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Nonlinear response of nitric oxide fluxes to fertilizer inputs and the impacts of agricultural intensification on tropospheric ozone pollution in Kenya

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Abstract

Crop yields in sub-Saharan Africa remain stagnant at 1 ton ha^{-1}, and 260 million people lack access to adequate food resources. Order-of-magnitude increases in fertilizer use are seen as a critical step in attaining food security. This increase represents an unprecedented input of nitrogen (N) to African ecosystems and will likely be accompanied by increased soil emissions of nitric oxide (NO). NO is a precursor to tropospheric ozone, an air pollutant and greenhouse gas. Emissions of NO from soils occur primarily during denitrification and nitrification, and N input rates are a key determinant of emission rates. We established experimental maize plots in western Kenya to allow us to quantify the response function relating NO flux to N input rate during the main 2011 and 2012 growing seasons. NO emissions followed a sigmoid response to fertilizer inputs and have emission factors under 1% for the roughly two-month measurement period in each year, although linear and step relationships could not be excluded in 2011. At fertilization rates above 100 kg N ha^{-1}, NO emissions increased without a concomitant increase in yields. We used the GEOS-CHEM chemical transport model to evaluate local impacts of increased NO emissions on tropospheric ozone concentrations. Mean 4-hour afternoon tropospheric ozone concentrations in Western Kenya increased by up to roughly 2.63 ppbv under fertilization rates of 150 kg N ha^{-1} or higher. Using AOT40, a metric for assessing crop damage from ozone, we find that the increased ozone concentrations result in an increase in AOT40 exposure of approximately 110 ppbh for inputs of 150 kg N ha^{-1} during the March–April–May crop growing season, compared with unfertilized simulations, with negligible impacts on crop productivity. Our results suggest that it may be possible to manage Kenyan agricultural systems for high yields while avoiding substantial impacts on air quality.

Keywords: African Green Revolution, fertilizer, greenhouse gas, nitrogen, soils, tropical agriculture

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Food security is a perennial challenge in sub-Saharan Africa. While global cereal production has nearly tripled since 1960, it has not increased in sub-Saharan Africa, where yields remain under 1 ton ha^{-1} (Hazell & Wood, 2008). Food shortages in sub-Saharan Africa affect 260 million people (Sanchez, 2010), more than twice as many as they did in 1970 (Sanchez, 2002). Much of the stagnation in food production can be attributed to extremely low fertilizer use over the last several decades [less than 7 kg nutrients ha^{-1} (UN, 2005)], which, in turn, has led to large negative nutrient balances, extensive mining of nutrients from soils by crops and declining soil fertility (Vitousek *et al*., 2009). Increased use of mineral fertilizer in these agricultural soils is seen as a critical step in increasing food security and improving soil fertility in sub-Saharan Africa (Vanlauwe & Giller, 2006). The Alliance for a Green Revolution in Africa (AGRA) has been working to increase fertilizer use sixfold across the continent within this decade, to an average of 50 kg ha^{-1} yr^{-1} (AGRA 2009). By later in the century, nitrogen (N) inputs may reach recommended rates, which vary regionally up to 120 kg N ha^{-1} yr^{-1} (Nziguheba *et al*., 2010).

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This increase in fertilizer use is likely to represent the largest perturbation to the nitrogen cycle in sub-Saharan Africa in the 21st century. Using existing estimates of cereal cropland in 2000 (Monfreda *et al.*, 2008) and assuming that existing fertilization rates are 5 kg N ha^{-1}, which should be conservative (Hazell & Wood, 2008), an increase in reactive N inputs of over 6 Tg N yr^{-1} would be needed just to reach application rates of 75 kg N ha^{-1} yr^{-1} on land already in cereal production. Such an increase would still fall considerably short of application rates in other parts of the world, which typically range from 100 kg N ha^{-1} to over 300 kg N ha^{-1} (Hazell & Wood, 2008; Monfreda *et al.*, 2008; Vitousek *et al.*, 2009), and excludes N inputs associated with future expansion of agriculture in the region, as well as inputs to noncereal crops. These increased N inputs will be accompanied by inevitable increases in soil emissions of nitric oxide (NO), a precursor to tropospheric ozone (IPCC, 2001). In soils, NO is produced during the microbial oxidation of ammonium to nitrate and during abiotic reactions; it is also a reaction intermediate in the microbial reduction of NO_3^- to atmospheric N_2 (Firestone & Davidson, 1989). In the 'hole-in-the-pipe' model (Firestone & Davidson, 1989), fluxes of NO and N_2O are controlled primarily by rates of N cycling (the 'flow' through the pipe) and secondarily by environmental factors such as oxygen concentration, pH, and soil diffusivity (which control the size of the 'holes' in the pipe, Davidson *et al.*, 2000). The increased 'flow' of N caused by addition of fertilizer tends to increase the rates of trace N gas emissions, sometimes by an order of magnitude or more (Firestone & Davidson, 1989).

Considerable attention has been given in the last 10 years to understanding how soil emissions of the greenhouse gas nitrous oxide (N_2O) change in response to incremental increases in N inputs (e.g., McSwiney & Robertson, 2005; Hoben *et al.*, 2010; Van Groenigen *et al.*, 2010; Shcherbak *et al.*, 2014; Hickman *et al.*, 2015). These studies revealed that the assumption that N_2O is emitted as a constant fraction of the added N – an assumption that underlies IPCC Tier I methods for estimating national greenhouse gas inventories – is incorrect. Instead, N_2O tends to be emitted as a nonlinear function of N inputs: At higher N input rates, a larger proportion of the added N is emitted as N_2O than at lower N input rates, particularly after crop N demand is met. Most N gradient studies find that N_2O emissions increase as an exponential function of N input rates (e.g., McSwiney & Robertson, 2005; Hoben *et al.*, 2010; Van Groenigen *et al.*, 2010; Hickman *et al.*, 2015; although note that 77 of the 233 site-years evaluated by Shcherbak *et al.* (2014) exhibited no change or a decline in the proportion of N inputs lost as N_2O with increasing input rates).

In spite of the attention paid to N_2O, the functional relationship between NO emissions and the amount of N added to soil has not been explored in depth. To date, measurements of NO in response to multiple rates of N additions are limited to one- or two-day dose–response studies in forests (Hall & Matson, 1999; Hall *et al.*, 2004) and one study in an agricultural system (Matson *et al.*, 1998), although that study reported emissions as the sum of NO and N_2O for the relevant treatments. That study used two fertilization rates (180 and 250 kg N ha^{-1}), which can be sufficient information to deduce whether the response is linear or nonlinear (Shcherbak *et al.*, 2014), but is not sufficient to identify the shape of the response. In addition, it provides no information on how NO fluxes may change in response to incremental increases in N additions below 180 kg N ha^{-1}, levels relevant to fertilizer use in sub-Saharan Africa. An early literature review of NO emissions found a linear relationship between NO and fertilizer inputs (Veldkamp & Keller, 1997), but did not employ a modern meta-analytical approach, relied on a small number of studies, and did not evaluate within-site responses to increasing N inputs (e.g., Shcherbak *et al.*, 2014). Veldkamp & Keller further stated that the result should be interpreted with caution and care as only 12 points were used and uncertainty was very high (Veldkamp & Keller, 1997). Bouwman (2002) and Stehfest & Bouwman (2006) conducted a broader literature review in which they binned data on both N_2O and NO emission responses and evaluated their drivers. Management was a key control: Emissions generally increased in response to increasing fertilizer rates, although the data exhibited high levels of variability. In fact, in the 2006 analysis, any level of fertilizer use above 1 kg N ha^{-1} was not significantly different from any other, reflecting high levels of variability in emission responses across studies (Stehfest & Bouwman, 2006). Higher soil organic matter and nitrogen content also lead to higher emissions, as did the length of the experiments and applying fertilizer by broadcasting rather than incorporating it (Bouwman, 2002; Stehfest & Bouwman, 2006).

In addition, while tropical agriculture is among the largest global contributors to fluxes of NO (Davidson & Kingerlee, 1997), NO emissions from agriculture in sub-Saharan Africa are very poorly understood. The only published field measurements of NO fluxes from African agricultural soils are from a preliminary study presenting data from a single season with a 16 kg N ha^{-1} treatment (Meixner *et al.*, 1997).

Understanding how NO emissions increase in response to N inputs is particularly important in the context of the increasing N inputs that will accompany agricultural intensification in the region, because of their potential to increase tropospheric ozone

concentrations. Tropospheric ozone formation in much of sub-Saharan Africa is sensitive to concentrations of atmospheric NO_x [NO + nitrogen dioxide (NO_2)]. Pulses of NO emissions from soils have been shown to cause large increases in tropospheric ozone concentrations in the region (Jaeglé *et al*., 2004), suggesting that increases in NO emissions from African agriculture can be expected to affect tropospheric ozone pollution. In other parts of the world, soil NO emissions from agricultural systems have been shown to substantially increase regional ozone levels (Aneja *et al*., 1995; Hall *et al*., 1996; Oikawa *et al*., 2015), and other anthropogenic impacts on soil NO emissions have been shown to have the potential to increase regional ozone concentrations (Hickman *et al*., 2010).

In addition to being a greenhouse gas, tropospheric ozone damages human health, and its potential impacts on agriculture are larger than the direct impacts of climate change in some regions, with projected global annual yield reductions for some crops of up to 26% by 2030 (Avnery *et al*., 2011). Indoor and outdoor air pollution is now the largest environmental health risk globally (WHO, 2014), with anthropogenic ozone contributing to roughly half a million premature deaths annually (Silva *et al*., 2013). Anticipating the potential effects that the order-of-magnitude increases in N inputs may have on air quality could be important for managing the impacts of agricultural intensification.

In this study, we address two questions. First, we address the question of whether NO emissions increase nonlinearly in response to N inputs by conducting a two-year fertilizer response trial in western Kenya, in which we measured NO flux responses to treatments of 0, 50, 75, 100, 150, and 200 kg N ha^{-1}. Second, we address the question of how agricultural intensification may affect tropospheric ozone concentrations and crop productivity in western Kenya by conducting a sensitivity analysis using the GEOS-CHEM chemical transport model.

Materials and methods

Experimental maize (*Zea mays*) plots were established in January 2011 in Yala, Kenya (34.51°E, 0.10°N, 1350 m above sea level, 1750-mm annual rainfall). The site was converted to regular agricultural use in the 1960s or 1970s, although it was likely originally converted in the early 20th century. The site is owned by the Kenya Broadcasting Corporation, and so access is generally more restricted than other fields in the region, potentially limiting grazing activity. It is possible that grazing occurred during fallow years and seasons, but there is no direct evidence of grazing, and measurements of total C and N for the experimental fields display relatively low levels of variability (total N ranged from 0.18% to 0.24%; total C ranged from 1.84% to 2.33%, with standard deviations of 0.01 and 0.14, respectively). Fields were left fallow from 1979 to 1989 and from 1994 to 2007; in other years maize, beans (multiple genera within the Fabaceae) and sweet potatoes (*Ipomoea batatas* (L.) Lam.) were grown by local farmers without mineral fertilizer. Soils are Oxisols derived from a Nyanzan basalt, with 12.4% silt, 52.2% sand, 35.2% clay, 1.9% organic C, 0.11% N, 62 μg g^{-1} Mehlich-III extractable P, a pH value of 6, and a cation exchange capacity of 15.4 meq 100 g^{-1}. Soil C and total N levels are comparable to levels in cropland in adjacent villages [1.87% C, 0.17% N in 2004, n = 45 (Clare Sullivan, personal communication)]. In Yala, maize yields averaged 5.1 tons ha^{-1} under a development program providing subsidized seed and fertilizer (Nziguheba *et al*., 2010), well in excess of the 1.8 tons ha^{-1} average for Kenya (Schroeder *et al*., 2013).

Experimental design

The experiment was conducted in 2011 and 2012 during the region's major growing season, which occurs during the first half of the year. Two seeds were planted in each planting hole at the start of the long rainy season on March 24, 2011, and April 5, 2012, and thinned within 2 weeks of emergence. An additional maize crop was sown in the plots without added fertilizer at the start of the short rainy season in October 2011. The same plots were used in 2011 and 2012, and received the same fertilizer treatments in both years.

Within each plot, rows were spaced at 0.75-m intervals, and plants were seeded by hand at 0.30-m intervals within rows following regional recommendations, for a plant population of 44 444 plants ha^{-1}. Kenya Seed Company hybrid maize varieties were used (WH505 in 2011 and WH403 in 2012); 90% of farmers use hybrids in the highland tropics and moist transitional zones of Kenya (Schroeder *et al*., 2013).

In fertilized plots, 1/3 of the fertilizer N was applied as diammonium phosphate (18% N) at planting (March 24, 2011, and April 5, 2012) within 5 cm of each seed, and the remaining 2/3 was applied as urea (46% N) 5 weeks later (April 26, 2011, and May 7, 2012), within 5 cm of each maize stem (Fig. 1). The field was weeded once during the week before the topdressing application and again several weeks later. Maize plants were harvested the weeks of August 7, 2011, and August 20, 2012.

Fertilizer treatments were applied in a randomized complete block design. Six levels of fertilizer treatment (0, 50, 75, 100, 150, and 200 kg N ha^{-1}) were applied in four blocks, each block consisting of six plots and each plot measuring 6 m × 3 m. It should be emphasized that application rates represent the amount of fertilizer applied to the entire plot (i.e., for a given treatment, the same amount of fertilizer is applied to a plot as would have been applied if the fertilizer were broadcast across the entire plot). Because fertilizer is targeted at the location of each seed and plant, the fertilizer can be thought of as being applied to these locations at rates that are effectively several times higher than the treatment level.

NO measurements

NO fluxes were measured from PVC chambers designed by Louis Verchot (personal communication). The chambers were

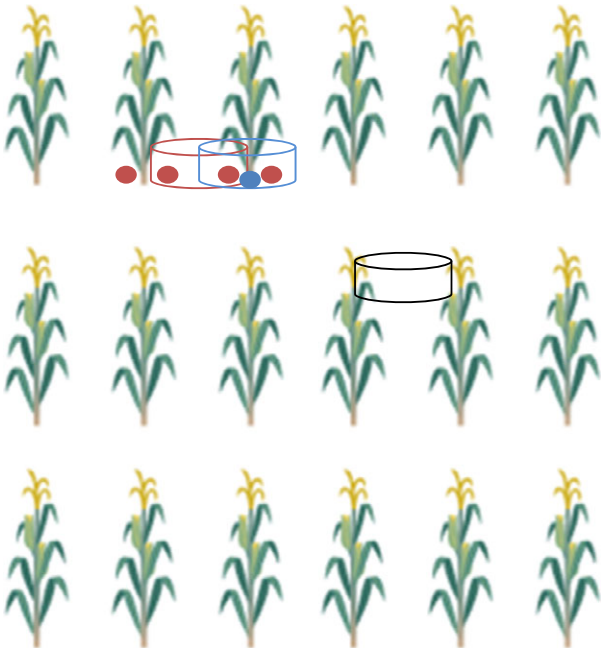

Fig. 1 Fertilizer and chamber positions. Maize rows were 75 cm apart, and plants were seeded every 30 cm within rows. At planting, fertilizer was applied with the seed (blue circle) of each plant, and a chamber was centered over the seeding hole (blue chamber). At topdressing, fertilizer was applied on either side of the plant stem (red circles), and the chamber was repositioned between maize plants, so that it covered all soil where one plant's worth of fertilizer was applied (red chamber). An additional chamber was positioned between rows in one plot within each block (black chamber).

25.5 cm in diameter, and chamber heights when covered and sealed ranged from 8 to 12 cm when covered, resulting in chamber volumes of ~4–6 L. The chambers did not include internal fans. One chamber was placed within a maize row in each treatment of each block (for four replicates per treatment). Measurements were conducted between March 25 and May 31 in 2011 and between April 8 and June 4 in 2012 (Table S1). Sampling was conducted at least five times during the 7 days following fertilizer applications and at least weekly during the rest of the measurement period. The measurement period ended 4–5 weeks after the second fertilizer application, when fluxes from fertilized plots were still elevated relative to the control. To capture fertilizer-induced fluxes, at planting each PVC chamber was centered over a planting station, where it remained in place until the second fertilizer application (Fig. 1). Just prior to the second fertilizer application, each chamber was moved from its position over a plant to a position between two maize plants within a row (Fig. 1); the chambers then remained in place until the end of the measurement period. Each chamber covered soil that was fertilized at the rate determined for a single plant for a given treatment. In each block, an additional chamber was inserted between maize rows in a randomly selected plot in 2011, and in two 0 kg N ha^{-1} and two 200 kg N ha^{-1} plots in 2012. Tests from 2012 showed that there were no fertilizer treatment effects on fluxes measured from these chambers ($P > 0.05$, where P is the P value, representing the statistical probability of the observed data given that the null hypothesis that there is no difference between groups is true), and they were considered representative of fluxes from soils between maize rows for all plots.

Emissions of NO were measured using a portable chemiluminescent detector that measures NO_2 and is equipped with a CrO_3 filter that can convert all NO to NO_2 (Unisearch Associates LMA-3D, Concord, ON, Canada). The flow-through chambers were fitted with two Swagelok inlets. The LMA-3D drew sample air through Teflon-coated tubing attached to one inlet. The second inlet was connected by Teflon-coated tubing to a column filled with Purafil, to scrub incoming ambient air of NO_x. Measurements of initial NO_2 concentrations were made, following which sample gas was passed through the CrO_3 filter before analysis, to allow for measurements of NO + NO_2 (NO_x) concentration. The total NO_x concentration was measured every 15 s for 5 min, following which the CrO_3 filter was taken off-line, and the final NO_2 concentration was measured. The initial and final NO_2 concentrations were used to estimate the linear change in NO_2 concentration within the chamber over time. The change in NO concentration over time was calculated by subtracting the change over time in NO_2 concentration from the change over time in NO_x concentration. Measurements were made between 09:00 hours and 13:00 hours. On each day, standard curves were conducted at least three times in the field (immediately before the day's measurements commenced, immediately after the day's measurements were completed, and at least once in between) using a standard gas with a known NO concentration (0.0992 ppm; Scott-Marin Co., Riverside, CA, USA) and corrected for the effects of temperature, pressure, chamber volume, changes in the N oxide mixing ratio, and changes in O_2 mixing ratios caused by different ratios of O_2-free standard gas and scrubbed ambient air (Hall *et al.*, 2008). Standard curves were constructed by using coupled rotameters to mix ambient air drawn through a Purafil column to scrub it of ambient NO_x with our NO standard, to produce 11 different NO concentrations. Linearity of the standard curves had R^2 values consistently above 0.99 in 2011 and above 0.965 in 2012, with three exceptions having values of at least 0.9. The linear relationship between the LMA-3D detector readings (mV) and standard gas concentration (ppb) was used to calculate chamber NO_x concentrations, accounting for linear drift in readings between standard curves.

Cumulative emissions represent the total emissions over a given period of time. Cumulative emissions were estimated by summing linearly interpolated daily emission rates and were used to derive a mean daily flux. Estimates of field-scale emissions were calculated using a weighted average of cumulative fluxes from chambers placed within rows and chambers placed between rows:

$$\text{Cumulative field-scale emissions}_k = \sum_{l=1}^{n}(0.227(\text{chamber}_{kl}) + 0.773(\text{between-row chamber}_l))/n \quad (1)$$

where chamber_{kl} is the flux (g NO–N ha^{-1}) from the chamber placed in the kth fertilizer treatment (or the control) and lth

block, between-row chamber$_l$ is the flux (g NO–N ha^{-1}) from the chamber placed between rows in the lth block, and where n is the number of replicate blocks. The proportion of the field allocated to fertilizer-induced emissions (0.227) is equal to the proportion of the field area described by a 12.75 cm radius extending from each stem (the radius of the chambers used). We assumed that chambers covering fertilizer applications captured all fertilizer-related emissions and that chambers placed between rows were representative from the remaining soil area in each plot. However, a gap remained between the edge of this 12.75 cm radius and the edge of the area covered by chambers placed between maize rows, and so it is possible that fertilizers affected soils outside of the area described by the 12.75 cm radius but not the soils covered by the between-row chambers (Fig. 1), which would result in an underestimate of the actual fertilizer-induced flux.

Emission factors for the loss of N fertilizer as NO were calculated using the cumulative field-scale emission estimates as follows: The difference between cumulative flux for the control and the cumulative flux for a given rate of fertilizer application was divided by the rate of fertilizer application and multiplied by 100:

$$\mathrm{EF} = (\mathrm{NO}_k - \mathrm{NO}_{\mathrm{control}})/k \times 100 \quad (2)$$

where EF is emission factor, NO is the estimated field-scale NO flux in kg NO–N ha^{-1}, k is the treatment in kg N ha^{-1}, and control is the unfertilized control treatment.

Mean daily field-scale emissions, which were used to develop scaling factors for NO emissions in GEOS-CHEM, were calculated by dividing the cumulative field-scale flux by the number of measurement days assuming no diurnal variation in flux. It is possible that this assumption may overestimate the mean daily flux, although diurnal variation in N oxide fluxes is often absent in tropical agroecosystems (Le Roux *et al*., 1995; Crill *et al*., 2000).

Analyses and modeling

Chambers were moved prior to the second fertilizer application from a position over a planting station (and over a plant) to a position between planting stations, leading to a change in the experimental unit (the soil area observed) and making separate analyses for the two periods necessary. To avoid pseudoreplication and issues with repeated measures of the same experimental unit, only the mean daily flux for each replicate during each time period (the period before the second fertilizer application and the period after) was used as a response variable (e.g., McSwiney & Robertson, 2005).

Linear, exponential, quadratic, sigmoid, and step functions describing the response of trace N gas emissions to N fertilization rates were compared:

$$Y_k = a + b \times N_k \quad (3)$$

$$Y_k = a \times e^{(b \times N_k)} \quad (4)$$

$$Y_k = a + b \times N_k + c \times N_k^2 \quad (5)$$

$$Y_k = (a \times b \times e^{(c \times N_k)})/(a + b \times (e^{(c \times N_k)}) - 1) \quad (6)$$

$$Y_k = a \text{ for } N < b; \quad Y_i = c \text{ for } N > b \quad (7)$$

where Y_k is the mean daily NO flux (in ng N cm^{-2} h^{-1}) at the kth fertilization rate (N, in kg N ha^{-1}), and where a, b, and c are nonzero constants. Likelihood estimates of the model parameters were determined by simulated annealing using the anneal function in the likelihood R package developed by Lora Murphy (http://www.sortie-nd.org/lme/lme_R_code_tutorials.html). Model comparison was conducted using Akaike's information criterion (AIC) and likelihood ratio-based r^2 values.

The GEOS-CHEM (version 9-1-3) chemical transport model was used to evaluate the impacts of fertilizer-induced NO emissions on atmospheric chemistry. The global model is run with a one-hour time step at a resolution of 4° latitude by 5° longitude with 47 vertical layers and a fully coupled ozone–$\mathrm{NO_x}$–volatile organic compound (VOC)–aerosol chemistry mechanism (Park *et al*., 2004). The model was run from June 2010 to December 2011, with 2010 as spin-up. The model spin-up started with initial emissions, transport, transformation, and deposition of chemical species in the atmosphere driven by meteorological data, which was then run until it reaches equilibrium state. Typically, this process takes several simulated months to years depending on model grid resolution. In this case, spin-up takes 6 months to complete.

The Berkeley-Dalhousie Soil $\mathrm{NO_x}$ Parameterization (BDSNP) scheme was employed to simulate fertilizer-induced NO emissions (Hudman *et al*., 2012). The BDSNP global model for soil NO emissions is designed to better resolve the episodic nature of soil NO emissions driven by meteorological conditions and fertilizer applications. In BDSNP, NO emissions are explicitly influenced by soil moisture history. This allows for representation of the biogeochemistry that induces emission pulses at the onset of precipitation following dry spells that is driven by both soil moisture and the length of the preceding dry spell. The scheme also includes a detailed spatial and temporal representation of N inputs from both chemical/manure fertilizer and atmospheric N deposition based on Potter *et al*. (2010).

The BDSNP scheme models soil NO fluxes using the following equation

$$E_{\mathrm{NO}} = A_{\mathrm{biome}}(A_{\mathrm{w,biome}}, N_{\mathrm{avail}}) \times f(T) \times g(\theta) \times P(l_{\mathrm{dry}}), \quad (8)$$

where E_{NO} represents the soil NO emission flux (ng N cm^{-2} s^{-1}); A_{biome} is a biome-specific emission coefficient; $A_{\mathrm{w,biome}}$ is the wet biome emission factor from Yienger & Levy (1995) as updated by Steinkamp & Lawrence (2011); N_{avail} is the N available for NO production (ng m^{-2}), including the standing pool N, fertilizer, and deposition N; $f(T)$ and $g(\theta)$ are empirically derived values for the dependence of soil NO flux on soil temperature and moisture, respectively; T and θ are soil temperature and water-filled pore space; $P(l_{\mathrm{dry}})$ is a soil pulsing factor, in which the magnitude of a precipitation-induced NO pulse is a function of the dry spell (l_{dry}).

To understand the sensitivity of tropospheric ozone concentrations to fertilizer-induced emissions of NO from soils in

western Kenya, we conducted model simulations for five fertilization rates (50, 75, 100, 150, and 200 kg N ha^{-1}) plus an unfertilized control, in which simulated emissions were constrained by our field measurements of NO.

We implemented the field-measured NO fluxes in GEOS-CHEM to assess the impacts of N inputs on atmospheric ozone concentrations in western Kenya. GEOS-CHEM simulates soil emissions in the form of NO and its interconversion with NO_2 after it is emitted to atmosphere. Soil emissions in GEOS-CHEM are in the form of NO, which then experiences conversion to NO_2 under canopy reduction, including the uptake of NO_2 by canopies. Within a given grid cell over a model time range (e.g., a growing season), we model the average changes in soil NO flux relative to the baseline BDSNP flux that is equivalent to the change in the average daily flux observed at a given fertilizer application rate in the field experiment relative to the unfertilized control. To be specific, the temporal variation of model flux at the hourly time step (t) is represented by the following equation in the model:

$$(E_k)_{i,j,t} = (E_0)_{i,j,t} + (M_k - M_0) \times (\mathrm{AGFRC})_{i,j} \times \frac{(E_0)_{i,j,t}}{(\bar{E}_0)_{i,j}}, \quad (9)$$

where k is the fertilizer application rate; E_0 denotes control model soil NO emission flux (the baseline BDSNP calculated emission without fertilizer application); $\bar{E}_0$ represents mean soil NO flux from model control runs for that grid cell, averaged over the simulation period, with both calculated directly from the default BDSNP scheme; M_k represents mean measured fertilizer-induced NO emission flux (for both 2011 and 2012) for a specific k; and M_0 is the mean field measurement NO emission flux with zero fertilizer application rate from the years 2011 and 2012; AGFRAC denotes the agricultural fraction for each grid cell following MODIS/Koppen landtypes.

Using this additive equation allows us to implement the relative effects of fertilizer applications on NO fluxes as measured in the field (presented here as mean daily emissions) while preserving both the spatial variation and temporal variation (represented by $(\bar{E}_0)_{i,j}$ and $(E_0)_{i,j,t}$) of NO fluxes as calculated with the BDSNP scheme. The additive equation also ensures that for the total fertilizer NO flux over Yala, West Kenya, the relative difference in fertilizer-induced NO flux between a model run for a given fertilization rate and the control run is the same as the relative difference between the observed fluxes for the two corresponding fertilization rates in the field experiment. GEOS-CHEM does not vary VOC emissions from cropland as a function of crop productivity.

Although the model is run globally, we present results only for the local atmosphere, in the grid cell containing our experimental plots. We propagated uncertainty from the field measurements into the simulated impact estimate by conducting additional simulations in which the mean NO flux for a given treatment (M_k) was replaced with the 95% confidence intervals in measured NO fluxes during the period following the second fertilizer application.

The AOT40 cumulative exposure parameter is a metric for assessing crop damage from ozone, where the decline in crop yield is a function of the crop's cumulative exposure (in ppbh) to ozone concentrations above 40 ppbv over a three-month period during the growing season (Mills *et al.*, 2007). For the estimation of the AOT40 critical load, we used model output of the 4-hour mean O_3 concentrations for the period from 13:00 to 17:00 local time. The daily AOT40 for grid cell i is calculated as $(C_i - 40) \times 4$, where C_i is the mean hourly ozone concentration for the four-hour period between 13:00 and 17:00 local time in ppbv h. When C_i is less than 40 ppbv, the AOT40 value for that day in that grid cell equals 0. The calculated AOT40 critical load for a grid cell was the sum of ppbv h exceedance of 40 ppbv during the three-month period evaluated. We present AOT40 results only for the grid cell containing our experimental plots.

Frequentist analyses were conducted to provide traditional evaluations of treatment differences. We conducted a mixed-model ANOVA on mean NO flux following the first application (9 days of measurements from March 23 to April 13) and a second mixed-model ANOVA on mean NO flux following the second fertilizer application (all subsequent measurements). Response variables were log transformed when necessary to meet the assumptions of ANOVA. Post hoc tests using the Benjamini, Hochberg, and Yekutieli method for controlling the false discovery rate were conducted for significant ANOVA results to identify treatment differences. All analyses were conducted using the R programming language.

Results

Fertilization rate did not affect NO emissions for the period between the first and second fertilizer applications in either 2011 or 2012, but there was an overall effect of fertilization rate on mean NO fluxes in both years following the second fertilizer application ($P < 0.0001$ in both years; Fig. 2). A sigmoid function provided the best fit to the data in both 2011 and 2012 for the period following the second fertilizer application, but the improvement over linear and step models was only sufficient to choose among models in 2012 (Table 1; Fig. 3).

Mean fluxes from fertilized soils in the 150 and 200 kg N ha^{-1} treatments following the second fertilizer application were higher than fluxes from all other treatments ($P < 0.02$), with mean fluxes of 74.1 and 71.2 g NO–N ha^{-1} day^{-1} for the 200 kg N ha^{-1} treatments in 2011 and 2012, and 84.1 and 70.2 g NO–N ha^{-1} day^{-1} for the 150 kg N ha^{-1} treatment, compared to 1.9 and 3.2 g NO–N ha^{-1} day^{-1} from unfertilized soils. This result is in line with the likelihood parameterization of the step model, which identified a threshold between 100 and 150 kg N ha^{-1} in both years (Fig. 3). Although the measurement periods before and after the second fertilizer application were roughly identical in duration, the majority of fluxes in all treatments except for the 2011 control occurred following the second fertilizer application, including over 90% of emissions from treatments of 150 kg N ha^{-1} or more in 2011 and from treatments of 100 kg N ha^{-1} or more in 2012. Emission factors were less than 1% of the added

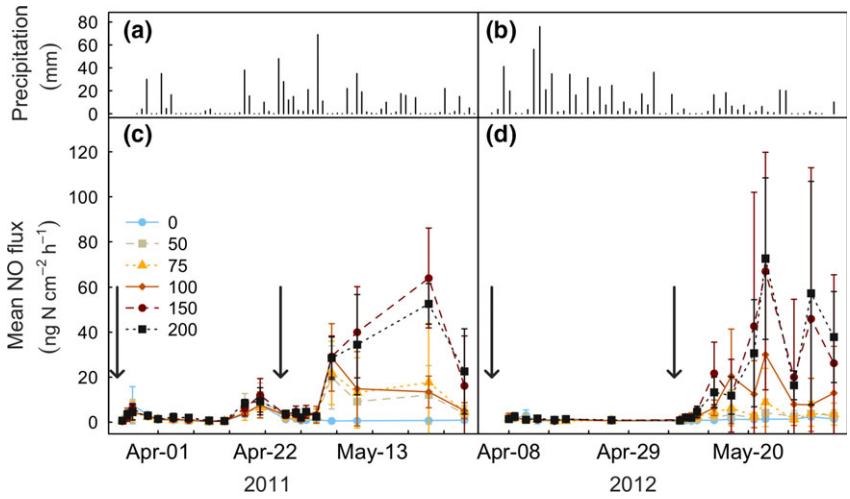

Fig. 2 NO fluxes following fertilization in 2011 and 2012. Time series of daily precipitation (a and b) and NO flux for each treatment (c and d) during measurement periods in 2011 and 2012. Arrows indicate dates of fertilizer application and error bars represent the standard error of the treatment means on each measurement date.

Table 1 Model parameters, R^2, and corrected AIC values for models describing the mean NO flux response to N fertilization rate (F) for the 5–6 weeks following the second fertilizer application to maturity in 2011 (April 26, 2011, to May 31, 2011, and May 7, 2012, to June 4, 2012)

	2011			2012		
Model	Parameter estimates	AIC	R^2	Parameter estimates	AIC	R^2
Linear ($a + (b \times F)$)	a = 1.10 b = 0.413	217.0	0.65	a = −7.70 b = 0.412	227.4	0.55
Exponential ($a \times e^{(b \times F)}$)	a = 15.7 b = 0.00844	221.4	0.58	a = 9.31 b = 0.0108	229.0	0.52
Sigmoid ($a \times b \times e^{(c \times F)})/(a + b \times (e^{(c \times F)} - 1)$)	a = 84.8 b = 4.25 c = 0.0304	216.9	0.68	a = 72.8 b = 0.154 c = 0.0583	225.0	0.62
Step b for $F < a$, c for $F > a$	a = 125 b = 21.5 c = 79.0	218.0	0.67	a = 125 b = 12.3 c = 70.8	228.0	0.58
Quadratic	a = 23.2 b = 0.481 c = −0.000351	218.9	0.65	a = −2.93 b = 0.247 c = 0.000826	228.8	0.56

Parameter estimation for the models was conducted using simulated annealing.

fertilizer N lost as NO during the measurement period in either year across all treatments (Table 2). There was a weak positive relationship between precipitation and NO flux during the first month of the growing season (R^2 = 0.19 and 0.13 in 2011 and 2012, $P < 0.05$) and a weak negative relationship after the second fertilizer application (R^2 = 0.08 and 0.06 in 2011 and 2012, $P < 0.05$; Fig. S2). Soil nitrate concentrations and potential net nitrification varied in response to fertilizer application in 2011, and a measure of nitrate production increased in response to fertilizer applications in 2012 (Hickman *et al.*, 2015).

In both years, grain yields responded to fertilizer additions, increasing from roughly 6 to roughly 9 tons ha^{-1}, with increases generally leveling off after additions of 100 kg N ha^{-1} (Hickman *et al.*, 2015). This leveling of grain yields represents a threshold above which larger volumes of NO are emitted without any change in grain production (Fig. 4).

Fertilizer-induced increases in NO flux simulated using GEOS-CHEM resulted in increased tropospheric ozone concentrations in western Kenya. Mean afternoon 4-hour ozone concentrations during the early growing season in the GEOS-CHEM simulations increased by 2.6 ppbv under

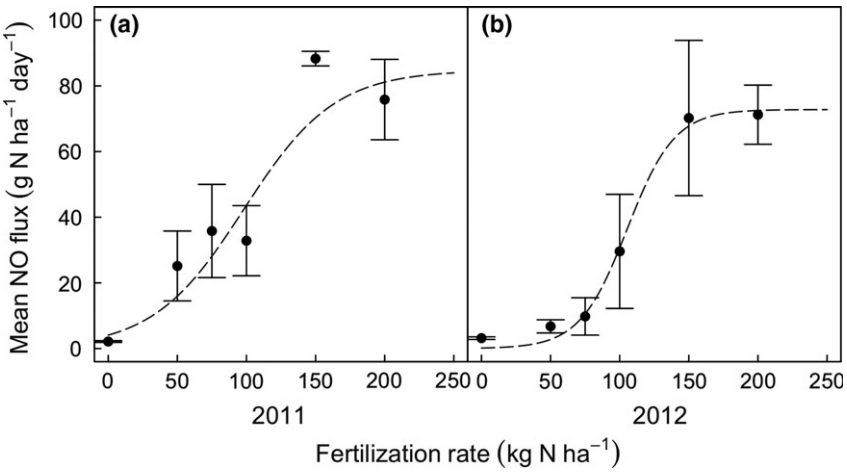

Fig. 3 Response function relating NO emissions to N input rate for the growing season period following the second fertilizer application in (a) 2011 and (b) 2012. The sigmoidal model is presented, though note that in 2011, the fit for the sigmoidal model was not significantly better than the fit for linear or step models. Error bars represent the standard error of the treatment means. Data are for fluxes from chambers placed within maize rows.

Table 2 Estimates of cumulative NO fluxes and emission factors during the measurement period

Treatment (kg N ha^{-1})	Cumulative NO* (g NO–N ha^{-1})	Emission factor (%)†	Field-scale cumulative NO‡ (g NO–N ha^{-1})
2011			
0	270	NA	290
50	1070	0.36	470
75	1360	0.32	530
100	1270	0.22	510
150	3300	0.45	970
200	2950	0.30	890
Between-row	289	NA	NA
2012			
0	157	NA	170
50	252	0.04	190
75	332	0.05	210
100	872	0.16	330
150	1980	0.28	590
200	2010	0.21	590
Between-row	177	NA	N/A

*Cumulative fluxes were calculated using linear interpolations of fluxes between measurements, assuming no diurnal variation in flux. Cumulative flux is calculated from measurements of soils within maize rows only.

†Emission factors represent the percentage of fertilizer N lost as NO, based on field-scale cumulative NO fluxes.

‡Field-scale fluxes are area-weighted estimates of fluxes from soil within maize rows and fluxes from soil between maize rows.

the 150 kg N ha^{-1} fertilizer treatments to 32.6 ppbv (1 ppbv O_3 ~2 μg m^{-3} O_3), but ozone increased by 1 ppbv or less for fertilizer applications up to 100 kg N ha^{-1}. As a result, AOT40 values for the grid cell increased from 187 ppbh for the unfertilized control to 229 and 297 ppbh respectively for the 100 and 150 kg N ha^{-1} treatments. In comparisons of the simulated and observed emissions, NO emissions from the agricultural fraction of the grid cell containing Yala, Kenya, appeared consistently higher than the mean of both seasons of measured fluxes (Fig. S1).

The upper 95% confidence interval resulted in an increase in mean afternoon ozone concentrations of up to 3.42 ppbv and an increase in AOT40 exposure of 151 ppbh for the 150 kg N ha^{-1} treatment, resulting in an AOT40 of 338 ppbh.

Discussion

There is considerable evidence that rates of NO_3^- leaching losses (e.g., Andraski *et al*., 2000; Gehl *et al*., 2005) and N_2O emissions (Van Groenigen *et al*., 2010; Shcherbak *et al*., 2014) respond nonlinearly to increasing rates of N additions; we found that this is also true for NO fluxes. In general, as N inputs increase, rates of N losses can be expected to increase more rapidly once N is no longer limiting to crop growth. Previous efforts examining the linearity of NO flux responses to fertilizer inputs found nonlinear emission responses along a forest elevation gradient in Borneo (NO only) and in Hawaiian rainforests (N_2O + NO), but these studies included only one or two measurements after fertilization and did not characterize the relationship between N inputs and NO flux (Hall & Matson, 1999; Hall *et al*., 2004). As noted previously, an early literature review of NO emissions found a linear relationship between NO and fertilizer inputs, but did not employ a modern

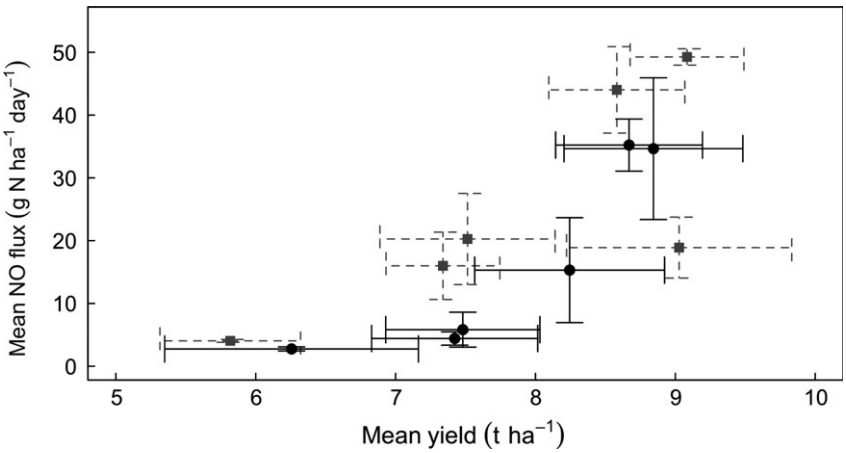

Fig. 4 Mean daily NO flux as a function of mean yield for each N input rate in 2011 (grey squares) and 2012 (black circles). NO fluxes are based on cumulative emissions over the entire measurement period. Error bars represent the standard error of the treatment means.

meta-analytical approach and relied on a small number of studies (Veldkamp & Keller, 1997), and variability in emission responses was so high in another meta-analysis that almost all binned treatment levels were not significantly different form one another (Stehfest & Bouwman, 2006).

The sigmoid shape of the relationship between NO flux and N input rate observed here was likely driven by different biogeochemical dynamics at low and high rates of N input. At low rates, plant uptake presumably acted to limit N availability to nitrifying bacteria. We hypothesize that at high rates of N additions, existing nitrifying populations' ability to nitrify ammonium is effectively saturated and that a slow rate of population growth limits their ability to quickly take advantage of available ammonium. In addition to their slow growth rates (Robertson & Groffman, 2007), these populations face competition from plant uptake of urea and ammonium. Given that harvested plant biomass contains more N than was added as fertilizer in both the 150 and 200 kg N ha^{-1} treatments (Hickman *et al*., 2015), we hypothesize that slow population-level responses to increased resource availability combined with competition from plants both make contributions to the plateauing of NO fluxes at high fertilization rates. This pattern is broadly similar to that posited by Kim *et al*. (2013) for N_2O responses to fertilizer applications, in which N_2O emissions increase linearly at low N addition rates when N_2O emissions reflect competition for N between plants and microbes, becomes exponential when N addition exceeds plant uptake, and then plateaus when inputs of N exceed the capacity of the microbial community to use it. Additional detailed research into short- and long-term microbial population responses to fertilization will be important for improving our mechanistic understanding of the dynamics of NO production and emission in response to N inputs.

It is worth emphasizing that the same plots were used in both years, but that a legacy effect of fertilizer applications in the first year may not be expected in the second year. One reason for this expectation is that an additional maize crop was sown in the plots during the short rainy season between the 2 years of measurements, without fertilizer additions, as is local practice. This short season of maize is likely to have depleted soil nitrogen concentrations and could contribute to the similar emission responses in the first and second years of fertilization. In addition, the N harvested in plant biomass exceeded the N added as fertilizer in all treatments (Hickman *et al*., 2015), further suggesting that a legacy effect of fertilization in the second year would be unlikely to be observed.

Although the sigmoid model provides a significantly better fit than any other model tested in 2012, in 2011, there was no significant difference between linear, step, and sigmoid models. This lack of a difference could be due to the high spatial variability of fluxes in 2011, which could be masking the presence of a sigmoid model. Alternatively, it remains possible that emissions respond differently in different years, although we lack any statistical evidence that this is the case. We also believe it is important to note that we do not currently have evidence that a sigmoidal response is a general property of soils outside our experimental site.

The observed fluxes from fertilized soil in this study (Table 2) are of the same order of magnitude as fluxes from agricultural systems receiving similar rates of N inputs in other parts of the world (Bouwman, 2002; Stehfest & Bouwman, 2006). This result is in contrast to the proportion of N lost as the greenhouse gas nitrous

oxide (N_2O) – which is produced during the same processes as NO – which was about 0.1% at this site (Hickman *et al*., 2015). In fact, N_2O emissions at our site were an order of magnitude or more lower than N_2O emissions from similarly fertilized sites elsewhere, although other sites in Kenya (Hickman *et al*., 2014a) and across sub-Saharan Africa (Hickman *et al*., 2014b) also have low emission factors for N_2O [although there are important exceptions (e.g., Millar *et al*., 2004)]. Cumulative N_2O fluxes from an entire year at this site are roughly an order of magnitude smaller than cumulative NO fluxes during the first 10 weeks of the growing season (Hickman *et al*., 2015). We hypothesize that this difference is related to the water-filled pore space at the site, which did not exceed 60% during the 2012 growing season, when regular measurements of water-filled pore space were made (Hickman *et al*., 2015). The low levels of water-filled pore space likely prevented extensive formation of the anaerobic conditions required for denitrification to occur, resulting in relatively low N_2O emissions (Davidson & Verchot, 2000), although it is also possible that plant uptake or leaching limited the availability of nitrate to denitrifiers. Bouwman (2002) found that that properties that contribute to low-level water-filled pore space such as coarse texture and effective drainage may be associated with higher levels of NO emissions, although the association was not significant, and was not observed in a later meta-analysis (Stehfest & Bouwman, 2006).

It is also important to note that NO flux measurements in this study were stopped 4–5 weeks following the second fertilizer application, when NO fluxes remained substantially elevated relative to controls (Fig. 2c, d). Indeed, earlier meta-analyses have suggested that emissions of NO increase as a function of the duration of experimental measurements (Bouwman, 2002; Stehfest & Bouwman, 2006). Consequently, our calculations are underestimates of actual fertilizer-induced fluxes and emission factors, and should be interpreted as lower limits; the difference between NO and N_2O fluxes may be even larger than presented here. In addition, our use of split applications and spatially targeted fertilizer applications should result in lower NO fluxes than might be expected from the uniform broadcasting of fertilizer (Adviento-Borbe *et al*., 2007); hence, agricultural systems under other management approaches could exhibit higher rates of NO emissions.

Emissions of NO + N_2O emissions constitute a small loss pathway of added N from our experimental plots, representing less than 1% of the added fertilizer (Hickman *et al*., 2015). In contrast, concentrations of nitrogen in the maize grain and by-product exceeded fertilizer addition rates for all treatments (Hickman *et al*., 2015). In African agroecosystems, crop residue may not be returned to agricultural soils, as residues often face competing uses such as livestock feed and fuel (Valbuena *et al*., 2012). These competing uses mean that when crop productivity is high, the net N budget in these systems may be negative even with substantial additions of fertilizer. Expanded studies that include N losses via leaching, and which use isotopically labeled fertilizer to trace the fate of added N, would help to better constrain how nitrogen budgets may change in response to agricultural intensification in the region.

Agriculture in western Kenya is dominated by maize, which is moderately sensitive to ozone, and pulses, vegetables, and fruits such as tomatoes, which are more sensitive to ozone. For the most ozone-sensitive crops, the AOT40 critical level (at which direct adverse effects resulting in a 5% yield decline are expected to occur) can be as low as 1600 ppbh, but is more commonly 3000–4000 ppbh (Mills *et al*., 2007). For our simulation of western Kenya, the 0 kg N ha^{-1} treatment produced an AOT40 of 187 ppbh, and the 150 kg N ha^{-1} treatment produced an AOT40 of 297 ppbh during the growing season, well below the critical level for even the most sensitive crops. Although the air quality and crop productivity impacts of increased fertilizer use in western Kenya appear to be largely negligible, it would be premature to conclude that the impacts will also be negligible in other areas of sub-Saharan Africa.

The local ozone impact assessment also does not account for the likely increases in ozone precursor emissions associated with expected changes in industrial activities in future decades in sub-Saharan Africa (e.g., IPCC, 2001). Generally, in the future, if growing season carbon monoxide (CO) and VOC concentrations increase as a result of increased fossil fuel combustion or increased biomass burning, the efficiency of fertilizer-induced NO emissions contributions to ozone production would be expected to increase as well. However, increases in both fossil fuel combustion and biomass burning emissions of NO_x would be expected to reduce the sensitivity of ozone formation specifically to fertilizer-induced NO emissions.

The largest changes in soil NO fluxes occurred in response to fertilizer additions between 75 and 150 kg N ha^{-1} (Fig. 3). Many recommended fertilization rates for smallholder agriculture in sub-Saharan Africa are between 75 and 120 kg N ha^{-1} (Nziguheba *et al*., 2010), making agriculture in the region potentially susceptible to substantial increases in NO flux with relatively small changes in N input (although in western Kenya, broad fertilizer recommendations are currently for 45 kg N ha^{-1}, NAFIS, 2012). This threshold is also present in the relationship between NO flux and yield, with fluxes increasing at fertilization rates above 100 kg N ha^{-1} without a concomitant increase in

yields (Fig. 4). It appears, therefore, that crops can be managed to maximize yield while avoiding the largest increases in NO emissions. However, the threshold-like nature of the sigmoid response function may make managing NO fluxes challenging, because if fertilizer inputs modestly exceed the initial threshold, emissions may quickly reach their maximum.

It is worth noting that fertilizer-induced emissions may increase atmospheric NO in sub-Saharan Africa at a time of year when NO concentrations tend to be low historically. The largest emissions of soil NO fluxes in sub-Saharan Africa occur in a pulse following the onset of the rainy season (Jaeglé *et al*., 2004), while emissions from biomass burning will tend to occur during the dry season (Scholes *et al*., 2011). In our field study, the majority of fertilizer-induced emissions occurred following the second fertilizer application, which is typically 5–8 weeks after the onset of rains and thus displaced temporally from both biomass burning and the onset of the rainy season, representing a potentially new source of NO_x.

These are just the second published field measurements of NO fluxes from African agriculture and the first for fertilization rates above 16 kg N ha^{-1} (Meixner *et al*., 1997). Further quantification of the duration of fertilizer-induced NO emissions and of the threshold for rapid increases in NO emissions across different soils and agro-ecological zones is essential for developing a robust estimate of regional NO fluxes under agricultural intensification and ultimately their effects on air quality. For example, sandier soils may be expected to emit NO at higher rates than clayey soils (Skiba & Ball, 2002). More generally, the sigmoidal response of NO emissions to increasing N inputs may be a common property to soils around the world, but that remains to be tested in temperate and subtropical regions, or in tropical sites outside our own.

Currently, African agriculture is estimated to be responsible for just 6% of global anthropogenic N_2O emissions (Hickman *et al*., 2011), and mitigation of N_2O from smallholder agriculture has been receiving increasing attention (Rosenstock *et al*., 2013; Scholes *et al*., 2014). Emissions of NO from smallholder agriculture are also thought to be small, but very few direct measurements exist. Given the potential for NO emissions to lead to increase in regional ozone and the order of magnitude higher fluxes of NO than N_2O from this site, it may be important to produce more accurate characterizations of NO fluxes across different climates and soils where substantial agricultural intensification is expected. Increasing food production in sub-Saharan Africa must remain a first-order priority, and an improved understanding of the environmental impacts of agricultural intensification will help to inform efforts toward sustainable development in the region.

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Supporting Information

Additional Supporting Information may be found in the online version of this article:

Figure S1. Comparison of simulated and observed fertilizer-induced NO fluxes from western Kenya.
Figure S2. Relationship of soil NO flux to precipitation.
Table S1. NO sampling dates at the Yala, Kenya experimental site.