REGULAR ARTICLE

Effects of organic and mineral fertilizer nitrogen on greenhouse gas emissions and plant-captured carbon under maize cropping in Zimbabwe

Farai Mapanda • Menas Wuta • Justice Nyamangara • Robert M. Rees

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Abstract Optimizing a three-way pact comprising crop yields, fertility inputs and greenhouse gases may minimize the contribution of croplands to global warming. Fluxes of N₂O, CO₂ and CH₄ from soil were measured under maize (*Zea mays* L.) grown using 0, 60 and 120 kg N hm⁻² as NH₄NO₃-N and composted manure-N in three seasons on clay (Chromic luvisol) and sandy loam (Haplic lixisol) soils in Zimbabwe. The fluxes were measured using the static chamber methodology involving gas chromatography for ample air analysis. Over an average of 122 days we estimated emissions of 0.1 to 0.5 kg

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F. Mapanda (⊠)
Department of Research and Specialist Services, Chemistry and Soil Research Institute,
P.O. Box CY550, Causeway, Harare, Zimbabwe e-mail: faraimaps@yahoo.com

M. WutaDepartment of Soil Science and Agricultural Engineering,University of Zimbabwe,P.O. Box MP167, Mt. Pleasant, Harare, Zimbabwe

J. Nyamangara International Crops Research Institute for the Semi-Arid Tropics, Matopos Research Station, P.O. Box 776, Bulawayo, Zimbabwe

R. M. Rees Scottish Agricultural College, West Mains Road, Edinburgh EH9 3JG, UK N_2 O-N hm⁻², 711 to 1574 kg CO₂-C hm⁻² and -2.6 to 5.8 kg CH_4 -C hm⁻² from six treatments during season II with the highest fluxes. The posed hypothesis that composted manure-N may be better placed as a mitigation option against soil emissions of GHG than mineral fertilizer-N was largely supported by N₂O fluxes during the wet period of the year, but with high level of uncertainty. Nitrogen addition might have stimulated both emissions and consumption of CH₄ but the sink or source strength depended highly on soil water content. We concluded that the application of mineral-N and manure input may play an important role with reference to global warming provided the season can support substantial crop productivity that may reduce the amount of N₂O loss per unit yield. Confidence in fluxes response to agricultural management is still low due to sporadic measurements and limited observations from the southern African region.

Keywords Cattle manure \cdot Greenhouse gas \cdot Maize \cdot Mineral fertilizer \cdot Plant captured carbon

Introduction

Maize production and mineral fertilizer use in southern Africa are likely to become more closely linked than they have been in the immediate past (Heisey and Mwangi 1996) mainly due to expansion of maize production in line with current national

policies to reduce food imports. This linkage is likely to cause a shift in the local and regional nitrogen (N) and carbon (C) balance as it may affect both primary productivity and soil emissions of greenhouse gases (GHGs). Equally important are organic soil amendments such as cattle manure that are extensively used in most smallholder farming systems in Africa. Economic reasons, compatibility with capacity, soil conditioning and pollution reduction are often used to justify the use of organic fertilizers (e.g. Odhiambo and Magandini 2008; Svotwa et al. 2009). However, there have been limited observations from Africa to support that the use of these organic soil amendments as sources of plant-N may also reduce soil emission of GHGs such as nitrous oxide (N₂O) and methane (CH₄) compared with the use of mineral-N fertilizers.

The lack of work addressing GHG emissions on the basis of agricultural productivity rather than cultivated area alone has been lamented by Flynn and Smith (2010), and such missing link may relate to Burneya et al. (2010)'s suggestion that investment in yield improvement compares favourably with other commonly proposed climate change mitigation strategies. The use of manure-N to increase food security and as a climate change mitigation strategy has been widely debated in Africa and elsewhere. It is generally accepted that under the current regional farming systems' setup the use of cattle manure alone may not sustain the food requirements of southern Africa. The reason is partly that an overwhelming majority of farmer households own none or small herds of cattle. Cattle manure use has often resulted in relatively low maize yields in the short-term, as a result of N-immobilization in soil (e.g. Ma et al. 1999; Nyamangara et al. 2003a). Such response could imply low plant-capturing of atmospheric CO_2 which may be important in the short term. In the long term however, Lasco et al. (2006) highlighted that for annual crops increase in biomass in a single year is assumed equal to biomass losses from harvest and mortality in that same year, thus there may be no net accumulation of biomass C.

The use of inorganic N-fertilizers has been implicated by Khan et al. (2007) and Mulvaney et al. (2009) in loss of soil organic C through increased respiration and GHG emissions. In addition, this loss would also decrease soil productivity and agronomic efficiency of applied-N, and would therefore shift the N and C balance in favour of GHG emissions. Such experience would be far more detrimental for southern Africa largely because the organic matter content of soils from arable fields in the region is on average less than 2% (i.e., <1% soil organic C) (Nyamangara 2002). For Zimbabwe at least 70% of total arable land is covered by the highly weathered sandy soils (Anderson et al. 1993), with low physical protection of soil organic C. On the other hand, solid manure may be a potential mitigation strategy that can reduce GHG emission from croplands (e.g. Desjardins et al. 2005). This option can be improved by manure pretreatment by composting (Petersen 1999), although the composting itself may be an important source of GHG (Hao et al. 2001). Many of these worries have however not been confirmed in southern Africa.

The latest (2006) IPCC guidelines for national GHG inventories gives a default N₂O emission factor for N additions from both mineral fertilizers and organic amendments as 0.01 kg N₂O-N kg⁻¹ applied N (de Klein et al. 2006). This factor is a revision downward from the 1997 IPCC factor (1.25% of applied N). Similarly for CH₄, a baseline emission factor of 1.3 kg CH_4 hm⁻² day⁻¹ is available in the same guidelines only as a starting point, with scaling factors of 0, 0.25, 0.28 and 1, for upland, drought prone, regular rain-fed and continuously flooded water regimes, respectively. Zimbabwe and many other African nations under the United Nations Framework Convention on Climate Change have adopted this emission factor approach for reporting national GHG inventories. However, considering the limited number of observations made from southern Africa during this period, it is highly likely that there were few data inputs from this region.

The objectives of our study were therefore to determine the fluxes of N₂O, CO₂ and CH₄ from soils under maize, and to relate these fluxes to both Nsource (composted cattle manure and mineral fertilizer) and crop productivity. We hypothesised that composted manure-N is better placed as a mitigation option against soil emissions of GHG than mineral fertilizer-N that has generally been implicated in the depletion of soil organic C and ultimate decrease in agronomic efficiency of applied-N. An equivalent N-rate from composted cattle manure would therefore yield less GHG emissions from croplands under maize because of the possible longer N residence time in soil that normally gives manure some of its residual effects on the preceding crops (e.g. Nyamangara et al. 2003a).

Materials and methods

Study sites

The study was conducted during Cropping Seasons I (2006/2007), II (2007/2008) and III (2008/2009) at the University of Zimbabwe Farm (UZ-Farm) located 15 km north of Harare (31° 00' 48" E; 17° 42' 24" S), and the Domboshawa Training Centre (DT-Centre) located 30 km north-east of Harare (31° 00' 30"E; 17° 42' 03"S). The UZ-Farm and DT-Centre experience cold-dry winters and hot-wet summers (subtropical). The amount and distribution of rainfall received at the two sites during the study period are shown in Fig. 1a,b. January was the wettest of all rainy months, especially in season II (2007/2008) where close to 40% and 30% of total rainfall were received in January at the UZ-Farm and DT-Centre, respectively. The warmest period of each year was October-December (Fig. 1c,d). The red clay soil at the UZ-Farm is classified (FAO) as Chromic luvisol derived from dolerite, while the brown sandy-loam soil at DT-Centre is Haplic lixisol derived from granite. Other site characteristics and soil properties are given in Table 1.

Experimental treatments and management

Two identical experiments were conducted on croplands that had been fallowed for at least 10 years, one at the UZ-Farm and the other at the DT-Centre. The treatments were:

- 1. No fertilizer-N and no manure-N applied (control)
- 2. NH_4NO_3 -N, applied at 60 kg hm⁻²
- 3. NH_4NO_3 -N, applied at 120 kg N hm⁻²
- Cattle manure-N, applied at 60 kg N hm⁻² plus NH₄NO₃-N at 60 kg N hm⁻² (combination)
- 5. Cattle manure-N, applied at 60 kg N hm^{-2}
- 6. Cattle manure-N, applied at 120 kg N hm^{-2}

Experimental plots (5 $m \times 6$ m) were laid out with six treatments arranged in a Randomized Complete Block Design with four replicates. Manure from pasture-fed beef cattle was collected and aerobically heap composted under a shed for three months (September–November). Before weighing and land application the composted manure was analysed for total-N and C content (Table 2), and water content for moisture correction in each season. Experimental plots were ploughed to about 0.2 m soil depth and disced before sowing each season. Sowing positions were marked at 0.9 m×0.45 m spacing using hoes, and a locally common maize variety (SC513, with 57 days to silk and 126 days to maturity (Seed-Co 1998)) was sowed (to two plants per position). Mineral-N fertilizer (NH₄NO₃, 34.5% N) was applied at 0, 60 and 120 kg N hm⁻², 50% at sowing and the remaining 50% at six weeks after sowing (next to crop) each season. Manure (60 and 120 kg N hm^{-2}) was strip applied at sowing alongside each sowing line and buried. In addition, annual basal dressings of P (30 kg hm^{-2} , as single super phosphate) and K $(30 \text{ kg hm}^{-2}, \text{ as muriate of potash})$ were applied in sowing holes on all experimental plots before sowing the seed. Basal dressing concurred with sowing to minimise mechanical operations, and the seed was placed at sufficient distance from fertilizers within each hole to reduce salt stress during crop emergence. This method of application is the most common for maize in both commercial and smallholder farming systems where graduated fertilizer cups or some fertilizer metering devices on traction implements are used for spot application in southern Africa. The rates applied closely related to the local recommendations of 300–400 kg hm⁻² of N: P: K (8.0: 7.0: 6.3) at sowing and 250-300 kg hm⁻² NH₄NO₃ from four or six weeks after sowing for a maize target yield of $6000-7000 \text{ kg hm}^{-2}$ (ARI 2002). Weed control was done manually using hand hoes.

Sampling

Gaseous emissions from soil were trapped using open-bottom and transparent polythene chambers with an area of 0.40 m x 0.28 m, (0.2 m high) and a net volume of 0.019 m³, using a method similar to that reported by Rees et al. (2006) and Mapanda et al. (2010). Each chamber was placed above the sampling area (located randomly) within a plot, and positioned in a way that it protruded into the intra-row spacing with its width covering more than half of this spacing. This was partly to get as close as possible to where the fertilizer and manure were applied (without disturbing crop roots), and also to use crop canopy to reduce excessive heating of chambers from direct sunlight. To avoid gas loss between the soil and chamber edges a small chisel was used to fasten this seal with surrounding soil, taking precaution not to



Fig. 1 Daily rainfall received and some key events timelines at the UZ-Farm (a) and DT-Centre (b), and the daily maximum and minimum air temperatures at the respective sites (c, d) in 36 months of the study starting June (J) 2006

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Table 1 General character-
istics of the study sites,
including climate data cov-
ering the period 2005 -
2010 and soil properties
(mean±standard deviation)
in the $0 - 0.1$ m depth at the
UZ-Farm and DT-Centre in
Zimbabwe

Characteristic	UZ-Farm	DT-Centre
Altitude, m	1505	1540
Mean annual rainfall, mm yr ⁻¹	748±176	824±226
Mean maximum temperature, °C	26.1 ± 0.7	27.2 ± 0.7
Mean minimum temperature, °C	12.4 ± 0.4	$10.4{\pm}1.9$
Soil type, FAO	Chromic luvisol	Haplic lixisol
Soil parent material	Dolerite	Granite
Slope,%	2-3	2-3
Soil pH	6.5 ± 0.1	$5.4 {\pm} 0.2$
Bulk density, g cm ⁻³	$1.27 {\pm} 0.03$	$1.78 {\pm} 0.03$
Soil organic C,%	1.63 ± 0.23	$0.76 {\pm} 0.10$
Cation exchange capacity, cmol ⁽⁺⁾ kg ⁻¹	9.5±1.5	5.2 ± 1.4
Clay content,%	52±1.4	15±1.4

disturb the surface inside the chamber perimeter. The emitted gas in each chamber was collected into preevacuated 20 cm³ glass vials using a 50 ml-graduated syringe, once immediately after securing the chamber on the sampling area and once after one-hour of trapping the gas. In addition, a separate linearity test was latter carried out once by similarly collecting the gas from three chambers at 10 minutes intervals for 60 minutes and plotting the fluxes against time.

Gas sampling was carried out at intervals shown in Fig. 1a,b, in order to compare the relative treatment effects on GHG fluxes during the rainy season only since high moisture content during this period would be expected to trigger more considerable GHG fluxes than during the dry period (Rees et al. 2006; Dick et al. 2008). It was assumed that GHG fluxes during the dry seasons would be very low and comparable across treatments due to a possible low microbial activity in dry soils and insignificant sources of CH_4 for uptake by soil microorganisms. In addition, sampling during the dry period using the employed chamber insertion method would increase chances of gas leakage or contamination by lateral diffusion beneath the base

(Rochette and Eriksen-Hamel 2008), causing nonlinearity and systematic underestimation in the fluxes (Kroon et al. 2008). Gas sampling from the plots of different treatments was done almost at the same time, with a 2 to 3 minutes lag in sampling from one chamber to the next. This time limit however could not allow for chamber replication within each plot, and partially addressed the effect of potential diurnal variations in the fluxes, especially for CO_2 which would then be negligible (Tang et al. 2005; Yang et al. 2010).

Soil samples were collected, initially and following each gas sampling, using a bucket auger at 0-0.15 m depth, and at two places within an area where a gas chamber was placed in each plot. Soil temperature was measured in-situ at three randomly selected positions within each plot using digital soil thermometers with 0.1 m long stainless steel probes, while air temperature was measured at a height of approximately 1 m above ground. Both soil temperature and air temperature were measured at the first and second gas collection time from each plot. Relative to temperatures inside the chambers (sporadically measured soon after the second gas collection) air temperatures were lower by between $0.8-11.7^{\circ}$ C (mean: 7.9° C). The samples

Table 2Total C and N, and
the C/N ratio of the N-
sources used in the experi-
mental plots at the two
study sites during the three
cropping seasons

N-source	Total C g kg ⁻¹	Total N g kg ⁻¹	C/N
Cattle manure (Season I: 2006/2007)	326	16	20
Cattle manure (Season II: 2007/2008)	312	12	26
Cattle manure (Season III: 2008/2009)	280	13	22
NH ₄ NO ₃ (Seasons I, II, and III)	-	345	_

were analysed for water content (SWC), mineral-N $(NH_4^+-N \text{ and } NO_3^--N)$, pH and organic C.

The maize crop was harvested at 22–24 weeks after sowing in each season, by cutting all above ground crop material within a net plot area of 3 m x 3 m. Harvested materials were subdivided into grain, shelled-cob and maize residue, and weighed for aboveground biomass. Sub-samples from each subdivision were collected for moisture correction and estimation of total plant N and C.

Analysis of samples

Nitrous oxide, CO₂ and CH₄ were quantified by Gas Chromatography (GC model: Hewlett Packard 5890, Series II, Avondale, PA, USA) at Scottish Agricultural College (SAC) in the UK. Nitrous oxide was determined using an Electron Capture Detector maintained at 380°C; CO₂ was analysed using a Thermal Conductivity Detector, and CH₄ using a Flame Ionisation Detector. The least detected level values for the specific gases were 0.24 ppm for N_2O_1 , 350 ppm CO₂ and 0.84 ppm CH₄. The fluxes of N₂O, CH₄ and CO₂ were calculated as the differences in concentration between sampling time zero and sampling after one hour. However, a four point sampling in time would be more suitable than this two-point approach in future studies in order to reduce uncertainties in the estimated fluxes. Atmospheric pressure and temperature during the time of sampling were taken into account in the calculations. In order to check the integrity of sample containers being used in this study, batches of standard samples were sent from the UK to Zimbabwe and returned (within 10 weeks) with field samples for analysis. The concentrations of 16 vials containing CO₂, CH₄ and N₂O were consistently between 92–100% of the original value, with a mean of 98%.

Soil water content (SWC), NH_4^+ -N and NO_3^- -N analyses were carried out immediately from fresh samples, while pH and organic C analyses were done after air drying of samples and sieving through a 2 mm and a 0.5 mm sieve, respectively. Soil analyses were done using the methods described by Okalebo et al. (1993). Mineral-N was extracted by mechanically shaking 5 g of a soil sample with 50 ml of 2 M KCl for one hour, and filtering. Ammonium-N was determined after steam distillation of the extract in MgO that is, trapping the NH_4^+ -N in boric acid plus

indicator (bromocresol-methyl red) solution. The distillate (50 ml) was titrated with 0.005 M H₂SO₄ in a micro-burette. Nitrate-N was determined in the same sample by adding Devarda's alloy to reduce NO₃⁻-N to NH₄⁺-N and distilling again into fresh boric acid, followed by titration with 0.005 M H₂SO₄. The SWC was determined gravimetrically as soil weight loss on oven drying at 105°C till constant weight. Soil pH was measured in a distilled water suspension with a pH meter (model: Corning 215) after an hour of mechanical shaking, while total organic C was extracted by wet oxidation using concentrated H₂SO₄ and K₂Cr₂O₇, and determined by titrating with Fe(NH₄)₂(SO₄)₂·6H₂O solution.

Plant moisture and C analyses were carried out using the methods also described by Okalebo et al. (1993). Dry matter was determined by weight difference upon oven drying at 70°C till constant weight. Total N content was determined using the semi-micro Kjeldahl method (Bremmer and Mulvaney 1982), while plant C was estimated from organic matter (loss in weight after slow ignition in a muffle furnace at 650°C over 12 hours). A conversion factor of 1.724 was used to convert organic matter to organic C based on the assumption that organic matter contains 58% organic C (i.e., g organic matter/1.724=g organic C) (Okalebo et al. 1993; Nelson and Sommers 1996). Three replicates were made by sub-sampling each sample in the laboratory. Before ashing the samples were pre-heated in an oven at 70°C to correct for any absorbed moisture.

Data analysis

The linearity test conducted using samples collected at 10 minutes intervals for 60 minutes gave some coefficients of regression (r^2 values) of between 0.88 and 0.97 (average: 0.92), thus on average about 8% of error originating from deviations of linearity. A total measurement uncertainty of at least 20% was estimated from the study (chamber height: 5%; time: temperature: 3%; linearity: 8%; transport: 2%; GC calibration and measurements: 2%) based on theoretical confidence estimate (e.g. Rochette and Eriksen-Hamel 2008; Venterea 2010). Homogeneity of variance and normality tests were carried out on gas, soil and plant data using the Levene's and Kolmogorov-Smirnov's Tests, respectively, at 5% level. Two-way analysis of variance was carried out to establish any significant



Fig. 2 Soil emissions (and consumption) of $N_2O(a, b)$, $CO_2(c, d)$ and $CH_4(e, f)$ from the experimental plots of six treatments at the UZ-Farm and DT-Centre in 3 cropping seasons

treatment and season effects (P < 0.05). However, most of the data did not meet all assumptions of the Fisher-founded Analysis of Variance even after transformation, and in such cases the Kruskal-Wallis one-way analysis of variance by ranks (Genstat 2003) was used to establish any significant treatment responses (P < 0.05). The Mood's Median Test was also used in significance tests on CO₂ and CH₄ fluxes data because it was more robust against outliers than the Kruskal-Wallis Test.

A pair-wise separation of significantly different treatment means was done using the Mann-Witney test. Bivariate correlation analysis (two-tailed) was performed using the Pearson correlation coefficients, while regression analysis was conducted to measure the relative importance of each soil factor on GHG fluxes. Fluxes of CO_2 and CH_4 were not considered for the ratios of yield to fluxes useful to judge agriculture management impact with reference to global warming because soil respiration is not included in the national GHG inventory but primarily an indication of soil biological activity, while CH_4 contained very high standard errors. Genstat 7.2 (Discovery Edition, Lawes Agricultural Trust UK) and SPSS 8.0 (SPSS Inc., USA) statistical packages were used in the statistical analysis of data.

Results

Soil N₂O fluxes

The pattern of N₂O fluxes in the few measurements taken was largely similar for all treatments with a few exceptions of those treatments that received NH₄NO₃-N that had up to 32 μ g N₂O-N m⁻² hour⁻¹ at the UZ-Farm, and up to 30 μ g N₂O-N m⁻² hour⁻¹ at the DT-Centre (Fig. 2a,b). Spatial variability in N₂O fluxes was considerably high but much of the highest N₂O fluxes particularly on plots that received NH₄NO₃-N were noted between December and January (rainfall peak period, Fig. 1) of Season II at the UZ-Farm. A considerable decrease in N₂O emissions (*P* <0.05) was noted in Season III, in which no emissions exceeded 10 μ g N₂O-N m⁻² hour⁻¹ in all measurements,.

The total relative emissions of N_2O from the six treatments, coarsely estimated over a period of 122 and 116 days during Seasons II and III, respectively are shown in Table 3. No linear relationship could be established between N-rate and N_2O emissions but the effect of N-source was apparent with NH_4NO_3 contributing emission increments of up to 0.31 and 0.19 kg N_2O -N per season from 60 kg N hm⁻² at the

Table 3 Total soil emissions or consumption of N_2O , CO_2 and CH_4 from six treatments at two sites, estimated as area under the curve of the mean (and median) fluxes from the 5 and 6

UZ-Farm and DT-Centre, respectively, in Season II. These translated to 0.5% and 0.3% of applied N, respectively, during this wet period representing about a third of the year, but with a high level of uncertainty. Sole manure-N contributed relatively fewer N₂O emissions (0.1% of applied N from 120 kg N hm⁻² at the UZ-Farm and <0% for the remaining sole manure treatments). The results also showed with low confidence that the treatment with a combination of N-sources lost 0.04% and 0.01% of applied N as N₂O-N at the UZ-Farm and DT-Centre, respectively, during the wet period of Season II while the 60 kg manure-N hm^{-2} treatment contributed even less N₂O emissions than the control plots that received only 30 kg P hm^{-2} and 30 kg K hm^{-2} annually at both sites (Table 3). In Season III however, the same control plots and 120 kg manure-N hm⁻² gave relatively higher N₂O emission inventories than the rest of the treatments.

Soil emissions of CO2

Soil respiration (mean ranges: $1.8-64.6 \text{ mg m}^{-2} \text{ hour}^{-1} \text{ CO}_2\text{-C}$ at UZ-Farm, and $0.1-90.3 \text{ mg m}^{-2} \text{ hour}^{-1} \text{ CO}_2\text{-C}$ at the DT-Centre), like N₂O showed some consid-

measurements in the second (122 days) and third (116 days) cropping seasons, respectively

Treatment	University of	f Zimbabwe Farn	1	Domboshawa Training Centre		
	N ₂ O-N g hm ⁻²	CO ₂ -C kg hm ⁻²	CH ₄ -C kg hm ⁻²	N ₂ O-N g hm ⁻²	CO ₂ -C kg hm ⁻²	CH ₄ -C kg hm ⁻²
Season II: 2007-2008						
0 kg N hm ⁻² (control)	103 (108)	711 (520)	0.15 (1.28)	324 (308)	774 (786)	5.84 (8.12)
60 kg hm ⁻² (NH ₄ NO ₃ -N)	408 (383)	750 (908)	-0.41 (-1.58)	515 (383)	1155(1142)	-1.70 (-0.15)
120 kg hm ⁻² (NH ₄ NO ₃ -N)	289 (266)	1241(1347)	-0.65 (-3.50)	408 (361)	1574(1408)	-5.53 (-2.50)
60+60 kg hm ⁻² (combined)	157 (121)	742 (771)	-2.51 (-2.16)	335 (306)	967 (936)	-2.61 (-2.48)
60 kg hm ⁻² (manure-N)	59 (45)	896 (903)	-2.58 (-4.35)	257 (243)	928 (887)	0.16 (-1.17)
120 kg hm ⁻² (manure-N)	262 (135)	1219(1176)	1.08 (0.66)	267 (246)	1191(1015)	-1.32 (-2.72)
Season III: 2008-2009						
0 kg N hm ⁻² (control)	63 (93)	384 (375)	0.07 (-0.16)	50 (39)	285 (297)	-0.18 (0.05)
60 kg hm ⁻² (NH ₄ NO ₃ -N)	22 (16)	419 (412)	-0.02 (-0.14)	32 (10)	162 (133)	-0.87 (-0.55)
120 kg hm ⁻² (NH ₄ NO ₃ -N)	18 (17)	452 (475)	-0.72 (-0.34)	31 (26)	234 (167)	-0.33 (-0.53)
60+60 kg hm ⁻² (combined)	37 (37)	639 (641)	0.02 (-0.13)	32 (31)	359 (345)	-0.09 (-0.21)
60 kg hm ⁻² (manure-N)	34 (38)	621 (611)	-0.40 (-0.04)	45 (34)	340 (339)	-0.57 (-0.40)
120 kg hm ⁻² (manure-N)	67 (26)	601 (647)	-0.81 (-1.17)	58 (62)	410 (409)	-0.44 (-0.11)

erable spatial variability and largely similar patterns across the treatments (Fig. 2c,d). The median CO₂ emissions however responded to N-rate (P<0.05) from both N-sources. Soil respiration showed a positive linear relationships (P<0.05) with NH₄NO₃-N rate (r^2 , 0.41 and 0.74 at the UZ-Farm and DT-Centre, respectively) and with manure-N rate (r^2 , 0.46 and 0.66 at the UZ-Farm and DT-Centre, respectively) in Season II, and this was agreeable from at least 73% of this season's data. In Season III the highest CO₂ emissions were from plots that received manure-N, while plots with NH₄NO₃ had lower soil respiration for the greater part of the beginning of Season III (Fig. 2c,d) and overall at the DT-Centre (Table 3).

Soil emissions and consumption of CH₄

The average CH₄ emissions (and consumption) ranged from 1.7–1130 μ g CH₄-C m⁻² hour⁻¹ (consumption: -0.1 to-565 μ g CH₄-C m⁻² hour⁻¹) at the UZ-Farm, and 0.5–1197 μ g CH₄-C m⁻² hour⁻¹ (consumption:

-0.3 to $-773 \ \mu g \ CH_4$ -C m⁻² hour⁻¹) at the DT-Centre (Fig. 2e,f). Methane fluxes showed high spatial variability and varied considerably across seasons (P < 0.05), with Season II having the highest fluxes. A considerable decrease in CH₄ fluxes was noted from all treatments in February at both sites (emissions: 1.9-8.7 μ g m⁻² hour⁻¹; consumptions:-0.1 to-8.3 μ g m⁻² hour⁻¹ CH₄-C), following a major weeding phase and a mid-season rainfall break (Fig. 1a,b). Methane fluxes, unlike other GHG, responded bilaterally to N-rate, but with a high level of uncertainty. When CH₄ emissions and consumption were analysed separately, the magnitude of each increased with N-rate (P < 0.05). At both sites there were positive linear relationships between CH₄ consumption and NH₄NO₃-N rate in Seasons II and III $(r^2, 0.15-0.53)$, and also between CH₄ consumption and manure-N rate $(r^2, 0.12-0.47)$. The relationships were more distinct at the UZ-Farm than at DT-Centre. Similarly, CH₄ emissions (medians), increased with NH₄NO₃-N rate at the UZ-Farm (r^2 , 0.70) in Season II, but the relationship was poor in



Fig. 3 Soil water content (SWC) (a, b) and soil temperature (c, d) from the experimental plots of six treatments at the UZ-Farm and DT-Centre in 3 cropping seasons

Treatment	University of Zimbabwe Farm (UZ-Farm)				Domboshawa Training Centre (DT-Centre)			
	NH4 ⁺ -N mg kg ⁻¹	NO ₃ ⁻ -N mg kg ⁻¹	рН	OC/% %	NH4 ⁺ -N mg kg ⁻¹	NO ₃ ⁻ -N mg kg ⁻¹	рН	OC %
Season II (2007/20	008)							
No N applied (control)	8.1 (2.3-17)	2.3 (1.0-4.1)	5.6 (5.2-6.3)	1.5 (1.2-1.9)	8.5 (1.1-16)	3.2 (0.2-13)	5.0 (4.8-5.2)	0.6 (0.3-0.8)
NH_4NO_3-N , 60 kg hm ⁻²	8.6 (4.2-16)	3.6 (1.0-9.5)	5.7 (5.5-5.9)	1.6 (1.1-1.9)	11 (0.8-19)	3.5 (0.5-14)	4.8 (4.4-5.5)	0.6 (0.3-0.7)
NH_4NO_3-N , 120 kg hm ⁻²	8.4 (2.2-13)	2.8 (1.1-5.1)	5.7 (5.3-6.0)	1.4 (1.0-1.9)	7.5 (0.9-15)	4.3 (0.5-16)	4.8 (4.4-5.4)	0.6 (0.5-0.7)
Combined, 120 kg hm ⁻²	6.8 (2.5-15)	3.5 (1.8-7.6)	5.7 (5.1-6.1)	1.4 (1.0-1.8)	11 (0.9-18)	2.8 (0.3-11)	4.8 (4.5-5.1)	0.5 (0.3-0.7)
Manure-N, 60 kg hm ⁻²	8.1 (2.4-21)	2.6 (1.5-4.3)	5.7 (5.3-6.1)	1.5 (1.2-1.9)	6.2 (0.1-17)	2.3 (0.1-7.6)	5.0 (4.8-5.6)	0.6 (0.4-0.8)
Manure-N, 120 kg hm ⁻²	12 (3.9-24)	4.5 (1.1-9.7)	5.7 (5.2-6.4)	1.5 (1.1-2.3)	6.6 (0.7-16)	4.0 (0.6-12)	4.9 (4.6-5.3)	0.6 (0.4-0.7)
Season III (2008/2	2009)							
No N applied (control)	4.4 (0.1-13)	4.1 (1.8-8.4)	5.5 (5.3-5.8)	1.4 (1.1-1.7)	9.5 (2.5-25)	1.5 (0.1-3.4)	4.8 (4.5-5.1)	0.5 (0.3-0.5)
NH_4NO_3-N , 60 kg hm ⁻²	7.2 (3.1-12)	7.1 (0.1-14)	5.5 (5.2-5.8)	1.6 (1.4-1.8)	6.8 (3.3-10)	3.1 (0.1-6.6)	4.8 (4.4-5.3)	0.5 (0.4-0.7)
NH_4NO_3-N , 120 kg hm ⁻²	10 (1.1-24)	5.7 (1.4-11)	5.6 (5.3-5.9)	1.5 (1.3-1.7)	8.5 (5.8-13)	2.5 (0.1-7.6)	4.6 (4.4-5.1)	0.6 (0.4-0.7)
Combined, 120 kg hm ⁻²	4.8 (1.0-10)	4.7 (1.8-7.7)	5.6 (5.5-5.8)	1.5 (1.2-1.9)	6.7 (1.8-12)	3.7 (0.1-8.8)	4.9 (4.8-5.2)	0.6 (0.4-0.9)
Manure-N, 60 kg hm ⁻²	6.6 (0.1-27)	5.6 (2.1-9.3)	5.7 (5.6-5.8)	1.5 (1.3-1.8)	5.0 (3.4-6.7)	2.7 (0.1-6.5)	4.9 (4.6-5.2)	0.6 (0.3-1.0)
Manure-N, 120 kg hm ⁻²	6.4 (0.1-14)	8.2 (3.9-11)	5.6 (5.3-5.9)	1.7 (1.5-2.0)	7.6 (2.5-12)	3.3 (0.1-8.3)	4.9 (4.5-5.2)	0.6 (0.4-0.8)

Table 4 Means (and ranges) of NH₄⁺-N, NO₃-⁻N, pH and organic carbon (OC) of soils from experimental plots of different treatments measured during the time of gas sampling in Seasons II and III at the UZ-Farm and DT-Centre

Season III at the same site and in both seasons at the DT-Centre (r^2 , <0.2).

The relative net CH₄ fluxes from the six treatments, coarsely estimated over a period of 122 and 116 days during Seasons II and III, respectively, are also given in Table 3. Without disregarding the limited confidence as a result of the high uncertainty the application of NH₄NO₃-N, manure-N and combination of these could have largely increased the capacity of the soils at both sites to act as CH₄ sinks in both Seasons II and III, with the exception of 120 kg manure-N hm⁻² in Season II at UZ-Farm.

Soil factors-GHG fluxes relationships

The variations in soil water content (SWC) and soil temperature during the seasons were more closely related to seasonal rainfall and temperature patterns than to applied treatments (P>0.05) (Fig. 3a,b). The SWC ranged from 6.9–24.2% at the UZ-Farm and 3.3– 13.3% at the DT-Centre, while soil temperature in the 0-0.1 m depth ranged from 19.3-32.8°C at the UZ-Farm and 23.0-30.7°C at the DT-Centre. The average and ranges of soil mineral N (NH_4^+ -N and NO_3^- -N), pH and organic C from the six treatments during Seasons II and III are given in Table 4. Emissions of N₂O, CO₂ and CH₄ were significantly correlated with SWC, soil temperature and pH (P < 0.05), but not with the other measured soil factors. The regression analysis revealed a few distinct relationships between GHG fluxes and SWC or soil pH at the DT-Centre (Fig. 4). Consumption of CH₄ decreased with increasing SWC above 9% which is the general water holding capacity of this soil (Nyamangara et al. 2003b; but see Vogel et al. 1994), while CH₄ emissions increased considerably towards and above this capacity.

Crop productivity-GHG fluxes relationships

The measured crop biomass (grain and aboveground residues), total-N uptake and captured C in maize from six treatments over three seasons at the two sites are shown Fig. 5. In all seasons the productivity of maize significantly increased (P < 0.01) with increasing NH₄NO₃-N rate at both sites, but was less responsive to manure-N rate above the 60 kg N hm^{-2} . Season II had the least yields, particularly at the DT-Centre where much of the rains were concentrated in January (Fig. 1b), while the highest yields were found in Season III at both sites. This was one major contrast with GHG emissions in which the highest fluxes were found in Season II. Total N removed as grain ranged from $18-71 \text{ kg hm}^{-2}$ at the UZ-Farm and 6-66 kg hm⁻² at the DT-Centre, and constituted about 66-87% and 43-83% of total N uptake at the UZ-Farm and DT-Centre, respectively. The amount of C partitioned to grain (825-3190 kg hm⁻² at UZ-Farm and 272-2651 kg hm⁻² at DT-Centre), stover (1340-3762 kg hm⁻² at UZ-Farm and 359-2703 kg hm⁻² at DT-Centre) and shelled-cob (186-562 kg hm⁻² at UZ-Farm and 63-392 kg hm⁻² at DT-Centre), also increased with NH₄NO₃-N rate.

Linking maize productivity (Fig. 5) with N₂O emissions (Table 3) to give some estimated ratios of grain yield, total grain N and total grain C to N₂O fluxes revealed with a high level of uncertainty that the application of NH_4NO_3 largely resulted in relatively lower N₂O emissions per unit of produce compared with the control treatment (Table 5). Similarly, manure-N application had the same effect at 60 kg N hm⁻², but doubling this rate did not show a

further increase in yield per unit loss of N_2 O-N. This was generally consistent at both sites and in both Seasons II and III.

Discussion

Despite the sporadic measurements presented in this paper, the study was among the few reported in the southern Africa region (e.g. Chikowo et al. 2004; Rees et al. 2006) and more so on fertilizer input management since much of the available information has largely been descriptive or only model-based. Much of the attention was therefore focused on relative rather than absolute GHG responses to treatment and budgets. The posed hypothesis that composted manure-N may be better placed as a mitigation option against soil emissions of GHG than mineral fertilizer-N was largely supported with high uncertainty during Season II, particularly for N2O fluxes during the wet period of the year (Table 3). However, for a rational compromise between N₂O emissions and crop productivity NH4NO3-N was relatively more promising (Table 5) on condition that the extremes of rainfall intensity and poor rainfall distribution are not encountered, as was noted during Season III.

The soil emissions of N_2O reported in this study were generally low and consistent with other GHG flux studies in Africa involving continuous cereal or cereal/legume rotations on regular croplands and in some agroforestry systems (e.g. Chikowo et al. 2004; Baggs et al. 2006; Dick et al. 2008; Halvorson et al. 2008). It is possible that the sampling design used



Fig. 4 Relationships between: CH_4 emissions/consumption and SWC (**a**), CO_2 emissions and pH of soils that received NH_4NO_3-N (**b**), and CO_2 emissions and pH of soils that received manure-N (**c**) at the DT-Centre

was not particularly good at fully identifying hotspots of N₂O production associated with the spot application of fertilizer used, and long path-length methods (not available in this study) may be more suitable in such a design. However, in terms of area coverage (assuming each hotspot cover a 0.05–0.08 m radius beyond the reach of a chamber, maize stem position included), the missed area represented only 2–5% of a hm² (calculated from the total sowing stations in a hm²). In a study in Mali where N was applied by broadcasting under continuous cereals applied urea (50 kg hm⁻², 46% N) gave up to 1.5 kg N₂O-N hm⁻² year⁻¹, while added manure gave up to 0.9 kg N₂O-N hm⁻² year⁻¹ (Dick et al. 2008). Apparently, this was one of the very limited studies in Africa that looked into both wet and dry seasons and estimated annual N₂O emissions of 1.54 kg N hm⁻² from mineral fertilizer application and 0.97 kg N hm-2 from animal manure. However, similar urea broadcasting at 60 kg hm⁻² by Kimetu et al. (2006) only yielded up to



Fig. 5 Partitioned aboveground plant biomass (a, b), N-uptake (c, d) and C captured (e, f) by maize grown on experimental plots under six treatments at the UZ-Farm and DT-Centre

2.9 μ g N₂O-N and an annual total of 0.1 kg N₂O-N hm⁻² that is less than some of the N₂O inventories from our study. There could therefore be a problem of heterogeneity in N inputs for area based measurements and in some parts of Europe some grazed pastures can have cattle urine patches that add 1000 kg N hm⁻², and yet many N₂O measurements studies are carried out using randomly located chambers (Rees RM 2010, personal communication).

Methane fluxes under the six treatments were the most inconsistent as N input stimulated both emissions and consumption of CH4 with Seasons II and III at both sites. The overall net fluxes (Table 3) would therefore reflect the relative net influence that also strongly depended on SWC variability within each season (Fig. 4a). The increase in CH₄ emissions by soil with addition of water and N were also noted by Mosier et al. (2003), who attributed this to increased soil respiration, conditions under which a microbial population developed that tended to increase the utilization of atmospheric CH₄. However, Vanitchung et al. (2005), who reported CH₄ emissions of up to 61.5 mg CH₄-C m⁻² day⁻¹ from N-fertilized upland soils under maize, argued that NH₄⁺-N inhibits CH₄ consumption and high SWC can limit O2 and CH4 diffusion between atmosphere and soil, thus, reducing CH_4 consumption. In our study there was no significant correlation between NH_4^+ -N and CH_4 fluxes. A review by Bodelier and Laanbroek (2004) however, showed that N can stimulate both emissions and consumption of CH_4 in soil, and indicated that mineral-N seems to be a prerequisite for the occurrence of CH_4 consumption and might initiate and stimulate the enzymatic machinery in a yet unknown way.

Conclusion

The level of uncertainty with reference to the response of GHGs to mineral-N and manure-N was very high due to sporadic measurements and the limited number of observations from the region in general. Without disregarding this limited confidence the posed hypothesis that composted manure-N may be better placed as a mitigation option against soil emissions of GHG than mineral fertilizer-N was largely supported by N₂O fluxes during the wet period of the year. It may be possible to reduce the overall contribution of NH₄NO₃-N to N₂O emissions per unit amount of productivity by increasing the fertilizer rate to 120 kg N hm⁻², the local general recommendation for N fertilizer for maize, provided

Treatment	UZ-Farm			DT-Centre			
	Yield	Total-N	Total-C kg g ⁻¹ 1	Yield N ₂ O-N	Total-N	Total-C	
Season II (2007/2008)							
0 kg N hm ⁻² (control)	14	0.17	8.0	1	0.02	0.8	
NH ₄ NO ₃ -N, 60 kg hm ⁻²	7	0.08	3.7	2	0.02	0.9	
NH ₄ NO ₃ -N, 120 kg hm ⁻²	15	0.20	8.6	4	0.06	2.1	
Combined, 120 kg hm ⁻²	29	0.35	17	5	0.05	2.6	
Manure-N, 60 kg hm ⁻²	43	0.50	25	4	0.05	2.4	
Manure-N, 120 kg hm ⁻²	12	0.16	6.8	4	0.05	2.2	
Season III (2008/2009)							
0 kg N hm ⁻² (control)	42	0.47	25	31	0.40	18	
NH ₄ NO ₃ -N, 60 kg hm ⁻²	188	2.36	108	100	1.32	58	
NH ₄ NO ₃ -N, 120 kg hm ⁻²	290	3.93	164	148	2.13	86	
Combined, 120 kg hm ⁻²	149	1.93	86	118	1.61	68	
Manure-N, 60 kg hm ⁻²	116	1.35	67	70	0.88	40	
Manure-N, 120 kg hm ⁻²	71	0.86	41	55	0.68	32	

Table 5Estimated ratios of grain yield, total grain-N and total grain-C to soil emissions of N_2O over an average period of 122 and116 days in Seasons II and III, respectively at two sites

the season can support substantial crop productivity. In future studies it will be necessary to increase temporal resolution, number of gas samples per flux and spatial representativeness of GHG measurements.

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