

Greenhouse gas and ammonia emissions from soil: The effect of organic matter and fertilisation method

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Abstract

Greenhouse gas (GHGs) emissions into the atmosphere derived from the use of fertilisers is a serious issue for the sustainability of agricultural systems, also considering that the growing global demand for food requires an increasingly productive agriculture. Emissions dynamics are very variable and are determined by many factors and their reciprocal interactions. Among driving factors, soil type (mineral, organic and microbiological composition), fertilisation method, climate, and the cropping system. In the present experiment, the combined effect of soil organic matter (SOM) and fertilisation method on the emissions of GHGs and

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ammonia (NH₃) was investigated. Liquid fraction of digestate from pig slurries, compost from organic fraction of municipal solid wastes, and urea were applied on bare soil with two levels of organic matter (OM1: 1.3% and OM2: 4.3%). Emissions were directly monitored by a static chamber system and a portable gas analyser. Results show that soil organic matter as well as the composition of the fertilisers affect greenhouse gasses emissions. Emissions of methane (CH₄) produced by digestate and compost during experimental period were higher in correspondence of lower organic matter content (0.58-0.49 kg CH₄ C/ha/day and 0.37-0.32 kg CH₄ C/ha/day for digestate and compost respectively), contrary to what was observed for urea. For all fertilisers, carbon dioxide (CO₂) and nitrous oxide (N₂O) emissions were higher in correspondence of higher organic matter level. In particular, CO2 emissions were 11.05%, 67.48% and 82.84% higher in OM2 than OM1 for digestate, urea and compost respectively. Likewise, N₂O emissions were 87.45%, 68.97% and 92.11% higher in OM2 than OM1 for digestate, urea and compost respectively. The obtained results show that the content of organic matter in soils plays a key role on the emissions of GHGs, generally enhancing the levels of gas emissions.

Introduction

Several strategies were developed and proposed in the last decades to reduce the environmental impacts from agriculture. In particular, fertilisation is one of the most studied practices due to its detrimental effects on the environment, such as groundwater pollution, eutrophication and greenhouse gasses (GHGs) emissions. An alternative to chemical fertilisers is the use of recycled organic waste materials, as slurries and manure, characterised by low environmental impact and satisfactory crop yields (Alburquerque *et al.*, 2012; Walsh *et al.*, 2012).

In addition to slurry, organic wastes from household and food processing industries are increasingly used as fertilisers in agricultural systems (Alluvione *et al.*, 2010). Of increasing relevance in this context is the combined anaerobic fermentation of organic wastes with slurry in biogas (Wulf *et al.*, 2002) and compost plants. On the other hand, the inputs of organic matter (OM) into the soil play a key role in the productivity of arable land by providing nutrients, through decomposition, and by maintaining soil fertility through OM turnover (Palm *et al.*, 2001). Researchers (Miller and Wali, 1995) have increasingly emphasised the benefits of a balanced fertilisation, by using organic amendment (*e.g.*, crop residues, manure, compost) for enhancing or maintaining soil OM level in soils. However, the efficient and appropriate use of organic fertilisers coming from organic wastes requires more in-depth





knowledge both in terms of quality and fertiliser value (Rowell *et al.*, 2001) aiming to support crop production and protect the environment while saving the soil resource (Mamo *et al.*, 1999). Moreover, a deep knowledge is also required for managing organic fertilisers.

Digestate management plays an important role on the real GHGs impact reduction. Due to its composition, rich in easily available nitrogen (N) for plants and organic carbon (C) (Alburquerque *et al.*, 2012), digestate can increase emissions of ammonia (NH₃) and GHGs such as carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O). An excessive application of digestate to agricultural soil without taking into account strategy to minimise losses through emissions can represent a point of weakness of the system. Within this context, the definition of appropriate management techniques represents one of the best opportunities for GHGs mitigation (Pezzolla *et al.*, 2012).

Bouwman et al. (2010) suggested that the recycling of N in animal manure, human excreta and compost to reduce inorganic fertiliser decreased N₂O emissions from agricultural ecosystems. In a Spanish typic xerofluent with a sandy loam texture, Lopez-Fernandez et al. (2007) demonstrated that organic fertilisers reduced N₂O emissions by 74% (compost) to 27% (pig slurry) in comparison with urea. This reduction was due to the consumption of N₂O by denitrifying bacteria during the irrigation period, which was driven by the addition of labile organic C (Vallejo et al., 2006). In contrast, Hayakawa et al. (2009) observed that adding poultry manure and especially pelleted poultry manure to an andisol increased N₂O emissions by approximately 2 and 7 times, respectively, but reduced NO emissions by 49% and 56%, respectively, compared with inorganic fertiliser. These inconsistent results and reports in the literature may reflect differences in manure composition, C:N ratios, incorporation method and depth into the soil, and the effect of their interaction with soil properties, such as soil organic carbon (SOC) and texture, on N2O production under different environmental, soil moisture and temperature conditions (Huang et al., 2004; van Groenigen et al., 2004; Stehfest and Bouwman, 2006).

For a better understanding of the emission dynamics from agricultural lands, particular attention has to be addressed to the system in absence of crops, which of course affect N and C cycles through uptake and assimilation processes. As affirmed by several authors, nowadays available data are scarce and referred only to specific areas and crops (Le Mer and Roger, 2001; Oertel et al., 2016). Authors affirm there is an inadequate data availability in Mediterranean area, and bare soil in general, with a strong bias towards temperate climate regions. Le Mer and Roger (2001) observed that available data on CH4 emissions are mainly focused on wetlands that represent the main source of CH4 from soils. In this way, upland CH4 emission dynamics are less explored. Despite the fact that N₂O emissions are widely explored, contradictory results are observed regarding the effect of soil organic matter on N₂O emissions. Velthof et al. (2003) observed that an addiction of organic c on arable soils encourage N2O emissions through denitrification. However, authors recommend further investigation on the interaction between manure/fertiliser composition and soil characteristic and utilisation. Instead, Oertel et al. (2016) reported a different behavior and described how the addiction of OM into the arable soils decrease N2O emissions. Considering the often discordant results, but also the great variability of soil and fertiliser compositions, and the influence of local climate factors (temperature, rainfall, wind, etc.), GHGs emissions dynamics need more indepth specific investigations. Moreover, as affirmed by Minoli et al. (2015), also NH₃ emission dynamics need a deep-in-knowledge assessment mainly due, especially for Italy, to inconsistencies in the measurement methods. The aim of this research is to study the emissions (GHGs and NH₃) of liquid fraction of digestate and compost after incorporation into bare soil, and to investigate the effect of organic matter in emission dynamics.

Materials and methods

Experimental field was located at the ITAGR (*Istituto Tecnico Agrario Statale*) via delle Cascine, Firenze (43°47'02.3"N 11°13'13.4"E), Italy. The experiment was conducted on 24 pots (9.5 L volume) 24 cm high and diameter of 24 cm, placed in the open field and exposed to the environmental conditions. Each pot was filled with 8 kg of a silty-clay soil (24% clay, 31% silt and 45% sand) from experimental fields of *Consiglio per la ricerca in agricoltura e l'analisi dell'economia agraria - Centro di ricerca per l'agrobiologia e la pedologia* (CREA-ABP) located in Scarperia, Firenze (43°58'56" N, 11°20'53" E). The experiment was set on bare soil in order to investigate the effect of the different fertilisers excluding any possible interference of the crop.

A layer of 30 cm of soil was taken from the experimental site including top and sub soil layer, and mixed before filling the pots in order to homogenise it. Soil sample was analysed in laboratory for elemental characterisation (Table 1). Experimental design consisted of two contrasting levels of soil organic matter - OM1 1.3% (that was the original OM content in the soil) and OM2 4.3% - with four treatments. Enrichment of OM into the soil was performed by adding 320 g pot⁻¹ of commercial manure, GoldenAgro Ecolife, (from poultry, piggery and horse manure) with 25% of organic C content and 2% of total N, which did not significantly affected soil mineral composition.

Treatments included two types of organic fertilisers (liquid fraction of digestate from pig slurries and compost from organic fraction of municipal solid waste) as well as one organo-mineral fertiliser (urea), with the non-fertilised pots as control treatment. Replicates were carried out in a randomised block design. The digestate was produced by *Fattoria di Corte Marchesi De' Frescobaldi* farm (Florence, Italy, 43°58'29" N, 11°23'21" E), while the compost derived from composting plant of *Alia Servizi Ambientali Spa* (Florence, Italy, 43°55'580.95" N, 11°21'00.09" E). The amount of each fertiliser varied according to its N content (Table 2) and was calculated on the base of a pre-defined quantity of 150 kg N/ha. Fertilisers were incorporated into the soil by manually replacing injection, for digestate and mechanical harrowing incorporation for compost and urea. Immediately after fertilisation, the anchors were placed into the soil (10 cm depth) and the cham-

Table 1. Soil characterisation.

	Unit	Soil
Texture		
Silt	%	31
Clay	%	24
Sand	%	45
N total	%	0.14
P total	%	0.07
K total	%	0.23
рН		8.06

bers were connected. Emission measurements were conducted three times in the first week after fertilisation (0 h, 48 h and 96 h) and once a week in the following three weeks to investigate the emission trend (26 days of measuring period). In accordance to Parkin and Venterea (2010), measurements were performed in mid-morning - early evening (times more closely corresponding to the daily average temperatures) to account diurnal variability. Experimental pots remained opened between successive measurements to enable volatilisation, as these conditions would be the closest to the ones occurring naturally. CO2, CH4, N2O and NH3 emission rates were measured by means of a static chambers system (Parkin and Ventera, 2010), equipped by two thermocouples per chamber, and a portable gas analyser XCGM 400 (Madur) that use nondispersive infrared sensors (NDIR) technology for CO₂, CH₄ and N₂O analysis and electrochemical technology for NH₃. Chambers are composed of two parts: the lid of the chamber (cylinder of 20 cm of diameter and 25 cm high) and the anchor system (cylinder of 20 cm diameter and 15 cm high). Samplings were performed by holding a needle, connected to XCGM 400, inside the chamber for 1-min recording gas accumulation at time 0 (immediately after chamber closing) and at time 1 (after 1 h).

Gas fluxes were calculated starting from the gas concentration into the chamber, chamber dimensions (area and volume), closing time and molecular weight of each gas. As temperature had a similar trend inside each chamber (data not shown), the whole experiment was assumed to be at standard temperature and pressure (STP) conditions and the molar volume of the air is assumed as 22.4 L.

An automatic meteorological station placed 20 meters far from the experimental field continuously monitored air temperature, atmospheric pressure and precipitations (Figure 1). However, during the experiment any precipitation were observed. In the second and the third day after fertilisation, two hours prior to the gas measurements 10 mm of water were added to each pot for accelerating the beginning of the emissions process.

The observed data were statistically processed using STATIS-TICA 13.0 (StatSoft, DELL, USA). In order to test the differences of measured (calculated) parameters between the samples Duncan's multiple range tests with the confidence of $P \le 0.05$ was performed.

Table 2. Elementa	l characterisation	of tested	fertilisers.
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	Urea	Digestate	Compost	
N content total%	46	0.319	2.27	
N-NH4+%	-	0.284	0.15	
N-NO ₃ %	-	0.035	0.0013	
P content total%	-	1.84	0.34	
K content total%	-	6.94	0.97	

Results

Carbon dioxide

Observed data from 26-measurement days showed that CO_2 was the most emitted gas from all fertilisers, although a high variability in the amount of emissions was observed (Table 3).

The highest rate of CO₂ emissions was produced by digestate. In particular, emissions were more than ten times higher than the other treatments in OM1 (23.24 Kg CO2-C ha-1 day-1), and more than three-to-four times than other treatments in OM2 (26.14 Kg CO₂-C ha⁻¹ day⁻¹). As for digestate, emissions from other fertilisers were positively affected by the increase of OM into the soil. In all treatments, emissions were higher compared to control with the exception of compost in OM1 that produced less CO₂ than control. Emissions trend show a specific behavior for each treatments (Figure 2). Urea and compost (and control) emit 16-30 Kg CO₂-C/ha/day and, except for urea in OM2, emissions increased until the third-fourth day and then decreased following a similar trend. In OM2, urea produced the highest amount of emissions in the first days and then emissions decrease regularly. Digestate showed the highest daily emission of 327 (OM2) and 259 (OM1) of Kg CO2-C ha^{-1} day^{-1}. At the end of the measurement period, CO₂ emissions were still observed.

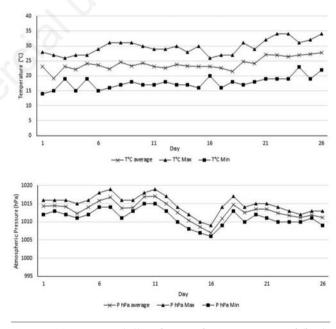


Figure 1. Temperature (°C) and atmospheric pressure trend (hPa).

Table 3. Cumulative emission fluxes on 26-days measuring period for each fertiliser and OM rate.

	kg CO ₂ -C ha ⁻¹		kg CH₄-C ha ^{−1}		kg N ₂ O-N ha ⁻¹		kg NH₃-N ha ⁻¹	
	OM1	OM2	OM1	OM2	OM1	OM2	OM1	OM2
No-fertiliser	38.50 ^g	129.19 ^e	8.06 ^d	8.06 ^d	0.04 ^c	0.31 ^{bc}	0.00 ^e	0.06 ^{de}
Digestate	604.12 ^b	679.75 ^a	15.07 ^a	12.65 ^b	0.96 ^b	7.65 ^a	0.61 ^b	0.59 ^b
Urea	67.04 ^f	206.67 ^c	8.95 ^d	11.17 ^{bc}	0.09 ^c	0.29 ^{bc}	0.09 ^{de}	1.15ª
Compost	29.22 ^h	169.35 ^d	9.62 ^{cd}	8.38 ^d	0.03 ^c	0.38 ^{bc}	0.26 ^{cde}	0.54 ^{bc}

Values marked with the same letter for each gas do not differ significantly according to Duncan's multiple range tests.



Methane

In contrast with previous results, digestate and compost produced more CH_4 emissions in correspondence of the lower OM content of soil. If for digestate differences are significant in compost they are negligible (Table 3). CH_4 emissions from urea were still higher in OM2 than in OM1. For all fertilisers, emissions decreased immediately after spreading; at day 5, an increase in the emissions from urea in OM2 and from digestate, and compost, in OM1 were observed (Figure 3). As for CO_2 , at the end of measurement period CH_4 emissions were still occurring.

Nitrous oxide

In accordance to CO_2 fluxes, N_2O emissions were positively correlated to OM content of soil. However, significant differences were observed only for digestate that produced roughly seven times more N_2O in OM2 than in OM1 (Table 3). For all treatments N_2O was produced a few days after fertilisers spreading in correspondence of irrigation. A peak of emissions in the third day was observed; then emissions decreased regularly until complete depletion in the first week, for urea, and in the second week for digestate and compost (Figure 4).

Ammonia

Any influence of OM on NH₃ emissions from bare soil was observed (Table 3). All fertilisers produced a similar amount of NH₃ emissions. The only exception was represented by urea in OM2 that showed a higher production of NH₃. However, the main part of the emissions were produced by urea in OM2 during the first day after fertilisation. For all fertilisers emissions occurred only during the first week, with complete emission depletion on the fifth day. Urea in OM2 and compost in both OM levels had the highest emissions rate on the first day and a regular decrease in the following days. Urea on OM2 and digestate in both OM levels had a peak of emissions on the third day with a consequentially complete depletion on the fifth day, as other treatments (Figure 5).

Discussion

In this experiment, GHGs and NH₃ emissions were measured in absence of crop, so that no C and N removal from plant uptake occurred and soil nutrients content was assumed constant during the measurement period. This may have caused higher emission

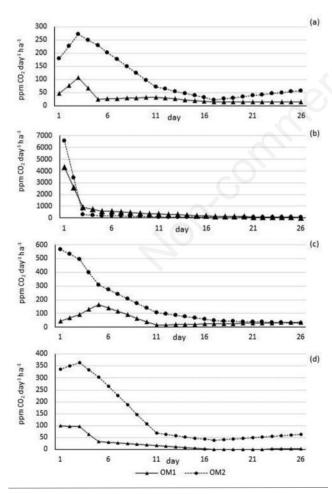


Figure 2. Daily CO₂ emission trend (parts per million) on 26-day measuring period for control (A), digestate (B), urea (C) and compost (D) at OM1 (\blacktriangle) and OM2 (\bigcirc).

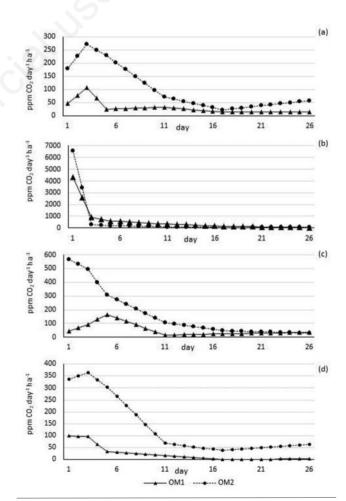


Figure 3. Daily CH₄ emission trend (parts per million) on 26-day measuring period for control (A), digestate (B), urea (C) and compost (D) at OM1 (\blacktriangle) and OM2 (\blacklozenge).



compared to open field conditions. However, especially for compost, fertilisers are often applied several weeks before crop sowing. In this period, between soil fertilisation and the presence of the crop in the field, C and N mineralisation and nitrification, with consequent emissions, may occur. In this context, a careful evaluation of most appropriate agronomic strategies to mitigate the risk of emissions is needed. In addition, soil temperature into the plot might be higher than in open field conditions, thus causing higher emissions. Nevertheless, the relative difference among treatments is not affected. Further studies on emission dynamics from open field bare soil are needed for a more in depth understanding of the process.

Carbon dioxide emissions

 CO_2 is produced in soil as result of decomposition of organic material by microorganisms and root respiration (Schlesinger and Andrews, 2000). In accordance to that, results show that an enrichment in soil OM content positively affects CO_2 emissions. As affirmed by several authors, CO_2 emissions dynamics from agricultural soil are affected by a wide range of factors (Six *et al.*, 1999; La Scala *et al.*, 2000; Paustian *et al.*, 2000). In this respect, OM represents one of the main ones due to its influence on soil respiration. A higher soil OM is able to increased soil respiration and consequently CO_2 emissions, as observed in the experiment. Digestate produced higher emissions compared to urea. In particular, this is due to digestate composition, rich in water, which allows the infiltration into the soil. An enrichment of water content of soil combined to the mild air temperatures occurred probably encouraged the proliferation of soil microorganisms and consequentially soil respiration. However, as observed by Maucieri *et al.* (2016), CO_2 emissions immediately decreased after fertiliser spreading in both OM levels and differences between OM1 and OM2 were not statistically significant.

Urea produced a higher level of CO_2 compared to compost, and the role of OM was evident. In fact, cumulative CO_2 emissions in OM2 were more than 3 times higher than in OM1. This effect was also enhanced by irrigation that ensured hydrolysis of urea with a consequent production of CO_2 . As observed by Schlesinger and Andrews (2000) CO_2 emissions are related to soil respiration following organic residues degradation. In agricultural soils the presence of crops and crop residues continuously provide organic materials for degradation. These observations are in accordance to ours were CO_2 emissions were still occurring, in all treatments, at the end of measuring period.

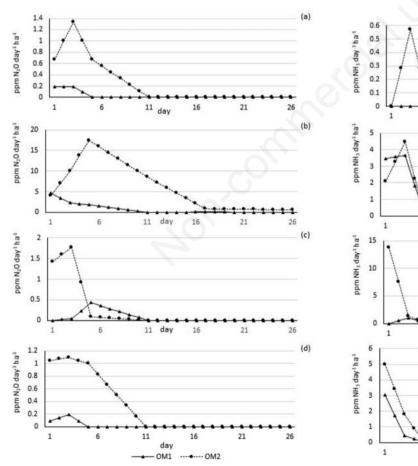


Figure 4. Daily N₂O emission trend (parts per million) on 26-day measuring period for control (A), digestate (B), urea (C) and compost (D) at OM1 (\blacktriangle) and OM2 ($\textcircled{\bullet}$).

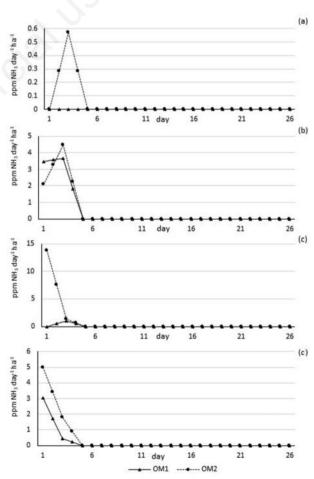


Figure 5. Daily NH₃ emission trend (parts per million) on 26-day measuring period for control (A), digestate (B), urea (C) and compost (D) at OM1 (\blacktriangle) and OM2 (\blacklozenge).



Methane emissions

Results obtained from manures (digestate and compost) showed that CH₄ had an opposite trend compared the other gasses monitored. In particular, digestate and compost produced more emissions in OM1 than in OM2. As described by Le Mer and Roger (2001) CH₄ emissions from soil are again affected by many factors and a negative correlation between CH4 emissions and C/N ratio was reported. An enrichment of available C stimulates the population soil microorganisms that use a great part of C for their metabolism with a reduction of available C for CH₄ production (Bernet et al., 2000; Norberg et al., 2016). In this respect, the composition of manure used to obtain the two levels of OM, which represent the 25% of total organic C, partially explain the behavior of CH₄ emissions from organic fertilisers. In addition, the composition of organic fertilisers, rich in total organic C (34.5% and 25.6% for digestate and compost, respectively), may have reduced CH₄ emissions. Moreover, an addiction of liquid (digestate) and fine milled (compost) fertilisers to the soil may had created compaction and so anaerobic conditions that modified the balance between denitrifying and methanogenic bacteria, in favor of the first ones (Saggar et al., 2004; Bunemann et al., 2006). In the case of urea, that does not contain organic C, the positive correlation between OM level and CH₄ emissions was confirmed.

Nitrous oxide emissions

Results obtained demonstrated that N2O emissions are positively affected by the OM content of soil. For all tested fertilisers N₂O emissions in OM2 were higher than in OM1. In particular, digestate produced the highest emissions and this was due to its high water content and irrigation that determines anaerobic conditions with consequent higher N2O losses compared to the other fertilisers (Wulf et al., 2002). Moreover, the higher amount of organic C available into the soil in OM2 probably encouraged denitrification activity and N degradation (Velthof et al., 2003). The high rate of readily available N compounds of digestate and the mild temperature occurred during the experiment (average of 28.4°) enhanced N losses in the first two weeks after fertilisation. On the other hand, compost emitted a N₂O rate comparable with the control, probably due to its low water content and its stable chemical composition. This result, in fact, is in accordance with the findings of Dalal et al. (2010), confirming that the application of compost can be considered an efficient strategy to reduce N2O emissions. Moreover, differences on emissions between the two fertilisers are in accordance to Aguilera et al. (2013) that found more N₂O emissions from liquid than solid organic fertilisers. Finally, concerning urea, its low water content reduces the risk of anaerobic conditions at soil level and the consequent N2O emissions that are comparable with those of compost. Further, during hydrolysis the majority of N contained in urea is transformed into NH₃ with a reduction of N available for denitrification.

Ammonia emissions

 NH_3 emissions were nearly five times higher in OM2 than OM1 treated with urea. Again, this confirms that higher organic C content into the soil modifies the C/N ratio and encourages bacteria activity with greater degradation of N and NH_3 losses. Moreover, as observed by Rochette *et al.* (2013), the increase of soil pH caused by urea hydrolysis encouraged NH_3 volatilisation losses. Further, NH_3 emissions were also favored by irrigation. On the other hand, contribution of manure, used for soil OM enrichment to NH_3 emissions, can be consider negligible due to its neutral (7) pH.

Digestate and compost are an exception: digestate showed the highest rate of NH₃ emissions of them. However, no differences between emissions in the two OM levels were observed. As on digestate, also on compost no significant differences were observed between the OM levels. This suggests that OM content of soil does not affect NH₃ volatilisation dynamics. Moreover, the neutral pH of digestate (7.7) and compost (6.8) had reduced NH₃ volatilisation losses compared to urea.

Conclusions

This experiment was performed to evaluate the effect of soil organic matter on GHGs emissions that occur from soil after fertilisation with different fertilisers. A wide range of factors affects emission dynamics into the soil, however, organic matter is one of them and plays a key role, generally enhancing the levels of GHGs emissions. In addition, fertiliser spreading emphasises emissions dynamics from soil. In this regard, compost represents an alternative to mineral fertilisers for GHGs and NH₃ mitigation. In particular, compared to urea, reduced CH₄ and N₂O, and comparable CO₂ and NH₃ make compost an interesting strategy for sustainable fertilisation management.

However, further investigations in open field are needed to exclude the influence of pot. Likewise, CH₄ emission dynamics from digestate and compost require additional studies that consider soil microorganisms population.

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