Highlights

- Nitrification was the dominant biological process driving N_2O production.
- CO_2 respiration was strongly influenced by the availability of labile C.
- Fertilisation had no effect on soil-borne CH_4 emissions
- Global warming potential of biobased fertilisers did not exceed that of mineral fertilisers.

Greenhouse gas emissions from a sandy loam soil amended with digestate-derived nitrogen fertilisers – a microcosm study

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Abstract

Nutrient recovery from anaerobic digestion systems provides several side streams that are useful as biobased fertilisers (BBFs). A microcosm approach was employed to assess the short-term greenhouse gas emissions from a sandy-loam soil enriched with 18 BBFs in comparison with mineral fertilisers (urea and calcium ammonium nitrate). In total, 20 different fertilisers were homogeneously incorporated into an arable sandy loam soil at a rate of 170 kg nitrogen (N) ha^{-1} and incubated at 80% water-filled pore space. Over 18 days, the fluxes of nitrous oxide (N_2O), methane (CH_4), and carbon dioxide (CO_2) released in the headspace of the microcosms were measured using a Gasera One Multi-gas analyser. Cumulative N_2O emissions from the BBF treatments were either comparable or lower (0.04 – 0.09 %N applied) than the mineral fertilisers (0.10 – 0.14 %N applied). Nitrification of the initial ammonium-N present in the BBFs was likely the dominant biological process driving N_2O production. The application of digestate and evaporator concentrates led to an increase in CO_2 emissions (8–51% of applied carbon (C)), mostly in the first days of the incubation. Meanwhile, the solid fraction of digestate exhibited slow mineralisation patterns (3–7 % of applied C). The variability in CO_2 respiration was strongly influenced by the availability of labile C. Fertilisation had no effect on soil-borne CH_4 emissions. Estimation of global warming potential, with respect to added N, suggests that BBFs obtained from the post-digestion treatment of digestate have a lower environmental impact compared to the unprocessed digestate due to lower N_2O emissions.

Keywords: biobased fertilisers, digestate, N_2O emission, microcosm, global warming potential

1. Introduction

Anaerobic digestion (AD) of organic wastes enables the production of biogas as a renewable energy carrier and provides a promising alternative to the use of fossil fuels (Holm-Nielsen et al., 2009). By converting food and animal wastes to energy, AD plays a significant role in reducing greenhouse gas (GHG) emissions from conventional energy sources. In addition, evidence suggests that the digestate, which is the residual matter after AD, may be useful as a fertiliser or soil improver because it retains most of the plant nutrients contained in the initial feedstock (Möller, 2009). Therefore, its use in agriculture is expected to improve soil fertility while reducing farmers' input of fossil-dependent mineral fertilisers.

The increase in soil available nitrogen (N) from the application of N fertilisers enhances nitrification and denitrification, which are soil processes that release nitrous oxide (N_2O) into the atmosphere (IPCC, 2006; Senbayram et al., 2010). N_2O is critical from the climate perspective because it is an ozone-depleting gas, with a global warming potential (GWP) 296 times that of carbon dioxide (CO_2) and 12 times that of methane (CH_4) in a 100-year time horizon (IPCC, 2007). Recent data revealed that transformations of N in agricultural soils by nitrifying and denitrifying microorganisms account for approximately 70% of the annual N_2O budget globally (Tian et al., 2019). This represents a major increase compared to the 50% contribution estimated in the early nineties (Bouwman, 1990). Therefore, for digestate-derived bio-based fertilisers (BBFs) to be used sustainably in agriculture as N fertilisers, it is necessary to ensure that their environmental impact is minimal. Moreover, fertiliser N lost from soils in gaseous form (N_2O, nitric oxide, and dinitrogen) reduces the fertiliser efficiency (Holland and Weitz, 2003).

Besides N availability, other factors that influence the magnitude of N_2O emission from soil include moisture content, pH, and carbon (C) supply (Akiyama et al., 2005; Dalal et al., 2003). In particular, the soil moisture content plays a crucial role as it impacts soil

aeration, diffusion of dissolved nutrients, and the rate of microbial activities (Hütsch et al., 1999). Nitrification by heterotrophic microorganisms proceeds under sufficiently aerobic conditions while heterotrophic denitrification increases as oxygen availability become restricted (Hütsch et al., 1999; Le Roux et al., 2013). The addition of organic substrates with high organic C concentration is likely to favour denitrification since heterotrophic denitrifiers utilize organic C as electron donors (Hattori, 1983). Digestate, however, have lower availability of labile C since a large fraction of the easily degradable organic matter in the feedstock is consumed during AD (Alburquerque et al., 2012). This partly explains why some studies found that N_2O emissions from the soil after the application of digestate are generally lower than those after application of untreated feedstock (Cayuela et al., 2010; Johansen et al., 2013; Möller, 2009). Differences in N_2O emission rates from those studies were related to the form of N in the digestate (mineral N or organic N) as well as the quantity and quality of organic C.

Bodelier and Laanbroek (2004) demonstrated that the application of N fertiliser could indirectly stimulate the oxidation of CH_4 because the increase in available N increases the activity of methanotrophic and nitrifying bacteria in the soil. Existing literature on CH_4 emissions after digestate fertilisation is often focused on paddy fields since they are the main sources of CH_4 from soils (Odlare et al., 2012; Singla and Inubushi, 2014; Walling and Vaneeckhaute, 2020). In the few studies that have explored CH_4 emission dynamics in digestate-fertilised upland soils, emission rates were related to the soil moisture content and the availability of labile C (Czubaszek and Wysocka-Czubaszek, 2018; Pezzolla et al., 2012; Rosace et al., 2020). As such, organic C mineralization into CO_2 and CH_4 is useful as a measure of soil microbial activity and the intensity of N transformations (Liu et al., 2019; Shao et al., 2014).

In recent years, emphasis has been placed on nutrient recovery and reuse (NRR) technologies which enable the processing of digestate into concentrated end-products with high fertilisation value (Vaneeckhaute et al., 2017). At the basic refinement level, phase partitioning of digestate is carried out to obtain a phosphorus- (P) rich solid fraction (SF) and an N-rich liquid fraction (LF). The SF is sometimes subjected to drying or composting. Meanwhile, further processing of the LF using advanced NRR technologies such as N-stripping, vacuum evaporation, membrane filtration, among others, can deliver multiple cascades of nutrient-rich BBFs (Brienza et al., 2021; Logan and Visvanathan, 2019). Examples of such BBFs include ammonium sulphate solution (Brienza et al., 2020; Sigurnjak et al., 2019), ammonia water (Jamaludin et al., 2018; Vondra et al., 2019), evaporator concentrate (Vondra et al., 2019), reverse osmosis concentrate and permeate water (mineral Logan and Visvanathan, 2019). Based on the compositional differences of these novel BBFs, compared to the unprocessed digestate, it can be assumed that their behaviour as fertilisers could differ considerably. While a few studies have investigated the soil fertilisation potential of these novel BBFs (Ehlert et al., 2019; Sigurnjak et al., 2017), there is a paucity of data on their GHG emission potential when applied to the soil.

To close this knowledge gap, the short-term and long-term effects of the application of digestate-derived BBFs on soil GHG production ought to be evaluated. In this context, this work aimed to evaluate and compare the short-term N_2O, CO_2 and CH_4 emissions from a sandy-loam soil fertilised with (i) untreated anaerobic digestate (ii) BBFs derived from different post-digestion treatment processes of digestate (iii) two mineral N fertilisers – urea and calcium ammonium nitrate (CAN). It has been previously shown that soil processes such as respiration, nitrification, and denitrification respond sensitively to C and N availability as well as changes in redox conditions (Le Roux et al., 2013). Therefore, it is predicted that the differences in the forms and availabilities of N and C in the digestate-derived BBFs will

influence the production of GHGs after their addition to soil. We hypothesized that the short-term emissions of N_2O, CO_2, and CH_4 from different BBF-amended soils are variable and this variability is due to differences in concentrations of ammonium-N (NH_4^+-N) and labile C.

2. Materials & Methods

2.1 Origin of the biobased fertilisers

Digestate samples were obtained from five full-scale AD plants. The digestates were treated to produce thirteen different biobased fertilisers, depending on the type of NRR technology present at each plant (Table 1).

Groot Zevert Vergisting (GZV, Beltrum, the Netherlands) operates a mesophilic (~35 ºC) AD plant that is fed with pig slurry (81% w/w) and residue from the agro-food industry (a.o. grain and rice husk, potato skins and coffee grounds, 19% w/w). A decanter centrifuge is used to dewater the digestate (D-GZV) to obtain the solid fraction (SF-GZV). Part of the SF is further processed in an installation to remove and recover P which includes washing the SF with water and sulphuric acid to obtain an SF with a reduced P content and a fibrous structure ($SF\text{-}GZV_{P\text{-}poor}$). The N-rich LF is treated through micro-filtration followed by reverse osmosis to produce an N-potassium (K)-rich concentrate (RO-GZV) and permeate water.

Am-Power (AmP, Pittem, Belgium) treats residues from the food processing industry and source-segregated food waste via thermophilic (~55 ºC) AD with a retention time of about 60 days. The digestate (D-AmP) from this installation is dewatered to obtain a solid fraction (SF-AmP). The solid fraction is passed through a fluidized bed dryer at 60°C to obtain a dried solid fraction (SFD-AmP). The LF of digestate is sent to a vacuum evaporator to evaporate water, leaving behind an evaporator concentrate rich in N and K (E-AmP). Ammonium-rich condensed water from the vacuum evaporator is passed through a reverse osmosis unit resulting in a reverse osmosis concentrate (RO-AmP) and permeate water.

Waterleau NewEnergy (WNE, Ieper, Belgium) operates an AD plant used for the mesophilic (~35 ºC) digestion of residues from agro-industry (potatoes and grain, 40% w/w), sludge from industrial wastewater treatment plants (15% w/w) and animal manure (45% w/w). Digestate (D-WNE) is passed through a decanter to obtain a SF which is then dried in a Hydrogone dryer to obtain a solid organic fertiliser (SFD-WNE). The evaporated water from the dryer, together with the LF of digestate (LF-WNE) is treated in a biological aerobic reactor to reduce the chemical oxygen demand. Ammonium is then transferred to the gas phase via evaporation resulting in a K-rich concentrate (E-WNE). The ammonia-rich gas is condensed with water vapour and condensed ammonia water (AW-WNE) is recovered.

Benas (BNS, Ottersberg, Germany) treats energy crops (silage maize, silage rye and corn, 85% w/w) and poultry litter (15% w/w) using thermophilic digestion. The ammonia content of a side stream of digestate (D-BNS) is lowered using a modified stripping process to obtain ammonium nitrogen to which gypsum is added to produce a concentrated marketable ammonium sulphate solution (AS-BNS).

Acqua & Sole (A&S, Vellezzo Bellini, Italy) processes sewage sludge from wastewater treatment plants (86% w/w) and coproducts (digestate from anaerobic treatment of source-segregated domestic food waste, 14% w/w) in a thermophilic (~55 ºC) AD. The process is equipped with an ammonia stripping unit, whereby biogas acts as a stripping agent. Ammonia is extracted from biogas by adding acid (H_2SO_4) resulting in an inorganic ammonium sulphate solution (AS-A&S). The digestate from the plant is denoted as D-A&S.

GZV, AmP, WNE, BNS, and A&S are demonstration plants within the EU project SYSTEMIC and more information is available on www.systemicproject.eu and in Brienza et al. (2021).

2.2 Soil characteristics

The soil samples for the incubation were collected from the top layer (0–25 cm) of an arable field in Bottelare, Belgium. Composite samples of the sandy-loam (55% sand, 6% clay, 39% silt) soil was taken in April 2020 with the following characteristics: pH-H_20 7.5, total N (TN) 0.76 g/kg dry weight (DW), total carbon (TC) 10.4 g/kg DW. This soil was used in the incubation experiments with BBFs from GZV and AmP. Soil was taken again from the same location in April 2022 having a slightly different composition (pH-H_20 7.11, TN 1.30 g/kg DW, TC 12.8 g/kg DW) and used for the incubation experiments with BBFs from WNE, BNS, and A&S. The soils were air-dried until constant mass, sieved (2 mm) then stored in a cool dry room before being used in the experiments.

2.3 Analytical methods for fertiliser characterisation

The dry matter (DM) content was determined by drying to constant weight (48 h) at 80 °C and was calculated as a percentage of wet weight. Organic matter (OM) was measured on dried solids by incineration at 550 °C in a muffle furnace for 4 h (Dean, 1974; Santisteban et al., 2004). TC was determined using a PRIMACS100 Analyzer series (Skalar B.V., Netherlands). TN was determined using the Kjeldahl destruction method (EN13654-1, 2002). Ammonium-N (NH_4^+-N) was determined spectrophotometrically after 1M KCl extraction at a sample to solution ratio of 1:10. For the determination of dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) in the BBFs, fresh samples were weighed into a 50 cm^3 centrifuge flask and extracted with 0.01 M $CaCl_2$ (sample to solution ratio of 1:10) by shaking for 2 h followed by centrifugation for 10 min at 3000 rpm (Houba et al., 1990). TDN and DOC in the extracts were measured using the Dumas Dry Combustion Method for TN and TC content (Bertsch and Ostinelli, 2019).

2.4 Microcosm setup

The incubation experiments were conducted in soil microcosms which enable studying the effects of amendment addition on soil respiration under controlled conditions. Each microcosm consisted of a 1L Duran bottle adapted with a GL45-thread Smart Cap (model: SW45-2A). The smart cap has two 2 mm threaded openings that can either be closed with blind plugs or fitted with valves that enable gas sampling. The incubation experiments were carried out in four batches from February to June 2021 at a mean room temperature of 20 ºC (diurnal temperature range: 18.5 – 21.5 ºC). Each batch included four or five BBFs from the demonstration plants, one blank (unfertilized control soil), and two mineral fertilisers (urea and CAN as positive controls). The same urea (46% urea N; Yara Benelux B.V.) and CAN (30% N) was used in all four incubation batches.

The soil was pre-incubated for one week at 40% water-filled pore space (WFPS) to activate the soil microorganisms. Next, 568 g of pre-incubated soil was thoroughly mixed with a biobased or mineral fertiliser in a steel bowl and then transferred into the microcosm. Prior to mixing, the mineral fertiliser granules were ground to <0.5 mm. The soil-fertiliser mixtures were carefully packed to attain an equivalent bulk density of 1.3 kg m^{-3}. All fertilisers were applied at a rate of 170 kg N ha^{-1}. The equivalent amounts of NH_4^+-N, organic N (N_{org}), TC applied in each treatment are summarized in Table 2. The moisture content in each bottle was brought to 80% WFPS and maintained throughout the experiment according to Cayuela et al. (2010). A 2 mm opening at the top of the microcosm was left uncovered to allow for aerobic respiration. The microcosms were laid out in a randomised block design with three replicates per treatment.

206 **2.5 Measurement**

207 Over an incubation period of 18 days, emissions of CO_2, N_2O, and CH_4 were
208 measured using the Gasera One Multi-gas analyser (Turku, Finland) equipped with a photo-
209 acoustic infrared analyser. Measurements were performed on days 0, 1, 2, 4, 7, 9, 11, 14, 16,
210 18. Measurements on day 0 were taken on average 2.5 hours after fertiliser incorporation. The
211 analyser was connected to the microcosm using two 1 m-long non-reactive Teflon tubes with
212 a 2 mm internal diameter. During measurement, the gases were pumped out from the
213 headspace (at 800 mL min^{-1} flow rate), passed through the analyser then returned to the
214 microcosm in a closed loop. This method ensures non-intrusive sampling and reduces the risk
215 of systematic errors. The gas concentration in the headspace of the microcosms was measured
216 at 4, 8, 12, and 16 minutes after connecting the tubes to the microcosm. During each 4 min
217 time step, the analyser detected the change in concentration of the measured gases. Fluxes of
218 CO_2, N_2O, and CH_4 were then calculated from the change in concentration over time
219 considering the volume of the headspace, tubing, and area of the soil surface. Sample sets
220 with a linear regression value of $R^2 < 0.90$ were rejected. At the end of the incubation period,
221 soil mineral N (NH_4^+-N and NO_3^--N) in each treatment was analysed in a 1:10 ($w\ v^{-1}$)
222 suspension of soil and 1 M KCl and shaken end-over-end for 30 min. The extracts were
223 filtered (Whatman No. 45) and analysed for their NH_4^+-N and NO_3^--N contents with a
224 continuous flow auto-analyser (Chemlab System 4, Skalar, the Netherlands).

225 **2.6 Calculations**

226 Gas concentrations measured in ppm were converted to emission flux using the ideal
227 gas law according to Equation (1) (Comeau et al., 2018):

228 $$Flux = \frac{\Delta gas}{\Delta t} \times \frac{P \times M \times n}{R \times T} \times \frac{V}{A} \qquad \text{Equation (1)}$$

Where flux is the elemental flux which is released as gas in μg m^{-2} h^{-1}; $\frac{\Delta gas}{\Delta t}$ is the slope of the linear regression of gas concentration (ppm) vs. time (h); P is the sampling pressure of the device (0.838 atm); M is the elemental molar mass (e.g. 12 for C, 14 for N); n is the number of atoms of the element in the gas (e.g. 2N in N_2O); R is the ideal gas constant (0.08206 L atm mol^{-1} K^{-1}); T is the average atmospheric temperature (294 K); V is the sum volume of the headspace, tubing, and analyser cell (0.623 L); A is the surface area of soil in the microcosm (0.0069 m^2).

The cumulative flux for each gas was calculated using a linear interpolation between two consecutive measurement days (Cai et al., 2013). Cumulative fluxes obtained with the soil control were subtracted for all cumulative fertiliser emissions.

Net N release (N_{rel}) in the soil at the end of the incubation was calculated according to Equation (2) (De Neve and Hofman, 1996):

$$N_{rel}\ (\%) = \frac{[(Mineral\ N_{fertiliser}) - (Mineral\ N_{control})]}{total\ N\ applied} \times 100 \qquad \text{Equation (2)}$$

where mineral $N_{fertiliser}$ is the soil mineral N content of the fertiliser treatment and mineral $N_{control}$ is the soil mineral N content of the unfertilised control soil.

2.7 Statistical analysis

The data were subjected to one-way analysis of variance (ANOVA) and when significant ($p < 0.05$), means were compared using Tukey's test. In addition, a principal component analysis (PCA) was performed to evaluate the relationships between the fertilisers' characteristics (pH, TN, NH_4, OM, TC, C/N, DOC, DOC/TC, TDN/TN) and cumulative GHG emissions. PCA is an exploratory statistical tool that is used to quickly visualize and analyse correlations between variables. Pearson's correlation analysis was performed to test the relationships between product characteristics and cumulative GHG emissions. All analyses were performed using XLSTAT 2021 software (Addinsoft, 2021).

254 **3. Results**

255 **3.1 Composition of the biobased fertilisers**

256 The studied BBFs differed considerably in their physicochemical composition (Table
257 3). The pH of most BBFs was alkaline (7.0 – 9.4) and any deviations from this range were
258 attributed to the use of sulphuric acid during digestate processing, e.g., in SF-GZV$_{P\text{-}poor}$ with
259 pH 5.5. On a fresh weight (FW) basis, OM constituted between 17 and 67% of the SFs of
260 digestate. The low OM content (<3% FW) in the R, LF, AW, and AS fertilisers indicates
261 these BBFs are dominantly mineral in nature and are, hereinafter, collectively referred to as
262 organo-mineral BBFs. DM content in the whole digestate varied between 5.2% in D-WNE
263 and 9.3% in D-A&S. For the organo-mineral BBFs, DM was below 5% except in the
264 ammonium salt solutions with 21 and 38 %DM due to their high salt content. The large
265 variation in DM content of the SFs of digestate (26 – 94%) was attributed to the type of
266 dewatering equipment used and whether a drying step was included during processing.
267 Nitrogen was present mostly (>95%) in mineral form in the R, AW, and AS fertilisers.
268 This, in addition to their high total N content, makes these BBFs comparable to CAN and urea
269 in terms of potential N availability to crops. Unlike in AmP, the LF of digestate fed to the
270 evaporator implemented at WNE is not acidified, resulting in a lower NH_4-N content in E-
271 WNE, compared to E-AmP (Table 3). Organic N was the dominant fraction in E-WNE, SFD-
272 AmP, SFD-WNE, and SF-GZV$_{P\text{-}poor}$, corresponding to 97%, 95%, 77%, and 73% of total N,
273 respectively.
274 All five SFs of digestate had high TOC content, ranging from 85 g/kg in SF-AmP to
275 335 g kg^{-1} in SFD-WNE. Lower TOC levels were measured in the whole digestate (15 – 30
276 g/kg) while the organo-mineral BBFs were characterised by very low amounts of TOC (<5 g
277 kg^{-1}). The variation in TN and TC content among the BBFs was reflected in the C/N ratio. As

expected, the C/N ratio was high in the SFs of digestate (11 – 27), low in the whole digestate and evaporator concentrates (2.3 – 8.4), and less than 1 in the organo-mineral BBFs.

A higher relative concentration of labile C, indicated by the DOC/TC ratio, was observed in D-GZV, D-WNE, D-BNS, and E-AmP, with 0.19, 0.33, 0.17, and 0.34, respectively. Meanwhile, in the SF fertilisers, DOC constituted a much lower fraction of TC, ranging between 0.01 – 0.03. The TDN concentration of AW and AS fertilisers were not analytically determined since N in those fertilisers is present almost entirely in dissolved form as NH_4^+-N. Concentrations of TDN in the BBFs varied widely and ranged between 1.3 to 76 g kg^{-1} FW. This variation was also reflected in the TDN/TN ratio.

3.2 N_2O emission

N_2O emission dynamics differed considerably among the different treatments. However, the overall trend of N_2O fluxes indicated a gradual decrease towards background levels (Figure 1), in agreement with studies by Cayuela et al. (2010) and Dietrich et al. (2020). Daily mean N_2O fluxes ranged between 5 to 246 µg N_2O-N m^{-2} h^{-1} and peaked within the first four days after fertiliser application in all treatments, except E-WNE which peaked on day 11. Average daily N_2O emissions from the CAN and urea followed similar flux patterns in the four incubation batches and were not significantly different from each other (p<0.01). Within each plant, the highest N_2O peaks were observed in the D fertilisers except for AmP where the highest peak was measured in E-AmP on day 0.

Cumulative N_2O (N_2O_{cum}) emissions among the different groups of fertilisers were not easily differentiated, at least not statistically. Soil amended with urea showed a significantly higher N_2O_{cum} release than most other treatments, except for CAN, D-AmP, D-WNE, E-AmP, E-WNE, and AW-WNE (Table 4). It is important to note that the N_2O_{cum} data for the mineral fertilisers are means of the measurements in the four incubation batches which ranged

between 0.11 to 0.14 % of urea N applied and 0.10 – 0.12 % of CAN N applied. The SF with depleted P (SF-GZV$_{P\text{-}poor}$) and the AS fertilisers induced the lowest N_2O_{cum} emissions (0.04 % of applied N) compared to the other fertilisers. However, this value was not significantly different from SF-GZV, AS-A&S, AS-BNS, D-BNS, LF-WNE, and R-AmP. N_2O_{cum} emissions from the D fertilisers from the five plants varied between 0.06 – 0.09 % of applied N. When considering the end-products originating from the individual biogas plants, the D fertilisers emitted more N_2O_{cum} compared to the fertilisers derived from D processing, although the difference was not statistically significant in A&S and BNS (Table 4).

The net N_{rel} from the BBFs and mineral fertilisers expressed as a percentage of applied total N is shown in Table 4. This parameter indicates the amount of fertiliser-derived available N present in the soil at the end of the incubation period under the conditions of the experiment. There were large variations in the net N_{rel} within the different fertiliser groups. The highest N_{rel} was observed in the mineral fertilisers (102 – 108%) and AW-WNE (108%). N immobilisation occurred in the SF with depleted P (SF-GZV$_{P\text{-}poor}$). The net N_{rel} was significantly negatively correlated with C/N ratio ($r = 0.67$; $p < 0.01$).

3.3 CO_2 emission

Figure 2 shows the cumulative CO_2 emissions from BBFs where greater than 300 kg C/ha was applied. At the end of the incubation, the D fertilisers mineralised between 13 and 52% of applied C. The highest cumulative CO_2 emission was from the D-WNE treatment ($p<0.01$). Soils amended with SFs of digestate showed a significantly lower release of CO_2 than other soils, with 3 to 8% of applied C mineralised. CO_2 emissions of treatments with AmP, A&S, and BNS fertilisers were not significantly different from each other, probably due to the high variability in the measurements. The CO_2 emission data for CAN, R, LF, AW and AS fertilisers were not shown because they contain little or no organic C, therefore, amounts

of C added to soil after their application was deemed to be negligible. Any additional CO_2 emitted was attributed to the positive priming effect of native soil organic C which stimulates mineralisation (Fontaine et al., 2003). Urea which contains 20% C showed rapid mineralisation (>70%) within the first 2 days of incubation in all the batches due to its fast hydrolysis after application to soil.

3.4 CH_4 emission

Table 4 indicates that for most of the fertilisers studied, cumulative CH_4 emissions were lower than the control. The exceptions were E-AmP and E-WNE with net positive emission of 4 and 1 mg m^{-2}, respectively. However, no significant difference (p<0.05) was observed among the treatments due to high variability in the flux measurements.

3.5 Principal component and correlation analyses

The overall grouping of individual observations and variable correlations is depicted in Figure 3. CH_4 was not included as a variable in the principal component analysis (PCA) since there was no significant difference in CH_4 emission among the treatments. The first two factors explained 61% of the total variance in all variables. The grouping of individual observations shows a separation of the different BBFs into three distinct groups based on their properties in relation to cumulative N_2O and CO_2. Separation along F1, which accounts for 24% of the total variation, was explained by differences in TN, TC, NH_4, OM, C/N, DOC, TDN/TN. The second factor (F2) which accounts for 36% of the total variation, was described by differences in N_2O_{cum} and CO_{2cum} emissions.

The D and E fertilisers were grouped at the upper part of the diagram indicating BBFs with the highest average DOC concentrations, pH, and N_2O_{cum} and CO_{2cum} emissions. The SF fertilisers were clustered along the positive quadrant of the F1 axis where the fertilisers with

the highest average TC and C/N ratio are represented. The AS, AW, R and LF fertilisers were found more displaced along the left side of the F1 axis, where TN, NH_4^+, and TDN/TN are the dominant variables.

Significant linear correlations were established between N_2O_{cum} emissions and the characteristics of the different fertiliser groups. When omitting fertilisers LF, R, AW, AS, which are outliers regarding TC (i.e., <5%), N_2O_{cum} correlated negatively with C/N ratio ($r = -0.68$, $p < 0.05$) and positively with TDN/TN ratio ($r = 0.75$, $p < 0.01$). Also, N_2O_{cum} emission from the SF fertilisers was positively related to TN ($r = 0.92$, $p < 0.05$) and DOC ($r = 0.70$, $p < 0.05$). In the dominantly mineral fertilisers (i.e., LF, R, AS, AW), pH appeared to be positively correlated with N_2O_{cum} emissions ($r = 0.81$), but this relationship was not statistically significant ($p = 0.10$).

Cumulative CO_2 emission in SF, D, and E fertilisers was correlated positively with TN (g kg^{-1} DW) ($r = 0.85$, $p < 0.01$), TDN/TN ratio ($r = 0.57$, $p < 0.05$), and DOC/TC ratio ($r = 0.83$, $p < 0.01$), and negatively to C/N ratio ($r = 0.60$, $p < 0.05$).

4. Discussion

4.1 Physicochemical properties of the biobased fertilisers

The high OM and/or N contents of the studied BBFs underline their potential as soil improvers or fertilisers. Elevated OM contents in the SFs of digestate make them better suited as organic soil improvers (Egene et al., 2020; Peters and Jensen, 2011) with the potential to increase C sequestration in soils (Veeken et al., 2017). Drying of the SF of digestate (as in SFD-AmP and SFD-WNE), concentrates the N (24 and 31 g kg^{-1}, respectively), making them also applicable as N or P fertilisers (Regelink et al., 2021). On the other hand, ammonia stripping of the LF of digestate produces pure mineral N fertilisers – as in AW-WNE, AS-

A&S and AS-BNS with total N contents of 53, 76, and 41 g kg^{-1}, respectively. The large variation in total N within the D fertilisers was attributed to differences in the N contents of the feedstock. The D with the highest total N content was obtained from GZV where animal waste constituted a high proportion (81% w/w) of the feedstock. On the other hand, D obtained from the processing of industrial food waste had the lowest total N content.

The pH of the studied BBFs was mostly alkaline which can influence soil pH and processes, including nutrient availability and nitrification rate. Fertilisers with a strong alkaline character, as was measured in AW-WNE (pH 9.7), indicates a high risk of NH_3 volatilisation when applied to soils. Low pH in some BBFs was related to the use of sulphuric acid during digestate processes. For example, SF-$GZV_{P\text{-}poor}$ (pH 5.5) was treated with sulphuric acid to lower its P content. Similarly, the digestate acidification step before vacuum evaporation explains the slightly acidic pH of E-AmP (pH 6.2).

For most of the BBFs, the TDN concentration, which represents the sum of dissolved organic N and mineral N (Christou et al., 2005), was higher than the NH_4^+ concentration. This indicates the presence of a sizeable dissolved organic N pool in the BBFs, especially in E-WNE. As explained in section 2.1, E-WNE is the concentrate that is obtained after NH_3 is evaporated from the LF of digestate. This explains the low NH_4^+ content in the fertiliser.

The PCA of variables related to the cumulative N_2O and CO_2 emissions showed a clear separation among the different groups of BBFs. TC and C/N ratio were the most important variables for separating the SF fertilisers from the others (along F2), while DOC and DOC/TC ratio differentiated the D and E fertilisers from the LF, R, AW and AS fertilisers. Except for SF_$GZV_{P\text{-}poor}$, the TOC/N ratio in the BBFs was below 20 which is favourable for N mineralisation (Mendham et al., 2004; Wagner and Wolf., 1999). In organic substrates with a high C/N ratio as in SF_$GZV_{P\text{-}poor}$ (27), mineralisation is slow and N immobilisation may dominate (Egene et al., 2020).

4.2 N_2O emissions and N mineralisation

The principal factors that regulate soil-borne N_2O emissions are soil mineral N concentration, availability of decomposable organic C, soil moisture, soil temperature, soil pH, and the activity of (de)nitrifying organisms (Dalal et al., 2003; Šimek and Cooper, 2002; Wang et al., 2021). In this study, we aimed to create the conditions optimal for N_2O production by using soil with a neutral pH, pre-incubating the soil for one week to activate microorganisms, and maintaining a high WFPS (80%) (Cayuela et al., 2010). As such, differences in N_2O flux from the different treatments may be attributable to differences in mineral N and labile organic C availability. The N_2O emissions in the first days of incubation were likely driven by nitrification of the initial NH_4^+ present in the fertilisers (Alburquerque et al., 2012a; Askri et al., 2016; de la Fuente et al., 2013; Egene et al., 2020). Some studies (Askri et al., 2016; Pampillón-González et al., 2017) on digestate fertilised soils reported positive correlations between N_2O_{cum} emissions and the initial NH_4^+ content in the digestate. However, this was not observed in the current study. This may be because NH_4^+ was not a limiting factor in most of the fertilisers investigated, except for E-WNE which has a low NH_4^+/TN ratio of 0.026. Moreover, the mineral N content at the end of the incubation in all treatments mainly consisted of NO_3^--N (Table 4) which supports our assumption that NH_4^+ in the treatments was nitrified (or immobilized) during the 18-day incubation.

The urea fertilised soil produced the highest N_2O_{cum} emission with 0.12% of applied N, although this value was not statistically differentiated from CAN, D-AmP, D-WNE, E-AmP, E-WNE, and AW-WNE. Generally, mineral N fertilisers quickly dissolve after addition to soil leading to increased NH_4^+ availability followed by nitrification and N_2O production (Saggar et al., 2013a; van der Weerden et al., 2016). The hydrolysis of urea or the dissolution of CAN in the soil can result in the loss of NH_3 which is a precursor to the formation of N_2O (Forrestal et al., 2016; Huang et al., 2014; Saggar et al., 2013b). It is, therefore, conceivable

that the high N_2O emissions observed in urea and CAN may be due to the combination of direct N_2O production (from nitrification of NH_4^+) and the indirect N_2O release (due to NH_3 oxidation). This phenomenon could also explain the high N_2O emission from the soil amended with NH_3-water (AW-WNE).

Despite their high mineral N contents (~100%), significantly lower N_2O emissions were measured in AS-BNS and AS-A&S compared to the mineral fertiliser treatments. This was attributed to the low pH of the AS fertilisers which inhibits N_2O production from nitrification (Dalal et al., 2003). In contrast, the hydrolysis of urea may have caused alkalinisation of the soil, especially in the microsites close to the urea granules (Clayton et al., 1997), thereby creating conditions more favourable for N_2O production from nitrification (Dalal et al., 2003). Similar observations were found in other studies that compared N_2O emissions between mineral AS, urea, and nitrate fertilisers (Clayton et al., 1997; Tierling and Kuhlmann, 2018). According to Clayton et al. (1997), N_2O_{cum} emissions from a clayey-loam soil fertilised with AS, urea, and calcium nitrate over 12 months were 0.2, 0.8, and 0.5% of applied N, respectively. Meanwhile, Tierling and Kuhlmann (2018) performed a 21-day incubation of a loamy-sand soil supplemented with AS, urea, and potassium nitrate fertilisers and reported N_2O_{cum} emissions of 0.07, 0.26, and 0.02% of applied N, respectively. In both studies, differences in N_2O production between the fertilisers were also attributed to pH effects in the soil.

Cumulative N_2O emissions from the D, SF, E, LF and R fertilisers could hardly be differentiated, at least not statistically. The exception was the SF with depleted P (SF-$GZV_{P\text{-}poor}$) which induced significantly lower N_2O emissions compared to the other fertilisers. As previously described, the low emissions may have been caused by the acidic pH (5.5) of SF-$GZV_{P\text{-}poor}$. However, its high C/N ratio (27) may have also played an important role in limiting nitrification (Egene et al., 2020) and consequently, N_2O production. Elevated C/N

ratio in organic substrates slows down their decomposition and subsequent release of DOC and NH_4^+ through mineralisation, both of which are linked to increased N_2O emissions (Huang et al., 2004). Among the SF fertilisers, differences in C/N ratio (r = -0.87) and DOC (r = 0.70) could explain the variation in N_2O emission. Similar results were reported by Huang et al. (2004) who found that N_2O_{cum} of N_2O were negatively correlated with C/N ratio and positively correlated with DOC of solid organic residues after a 21-day incubation study.

The pH effect described above was not apparent in E-WNE which has a slightly acidic pH of 6.2 but produced N_2O_{cum} emission comparable to the mineral fertilisers (Table 4). Remarkably, soil amended with E-WNE emitted less than the control at the start of incubation before showing rapid N_2O release from the ninth day (Figure 1). This was attributed to its low initial NH_4^+ (0.26 g kg^{-1}) meaning there was almost no readily available N to be nitrified. This N deficiency enhanced microbial decomposition of labile organic matter to obtain N, otherwise known as "microbial mining" (Craine et al., 2007; Moorhead and Sinsabaugh, 2006) which resulted in temporary N immobilisation in the first days of the incubation. The high TDN concentration in E-WNE (7.9 g kg^{-1}) indicates that microorganisms could easily access the dissolved organic N in the fertilisers to release NH_4^+. At this point, nitrification of the released mineral N could progress rapidly.

Despite the short duration of our incubation experiment (18 days), the N_2O_{cum} values for D fertilisers were strongly agreed with results from a 110-day field study by Baral et al. (2017) who measured N_2O_{cum} of 0.10% of applied N due to digestate fertilisation applied at 167 kg N ha^{-1}. Nitrification of NH_4^+-N in fertilised "hotspots" within the soil, characterized by enhanced microbial activity and oxygen demand, was determined as the principal factor controlling N_2O production, with most of the emissions occurring in the first 35 days. After a one year investigation of N_2O emissions from mineral and organic fertilisers, Meijide et al. (2009) also reported N_2O_{cum} emissions of 0.12 and 0.11% of applied N from digestate and

478 urea fertilised agricultural fields, respectively. The authors determined that nitrification and
479 denitrification occurred at different stages of the experiment but concluded that environmental
480 factors, mainly WFPS, strongly influenced N_2O emission rates.

481 Overall, the results from our incubation study show that the differences in N_2O
482 emission flux among the BBFs were small and in some cases, marginal. Therefore, the rate of
483 N_2O emissions was probably more affected by the soil type and condition than by the fertiliser
484 properties. In a study by Abubaker et al. (2013), large differences in N_2O emissions were
485 found between different biogas residues when incubated for 24 days a sandy and clayey soil.
486 However, the same digestate showed comparable N_2O_{cum} emissions when they were
487 incubated in loamy soil, with values between 0.08 to 0.09% of applied N. The characteristics
488 of the soil used in our study closely resemble the loam soil used in Abubaker et al.'s (2013)
489 study, at least in terms of soil texture. This suggests that the BBFs discussed in this study may
490 induce different N_2O emission fluxes when incubated in differently textured soils.

491

492 **4.3 CO_2 emissions**

493 Cumulative CO_2 emissions from the soils amended with the D, E, and SF fertilisers
494 were related to the proportion of readily available C, as evidenced by the strong positive
495 correlation between CO_{2cum} emission and DOC/TC ratio ($r = 0.83$). Cysneiros et al. (2008)
496 and Jacobi et al. (2009) have previously shown that considerable amounts of volatile fatty
497 acids are formed as intermediates during AD. These organic compounds are easily
498 metabolized by soil microorganisms within a few days, releasing CO_2 in the process. The
499 slower C mineralisation in the SF treatments (3.5 – 7% of applied C) suggests that the organic
500 C in SF fertilisers is more stable than those in the D and E fertilisers. This may be because
501 solid-liquid separation of the whole digestate resulted in the separation of the stable
502 particulate C, mainly associated with the solid phase, from the easily degradable C which

503 remained mostly in the liquid phase. These results reaffirm the findings from other incubation
504 studies with biogas residues, that the availability of labile C favours the production of soil-
505 borne CO_2 (Askri et al., 2016; Cardelli et al., 2018; Mukherjee et al., 2016).
506 It is worth noting that the enhanced degradation of native soil C (priming effect)
507 and/or the reduction of carbonates in the fertilisers may have contributed to the CO_2 emissions
508 in the BBF-fertilised soils (Kuzyakov et al., 2000; Yoshida et al., 2015). However, the
509 differentiation of the origins of soil-borne CO_2 emissions was not investigated in this study.
510

511 **4.4 CH_4 emissions**

512 The low CH_4 emissions from the treatments highlight the fact the incubations were
513 carried out under sufficiently aerobic conditions. Our results are in agreement with studies by
514 Odlare et al. (2012) and Pampillón-González et al. (2017) who reported negative or negligible
515 CH_4 emissions from the soil after the application of biogas residues. In this study, CH_4
516 oxidation was likely driven by the presence of methanotrophic (CH_4 oxidizing) bacteria in the
517 soil whose activity was stimulated by the addition of N fertiliser. Conrad (1996) and Steven et
518 al. (2006) testified that agricultural soils are common habitats for methanotrophic bacteria
519 who, in the presence of oxygen, utilize CH_4 as a source of carbon and energy.
520

521 **4.5 Global warming potential**

522 The global warming potential (GWP) of N_2O and CH_4 emissions were determined and
523 expressed as CO_2 equivalents per 100 grams of N added, using a conversion factor of 298 for
524 N_2O and 25 for CH_4 (IPCC, 2007). CO_2 emission was not considered for GWP emissions
525 calculation since, from the life cycle assessment perspective, the biodegradation of organic
526 matter releases biogenic carbon (USEPA, 2010; WRI, 2014). Therefore, the mineralization of
527 BBFs in soils does not contribute to the net increase of CO_2.

As shown in Figure 4, the GWP of the BBFs was either equal to or lower than the GWP of the mineral fertilisers. In all the fertilisers, N_2O emissions contributed significantly more to GWP than CH_4 emissions. Generally, CH_4 was taken up rather than emitted, however, the benefit gained by CH_4 consumption was offset by the increase in N_2O emissions. The fertilisers derived from the NRR processing of digestate appear to decrease the GWP relative to the unprocessed digestate fertilisers. This trend is particularly noticeable in fertilisers from WNE and AmP.

GWP values varied between 0.08 and 0.35 kg CO_2 eq kg^{-1} N and are hence low as compared to values obtained from long-term field studies. Over ten months, Zilio et al. (2022) measured net N_2O_{cum} emissions between 1.2 and 3% of N applied, from digestate+AS and urea+AS fertilised fields, corresponding to 3.80 and 9.84 kg CO_2 eq kg^{-1} N, respectively. The authors concluded that the environmental impact in terms of GHG emissions from fertilisation with the tested BBFs or urea were comparable, in agreement with findings from this study. Meanwhile, Walling and Vaneeckhaute (2020) found in their review that N_2O-derived GWP due to digestate fertilisation can range between 0.15 to 17.6 kg CO_2 eq kg^{-1} N, depending on the application technique. This means that the impact of GHG emissions related to the application of digestate N fertilisers could still exceed the impact of synthetic N fertilisers and hence, N_2O emissions from N fertilising products from digestates remain a point of environmental concern.

4.6 Limitations of the laboratory incubation approach

The microcosm approach employed in this study enables the close monitoring and quantification of fertilisation effects on soil GHG emissions and C and N turnover processes. However, the standardized conditions (for temperature and moisture) under which the incubations were performed greatly differ from field conditions. Generally, field

552 measurements give higher N_2O emissions due to pulses of N_2O release after a rainfall event or
553 from management practices such as tillage (Wang et al., 2021). The method of fertiliser
554 application also influences the N_2O production dynamics as reported by Velthof and
555 Mosquera (2011) who found that injection of slurry increased the average emission factor of
556 N_2O in comparison to surface application.

557 Furthermore, our incubation was performed only on sandy-loam soil even though
558 fertilisation effects on GHG emissions are modulated by soil texture (Pelster et al., 2012). A
559 meta-analysis by Charles et al. (2017) found that N_2O emissions from fertilisation were 2.8
560 times greater in fine- than in coarse-textured soils. Future studies should investigate the effect
561 of soil texture on GHG emissions from BBF enriched soils through similar microcosm
562 incubation experiments. Finally, other pathways of N losses such as NH_3 and N_2 emissions as
563 well as NO_3^- leaching were currently not explored. Quantifying these loss pathways is
564 necessary to get a full picture of soil N cycling after fertilisation with BBFs and should be
565 investigated in future studies.

566 **5. Conclusions**

567 The key finding from this study was that none of the biobased fertilisers (BBFs)
568 emitted more N_2O than the mineral N fertilisers (urea and calcium ammonium nitrate). Soil-
569 borne N_2O emission from the BBFs was attributed to nitrification of the initial ammonium N
570 shortly after the fertilisers were applied. Differences in C/N ratio and TDN/TN ratio could
571 partly explain the variation in N_2O emissions in the unprocessed digestate, evaporator
572 concentrates, and solid and liquid fractions of digestate. CO_2 respiration in the BBF
573 treatments was strongly influenced by the availability of labile C while CH_4 emissions due to
574 fertilisation were negligible. Global warming potential (GWP) of the BBFs was comparable
575 or lower than that of the mineral fertilisers. Furthermore, the GWP of BBFs derived from the

processing of digestate was generally lower than that of whole digestate. These findings not only revealed the important factors driving short-term GHG emissions in BBF-fertilised soils, but also suggested that the refinement of digestate into concentrated fertilising products does not increase the risk of soil-borne GHG emissions.

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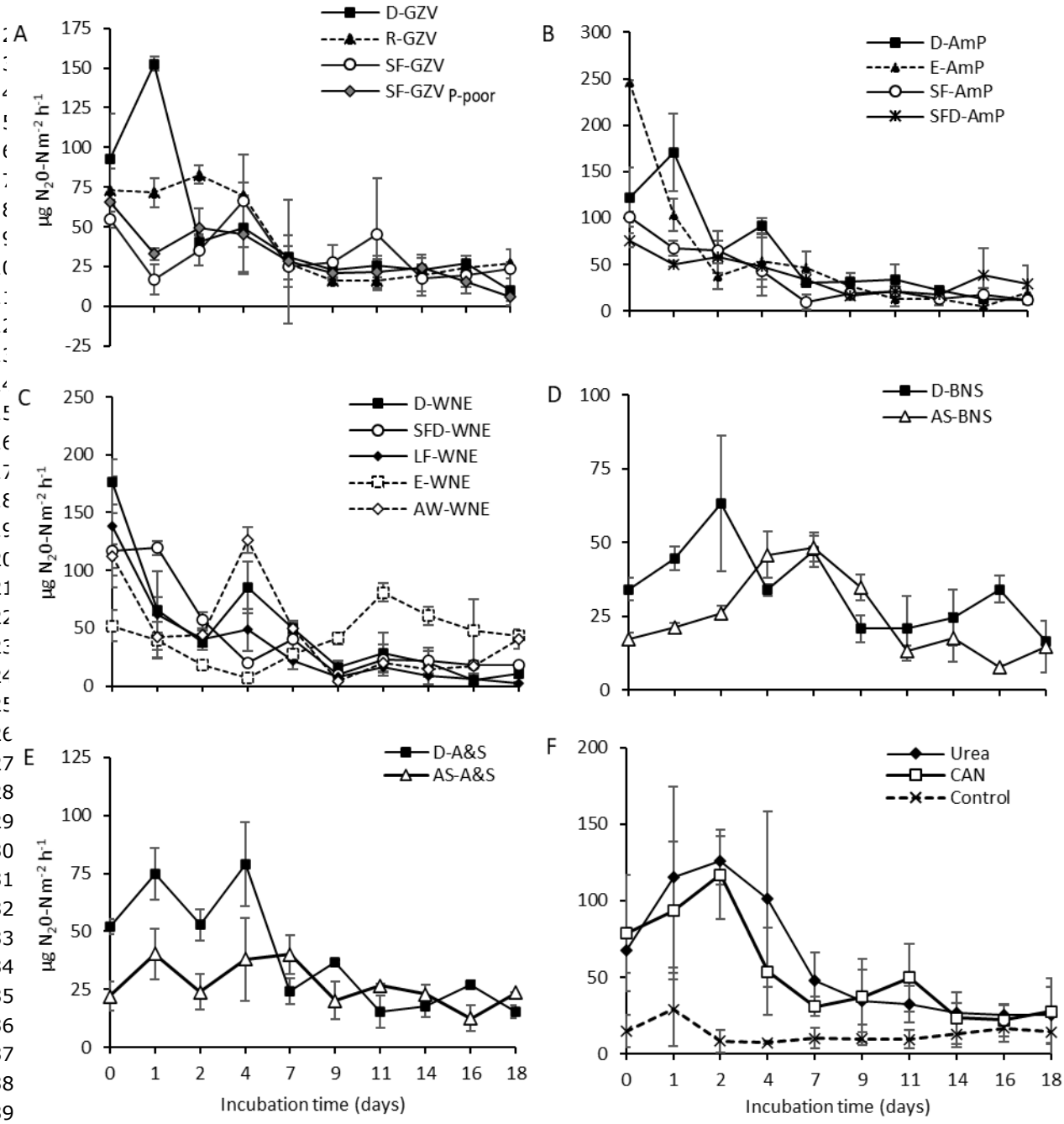

Figure 1. Kinetics of N2O emission rates measured during incubation of digestate-derived biobased fertilisers (A-E) and mineral N fertilisers (F), applied to a sandy-loam soil. Values are means with standard deviation represented by vertical bars; n = 3 for the BBFs; For control, urea and CAN, data points represent the means of measurements in the four incubation batches, n = 9). For abbreviations, refer to Table 1 in Materials and methods.

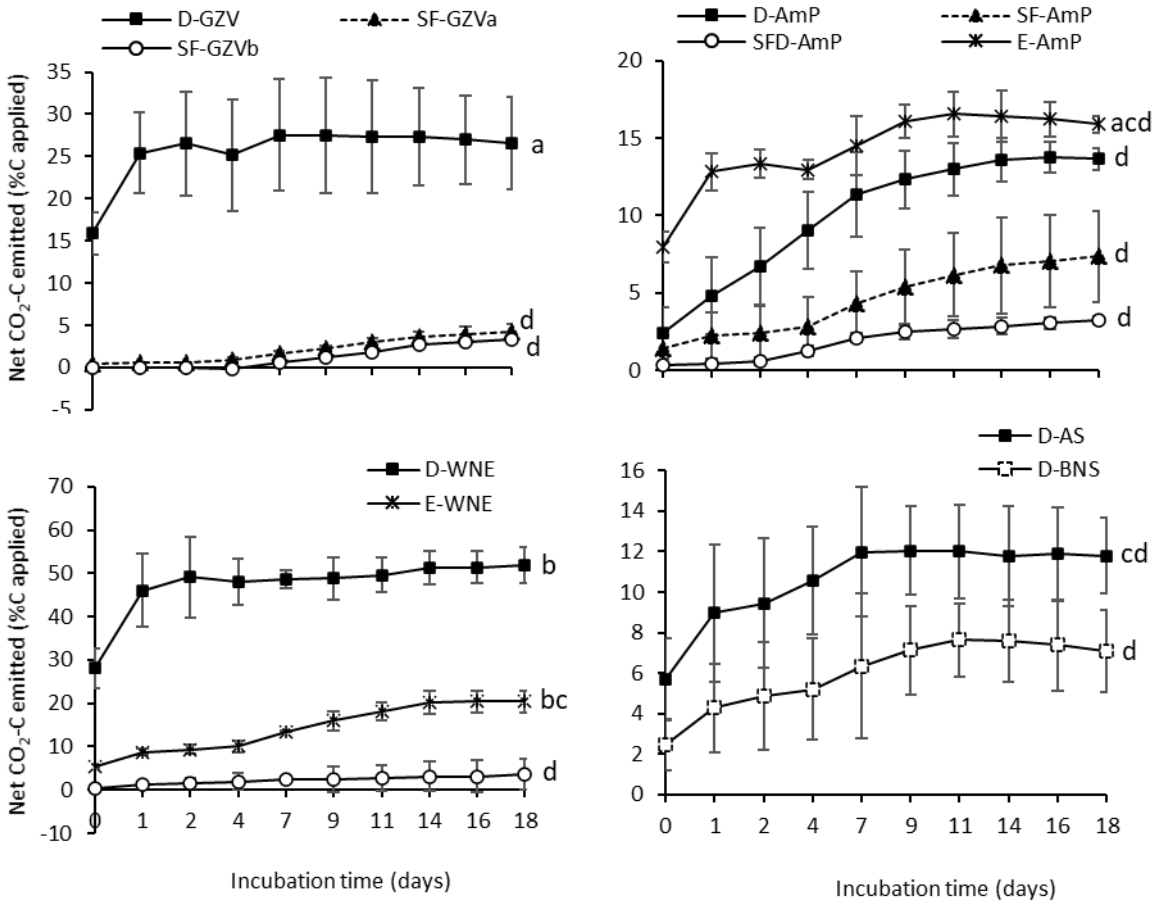

Figure 2. Cumulative CO_2 emission measured during incubation of digestate-derived biobased fertilisers applied to a sandy-loam soil. Different lower-case letters indicate significant differences between C mineralisation means according to Tukey's test (p<0.05). Values are means with standard deviations represented by vertical bars (n = 3). For abbreviations, refer to Table 1 in Materials and methods.

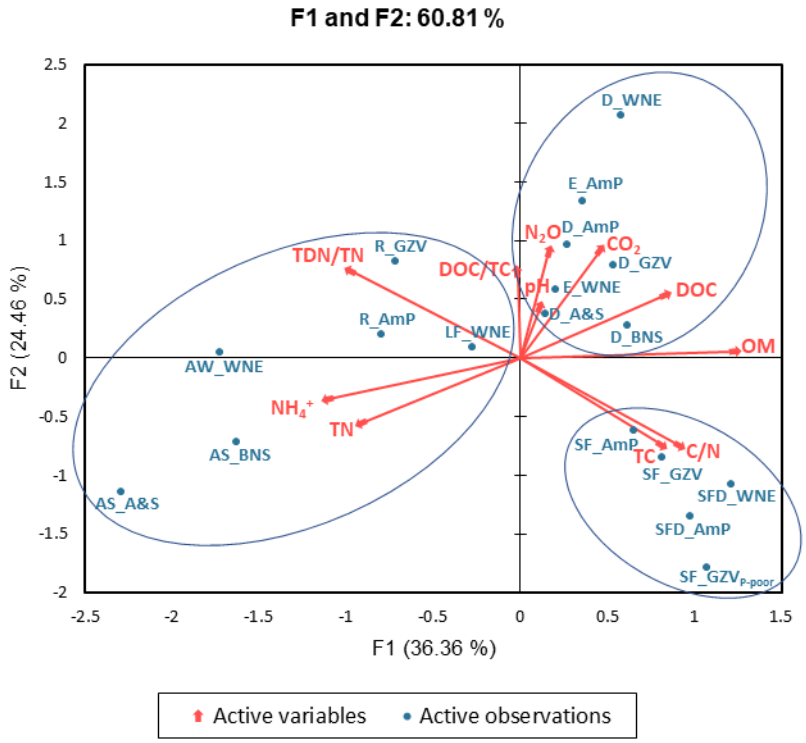

Figure 3. Biplot showing ordination of the BBFs (blue text) based on a PCA of variables (red text) related to cumulative N_2O and CO_2 emissions. F1 explains 36% of the variance in the data and F2 explains 24% of the variance in the data. Variables far from the centre and close to each other are significantly positively correlated (Pearson's correlation; r close to 1); Variables in orthogonal positions are not correlated (r close to 0); variables on opposite sides of the origin are significantly negatively correlated (r close to -1). The arrows point in the direction of treatments with an above-average signal. Variable abbreviations: OM: organic matter; TN: total N; TC: total C; DOC: dissolved organic carbon; TDN: total dissolved N; C/N: carbon to nitrogen ratio. For abbreviations of BBFs, refer to Table 1 in Materials and methods.

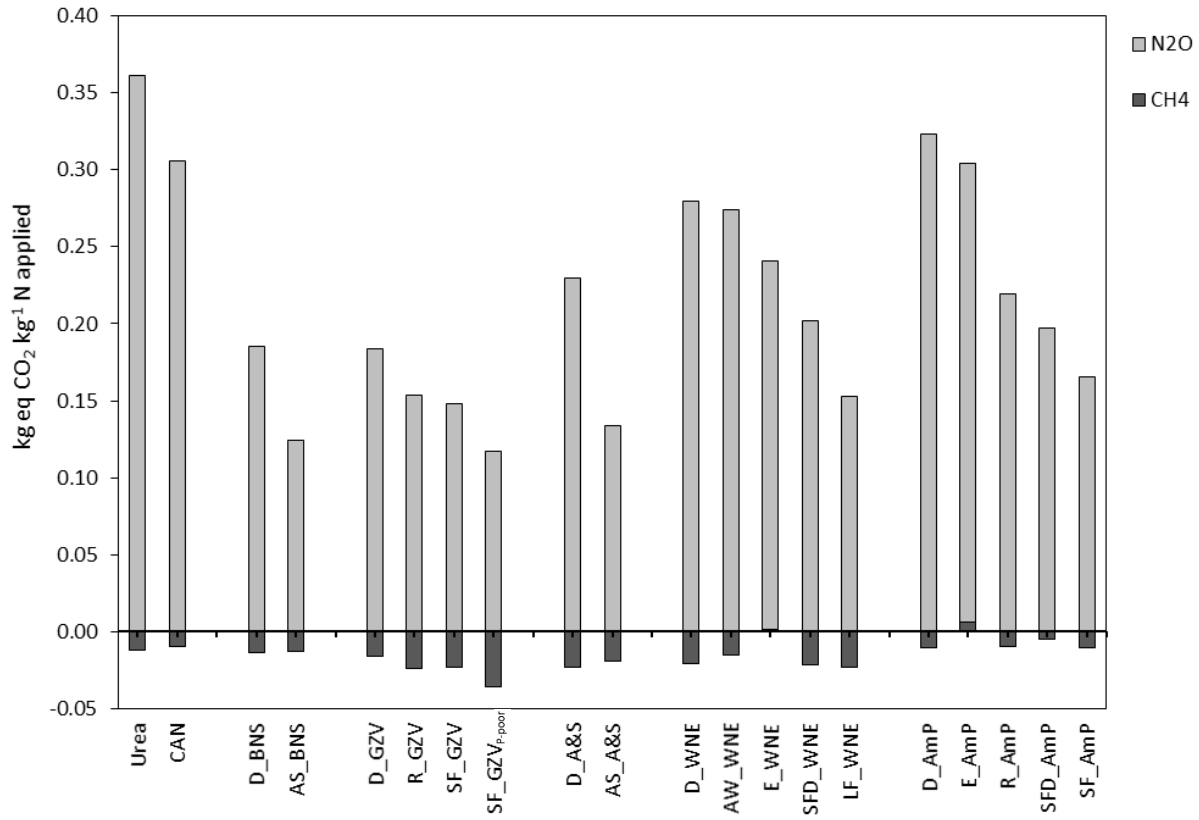

Figure 4. Global warming potential of mineral and biobased fertilisers calculated as the sum of grams of cumulative N_2O and CH_4 (expressed as grams of CO_2 equivalents) per 100 grams of N applied to the soil. Results are based on aerobic incubation experiments conducted over 18 days. For abbreviations, refer to Table 1 in Materials and methods.

Table 1. Overview of feedstock and produced biobased fertilisers at five biogas plants

Inputs	Code	Fertiliser and processing information
Pig slurry (81% w/w) and residues from agro-food industry (a.o. grain and rice husk, potato skins and coffee grounds, 19% w/w).	D-GZV	Digestate, unprocessed
	SF-GZV	Solid fraction (SF) of digestate, separated via decanter centrifugation
	SF-GZV$_{P\text{-}poor}$	Low phosphorus (P) soil improver, obtained after leaching P from GZV-SF with water and sulphuric acid
	R-GZV	Reverse osmosis concentrate, obtained after the liquid fraction (LF) of digestate is treated via dissolved air floatation and membrane filtration
Residues from food processing industry and source-segregated food waste	D-AmP	Digestate, unprocessed
	SF-AmP	Solid fraction of digestate, separated via decanter centrifugation
	SFD-AmP	Dried SF of digestate, obtained after drying AmP-SF in fluidized bed dryer at 60 °C
	E-AmP	Evaporator concentrate, obtained after the LF of digestate is passed through a vacuum evaporator
	R-AmP	Reverse osmosis concentrate, obtained after ammonia water from vacuum evaporator is treated via reverse osmosis.
Residues from agro-industry (potatoes and grain, 40% w/w), sludge from industrial wastewater treatment plants (15% w/w) and animal manure (45% w/w)	D-WNE	Digestate, unprocessed
	LF-WNE	LF of digestate, separated via decanter centrifugation
	E-WNE	Evaporator concentrate, the fraction of LF of digestate retained after NH_3 removed via evaporation
	SFD-WNE	Dried SF of digestate, obtained after drying the SF of digestate in a Hydrogone dryer
	AW-WNE	Condensed ammonia water, obtained after NH_3-rich gas is condensed with water vapour
Sewage sludge from wastewater treatment plants (86% w/w) and coproducts (digestate from anaerobic treatment of source-segregated domestic food waste, 14% w/w)	D-A&S	Digestate, unprocessed
	AS-A&S	Ammonium sulphate solution, obtained after ammonia is extracted from biogas using H_2SO_4
Energy crops (silage maize, silage rye and corn, 85% w/w) and poultry litter (15% w/w)	D-BNS	Digestate, unprocessed
	AS-BNS	Ammonium sulphate solution, obtained after gypsum is added to ammonia stripped from digestate

Table 2. Fertiliser and equivalent amounts of NH_4^+-N, organic N (N_{org}), and total carbon (C) added to soil at the total N application rate of 170 kg ha^{-1}

Fertiliser groups	Fertiliser	NH_4^+-N	N_{org}	C added
		kg ha^{-1}		
Digestate (D)	D-GZV	113	57	595
	D-AmP	109	61	1334
	D-WNE	89	81	392
	D-A&S	108	62	671
	D-BNS	81	89	1000
Solid fractions of digestate (SF)	SF-GZV	154	16	2838
	$SF\text{-}GZV_{P\text{-}poor}$	46	124	4489
	SF-AmP	39	131	1778
	SFD-AmP	8.0	162	2047
	SFD-WNE	39	131	1814
Evaporator concentrates (E)	E-AmP	138	32	570
	E-WNE	4.0	156	748
Liquid fraction of digestate (LF)	LF-WNE	95	75	151
Reverse osmosis concentrates (R)	RO-GZV	162	8	86
	RO-AmP	143	27	197
Ammonia water (AW)	AW-WNE	170	0	0
Ammonium sulphate solutions (AS)	AS-A&S	170	0	0
	AS-BNS	169	1	0
Mineral fertilisers	CAN	170	0	0
	Urea	170	0	74

Table 3. Main physicochemical characteristics of biobased and mineral fertilisers included in the study. DM: Dry matter; FW: fresh weight; OM: organic matter; TN: total N; TC: total C; DOC: dissolved organic carbon; TDN: total dissolved N

Fertiliser	pH	DM	OM	TN	TC	NH_4^+	TDN	DOC	C/N	DOC/TC	TDN/TN
	-	%	%FW	g kg^{-1} FW					-		
D-GZV	8.20	7.9	5.7	8.12	30.0	5.42	5.30	5.13	3.7	0.19	0.63
D-AmP	8.10	8.1	5.0	3.44	29.0	2.20	2.44	3.20	8.4	0.09	0.93
D-WNE	8.57	5.2	3.2	6.50	17.0	3.41	4.91	5.05	2.7	0.33	0.78
D-A&S	8.60	9.3	5.5	6.95	29.0	4.40	1.27	4.40	4.1	0.05	0.63
D-BNS	8.30	8.1	6.5	5.10	33.0	2.42	5.19	2.80	6.5	0.17	0.55
SF-GZV	8.80	33	25	11.8	136	7.24	2.97	3.30	17	0.02	0.41
$SF\text{-}GZV_{P\text{-}poor}$	5.50	27	24	4.50	120	1.22	0.53	1.32	27	0.00	0.29
SF-AmP	8.30	26	17	9.10	100	2.10	3.01	2.40	11	0.03	0.26
SFD-AmP	8.10	47	47	24.0	310	1.10	2.44	1.00	13	0.01	0.04
SFD-WNE	7.90	94	67	31.4	343	7.14	8.73	3.20	11	0.03	0.10
E-AmP	6.20	6.3	6.3	7.80	29.0	6.30	8.77	7.70	3.7	0.34	0.99
E-WNE	7.00	17	9.5	10.0	51.0	0.26	2.96	7.90	3.4	0.07	0.81
LF-WNE	8.85	2.4	1.2	4.94	5.90	2.77	1.10	4.34	1.2	0.25	0.88
R-GZV	8.30	3.6	1.0	9.10	5.70	8.65	8.85	-	0.6	-	0.97
R-AmP	7.30	1.5	1.4	3.10	3.60	2.60	3.04	-	1.2	-	0.98
AW-WNE	9.70	<1	0.0	53.2	0.50	53.2	-	-	-	-	1**
AS-A&S	5.90	38	0.0	76.1	0.10	75.9	-	-	-	-	1**
AS-BNS	6.30	21	0.0	41.3	0.26	41.0	-	-	-	-	1**
CAN	7.39	99	0.0	300	-	-	-	-	-	-	-
Urea	7.91	99	0.0	460	200*	-	-	-	-	-	-

*based on the molecular composition of urea

**assumed values since NH_4^+-N≈TN

Table 4. Soil concentrations of NH_4^+ and NO_3^- and net* mineral N release (N_{rel}) at the end of the incubation (18 days); and net* cumulative fertiliser-derived N_2O and CH_4 emissions

Fertiliser	NH_4^+	NO_3^-	N_{rel}	N_2O_{cum}	CH_{4cum}
	mg kg^{-1}		% N applied		mg m^{-2}
D_GZV	1	122	88	**0.06^{bcde}**	-1^{a}
D_AmP	1	151	97	0.11^{ab}	-7^{a}
D_WNE	2	105	75	0.09^{abcde}	-14^{a}
D_A&S	2	77	45	*0.08^{bcdefg}*	-16^{a}
D_BNS	2	67	34	**0.06^{efgh}**	-9^{a}
SF_GZV	1	93	57	**0.05^{fgh}**	-16^{a}
$SF\_GZV_{P\text{-}poor}$	0	38	-3	**0.04^{h}**	-24^{a}
SF_AmP	1	91	54	**0.06^{fgh}**	-7^{a}
SFD_AmP	1	58	23	*0.07^{defgh}*	-3^{a}
SFD_WNE	1	60	26	*0.07^{cdefgh}*	-15^{a}
E_AmP	0	118	84	0.10^{abc}	4^{a}
E_WNE	2	90	56	0.08^{abcdef}	1^{a}
LF_WNE	1	125	89	**0.05^{fgh}**	-16^{a}
R_GZV	1	117	83	**0.05^{fgh}**	-16^{a}
R_AmP	1	121	87	0.07^{bcdefgh}	-6^{a}
AW_WNE	2	135	108	0.09^{abcde}	-8^{a}
AS_A&S	2	112	82	**0.04^{fgh}**	-13^{a}
AS_BNS	2	117	88	**0.04^{gh}**	-9^{a}
CAN	1	135	108	0.10^{abcd}	-6^{a}
Urea	1	130	102	0.12^{a}	-8^{a}

In a column, values followed by the same letter do not differ significantly according to Tukey's test (p<0.05).

N_2O_{cum} values in bold are significantly lower than CAN and urea; italicized values are significantly lower than urea but not different from CAN.

*After subtracting the control