



Comparative Effectiveness of Biogas Residue Acidification and Nitrification Inhibitors in Mitigating CO₂ and N₂O Emissions from Biogas Residue-Amended Soils

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Abstract Owing to their high carbon and nitrogen contents, biogas residues may lead to higher carbon dioxide (CO₂) and nitrous oxide (N₂O) emissions from soils. Acidification of biogas slurry and application of nitrification inhibitors (NIs) could mitigate the emission of these gases. An incubation experiment was therefore carried out to investigate the effect of NIs, DMPP (3, 4-dimethylpyrazole phosphate), and PIADIN (active ingredients: 3.00–3.25% 1,2,4-triazole and 1.50–1.65% 3-methylpyrazole), on CO₂ and N₂O emissions from soils fertilized with biogas residues and acidified biogas residues. Biogas residues produced higher ammonium-nitrogen (NH₄⁺-N) and nitrate-nitrogen (NO₃⁻-N) concentrations in soils which resulted in higher emissions of CO₂-C and N₂O-N than that from acidified biogas residues. Both DMPP and PIADIN significantly decreased the emissions of CO₂-C (8.1–55.8%) and N₂O-N (87–98%) and maintained lower NH₄⁺-N and NO₃⁻-N concentrations when compared to control (without nitrification inhibitors). However, the DMPP had a higher

reduction capability for CO₂-C emissions than PIADIN in acidified biogas residue applied soil. In conclusion, the acidification of biogas residues and application of NIs are effect in reducing gaseous emission from biogas residue fertilized soils and thus could improve the fertilizer effectiveness of the residues.

Keywords Acidified biogas residues · Nitrification inhibitors · N₂O and CO₂ emissions · Nutrient cycling

1 Introduction

Carbon dioxide (CO₂) and nitrous oxide (N₂O) are the primary greenhouse gases (GHGs) present in the Earth's atmosphere (IPCC, 2010). CO₂ could hang around for a long time, between 300 and 1000 years, once it is added to the atmosphere (Alan, 2019). The lifetime of atmospheric CO₂ concentration, with an increase of about 120 ppm over the past 250 years, has risen to a current global average of approximately 409 ppm, and future rapid increase is expected, with values likely to reach 550 ppm by mid-century and 1000 ppm by the end of this century (IPCC, 2014). Similarly, N₂O is a long-lived GHG, has a lifetime of 116 ± 9 years (Prather et al., 2015), and is a major stratospheric ozone-depleting substance (Thompson et al., 2019). Its concentration in the atmosphere has also risen steadily since the mid-twentieth century (IPCC, 2013), from approximately 290 ppb in 1940 to 330 ppb in 2017 (Park et al., 2012).

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Agricultural practices, particularly the use of nitrogenous fertilizers, substantially contribute to enhancing N₂O emission and thus increasing the concentration of reactive nitrogen (N, N₂O) in the atmospheric environment (Bouwman et al., 2013). In soils, N₂O is produced as a by-product of nitrification and denitrification processes which are carried out by different types of microbes (Bremner, 1997). Nitrification is the biological oxidation of NH₄⁺ to nitrite (NO₂⁻) and further to nitrate (NO₃⁻). Denitrification is a microbially facilitated process in which NO₃⁻ is reduced, through a series of intermediate gaseous N oxide products, to molecular nitrogen (N₂) (Köster et al., 2013). To meet the ambitious climate change adaptations, CO₂ and N₂O emissions should be minimized (IPPC, 2018).

Various techniques are used to reduce the CO₂ and N₂O emissions while meeting the growing demand for food and other agricultural products (Thompson et al., 2019). One of the approaches is to produce biogas through fermentation of renewable sources, including organic manures, plant materials, food waste, etc. The use of biogas as an energy source could reduce dependency on fossil fuels and is expected to have no or even a positive effect on the atmospheric greenhouse gas balance (Herrmann, 2013). Biogas production plays an important role in the European bio-energy supply and has increased rapidly in Germany in recent years. According to the Agency of Renewable Energies, there are 837 biogas production factories in the northern part of Germany. It is evident that the recycling of the biogas residue (BR) from such a large number of biogas production factories installed in the state of Schleswig–Holstein became a problem. Mostly BR is applied to soil as organic fertilizers (Köster et al., 2014; Koszel & Lorencowicz, 2015) and is considered an essential component of cropping systems due to its high fertilization value (Möller & Stinner, 2009). The application of BR as a fertilizer improved soil fertility, plants quality, and their immunity to biotic and abiotic stress agents (Kouřimská et al., 2012).

In addition to improving soil quality, the BR application to soil, due to their high carbon and ammonium content, may increase the CO₂ and N₂O emissions and NO₃⁻ leaching from the soils (Hennig & Gawor, 2012). N₂O emissions and NO₃⁻ leaching from BR may be minimized by their acidification before soil application and by using nitrification

inhibitors (NIs). While application of NIs can further reduce NO₃⁻ leaching from BR applied soils by suppressing autotrophic nitrification and subsequent denitrification, which will ultimately also reduce N₂O emission. In fertilizer (mineral, slurry, and organic manure) applied to soil, the use of NIs has shown reduced N₂O emissions (VanderZaag et al., 2011) and thereby increased N use efficiency of the applied fertilizers (Subbarao et al., 2006).

We hypothesized that (a) application of ABR to the soil will decrease soil pH and show lower CO₂ and N₂O emissions than the application of BR and (b) NI application to ABR-amended soil will further lower the gaseous emission from the soil. Keeping this in view, an incubation pot experiment was conducted to investigate CO₂ and N₂O emissions as well as NH₄⁺ and NO₃⁻ dynamics in the soils amended with BR and ABR and applied with DMPP and PIADIN nitrification inhibitors.

2 Material and Methods

2.1 Collection and Preparation of Soil and Biogas Residues

The biogas residues (BR) were collected from a large commercial biogas company in Germany in May 2019. Its digesters were used to feed with the following materials: 18-t corn silage, 55-t dry chicken feces, 4-t whole crop silage (rye), and 7 m³ swine manure. For the incubation experiment, BR was sampled directly from the biogas residue storage pool. Acidified biogas residues (ABR) were prepared by lowering the pH of BR from 7.9 to 5.5 with the addition of H₂SO₄.

The soil was collected from an upper 20-cm layer of a natural grassland (which is adjacent to an agricultural farm and its soil has the same characters as that of agricultural soil) in Grevenkrug, Schleswig–Holstein (54° 11' 09.1" N and 10° 00' 36.6" E). The soil was sandy in texture, with 5% silt and 95% sand. The water-holding capacity (WHC) of the soil was 24.34% and bulk density was 1.4 g cm⁻³. The soil was air-dried and sieved through a 2-mm sieve to remove visible plant residues, roots, and stones. The total soil C and N contents in the soil were determined using a CN analyzer (Flash EATM 1112, Thermo Fischer Scientific,

Waltham, Massachusetts, USA). The fresh BR was got analyzed from Raiffeisen Laborservice (Ormont, Germany) for the salient characteristics. The salient characteristics of the soil and fresh BR are given in Table 1.

2.2 Treatments and Experimental Design

Three treatments of biogas residues (unamended, BR and ABR) were tested against three treatments of nitrification inhibitors (control, DMPP (3, 4-dimethylpyrazole phosphate), and PIADIN (active ingredients: 3.00–3.25% 1,2,4-triazole and 1.50–1.65% 3-methylpyrazole)), yielding 9 treatment combinations in total. The soil was filled in cylindrical pots (15-cm diameter and 33-cm length) up to 20-cm height while adjusting the bulk density to 1.4 g cm⁻³. Both BR and ABR were applied to the respective pots at the rate of 27.8 g kg⁻¹ soil (equivalent to 0.1 g NH₄⁺-N kg⁻¹ soil), whereas unamended treatment did not receive any amendment. The DMPP and PIADIN were applied at the rate of 5 mg kg⁻¹ soil (5% of the applied NH₄⁺-N), whereas no NI was added to the control pots. The pots were incubated for 57 days in a climatic chamber at a constant temperature (15 °C), soil moisture (80% WHC), and air humidity (50%). Deionized water was added daily to maintain the desired soil moisture level. The experiment followed a two-factorial completely randomized design with four replicates.

Table 1 Characteristics of experimental soil and fresh biogas residues

| Characteristic | Soil | Biogas residues |
|--|------|-----------------|
| Water content (%) | – | 90.3 |
| Total carbon (C, g kg ⁻¹) | 11.6 | 31.4 |
| Total nitrogen (N, g kg ⁻¹) | 0.8 | 5.6 |
| Organic N (g kg ⁻¹) | 0.7 | 2.0 |
| NH ₄ ⁺ -N (mg kg ⁻¹) | 2.16 | 3600 |
| NO ₃ ⁻ -N (mg kg ⁻¹) | 4.8 | 0 |
| pH ^a | 6.5 | 7.9 |

^aIn soil:CaCl₂ (1:4) extract

2.3 Collection and Measurement of N₂O and CO₂

The N₂O and CO₂ samples were collected daily during 1st week, once after 2 days during the 2nd week, and once after 3 days during rest of the incubation period. Before collecting gas samples, the pots were tightly closed with air-tight lids having one rubber membrane, which served as a contact between the sample collecting syringe and the incubated environment. The samples were collected every 0, 20, 40, and 60 min. A 10-ml syringe with a hypodermic needle was placed in the pre-evacuated 2-ml headspace of Chromacol glass vials to collect the gas samples. The glass vials had a chloro-butyl rubber septum. Each gas sampling was carried out between 09:00 and 11:00 am. Except for the times when samples were being taken, the pots were left open. The concentrations of CO₂ and N₂O in the gas samples were measured by gas chromatography (Agilent 7890A GC, Agilent, CA, United States). An electron capture detector (ECD), adjusted to a temperature of 300 °C with N₂ as a carrier gas, was used to measure N₂O concentration. A thermal conductivity detector (TCD), adjusted to a temperature of 250 °C with He as a carrier gas, was used to measure CO₂ concentration (Guo et al., 2021a). For each gas measurement, the gas chromatograph was calibrated with respective certified gas standards. The rate of CO₂ and N₂O emissions from each pot (ppm/min) during lid closure was calculated using headspace volume and a linear relation between the CO₂ and N₂O concentration and time (Venterea et al., 2020). The emission rates of CO₂-C (μg h⁻¹ kg⁻¹) and of N₂O-N (ng h⁻¹ kg⁻¹) were calculated with the following equations:

$$EN_2O - N = \frac{R \times 60 \times V_{\text{gas}} \times AR}{W_{\text{soil}} \times V_m} 2 \times 1000 \quad (1)$$

$$ECO_2 - C = \frac{R \times 60 \times V_{\text{gas}} \times AR}{W_{\text{soil}} \times V_m} \quad (2)$$

where ECO₂ and EN₂O are emission rates of CO₂-C (μg h⁻¹ kg⁻¹) and N₂O-N (ng h⁻¹ kg⁻¹), respectively; *R* is the rate of CO₂ and N₂O emissions from each pot (ppm/min); *V*_{gas} is the gas volume in pot (L); *W*_{soil} is the weight of dry soil in pot (kg); *AR* is the relative atomic mass of C and N, i.e., 12 and 14, respectively;

and V_m is the molar volume of gas which is 23.7 L/mol at 15 °C.

Total N_2O and CO_2 emissions during the incubation period were calculated by adding the total daily N_2O and CO_2 emissions. For this purpose, the emission rates of CO_2 -C ($\mu\text{g h}^{-1} \text{kg}^{-1}$) and N_2O -N ($\text{ng h}^{-1} \text{kg}^{-1}$) were multiplied by the hours, i.e., 24 h for the 1st week, 48 h for the 2nd week, and 72 h for the last 6 weeks. The summation of all these gave the total emissions of CO_2 (mg kg^{-1}) and N_2O ($\mu\text{g kg}^{-1}$).

2.4 Soil Sampling and Measurement of NH_4^+ , NO_3^- , and pH

For the measurement of NH_4^+ -N, NO_3^- -N, and pH, soil samples (each 50 g approx.) were collected up to 20-cm depth using a specialized soil auger on days 1, 15, 29, 43, and 57 of incubation. Each soil sample was divided into two subsamples; the first was oven-dried at 105 °C for 8 h to calculate the water content, while the other was used for the determination of NH_4^+ -N, NO_3^- -N and pH. For soil mineral N analysis, 10-g fresh soil was extracted with 40 mL of 0.0125 M $CaCl_2$ solution (1:4) for 1 h on a reciprocating shaker. The suspensions so obtained were centrifuged for 10 min, filtered through Whatman filter paper No. 42, and stored at 4 °C. The concentrations of NH_4^+ and NO_3^- were measured by a continuous flow autoanalyzer (San⁺⁺ Automated Wet Chemistry Analyzer—Continuous Flow Analyzer (CFA), Skalar, The Netherlands). For pH measurement, 10-g air-dried and sieved soil was mixed with 25 mL of 0.0125 M $CaCl_2$ solution (1:2.5) and shaken for 1 h. After centrifugation of the suspensions, the pH of the upper clear liquid was measured using a pH meter.

2.5 Statistical Analysis

Data were verified for normal distribution, treatment means for total N_2O -N, and CO_2 -C emissions over the incubation period were compared using a two-way analysis of variance. pH over the different treatment at the same day was compared using a two-way analysis of variance. The significance of differences between individual treatment means was determined using Tukey's honestly significant difference (HSD) test at $P \leq 0.05$. Tukey's HSD test was performed by R statistical software (Oakland, CA, USA). R was used to create the artwork.

3 Results

3.1 Rate of CO_2 -C and N_2O -N Emissions

In unamended soil, the rates of CO_2 -C and N_2O -N emissions were substantially lower than the biogas residues amended soils and there was no consistent pattern of increase or decrease with the passage of time during the incubation period (Figs. 1 and 2). However, rates of both CO_2 -C and N_2O -N emissions were substantially higher in BR- and ABR-amended soils than unamended soil, with BR application showing more increase than ABR application. In BR- and ABR-amended soils, rates of emissions reached maximum by the end of the first or mid of the 2nd week, and thereafter decreased gradually, reaching the minimum value at the end of the incubation period. Application of DMPP and PIADIN to BR- and

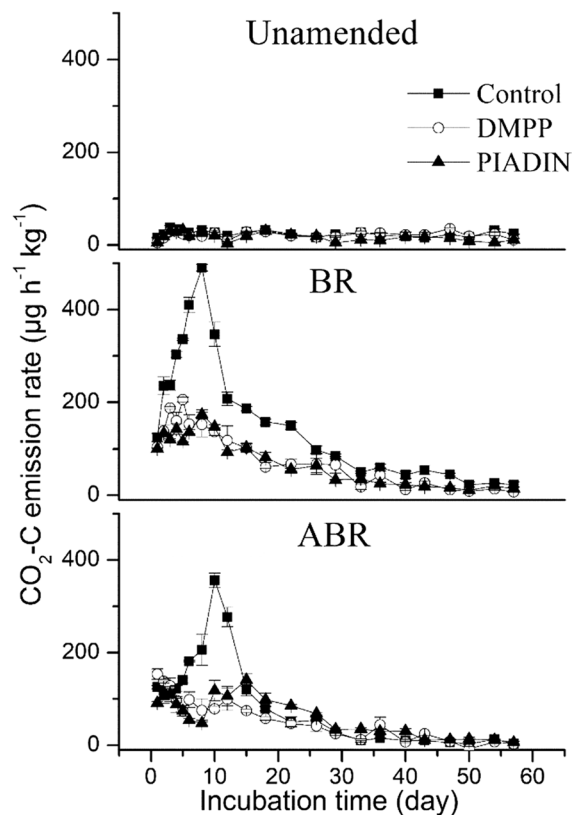


Fig. 1 Rate of CO_2 -C emissions from unamended, biogas residues (BR)- and acidified biogas residues (ABR)-amended soils applied with control, DMPP, and PIADIN nitrification inhibitors. The vertical bars indicate the standard error of the means ($n=4$)

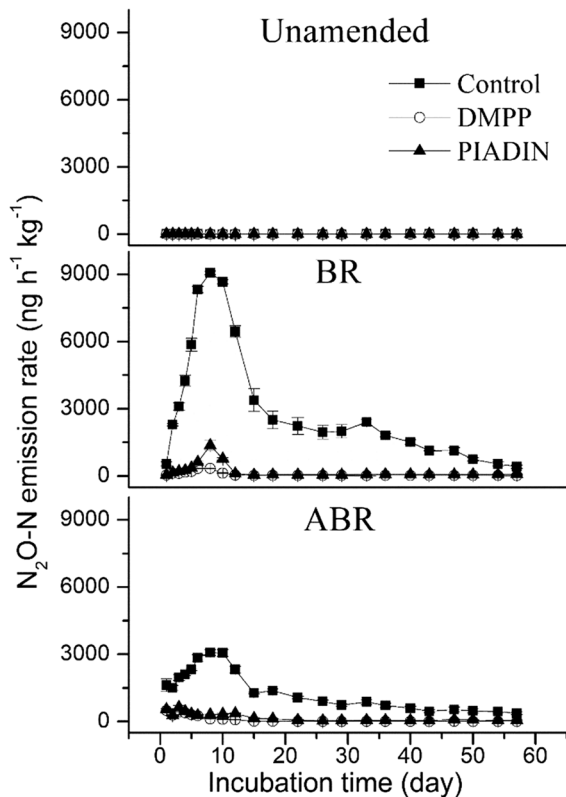


Fig. 2 Rate of N_2O -N emissions from unamended, biogas residues (BR)- and acidified biogas residues (ABR)-amended soils applied with control, DMPP, and PIADIN nitrification inhibitors. The vertical bars indicate the standard errors of the means ($n=4$)

ABR-amended soils decreased the emissions rates of both gases.

3.2 Total CO_2 -C and N_2O -N Emissions

Irrespective of whether NIs were applied or not, total CO_2 -C emission was very low from unamended soil than that from BR- and ABR-amended soils. The total CO_2 -C emission was the highest from BR-amended soil (169 mg kg^{-1} soil), followed by ABR-amended soil (81 mg kg^{-1} soil) and the lowest from unamended soil (37 mg kg^{-1} soil) (Table 2). Compared to unamended soil, the application of BR and ABR increased total CO_2 -C emission by 3.60- and 1.21-fold, respectively. Total N_2O -N emission was also significantly higher from BR- and ABR-amended soils than that from unamended soil (Table 3). The mean total N_2O -N emission was the highest from

Table 2 Total CO_2 -C (mg kg^{-1} soil) emission from unamended, biogas residues (BR)-, and acidified biogas residues (ABR)-amended soils applied with control, DMPP, and PIADIN nitrification inhibitors

| NI | Unamended soil | BR-amended soil | ABR-amended soil |
|---------|---------------------|---------------------|---------------------|
| Control | $37 \pm 1e$ | $169 \pm 8a$ | $81 \pm 3b$ |
| DMPP | $30 \pm 5 (-17.8)f$ | $76 \pm 7 (-55.0)c$ | $50 \pm 5 (-38.1)d$ |
| PIADIN | $26 \pm 0 (-29.5)f$ | $75 \pm 3 (-55.8)c$ | $75 \pm 4 (-8.0)c$ |

Values (mean \pm SE, $n=4$) followed by different letters are significantly different at $P=0.05$. The values in parenthesis represent % decrease (-) or increase (+) over the respective controls

BR-amended soil ($3678 \mu\text{g kg}^{-1}$), followed by ABR-amended soil ($1464 \mu\text{g kg}^{-1}$), and the lowest from unamended soil ($5 \mu\text{g kg}^{-1}$). Compared to unamended soil, the application of BR and ABR increased the total N_2O -N emission by 73- and 29-folds, respectively.

ABR-amended soil showed half CO_2 -C emission of what did the BR-amended soil (Table 2). The NIs (DMPP and PIADIN) significantly lowered total CO_2 -C emission compared to control, but their relative effectiveness depended upon the residue types (Table 2). In BR-amended soil, DMPP and PIADIN were equally effective in reducing CO_2 -C emission, with reduction amounted to be 55% of that from control. However, in ABR-amended soil, DMPP was more effective in reducing CO_2 -C emission, showing a 38% decrease over control, than PIADIN which showed only an 8% decrease. Overall, the CO_2 -C emission-reducing capacity of both the NIs was higher in BR-amended soil than that in ABR-amended soil.

ABR-amended soil showed 60% lower total N_2O -N emission than BR-amended soil (Table 3). The application of NIs further much lowered the total N_2O -N emission compared to control, with DMPP having higher reduction efficiency than PIADIN under both BR- and ABR-amended soils. The mean reduction in total N_2O -N emission in BR- and ABR-amended soil by DMPP and PIDIN was 96 and 90%, respectively.

3.3 Soil NH_4^+ -N and NO_3^- -N Concentrations

The application of both BR and ABR substantially increased NH_4^+ -N and NO_3^- -N concentrations

Table 3 Total N_2O -N emission (mg kg^{-1} soil) from unamended, biogas residue (BR)-, and acidified biogas residue (ABR)-amended soils applied with control, DMPP, and PIADIN nitrification inhibitors

| NI | Unamended soil | BR-amended soil | ABR-amended soil |
|---------|---------------------------------|----------------------------|----------------------------|
| Control | $5.04 \pm 0.35\text{e}$ | $3678 \pm 64\text{a}$ | $1464 \pm 72\text{b}$ |
| DMPP | $8.48 \pm 0.53 (+68.3)\text{e}$ | $84 \pm 4 (-98)\text{d}$ | $87 \pm 6 (-94)\text{d}$ |
| PIADIN | $5.31 \pm 0.24 (+5.4)\text{e}$ | $233 \pm 28 (-94)\text{c}$ | $187 \pm 15 (-87)\text{c}$ |

Values (mean \pm SE, $n=4$) followed by different letters are significantly different at $P=0.05$. The values in parenthesis represent % decrease (-) or increase (+) over the respective controls

compared to control (Fig. 3). With the passage of time, ABR application showed a slow gradual decline in NH_4^+ concentration and a rise in NO_3^- concentration as compared to BR-amended soil. Similarly, the residue-amended soils applied with NIs showed a gradual decline in NH_4^+ -N concentration and rise in NO_3^- -N concentration, whereas these changes were

quite sharp in control soils. Moreover, DMPP more strongly retarded the fall in NH_4^+ -N concentration and rise in NO_3^- -N concentration than PIADIN in both BR- and ABR-amended soils. The peak NO_3^- -N concentrations were lower in NI-treated soils as compared to control and DMPP produced the lowest NO_3^- -N concentration.

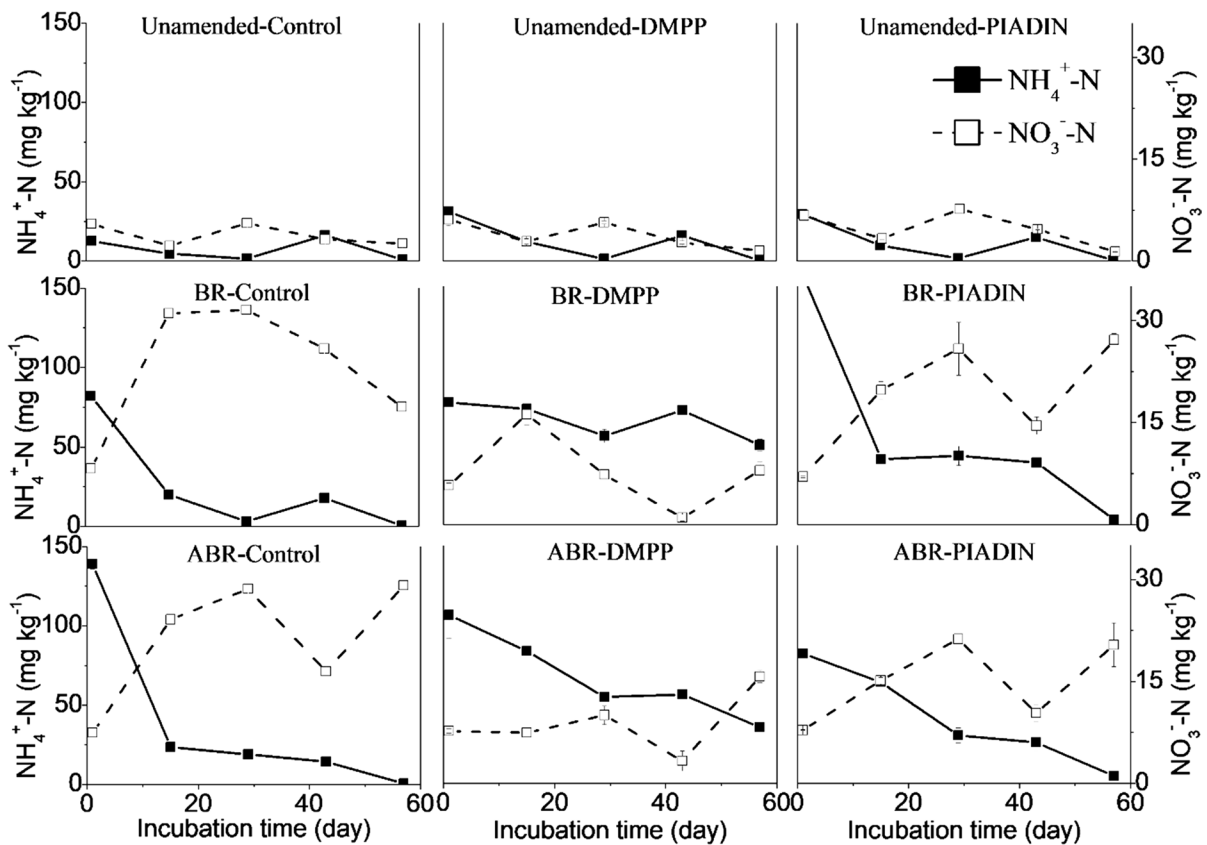


Fig. 3 Time-dependent change in NH_4^+ -N and NO_3^- -N concentrations in unamended, biogas residue (ABR)- and acidified biogas residue (ABR)-amended soils applied with control,

DMPP, and PIADIN nitrification inhibitors under controlled environment. The vertical bars indicate the standard errors of the means ($n=4$)

3.4 Soil pH

The application of BR did not affect the soil pH throughout the course of the experiment (Fig. 4). However, ABR application lowered the soil pH as compared to unamended soil and the mean decrease during the incubation period was 0.34 units. The application of DMPP and PIADIN had no influence on the soil pH.

4 Discussion

4.1 Effect of Biogas Residues

The application of biogas residues to agricultural soils as an organic fertilizer has become a common practice and is further growing with the increase in

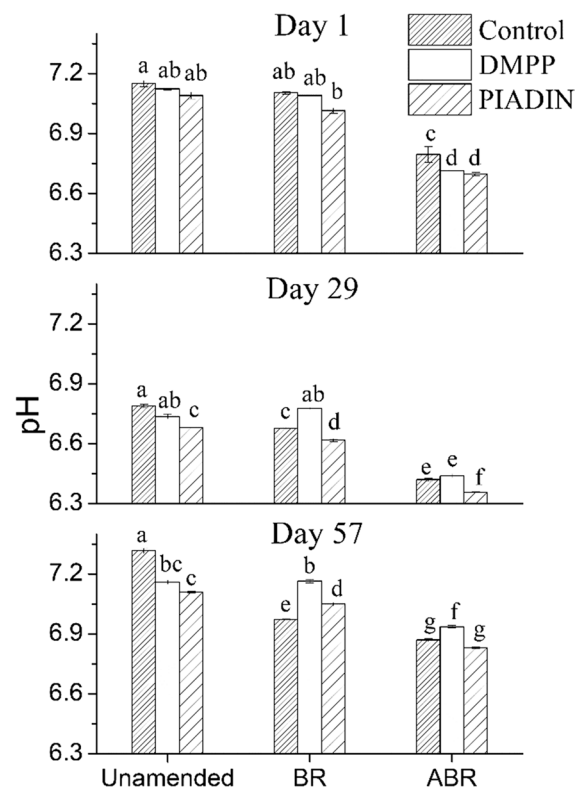


Fig. 4 Changes in pH of unamended, biogas residues (BR)- and acidified biogas residues (ABR)- amended soils applied with control, DMPP, and PIADIN nitrification inhibitors. The vertical bars indicate the standard errors of the means ($n=4$). The values indicated with the same lowercase letter(s) on the same days are not significantly different at $P=0.05$

the number of biogas plants in some European countries (Köster et al., 2015; Wolf et al., 2014). The application of BR no doubt improves soil organic matter and N availability to crops, but on other sites, it can also provoke CO_2 and N_2O emissions from soils (Köster et al., 2011, 2015; Senbayram et al., 2014). Thus, high application rates of BR to cultivated lands could be linked to environmental problems such as high levels of CO_2 and N_2O in the atmosphere and NO_3^- leaching to groundwaters (Qu et al., 2014). This study revealed that BR application to soil significantly increased CO_2 and N_2O emissions (Figs. 1 and 2; Tables 2 and 3). A sharp decline in $\text{NH}_4^+\text{-N}$ concentration and a rise in $\text{NO}_3^-\text{-N}$ concentration was recorded in BR-amended soil (Fig. 3). Concurrent presence of NH_4^+ , NO_3^- , and high level of labile C in the BR could have hastened the nitrification and denitrification processes in the soil (Jaeger et al., 2013) and thus increased CO_2 emissions (Köster et al., 2015) and N_2O emissions (Senbayram et al., 2009) compared with unamended soil. The availability of a high level of NO_3^- as a result of nitrification together with labile C under anaerobic soil conditions serves as a driving force for N_2O emissions (Senbayram et al., 2009). Groffman and Crawford (2003) reported that CO_2 efflux and denitrification activity can be positively correlated, and hence, increased denitrification activity also increases CO_2 efflux. It is generally accepted that the application of organic fertilizers stimulates soil microbial biomass, basal respiration (Ros et al., 2003), and enzyme activities (Chu et al., 2007). Soil microbial processes also produce gases such as N_2O (IPCC, 2013), and residual organic carbon substrates favor soil microbial denitrification (Robertson & Groffman, 2007). In conclusion, BR application to soil significantly increases $\text{CO}_2\text{-C}$ and $\text{N}_2\text{O}\text{-N}$ emissions from soils.

4.2 Acidification of BR and the Gaseous Emission

Soil N dynamics in BR-amended soils could depend on the BR composition and stability (Albuquerque et al., 2012). Hence, through changing the soil characteristics, BR may affect the nitrification process and hence the amounts of NO_3^- lost by denitrification or leaching (Peter et al., 2004). Among the soil characteristics, pH is a master variable that affect microbial transformations in soils. Nitrification is strongly influenced by pH (Mackens et al., 2021), with maximum

rates occurring at pH 7.5 (Eric et al., 2002). Oxidation of NH_4^+ is completely inhibited at pH 5 and increases with a higher pH (Wang et al., 2018). Our result showed that application of ABR lowered soil pH than unamended soil, but this pH effect was not observed for BR-amended soil (Fig. 4). Accordingly, ABR application resulted in half $\text{CO}_2\text{-C}$ and 60% less $\text{N}_2\text{O-N}$ emissions from the soil compared to BR application (Tables 2 and 3). This is well explained by a slow gradual decline in NH_4^+ concentration and a rise in NO_3^- in ABR-amended soil as compared to BR-amended soil (Fig. 3). Thus, it could be inferred that ABR application retarded the nitrification process through a pH-driven shift in the microbial community structure and/or microbial activities (Ottosen et al., 2009). Fangueiro et al. (2013) also reported that lowering the pH led to decreased CO_2 emission from soil, and the effect is due to the low microbial activities in the acidified soil (Fangueiro et al., 2015). In addition, since a small amount of H_2SO_4 could lower the pH of BR from 7.9 to 5.5, the cost of acidification is very low. In conclusion, ABR application to soil significantly decreases $\text{CO}_2\text{-C}$ and $\text{N}_2\text{O-N}$ emissions from soils compared to BR.

4.3 Nitrification Inhibitors and the Gaseous Emissions

Application of NIs is recognized as one of the mitigation strategies that have been proven to be highly effective in reducing N fertilizer losses, increasing N use efficiency, and crop yields under different cropping systems (Moir et al., 2012; Zhang et al., 2015). Therefore, we tested the compatibility of using the most common NIs DMPP and PIADIN with BR and ABR for reducing CO_2 and N_2O emission from soils. Our result showed that NIs reduced CO_2 and N_2O emissions in BR- and ABR-amended soil (Figs. 1 and 2; Tables 2 and 3). For reducing CO_2 emission, the efficiency of NIs was relatively less in ABR-amended soil than BR-amended soil and DMPP was more effective than PIADIN only in ABR-amended soil (Table 2). However, NIs were equally effective in reducing N_2O emission in BR- and ABR-amended soil, and DMPP was relatively more effective than PIADIN under both conditions (Table 3). The application of PIADIN has been reported to reduce N_2O emissions by 37–62% during the weeks following biogas residue application

to soil (Wolf et al., 2014). In fact, DMPP and PIADIN maintained $\text{NH}_4^+\text{-N}$ concentration at a higher level which showed that NIs retarded the nitrification process and kept $\text{NO}_3^-\text{-N}$ concentration at a low level (Fig. 3). Most NIs retard microbial oxidation of NH_4^+ by depressing the activities of nitrifiers in soil (Wolf et al., 2014). Thus, NIs could have inhibited nitrification through suppressing the activity of ammonia-oxidizing bacteria or relevant enzymes, effectively delaying the oxidization process that transforms NH_4^+ into NO_3^- . The decrease of $\text{CO}_2\text{-C}$ by applied NIs (Guo et al., 2021b) mostly was caused by the inhibition of microbial activities (Wolf et al., 2014). We found long-lasting higher $\text{NH}_4^+\text{-N}$ concentration and lower $\text{CO}_2\text{-C}$ and $\text{N}_2\text{O-N}$ emissions from DMPP-treated soil as compared to PIADIN-treated soil (Fig. 3; Tables 2 and 3). This implies that DMPP was more effective than PIADIN in retarding the nitrification process and mitigating the gaseous emission from both BR- and ABR-amended soils under given experimental conditions. Chen et al. (2010) and Fangueiro et al. (2009) also reported that DMPP maintained the highest soil NH_4^+ content and a low soil NO_3^- content for a longer time than the other NIs and resulted in the highest reduction in N_2O emissions.

5 Conclusion

Application of both BR and ABR substantially increased soil NH_4^+ content, but ABR-amended soil showed much lower $\text{CO}_2\text{-C}$ and $\text{N}_2\text{O-N}$ emissions than BR-amended soil. DMPP and PIADIN were equally effective in reducing $\text{CO}_2\text{-C}$ emission from BR-amended soil but DMPP was more effective than PIADIN in ABR-amended soil. DMPP almost completely diminished the N_2O emission from both BR- and ABR-amended soils while the efficacy of PIADIN was relatively lower than DMPP in both cases. Acidification of BR did not further improve the efficacy of NIs, rather it had a slightly negative effect on the performance of PIADIN. Thus, it is concluded that although acidification of BR had an ameliorating effect on CO_2 and N_2O emissions from soils, it is not required when NIs have already been applied to the soils. However, acidification of BR could be beneficial in lowering N_2O emission from the soils.

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Data Availability The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Code Availability Not applicable.

Declarations

Conflict of interest The authors declare no competing interests.

Ethical Approval Not applicable.

Consent to Participate Not applicable.

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