. (2021), and are 346 referred to as the COV3ER-2016 dataset in the following sections. The data were taken from the 347 repository associated with this publication (https://doi.org/10.15454/IRZ9XX), and are not 348 detailed here.

349 Similarly to what was done in this study with net plant photosynthesis (Figure 1), ripening, 350 senescence 1, and senescence 2 periods were determined based on measured net ecosystem 351 exchange (Appendix D). For each of these periods, the standard emission factors estimated in this study were used to compute the SEF-based whole plant VOC emissions using air temperature and incoming photosynthetically active radiation as measured in COV3ER-2016 and equations 5-7. These SEF-based whole plant VOC emissions were compared to hourly measured fluxes in COV3ER-2016 which were scaled to $\mu g g^{-1}(DM) h^{-1}$ by multiplying the fluxes in nmol m⁻² s⁻¹ by *ion_mass* × 3600/1000 × *AGB*, where AGB is the total above ground biomass that was 1224 g m⁻² during that period.

358 2.14. OH reactivity

359 In order to evaluate the impact of the measured BVOC emissions, and their change with plant 360 stages, on the atmospheric chemistry, we evaluated their potential OH reactivity. Once emitted, 361 BVOCs can reduce the atmospheric reactivity mainly through their reaction with the OH radical, 362 which leads to an accumulation of other compounds such as methane. As the reactivity with the 363 OH radical strongly depends on the compound, the impact on atmospheric reactivity depends not 364 only on the emissions in terms of quantity but also on its composition. Thus, in order to evaluate 365 this impact, measured BVOC concentrations of the compounds identified in Table 2 were used to 366 calculate a theoretical OH reactivity (cROH for calculated OH reactivity), which consists of the 367 sum of the reaction frequencies of all chemical compounds with OH. In practice cROH was 368 calculated as the sum of the products of each compound concentration $[X_i]$ (in molecule cm⁻³) by the reaction rate coefficient of this compound with OH, k_{OH+X_i} (in cm³ molecule⁻¹ s⁻¹): 369

$$cROH = \sum k_{OH+X_i}[X_i]$$
(8)

This calculated OH reactivity represents the expected total loss rate of OH, which is the inverse of OH lifetime (s^{-1}). The relative uncertainty in *cROH* was computed as the sum of relative 373 uncertainties in concentration (assumed equal to that on mixing ratio) and in k_{OH+X_i} which was 374 retrieved from the literature (see Table G1, Appendix G for details on k_{OH+X_i}).

375 **3. Results**

376 **3.1. Meteorological variation during the campaign**

377 Air temperature, photosynthetically active radiation (PAR) and air relative humidity (RH), 378 presented similar temporal variability for both wheat chambers, with a clear diurnal dynamics 379 pattern (Figure 2). On average, the air temperature during measurements was 2.3 °C larger inside 380 the chambers than above the canopy during daytime, but maximum differences reached 10°C, 381 denoting a noticeable impact of chambers on the plant microclimate. Maximum diurnal 382 temperatures remained in general between 30 and 40°C during the entire measurement period, exceptions are: June 19th and 20th, during which the temperature increased above 40°C; and July 383 384 01st, during which the temperature remained below 30°C, concomitantly with a low PAR. It can also be noted that the period from June 27th to July 2nd was marked by poor weather conditions 385 386 with some rainfall events. During that period, temperature presented a less pronounced diurnal 387 pattern with smaller temperature ranges. The PAR transmissivity of the chamber was evaluated to be 89% (Pape et al., 2009). During daytime, PAR was on average 264 µmol m⁻² s⁻¹ higher above 388 389 the canopy than inside the chambers. This was expected due to the presence of plants surrounding 390 the sensor in the chamber and the chamber itself. The relative humidity inside the chambers was 391 close to the one measured above the canopy (0.1 to 1.8% higher inside the chambers during 392 daytime) and hence was representative of the ambient air. Although the chambers were affected 393 by temperature, it is important to keep in mind that they remained open most of the time and therefore the conditions inside the chambers were affected only during the short periods ofclosure (12 minutes every hour).



ICOS site - - wheat 1 ---- wheat 2

396

Figure 2 Environmental conditions measured inside each chamber (*Wheat_1*, and *Wheat_2*) and at 1 meter above canopy (ICOS site). PAR is given in μ mol m⁻² s⁻¹, relative humidity (RH) in %, rain in mm and

400

³⁹⁹ temperature in °C.

401 **3.2. BVOC fluxes variation between developmental wheat periods**

402 The overall fluxes for the different developemental periods were generally well reproduced 403 (qualitatively and quantatively) between the two wheat plants (Figure 3). Althought the overall 404 BVOC emission rate was generally higher for *Wheat_2* plant, compared to *Wheat_1*, especially 405 during *Ripening* (emission rate about twice as large), it remained of the same order of magnitude. 406 For both plants the overall emission rate increased considerably during the first period of 407 senescence (Sen1), decreased slightly during the seconde period of senecence (Sen2) and then 408 declined abruptly after harvest. Net deposition was also observed, ocurring mainly during 409 *Ripening* and *Sen1*, and after harvest in the case of methanol.



410

Figure 3: Overall BVOC fluxes and composition for each developmental period of wheat plants. We show for comparison all 12 compounds that were among the 5 most exchanged during at least one developmental stage. 7The category "others" includes the fluxes of all the other detected ions. # Acetic acid not corrected for m/z 43

414 fragment. * Hexadiene could also correspond to a fragment of hexenol, a green leaf volatile (GLV).

415 **3.2.1.** Qualitative BVOC fluxes variation

416 The most exchanged compounds for each developmental period and their contribution to overall 417 fluxes is depicted in Figure 3. All compounds that were among the top 5 compounds for each 418 developmental stage were selected, which represented 12 compounds in total. Together, these 419 major compounds represented about 80% of the net overall fluxes for each period, except harvest. 420 It can be noted that the composition of these most emitted compounds varies according to the 421 stage of development. In general, the most emitted compounds were: methanol, acetaldehyde, 422 acetic acid and acetone. Methanol was the most emitted compound for all periods, excepted 423 harvest, contributing to 60%, 59% and 49% of the overall BVOC flux during Ripening, Sen1 and 424 Sen2 (average of both chambers), respectively (see Appendix E). During *Ripening*, acetone was 425 the second most emitted compound, contributing 9% to the overall fluxes. During senescence, 426 acetone, acetaldehyde and acetic acid were the most emitted compounds after methanol, 427 contributing, respectively 8%, 3% and 1% to the overall net fluxes during Sen1 and 8%, 10%, 428 3% during Sen2 (see Appendix E). The remaining most emitted compounds each presented a 429 minor contribution to the overall fluxes. These ions were: m/z 69.069 (Isoprene; Methyl butenol 430 fragment), m/z 73.064 (Methyl ethyl ketone), m/z 83.084 (Hexadiene), m/z 108.957 (NO₄P) and 431 m/z 125.959 (NO₅P). The likely fragments of acetic acid, isoprene and butanol fragments, at m/z432 43.018, 41.039, 57.069, respectively, also appeared among the most exchanged compounds. If 433 m/z 43.018 is accounted as acetic acid, this increases its contribution to the overall flux, 434 especially during Sen2 where it reaches 7.3% of the overall fluxes (Appendix E). After harvest, 435 no compounds made a significant individual contribution to overall emissions, apart from 436 methanol which was mainly taken up and represented around 36% of the overall flux.

437 **3.3. Fluxes temporal variation for individual BVOC**

In general, the temporal fluxes variation of the most emitted BVOCs showed similar trends for both wheat plants, despite a few differences being observed mostly after harvest (Figure 4). However, *Wheat_2* showed emission rates higher than *Wheat_1* for all compounds, except during *Sen2* for a few compounds. This difference was small for methanol but sometimes reached a factor of 2 for hexadiene, acetone, acetaldehyde and isoprene. Clear diurnal dynamics were observed for most compounds throughout the whole measurement period, except for acetic acid during *Ripening* and *m/z* 108.957 and 125.959 ions during *Sen2*.

Several temporal trends can be observed among the different compounds. For example, some compounds, such as methanol, acetaldehyde, acetone, isoprene, hexadiene and hexanal, presented a gradual increase in emission rates during *Sen1*, while for m/z 108.957 and 125.959 ions, emission rates gradually decreased at the beginning of senescence and reached a minimum during *Sen2* and after harvest. Some small amounts of deposition were also noticed for some compounds including acetaldehyde and acetic acid, occurring mainly during *Ripening* and *Sen1*. An important deposition of methanol was observed mainly after harvest (Figure 4).



Figure 4: Fluxes variation during the measurements period for some of the most exchanged compounds. Acetic acid was not corrected for m/z 43 fragment in this figure. Hexadiene could also correspond to a fragment of hexenol, a green leaf volatile (GLV).

In order to better analyze the BVOC flux variation during the investigated periods, flux statistics over each stage and for each major compound are depicted in Figure 5. Overall, most compounds presented a larger averaged emission during *Sen1*. However we observed 5 types of behaviors: (i) a significant increase in average emission rates from *Ripening* to *Sen1*, followed by a significant 460 decrease during Sen2, and an abrupt decrease during harvest. This behavior was observed for 461 methanol, isoprene, hexenal, hexenone, hexadiene and m/z 101.092. In the case of methanol, the 462 flux turned from a net emission to a net deposition during harvest; (ii) a significant increase from 463 *Ripening* to *Sen1*, but a further increase during *Sen2*, and a drastic decrease during harvest. Such 464 was the case for acetaldehyde and acetic acid; (iii) a significant increase from *Ripening* to *Sen1*, 465 no significant variation during Sen2, and a decrease during harvest. This behavior concerns 466 acetone and MEK, the latter of which showed a peak in emissions two days after harvest; (iv) m/z467 108.957 and 125.959 showed a significant decrease from Ripening to Sen1, from Sen1 to Sen2, 468 and from Sen2 to harvest; (v) no significant variation from Ripening to Sen1 and to Sen2, and a 469 significant decrease from Sen2 to harvest, being the case for monoterpenes.

470 BVOC emissions from plants are known to depend strongly on temperature and light conditions. 471 Given the large variation of these climatic factors between the different periods investigated, the 472 flux differences observed between the different periods could be either due to plant development 473 or to variation in temperature and light conditions. The standard emission factors (SEF), 474 calculated for each compound during each developmental stage (Figure 5) can be seen as fluxes 475 at standard conditions of temperature and light. Thus, the SEF allow comparing the fluxes 476 between the different developmental stages while eliminating the effects of temperature and light. 477 Figure 5 shows that SEF varied with plant development, but SEF variations were often different 478 when compared to the measured fluxes. Overall, SEF were higher during Sen2, contrary to the 479 measured fluxes which were either smaller or of similar magnitude to that during *Sen1*. Based on 480 SEF, different behaviors are identified: compounds for which SEF increased between periods 481 (acetaldehyde, acetic acid, acetone, isoprene, hexanal), those for which SEF decreased (m/z482 108.957, 125.959 and monoterpenes), those for which SEF decreased during Sen1 and then



483 increased during *Sen2* (methanol), and those for which only during *Sen2* SEF decreased (m/z484 101.092) or increased (MEK), while for hexadiene SEF remained stable among all periods.

485

486 Figure 5. Top: Mean fluxes (µg g⁻¹ h⁻¹) estimated for each developmental period (dots), corresponding 95% 487 confidence interval (error bars), and mean fluxes over the entire measurement period (grey bar). Bottom: 488 standard emission factor SEF at standard temperature (30°C) and light (1000 µmol m² s⁻¹) estimated for each 489 developmental period (dots), corresponding 95% confidence interval (error bars), and SEF estimated for the 490 whole measurement period (grey bar). SEF were obtained by fitting the measured flux with the temperature 491 and light dependency (TP) or the temperature dependency only (Tonly) model given by (Guenther et al., 492 1995) as explained in the text. The model with highest R^2 was selected. The R^2 coefficients are provided in 493 Appendix C. SEF are not shown for harvest since there was no plant left in the chamber, apart from a small 494 portion of the plant stems. Compounds were grouped by similar scale of mean emission to facilitate 495 visualization, only the y-scale changes between groups. Hexadiene could also correspond to a fragment of 496 hexenol, a green leaf volatile (GLV). For acetic acid, an alternative evaluation of the SEF is given in the 497 dashed rectangle, for which m/z 43 was considered a fragment of acetic acid.

498

499 **3.4.** Comparison of modelled VOC fluxes with eddy covariance fluxes in COV3ER-2016

500 The SEF-based whole plant VOC emissions compared overall quite well with the COV3ER-2016 501 whole ecosystem fluxes (Figure 6). This is especially true for acetone, during ripening and early 502 senescence (Sen1), where with a slope of 0.8 and 1.1 in x-y regressions. Acetaldehyde SEF-based 503 whole plant VOC emissions were lower than whole ecosystem fluxes during *Rip* and *Sen1* (by a 504 factor of 5 to 2), while methanol plant fluxes were larger than whole ecosystem fluxes during the 505 same period (by a factor of ~2). During maturation and chlorosis (Sen2) the SEF-based whole 506 plant VOC emissions were systematically larger than COV3ER2016 whole ecosystem fluxes, by 507 a factor of ~2. For acetic acid, the SEF-based whole plant VOC emissions were systematically 508 larger than the whole ecosystem fluxes measured in 2016, although the orders of magnitude were 509 similar during *Rip* and *Sen1*. See Appendix F for details on linear regressions.



511 Figure 6. Comparison between measured whole ecosystem VOC fluxes in COV3ER-2016 (red) and SEF-based

514

⁵¹² whole plant VOC emissions as derived in this study (blue) over the ripening (Rip), and senescence periods 513 (Sen.1 and Sen.2). Here acetic acid fluxes are not corrected for m/z 43 fragments in both datasets.

515 **3.5. OH reactivity**

516 ROH showed a diurnal variability (Fig. 6), with maxima during day-time and minima during night-time, following temperature and PAR profiles, and thus the variability of total BVOCs 517 fluxes. Similarly to what was described in section 3.2.1 on BVOCs fluxes variation, ROH 518 519 remained of the same order of magnitude for both wheat chambers, with higher values during Sen1 (19th- 20th of June 2017). Average day-time ROH was similar for both plants with 2.4 ± 3.0 -520 521 2.5 ± 2.4 s⁻¹ for wheat 1 and wheat 2, respectively. Maxima of 13.6 and 12.7 s⁻¹ were recorded for 522 wheat 1 and wheat 2, respectively, at Sen1. Interestingly, higher values of ROH were recorded for 523 wheat 1 compared to wheat 2 during Sen2. These values remain in the lower ranges of OH 524 reactivity compared to other ecosystems, especially for measurements from dynamic chambers 525 (Bsaibes et al., 2020; Kim et al., 2011; Nölscher et al., 2013; Sinha et al., 2008), bearing in mind 526 that flow rates and chamber setups may modify the absolute values of the reactivity. We evaluated that the uncertainty in calibration factors may lead to potentially underestimating the 527 528 OH reactivity by 50% with an overall uncertainty of 25% (Fig. 7).



28

530 Figure 7. Calculated OH reactivity of the outlet air of the two wheat chambers. The effect of sensitivity 531 corrections and considering hexadiene as an hexenol fragment were evaluated here.

Regarding the contribution of the main emitted compounds, methanol which was the most emitted compound in general, accounted for 12 - 17% of the cROH, acetaldehyde represented 16%, while other mainly emitted OVOCs accounted for much less (acetone 0.3- 0.4%, acetic acid 0.3- 0.4%, etc.). However, even though isoprene had a minor contribution to the overall flux, its contribution to cROH exceeded that of the mentioned OVOCs and reached 34- 36%, on average. Overall, senescence induced a marked increase in OH reactivity of up to 4-fold during senescence

538 1 and 2-fold during senescence 2 compared to the ripening period.

539 4. Discussion

540 **4.1. Flux dynamics in relation with vegetation development**

541 Grass species, which include wheat as the most widespread cultivated grass species, are known to 542 emit relatively large amounts of oxygenated VOCs and some monoterpenes (Fukui and Doskey, 543 2000; Karl, 2009; Kirstine et al., 1998). Indeed, in this study oxygenated compounds dominated 544 the BVOC exchanges for wheat plants, with methanol being the most emitted compound during 545 all developmental periods followed by acetone, acetaldehyde and acetic acid (Figure 3). These 546 findings are also in good agreement with recent literature studies on grass species including 547 wheat (Bachy, 2018; Bachy et al., 2016; Gonzaga Gomez et al., 2019; Graus et al., 2013; 548 Mozaffar et al., 2018).

549 Our study showed that many BVOC species were released in larger amounts as the plants entered 550 senescence (*Sen1*), with emission rates decreasing thereafter as plant leaves turned yellow (*Sen2*). 551 It has been suggested that, for some BVOC, higher emissions occurring during senescence may 552 originate from the breakdown of cellular structures, cell organelles and macromolecules to 553 nutrients remobilization (Mozaffar et al., 2018; Rottenberger et al., 2005). In addition, chlorosis 554 is likely to increase BVOC diffusion through a degraded epidermal layer and cuticle (Mozaffar et 555 al., 2018). Thus, BVOC emissions are expected to rise as the leaves turn yellow and degradation 556 increases. However, our results showed a decrease in BVOC emissions during wheat chlorosis 557 (Sen2), which was probably due to unusual weather conditions during this period (i.e. heavy 558 rainfall and low temperatures). Indeed, emissions are likely to decrease when the temperature 559 decreases given the chemical properties of certain compounds, such as high solubility, or their 560 origin within plants, such as storage organs and enzymatic reactions (Cojocariu et al., 2004; 561 Hayward et al., 2004). Standard emission factors are in this case useful to distinguish the share of 562 flux variation due to temperature or endogenous plant variation. Most compounds showed an 563 increase in SEF during chlorosis (Sen2), except for m/z 101.092, 108.957, 125.959 and 564 monoterpenes. Thus, senescence induced higher emissions in wheat plants despite the presence of 565 rain, which may have increased deposition of soluble compounds (Bachy, 2018; Holzinger et al., 566 2001).

567 In the following sections the most exchanged compounds are discussed more in details and 568 compared with literature findings.

569 **4.2.** Compounds with increasing emissions during senescence

570 **4.2.1. Methanol**

571 Methanol emission rates have already been found to increase with senescence for maize 572 (Mozaffar et al., 2018) and wheat plants (Bachy, 2018) in previous studies. In those studies, 573 emission rates of methanol increased slowly at the beginning of senescence reaching a maximum 574 emission rate during chlorosis. This is well in line with our results where methanol emissions 575 increased during the first phase of senescence (Sen1). However, emissions decreased during 576 chlorosis (Sen2), contrary to previous studies. Methanol emitted by plants is known to originate 577 from enzymatic reactions of pectin demethylation in the cell wall by Pectin Methyl Esterase 578 (PME) activity (Fall, 2003), a process occurring during growth but also during other events 579 impacting the cell wall structure such as senescence (Bachy et al., 2016; Karl et al., 2005; 580 Mozaffar et al., 2018). Thus, an increase in methanol emissions is expected with the progress of 581 senescence. Poor weather conditions during chlorosis, with a decrease in temperature and some 582 rain (Figure 2), hence explains the decrease in the measured methanol fluxes during chlorosis. 583 Indeed, due to the low temperatures, enzymatic activity was very probably inhibited, while 584 methanol solubility was improved during that period. Moreover, methanol being highly soluble 585 (≥100 mg/mL at 70° F; NTP, 1992) it is readily deposited on wet surfaces (Bachy, 2018; 586 Holzinger et al., 2001; Laffineur et al., 2012; Wohlfahrt et al., 2015). When normalized for 587 temperature, methanol emissions actually increased during chlorosis (Sen2), despite a probable 588 higher deposition due to the presence of wet surfaces.

589 **4.2.2.** Acetone

Increase in acetone emissions during plant senescence and biomass decay have previously been reported in literature (Bachy, 2018; T. Karl et al., 2003; Mozaffar et al., 2018; Warneke et al., 1999). Although acetone fluxes were bidirectional in the present study, average net flux always resulted in net emissions for all the investigated periods. Contrary to our observations, in the study of Bachy et al. (2018), acetone was on average deposited before the senescence of wheat but was emitted during senescence. This difference may result from an acetone uptake by soil in Bachy et al. (2016) since their measurements were at the ecosystem scale. 597 Schade and Goldstein (2001) found temperature to be the main environmental driver regulating 598 acetone emissions. This is consistent with the decrease in acetone emissions during the chlorosis 599 period, when temperatures were lower. Therefore, once normalized for temperature, emissions 600 increased during chlorosis and exceeded those of the first senescence period.

601 Acetone is known to be produced in plants via the cyanogenic pathway (Fall, 2003). In this 602 pathway, amino acids are converted into cyanogenic glycoside which is stored in the cell 603 vacuoles. Impacts against cell wall structure, resulting from the senescence process, may enhance 604 the contact of cyanogenic glycoside with β -glucosidase, a cell wall enzyme. This reaction leads to 605 acetone cyanohydrin that subsequently reacts with another cell wall enzyme, hydroxynitrile lyase, 606 to form acetone and hydrogen cyanide. This mechanism together with abiotic processes, through 607 the Maillard reaction that was also reported for acetone (Warneke et al., 1999), may explain the 608 observed increase in acetone emissions as senescence progresses. Indeed, Warneke et al. (1999) 609 showed that the thermochemical Maillard reaction can produce oxygenated VOCs (OVOCs) even 610 at typical ambient temperature (20-40°C). The wetting of leaves acts then as a desorption process 611 that replaces OVOCs molecules attached to the surface of plants by highly polar water molecules 612 in the aqueous phase. OVOCs can then be released to the air by Henry equilibrium. The wetting-613 drying cycle was shown to be an efficient emission process that can last several tens of cycles 614 (Warneke et al., 1999). Since plants were not exposed to this wetting-drying cycle in our study, 615 relative humidity may have contributed to desorption of OVOC attached to the plants surface as 616 well demonstrated by Mozaffar et al. (2018), either through a water microlayer on the plant 617 surface or through interactions with polar water vapour molecules.

618 4.2.3. Acetaldehyde

619 The sharp increase in acetaldehyde emissions during leaf senescence in this study is in good 620 agreement with previous studies on maize (Mozaffar et al., 2018), wheat (Bachy, 2018) and tree 621 species (Rottenberger et al., 2005). Although acetaldehyde emissions from plants are highly 622 dependent on temperature, (Bachy, 2018; Cojocariu et al., 2004; Das et al., 2003; Hayward et al., 623 2004; Karl et al., 2005), acetaldehyde emissions increased during senescence, and mainly 624 chlorosis, resulting from a senescence effect (Figure 5). Similarly to our observations, in the 625 study of Bachy (2018) over a wheat field, acetaldehyde emissions increased from the early stages 626 of senescence to reach higher levels during leaf chlorosis. In their study, acetaldehyde 627 contribution to the overall BVOC emissions during beginning of senescence (2%) and chlorosis 628 (6%) was similar to our findings, being 3% and 10% during Sen1 and Sen2, respectively (see 629 Appendix E). Mozaffar et al. (2018), investigating BVOC emissions from senescent maize leaves 630 under controlled environmental conditions, found a delayed increase in acetaldehyde emissions, 631 with a pronounced emission increase only 2 days after leaf chlorosis started. Although missing 632 data do not allow a strict comparison of our study with Mozaffar et al. (2018), acetaldehyde emissions increased on 24th and 25th June (Figure 4), which is about 2 days after photosynthesis 633 634 went down to zero and chlorosis started (Figure 1).

In terms of processes, the peroxidation of fatty acid by reactive oxygen species (ROS) might be the main mechanism for the production of acetaldehyde (Jardine et al., 2009) during the senescence period, as discussed by Mozaffar et al. (2018). It has also been suggested that acetaldehyde emissions could originate from internal pools (Hayward et al., 2004), and increased emissions during leaf senescence could result from the breakdown of cellular structures and 640 degradation of cell organelles (Rottenberger et al., 2005), although both studies were based on641 tree species.

642 **4.2.4.** Acetic acid

643 The increase of acetic acid emissions during wheat senescence (Figure 5) observed here is 644 consistent with the study of Mozaffar et al. (2018) for maize leaf emissions. On the contrary, in 645 the study of Bachy et al. (2018), acetic acid fluxes resulted in an average net uptake during wheat 646 senescence. Given the ecosystem scale of their flux measurements, the authors invoked the 647 possible role of soil as an important acetic acid sink to explain the net uptake during senescence. 648 Indeed, it has been demonstrated that soil may act as an important sink for acetic acid (Bachy et 649 al., 2016). This hypothesis could explain the divergence between the ecosystem scale (Bachy, 650 2018) and plant scale studies (this study and Mozaffar et al., 2018). A further explanation would 651 be the ambient level of acetic acid. Indeed the deposition flux of a deposited compound will 652 increase with increasing its ambient level as is well known for instance with ammonia (Sutton et 653 al., 1995).

654 In terms of processes, the abiotic Maillard reaction was shown to be very effective for producing 655 acetic acid (Warneke et al., 1999). Mozaffar et al. (2018) showed good consistency of the 656 increase in acetic acid emissions with that mechanism during leaf senescence. Another process 657 that may favor acetic acid emissions is the decrease of leaf pH. Indeed, it has been demonstrated 658 that decrease in apoplastic pH leads to acetic acid emissions by displacing the acid-base 659 equilibrium towards the acid form (its conjugate base being acetate) and subsequently promoting 660 the aqueous-to-gaseous transfer by Henry equilibrium (Gabriel et al., 1999). Hill et al. (2002) found a decrease in apoplastic pH with increasing leaf age (old leaves have a lower apoplastic pH 661 662 than young leaves). Thus, the increase in acetic acid emissions during senescence may have resulted from a combination of a decrease of apoplast pH in senescent wheat leaves and theMaillard reaction.

665 4.3. Acetic acid and methanol uptake during wheat development

666 Acetic acid uptake from other cereal species (Bachy et al., 2016; Kesselmeier et al., 1998) and 667 wheat (Bachy, 2018; Gonzaga Gomez et al., 2019) has been reported before and is well in line 668 with our results during *Ripening*. As already discussed, acetic acid exchanges result from both, 669 gas-to-liquid Henry equilibrium and acid-base equilibrium in the apoplast, as well as on any wet 670 surface. As a result, acetic acid can either be emitted or taken up by plants depending on the 671 concentration gradient between the plant and the atmosphere. If acetic acid concentration in the 672 atmosphere is larger than in the plant it is deposited. During plant development, acetate and acetic 673 acid may be converted to acetyl-CoA in the symplast and enter the plant metabolism, such as 674 Krebs cycle (TCA, TriCarboxylic Acids cycle) (Seco et al., 2007). Thus this process allows 675 maintaining a concentration gradient and, consequently, the continuous uptake of acetic acid by 676 the living plant. This process ends with senescence, which may explain the switch from 677 bidirectional acetic acid exchange to emission during that stage. Acetic acid deposition to wet 678 surfaces in the chamber does not seem to be a dominant process. Otherwise, we would have 679 expected some deposition after the rainfall events of 27 and 30 June, which was the case for 680 acetone and methanol. On the contrary, acetic acid deposition was clear in Sen2 when no rainfall 681 was observed (Figure 4).

Methanol uptake observed after harvest in this study may have resulted from its deposition and dissolution on wet surfaces following rainfall events. Indeed, methanol which is soluble in water can be taken up on water films that appear on the plant parts under wet conditions such as reported before (Bachy, 2018; Holzinger et al., 2001; Laffineur et al., 2012; Wohlfahrt et al.,

2015). In addition, after harvest the amount of biomass in the cuvette was small, presenting no 686 687 significant methanol emission to compensate deposition.

688

4.4. *m/z* 73.064 emission during harvest

689 The m/z 73.064 ion may correspond to methyl ethyl ketone (MEK). It has been suggested that 690 MEK emissions from plants may come from reduction reactions of isoprene oxidation products 691 produced during oxidative stress (Cappellin et al., 2019). In this study the ion m/z 73.064 showed 692 a gradual increase in emission rates during the senescence stages and a noticeable peak in 693 emissions two days after cutting wheat plants (Figure 4). A possible explanation is the reduction 694 reaction of isoprene-hydroxy-hydroperoxides (ISOPOOH, an isoprene oxidation product) to 695 MVK and then to MEK by an enzyme, alkenal-one oxidoreductase (AOR), that is ubiquitous in 696 terrestrial plants (Canaval et al., 2020). These authors have shown that this MEK formation 697 process responds to stomatal opening in leaving plants. During senescence and after harvest the 698 AOR enzyme may be more accessible to the ambient air, because of cells breakdown during 699 senescence, therefore leading to the observed increase in MEK emissions at the senescence stage. 700 Moreover, the same study reports that AOR is present in stem flows (xylem and phloem), which 701 would explain the burst observed after harvest. This would be consistent with the observation of 702 much larger MEK than MVK fluxes at all stages. Unfortunately, ISOPOOH could not be 703 measured with our PTR-TOF-MS, as it requires a specific setup of the drift tube to minimize 704 metal-catalysed decomposition of ISOPOOH Canaval et al. (2020).

705 In addition, a significant difference in MEK emissions is observed between the two plants after 706 harvest. This is also observed for other compounds including isoprene. Since these plants belong 707 to the same variety, a possible explanation for these differences in emissions between the two 708 wheat plants may be an important soil spatial heterogeneity of the field and therefore a different availability of nutrients, water and also light for each plant. These different conditions may result,
for each plant, in a more or less important production of isoprene as well as of the AOR enzyme
responsible for the reduction of ISOPOOH to MEK.

712 **4.5. Terpenes exchanges**

Isoprene emissions increased gradually as senescence started (*Sen1*) and decreased when wheat plants entered chlorosis (*Sen2*) (Figure 4). However, when considering emissions in standard conditions (SEF) an additional increase is found during chlorosis (*Sen2*) (Figure 5). Isoprene increase with plant senescence has been reported before for wheat (Bachy, 2018) and maize (Mozaffar et al., 2018).

718 Much smaller, but still significant, emissions were measured for the m/z 137.133 compounds 719 (potentially monoterpenes), generally an order of magnitude lower than isoprene emissions. A 720 clear significant decrease in standard emission factors is noticed when plants entered senescence 721 (Figure 5). This is consistent with literature where these compounds were found to present higher 722 emissions during the early developmental stages of leaves and reduced emissions upon maturity 723 and senescence for several plant species (Bracho-Nunez et al., 2011; Holopainen et al., 2010; 724 Mozaffar et al., 2018). This relation between monoterpene emissions and plant development has 725 been related to the antimicrobial or antifungal properties of these compounds and their great 726 importance in young leaves which are more susceptible to herbivores and pathogen attacks than 727 mature leaves (McCall and Fordyce, 2010). However, in the study of Bachy (2018) at the 728 ecosystem level, monoterpenes emissions increased when wheat plants entered senescence. 729 Monoterpenes emissions from soils have been reported before (Abis et al., 2018; Hayward et al., 730 2001). Thus, the increase in monoterpenes emissions found in Bachy (2018) may have resulted 731 from soil emissions, which might explain the contradiction with our results.

4.6. *m/z* 108.957 and 125.959: compounds decreasing emissions with wheat senescence

733 Both m/z 108.957 and 125.959 compounds presented the same flux temporal trend with emission 734 rates decreasing gradually as plants entered senescence and reaching minimum values from the 735 second senescence period onwards (Figure 4). These ions may correspond respectively to 736 nitrogen compounds with the chemical formula NO₄P⁺ and NO₅P.H⁺. However, since this is not a 737 sure identification but rather some candidates that correspond very precisely to the mass, they 738 may actually correspond to a single compound since they are quite well correlated to each other. 739 To our knowledge, this is the first time these compounds are being reported in the literature 740 regarding studies on BVOC emissions from crops. It is unlikely that they are chamber 741 contaminants since they were not emitted by the empty chamber itself. In addition, if they were 742 coming only from the chamber, they would remain stable throughout the experiment, while a 743 clear daytime cycle is observed as well as a decrease during senescence.

744 **4.7. GLV exchanges during wheat development**

745 In earlier studies "green leaf volatiles" (GLV) compounds appeared to dominate BVOC 746 emissions from wheat plants (Butter et al., 1985; König et al., 1995; Piesik et al., 2011). The ions 747 m/z 99.079 and 101.092 were also detected in this study, and might represent hexenal and 748 hexenol compounds, respectively, which are part of the GLV. In contrast with earlier studies, 749 these compounds do not appear among the most emitted compounds in this study (Figure 3). 750 Hexadiene (m/z 83.084) may also be a fragment of hexenol which shows larger concentrations 751 than hexenol itself (Pang, 2015). Assuming m/z 83.084 is a fragment of hexenol, GLV fluxes 752 become much larger and in better agreement with the literature. GLV compounds have antibiotic 753 properties and inhibit the invasion of bacteria and other microorganisms into damaged tissues 754 (Croft et al., 1993). This is why they are known to be released from plants following mechanical tissue damage (Fall et al., 1999). Thus, in previous studies plants may have suffered further tissue
damage, which could explain the larger emissions of these compounds.

757 According to our results, the average emissions of these compounds seem to increase with onset 758 of senescence, which is well in line with literature findings. GLV production is known to 759 originate from the oxidation of fatty acids, catalyzed by 13-lipoxygenase (13-LOX) (Dudareva et 760 al., 2013). Fall et al. (1999) found an increase in emissions of (Z)-3-hexenal as detached aspen 761 leaves dried out. The authors proposed that during leaf drying, cellular water levels declined until 762 cellular structures began to collapse. This collapse was likely to induce the formation of hexenal 763 and hexanal compounds by increasing the oxidation of fatty acids, such as a-linolenic acid, which 764 may be released from membrane lipids. Holopainen et al. (2010) reported GLV dominating 765 BVOC emissions during the later stages of senescence and leaf abscission of Betula pendula 766 Roth, and suggested that the disintegration of cellular organelles and dying cells were related to 767 these emissions. Mozaffar et al. (2018) also showed increased hexenal emissions during maize 768 leaf senescence, and suggested that it could result from an increase in fatty acid oxidation in order 769 to provide energy for the senescence process.

770 **4.8. Robustness of the inferred standard emission factors**

The comparison between SEF-based whole plant VOC emissions and COV3ER-2016 whole ecosystem fluxes allows us to challenge the robustness of the SEF estimated in this study and especially their evolution over the plant developmental stages. This comparison allows evaluating the representativeness of the measurements made with the two chambers and the intra-specific variability of the VOCs emissions, and also evaluating the variation of the VOCs emissions during the investigated development stages of wheat. However, the eddy covariance method, unlike the plant chamber measurements, takes into account not only plant VOCs exchange but also soil exchange. In addition, we should bear in mind that different wheat varieties between the
two studies might explain some observed differences in VOCs emissions.

780 For methanol, the larger SEF-based whole plant VOC emissions (representative of the whole 781 plant emissions) compared to the whole ecosystem fluxes may be explained by a significant sink 782 at the ground surface, due for instance to methanol dissolution in soil water. Indeed, the 783 contribution of soil to methanol uptake, under wet or dew conditions often present at night, is 784 well documented in the literature (Bachy et al., 2016; Holzinger et al., 2001; Karl et al., 2004). In 785 COV3ER-2016, the soil water content at 10 cm was around 30% humidity in volume, which is 786 quite wet. The canopy wetness as measured by the wetness sensor indicated that around 20% of 787 the day the canopy was wet. Overall, ripening was the wettest period.

Regarding acetic acid emissions, the SEF-based whole plant emissions did not match the EC fluxes. Similarly to methanol, this is most likely due to the strong contribution of the soil to acetic acid uptake, which was probably high enough to dominate the exchange of this compound and overlook plant emissions during senescence. Indeed, Bachy et al. (2016) showed that the soil was an important sink for acetic acid.

793 For all compounds, the observed differences between SEF-based whole plant emissions and EC 794 fluxes, especially large during Sen2, may also be explained by the temperature gradient in the 795 canopy and source location. Indeed, if the air temperature is replaced by the soil temperature in 796 the SEF model to mimic emissions by the bottom of the canopy, the modelled fluxes of methanol, 797 acetaldehyde and acetone fit much better to the measured ones during the senescence 2 phase 798 (Appendix F, Figure F.3 and Table F.1). This may be an indication of Sen2 emissions rather 799 coming from the bottom leaves that are decomposing the most. In the chamber measurements, 800 these leaves were exposed to the same temperature as the entire plant due to efficient mixing in the plant cuvette, which is not the case for the whole canopy that exhibits a large temperature gradient between the cooler ground and the hotter top of the canopy. Moreover, this temperature gradient is likely to increase with senescence due to vanishing transpiration leading to a lower capacity to dissipate solar radiation into evaporation.

805 Comparison of the SEF and γ_{age} estimated in this study, in COV3ER2016, in Bachy et al. (2020) 806 and in Guenther et al. (2012), shows high similarities in SEF between this study and Guenther et 807 al. for methanol and acetone, but lower SEF and higher γ_{age} for acetaldehyde in this study 808 compared to Guenther (Table 3). One the contrary, COV3ER2016 compares very well with 809 Bachy et al. (2012), both in terms of SEF and γ_{age} for methanol and acetaldehyde. For 810 acetaldehyde this study COV3ER-2016 and Bachy et al. all agree well in terms of SEF and γ_{age} , while acetone emissions are larger in COV3ER2016 than in the three other datasets, and γ_{age} is 811 812 lower than 1 in COV3ER-2016.

This comparison suggests that methanol emissions by chamber measurements give larger emissions (by a factor of ~3 to ~4) compared to whole ecosystem fluxes, probably due to soil and plant recapture which would correspond to a large fraction of the emissions. Moreover, the effect of senescence on methanol emissions is negligible in chamber measurements but large and consistent at the canopy scale (factor of 3). The reason is still unclear but may be linked to increased soil emissions (or decreased soil and plant recapture) during senescence.

	Standard emisssion factor μg m ⁻² h ⁻¹				Yage -					
	This study	COV3	ER-2016	G2012	B2020	This study	COV3	ER-2016	G2012	B2020
Compound		Та	Tsoil				Та	Tsoil		
methanol	914	235	306	900	252	1.01	2.4	3.0	1.02	2.7
acetaldehyde	18	18	23	80	19	6.90	6.4	8.1	1.00	5.6
acetone	85	106	152	80	15	1.30	0.6	0.7	1.00	-

Table 3. Standard emission factors (SEF) and γ_{age} compared to existing dataset for wheat. G2012 stands for Guenther et al. (2012), B2020 for Bachy et al. (2020) and COV3ER-2016 for Loubet et al. (2021).

821

For acetaldehyde, whole plant emissions and whole ecosystem emissions are very similar and a quarter of what is used in Megan 2.1 for crops. Senescence consistently induced an increase in acetaldehyde emissions by a factor of 6 to 8 depending on the study, while Megan 2.1 did not attribute any aging effect on acetaldehyde emissions. This consistently suggests a revision of the emission factors and aging effects for acetaldehyde. For acetone, this study suggests Megan 2.1 SEF are valid, while the aging factor is unclear and diverges between studies.

Overall, this comparison suggests a real effect of senescence on the exchange of VOCs from wheat plants leading to a clear increase in the emissions of acetaldehyde during this developmental stage, and for methanol but at the ecosystem scale only. It also indicates that the VOC fluxes measured on the two wheat plants in this study are well representative.

832 **5.** Conclusions

In this study, BVOC exchanges from wheat plants were investigated from ripening to senescence and after harvest, using 2 dynamic chambers, which constitutes a low number of replicates. With regard to the emissions composition during the different investigated periods, methanol was the most emitted compound (49 - 59% of the overall flux) followed by acetone, during ripening and beginning of senescence (7.5 – 8.2% of the overall flux), and acetaldehyde, during the chlorosis 838 phase of senescence (9.7 of the overall flux). We showed that the composition of BVOC 839 emissions varied with wheat plant development. We noticed an increase in the contribution of 840 acetaldehyde and acetic acid to the overall emissions as senescence progressed (from 1.6 to 9.7% 841 and from 1.9 to 7.3% of the overall flux, respectively). We also demonstrated that the amounts of 842 BVOC exchanges varied significantly from one development period to another. The overall 843 BVOC emissions appeared to be twice as large during senescence compared to ripening. In 844 general, once normalized for temperature and light conditions, emissions of the major compounds 845 increased as senescence progressed. After harvest, BVOCs were emitted in small (3 times less 846 than during the ripening on average) but significant amounts, most likely from wheat stems. This 847 suggests that after harvest, the wheat stems left in the field may be a non-negligible source of 848 BVOC. OH reactivity of the emitted BVOC was calculated and showed a small reactivity on 849 average compared to measurements in isoprene or monoterpenes emitter canopies. The OH 850 reactivity however showed a peak of 12 s⁻¹ during the first stage of senescence and a significant 851 contribution after harvest. Overall, senescence induced a marked increase in OH reactivity of up 852 to 4-fold during senescence 1 and 2-fold during senescence 2 compared to the ripening period.

Our measurements lasted only 4 days after the harvest. In order to consolidate our results, it may be important to reproduce these measurements under similar conditions (soil, climate, agricultural practices) on the same species but using more measuring chambers to enable statistical analyses. Moreover, since the impact on atmospheric chemistry is highly dependent on the species of compounds emitted, a good characterization of the emissions, including low emitting compounds, is necessary. It would therefore be very useful to use GC-MS or a fast-GC in conjunction with PTR-MS BVOC flux measurements in order to carry out an accurate identification of the compounds. This would allow to better attribute fragments in particular of acetic acid at m/z 43
and green leaves volatiles at m/z 83.

BVOC emissions, and in particular oxygenated compounds, varied in composition and amounts with the development of wheat. This suggests that the current practice of assigning standard emission factors (SEF) by default to the entire plant season without considering larger emissions during plant senescence, may lead to an underestimation of BVOC emissions by wheat plants and possibly other crop species.

Comparison between whole plant emissions and ecosystem scale emissions suggests that methanol recapture in the canopy may represent a large fraction of the plant emitted methanol, while acetaldehyde emitted at the plant and ecosystem scales are comparable between the two approaches. It also clearly demonstrates a 5-to-8-fold increase of acetaldehyde emissions during senescence.

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883 Data access

884 Data are accessible in dataINRAE repository.

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