

ORIGINAL ARTICLE

Contrasting effects of different pH-raising materials on N₂O emissions in acidic upland soils

Yi Cheng¹  | Huimin Zhang¹ | Zhaoxiong Chen¹ | Jing Wang^{2,3} |
Zejiang Cai^{4,5} | Nan Sun⁴ | Shenqiang Wang⁶ | Jinbo Zhang^{1,7,8}  |
Scott X. Chang^{9,10} | Minggang Xu⁴  | Zucong Cai¹ | Christoph Müller^{11,12}

¹School of Geography, Nanjing Normal University, Nanjing, China

²College of Forestry, Nanjing Forestry University, Nanjing, China

³Co-Innovation Center for Sustainable Forestry in Southern China, Nanjing Forestry University, Nanjing, China

⁴Institute of Agricultural Resources and Regional Planning, Chinese Academy of Agricultural Sciences/National Engineering Laboratory for Improving Quality of Arable Land, Beijing, China

⁵Qiyang Agro-ecosystem of National Field Experimental Station, Chinese Academy of Agricultural Sciences, Hunan, China

⁶State Key Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, Chinese Academy of Sciences, Nanjing, China

⁷Jiangsu Center for Collaborative Innovation in Geographical Information Resource Development and Application, Nanjing, China

⁸State Key Laboratory Cultivation Base of Geographical Environment Evolution (Jiangsu Province), Nanjing, China

⁹State Key Laboratory of Subtropical Silviculture, Zhejiang A&F University, Hangzhou, China

¹⁰Department of Renewable Resources, University of Alberta, Edmonton, Alberta, Canada

¹¹Institute of Plant Ecology, Justus Liebig University Giessen, Giessen, Germany

¹²School of Biology and Environmental Science and Earth Institute, University College Dublin, Belfield, Ireland

Correspondence

Jinbo Zhang, School of Geography,
Nanjing Normal University, Nanjing
210023, China
Email: zhangjinbo@njnu.edu.cn

Christoph Müller, Institute of Plant
Ecology, Justus Liebig University Giessen,
Heinrich-Buff-Ring 26, 35392 Giessen,
Germany
Email: cmueller@uni-giessen.de

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Abstract

Acidic soils, occupying ca. 40% of the world's arable soils, often need to be managed (e.g., to raise their pH and to improve crop productivity); however, the environmental impact of raising soil pH is often difficult to assess. Increasing soil pH stimulates the reduction of N₂O to N₂, thus lowering N₂O emissions associated with denitrification, but can also increase autotrophic nitrification rates and related N₂O emission. Using a ¹⁵N tracing technique, we provide process-based insights into the effects of two acid-neutralizing materials (quicklime [CaO] vs. pig manure) on N₂O emissions in an acidified upland soil that had experienced excessive N application. Without pH adjustments we found that N₂O emissions, stimulated by supply of reactive N, were related to denitrification- and heterotrophic nitrification-derived N₂O emissions, whereas autotrophic nitrification-derived N₂O emissions declined with decreasing soil pH. These effects were reversed by increasing soil pH via liming. However, increasing the soil pH via application of pig manure significantly increased soil N₂O emissions from both nitrification and denitrification. Our study highlights that pH-amelioration practices may enhance N₂O emissions depending on the type of material applied to the

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soil. Therefore, both pH remediation and greenhouse gas mitigation options need to be considered together to avoid adverse environmental effects. The effect of different acid-neutralizing materials on soil N₂O emissions should be incorporated into ecosystem models to better estimate global N₂O emissions when pH amelioration is practised.

Highlights

- Enhanced N₂O emission by N input was from denitrification and heterotrophic nitrification.
- Chemical N input and liming have reversible effects on N₂O emission.
- Soil N₂O emission was decreased by liming but increased by animal manure input.
- Careful consideration of pH raising substrates is needed to avoid adverse effects.

KEYWORDS

¹⁵N tracing, denitrification, N₂O emissions, nitrification, quicklime, soil acidification

1 | INTRODUCTION

Nitrous oxide (N₂O) is an important greenhouse gas with a global warming potential of 298 times that of CO₂ over a 100-year time period, contributing to positive radiative forcing and ozone destruction in the stratosphere (Kanter et al., 2013; Stocker et al., 2013). Globally, agricultural soils have been found to contribute approximately 50% of anthropogenic N₂O emissions, mainly due to the input of chemical nitrogen (N) fertilizers (Bouwman, Boumans, & Batjes, 2002; Tian et al., 2019). A global meta-analysis of 1,104 field measurements further indicated that N₂O emissions in acidic soils are highly sensitive to changing N fertilization practices compared to neutral-alkaline soils (Wang et al., 2018).

Approximately 40% of the world's arable soils are acidic (i.e., pH < 5.5), with a tendency to become even more severe in recent years (Bian, Zhou, Sun, & Li, 2013; Von Uexkuell & Mutert, 1995). There are global concerns regarding acidified arable land, particularly in China (Guo et al., 2010; Hajkovicz & Young, 2005), because soil acidification has adverse effects on plants and soil microorganisms due to aluminium toxicity and deficiencies of some nutrients (Kunhikrishnan et al., 2016). Liming is recommended to alleviate soil acidification (Goulding, 2016; Holland et al., 2018). The application of animal manure may also have a liming effect due to its ash alkalinity (Wang et al., 2017), with the added advantage that the animal manure supplies some of the N required by crops. Increasing soil pH by liming and/or animal manure can affect N transformation rates such as denitrification and autotrophic

and heterotrophic nitrifications, with all of them involved in the production of N₂O (Zhang, Müller, & Cai, 2015). It has been suggested that increasing soil pH may be a viable abatement technique to mitigate N₂O emission from acid soils (Wang, Guo, et al., 2018). However, the effects of different acid-neutralizing materials (e.g., quicklime vs. animal manure) on N₂O emissions from acidic soils are unclear. A better process-based understanding is pivotal to accurately estimate global N₂O emissions from acid soils undergoing pH-raising amelioration treatments.

The effect of liming on soil N₂O emissions is complex (McMillan et al., 2016; Senbayram et al., 2019). An important mitigation effect appears to be the shifting of the N₂O to N₂ ratio during denitrification towards N₂ under less acidic conditions (Liu, Mørkved, Frostegård, & Bakken, 2010; Šimek & Cooper, 2002). Although increased soil pH often stimulates the reduction of N₂O (lower N₂O/N₂ ratio), reduction may be partially or completely counterbalanced by increased total denitrification rates under higher soil pH (Saggar et al., 2013). It has also been shown that liming decreases the relative proportion of N₂O emissions via autotrophic nitrification, but enhances autotrophic nitrification, which increases the production of NO₃⁻, and therefore the N₂O emission resulting from the coupling of nitrification–denitrification processes (Barton, Gleeson, Maccarone, Zúñiga, & Murphy, 2013; Senbayram et al., 2019). Thus, there is considerable debate over whether liming would be a viable mitigation strategy to reduce N₂O emissions from N-fertilized acidic arable soils (Higgins, Laughlin, & Watson, 2013; Qu, Wang, Almoy, & Bakken, 2014;

Senbayram et al., 2019). The question is how liming affects denitrification-, autotrophic nitrification- and heterotrophic nitrification-derived N_2O emissions. In addition to the changed pH, animal manure application can stimulate N_2O emissions through the supply of labile carbon (C) and N, thus potentially increasing denitrification activity, which may outweigh the N_2O emission savings due to a decreased N_2O/N_2 ratio as a result of increasing pH (Saggar et al., 2013; Wang, Chadwick, Cheng, & Yan, 2018). Thus, understanding how liming and animal manure affect N_2O production through denitrification and autotrophic and heterotrophic nitrification is critical for developing more reliable process-based N_2O emission estimation models and specific N_2O emission mitigation strategies.

Here, we investigated how long-term application of quicklime (CaO) and pig manure influences gross N transformation rates and associated N_2O emissions under aerobic conditions in an acidified upland soil caused by excessive N application. We hypothesized that (a) the stimulation of N_2O emission by chemical N fertilizer application-induced soil acidification would be completely reversed by quicklime application, given that both applications mainly affect soil pH, and (b) different acid-neutralizing materials (quicklime vs. pig manure) have different effects on soil N_2O emissions due to the interactive effects of pH, and C and N availability following animal manure application.

2 | MATERIALS AND METHODS

2.1 | Site description and experimental design

The long-term field experiment was initiated in 1990 at Qiyang Experimental Station ($26^{\circ}45'12''N$, $111^{\circ}52'32''E$) at the Chinese Academy of Agricultural Sciences, Hunan Province, China, and is still running now. The site has been managed according to a typical agriculture practice in the area, with a summer maize (*Zea mays* L.)–winter wheat (*Triticum aestivum* L.) rotation system. In each year, winter wheat was sown in strips in early November and harvested in early May in the following year. Summer maize was sown between the wheat strips in early April and harvested in July. The site is characterized by a subtropical monsoon climate with an annual average temperature of about $18^{\circ}C$ and an annual average precipitation of approximately 1,250 mm (He et al., 2015). The soil is classified as Ferric Acrisols (WRB) originated from the Quaternary red clay parent material (He et al., 2015). In the region, soil acidification is a natural process as a result of intensive leaching, whereas increased input of chemical N fertilizers for achieving high yields has been accelerating the process (Cai et al., 2015). Prior to

establishing the long-term field experiment, the field was under a wheat–maize rotation for 3 years without fertilization to achieve low and uniform nutrient levels. The soil (0–20 cm) at the beginning of the long-term experiment had a pH of 5.7, organic C of 6.1 g kg^{-1} , total N of 1.1 g kg^{-1} , total P of 0.5 g kg^{-1} , total K of 13.7 g kg^{-1} , available N of 79.0 mg kg^{-1} , available P of 13.9 mg kg^{-1} and available K of 104 mg kg^{-1} .

The long-term experiment included 11 treatments: UC (unfertilized control); NK, NP and NPK (mineral fertilizer, where N, P and K stand for nitrogen, potassium and phosphorus, respectively); NKL, NPL and NPKL (mineral fertilizer + L = quicklime); NPKS (mineral fertilizer + S = straw); NPKSL (mineral fertilizer + straw + quicklime); NPKM (mineral fertilizer, 30% of applied N, + M = pig manure [70% of applied N]); and M (pig manure only). For the treatments receiving N fertilizer, the total amount of N (manure and urea) application was the same each year. For the NPKM treatment, 30% of the total N was applied as urea and the remaining 70% was applied as pig manure. The pig manure with an average water content of around 70% was collected from local farms. The pig manure contained 82.7 cmol kg^{-1} ash alkalinity, 368 g kg^{-1} organic C, 18.2 g kg^{-1} total N, 13.7 g kg^{-1} total P and 13.3 g kg^{-1} total K, with a pH of 8.8. For the NPKS and NPKSL treatments, half of the crop residues were left on the soil surface each year, considering that returning all straw with wide C/N ratios to the soil would result in high microbial N demand and subsequently severe N limitation for crop production (Chen, Liu, Tian, & Zhang, 2014). The chemical fertilizers were applied in the form of urea ($300\text{ kg N ha}^{-1}\text{ year}^{-1}$), superphosphate ($53\text{ kg P ha}^{-1}\text{ year}^{-1}$) and potassium chloride ($100\text{ kg K ha}^{-1}\text{ year}^{-1}$). Annually, 30% of the fertilizers were applied in the winter wheat season (November–May) and 70% in the summer maize season (April–July). Both chemical fertilizers and manure were applied by band placement at a depth of 10 cm after sowing of each crop. Because of rapid soil acidification in plots subjected to annual inputs of chemical N fertilizers since 1990, in 2010, half of the plots in the NK, NP, NPK and NPKS treatments received $2,250\text{ kg ha}^{-1}$ quicklime according to the same N fertilization amount to alleviate soil acidification, followed by the addition of $1,500\text{ kg ha}^{-1}$ quicklime in 2014 (Wang et al., 2017). Quicklime powder was broadcasted in the fallow season (August–October) and mixed with the soil by subsequent manual ploughing (10 cm).

Fresh soil samples (0–20 cm) were collected in October 2015 after the maize harvest using a 5-cm-diameter soil auger. A total of nine soil cores were randomly taken and homogenized to produce one composite soil sample from each plot. The soil samples were immediately sieved through a 2-mm mesh, homogenized thoroughly and then divided into two

subsamples. One subsample was stored at 4°C for less than a week prior to conducting the ^{15}N tracing incubation experiments; another was air-dried for the determination of soil pH, total C and N concentrations (Figure 1).

2.2 | ^{15}N tracing experiment

A ^{15}N tracing experiment was conducted in triplicate with ^{15}N -labelled NH_4^+ and ^{15}N -labelled NO_3^- . Fresh soil samples (20 g, oven-dried basis) were placed in 250-mL flasks and sealed. The flasks were then preincubated in the dark at 25°C in the laboratory for 1 day to allow equilibration. After preincubation, 2 mL of either $^{15}\text{NH}_4\text{NO}_3$ or $\text{NH}_4^{15}\text{NO}_3$ solution (10 atom% ^{15}N excess) were added to each soil sample by pipetting the solutions homogeneously over the soil surface, reaching final concentrations of 50 mg of $\text{NH}_4^+\text{-N}$ and 50 mg of $\text{NO}_3^-\text{-N}$ kg^{-1} soil. Subsequently, the moisture content was adjusted to 60% water-holding capacity by adding deionized water. The flasks were then sealed with rubber stoppers and incubated at 25°C in the dark for an additional 6 days. During the incubation, the samples were aerated for 30 min each day to maintain aerobic conditions inside the flasks, and any water loss was replaced every 3 days with deionized water as required. Incubation conditions mimicked the actual conditions of upland soils.

Gas samples were taken from the headspace of the flasks on days 2, 4 and 6. Before each gas sampling event, the flasks were opened for 30 min to renew the atmosphere inside and immediately sealed for 6 hours using a silicone sealant. Before sampling, the headspace gas was mixed by withdrawing and back injecting headspace gas five times using a 20-mL gas-tight syringe with a stopcock. There were two groups of flasks with the same soil

samples used for N_2O and NO sampling, respectively. For one group of the flasks, 40-mL gas samples were collected using a 50-mL gas-tight syringe with a stopcock from the headspace of each flask at the end of 6-hr incubations and immediately injected into two pre-evacuated vials (18.5 mL), to determine the concentrations of N_2O and CO_2 and isotopic composition of the N_2O . For another group of the flasks, 40-mL gas samples were also collected and transferred to a multi-layer foil sampling bag (2 L) for NO analysis. After headspace samples were taken, three flasks were randomly selected from each labelling treatment, and the soils were extracted by 2 M KCl (at a soil:solution ratio of 1:5) for determination of the concentration and isotopic composition of NH_4^+ and NO_3^- . The extraction procedure was also performed 0.5 hr following ^{15}N addition to avoid disturbance of abiotic N immobilization. After KCl extraction, residual soils were washed with deionized water three times until any residual inorganic N was removed, oven-dried at 60 °C to a constant weight, and ground to pass through a 0.15-mm sieve for ^{15}N analysis of insoluble organic N.

2.3 | Analyses

Prior to NO determination, gas samples drawn from flasks were diluted to 1 L with high-purity N_2 . The NO concentrations were measured using a NO_x analyser (ThermoFisher 42i, Chemiluminescence Detector, ThermoFisher, Franklin, MA, USA). The N_2O and CO_2 concentrations were determined using an Agilent 7,890 gas chromatograph (Santa Clara, CA, USA). The isotopic compositions of the N_2O samples were determined via mass spectrometry (Thermo Finnigan, MAT 253, Waltham, MA, USA). The concentrations of NH_4^+ and NO_3^- in the KCl extracts were determined using a continuous-

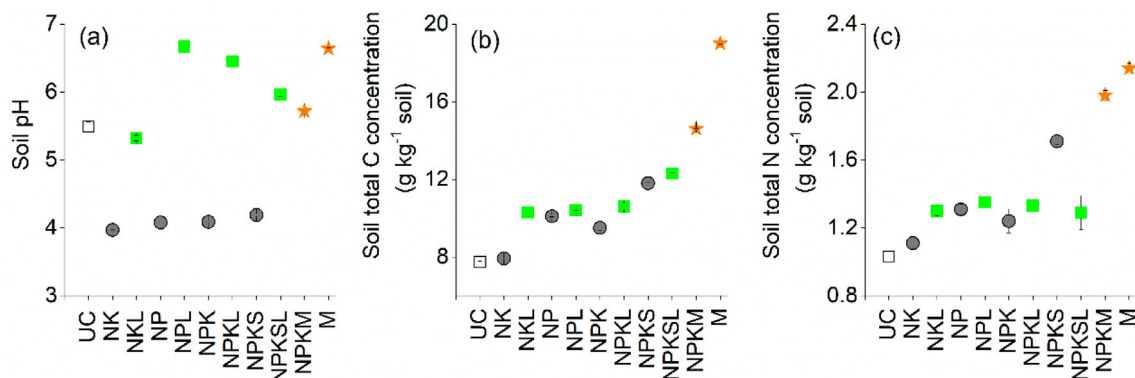


FIGURE 1 Soil properties (0–20 cm) after 25 years of repeated fertilizer experiment in an upland acidic soil. UC, unfertilized control; NK, NP, NPK, mineral NK, NP, NPK fertilizer alone, respectively; NKL, NPL, NPKL, mineral NK, NP, NPK fertilizer plus quicklime, respectively; NPKS, mineral NPK fertilizer plus straw; NPKSL, mineral NPK fertilizer plus straw and quicklime; NPKM, mineral NPK fertilizer (30% of applied N) plus swine manure (70% of applied N) each crop season; M, manure only. Error bars are standard deviations of the means ($n = 3$) [Color figure can be viewed at wileyonlinelibrary.com]

flow analyser (SA1000, Skalar, Breda, the Netherlands). NH_4^+ and NO_3^- were separated for ^{15}N measurements by distillation with magnesium oxide and Devarda's alloy, respectively (Bremner, 1996). The isotopic compositions of NH_4^+ , NO_3^- and insoluble organic N were determined by an automated C/N analyser isotope ratio mass spectrometer (Europa Scientific Integra, Sercon 20–22, Crewe, UK). Soil total C and N concentrations were determined by dry combustion using an elemental analyser (Vario MAX CN Elemental Analyzer, Elementar, Hanau, Germany). Soil pH was determined in deionized water (soil:water, 1:2.5) using a pH metre (Mettler Toledo FE20, Shanghai, China).

2.4 | ^{15}N tracing model and statistical analyses

Soil gross N transformation rates were quantified using the ^{15}N tracing analysis model developed by Müller, Rütting, Kattge, Laughlin, and Stevens (2007) (Figure S1). The model included 10 simultaneously occurring gross N transformations: (a) M_{Nrec} , mineralization of recalcitrant organic-N to NH_4^+ , (b) M_{Nlab} , mineralization of labile organic-N to NH_4^+ , (c) $I_{\text{NH}_4\text{-Nlab}}$, immobilization of NH_4^+ to labile organic-N, (d) $I_{\text{NH}_4\text{-Nrec}}$, immobilization of NH_4^+ to recalcitrant organic-N, (e) $R_{\text{NH}_4\text{ads}}$, release of adsorbed NH_4^+ , (f) A_{NH_4} , adsorption of NH_4^+ on cation exchange sites, (g) O_{NH_4} , oxidation of NH_4^+ to NO_3^- , (h) O_{Nrec} , oxidation of recalcitrant organic-N to NO_3^- (heterotrophic nitrification), (i) I_{NO_3} , immobilization of NO_3^- to recalcitrant organic-N, and (j) D_{NO_3} , dissimilatory NO_3^- reduction to NH_4^+ (DNRA) (Figure S1). The *N trace* model employs a Markov Chain Monte Carlo (MCMC) method, which can generate reliable results for a large number of parameters. The average NH_4^+ and NO_3^- concentrations and ^{15}N excess values (average \pm standard deviations) from the two ^{15}N treatments were supplied to the model (Figure S2 and S3). The model determines gross N transformation rates by simultaneously optimizing the kinetic parameters for various N transformations by minimizing the misfit between modelled and observed NH_4^+ and NO_3^- concentrations and their corresponding ^{15}N enrichments (Figure S2 and S3) (Müller, Stevens, & Laughlin, 2004). According to the kinetic settings and the final parameters, average gross N transformation rates were calculated over the 6-day period and expressed in units of $\text{mg N kg}^{-1} \text{ soil day}^{-1}$.

Cumulative emissions of NO, N_2O and CO_2 were estimated by successive linear interpolations across sampling intervals. The relative contribution of different processes to the N_2O production was calculated using the equations developed by Stevens, Laughlin, Burns, Arah, and

Hood (1997), and modified and extended by Rütting, Clough, Müller, Lieffering, and Newton (2010). Three pools were considered as possible substrates for N_2O , which differed in their ^{15}N atom fraction, α_d (NO_3^- pool, assumed to be the e-acceptor denitrification), α_a (NH_4^+ pool, assumed to be driving autotrophic nitrification) and α_h (N pool at natural abundance, assumed to be the substrate for oxidation of organic N). The ^{15}N atom fraction of N_2O ($\alpha_{\text{N}_2\text{O}}$) is determined by:

$$\alpha_{\text{N}_2\text{O}} = d\alpha_d + n_a\alpha_a + n_h\alpha_h, \quad (1)$$

where d , n_a and n_h indicate the fractions of N_2O derived from the NO_3^- pool via denitrification, the NH_4^+ pool via autotrophic nitrification and the organic N pool via heterotrophic nitrification, respectively. The sum of d , n_a and n_h was assumed to be 1 in this equation. Inserting the ^{15}N atom% excess from the NO_3^- , NH_4^+ and organic N pools in the paired $^{15}\text{NH}_4\text{NO}_3$ and $\text{NH}_4^{15}\text{NO}_3$ treatments into Equation (1) allows the calculation of d , n_a and n_h (via the solver routine available in Microsoft-Excel).

Paired sample *t*-tests were used to compare significant differences in soil properties, cumulative CO_2 , N_2O and NO emissions, NO/ N_2O ratios and gross N transformation rates between NKL, NPL, NPKL and NPKSL treatments compared to their respective quicklime-free treatments (NK, NP, NPK and NPKS), and between NPK and NPKM treatments. One-way ANOVA with a least significant difference (LSD) test was used to assess differences in various variables among all treatments. All statistical analyses were performed with SPSS 16.0. All results are reported as means \pm standard deviations on a soil dry weight basis.

3 | RESULTS

3.1 | Soil properties

In comparison with UC, long-term application of NK, NP, NPK and NPKS (N-containing treatments) significantly decreased soil pH from 5.49 to approximately 4.10, whereas soil pH was maintained close to or above the level of UC after application of either quicklime (NKL, NPL, NPKL and NPKSL, NL-containing treatments) or animal manure (NPKM and M, M-containing treatments) (Figure 1). Compared with UC, the long-term application of NK, NP, NPK and NPKS generally increased soil total C and N concentrations (Figure 1). However, the application of quicklime (NKL, NPL, NPKL and NPKSL) in most cases did not further increase soil total C and N concentrations compared

TABLE 1 Gross and net N transformation rates (mean \pm standard deviation) after 25 years of repeated fertilizer experiment in an upland acidic soil

Treatment	N transformation rates (mg N kg ⁻¹ soil day ⁻¹)								
	M _N	I _{NH4}	O _{NH4}	O _{Nrec}	I _{NO3}	D _{NO3}	Net Amm	Net nit	Net min
UC	0.53 \pm 0.16	0.005 \pm 0.003	1.39 \pm 0.05	0.037 \pm 0.018	0.070 \pm 0.045	0.11 \pm 0.07	-0.77 \pm 0.18	1.25 \pm 0.05	0.49 \pm 0.13
NK	0.08 \pm 0.06	0.009 \pm 0.004	0.002 \pm 0.003	0.083 \pm 0.028	0.243 \pm 0.031	0.02 \pm 0.01	0.08 \pm 0.06	-0.17 \pm 0.01	-0.10 \pm 0.05
NKL	0.34 \pm 0.22	0.44 \pm 0.24	1.42 \pm 0.03	0.032 \pm 0.023	0.002 \pm 0.001	0.36 \pm 0.05	-1.15 \pm 0.01	1.08 \pm 0.01	-0.07 \pm 0.00
NP	0.64 \pm 0.35	0.76 \pm 0.47	0.20 \pm 0.05	0.072 \pm 0.032	0.004 \pm 0.003	0.03 \pm 0.03	-0.29 \pm 0.15	0.23 \pm 0.05	-0.05 \pm 0.10
NPL	0.23 \pm 0.15	1.06 \pm 0.18	1.24 \pm 0.05	0.013 \pm 0.011	0.005 \pm 0.003	0.61 \pm 0.05	-1.46 \pm 0.02	0.64 \pm 0.00	-0.82 \pm 0.02
NPK	0.51 \pm 0.24	0.001 \pm 0.000	0.33 \pm 0.02	0.019 \pm 0.019	0.003 \pm 0.002	0.09 \pm 0.03	0.28 \pm 0.25	0.25 \pm 0.01	0.53 \pm 0.26
NPKL	0.37 \pm 0.24	0.43 \pm 0.21	1.87 \pm 0.06	0.024 \pm 0.019	0.003 \pm 0.002	0.20 \pm 0.06	-1.74 \pm 0.03	1.70 \pm 0.02	-0.04 \pm 0.05
NPKS	0.65 \pm 0.21	0.001 \pm 0.000	0.07 \pm 0.04	0.089 \pm 0.049	0.002 \pm 0.002	0.08 \pm 0.06	0.65 \pm 0.23	0.08 \pm 0.03	0.73 \pm 0.26
NPKSL	0.21 \pm 0.10	1.22 \pm 0.22	1.02 \pm 0.01	0.135 \pm 0.011	0.002 \pm 0.002	0.09 \pm 0.01	-1.94 \pm 0.12	1.07 \pm 0.02	-0.88 \pm 0.11
NPKM	0.57 \pm 0.31	1.08 \pm 0.24	4.98 \pm 0.13	0.012 \pm 0.010	0.003 \pm 0.002	0.88 \pm 0.09	-4.62 \pm 0.03	4.11 \pm 0.05	-0.50 \pm 0.08
M	2.24 \pm 0.68	0.85 \pm 0.52	9.58 \pm 0.19	0.046 \pm 0.049	0.006 \pm 0.004	1.47 \pm 0.18	-6.71 \pm 0.15	8.15 \pm 0.06	1.43 \pm 0.21

Abbreviations: D_{NO₃⁻}, dissimilatory NO₃⁻ reduction to NH₄⁺; I_{NH₄}, immobilization of NH₄⁺ to organic-N; I_{NO₃}, immobilization of NO₃⁻ to recalcitrant organic-N; M, manure only; M_N, mineralization of organic-N to NH₄⁺; Net Amm, net NH₄⁺ production rate; Net Min, net (NH₄⁺+NO₃⁻) production rate; Net Nit, net NO₃⁻ production rate; NK, NP, NPK, mineral NK, NP, NPK fertilizer alone, respectively; NKL, NPL, NPKL, mineral NK, NP, NPK fertilizer plus quicklime, respectively; NPKM, mineral NPK fertilizer (30% of applied N) plus swine manure (70% of applied N) each crop season; NPKS, mineral NPK fertilizer plus straw; NPKSL, mineral NPK fertilizer plus straw and quicklime; O_{NH₄}, oxidation of NH₄⁺ to NO₃⁻ (autotrophic nitrification); O_{Nrec}, oxidation of recalcitrant organic-N to NO₃⁻ (heterotrophic nitrification); UC, unfertilized control.

with their respective quicklime-free treatments. In contrast, soil total C and N concentrations were significantly higher in NPKM and M treatments than in NPK and UC treatments.

3.2 | Gross N transformation rates

The observed and modelled concentrations and ¹⁵N enrichment values for NH₄⁺ and NO₃⁻ were in good agreement for all treatments (Figures S2 and S3), indicating the modelled gross N transformation rates were reliable. Gross N mineralization rates were significantly greater in M treatments compared to the other treatments but not different among the various M treatments (Table 1). Gross NH₄⁺ immobilization rates were consistently greater in NKL, NPL, NPKL and NPKSL treatments than their respective quicklime-free treatments. Animal manure application (NPKM and M) also resulted in a significant increase in gross NH₄⁺ immobilization rates compared with NPK and UC treatments. Gross autotrophic nitrification rates were almost completely suppressed by the application of NK, NP, NPK and NPKS (N-containing treatments), but were maintained at a similar level to UC treatment due to the application of NKL, NPL, NPKL and NPKSL

(NL-containing treatments) (Table 1). Animal manure application (NPKM and M) led to an approximately 3–6-fold increase in gross autotrophic nitrification rates in comparison with UC. Both gross heterotrophic nitrification and NO₃⁻ immobilization rates were generally negligible for all treatments. The DNRA rates were negligible in UC, NK, NP, NPK and NPKS treatments, but were enhanced by quicklime application except for NPKS. Manure application resulted in a more pronounced increase in DNRA rates than the quicklime application. Gross N mineralization rates showed a quadratic response function with increasing total C and N concentrations (Figure S4a). The response of gross autotrophic nitrification rates to soil pH was different with the two acid-neutralizing substances (Figure S4b). There was a linear and positive relationship between gross autotrophic nitrification rates and soil pH when quicklime was used to alleviate soil acidity, whereas an exponential and positive relationship between gross autotrophic nitrification rates and soil pH was observed when manure was used as ameliorant. Such results indicated that gross autotrophic nitrification rates could be stimulated to a greater degree by manure than by quicklime when soil pH was increased to a similar value. Gross NH₄⁺ immobilization rates were positively correlated with soil pH (in fact

logarithmic if the H^+ ion concentrations are taken into account) and positively correlated with total C concentrations, plateauing at C concentrations of 14 g C kg^{-1} (i.e., in the form of a cubic response function, Figure S4c,d). The DNRA rates were positively correlated with soil pH and total C concentrations (Figure S4e,f).

3.3 | Soil CO_2 , N_2O and NO emissions

Cumulative CO_2 emissions over the whole incubation period were highest in the M treatment, followed by NPKM and NPKSL treatments (Figure 2a). The cumulative CO_2 emissions were generally greater in NKL, NPL, NPKL and NPKSL treatments than in their respective quicklime-free counterparts, although not significantly. Compared with their respective quicklime-free treatments (NK, NP, NPK and NPKS), the cumulative NO and N_2O emissions were reduced by quicklime application (NKL, NPL, NPKL and NPKSL treatments) by 20–58% and 28–38%, respectively, although not significantly in the latter (Figure 2b,c). In contrast, manure applications (NPKM and M) led to around 28% decrease in NO emissions and 87–828% increase in N_2O emissions compared

with NPK and UC treatments. The $\text{NO}/\text{N}_2\text{O}$ ratio was 1.2 and 0.3 in the NPKM and M treatments, respectively, and both were significantly lower compared to other treatments (2.8–5.6) (Figure 2d). The response of cumulative N_2O emissions to soil parameters varied with the pH amelioration substance (Figure S5). Cumulative N_2O emissions exhibited an either exponential or linear decline with soil pH, total C concentration, cumulative CO_2 emissions and gross autotrophic nitrification rates when quicklime was used to alleviate soil acidification. However, the trends were reversed when manure was used as ameliorant. Both cumulative NO emissions and the $\text{NO}/\text{N}_2\text{O}$ ratios were negatively correlated with soil pH (Figure S6a,b). In addition, cumulative NO emissions showed a steep decline with increasing gross autotrophic nitrification rate and cumulative CO_2 emissions and then levelled out (Figure S6c,d).

3.4 | Sources of N_2O emissions

The comparison of the ^{15}N enrichment of N_2O , NH_4^+ , NO_3^- and organic N at different incubation times allowed the identification of N_2O production pathways

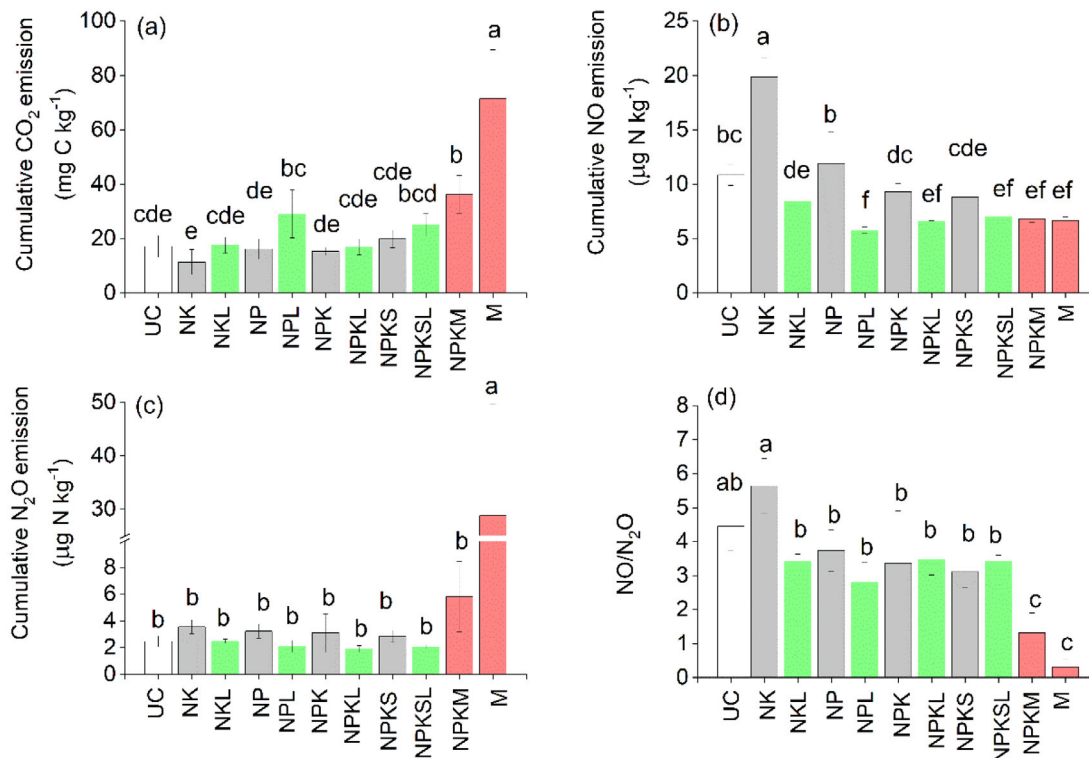


FIGURE 2 Cumulative emissions of CO_2 (a), NO (b) and N_2O (c) and the $\text{NO}/\text{N}_2\text{O}$ ratio (d) during the 144-hr incubation period following application of differentially labelled NH_4NO_3 to an upland acidic soil previously treated with repeated applications of different types of fertilizers with or without quicklime. Because all three gas concentrations were not different between the $^{15}\text{NH}_4\text{NO}_3$ and $\text{NH}_4^{15}\text{NO}_3$ labelled treatments, results for the two labelling types were merged. Different letters indicate significant differences among the treatments ($p < .05$). Error bars are standard deviations of the means ($n = 6$) [Color figure can be viewed at wileyonlinelibrary.com]

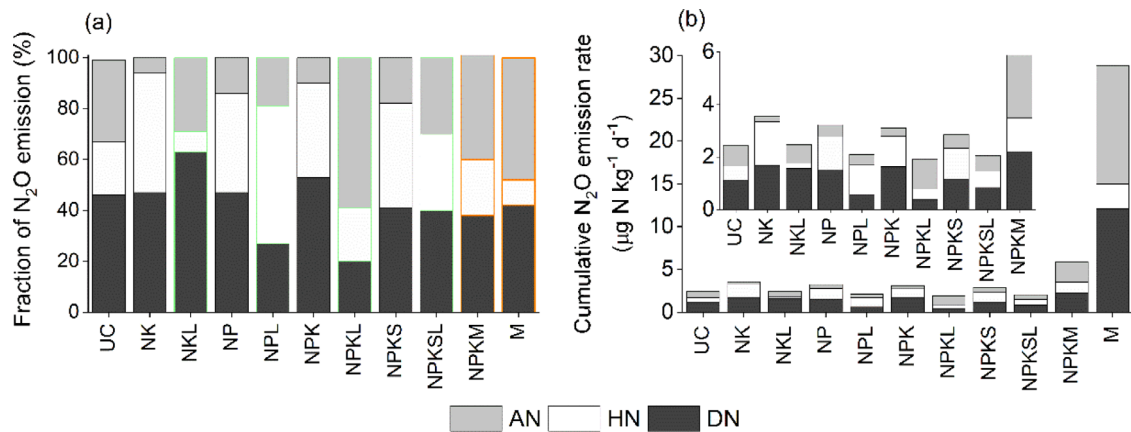


FIGURE 3 The time-weighted average contribution of autotrophic (CAN) and heterotrophic nitrification (CHN) and denitrification (CDN) to N₂O production (a), and cumulative N₂O flux from autotrophic nitrification (AN), heterotrophic nitrification (HN) and denitrification (DN) (b) in an upland acidic soil that has previously received repeated applications of different types of fertilizers with or without quicklime. Insert (small figures) shows that NPKM and M treatments were not included. NPKM, mineral NPK fertilizer (30% of applied N) plus swine manure (70% of applied N) each crop season; M, manure only [Color figure can be viewed at wileyonlinelibrary.com]

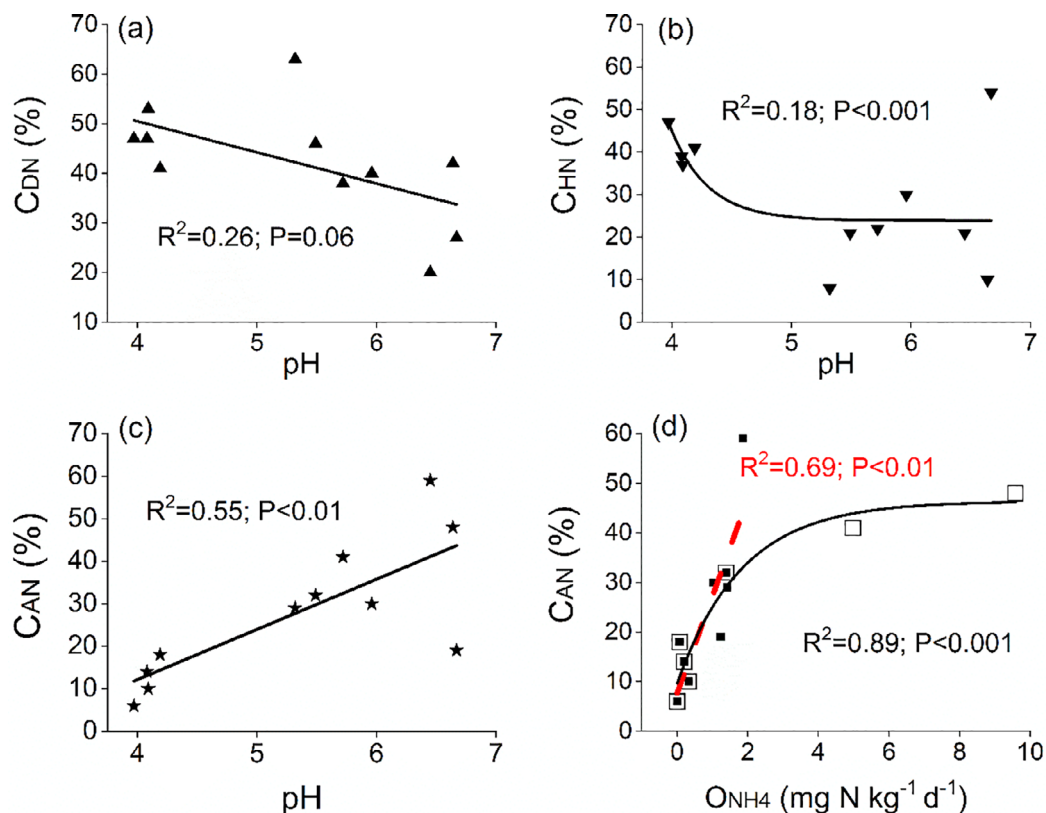


FIGURE 4 Relationships between soil pH and the contribution of denitrification (CDN, a), heterotrophic nitrification (CHN, b) and autotrophic nitrification (CAN, c) to N₂O production, and between soil gross autotrophic nitrification rate (O_{NH4}) and CAN (d). Dashed line with red colour denotes that NPKM and M treatments were excluded from the analysis. NPKM, mineral NPK fertilizer (30% of applied N) plus swine manure (70% of applied N) each crop season; M, manure only [Color figure can be viewed at wileyonlinelibrary.com]

(Figure S3 and S7). During the whole incubation period, ¹⁵N enrichment of N₂O was between the ¹⁵N enrichment of NH₄⁺ and NO₃⁻ for both ¹⁵NH₄NO₃ and NH₄¹⁵NO₃ labelling treatments (Figure S3). In the UC treatment,

the average contribution of denitrification and autotrophic and heterotrophic nitrification to N₂O production was 46, 32 and 21%, respectively, whereas denitrification and autotrophic and heterotrophic nitrification were

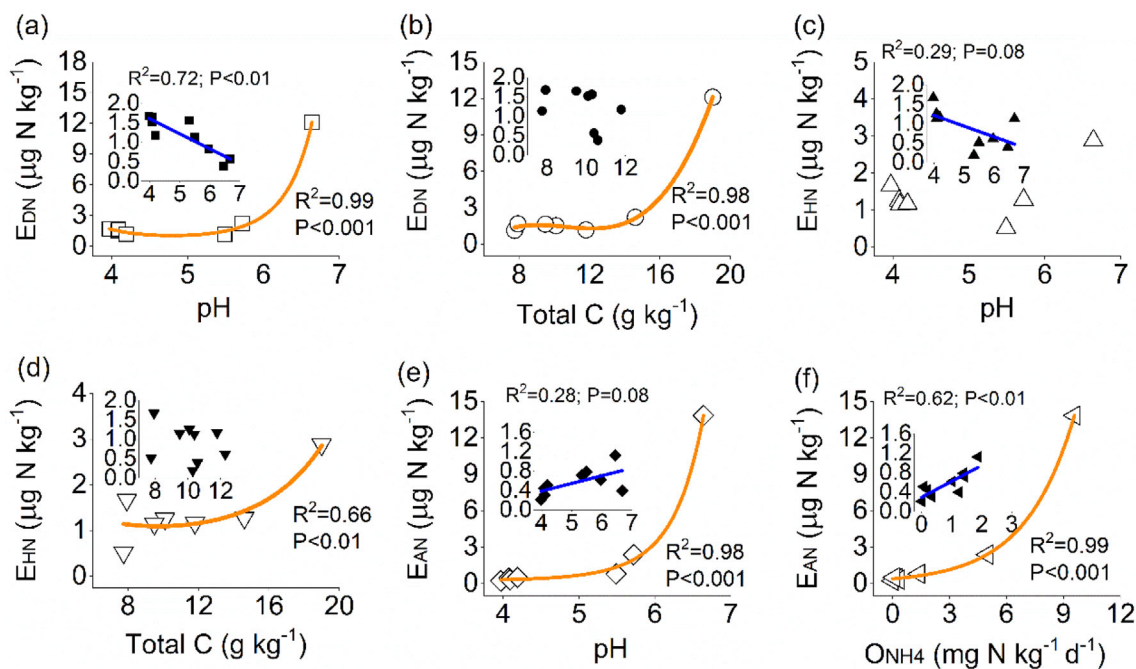


FIGURE 5 Relationships between soil pH and total C concentration and cumulative N₂O flux from denitrification (EDN, a, b) and heterotrophic nitrification (EHN, c, d) and between soil pH and gross autotrophic nitrification (O_{NH₄}) and cumulative N₂O flux from autotrophic nitrification (EAN, e, f). Insert (small figures) shows that NPKM and M treatments were excluded from the analysis, and big figures show that NKL, NPL, NPKL and NPKSL treatments were excluded from the analysis. NPKM, mineral NPK fertilizer (30% of applied N) plus swine manure (70% of applied N) each crop season; M, manure only; NKL, NPL, NPKL, mineral NK, NP, NPK fertilizer plus quicklime, respectively; NPKSL, mineral NPK fertilizer plus straw and quicklime [Color figure can be viewed at wileyonlinelibrary.com]

responsible for 41–53%, 6–18% and 37–47% of N₂O production in NK, NP, NPK and NPKS treatments, respectively (Figure 3a). In NKL, NPL, NPKL and NPKSL treatments, denitrification and autotrophic and heterotrophic nitrification contributed 20–63%, 19–59% and 8–54% of N₂O production, respectively. In NPKM and M treatments, denitrification and autotrophic and heterotrophic nitrification contributed 38–42%, 41–48% and 10–22% of N₂O production, respectively (Figure 3a). The contribution of denitrification and heterotrophic nitrification to N₂O production decreased linearly and exponentially with increasing soil pH, respectively (Figure 4a,b), whereas the contribution of autotrophic nitrification to N₂O production was linearly and positively correlated with soil pH (Figure 4c). In addition, the contribution of autotrophic nitrification to N₂O production increased linearly and exponentially with the increase of autotrophic nitrification rates after quicklime and manure application, respectively (Figure 4d).

In the UC treatment, the cumulative N₂O production from processes of denitrification and autotrophic and heterotrophic nitrification were 1.1, 0.8 and 0.5 μg N kg⁻¹, respectively (Figure 3b). In NK, NP, NPK and NPKS treatments, the cumulative N₂O production from denitrification and autotrophic and heterotrophic nitrification was 1.2–1.7, 0.2–0.5 and 1.2–1.7 μg N kg⁻¹, respectively.

In NKL, NPL, NPKL and NPKSL treatments, the cumulative N₂O production from denitrification and autotrophic and heterotrophic nitrification showed tendencies of decrease (0.4–1.6 μg N kg⁻¹), increase (0.4–1.1 μg N kg⁻¹) and decrease (0.2–1.1 μg N kg⁻¹) compared with their respective quicklime-free treatments (NK, NP, NPK and NPKS), respectively (Figure 3b). In contrast, in NPKM and M treatments, the cumulative N₂O production from denitrification and autotrophic and heterotrophic nitrification was as high as 2.2–12, 2.4–14 and 1.3–2.9 μg N kg⁻¹, respectively. Cumulative N₂O production from denitrification decreased linearly with increasing soil pH when quicklime was used to alleviate acidification, but increased exponentially with increasing soil pH and total C concentration when manure was used as ameliorant (Figure 5a, b). Cumulative N₂O production from heterotrophic nitrification was negatively and linearly correlated with soil pH when quicklime was used to alleviate acidification, but was positively and exponentially correlated with total C concentration when manure was used as ameliorant (Figure 5c,d). With increasing pH and gross autotrophic nitrification rates, cumulative N₂O production from autotrophic nitrification increased linearly and exponentially when quicklime and manure were used to alleviate acidification, respectively (Figure 5e,f).

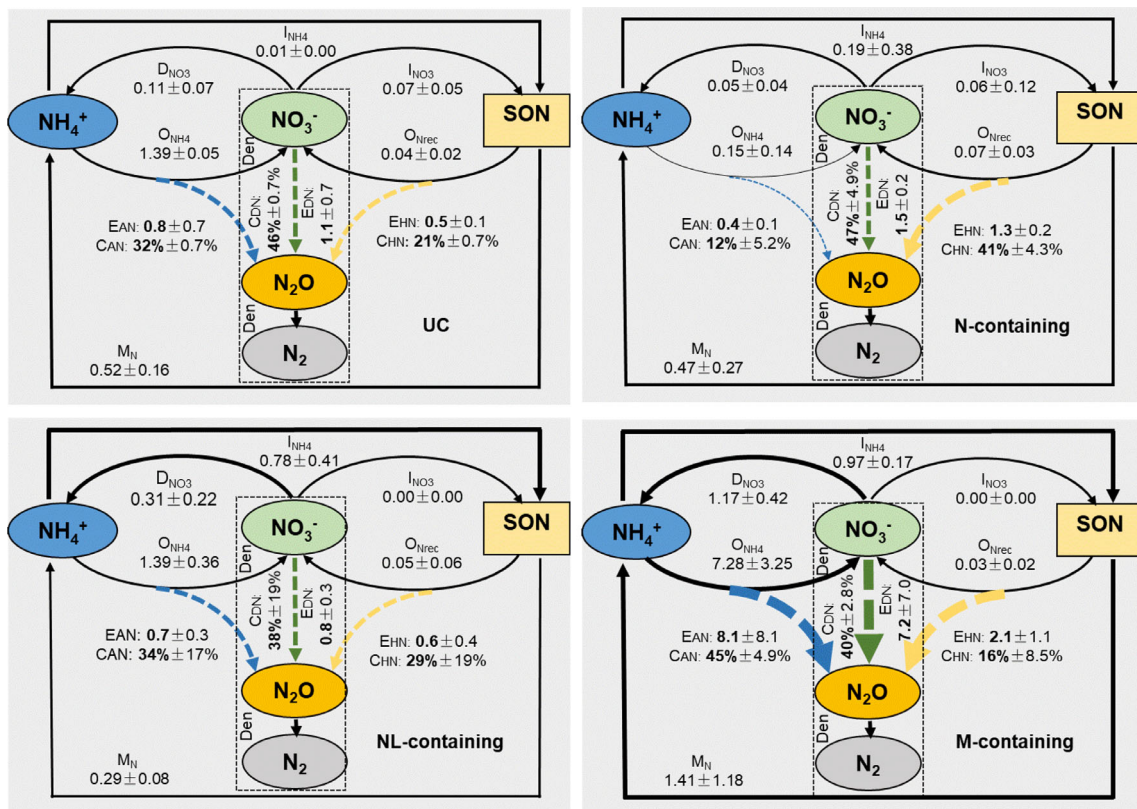


FIGURE 6 Schematic showing how the quicklime and animal manure application affects N_2O emission differently. The data in the UC, N-containing, NL-containing and M-containing treatments represent the value from original UC treatment, the average value from the original NK, NP, NPK and NPKS treatments, NKL, NPL, NPKL and NPKSL treatments, and NPKM and M treatments, respectively. SON, soil organic N pool; Den, denitrification. CDN, CHN and CAN are the contributions of denitrification, heterotrophic nitrification and autotrophic nitrification to N_2O production, respectively. EDN, EHN and EAN are the cumulative N_2O fluxes from denitrification, heterotrophic nitrification and autotrophic nitrification, respectively. UC, unfertilized control; NK, NP, NPK, mineral NK, NP, NPK fertilizer alone, respectively; NKL, NPL, NPKL, mineral NK, NP, NPK fertilizer plus quicklime, respectively; NPKS, mineral NPK fertilizer plus straw; NPKSL, mineral NPK fertilizer plus straw and quicklime; NPKM, mineral NPK fertilizer (30% of applied N) plus swine manure (70% of applied N) each crop season; M, manure only [Color figure can be viewed at wileyonlinelibrary.com]

4 | DISCUSSION

It is well known that excessive N use contributes substantially to soil acidification (Guo et al., 2010). Our results showed that 25 years of chemical N fertilizer application (NK, NP, NPK and NPKS, N-containing treatments) resulted in a significant decline in soil pH from 5.49 to 4.10 (Figure 1). Meanwhile, soil pH was maintained close to or above the original level after application of either quicklime (NKL, NPL, NPKL and NPKSL, NL-containing treatments) or animal manure (NPKM and M, M-containing treatments). Such results demonstrated that animal manure has the same potential to alleviate N-induced soil acidification with quicklime. Changes in soil pH have been found to affect N_2O emissions through changing microbial-mediated N transformation processes (Li, Sørensen, Olesen, & Petersen, 2016; Zhang, Zhao, Cai, Müller, & Zhang, 2018). However, the effects of the two contrasting acid-neutralizing materials (quicklime vs. animal manure) on soil N_2O emissions and their underlying mechanisms have not been addressed explicitly. Our study

clearly shows that quicklime and animal manure applications have contrasting effects on soil N_2O emissions in an acidified upland red soil (Figure 6). Our findings of quicklime-induced decrease and animal manure-induced increase in N_2O emissions are in contrast to the prevailing view that increasing soil pH can be a viable strategy for lowering N_2O emissions in acidic soils (Qu et al., 2014; Russenes, Korsæth, Bakken, & Dorsch, 2016; Wang, Guo, et al., 2018), thus highlighting extreme caution in applying pH-raising substances to mitigate N_2O emissions. Our study also provides a compelling process-based understanding of how N_2O emissions change in response to application of quicklime and animal manure (Figure 6).

4.1 | Potential mechanisms to explain the effects of quicklime and animal manure application on soil N_2O emissions

We found that increasing soil N_2O emissions following long-term application of chemical NK, NP, NPK and NPKS

fertilizers was attributed to enhanced denitrification- and heterotrophic nitrification-derived N_2O emissions, which offset reduced autotrophic nitrification-derived N_2O emissions (Figure 6). The opposite effect was observed in all lime treatments (i.e. NKL, NPL, NPKL and NPKSL) compared with NK, NP, NPK and NPKS treatments. We found that both denitrification- and heterotrophic nitrification-derived N_2O emissions were negatively correlated with soil pH, whereas autotrophic nitrification-derived N_2O emissions were positively correlated with soil pH when quicklime was used to alleviate acidification (Figure 5). This is in line with other studies, showing a pH-associated stimulation of N_2O reduction (lower N_2O/N_2 ratio) and in turn reduced N_2O emissions via denitrification (Mukumbuta, Uchida, & Hatano, 2018; Qu et al., 2014), as well as lower N_2O emissions via heterotrophic nitrification (Li, Chapman, Nicold, & Yao, 2018; Zhang et al., 2015; Zhang et al., 2018), but increased N_2O emissions via autotrophic nitrification (Zhang et al., 2013). Recent studies on the same site indicated that ammonia-oxidizing bacteria (AOB) rather than ammonia-oxidizing archaea (AOA) were mainly responsible for increased autotrophic nitrification after long-term liming despite a general dominance of AOA in these acidic soils (Zhang et al., 2017).

Another important factor to explain the reduced N_2O emissions due to liming is the aerobic state of the soil. Under anaerobic conditions, increasing soil pH by liming promotes the reduction of N_2O (lower N_2O/N_2 ratio) through denitrification when most of the N_2O originates from denitrification (Mukumbuta et al., 2018; Qu et al., 2014; Russenes et al., 2016). This was due to the fact that the activity of the N_2O reductase enzyme generally increases with increasing pH values (Saggar et al., 2013; Šimek & Cooper, 2002). Further study showed that the low N_2O reductase activity in acid soils could not be ascribed to the low number of *nosZ* transcripts (Liu et al., 2010). However, under aerobic conditions and increasing soil pH, N_2O reduction is restricted by the availability of NO_2^- (Feng, Yan, Hütsch, & Schubert, 2003) and only noticeable when N_2O via autotrophic nitrification is the dominant N_2O source (Barton et al., 2013; Mørkved, Dorsch, & Bakken, 2007). Overall, these explanations were prevailing but split. Instead, our results integrated the above explanations and provided a full picture of how increased soil pH following quicklime application changed N_2O emission in an acidified upland soil caused by chemical N application (Figure 6).

In contrast to liming, animal manure application significantly increased denitrification-, autotrophic- and heterotrophic nitrification-derived N_2O emissions (Figure 6). Our results are in contrast with the common viewpoint that organic material input stimulates N_2O emissions via denitrification under aerobic conditions (Charles

et al., 2017; Chen, Li, Hu, & Shi, 2013; Li et al., 2016). Autotrophic nitrification-derived N_2O emissions were positively correlated with soil pH and gross autotrophic nitrification rates (Figure 5e,f), showing a stimulating effect of manure on autotrophic nitrification rates and associated N_2O emissions, probably by increased soil pH (Figure S4b). Other possible explanations for manure-induced stimulation of autotrophic nitrification and N_2O emission could be the enhanced substrate (NH_4^+-N) availability from what the pig manure itself contains, the mineralization of pig manure and increased soil N mineralization due to a priming effect (Table 1). This is in line with previous findings at the same site that the NPKM treatment had the highest copy numbers of AOB and AOA *amoA* genes among the treatments that received mineral fertilizers (He et al., 2007). The positive relationship between denitrification-derived N_2O emissions, soil pH and total C concentrations (Figure 5a,b) showed that the stimulation of denitrification to soil N_2O emissions with animal manure application outweighed any possible decline in the N_2O/N_2 ratio with pH increase, possibly due to the C-induced activity and associated increase of the anaerobic microenvironment (Saggar et al., 2013). Also the pH-stimulated effect on autotrophic nitrification rates and NO_3^- build-up (Table 1) in conjunction with increased C availability further enhanced denitrification activity (Senbayram et al., 2019). Heterotrophic nitrification-derived N_2O emissions were positively correlated with soil total C concentrations, but not with increased soil pH (Figure 5c,d), which is in line with other studies (Zhang et al., 2015; Zhang et al., 2018). Next to the observed C-induced increase of heterotrophic nitrification-derived N_2O emissions it is, however, possible that soil pH decreased the relative proportion of heterotrophic nitrification-related N_2O emissions but this was masked by the overall C-stimulated activity increase. Thus, complex interactions among soil pH, available C input and relative N_2O emissions seem to control N_2O emissions from this acidified upland acidic soil under animal manure application.

4.2 | Potential mechanisms for individual N_2O production processes in response to quicklime and animal manure application and implications for N_2O mitigation

Studies found that nitrification-related N_2O emissions could be dominant under aerobic conditions (Mathieu et al., 2006; Stevens et al., 1997). Our study showed that nitrification (autotrophic + heterotrophic) and denitrification contributed almost equally to N_2O emissions in

the UC and N-containing treatments in an upland red soil. Meanwhile, long-term quicklime and animal manure application decreased the contribution of denitrification to N_2O emissions. There was a negative relationship between the contribution of denitrification to N_2O emissions and soil pH (Figure 4a). A shift in microbial N_2O source in response to a short-term change in pH has been reported by Baggs, Smales, and Bateman (2010), who observed that liming of a pH 4.5 soil to pH 7 shifted the predominance away from denitrification to autotrophic nitrification in an arable soil. Previously we showed via a regression analysis that the contribution of denitrification to N_2O production decreased with increasing soil pH, with a threshold of approximately pH 4.4, below which denitrification dominated N_2O production (Cheng, Zhang, Wang, Cai, & Wang, 2015). Moreover, a global meta-analysis from agriculture revealed that pH was a critical factor regulating N_2O production but the authors failed to present the underlying mechanisms (Wang, Guo, et al., 2018). Results from this long-term study demonstrated that soil pH is a key predictor of the main N_2O production pathways. Understanding and accurately identifying the dominating N_2O production source is of particular importance to developing targeted N_2O mitigation strategies. For instance, in manure-containing treatments, autotrophic nitrification accounted for 45% of N_2O emissions, whereas denitrification contributed to 40% of N_2O emissions. Although a nitrification inhibitor could not directly affect denitrification, the application of a nitrification inhibitor, which depresses autotrophic nitrification, would also limit denitrification via reduced nitrification–denitrification transformations, that is, decreasing NO_3^- concentrations. A recent study even found that the effectiveness of nitrification inhibitors used for mitigating N_2O emissions seems to be more pronounced under conditions favouring denitrification (Wu et al., 2017). Nguyen et al. (2017) further demonstrated that the effectiveness of nitrification inhibitors in reducing denitrification-derived N_2O emissions depended on whether denitrification is controlled by NO_3^- produced during nitrification.

5 | CONCLUSIONS

We showed that long-term N applications, causing soil acidification and an associated increase in N_2O emissions, could be completely reversed by increasing soil pH via liming. However, application of animal manure, also used for pH amelioration, had the opposite effects on N_2O emissions. This shows that we need to understand the full complexity of the effects of a substance used to ameliorate soil conditions (such as pH) before this can be

recommended. Thus, careful consideration of pH-raising substrates is needed to avoid adverse environmental effects. Our study provides a full account of the effect of two acid-neutralizing materials (quicklime vs. pig manure) on N transformation processes in the soil and associated N_2O emissions. Co-application of nitrification inhibitors in combination with various acid-neutralizing materials should be tested to avoid negative effects on N_2O emissions. Thus, acid-neutralizing materials need to be carefully chosen and the effect of these substances on the overall elemental cycles in soils should be taken into account in models that aim to predict global N_2O emissions. However, it should be noticed that the soil used in this study was sampled only once from the field and the soil microbial community was not analysed. Further research is therefore required to link microbial community composition or potential function to the N_2O emission processes in response to the input of acid-neutralizing materials with high-frequency soil sampling from the field.

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DATA AVAILABILITY STATEMENT

I confirm that my article contains a Data Availability Statement even if no data is available (list of sample statements) unless my article type does not require one.

ORCID

Yi Cheng  <https://orcid.org/0000-0002-0559-1319>

Jinbo Zhang  <https://orcid.org/0000-0002-5659-7921>

Minggang Xu  <https://orcid.org/0000-0002-0759-3887>

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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