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## Nitrous oxide and carbon dioxide emissions following green manure and compost fertilization in corn

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# UNIVERSITÀ DEGLI STUDI DI TORINO

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1	Mitigating the impact of fertilization on global warming: can leguminous green manure and
2	compost help to reduce N <sub>2</sub> O and CO <sub>2</sub> emissions?
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Mitigating the impact of fertilization on global warming: can leguminous green manure and compost help to reduce N<sub>2</sub>O and CO<sub>2</sub> emissions?

#### ABSTRACT

23 Alternative nitrogen fertilizers that stimulate low greenhouse gas emissions from soil are 24 needed to reduce the impact of agriculture on global warming. Corn (Zea mais, L.) grown in a 25 calcareous silt loam soil in northwestern Italy was fertilized with a municipal solid waste compost 26 and vetch green manure (Vicia villosa, Roth.). Their potential to reduce N<sub>2</sub>O and CO<sub>2</sub> emissions was compared to that of urea (130 kg N ha<sup>-1</sup>). Gaseous fluxes were measured for two years in the 27 28 spring (after soil incorporation of fertilizers) and in summer. In spring, the slow mineralization of 29 compost reduced N<sub>2</sub>O emissions (0.11 % of supplied N) relative to urea (3.4 % of applied N), 30 without an increase in CO<sub>2</sub> fluxes. Nitrous oxide (2.31 % of fixed N) and CO<sub>2</sub> emissions from rapid 31 vetch decomposition did not differ from urea. When N2O and CO2 fluxes were combined, compost 32 reduced by 49% the CO<sub>2</sub> equivalent emitted following urea application. Vetch did not show such an 33 effect. In summer, no fertilizer effect was found on N<sub>2</sub>O and CO<sub>2</sub> emissions. Compost proved to be 34 potentially suitable to reduce CO<sub>2</sub> equivalent emitted after soil incorporation while vetch did not. 35 For a thorough evaluation, net greenhouse gas emissions assessment should be extended to the 36 entire N life cycle. Differences between calculated N2O emission factors and the default Tier 1 37 IPCC value (1%) confirmed the need for site- and fertilizer-specific estimations.

38

Abbreviations: ΔCO<sub>2</sub>eq, increase of emitted CO<sub>2</sub> equivalent due to the applied fertilizer N
respect to absence of fertilization; COM, fertilization with compost; CK, check plots not fertilized
with N; EF, nitrous oxide emission factor of fertilizer N applied; GHG, greenhouse gas; LGM,
fertilization with a leguminous green manure (hairy vetch); Ndfa, N derived from the atmosphere
and fixed by a legume; PD, potential denitrification; PMN, N potentially mineralizable in
anaerobiosis; SOC, soil organic carbon; SON, soil organic nitrogen; UR, fertilization with urea;
WFPS, water-filled pore space.

### **INTRODUCTION**

47	Optimal nitrogen (N) fertilization management is crucial not only to crop production
48	improvement and cropping systems energy efficiency (Fluck, 1992; Sauerbeck, 2001; Mosier,
49	2002), but also to ammonia and greenhouse gas (GHG) emission reduction (Freney, 1997; Bussink
50	and Oenema, 1998; Follett et al., 2005; Snyder et al., 2009). Greenhouse gases are produced during
51	mineral N fertilizer synthesis by burning fossil fuels (Jenssen and Kongshaug, 2003) and following
52	their application in the field. After N fertilizer distribution, nitrous oxide (N2O) and nitrogen oxide
53	emissions typically increase due to enhanced nitrification and denitrification processes (Byrnes,
54	1990; Mosier and Schimel, 1991; Stehfest and Bouwman, 2006). On the other hand, adequate
55	fertilization can contribute to soil carbon (C) sequestration through a greater crop residue soil return
56	(Halvorson et al., 1999; Follett, 2001; Alvarez, 2005). Similarly, green manures and organic
57	fertilizers (such as animal manure, slurry, and compost) increase soil C storage and sustain crop
58	nutrition with recycled and/or biologically (not industrially) fixed N (Campbell et al., 2001;
59	Grignani et al., 2007; Melero et al., 2007; Triberti et al., 2008).
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<ul> <li>60</li> <li>61</li> <li>62</li> <li>63</li> <li>64</li> <li>65</li> <li>66</li> <li>67</li> </ul>	Different N sources have already been evaluated for their crop production sustainability while reducing their global warming impact. Among them, leguminous green manure and compost from urban waste represent viable options as mineral N fertilizer substitutes (Bøckman, 1997; Eriksen et al., 1999; N'Dayegamiye and Tran, 2001; Tejada and Gonzalez, 2003; Tejada et al., 2008). In addition to microbial activity stimulation, soil fertility increase, pest control, and reduced soil erosion, leguminous green manures can prevent nutrient leaching during the non-crop growing season and supply low energy cost N to the subsequent crop (Crews and Peoples, 2004; Cherr et al., 2006a). Compost fertilization not only has a low groundwater N pollution risk (Eva Erhart, 2007), if

71 Organic N sources used to sustain crop nutrition can reduce N<sub>2</sub>O and CO<sub>2</sub> emissions after 72 soil incorporation depending on their N and C availability to soil microorganisms. (Granli and 73 Bøckman, 1994; Baggs et al., 2000; Huang et al., 2004). Many indicators can be used to estimate 74 such availability. Among all, soil mineral N, potentially mineralizable N in anaerobios (PMN), and 75 potential denitrification (PD) are common. Soil mineral N is an indicator of the N readily available 76 to nitrification and denitrification (Granli and Bøckman, 1994; Bertora et al., 2008). PMN and PD 77 are used, respectively, as indicators of organic N (Curtin and McCallum, 2004; Russell et al., 2006; 78 Monaco et al., 2008) and C fractions (Bijay et al., 1988; Hill and Cardaci, 2004; Ullah and 79 Faulkner, 2006; Bertora et al., 2007) that can be mineralized easily by soil microorganisms. 80 Moreover, PMN and PD can be used to detect changes in soil organic N (SON) and SOC evolution 81 under differing treatments shortly after their establishment, before equilibrium is attained, as the 82 more labile C and N fractions are known to be more responsive (Campbell et al., 2001). 83 The magnitude of the emission rates and their relative importance among different 84 management practices can vary between soils with different pH. Gaseous emissions from acidic 85 soils have been widely assessed, but less information is available for calcareous soils (Stehfest and 86 Bouwman, 2006). Soil environment, pH in particular, can be crucial determinants of N<sub>2</sub>O emissions 87 (Granli and Bøckman, 1994; Clough et al., 2004) and soil organic matter mineralization (Curtin et 88 al., 1998; Bertrand et al., 2007). The effect of compost application on gaseous emissions from 89 calcareous soil has already been evaluated in Mediterranean climate (Vallejo et al., 2006; López-90 Fernández et al., 2007), but few data are available from temperate climates. 91 Nitrous oxide and CO<sub>2</sub> emissions from soil can potentially occur throughout the year. In 92 temperate climates, emissions are usually concentrated in spring and in summer. In spring, high 93 gaseous emissions occur due to fertilization combined with tillage, in presence of elevated soil 94 moisture following seasonal precipitation. In summer, gaseous fluxes are usually stimulated by

95 warmer temperatures and dry/rewetting cycles following irrigation or rainstorms (Velthof et al.,

96 2002; Jabro et al., 2008; Kavdir et al., 2008; Lee et al., 2009). In this period, plant presence and root

development strongly influence soil environmental conditions and microbial activity (Smith and
Tiedje, 1979; Cheng et al., 2003). Though not exhaustive, N<sub>2</sub>O and CO<sub>2</sub> emissions during spring
and summer can be high and contribute to an important share of total year emissions. Carbon
dioxide fluxes do not represent the treatment net effect on the C balance between soil and
atmosphere, which corresponds to soil organic C (SOC) evolution over time (IPCC, 2007b), but
CO<sub>2</sub> emissions contribute to and can help explain SOC changes (Alluvione et al., 2009).

103 The objective of this research was to give a preliminary evaluation of  $N_2O$  and  $CO_2$ 104 emissions from soil following corn fertilization with compost or leguminous green manure. We 105 tested, using a calcareous soil in temperate climate, the hypothesis that fertilization of corn with 106 compost or leguminous green manure, as alternatives to urea, could reduce the stimulation of CO<sub>2</sub> 107 equivalents emitted as N<sub>2</sub>O and CO<sub>2</sub> after fertilizer incorporation, by influencing its N and C cycles. 108 We expected N<sub>2</sub>O fluxes to be reduced by supplying organic N not readily available to soil 109 microorganisms, as it must be mineralized prior to its availability for the nitrification and 110 denitrification processes. We expected increased N<sub>2</sub>O and CO<sub>2</sub> emissions with rising mineral N, 111 PMN and PD values. Moreover, we expected PMN and PD to detect increases in the SON and SOC 112 following different fertilization managements.

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#### **MATERIALS AND METHODS**

#### 115 Site description and experimental treatments

The field experiment was carried out at the agro-environment experimental station of the Department of Agronomy, Forest and Land Management of the University of Turin (44° 53' 1'' N; 7° 41' 10'' E; 232 m a.s.l.). The site is located in the western area of the Po plain (northwestern Italy) and is characterized by a silt-loam alluvial soil that is scarcely weathered (Typic Udifluvent). Selected chemical and physical properties of the plowed layer (0- to 30- cm) sampled in 2006 are reported in Table 1. The climate is temperate sub-continental, with a mean annual temperature of 11.9 °C and a mean annual precipitation of 734 mm, characterized by two main rainfall periods in
spring (April-May) and autumn (September–November).

124 Our study considered the following treatments: 1) compost mixture of park, garden, and 125 urban waste (COM), 2) winter leguminous green manure (LGM) of hairy vetch, 3) urea at a rate of 130 kg N ha<sup>-1</sup> (UR), and 4) a non-fertilized check plot (CK). Fertilized treatments were designed to 126 127 receive amounts of fertilizer N similar to urea. For compost the total N was considered as fertilizer N while for vetch only the fraction derived from biological N fixation was counted. Treated 48 m<sup>2</sup> 128 129 plots were established in 2006 and organized in a completely randomized design with three 130 replications. Silage corn was grown because it is a main regional crop. Table 2 reports key compost 131 and vetch composition parameters. In the compost, we determined total C by wet oxidation with 132 dichromate and total N by the Kjeldhal method. In the vetch, we analyzed tissue C and N content 133 with a CHN elemental analyzer (NA 1500 Nitrogen Analyzer from Carlo Erba Instruments -134 Thermo Fisher Scientific Inc., Waltham, MA). We analyzed fiber fractions (neutral detergent fiber, 135 NDF; acid detergent fiber, ADF; acid detergent lignin, ADL) according to the Robertson and Van 136 Soest (1981) method. Soluble C was computed by the difference between total C and C in the NDF 137 fraction (Thuriès et al., 2002; Gabrielle et al., 2004). Ash content was determined by loss on 138 ignition at 550°C.

139 The hairy vetch was shredded with a stalk shredder a few days before soil incorporation (17 May 2007 and 13 May 2008). Next, equal amounts of triple super-phosphate (100 kg  $P_2O_5$  ha<sup>-1</sup>) and 140 KCl (200 kg  $K_2O$  ha<sup>-1</sup>) were applied to all plots. Then, a moldboard plow was used to till all plots 141 142 (30 cm depth) and to incorporate the applied fertilizers. Corn was planted on the same date plots 143 were fertilized and tilled (4 June 2007 and 19 May 2008). Post-emergence herbicides were used in 144 all treatments, resulting in the plots being weed-free. A travelling gun sprinkler irrigation system 145 applied 40 mm of irrigation water once during each growing season (in 2007: 31 July, in 2008: 28 August), following the common farmers' practice in the region. The low N content of the irrigation 146 water corresponded to a 4 kg N ha<sup>-1</sup> addition for each irrigation event. 147

148 Each year, we quantified the epigeic biomass of the vetch before its incorporation. Carbon 149 and N in below-ground residue were counted as well (Unkovich and Pate, 2000; Rochette and 150 Janzen, 2005). As we did not measure the biomass of root vetch, we estimated its C and N content. 151 We considered a shoot C: root C ratio of 2.1 to be reasonable (Michalk and Mueller, 2003; Hamer 152 et al., 2008) even though it has been shown to change during vetch development (Gregory et al., 153 1995). The same ratio was used to estimate vetch root N (Unkovich and Pate, 2000; IPCC, 2007b). 154 The percentage of total N in the epigeic biomass derived from the atmosphere (Ndfa) has been 155 measured at 58% in like environment experimental plots (Zavattaro et al., 2003). We used the same 156 percentage for N in root biomass.

157

#### 158 Gaseous fluxes

159 Nitrous oxide and  $CO_2$  emissions were monitored in 2007 and 2008. Each year, we 160 concentrated flux measurements in two periods of the corn growing season when we were expecting 161 high gaseous fluxes: one in spring and one in summer. Spring measurements took place in 2007 for 162 29 days, (from 1 June to 28 June), and in 2008 for 31 days (from 16 May to 16 June). Summer 163 campaigns took place in 2007 for seven days (from 30 July to 6 August), and in 2008 for 12 days 164 (from 16 July to 24 July). In spring, fluxes were monitored a few days before fertilization, and daily 165 measurements were performed in the first week to follow. In subsequent weeks, frequency 166 decreased progressively while gaseous emissions approached the basal flux (absent peaks from 167 tillage, precipitation or irrigation). In summer, about two months after fertilization, fluxes were 168 monitored daily during the first week and three times during the second week. In 2008, no irrigation 169 occurred during the summer campaign because of high late spring precipitation.

We used a non-steady state closed chamber technique (Livingston and Hutchinson, 1995) to measure emissions. In each plot, three stainless-steel anchors, inserted 5 cm into the soil, were set in the inter-row of three non-adjacent rows a week before pre-fertilization measurements started. They were removed for tillage and re-inserted immediately after seeding where they remained until the

175mm; wall thickness: 6.2 mm) was scaled to each anchor with a rubber O-ring. Internal chamber gas176concentrations were measured using an Innova 412 photo-acoustic infrared gas analyzer177(LumaSense Technologies A/S, Ballerup, Denmark) re-circulating the gas sample through two178Teflon tubes (each 12.5 m long) attached to two sampling ports installed atop the chamber.179Consistent with the findings of Flechard et al. (2005), we found the instrument to over-estimate180N <sub>2</sub> O concentration due to high CO <sub>2</sub> and water vapor concentrations during chamber deployment181(data not shown). To solve this problem, N <sub>2</sub> O and CO <sub>2</sub> were measured separately and N <sub>2</sub> O was182measured by forcing the gas sample pumped from chamber to instrument through a soda lime filter183to eliminate almost all CO <sub>2</sub> (concentration below 40 µl Γ <sup>4</sup> ). In order to equilibrate the water vapor184concentration identically across all N <sub>2</sub> O samples, they were then bubbled in 400 ml of de-ionized185water maintained at 18°C. Nitrous oxide dissolution in water did not influence flux estimations186since we calculated the N <sub>2</sub> O dissolved to be in the range of six orders of magnitude lower than that187in the chamber headspace. The absence of effect was verified with a lab test (data not shown). Gas188concentrations were adjusted to account for the mixing of the chamber headspace with the previous189sample still present in the internal volume of the photo-acoustic infrared gas analyzer plus the190sampling tubes (Bertora et al., 2007). Volumetric concentrations of N <sub>2</sub> O and CO <sub>2</sub> measured by the191instrument	174	growing season ended. Every sampling day, a cylindrical PVC chamber (i.d.: 240 mm; height: 110
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181(data not shown). To solve this problem, $N_2O$ and $CO_2$ were measured separately and $N_2O$ was182measured by forcing the gas sample pumped from chamber to instrument through a soda lime filter183to eliminate almost all $CO_2$ (concentration below $40 \ \mu l \ \Gamma^1$ ). In order to equilibrate the water vapor184concentration identically across all $N_2O$ samples, they were then bubbled in 400 ml of de-ionized185water maintained at $18^{\circ}C$ . Nitrous oxide dissolution in water did not influence flux estimations186since we calculated the $N_2O$ dissolved to be in the range of six orders of magnitude lower than that187in the chamber headspace. The absence of effect was verified with a lab test (data not shown). Gas188concentrations were adjusted to account for the mixing of the chamber headspace with the previous189sample still present in the internal volume of the photo-acoustic infrared gas analyzer plus the190sampling tubes (Bertora et al., 2007). Volumetric concentrations of $N_2O$ and $CO_2$ measured by the191instrument were transformed to mass values using the ideal gas law and the recorded air192temperature (HOBO H08-031-08 from Onset Computer Corporation, Bourne, MA) and pressure193(measured by the Innova 1412) inside the chamber.194Fluxes of $CO_2$ and $N_2O$ were estimated from using two gas concentration measurements	179	Consistent with the findings of Flechard et al. (2005), we found the instrument to over-estimate
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to eliminate almost all CO <sub>2</sub> (concentration below $40 \ \mu l \ l^{-1}$ ). In order to equilibrate the water vapor concentration identically across all N <sub>2</sub> O samples, they were then bubbled in 400 ml of de-ionized water maintained at 18°C. Nitrous oxide dissolution in water did not influence flux estimations since we calculated the N <sub>2</sub> O dissolved to be in the range of six orders of magnitude lower than that in the chamber headspace. The absence of effect was verified with a lab test (data not shown). Gas concentrations were adjusted to account for the mixing of the chamber headspace with the previous sample still present in the internal volume of the photo-acoustic infrared gas analyzer plus the sampling tubes (Bertora et al., 2007). Volumetric concentrations of N <sub>2</sub> O and CO <sub>2</sub> measured by the instrument were transformed to mass values using the ideal gas law and the recorded air temperature (HOBO H08-031-08 from Onset Computer Corporation, Bourne, MA) and pressure (measured by the Innova 1412) inside the chamber. Fluxes of CO <sub>2</sub> and N <sub>2</sub> O were estimated from using two gas concentration measurements	181	(data not shown). To solve this problem, $N_2O$ and $CO_2$ were measured separately and $N_2O$ was
<ul> <li>concentration identically across all N<sub>2</sub>O samples, they were then bubbled in 400 ml of de-ionized</li> <li>water maintained at 18°C. Nitrous oxide dissolution in water did not influence flux estimations</li> <li>since we calculated the N<sub>2</sub>O dissolved to be in the range of six orders of magnitude lower than that</li> <li>in the chamber headspace. The absence of effect was verified with a lab test (data not shown). Gas</li> <li>concentrations were adjusted to account for the mixing of the chamber headspace with the previous</li> <li>sample still present in the internal volume of the photo-acoustic infrared gas analyzer plus the</li> <li>sampling tubes (Bertora et al., 2007). Volumetric concentrations of N<sub>2</sub>O and CO<sub>2</sub> measured by the</li> <li>instrument were transformed to mass values using the ideal gas law and the recorded air</li> <li>temperature (HOBO H08-031-08 from Onset Computer Corporation, Bourne, MA) and pressure</li> <li>(measured by the Innova 1412) inside the chamber.</li> <li>Fluxes of CO<sub>2</sub> and N<sub>2</sub>O were estimated from using two gas concentration measurements</li> </ul>	182	measured by forcing the gas sample pumped from chamber to instrument through a soda lime filter
<ul> <li>water maintained at 18°C. Nitrous oxide dissolution in water did not influence flux estimations</li> <li>since we calculated the N<sub>2</sub>O dissolved to be in the range of six orders of magnitude lower than that</li> <li>in the chamber headspace. The absence of effect was verified with a lab test (data not shown). Gas</li> <li>concentrations were adjusted to account for the mixing of the chamber headspace with the previous</li> <li>sample still present in the internal volume of the photo-acoustic infrared gas analyzer plus the</li> <li>sampling tubes (Bertora et al., 2007). Volumetric concentrations of N<sub>2</sub>O and CO<sub>2</sub> measured by the</li> <li>instrument were transformed to mass values using the ideal gas law and the recorded air</li> <li>temperature (HOBO H08-031-08 from Onset Computer Corporation, Bourne, MA) and pressure</li> <li>(measured by the Innova 1412) inside the chamber.</li> <li>Fluxes of CO<sub>2</sub> and N<sub>2</sub>O were estimated from using two gas concentration measurements</li> </ul>	183	to eliminate almost all CO <sub>2</sub> (concentration below 40 $\mu$ l l <sup>-1</sup> ). In order to equilibrate the water vapor
<ul> <li>since we calculated the N<sub>2</sub>O dissolved to be in the range of six orders of magnitude lower than that</li> <li>in the chamber headspace. The absence of effect was verified with a lab test (data not shown). Gas</li> <li>concentrations were adjusted to account for the mixing of the chamber headspace with the previous</li> <li>sample still present in the internal volume of the photo-acoustic infrared gas analyzer plus the</li> <li>sampling tubes (Bertora et al., 2007). Volumetric concentrations of N<sub>2</sub>O and CO<sub>2</sub> measured by the</li> <li>instrument were transformed to mass values using the ideal gas law and the recorded air</li> <li>temperature (HOBO H08-031-08 from Onset Computer Corporation, Bourne, MA) and pressure</li> <li>(measured by the Innova 1412) inside the chamber.</li> <li>Fluxes of CO<sub>2</sub> and N<sub>2</sub>O were estimated from using two gas concentration measurements</li> </ul>	184	concentration identically across all $N_2O$ samples, they were then bubbled in 400 ml of de-ionized
<ul> <li>in the chamber headspace. The absence of effect was verified with a lab test (data not shown). Gas</li> <li>concentrations were adjusted to account for the mixing of the chamber headspace with the previous</li> <li>sample still present in the internal volume of the photo-acoustic infrared gas analyzer plus the</li> <li>sampling tubes (Bertora et al., 2007). Volumetric concentrations of N<sub>2</sub>O and CO<sub>2</sub> measured by the</li> <li>instrument were transformed to mass values using the ideal gas law and the recorded air</li> <li>temperature (HOBO H08-031-08 from Onset Computer Corporation, Bourne, MA) and pressure</li> <li>(measured by the Innova 1412) inside the chamber.</li> <li>Fluxes of CO<sub>2</sub> and N<sub>2</sub>O were estimated from using two gas concentration measurements</li> </ul>	185	water maintained at 18°C . Nitrous oxide dissolution in water did not influence flux estimations
<ul> <li>concentrations were adjusted to account for the mixing of the chamber headspace with the previous</li> <li>sample still present in the internal volume of the photo-acoustic infrared gas analyzer plus the</li> <li>sampling tubes (Bertora et al., 2007). Volumetric concentrations of N<sub>2</sub>O and CO<sub>2</sub> measured by the</li> <li>instrument were transformed to mass values using the ideal gas law and the recorded air</li> <li>temperature (HOBO H08-031-08 from Onset Computer Corporation, Bourne, MA) and pressure</li> <li>(measured by the Innova 1412) inside the chamber.</li> <li>Fluxes of CO<sub>2</sub> and N<sub>2</sub>O were estimated from using two gas concentration measurements</li> </ul>	186	since we calculated the $N_2O$ dissolved to be in the range of six orders of magnitude lower than that
<ul> <li>sample still present in the internal volume of the photo-acoustic infrared gas analyzer plus the</li> <li>sampling tubes (Bertora et al., 2007). Volumetric concentrations of N<sub>2</sub>O and CO<sub>2</sub> measured by the</li> <li>instrument were transformed to mass values using the ideal gas law and the recorded air</li> <li>temperature (HOBO H08-031-08 from Onset Computer Corporation, Bourne, MA) and pressure</li> <li>(measured by the Innova 1412) inside the chamber.</li> <li>Fluxes of CO<sub>2</sub> and N<sub>2</sub>O were estimated from using two gas concentration measurements</li> </ul>	187	in the chamber headspace. The absence of effect was verified with a lab test (data not shown). Gas
<ul> <li>190 sampling tubes (Bertora et al., 2007). Volumetric concentrations of N<sub>2</sub>O and CO<sub>2</sub> measured by the</li> <li>191 instrument were transformed to mass values using the ideal gas law and the recorded air</li> <li>192 temperature (HOBO H08-031-08 from Onset Computer Corporation, Bourne, MA) and pressure</li> <li>193 (measured by the Innova 1412) inside the chamber.</li> <li>194 Fluxes of CO<sub>2</sub> and N<sub>2</sub>O were estimated from using two gas concentration measurements</li> </ul>	188	concentrations were adjusted to account for the mixing of the chamber headspace with the previous
<ul> <li>instrument were transformed to mass values using the ideal gas law and the recorded air</li> <li>temperature (HOBO H08-031-08 from Onset Computer Corporation, Bourne, MA) and pressure</li> <li>(measured by the Innova 1412) inside the chamber.</li> <li>Fluxes of CO<sub>2</sub> and N<sub>2</sub>O were estimated from using two gas concentration measurements</li> </ul>	189	sample still present in the internal volume of the photo-acoustic infrared gas analyzer plus the
<ul> <li>temperature (HOBO H08-031-08 from Onset Computer Corporation, Bourne, MA) and pressure</li> <li>(measured by the Innova 1412) inside the chamber.</li> <li>Fluxes of CO<sub>2</sub> and N<sub>2</sub>O were estimated from using two gas concentration measurements</li> </ul>	190	sampling tubes (Bertora et al., 2007). Volumetric concentrations of $N_2O$ and $CO_2$ measured by the
<ul> <li>193 (measured by the Innova 1412) inside the chamber.</li> <li>194 Fluxes of CO<sub>2</sub> and N<sub>2</sub>O were estimated from using two gas concentration measurements</li> </ul>	191	instrument were transformed to mass values using the ideal gas law and the recorded air
194 Fluxes of $CO_2$ and $N_2O$ were estimated from using two gas concentration measurements	192	temperature (HOBO H08-031-08 from Onset Computer Corporation, Bourne, MA) and pressure
	193	(measured by the Innova 1412) inside the chamber.
195 inside the chamber headspace—at the start and end of closing—and assuming a linear change in gas	194	Fluxes of $CO_2$ and $N_2O$ were estimated from using two gas concentration measurements
	195	inside the chamber headspace—at the start and end of closing—and assuming a linear change in gas
196 concentration over time. This assumption was frequently checked for each treatment by continuous	100	

 $197 \qquad \text{measurement of the CO}_2 \text{ and } N_2O \text{ concentration increases for a period of about 40 min.}$ 

198 Consequently, closure time varied according to flux intensities from about 15 min during emission

199 peaks to about 30 min during low emission periods.

202

#### 201 Soil temperature and moisture

203 growing season using a temperature probe (HOBO H08-031-08 from Onset Computer Corporation, 204 Bourne, MA). Soil samples from 0-7.5 cm depth were collected on each gas sampling day using a 205 soil corer (OakField Apparatus Inc., Oakfield, WI), and gravimetric water content was determined 206 after drying at 105°C for 24 hours. Water-filled pore space (WFPS) (Linn and Doran, 1984a) was 207 calculated using the soil bulk density (Blake and Hartge, 1986) measured at 0- to 7.5- cm in fall 2008 after corn harvest and a particle density of 2.79 Mg m<sup>-3</sup> (Zavattaro and Grignani, 2001). 208 209 210 Soil N and C availability indicators 211 Soil mineral N content, PMN, and PD were measured in each plot during gaseous flux 212 monitoring days: five times in spring (one day before fertilization, the day following fertilization 213 and than weekly until the end of the measurement campaign) and two times in summer (at the 214 beginning and end of the measurement campaign). Measurements were concentrated in the 0- to 215 7.5- cm layer as a previous field experiment (Monaco et al., 2009) showed that the soil surface can 216 be used as a proxy for the whole plowed layer. We confirmed the homogeneity of the soil mineral N 217 content throughout the 0- to 15- cm layer by monitorings conducted during the two 2007 campaigns 218 (data not shown). 219 Soil mineral N was extracted by shaking 16 g of moist soil with 80 ml of 1 M KCl solution 220 for 1 h. Subsequently, samples were filtered through a Whatman No. 1 paper, then extracts were frozen until they were analyzed for  $NO_3^--N$  and  $NH_4^+-N$  concentration by colorimetry with a 221 222 continuous flow analyzer (Evolution II, Alliance Analytical Inc., Menlo Park, CA). 223 Potentially mineralizable N in anaerobiosis was measured according to the method reported 224 by Monaco et al. (2008). Sixteen g of soil and 40 g of water were mixed in a gas tight syringe

Soil temperature (7.5 cm depth) was monitored in one LGM plot during the entire corn

equipped with a vacuum proof stopcock. Air was removed by adjusting the height of the piston and

226	samples were then incubated at 40 °C for seven days. At incubation start and end, inorganic N was
227	extracted with a final 1M KCl solution. Inorganic N was measured as described above.
228	Potential denitrification was measured following the method reported by Bertora et al.
229	(2008) in which undisturbed soil cores are incubated (at 25 °C) in water-saturated, oxygen-free, and
230	non-nitrate-limiting conditions in the presence of acetylene. The soil cores were sampled by
231	inserting a steel cylinder (i.d.: 5.8 cm) 7.5 cm into the soil (on average 257 g of dry soil were
232	sampled). Approximately 200 mg N kg <sup>-1</sup> dry soil were applied using 40 ml of KNO <sub>3</sub> solution
233	distributed over the soil cores stored in 500 ml glass jars to avoid nitrate limitation to denitrification
234	processes (Limmer and Steele, 1982). Anaerobic conditions were created by replacing the jar
235	headspace with N <sub>2</sub> two times after air removal (final absolute pressure of 20 kPa). In order to inhibit
236	the transformation of $N_2O$ to $N_2$ and to prevent nitrification, 10% of the headspace was replaced
237	with acetylene (Yoshinari et al., 1977; Davidson et al., 1986; Tiedje et al., 1989). After 24 h, and
238	again at 48 h, $N_2O$ was sampled from the headspace (25 ml gas in 10 ml evacuated vial) and
239	quantified using a Trace GC Ultra gas-chromatograph (Thermo Fisher Scientific Inc., Waltham,
240	MA) equipped with a thermal conductivity detector. Denitrification rates were calculated assuming
241	a linear increase in N <sub>2</sub> O concentration (Beek et al., 2004).

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#### Percent N lost and CO<sub>2</sub> equivalent emitted

In order to accurately compare  $N_2O$  fluxes from various fertilizer treatments regardless of the amount of N added, cumulative  $N_2O$  emissions, net of the  $N_2O$  emitted from CK, were used to calculate a  $N_2O$  emission factor of applied N (EF) (Table 4). Two EFs were calculated for vetch: one accounting for only fixed N, as it represents the fertilizer N added to the soil (Kelner et al., 1997; Drinkwater et al., 1998), and the other taking into account the full amount of N in the legume biomass (IPCC, 2007b).

Cumulative N<sub>2</sub>O and CO<sub>2</sub> emissions from fertilized treatments were used to calculate the
 CO<sub>2</sub> equivalents emitted (Robertson et al., 2000) after discounting emissions from CK to estimate

the increase in emissions due to fertilization ( $\Delta CO_2 eq$ ). We assumed that the increase in N<sub>2</sub>O and CO<sub>2</sub> emissions between fertilized treatments and CK was due only to the N addition. Carbon dioxide equivalents of N<sub>2</sub>O were calculated by multiplying the amount of N<sub>2</sub>O for its global warming potential (298 kg CO<sub>2</sub> equivalent per kg N<sub>2</sub>O) as suggested by the IPCC (2007a). As different amounts of N were distributed (Table 2), CO<sub>2</sub> equivalents were expressed on one kg of applied fertilizer N basis (for LGM, the amount of N fixed was used).

258

#### 259 Data analysis

Cumulative  $CO_2$  and  $N_2O$  emissions were calculated using a linear interpolation across sampling days. Since the campaigns were slightly longer in 2008 than in 2007, values were calculated on Day 24 after spring fertilization and Day 6 after the start of the summer campaign in both years. The variability among same-plot chambers was found to be significantly lower than the variability among same-treatment plots (data not shown). Therefore, triplicate gaseous flux measurements and the respective  $CO_2$  equivalent and  $N_2O$  EF inside each plot were averaged before subsequent analysis.

Data normality was verified using the Kolmogorov–Smirnov test. Since  $N_2O$  fluxes were log-distributed, the geometrical average of daily values and seasonal cumulates was calculated for same-plot chambers. Daily and cumulative  $N_2O$  fluxes, average soil  $NO_3^--N$  content, and PD were log-transformed (natural logarithm) before the ANOVA and the correlation analyses.

271 Analysis of variance was used to determine differences in cumulative  $CO_2$  and  $N_2O$  fluxes, 272 cumulative  $\Delta CO_2$ eq, average soil  $NO_3$ -N content, PMN, and PD by treatment and year. Seasons 273 were analyzed separately as different phenomena were observed. When significant, means were 274 separated using a Sidak post-hoc test. The relationship between (i) daily  $CO_2$  and  $N_2O$  fluxes, soil 275 temperature, and WFPS, and (ii) cumulative  $CO_2$  and  $N_2O$  emissions, average soil  $NO_3$ -N content, 276 PMN, and PD were analyzed using the Pearson bivariate correlation. Only data from the two spring

277 campaigns were used. All statistical comparisons were made at the  $\alpha = 0.05$  probability.

278 Calculations were made using SPSS 16.0 (SPSS Inc., Chicago, IL).

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280

#### RESULTS

#### 281 Composition parameters of compost and vetch and amounts of added C and N

282 Properties of applied compost and vetch, and amounts of N and C added to the soil varied 283 between years (Table 2). Utilized compost, produced in 2007, was deemed stable and fully mature 284 given its C:N ratio of less than 20 (Chefetz et al., 1996; Brinton, 2000; Silva et al., 2007). 285 Nonetheless, it continued to mature beyond the 2007 fertilization, yielding more stable compost for 286 the 2008 application. Consistent with Chefetz et al. (1996) results describing normal compost 287 evolution, organic matter, C:N ratio, and soluble C:total C ratio decreased while ash content and the 288 recalcitrant ADL fraction increased. Vetch was harvested at mid-flowering both years. In 2008, 289 however, soluble C:total C ratio was higher and ADL was lower. The colder and wetter climate in 290 the second year probably contributed to these differences, even though the vetch was harvested on 291 nearly the same date. Comparison of the two fertilizers, across both years, showed vetch to be 292 characterized by a higher C:N ratio and soluble C:total C ratio, with lower ADL and ash contents 293 than compost.

Based on the amount of compost and vetch biomass incorporated, the total C supplied to the soil was similar between the 2007 treatments while it was 50 % higher in LGM in 2008 (Table 2). The difference was even greater for soluble C (vetch to compost ratio was 2.3). While the amount of total N supplied with compost was comparable to that given with urea (130 kg N ha<sup>-1</sup>) in both years, the amount of N supplied with vetch was higher (both the total N and the Ndfa).

299

#### 300 Gaseous emissions

301 Nitrous oxide emissions in spring were enhanced by fertilization and tillage; fluxes followed
302 a parabolic pattern (Fig. 1a) (Baggs et al., 2000). Fluxes increased within a day after fertilizer

incorporation while emissions peaked after precipitation events. In summer, fluxes were nearlyabsent, even after the 2007 irrigation.

305	Applied N sources affected N <sub>2</sub> O emissions in spring, but not in summer. In spring,
306	cumulative emissions, on average, were almost six times higher in UR and LGM than in COM and
307	CK. A shorter duration of the N <sub>2</sub> O peak coupled with higher values resulted in no significant
308	difference in cumulative emissions between the springs of 2007 and 2008 (Table 3). In summer, no
309	treatment effect was found, and fluxes were lower in 2007 than in 2008. Nitrous oxide emission
310	factors of applied N calculated from spring emissions were on average 26 times higher in UR and
311	LGM than in COM. When EF was calculated considering the entire amount of N distributed with
312	the vetch in LGM (EF used by the IPCC (IPCC, 2007b)) rather than just the N fixed by the crop, the
313	EF of LGM did not vary from COM and was significantly lower than UR (Table 4).
314	Across all treatments, spring CO <sub>2</sub> emissions were enhanced by fertilization and tillage, with
315	fluxes following parabolic patterns similar to N <sub>2</sub> O (Fig. 1b) (Chatskikh and Olesen, 2007;
316	Chatskikh et al., 2008). Fluxes increased immediately after fertilization and tillage, and peaked two
317	weeks later. Emissions retreated back to base level prior to tillage at the end of the third or fourth
318	week depending on the year. In 2007, CO <sub>2</sub> emissions increased after the summer irrigation.
319	Cumulative CO <sub>2</sub> emissions varied among treatments in spring, but not in summer. In spring,
320	cumulative fluxes rose significantly from CK, to UR, to COM, and to LGM (Table 3). A longer
321	duration of the CO <sub>2</sub> emission peak coupled with lower values, resulted in no significant difference
322	in cumulative emissions between the springs of 2007 and 2008. In summer no difference was found
323	among treatments; emissions were higher in 2007 than 2008.
324	Daily and cumulative $N_2O$ fluxes were positively correlated with $CO_2$ emissions (daily
325	values: R=0.65, P<0.01; cumulative values: R=0.56, P<0.01).
326	When $N_2O$ and $CO_2$ emissions were combined, $\Delta CO_2eq$ emitted in spring were no different
327	for LGM with respect to UR, and 49% lower in COM. In summer no treatment effect was found.
328	

#### 329 Soil temperature and moisture

330 The average WFPS changed over time according to precipitation and irrigation events 331 during the different campaigns (Fig. 1). In 2007, the spring average WFPS was 0.62 (following 117 332 mm of rainfall during the monitored period); in the summer it increased from 0.34 pre-irrigation to 333 0.61 post-irrigation (40 mm of irrigation water and 30 mm of rainfall during the monitored period). 334 In 2008, precipitation was frequent; the average WFPS was 0.77 in spring (following 257 mm of 335 rainfall during the monitored period) and 0.49 in summer (21 mm of rainfall during the monitored 336 period). Treatments did not influence WFPS on any of the sampling dates (data not shown). Soil 337 moisture was significantly correlated to N<sub>2</sub>O emission (correlation between daily N<sub>2</sub>O-N emissions 338 and WFPS was significant, R=0.43; P<0.01), but not to CO<sub>2</sub> fluxes.

339 Soil temperature varied among seasons according to climatic conditions and crop presence. 340 The average soil temperature was 25.7 °C during spring 2007, which decreased from 24.3 °C pre-341 irrigation to 21.3 °C post-irrigation in summer. During the wetter 2008, average soil temperature 342 was 20.2 °C in spring and 21.5 °C in summer. Because of corn shading, soil temperature in summer 343 was not much different from the spring temperature. Soil temperature was not correlated to daily 344 N<sub>2</sub>O and CO<sub>2</sub> emissions.

345

#### 346 Soil N and C availability indicators and their correlations with gaseous emissions

347 Soil mineral N was composed almost exclusively of NO<sub>3</sub><sup>-</sup>-N; NH<sub>4</sub><sup>+</sup>-N never exceeded 2 kg ha<sup>-1</sup> (data not shown). Fertilization increased soil NO<sub>3</sub><sup>-</sup>N content in spring and in summer. In 348 349 spring, UR significantly increased (by 50%) the soil nitrate content relative to CK while COM and 350 LGM were intermediate (Table 5). A treatment effect was also present in summer when NO<sub>3</sub><sup>-</sup>N 351 content in CK was 17% lower than in LGM and UR. Comparing the two years, soil NO<sub>3</sub><sup>-</sup>N content 352 after fertilization was significantly higher in 2007 than in 2008 in both in spring and summer. 353 In spring, organic fertilizers (compost and vetch) increased the PMN by 20% with respect to 354 CK. Urea was lower than COM and not different from LGM (Table 5). In summer, PMN was still

355 16% higher in COM and LGM than in CK while UR was intermediate. Comparing the two years,

356 PMN in summer was significantly lower in 2007 than 2008.

Potential denitrification was significantly influenced by fertilizer addition. In spring, organic
fertilization (COM and LGM) increased the PD 50% with respect to UR while CK was
intermediate. In summer, UR was 2.5 times lower than the other treatments. Comparing the two
years, and similar to PMN, PD did not decrease in response to high 2008 precipitation. On the
contrary, PD in summer 2008 was 20% higher than in 2007.
No significant correlation was found between N<sub>2</sub>O or CO<sub>2</sub> emissions and soil NO<sub>3</sub><sup>-</sup>-N
content or PMN. Average PD showed a positive correlation with cumulative CO<sub>2</sub> emissions

364 (R=0.43; P=0.04), but not with cumulative  $N_2O$ .

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- 366

#### DISCUSSION

367 Gaseous emissions

368 The availability of N to soil microorganisms was probably the driving factor in spring N<sub>2</sub>O 369 emissions following fertilization. Losses were highest when N was supplied in a form readily 370 available for N<sub>2</sub>O-producing microorganisms such as urea (Bertora et al., 2008), and were almost 371 null with compost. Surprisingly, fluxes following vetch incorporation were no different from those 372 of urea (Table 4), suggesting that vetch tissues were likely more prone to mineralization than the 373 stable organic matter of compost, which had a lower soluble C:total C ratio and higher ADL and ash 374 content. Moreover, compost contained almost no inorganic N ready for the nitrification or 375 denitrification processes (data not shown). Mineralization of legume residue is known to enhance 376 N<sub>2</sub>O emissions (Rochette et al., 2004; Yang and Cai, 2005). Our results were similar to those of 377 López-Fernández (2007) and Meijide et al. (2007) who found a significantly lower N<sub>2</sub>O emission 378 with organic fertilizers (compost in particular) as compared to urea. Beside N availability, soil 379 moisture fostered N<sub>2</sub>O production, as showed by the significant correlation between daily N<sub>2</sub>O 380 fluxes and WFPS.

381 Two considerations arise when evaluating calculated EFs. First, the EF calculated for LGM 382 for which total N of the biomass is considered added N (recommended by IPCC (2007b)), was 383 smaller than that calculated when only fixed N was considered added N. Compared with other N 384 sources, fertilization with leguminous green manures suffers from the addition to the soil of N taken 385 up by the crop together with the fixed N, thus increasing N<sub>2</sub>O emissions. Second, the 1% default 386 Tier 1 emission factor proposed by the IPCC (2007b) to estimate N<sub>2</sub>O emissions from all N sources is high, relative to our results, for compost fertilization and low for vetch and urea. We remain 387 388 cautious regarding the result, as it requires confirmation by measurements integrating year round 389 N<sub>2</sub>O measurements. Our findings indicate the need for source and site-specific coefficients for the 390 compilation of national greenhouse gas inventories (Velthof et al., 2002; Flynn et al., 2005; 391 Helgason et al., 2005; Bertora et al., 2008; Halvorson et al., 2009). Treatment comparison biases in 392 our study could derive from variation in the percentage of N lost as N<sub>2</sub>O with the N fertilization 393 rate. Given that the percentage of N lost as N<sub>2</sub>O remains constant or rises with increasing N 394 fertilization (Granli and Bøckman, 1994; Mosier et al., 2006; Snyder et al., 2009), and since vetch 395 in both years and compost in 2007 added higher amounts of N to the soil than urea, then the EF 396 calculated for LGM and COM were either comparable or overestimated with respect to UR. 397 During summer, as opposed to spring, the year effect and absence of treatment effect 398 suggest that N<sub>2</sub>O emissions may be influenced more by climatic conditions than by the fertilizer 399 applied in spring. We expected N<sub>2</sub>O emission to increase after the 2007 summer irrigation, but no 400 peak was observed. This contrasted with the findings of other authors (Ball et al., 1999; Velthof et 401 al., 2002; Ruser et al., 2006; Werner et al., 2006). Result differences could be explained if N<sub>2</sub>O 402 emissions after dry-rewetting cycles occurred rapidly (possibly, within one day) before detection 403 (Steenwerth et al., 2005; Yanai et al., 2007; Bertora et al., 2008). We excluded the possibility that, 404 if denitrification was the main producer of N<sub>2</sub>O, lower N<sub>2</sub>O fluxes in summer 2007 than 2008 were 405 caused by a lower N<sub>2</sub>O:N<sub>2</sub> ratio (Granli and Bøckman, 1994) because higher WFPS was present in

summer 2007 than in that of 2008, but water drainage in the soil is swift enough to allow gases toescape from the soil.

408 Organic fertilizers increased soil  $CO_2$  fluxes in spring. Significantly higher emissions were 409 found in LGM than in CK while COM had an intermediate value. The results were likely partly 410 related to the amount of added C. We exclude the possibility that our experimental conditions could 411 have led to dissociation of soil carbonates and subsequent chemical  $CO_2$  release since the soil pH 412 was above the threshold carbonate dissociation value (7.2). Frequent rainfall events during spring 413 2008 did not increase cumulative  $CO_2$  emissions respect to spring 2007, probably because of the 414 consequent colder soil temperature.

415 Summer CO<sub>2</sub> emissions were influenced by climatic conditions and not by fertilizer applied 416 during the spring, as was the case with N<sub>2</sub>O emissions. Soil rewetting via irrigation following a dry 417 period in 2007 promoted SOC mineralization characterized by increased CO<sub>2</sub> fluxes (Jabro et al., 418 2008). The absence of an observed treatment effect in summer relative to spring was probably a 419 consequence of reduced SOC oxidation and increased root respiration. In both summers, basal respiration was only about 10 to 30 kg CO<sub>2</sub>-C ha<sup>-1</sup> d<sup>-1</sup> higher than when measured in spring. We 420 421 expected to observe higher differences due to the contribution of root respiration to CO<sub>2</sub> fluxes from 422 soil organic matter mineralization. Our fluxes are, however, in agreement with those of Rochette 423 and Flanagan (1997) and Rochette et al. (1999), who showed that increased CO<sub>2</sub> emissions from 424 summer root activity are offset by a decrease in SOC respiration. A similar increase in CO<sub>2</sub> fluxes between spring and summer was found by Mosier et al. (2006) and Alluvione et al. (2009) in 425 426 conventionally-tilled continuous corn. If any difference in soil organic matter respiration was 427 present among the various treatments, then it is possible that the N fertilization effect was masked 428 by root activity and C rhizodeposition oxidation (Sainju et al., 2008; Alluvione et al., 2009). 429 We found a positive and significant correlation between CO<sub>2</sub> and N<sub>2</sub>O emissions. This was 430 probably an outcome of the simultaneous interplay of mineralization and N<sub>2</sub>O production or of

431 denitrification enhancement due to anaerobic sites where high amounts of CO<sub>2</sub> were produced
432 (Granli and Bøckman, 1994).

433 When comparing N<sub>2</sub>O and CO<sub>2</sub> fluxes among treatments, it is important to consider that 434 observed differences were probably underestimated. Linear interpolation is known to be a less than optimal model for estimating soil gas fluxes since it does not account for the inevitable immediate 435 436 depleting effect of chamber deployment on gas fluxes (Hutchinson and Mosier, 1981; Healy et al., 437 1996). Despite this limitation, Venterea et al. (2009) suggest using linear interpolation when the 438 research goal is comparison between treatments as in our case. Thus, calculated EF and  $\Delta CO_2$ eq 439 must be used only as indicators of the potential of tested fertilizers to reduce the impact of 440 fertilization on global warming while their quantitative information needs to be considered with 441 caution.

442

#### 443 Soil N and C availability indicators and their correlations with gaseous emissions

444 Soil N and C availability was significantly influenced by the different N sources and by the 445 tendency of added materials to be mineralized.

The addition of readily mineralizable N with urea (Bertora et al., 2008) tended to increase nitrate content in spring relative to vetch and compost, which probably supplied mineral N to the soil more gradually according to their respective organic matter mineralization rates.

Across the two years, soil NO<sub>3</sub><sup>-</sup>-N content after fertilization was significantly lower in 2008 than in 2007 in both spring and summer, probably due to the high frequency of precipitation events that leached some N into deep soil layers.

Surprisingly, cumulative spring  $N_2O$  emissions were not correlated with average soil  $NO_3^-$ N content. Though this result is not common in the literature, it is reasonable in our experiment for a number of possible reasons. First, nitrate availability was probably higher and more different among treatments in deep soil layers (beyond 7.5 cm). In fact, many studies show that materials applied to the surface tend to move to the bottom of the ploughed layer by soil inversion from

457 tillage (Cousens and Moss, 1990; Swanton et al., 2000; Roger-Estrade et al., 2001). Second, a more 458 abundant facultative aerobe population and higher potential denitrification rates can be found below 459 the top soil layer in ploughed soils (Linn and Doran, 1984b; Groffman, 1985; Venterea et al., 2005), suggesting that the N<sub>2</sub>O we monitored was produced below 7.5 cm. A third possible reason for the 460 461 absence of nitrate and nitrous oxide flux correlation is the scale of phenomena. In fact, N<sub>2</sub>O is 462 known to be produced in soil microsites, where local conditions fostering nitrification or 463 denitrification can vary radically from the surrounding soil (Parkin, 1987; Granli and Bøckman, 464 1994; Loecke and Robertson, 2009). It is possible that at a microsite scale, high NO<sub>3</sub>-N content 465 occurred and enhanced N<sub>2</sub>O emissions through denitrification as opposed to dilution at the soil 466 sampling scale. This seems to be particularly true for LGM, where N<sub>2</sub>O was likely produced around 467 decomposing vetch tissue aggregates. Loecke and Robertson (2009) found higher N<sub>2</sub>O emissions 468 when residue was not uniformly distributed in the soil as a consequence of favorable local 469 conditions. Finally, it is also possible that N<sub>2</sub>O was mainly produced by nitrification with NO<sub>3</sub><sup>-</sup>N 470 content having no influence.

471 Potentially mineralizable N in anaerobiosis has been confirmed as a viable indicator to 472 monitor SON evolution under different treatments even in the brief period before equilibrium. In 473 fact, PMN measurements followed a pattern consistent with total SON evolution ---which was significantly higher in COM (1.22 mg N kg<sup>-1</sup>) versus LGM (1.11 mg N kg<sup>-1</sup>) and UR (1.08 mg N 474 475 kg<sup>-1</sup>) in fall 2008. Increased SON and PMN after compost fertilization were consequential to very 476 low mineralization rates of added organic compounds (Debosz et al., 2002; Ginting et al., 2003; 477 Hargreaves et al., 2008). Work by both N'Dayegamiye and Tran (2001) and by Kuo and Jellum 478 (2002) have confirmed SON increases following legume incorporation, although the change can be 479 limited over time (Cherr et al., 2006b). The low PMN in CK was likely related to the lower amount 480 of N returned to the soil from crop residue, which in turn, supplied lower amounts of mineralized N. 481 Though root biomass was not directly measured, we surmise that a lower amount of N was returned 482 by crop root since the total N taken up by the aboveground biomass was not different among

483 fertilized treatments, but it was significantly lower in CK (two year averages for silage corn N uptake: 146 kg N ha<sup>-1</sup> in CK, 180 kg N ha<sup>-1</sup> in COM, 201 kg N ha<sup>-1</sup> in LGM, and 210 kg N ha<sup>-1</sup> in 484 UR; treatment effect: P=0.01). The high PMN was not associated with CO<sub>2</sub> or N<sub>2</sub>O emission. 485 486 The lower PD of urea with respect to organic fertilizers both in spring and in summer was 487 probably due to two phenomena: (1) a rapid mineralization of labile C compounds in soil organic 488 matter following urea application (Kuzvakov et al., 2000; Huang et al., 2004), and (2) a 489 simultaneous and opposite increase in the treatments receiving compost and vetch tissues. The 490 increase in soil labile C after compost and green manure additions agrees with findings from other 491 authors (Chantigny, 2003; Huang et al., 2004; Melero et al., 2007). A tendency for higher PD in CK 492 than in UR might be the consequence of a higher root exudate production by N-stressed corn in the 493 non-fertilized treatment (Rees et al., 2005), as shown by silage corn N uptake. We believe that this 494 difference is not linked to the amount of crop residue returned to the soil. Aboveground biomass was low in CK and consistent among fertilized treatments (two year averages: 17.1 Mg d.m. ha<sup>-1</sup> in 495 CK, 20.1 Mg d.m. ha<sup>-1</sup> in COM, 21.6 Mg d.m. ha<sup>-1</sup> in LGM, and 22.0 Mg d.m. ha<sup>-1</sup> in UR; 496 497 treatment effect: P<0.01). In this paper, we report results from the second and third years after 498 treatment establishment. Therefore, it is likely that the difference in labile C amounts shown by PD 499 between mineral (UR) and organic (COM and LGM) fertilization was the result of a change that 500 occurred in the soil organic matter. Though total SOC measured in fall 2008 was not significantly 501 different among treatments (data not shown), PD was as expected with SOC increase when organic 502 fertilizers are applied.

Potential denitrification is an estimator of labile C available to soil microorganisms. In our experiment, labile C was positively correlated with  $CO_2$  emissions, but did not influence  $N_2O$ fluxes. Our set-up did not allow identification of the relative contribution of denitrification and nitrification to  $N_2O$  emissions. If denitrification was the driving process, then the amount of labile C supplied by soil organic matter was probably sufficient to support  $N_2O$  production, regardless of the treatment. On the contrary, if nitrification was the primary contributor, then the observed absence of

509 correlation between PD and  $N_2O$  would be expected since nitrifying bacteria are autotrophic. This 510 would also be consistent with the absence of correlation between soil nitrate content and  $N_2O$ 511 emissions that we found.

512

#### 513 CO<sub>2</sub> equivalents emitted

514 The calculated  $\Delta CO_2$ eq values provided useful information on the combined contribution of 515 fertilizer induced N<sub>2</sub>O and CO<sub>2</sub> emissions on global warming; however, they do not fully 516 characterize the effect of the studied fertilizers on global warming because soil C evolution, rather 517 than CO<sub>2</sub> fluxes, should be considered.

518 Compost application reduced  $\Delta CO_2$ eq emissions following its use as a corn fertilizer while 519 vetch did not (Table 3). Though fertilization after compost incorporation in the soil seems to have a 520 very low impact on global warming, emissions associated with the collection of the organic 521 materials and the composting process need to be included for a more comprehensive evaluation. 522 Also, the advantage of compost utilization could be reduced in the farmers' practice when compost 523 is added on the basis of an estimated mineralizable N. Fertilization with leguminous green manure 524 seems to be a valuable substitute for mineral N fertilizer as its greenhouse gas impact on global 525 warming is similar to urea, and emissions during crop management can be lower than during mineral fertilizer synthesis. 526

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#### CONCLUSIONS

529 Compost and vetch significantly affected soil N<sub>2</sub>O and CO<sub>2</sub> emissions. The amount and 530 quality of the organic matter they supplied regulated N and C mineralization rates and 531 consequently, the microbial processes producing N<sub>2</sub>O and CO<sub>2</sub>. During the first month in spring 532 after soil incorporation, the stable organic matter in compost mineralized slowly, thereby 533 significantly reducing N<sub>2</sub>O emissions and without increasing CO<sub>2</sub> emissions compared to urea. 534 Compared to compost, fresh vetch tissues decomposed faster and sustained N<sub>2</sub>O fluxes at a rate similar to urea while increasing CO<sub>2</sub> emissions. When N<sub>2</sub>O and CO<sub>2</sub> losses were combined, using
compost decreased CO<sub>2</sub> equivalents emitted per kg of fertilizer N applied by 49% relative to urea
while using vetch did not. In summer, there was no fertilizer effect detected on N<sub>2</sub>O and CO<sub>2</sub> fluxes.
Soil mineral N content, potentially mineralizable N in anaerobiosis, and potential
denitrification all agreed with expected soil organic matter evolution. What did differ from our
expectation was that these measurements did not add substantial information about the processes
leading to N<sub>2</sub>O and CO<sub>2</sub> emissions.

542 We conclude that compost proved to be efficient in reducing N<sub>2</sub>O emissions and 543 maintaining CO<sub>2</sub> fluxes, thereby reducing the global warming impact of fertilization. Hairy vetch 544 did not, as no reduction of N<sub>2</sub>O fluxes, relative to urea, was obtained. Further research is needed to 545 accurately compare tested fertilizers. Flux measurements need to be extended throughout the year 546 (to include off-peak and non-crop growing season emissions), and combined with the entire life 547 cycle of the fertilizer-be it compost (Hao et al., 2001) or urea production (Jenssen and Kongshaug, 548 2003) or hairy vetch field management. As GHG emissions during industrial N fixation are very 549 high, it is likely that both compost and vetch could be viable substitutes for urea. Furthermore, the 550 highly variable N emission factors we found, as compared to the default 1% value proposed by the 551 IPCC (2007b), confirm the need for site- and source-specific estimations.

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## 839 List of Figures

- Fig. 1. Daily N<sub>2</sub>O fluxes (a), daily CO<sub>2</sub> fluxes (b) and precipitation events (including irrigation), soil (VEPS) is the 0, to 7.5, an axii becau (c) during
- 841 temperature and water-filled pore space (WFPS) in the 0- to 7.5- cm soil layer (c) during
- 842 measurement campaigns.

Table 1. Selected soil chemical and physical properties in the 0- to 30- cm layer (plowed layer) at

the study site.	
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Soil texture	
Sand, %	36.0
Silt, %	56.5
Clay, %	7.5
Chemical properties	
pH (soil:water = $1:2.5$ )	8.1
Active CaCO <sub>3</sub> , g kg <sup>-1</sup>	24
Organic C, g kg <sup><math>-1</math></sup>	10.2
Total N, g kg <sup><math>-1</math></sup>	1.0
C.E.C., $\text{cmol}_{c} \text{ kg}^{-1}$	12.8
Exchangeable Ca, cmol <sub>c</sub> kg <sup>-1</sup>	11.4
Exchangeable Mg, cmol <sub>c</sub> kg <sup>-1</sup>	0.4
Exchangeable K, cmol <sub>c</sub> kg <sup>-1</sup>	0.1
Olsen P, mg kg $^{-1}$	16
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	Com	ipost	Ve	tch
	2007	2008	2007	2008
Dry matter, %	61.0	61.6	79.1	89.1
Organic Matter, % dm	51.1	45.4	89.5	88.2
Organic C, % dm	25.6	22.7	45.0	45.1
$NDF^{\ddagger}$ , % dm	33.9	30.5	56.0	44.6
$ADF^{\dagger}$ , % dm	23.2	21.1	41.0	31.7
ADL <sup>‡</sup> , % dm	11.2	12.7	11.0	7.9
Ash, % dm	39.1	47.9	10.5	12.7
Total N, % dm	2.1	2.3	2.7	3.5
C:N	12.2	9.8	17.0	12.9
Soluble C:total C <sup>†</sup>	0.34	0.33	0.37	0.49
Total supply, Mg d.w. ha <sup>-1†</sup>	7.3	4.9	2.9	2.6
Total C supply, kg ha <sup>-1‡</sup>	1877	1123	1910	1734
Soluble C supply, kg ha <sup>-1‡</sup>	635	369	714	856
Total N supply, kg ha <sup>-1 ‡</sup>	154	110	260	298
Estimated N fixation, kg N ha <sup>-1‡§</sup>			151	173

Table 2. Main properties of the compost and vetch incorporated into the soil in 2007 and 2008.

<sup>\*</sup> NDF: neutral detergent fiber, ADF: acid detergent fiber, ADL: acid detergent lignin according to

the Robertson and Van Soest (1981) method; soluble C was computed by the difference between

850 total C and C in the NDF fraction.

<sup>\*</sup> Only the measured aboveground biomass of the vetch is reported.

852 <sup>‡</sup> Shoot : root C and N ratios were estimated to be 2.1

853 § N fixation was estimated to be 58% of total vetch N.

854	Table 3. Cumulative $CO_2$ and $N_2O$ emissions and the corresponding increase in $CO_2$ equivalents
855	above that of CK ( $\Delta CO_2 eq$ ) for the different treatments during measurement campaigns
856	(main effect differences are indicated by upper case letters). The following were the studied
857	treatments: fertilization with compost (COM), leguminous green manure (LGM), urea (UR),
858	and the absence of N fertilization (CK).

		Spring		Summer			
	CO <sub>2</sub>	$N_2O$ $\ddagger$	$\Delta CO_2 eq^{\dagger}$	CO <sub>2</sub>	$N_2O^{\ddagger}$	$\Delta CO_2 eq^{\dagger}$	
	[kg CO <sub>2</sub> -C ha <sup>-1</sup> ]	[g N <sub>2</sub> O-N ha <sup>-1</sup> ]	[kg CO <sub>2</sub> eq ha <sup>-1</sup> kg <sup>-1</sup> fertilizer N]	[kg CO <sub>2</sub> -C ha <sup>-1</sup> ]	[g N <sub>2</sub> O-N ha <sup>-1</sup> ]	[kg CO <sub>2</sub> eq ha <sup>-1</sup> kg <sup>-1</sup> fertilizer N]	
СОМ	1499 AB <sup>‡</sup>	830 B	12.24 B	319	27	0.38	
LGM	1828 A	3802 A	27.95 A	313	48	0.39	
UR	1343 AB	4726 A	24.02 A	278	16	-0.70	
СК	1058 B	637 B	/	302	26	/	
2007	1533	1877	20.92	371	8	0.35	
2008	1331	1651	21.89	236	67	-0.31	
Average	1432	1760	21.40	303	28	0.02	
Year	0.19	0.52	0.33	< 0.01	< 0.01	0.30	
Fertilization	0.01	< 0.01	0.02	0.29	0.29	0.32	
Interaction	0.38	0.43	0.80	0.22	0.22	0.18	
SD	359	2	12.95	47	2	1.30	

<sup>\*</sup> Data normalization for the ANOVA was performed by log-transformation (natural logarithm).

#### 861 Back-transformed data are reported.

863 account for the amount of N distributed in the different treatments, values referred to one kg

864 of fertilizer N applied per ha. For the vetch, only the fixed N was counted as added fertilizer.

865 Carbon dioxide equivalents of N<sub>2</sub>O were calculated using a global warming potential of 298

866 kg CO<sub>2</sub> equivalent per kg of N<sub>2</sub>O (IPCC, 2007a). As reported N<sub>2</sub>O emissions are

geometrical averages,  $CO_2$  equivalents do not correspond to the arithmetical sum of  $CO_2$  and

868  $CO_2$  equivalent N<sub>2</sub>O values.

869 <sup>‡</sup> When the effect of the factor was significant, letters were used to separate between means

according to the results of the Sidak post-hoc test.

<sup>&</sup>lt;sup>\*</sup> Carbon dioxide equivalents emitted by the different treatments above the emissions from CK. To

871	Table 4. Nitrous oxide emission factor of applied N (EF) in fertilized treatments during spring
872	campaigns. In LGM, N <sub>2</sub> O EFs were calculated taking into account only the N fixed (values
873	calculated considering the total N in the vetch residue are reported in brackets). The
874	following were the studied treatments: fertilization with compost (COM), leguminous green
875	manure (LGM), or urea (UR).

	COM		LGM		UR	ł	Avg
2007	0.19		1.95 (1.13)		4.05		2.06 (1.79)
2008	0.03		2.67 (1.55)		2.78		1.83 (1.45)
Avg.	0.11	$A^{\dagger}$	2.31 (1.34)	B(A)	3.42	В	1.95 (1.62)
Year	0.70		(0.50)				
Fertilization	< 0.01		(<0.01)				
Interaction	0.40		(0.37)				
SD	1.22		(1.02)				

<sup>\*</sup> When the effect of the factor was significant, letters were used to separate between means

878 according to the results of the Sidak post-hoc test.

## 879 Table 5. Average soil NO<sub>3</sub><sup>-</sup>N content, potentially mineralizable N (PMN), and potential

- denitrification (PD) in the 0- to 7.5- cm layer in spring and summer. The following were the
- studied treatments: fertilization with compost (COM), leguminous green manure (LGM), or
- 882 urea (UR).

		Spring		Summer			
	NO <sub>3</sub> <sup>-</sup> -N <sup>¶</sup>	PMN	PD¶	NO3 <sup>-</sup> -N <sup>¶</sup>	PMN	PD¶	
	$[\text{kg NO}_3^-\text{-N ha}^-)]$	$[\text{kg NH}_4^+\text{-N ha}^-]$	$[kg N_2 O\text{-}N ha^{\text{-}1}]$	[kg NO <sub>3</sub> <sup>-</sup> -N ha <sup>-1</sup> ]	[kg NH <sub>4</sub> <sup>+</sup> -N ha <sup>-1</sup> ]	[kg N <sub>2</sub> O-N ha <sup>-1</sup> ]	
СОМ	3.94 ab <sup>§</sup>	10.21 c	0.66 b	1.45 ab	12.04 b	0.62 b	
LGM	4.36 ab	9.74 bc	0.67 b	2.60 b	12.36 b	0.68 b	
UR	5.14 b	8.94 ab	0.44 a	5.57 b	11.15 ab	0.28 a	
СК	3.41 a	8.17 a	0.54 ab	0.27 a	10.44 a	0.76 b	
2007	12.87	8.61	0.56	8.92	10.98	0.88	
2008	1.35	9.92	0.60	0.26	12.00	1.06	
Average	4.16	9.26	0.58	1.52	11.49	0.55	
Year	< 0.01	< 0.01	0.47	< 0.01	0.05	< 0.01	
Fertilization	0.01	< 0.01	0.03	0.02	0.05	0.03	
Interaction	0.52	0.18	0.55	0.71	0.44	0.12	
SD	1	1	1	48	1	2	

883

885 Back-transformed data are reported.

886 <sup>§</sup> When the effect of the factor was significant, letters were used to separate between means

887 according to the results of the Sidak post-hoc test.

<sup>&</sup>lt;sup>¶</sup> Data normalization for the ANOVA was performed by log-transformation (natural logarithm).

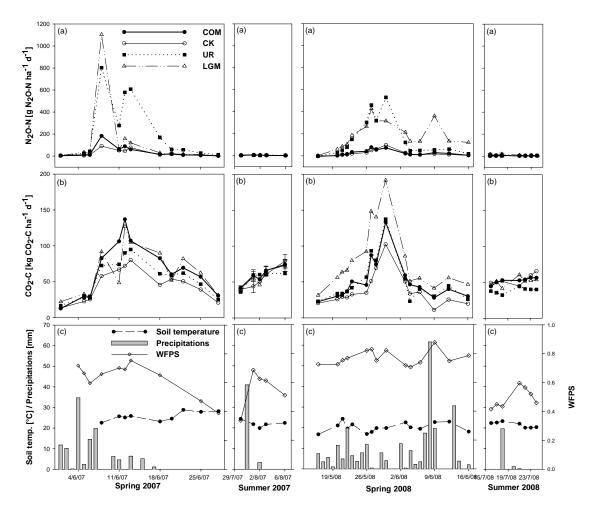


Fig. 1. Daily N<sub>2</sub>O fluxes (a), daily CO<sub>2</sub> fluxes (b), precipitation events (including irrigation), soil
temperature, and water-filled pore space (WFPS) in the 0- to 7.5- cm soil layer (c) during
measurement campaigns.