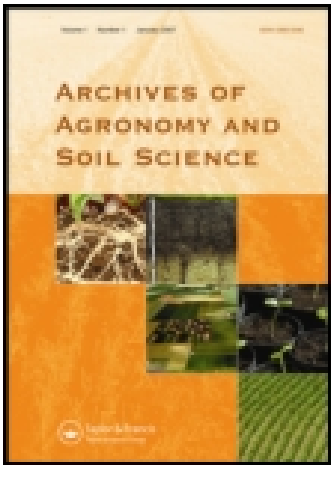

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Nitrous oxide emissions from wetland soil amended with inorganic and organic fertilizers

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Agricultural soils are a primary source of anthropogenic trace gas emissions, and the subtropics contribute greatly, particularly since 51% of world soils are in these climate zones. A field experiment was carried out in an ephemeral wetland in central Zimbabwe in order to determine the effect of cattle manure (1.36% N) and mineral N fertilizer (ammonium nitrate, 34.5% N) application on N_2O fluxes from soil. Combined applications of 0 kg N fertilizer + 0 Mg cattle manure ha^{-1} (control), 100 kg N fertilizer + 15 Mg manure ha^{-1} and 200 kg N fertilizer + 30 Mg manure ha^{-1} constituted the three treatments arranged in a randomized complete block design with four replications. Tomato and rape crops were grown in rotation over a period of two seasons. Emissions of N_2O were sampled using the static chamber technique. Increasing N fertilizer and manure application rates from low to high rates increased the N_2O fluxes by 37–106%. When low and high rates were applied to the tomato and rape crops, 0.51%, 0.40%, and 0.93%, 0.64% of applied N was lost as N_2O, respectively. This implies that rape production has a greater N_2O emitting potential than the production of tomatoes in wetlands.

Keywords: manure; fertilizer; N_2O; emission; wetland

Introduction

Nitrous oxide (N_2O) is a greenhouse and ozone-depleting gas whose atmospheric concentration is currently >310 nL L^{-1} and increasing at a rate of approximately 0.4% per annum (IPCC 2001). Although very much a trace component of the Earth's atmosphere, it is estimated to account for some 6% of the greenhouse warming (Ma et al. 2007). Nitrous oxide has a global warming potential of 270–320 times compared to carbon dioxide (CO_2) (Flessa et al. 2002). Much of the increasing atmospheric concentration of N_2O is thought to be a consequence of the continual conversion of land to cultivation (IPCC 2001) and increasing intensity of land use, primarily through greater use of N fertilizers (Mosier et al. 1998; Burke et al. 2002; McSwiney & Robertson 2005). The formation of N_2O in the soil as an intermediate product of the biological processes of nitrification and denitrification is believed to account for as much as 90% of the global atmospheric N_2O. These factors are exacerbated by there

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being no chemical sinks for N_2O in the troposphere, resulting in the mean residence time in the atmosphere of about 100–150 years (IPCC 2001).

Wetlands are important in crop production in the smallholder semiarid areas of subtropical Africa, because they have enough water for a longer period to allow crops to be grown throughout the year as compared to dry land cropping. Wetland cropping in southern Africa usually involves the production of leafy vegetables and tomato. Animal manure is applied in combination with mineral fertilizers due to the poor manure quality (Nyamangara et al. 2003). Vegetables are high value crops and smallholder farmers apply high fertilizer rates in order to eliminate the risk of yield depression due to the lack of plant available N. The relatively low recovery rate of applied N by vegetable crops means that there are risks of significant N losses to the environment (De Lannoy 2001; Lin et al. 2011). Usually, only about 70% of applied fertilizer nitrogen is recovered in the harvested biomass of vegetable crops (Lowrance & Smittle 1988; Reuter 2001). On average, 0.2–1.5% of applied N to agricultural soils is emitted as N_2O (Groot et al. 2006). Addition of cattle manures to wetland soils under vegetable cropping increases the amount of readily decomposable organic matter. This enhances the potential for denitrification (Nobre et al. 2001; Fierer & Schimel 2002) and increased emissions of N_2O (Wrage et al. 2004) through stimulation of microbial respiration, causing rapid oxygen consumption, and consequently an increase of anaerobic conditions (Van Groenigen et al. 2005).

Significant denitrification can take place when NO_3–N and readily decomposable organic compounds are available and the soil air contains less than 10% O_2 or less than 0.2 Mg L^{-1} of O_2 dissolved in the solution (Bedard-Haughn et al. 2006). Factors such as soil water content, water table, precipitation, soil temperature, soil organic C, and soil pH (Burke et al. 2002; Takaya et al. 2003; Ma et al. 2007) are the major regulators of N_2O emissions. Soil surface N_2O fluxes are also influenced by the form and quantity of added N (Wrage et al. 2004; McSwiney & Robertson 2005; Van Groenigen et al. 2005).

There is little scientific information about the effects of elevated fertilizer and manure derived N on losses through N_2O emissions in subtropical Africa. The impact of C addition on N_2O emissions is, however, not clear, in particular the combined effect of N fertilizer addition and other management practices (Rees et al. 2006). Few studies have reported *in situ* N_2O flux measurements from wetland vegetable cropping receiving cattle manure amendments (Van Der Salm et al. 2007). An understanding of the contribution of manures to global atmospheric N_2O loading is needed to evaluate agriculture's contribution to global warming. Consequently, a 2-year study with four cropping seasons of tomato and rape rotation was carried out at a wetland site in Zimbabwe in order to determine the effect of cattle manure and mineral N fertilizer application on N_2O emission from cultivated wetland soil.

Materials and methods

Site description

The study was conducted in 2007 and 2008 in a wetland garden at Dufuya (19° 17′ S; 29° 21′ E) wetland in Lower Gweru Communal Lands in central Zimbabwe. The experimental site is located in Agro-ecological Region III characterized by mean annual rainfall ranging from 650 to 800 mm and a mean annual temperature of 21°C (Vincent & Thomas 1960;

Mugandani et al. 2012). The soil is deeply weathered and is course-textured loamy sand in topsoils overlying sandy loam subsoils derived from granite and classified as Udic Kandiustalf (USDA) and Gleyic Luvisol (FAO) (FAO 1988; Nyamapfene 1991; Soil Survey Staff 1992). They are perennially moist in part of the soil profile and smallholder farmers have established vegetable gardens along the wetland. Vegetable production is all year round. The site had been under alternate rape, tomato, and maize crops for several years. Rape is cultivated as a leaf vegetable in Zimbabwe (De Lannoy 2001).

Soil sampling and analysis

Initial soil characterization was done by collecting 20 soil samples from randomly selected points of the experimental site at a depth of 0–20 cm using a soil auger. The soil samples were mixed thoroughly in a clean plastic bucket to obtain a composite sample. The composite sample was air-dried, sieved (<2 mm) and characterized (Table 1). Soil organic carbon was determined by the Walkley and Black method (Nelson & Sommers 1996). Soil texture was determined by the Bouyoucos hydrometer method (Bouyoucos 1965). Soil pH was determined by weighing a 15 g soil sample in a 200 mL honey jar to which 75 mL 0.1 M $CaCl_2$ were added. The mixture was shaken mechanically for 30 min and pH was determined using a digital pH meter (Orion 701, Orion Manufacturing, Ionia, USA).

Soil bulk density was determined by the core method (Black & Hartge 1986). Bulk density (D_b) was calculated using the following Equation (1):

$$D_b = \frac{M_s}{V_t}, \tag{1}$$

where M_s is the mass of oven dry solids and V_t is the total soil volume.

The soil cores were oven-dried at 105°C (to constant weight) for determination of mean gravimetric water content. Taking particle density (P_d) of soil to be 2.65 g cm^{-3}, total porosity was calculated (Equation (2)):

$$P_d(\text{total}) = 1 - \frac{D_b}{P_d} \tag{2}$$

Total N in soil was measured by the Kjeldahl method using concentrated H_2SO_4, K_2SO_4, and HgO to digest the sample (Bremner 1996).

Experimental manure

Aerobically composted cattle manure was collected from a cattle pen belonging to one of the smallholder farmers near the wetland. Smallholder farmers do not surface the floor on the cattle holding pen. As a result, the manure is mixed with soil during trampling. Ten randomly selected samples were collected from a pile of manure and thoroughly mixed in a plastic bucket. Three replicate composite samples were taken for laboratory analysis. The samples were air-dried, passed through a 2 mm sieve, and analyzed for organic C (Nelson & Sommers 1982), total N using the Kjeldahl procedure (Bremner & Mulvaney 1982; Stevenson 1982), and soil and ash content. Soil and ash contents were determined by ashing manure in a muffle furnace (450°C) for 16 h. The ash was dissolved in concentrated HCl acid and separated from mineral soil by filtering.

Table 1. Chemical and physical properties of the experimental soil.

Soil depth (cm)	Soil pH (H_2O)	Organic C (%)	Total N (Mg kg^{-1})	Sand	Clay	Silt	Total porosity $cm^3\ cm^{-3}$	Bulk density	Field capacity	Permanent wilting point	Saturation gravimetric water (g g^{-1})
				%				g cm^{-3}			
0–20	5.5	0.4	24	85	10	5	0.45	1.37	0.22	0.08	0.31
20–60	5.8	0.2	20	80	15	5	0.45	1.36	0.18	0.06	0.33
60–100	5.7	0.2	20	78	17	5	0.44	1.35	0.16	0.05	0.33

Land preparation and crop management

The land was prepared by digging using hand hoes to a depth of 30 cm and then leveling using a rake. Plots raised to a height of 15 cm, which measured 5 by 1.5 m, were then carefully marked out. The distance between the plots was 60 cm. Small 20 cm high ridges were established around each plot to avoid cross-contamination by surface runoff. Tomato (*Lycopersicon esculentum*, Mill *var. Heinz*) and rape (*Brassica napus*, L *var. Giant*) crops were used as test crops in the study. The cropping sequence in the field experiment was: September–October 2007 tomato (1), January–March 2008 rape (1), April–July 2008 tomato (2), and September–November 2008 rape (2). Spacing between rows was 45 cm and 15 cm within the rows for the rape crop. For the tomato crop, the plant spacing was 100 cm between rows and 40 cm within rows.

Experimental treatments and design

The following treatments were used:

(1) 0 kg N fertilizer ha^{-1}, 0 Mg smallholder cattle manure ha^{-1} (control).
(2) 100 kg N fertilizer ha^{-1}, 15 Mg smallholder cattle manure ha^{-1} (low rate).
(3) 200 kg N fertilizer ha^{-1}, 30 Mg smallholder cattle manure ha^{-1} (high rate).

A randomized complete block design with four replicates was employed. The blocking factor was the gradient of land (0.1%). Manure application rates were determined on a moisture-free basis. A basal application rate of 1000 kg ha^{-1} compound (multi-component) fertilizer S (5% N, 7.9% P, 16.6% K, and 8% S) (Cassidy 1967) was applied to all treatments before planting each crop to capture common practice. Cattle manure was broadcast only once in the two seasons before planting of the first crop (tomato) in the first season. The manure was evenly broadcast in the respective plots and then incorporated into the topsoil a few days before transplanting the crop. For treatments (2) and (3), N fertilizer (100 and 200 kg ha^{-1} N) was applied to each crop in two equal split applications. The first split application (50 kg and 100 kg ha^{-1} N) was broadcast evenly on soil surface and incorporated a day before planting. The second split application (50 and 100 kg ha^{-1} N) was done a month after transplanting. Nitrogen fertilizer was applied as ammonium nitrate (AN) (34.5% N).

Static chamber setup and N_2O flux measurement

Static gas-sampling chambers were used to collect emitted gas from plots. The static chambers were made of acrylic cylinders with one-end open (18 cm internal diameter, 20 cm height, and 1.5 mm wall thickness) (Holland et al. 1999; Meyer et al. 2001). The net enclosed surface area of each static gas chamber was 0.03 m^2. Four static gas chambers were randomly placed in each plot for gas sampling giving a 1.6% plot surface area under the chambers at each sampling event. This meant that each N_2O gas sampling and measurement was repeated four times (repeated measurement). The closed ends of the cylinders were tightly fitted in the center with 5 mm diameter self-sealing rubber septa to facilitate gas sampling with a syringe. Gas samples were collected at intervals of 2 weeks up to the last vegetable harvesting event. Because soil temperature is known to affect N_2O production, N_2O gas sampling was started at around 11.30 h when daily temperatures would have stabilized (Denmead et al. 1979; Blackmer et al. 1982; Conrad et al. 1983).

The open ends of the acrylic chambers fitted with chamber collars were manually inserted into the soil to a depth of 6 cm. Chamber collars were inserted into the soil a day before the gas sampling campaigns to reduce disturbance effects. Gas sampling was done at time 0 min to obtain the start values of atmospheric concentration of N_2O in the static chamber head space and after 30 and 60 min (Matthias et al. 1980; Kaiser et al. 1996). Gas samples were extracted by 10 mL Plastipak syringe (Becton Dickinson and Co., Franklin Lakes NJ, USA) and injected into 2 mL pre-evacuated gas testing vials that do not allow gaseous diffusion and exchange with the atmosphere. Gas samples were analyzed for N_2O using the method described by Mosier and Mack (1980) and Galle et al. (2003). The gas samples were analyzed for N_2O concentration by means of a Varian Model 3400 gas chromatograph (Varian, Walnut Creek CA, USA) equipped with an electron capture detector and a stainless steel column (3.66 m long by 3.18 mm i.d.) packed with 80/100 Porapack-Q. Carrier gas (10% CH_4, 90% Ar) flow rate was 30 mL min^{-1}. Air samples were emptied in 2 mL sampling loop and samples were injected automatically via a six-port gas-actuated sampling valve. The sampling loop was preceded by $CaSO_4$ (WA Hammond Drierite Co., Xenia OH, USA) trap for water absorption. Other analytical conditions were: detector temperature 390°C, oven temperature 60°C, and injection temperature ambient. Nitrous oxide was quantified by comparing sample peak area with that of a 1.17 nL L^{-1} custom standard (Matheson Gases, Ottawa ON, Canada); retention time was 2.07 (Mosier & Mack 1980; Galle et al. 2003).

Nitrous oxide production rates in static chambers were calculated from linear slope of gas concentration change (δCN/δt, increase or decrease) over the three sampling events (0, 30, and 60 min) on cropped plots under different treatments. Nitrous oxide fluxes (F_N) were calculated using the Hutchinson and Livingston (1993) model (Equation (3)):

$$F_{\mathrm{N}} = \frac{\delta \mathrm{CN}}{\delta \mathrm{t}} \frac{V}{A} \cdot \frac{M_{\mathrm{N}}}{V_{\mathrm{mol}}} \tag{3}$$

where $\delta CN/\delta t$ is the rate of change in N_2O concentration (μmol mol^{-1} min^{-1}), V is the chamber headspace volume (m^3), M_N is the molecular weight of N_2O (44 g mol^{-1}), $\boldsymbol{A}$ is the surface area (m^2), and V_{mol} is the volume of one mole of gas at 20°C (0.024 m^3 mol^{-1}). Further conversions were performed to calculate F_N fluxes in g ha^{-1} day^{-1} as follows: F_N g ha^{-1} day^{-1} = N_2O g h^{-1} × 24 h × A/10,000. Total N lost as N_2O (N kg ha^{-1}) was calculated using Equation (4):

$$\text{N loss } (\text{kg ha}^{-1}) = F_N \,\text{g ha}^{-1}\,\text{day}^{-1} \times T\,\text{days}/1000, \tag{4}$$

where T is the number of days with similar daily N_2O emissions rates. At the same time that gas samples were collected and soil temperature measurements were done 5 cm from each static chamber.

Soil mineral N measurements

At the same time that gas samples were collected, soil samples (from 0 to 20 cm soil layer; n = 4 for each treatment) were collected 10 cm from a gas chamber in each plot. The soil samples were taken to the laboratory for mineral nitrogen analysis. Soils were immediately extracted with 0.5 M K_2SO_4 (10 g soil in 50 mL). Soil slurries were shaken for 1 min, left to equilibrate overnight, and re-shaken for more than 1 h before filtering.

Filtrate was stored in 7 mL scintillation vials and frozen until analysis for NH_4–N and NO_3–N. Both analyses were performed on an Alpkem 3550 Flow Analyzer (OI Analytical, College Station TX, USA), using colorimetric techniques (Mosier & Mack 1980; Galle et al. 2003).

Dry matter yield

Four randomly selected plants were chosen and labeled in each plot for crop biomass sampling. Rape leaves and tomato fruits that reached horticultural maturity were harvested from the selected plants at every harvesting event and taken to the laboratory. The samples were rinsed, oven dried at 65°C, weighed and kept in a dry place. At the end of the growing season, the aboveground biomass of the selected plants was summed up. The composite samples were then ground to pass a 2 mm sieve and analyzed for N concentration using the semimicro Kjeldahl method (Bremner & Mulvaney 1982). Total N uptake was determined by multiplying the N concentration with dry matter yield as follows (Equation (5)):

$$\text{N uptake } (\text{kg ha}^{-1}) = \text{DM yield } (\text{kg ha}^{-1}) \times \text{concentration of N in DM } \left(\text{Mg N kg}^{-1}\,\text{DM}\right), \quad (5)$$

where DM is the dry matter.

Statistical analysis

Treatment and time effects on nitrate and ammonium N concentrations in soil, N_2O fluxes from soil, total N lost as N_2O, dry matter yield, and N uptake by the test crops were analyzed using two-way repeated measures ANOVA (GenStat 2003). Flux data were log-transformed if needed, to normalize the distributions before the statistical analysis. Differences between treatment means were judged significant at $p \leq 0.05$ as determined by Fisher's protected least significant difference test. The Pearson correlation coefficients between measured variables and their coefficients of determination values were calculated and the significance of the correlations between selected variables was established using GenStat statistical package.

Results and discussion

Weather conditions

The 2007–2008 summer rain season started at the end of September. About 98% (792 mm) of the total rainfall (808.2 mm) was received in the first half of the season (September–January, Figure 1).

The first tomato and first rape crops were cultivated during the first 6 months of the 2007–2008. Emissions of N_2O were considerably higher under these crops. The 2007–2008 winter season was generally frost-free and had maximum and minimum temperatures of 20°C and 15°C, respectively. The 2007–2008 summer season had a mean maximum and minimum temperature of 31.5°C and 24.5°C, respectively. The 2008–2009 rainy season started at the beginning of October when 36 mm of rainfall was recorded. The last quarter of the study period occupied about half of the 2008–2009 summer season (October–December 2009) during which the last rape crop was grown.

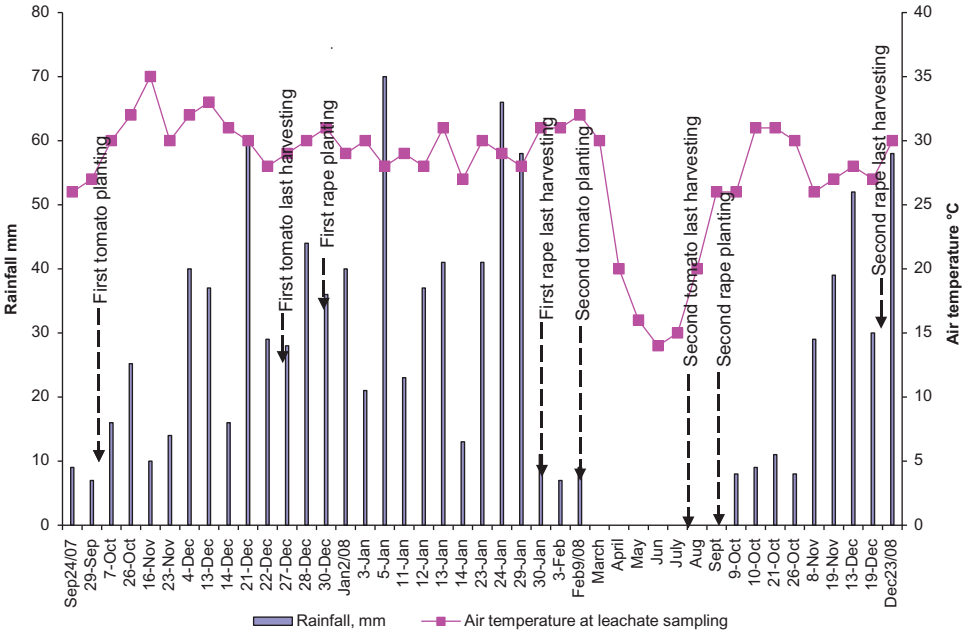

Figure 1. Daily rainfall and air temperature at the study site.

The first 3 months of the summer season accumulated 156 mm of rainfall. The summer season was characterized by hot and humid weather with a maximum and minimum air temperature of 30.5°C and 26.5°C, respectively. The field experiment was terminated in December 2008 when the last rape crop was harvested.

Mineralized N concentrations in soil

Concentrations of mineralized N in soil increased significantly ($p < 0.05$) with increasing application rates of mineral N and manure (Figures 2 and 3). Mineralized N concentration responses to manure and fertilizer amendments were studied in this experiment because organic N mineralization and the nitrification of NH_4^+ in soil mark the onset of N_2O emissions. The potential of added fertilizer to increase the concentration of N_2O in the atmosphere is determined by the capacity of the soil–fertilizer interactive system to release mineralized N in chemical reaction pathways for specific soil conditions. The mineralization of organic N in added manure yielding NH_4–N form of mineralized N and its subsequent nitrification to NO_3–N is suspected to have significantly contributed to the emission of N_2O (Christensen 1983) during denitrification of NO_3–N. Nitrous oxide generated in this way is believed to account for as much as 90% of the global atmospheric N_2O (Flessa et al. 2002; Ma et al. 2007).

Except for the first rape crop (Figures 2(b) and 3(b)), temporal variations in mineralized N concentrations in wetland soil on plots subjected to different rates of N fertilizer and cattle manure showed decreasing concentrations as the vegetative period progressed toward the end for the tomato and rape crops (Figures 2 and 3). When compared with the control, plots subjected to low (treatment 2) and high N (treatment 3) fertilizer and manure

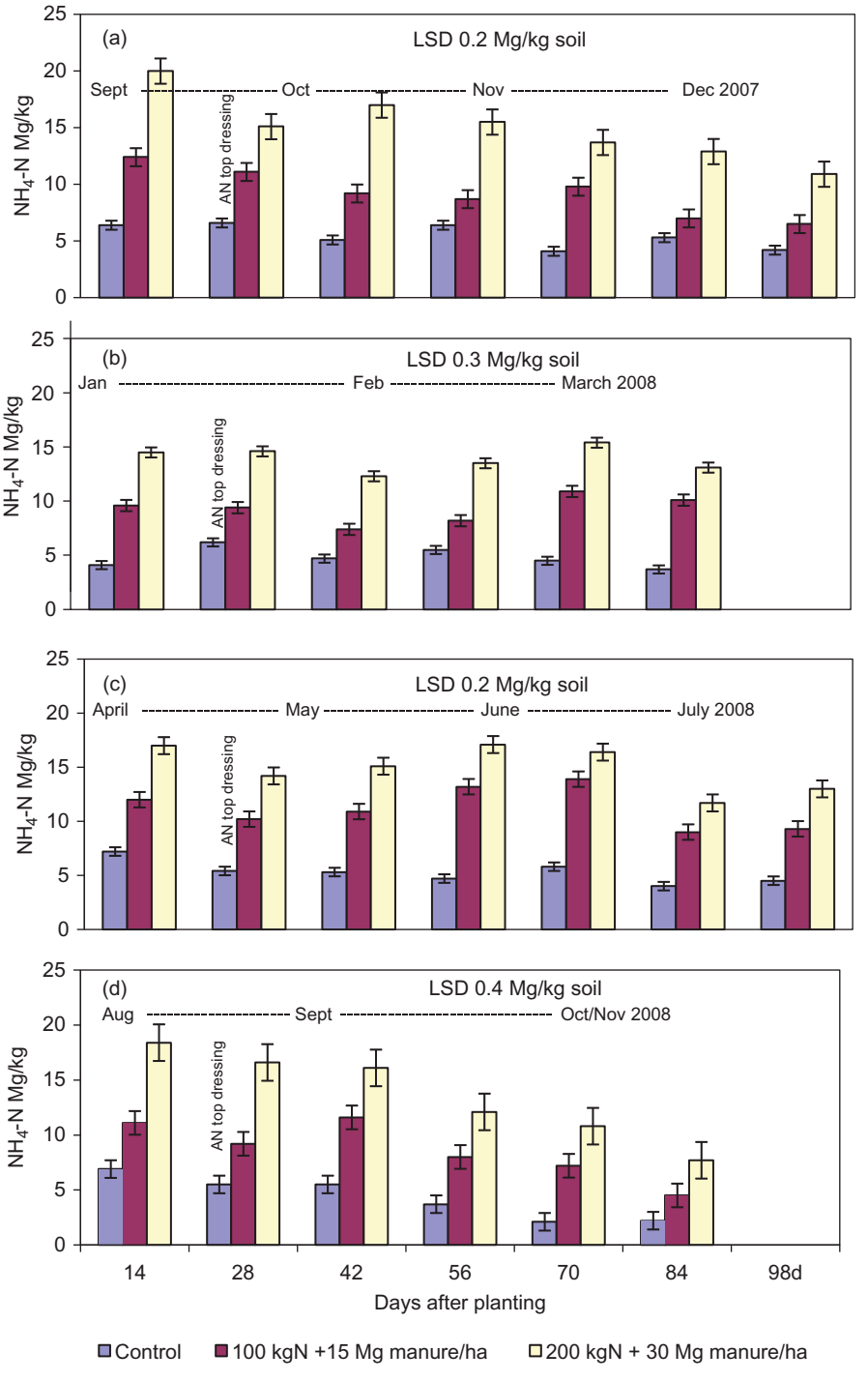

Figure 2. Ammonium nitrogen concentrations in soil during the 2007–2008 growing seasons following combined application of N fertilizer and manure, (a) first tomato, (b) first rape, (c) second tomato, and (d) second rape crops.

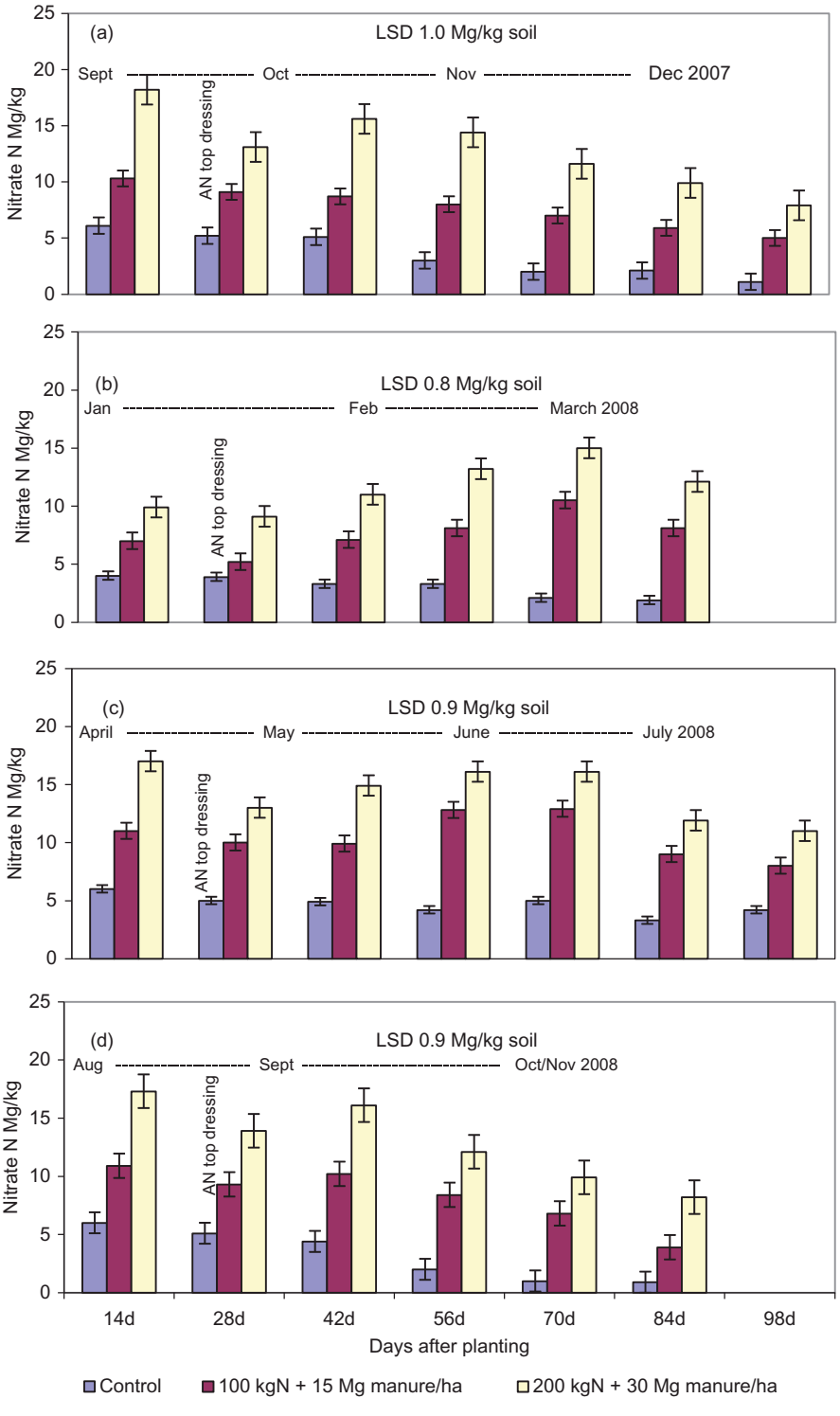

Figure 3. Nitrate concentration in soil during the 2007–2008 growing seasons following combined application of N fertilizer and manure.
Note: Crops (a)–(d), see Figure 2.

applications rates recorded 1.5 and 2–7 times higher mineralized N concentrations in soil for the tomato and rape crops, respectively.

Increasing N fertilizer and manure applications from low to high rates increased mineralized N concentrations in soil by 18–85% and 30–110% during the vegetative periods of tomato and rape crops, respectively. In related studies, Khalil et al. (2004), Wrage et al. (2004), and Van Groenigen et al. (2005) reported elevated organic N mineralization processes and associated N_2O emission with increasing manure applications when NO_3–N and readily decomposable organic compounds are not limiting.

The application of C-rich manure is suspected to have provided a source of C and energy for increased activity of heterotrophic nitrifiers (Flessa et al. 2002; Grant & Beer 2008). In addition, the high availability of N from N fertilizer applied to each crop ensured the presence of NH_3/NH_4^+ substrates in soil for nitrification (Petersen et al. 2006). It is suggested that the application of manure in combination with N fertilizer narrowed the C:N ratio in manure for net N mineralization. The high availability of N to microbes is suspected to have ensured that immobilization of mineralized N was kept low. The net result was an elevated content of mineralized N in plots that received higher fertilizer rates.

Nitrous oxide fluxes from soil

The mean differences in the emissions of N_2O recorded on plots that received different application rates of N fertilizer and cattle manure were significant ($p < 0.05$, Figure 4). Nitrous oxide fluxes in soil increased considerably with increasing application rates of N fertilizer and cattle manure. Doubling the rate of application of N fertilizer and manure from low to high increased N_2O fluxes from the soil by 21 (2.6 g ha^{-1} day^{-1})–106% (7.3 g ha^{-1} day^{-1}) and 29 (3.1 g ha^{-1} day^{-1})–107% (7.1 g ha^{-1} day^{-1}) for the tomato and rape crops, respectively.

Organic N in applied manure potentially increases N_2O emissions after undergoing heterotrophic microbial decomposition and mineralization (Venterea & Rolston 2000; Reuter 2001). The microbial degradation of nitrogenous organic substance (in manure crude protein) in soil may yield net mineralized N when N is turned into available/soluble forms (NH_4–N and NO_3–N) or immobilized N (assimilated into microbial cell substance, and therefore temporarily sequestrated from denitrification). However, whether organic N in applied manure is immobilized or mineralized depends on the concentration of available N in soil and manure against the content of C in applied manure (Mtambanengwe et al. 1998; Silva et al. 2005). In the current study, the application of mineral N fertilizer in combination with cattle manure effectively narrowed the C:N ratio of applied manure from 18:1 to 11:1 (Table 1). In related studies on dynamics of organic matter decomposition and organic N mineralization, Mtambanengwe et al. (1998) and Venterea and Rolston (2000) reported increased net N mineralization in decomposing organic substrates with narrower C:N ratios. This implies that the application of N fertilizer as a supplement to cattle manure in vegetable production enhances the potential of cattle manure to release mineralized N into the soil where it is subject to N_2O-releasing processes of nitrification and denitrification. In this context, the general recommendation that manure applications should be supplemented by mineral N fertilizer amendments to improve available N supply (Lowrence & Smittle 1988; Venterea & Rolston 2000; Reuter 2001) in soil has far reaching environmental consequences on the atmosphere. The practice enhances the applied manure's potential to release mineralized forms of N (Figures 2 and 3) by narrowing the C:N ratios (Table 2) into ranges favorable for net mineralized N that is

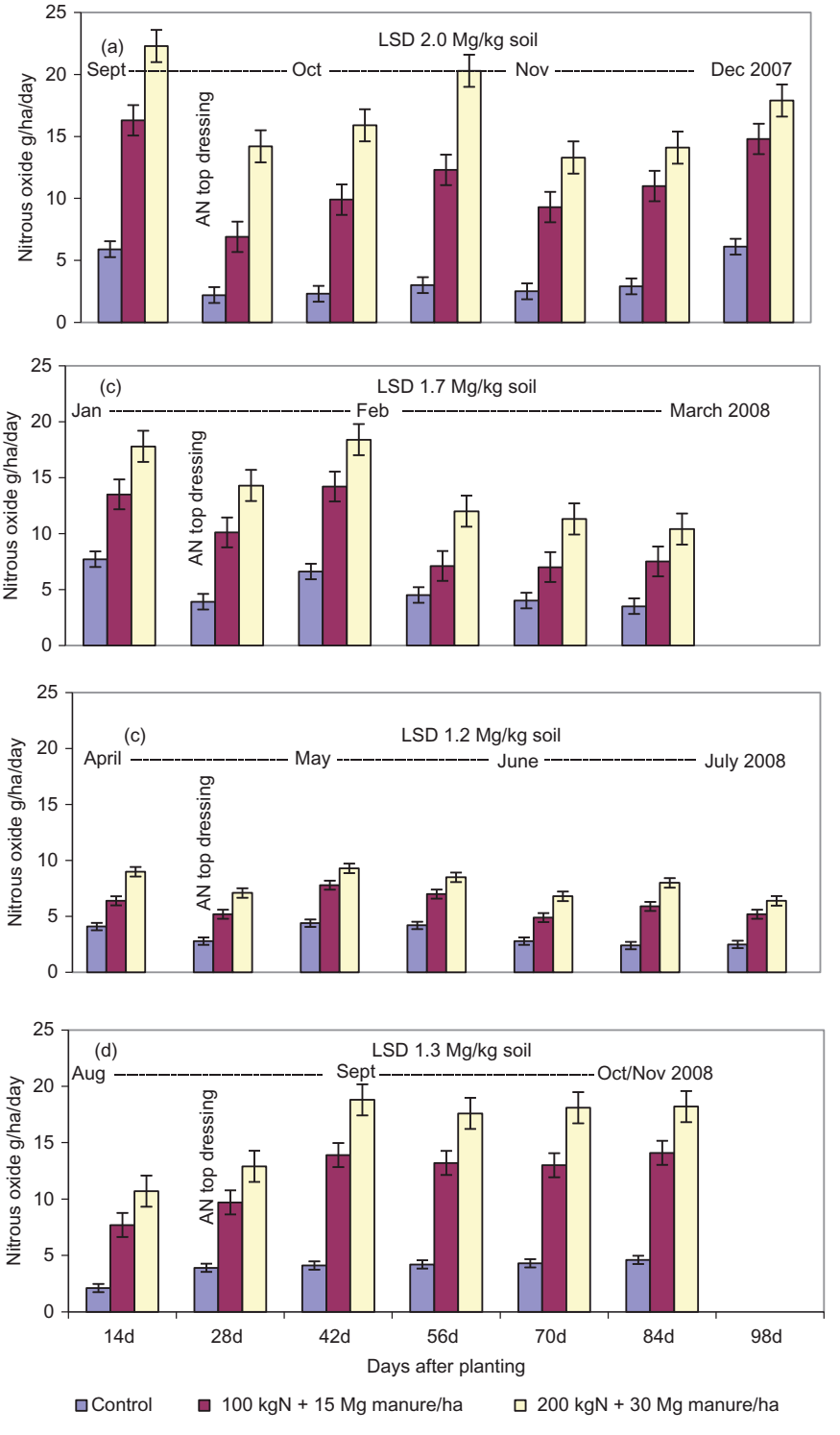

Figure 4. Nitrous oxide emissions in soil during the 2007–2008 growing seasons following combined application of N fertilizer and manure.
Note: Crops (a)–(d), see Figure 2.

Table 2. Selected chemical properties of cattle manure.

Organic C	Total N	C:N ratio	Soil + ash content	Soil and ash-free basis	
				Organic C	Total N
(%)				(%)	
22.82	1.36	17:1	77.18	61.3	6.4

exposed to N_2O-releasing microbial processes in soil. The lower N use efficiency associated with vegetable crops (Lowrence & Smittle 1988) meant that a larger pool of unused mineralized N in the soil (Table 5) was exposed to N_2O-emitting process of denitrification in the current study. Clearly, the results of the current study show that elevated fertilizer applications as a means of avoiding yield depression of vegetable crops in subtropical Africa potentially increase the risk of global N_2O concentration overload in the atmosphere and the associated problem of global warming and ozone depletion. Reduced N_2O emissions under such farming practices in the subtropics may be achieved by introducing cover crops that can trap some of the mineralized N from denitrification process.

In the current study, it was suspected that the application of manure in combination with N fertilizer provided N for bacteria biomass synthesis and NO_3–N formation in quantities beyond losses caused by temporary immobilization, leaching, gaseous emissions, formation of ligno-protein complexes of low biodegradability and crop uptake. Nitrate N is a substrate in the processes leading to emissions of N_2O (Rees et al. 2006) when soil conditions become anaerobic after water saturation of the wetland soil profile (Venterea & Rolston 2000; Soren et al. 2006).

Study results have shown that the patterns of N_2O fluxes were strongly seasonal (Figures 1 and 4). It was found by Nobre et al. (2001) that N_2O emission rapidly increased after wetting of soil in conditions where availability of N and C are not limiting. In response to soil wetting at the onset of the rainy season (October 2007 and 2008), N_2O fluxes from soil typically increased. In anaerobic conditions, denitrifying bacteria use nitrate as electron acceptor which is conducive for formation of N_2O, NO_2, and N_2. Fierer and Schimel (2002) concluded that the point at which soils are rewetted following a dry period coincides with the maximum activity of nitrifiers. The nitrification process does not only create a substrate (NO_3–N) for the N_2O-releasing microbial denitrification, it also generates N_2O in some of its stages (Nobre et al. 2001; Fierer & Schimel 2002; Mosier et al. 2003). Highest N_2O emissions were recorded during the early growth stages of the first tomato crop (Figure 4a) when cattle manure was recently applied despite the presence of dry weather (Figure 1) and field capacity soil moisture conditions that usually encourage lower N_2O emissions.

Correlation analysis between measured variables

Regression analysis (Table 3 and Figures 5 and 6) showed that soil moisture and NO_3–N concentration were negatively correlated under first tomato (Figure 5, $p < 0.05$, $r^2 = 0.17$) and second rape (Figure 6, $p < 0.05$, $r^2 = 0.18$) crops only. This implied that NO_3–N concentration dynamics in soil were dependent on the content of soil moisture under the first tomato and rape crops.

Table 3. Pearson correlation coefficients between physical and chemical characteristics.

Crop		NO_3–N	N_2O	NH_4–N
Tomato (1)				
	N_2O	0.81*	–	–
	NH_4–N	–	0.81*	–
	Soil H_2O	−0.41*	−0.07 NS	−0.33 NS
	Soil *T*°	−0.33 NS	−0.05 NS	0.30 NS
Rape (1)				
	N_2O	0.49*	–	–
	NH_4N	–	0.61*	
	Soil H_2O	−0.04 NS	−0.15 NS	−0.01 NS
	Soil T (°)	0.05 NS	−0.22 NS	0.11 NS
Tomato (2)				
	N_2O	0.77*	–	–
	NH_4N	–	0.75*	–
	Soil H_2O	−0.19 NS	−0.08 NS	−0.20 NS
	Soil T (°)	0.06 NS	0.19 NS	0.04 NS
Rape (2)				
	N_2O	0.35*	–	–
	NH_4N	–	0.30*	–
	Soil H_2O	−0.42*	0.51 NS	−0.45 NS
	Soil T (°)	−0.05 NS	0.34 NS	0.03 NS

Note: *Significant difference at $p < 0.05$; NS, not statistically significant; soil H_2O, soil water content; and soil T, soil temperature.

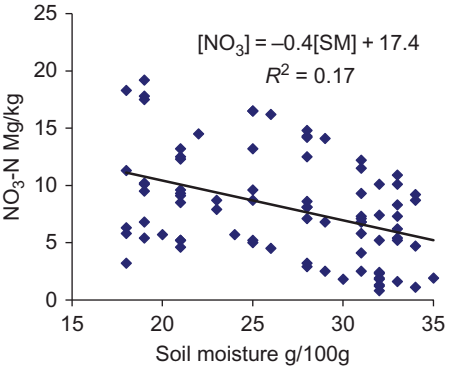

Figure 5. Regression analysis showing effect of soil moisture content on NO_3–N concentration under first tomato crop.

A significant correlation between NO_3–N in soil and soil moisture content was only observed under first tomato and rape crops probably due to the overlap in the vegetative periods of the crops from the dry winter period into the wet summer seasons (Figure 1) that introduced substantial changes in the moisture regimes of the wetland soil. The seasonal overlap had effects on soil moisture dynamics observed during the first tomato and second rape crops which were absent during the vegetative periods of the first rape (wet summer 2008 season) and second tomato (dry winter 2008 season) crops (Figure 1). Under the first rape crop, the soil profile was incessantly saturated (33 g water/100 g soil;

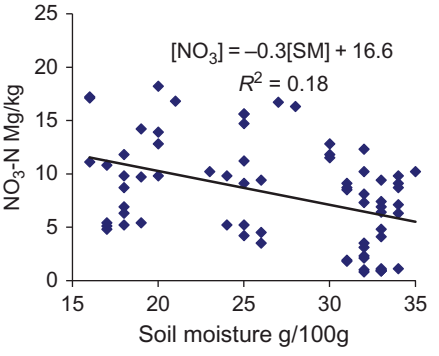

Figure 6. Regression analysis showing effect of soil moisture content on soil NO_3–N concentration under second rape crop.

Table 1) while the profile was consistently dry under second tomato crop thereby introducing no changes in the soil moisture profile.

Results of a multiple linear regression analysis have shown that a large proportion (r^2 values between 0.09 and 0.66; $p < 0.05$) of N_2O flux was influenced by variations in concentrations of NO_3–N and NH_4–N in soil (Figure 7–14). Both processes of

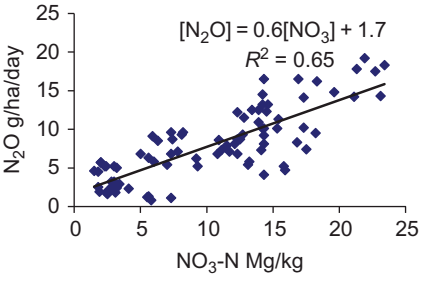

Figure 7. Regression analysis showing effect of soil NO_3–N concentration on N_2O emission under first tomato crop.

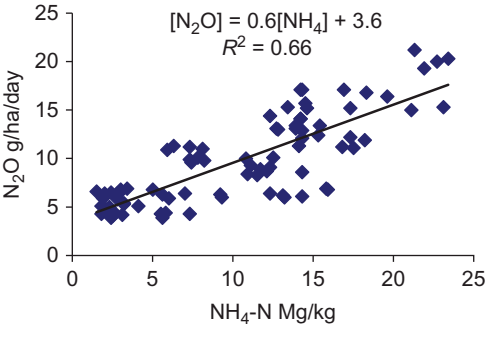

Figure 8. Regression analysis showing effect of soil NH_4–N concentration on N_2O emission under first tomato crop.

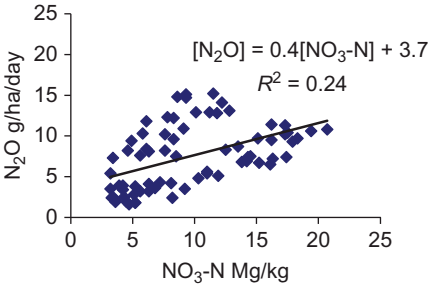

Figure 9. Regression analysis showing effect of soil NO_3–N concentration on N_2O emission under first rape crop.

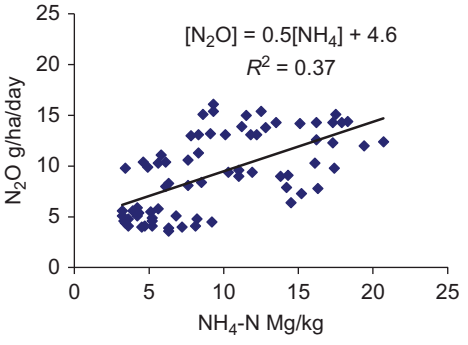

Figure 10. Regression analyses showing effect of soil NH_4–N concentration on N_2O emission under first rape crop.

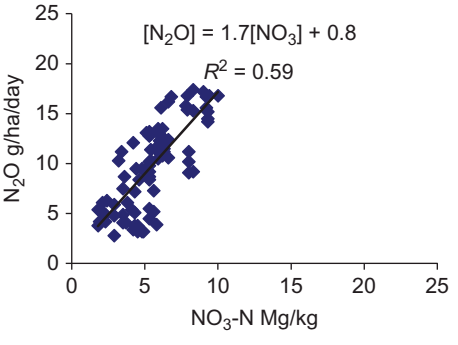

Figure 11. Regression analysis showing effect of soil NO_3–N concentration on N_2O emission under second tomato crop.

nitrification of NH_4–N and denitrification of NO_3–N are thought to contribute immensely to the emissions of N_2O although the later has been suggested to play a bigger role in the emissions (Venterea & Rolston 2000). In this study, NH_4–N and NO_3–N had comparatively equal influence on the variability found in N_2O emissions from soil (r^2 = 0.66 vs.

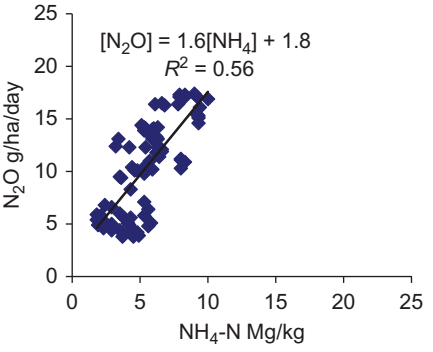

Figure 12. Regression analysis showing effect of soil NH_4–N concentration on N_2O emission under second tomato crop.

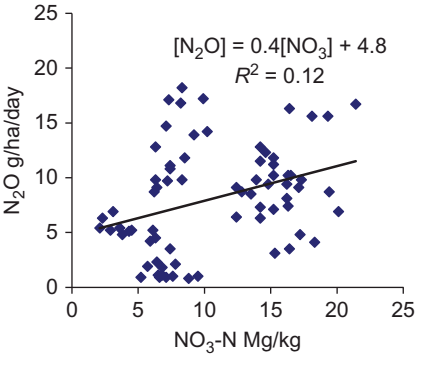

Figure 13. Regression analyses showing effect of soil NO_3–N concentration on N_2O emission under second rape crop.

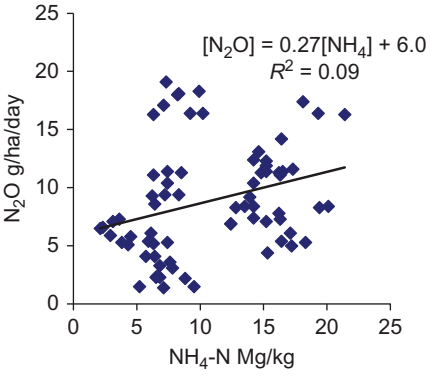

Figure 14. Regression analyses showing effect of soil NH_4–N concentration on N_2O emission under second rape crop.

0.65 for first tomato crop; r^2 = 0.37 vs. 0.24 for first rape crop; r^2 = 0.56 vs. 0.59 for second tomato crop; and r^2 = 0.09 vs. 0.12 for second rape crop).

The interactions between soil moisture, N_2O fluxes, NH_4–N, and NO_3–N concentrations in soil, soil temperature, and N_2O emissions from soil were not significant ($p > 0.05$) (Table 3). This implied that soil moisture and temperature generally exerted a weak influence on the variabilities in NH_4–N, NO_3–N concentrations in soil, and N_2O fluxes from soil. The presence of water saturated soil profiles for the greater part of the growing season of vegetable crops is a permanent distinguishing feature of wetlands making the impact of moisture variations in surface soils on N_2O emissions insignificant. Water has a very high specific heat capacity implying that a lot of incident and internal thermal energy capital is required to raise the temperature of a kilogram of saturated wetland soil by 1°C. Consequently, wet soil temperature regime response to atmospheric temperature changes occurs over very narrow ranges. It is, perhaps, for this reason that the effect of soil temperature on the concentrations of NH_4–N, NO_3–N, and N_2O fluxes in wetland soil was insignificant under all crops.

Total N lost as nitrous oxide

Significant differences in the total amounts of N lost as N_2O ($p < 0.05$) were recorded between treatments (Table 4). Total N lost as N_2O consistently increased with increasing application rates of mineral N fertilizer and cattle manure. In a related study, Burke et al. (2002) reported increased annual N_2O emissions with increasing manure and N fertilizer rates. Higher total N losses through N_2O emission were observed for manure in combination with inorganic fertilizer treatments in the first tomato crop (1.74 kg N ha^{-1}) and wet summer seasons in the first (1.21 kg N ha^{-1}) and second rape crops (1.31 kg N ha^{-1}). Lower total amount of N lost as N_2O was recorded in the second tomato (0.77 kg N ha^{-1}), a crop that grew under dry weather conditions of the 2008 April to July winter season. The percentage of N lost in N_2O emission was established by relating the total N applied in N fertilizer and cattle manure to the estimated amount of N lost in N_2O emissions. On average, annual losses of N as N_2O emission were 0.8, 1.8, and 2.5 kg N ha^{-1} when no fertilizer, low and high N fertilizer, and cattle manure were applied to tomato and rape crops. The percentages of N applied lost as N_2O–N when high and low manure; mineral N fertilizer rates were applied to tomato and rape crops under wetland conditions were generally lower than the global default value of 1.25% of the mineral N applied. In addition, percentage losses of N in N_2O of applied N in the high and low manure; N fertilizer + manure treatments were also lower than the global average rates of 0.2–2.5% N_2O-N of applied N computed from 35 studies on N_2O emissions in temperate agricultural systems (Mosier et al. 2003). It is suggested that this might be a result of high losses of applied N through nitrate leaching especially under wetland conditions and lower rates of N fertilizer applications in the subtropical Africa when compared with the rates in South-east Asia and Western Europe.

Generally, the proportion of applied N lost as N_2O was higher in the rape crop than in the tomato crop. When low and high N fertilizer + manure rates were applied to the tomato and rape crops 0.51%, 0.40% and 0.93%, 0.64% of applied N was lost as N_2O, respectively. This implies that rape production fertilized with N fertilizer and cattle manure has a greater potential to emit N_2O into the atmosphere than the production of tomatoes in wetlands at least for the adopted crop rotation and fertilizer application practice. In the current study, the growing periods for the tomato and rape crops were 98 and 84 days, respectively. Besides the fact that the two crops have different N

Table 4. Estimated total N loss through N_2O emission.

	Temporal interval (DAS)	Average rate of N_2O emission ($g\ ha^{-1}\ day^{-1}$)	Total N emitted ($kg\ ha^{-1}$)	Total N applied ($kg\ ha^{-1}$)	Emitted N_2O of applied N	Temporal interval (DAS)	Average rate of N_2O emission ($g\ ha^{-1}\ day^{-1}$)	Total N emitted ($kg\ ha^{-1}$)	Total N applied ($kg\ ha^{-1}$)	% emitted N_2O of applied N
Treatment			Tomato (1)					Rape (1)		
(1)	1–21	5.9	0.12	–	–	1–49	6.1	0.30	–	–
	22–49	2.5	0.07	–	–	50–84	4.0	0.14	–	–
	50–63	2.7	0.04	–	–	–	–	–	–	–
	64–98	6.1	0.21	–	–	–	–	–	–	–
Total			0.44	0	0	–	–	0.44	0	0
(2)	1–21	13.5	0.29	–	0.10	1–49	12.6	0.62	–	0.62
	22–49	9.7	0.28	–	0.10	50–84	7.2	0.25	–	0.25
	50–63	10.2	0.14	–	0.05	–	–	–	–	–
	64–98	14.8	0.52	–	0.20	–	–	–	–	–
Total	–	–	1.24	304	0.45	–	–	0.87	100	0.87
(3)	1–21	17.8	0.38	–	0.10	1–49	16.7	0.82	–	0.41
	22–49	18.8	0.53	–	0.13	50–84	11.2	0.39	–	0.20
	50–63	14.1	0.20	–	0.05	–	–	–	–	–
	64–98	17.9	0.63	–	0.15	–	–	–	–	–
Total	–	–	1.74	608	0.30	–	–	1.21	200	0.61
FPR	–	–	*	–	–	–	–	*	–	–
LSD	–	–	0.16	–	–	–	–	0.23	–	–
CV	–	–	13.40	–	–	–	–	12.20	–	–
			Tomato (2)					Rape (2)		
(1)	1–98	3.3	0.32	–	–	1–35	3.0	0.11	–	–
—	–	–	–	—	–	36–84	4.3	0.21	–	–
Total			0.32	0	–			0.32	0	–
(2)	1–98	6.1	0.60	–	0.6	1–35	8.7	0.31	–	0.31
—	–	–	–	—	–	36–84	13.6	0.67	–	0.67
Total			0.60	100	0.60			0.98	100	0.98

(*continued*)

Table 4. (*Continued*).

Treatment	Temporal interval (DAS)	Average rate of N_2O emission (g ha^{-1} day^{-1})	Total N emitted (kg ha^{-1})	Total N applied (kg ha^{-1})	Emitted N_2O of applied N	Temporal interval (DAS)	Average rate of N_2O emission (g ha^{-1} day^{-1})	Total N emitted (kg ha^{-1})	Total N applied (kg ha^{-1})	% emitted N_2O of applied N
	Tomato (1)					Rape (1)				
(3)	1–98	7.9	0.77	–	0.4	1–35	11.8	0.41	–	0.21
—	–	–	–	–	–	36–84	18.2	0.90	–	0.45
Total	–	–	0.77	200	0.40	–	–	1.31	200	0.66
FPR	–	–	*	–	–	–	–	*	–	–
LSD	–	–	0.14	–	–	–	–	0.24	–	–
CV	–	–	15.70	–	–	–	–	8.80	–	–

Notes: Treatment 1, 0 kg N fertilizer + 0 Mg cattle manure ha^{-1} (control); Treatment 2, 100 kg N fertilizer + 15 Mg cattle manure ha^{-1}; Treatment 3, 200 kg N fertilizer + 30 Mg cattle manure ha^{-1}; FPR, false-positive rate; LSD, least significant difference; and CV, coefficient of variation. *Significant difference at $p < 0.05$.

assimilative capacities and therefore different soil N sequestration potentials, the longer vegetative period of the tomato crop gave it a greater time for active N uptake from the wetland soil which effectively depleted the N reserve in soil available for denitrification and subsequent emission of N_2O in soil under the crop. The extended period for N uptake and its sequestration from the wetland soil by the tomato crop meant that there was a diminished residual N pool in soil for the emission of N_2O. This effectively meant that the rape crop's active period of soil N uptake was shorter than that of the tomato crop. This is suspected to have caused a greater reserve of residual N to be left in the soil subject to denitrification with an associated higher release of N_2O in soil than that recorded in soil under tomato crop. Generally, the uptake of N by the tomato crop during the four cropping events was 39% higher than that of the rape crop (Table 5). This clearly shows that the tomato crop, in addition to its extended period of active N uptake in the growing period, had a greater capacity to remove denitrifiable N from soil than the rape crop. The difference in the proportion of applied N that was lost as N_2O emissions between the tomato and rape crops seemed small. However, when considering that N_2O is a trace component of the Earth's atmosphere with concentrations of >310 nL L^{-1} (Ma et al. 2007) its emission fluxes were not expected to be considerably large. The relatively small amounts of total N lost per unit area as N_2O may explain why N_2O is responsible for only 4% of the greenhouse effect compared to 50% for CO_2 (Van Der Salm et al. 2006; Grant & Beer 2008). A number of previous studies have indicated that 0.07–2.7% of applied N can be evolved as N_2O (Wrage et al. 2004).

Nitrogen uptake and dry matter yield

Nitrogen uptake was monitored for all the treatments throughout the growing seasons of the four vegetable crops. Statistically significant differences in N uptake and dry matter yield ($p < 0.05$) were recorded in plots receiving varying N fertilizer and manure application levels (Table 5). Raised application rates of N fertilizer and manure from low to high increased dry matter build up per hectare by 26% and 18%; 23% and 22% for the first tomato and rape; the second tomato and rape crops, respectively. In single dose fertilizer applications to tomato and rape crops, N uptake represented 43–76% and 85–87% of applied N, respectively. Nitrogen uptake represented 78–84% for the tomato and 75–88% for the rape crops of the total N applied to each crop in double dose fertilizer treatments.

Conclusions

It can generally be concluded that the additions of mineral N fertilizer and animal manures to wetland soil in the subtropical Zimbabwe can be recognized as one of the major drivers of N_2O emissions into the atmosphere with global warming consequences. The study has emphasized the importance N fertilizer and cattle manure applications on loss of N as N_2O. The loss of N as N_2O emission was shown to constitute an important nutrient flux, and the variability in the losses was determined by varying application rates of mineral N fertilizer and manure. Wetland crop production systems that use lower fertilizer application rates of significantly reduce emission of N_2O and the associated risk of increasing global warming. In subtropical wetland vegetable production systems amended with mineral N fertilizer and cattle manure, the production of rape leaf has a greater N_2O emitting potential than the production of tomatoes.

Table 5. Dry matter yield and N uptake by aboveground plant biomass.

	DM yield (t ha^{-1})	N content (Mg g^{-1} DM)	N uptake (kg ha^{-1})	DM yield (t ha^{-1})	N content (Mg g^{-1} DM)	N uptake (kg ha^{-1})	DM yield (t ha^{-1})	N content (Mg g^{-1} DM)	N uptake (kg ha^{-1})	DM yield (t ha^{-1})	N content (Mg g^{-1} DM)	N uptake (kg ha^{-1})
Treatment	Tomato (1)			Rape (1)			Tomato (2)			Rape (2)		
(1)	3.0	9.6	28.7	10.1	1.0	9.8	2.9	12.2	35.4	14.5	2.3	32.9
(2)	7.7	16.9	129.9	16.4	5.3	86.9	7.7	9.9	76.2	20.8	4.1	85.3
(3)	9.7	32.6	316.3	19.3	7.8	150.5	9.5	17.6	167.7	25.4	6.9	175.3
FPR	*	*	*	*	*	*	*	*	*	*	*	*
LSD (5%)	0.1	0.6	34.9	0.3	0.8	14.4	0.1	0.3	17.7	0.3	0.7	13.1
CV (%)	0.9	1.7	12.7	1.2	7.8	7.7	0.4	0.9	6.2	0.7	5.0	4.4

Note: *Significant difference at $p < 0.05$; For Abbreviations, see Table 4.

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