African Green Revolution, NO, and ozone

Impacts of African agricultural intensification on nitric oxide fluxes and tropospheric ozone

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Keywords: Ozone, tropical agriculture, Africa, greenhouse gas, agricultural intensification, fertilizer, nitrogen, GEOS-Chem

Type of Paper: Letter
Abstract
Where a global green revolution had great successes in reducing food security globally, it largely bypassed sub-Saharan Africa (SSA), where yields remain stagnant at 1 ton ha\(^{-1}\) and 260 million people lack access to adequate food resources. An order-of-magnitude increase in fertilizer use is seen as a critical step in securing food security in a new African Green Revolution. This increase represents an unprecedented input of nitrogen (N) to African ecosystems—6 Tg N yr\(^{-1}\) to reach application rates of 75 kg N ha\(^{-1}\) yr\(^{-1}\) on existing agricultural land for cereals—and will likely be accompanied by increased soil emissions of nitric oxide (NO). NO is a precursor to tropospheric ozone, a powerful greenhouse gas and a pollutant that is harmful to human health and can reduce crop productivity. In order to understand how agricultural intensification will affect NO emissions in SSA, we established experimental maize plots in western Kenya’s Siaya District to quantify the response function relating NO flux to N input rate in 2011 and 2012. NO emissions followed a sigmoid response to fertilizer inputs and have short-term emission factors under 1%. In addition, at fertilization rates above 100 kg N ha\(^{-1}\), NO emissions increased without a concomitant increase in yields. Using the field results to constrain soil NO emissions in the GEOS-Chem chemical transport model, we show that increased NO fluxes from high fertilization rates caused tropospheric ozone increases up to 2.2 ppb and potential yield penalties for some crops of 2.5% in the most affected areas. However, impacts were small at fertilization rates of 100 kg N ha\(^{-1}\) or less. These results suggest that it may be possible to conduct order-of-magnitude increases in N applications in the region and manage agricultural systems for high yields without large impacts on air quality in the short-term.
Food security is a perennial challenge in sub-Saharan Africa (SSA). While global cereal production has nearly tripled since 1960, it has not increased in SSA, where yields remain under 1 ton ha\(^{-1}\) \{Hazell:2008ih\}, and food shortages affect 260 million people \{Sanchez:2010hb\}, more than twice as many as in 1970 \{Sanchez:2002uj\}. 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\(^{-1}\) \{:2005uc\}), which, in turn, has lead to large negative N balances, extensive mining of nutrients from soils, and declining soil fertility \{Vitousek:2009fe\}. Increased use of inorganic fertilizer in these agricultural soils is seen as a critical step in increasing food security and improving soil fertility in SSA \{Vanlauwe:2006db\}; the Alliance for a Green Revolution in Africa (AGRA) has been working to increase fertilizer use six-fold across the continent by 2015, to an average of 50 kg ha\(^{-1}\) yr\(^{-1}\) \{AGRA:2009tc\}. By later in the century, N inputs may reach recommended rates, which vary regionally up to 120 kg N ha\(^{-1}\) yr\(^{-1}\) \{Nziguheba:2010wt\}. This increase in fertilizer is likely to represent the largest perturbation to the nitrogen cycle in SSA in the 21\(^{st}\) century, with an increase in reactive N inputs of at least 6 Tg N yr\(^{-1}\) needed just to reach application rates of 75 kg N ha\(^{-1}\) yr\(^{-1}\) on existing agricultural land for cereals \{Monfreda:2008cb, Hazell:2008ih\}. These increased N inputs will be accompanied by inevitable increases in soil emissions of nitric oxide (NO), a precursor to tropospheric ozone \{IPCC:2007wb\}. In soils, NO is a reaction intermediate in the microbial reduction of NO\(_3^-\) to atmospheric N\(_2\); it can also be produced during the microbial oxidation of ammonium to nitrate and during abiotic reactions in soils \{Firestone:1989wb\}. In the “hole-in-the-pipe” model \{Firestone:1989wb\}, fluxes of nitric oxide (NO) and N\(_2\)O 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:2000uv}). 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:1989wb, Predotova:2010eh}.

Tropospheric ozone formation in much of SSA is sensitive to atmospheric NOX (NO + nitrogen dioxide [NO2]) concentrations, and recent studies using satellite retrievals show that soil NOX flux is one of the largest drivers of ozone formation in the region {Jaegle:2004jt}. 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 of up to 26% for some crops by 2030 {Avnery:2011kq}. Changes in soil NO emissions mediated by terrestrial ecosystem properties and management have been shown to alter regional ozone levels {Hickman:2010uz}, suggesting that the order-of-magnitude increases in N inputs expected in an African Green Revolution could have important impacts on atmospheric chemistry.

Although it is well established that N availability is the main driver of NO flux from soils and central to our theoretical understanding of NO emissions from soils {Firestone:1989wb}, a response function relating N input rate to NO flux has not been parameterized in any terrestrial ecosystem, and studies quantifying NO fluxes in response to multiple N input rates are limited to very brief dose-response studies in forests {HALL:1999wn, Hall:2004vc}. And while tropical agriculture is among the largest global fluxes of NO {Davidson:1997we}, NO emissions from agriculture in SSA are very
African Green Revolution, NO, and ozone

poorly understood: the only published field measurements of NO fluxes from African agricultural soils are from a single season of a preliminary study with a 30 kg N ha\(^{-1}\) treatment \{Meixner:1997vs\}.

In order to evaluate how agricultural intensification in sub-Saharan Africa may affect emissions of NO and to evaluate the basic relationship between N input and NO flux, we conducted a fertilizer response trial in Yala, in Siaya District in western Kenya. We incorporated the response functions observed in Yala in the GEOS-Chem chemical transport model to evaluate how changes in agricultural intensification may drive changes in tropospheric ozone concentrations across SSA.

Results

Fertilization rate did not explain NO emissions among treatments prior following the first application, 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. 1). A sigmoid function provided the best fit to the data in both 2011 and 2012, but the improvement over linear and step functions was only sufficient to choose among models in 2012 (Table 1; Fig. 1e-f).

Fluxes from fertilized soils in the 150 and 200 kg N ha\(^{-1}\) treatments were higher than fluxes from all other treatments (P<0.02), with mean fluxes of 49.3 and 35.2 g NO-N ha\(^{-1}\) day\(^{-1}\) for the 200 kg N ha\(^{-1}\) treatments in 2011 and 2012 and 44.0 and 34.7 ng NO-N cm\(^{-2}\) hr\(^{-1}\) for the 150 kg N ha\(^{-1}\). 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. 1). Although the measurement periods before and after the second fertilizer application were roughly identical in duration, the majority of fluxes in
African Green Revolution, NO, and ozone

all treatments except for the 2011 control occurred following the second fertilizer
application rates, including over 90% of emissions from treatments of 150kg N ha⁻¹ or
more in 2011, and over 90% of emissions from treatments of 100 kg N ha⁻¹ or more in
2012. Less than 1% of fertilizer N was 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 (R²
=0.19 and 0.13 in 2011 and 2012), and a weak negative relationship after the second
fertilizer application (R² =0.08 and 0.06 in 2011 and 2012). 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 in
these soils {Hickman:PytbE4lw}.

In both years, yields responded to fertilizer additions, increasing from roughly 6
to 9 tons ha⁻¹, with increases generally leveling off after additions of 100 kg N ha⁻¹
{Hickman:PytbE4lw}. This leveling of yields represents a threshold above which larger
volumes of NO are emitted without any change in grain production (Fig. 2).

When incorporated in the GEOS-Chem chemical transport model, the increases in NO
flux with increasing N input results in increased ozone concentrations in some parts of
SSA. Mean ozone concentrations during the early growing season increased by up to 2.2
ppbv in some areas (Fig. 3). In some cases, the increase in tropospheric ozone
concentrations resulted in an increase in the number of bad ozone days (defined as days
in which afternoon average surface ozone exceeded 40 ppbv) during a given month of
elevated fluxes (Table 3). Above 100 kg N ha⁻¹, some areas experienced an increase of up
to 9 days per month of AOT40 exposures in our simulations, compared to a maximum of
African Green Revolution, NO, and ozone

2 additional days per month below 100 kg N ha\(^{-1}\) (Table 3). In general, the impacts of agricultural intensification on ozone concentrations were smaller at low fertilization rates, and smaller at latitudes below the equator, with most of the large impacts occurring in east and central Africa.

**Discussion**

There is mounting evidence that rates of N losses respond non-linearly to increasing rates of N additions; we found that this is also true for NO fluxes in western Kenya. In general, as N inputs increase, rates of N losses can be expected to increase rapidly once N is no longer limiting to crop growth. Non-linear N losses in response to incremental increases in N addition have been observed in temperate agroecosystems for NO\(_3^-\) leaching [e.g., {Andraski:2000uc} and N\(_2\)O emissions {Bouwman:2002ig, McSwiney:2005fi, Hoben:2010ew, VanGroenigen:2010jq}], including in SSA {Hickman:PytbE4lw}. Previous efforts examining the linearity of NO flux responses to fertilizer inputs found non-linear emission responses along a forest elevation gradient in Borneo (NO only) and in Hawaiian rainforests (N\(_2\)O + NO), but included only one or two measurements after fertilization and did not characterize the relationship between N inputs and NO flux {HALL:1999wn, Hall:2004vc}. An early literature review of NO emissions found a linear relationship between NO and fertilizer inputs, but did not employ a modern meta-analytical approach and relied on a small number of studies {Veldkamp:1997vg}.

The sigmoid shape of the relationship observed here for NO was likely driven by different dynamics at low and high rates of N input. At low rates, plant uptake
African Green Revolution, NO, and ozone

presumably acted to limit N availability to nitrifying bacteria. At high input rates, nitrifier populations were likely unable to grow quickly enough to utilize the increased levels of available N \cite{Robertson:2007to}. These dynamics suggest that factors such as plant uptake that limit N availability to nitrifiers may be an important component of future models, as the parameters of the response curve may be expected to differ across varieties, crops, and years as a function of plant size.

The observed fluxes from fertilized soil in this study are of the same order of magnitude as fluxes from agricultural systems receiving similar rates of N inputs in other parts of the world \cite{Stehfest:2006co, Bouwman:2002ig}. This result was something of a surprise, since the proportion of N lost as the greenhouse gas nitrous oxide (N\textsubscript{2}O)—which is produced during the same processes as NO—at this site was about 0.1%, often an order of magnitude or more lower than N\textsubscript{2}O emissions from similarly fertilized sites elsewhere \cite{Hickman:PytbE4lw}. Indeed, cumulative N\textsubscript{2}O fluxes are roughly an order of magnitude smaller than NO fluxes even when measured over an entire year at this site, which has a history of low nutrient input and low soil N concentration (0.1%). It is important to note that NO flux measurements in this study were stopped 4-5 weeks following the second fertilizer application, when NO fluxes remained elevated relative to controls (Fig. 1c-d). Consequently, our calculations are underestimates of actual fertilizer-induced fluxes and annual emission factors, and should be interpreted as lower limits.

The AOT40 cumulative exposure parameter is a metric for assessing crop damage from ozone, where the decline in crop yield is a function of their cumulative exposure (in ppb h) to ozone concentrations above 40 ppbv during the growing season \cite{Mills:2007br}.
In the grid cell with the largest increase in ozone, the 150 kg N ha\(^{-1}\) treatment produced an additional AOT40 of 1500 ppb h during the month of elevated fluxes, sufficient to cause a 2 to 2.5% yield decline in ozone-sensitive crops such as wheat, cotton, soybean, and pulses \{Mills:2007br\}. In contrast, the largest increases in ozone under the 75 or 100 kg N ha\(^{-1}\) treatments produced an AOT40 of roughly 340 ppb h and a 0.5% yield decline in these crops. The increases in ozone concentrations over SSA and the enhancement in continental outflow of ozone may also have important implications for radiative forcing and regional climate since ozone is a powerful greenhouse gas \{IPCC:2007wb\}.

The largest changes in both soil NO flux and modeled tropospheric ozone formation occur in response to fertilizer additions between 75 and 150 kg N ha\(^{-1}\), the steep section of the sigmoidal response (Fig. 1). Many recommended fertilization rates for smallholder agriculture in SSA are between 75 and 120 kg N ha\(^{-1}\) \{Nziguheba:2010wt\}, making them potentially susceptible to substantial increases in NO flux with relatively small changes in N input; in western Kenya, broad fertilizer recommendations are currently for 45 kg N ha\(^{-1}\) \{NAFIS:tz\}. 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. 3). Since AOT40 impacts were very small at 100 kg N ha\(^{-1}\) or less, there may be room for order-of-magnitude increases in N applications in the region—and managing maize for high yields—without large impacts on air quality in the short-term.

The ozone results should be viewed as an initial exercise in evaluating potential impacts of agricultural intensification on atmospheric chemistry and air quality. These are just the second published field measurements of NO fluxes from African agriculture.
and the first for fertilization rates above 30 kg N ha\(^{-1}\), so this initial evaluation of the potential impacts of agricultural intensification on air quality extrapolates widely from a relatively small field data set. Further quantification of the duration of fertilizer-induced NO and of the threshold for rapid increases in NO flux across different soils and agro-ecological zones is essential for developing a robust estimate of regional NO fluxes under agricultural intensification, and ultimately of their effects on air quality. In addition, several simplifying assumptions made in the GEOS-Chem simulations are certain to make the model incorrectly simulate the impacts of increased fertilizer use on ozone. First, the GEOS-Chem simulation assumes the fertilizer-induced fluxes exist throughout the simulation period, but observed fertilizer-induced fluxes may not extend beyond 4-5 weeks; for this reason, we present the ozone impacts as monthly averages. Secondly, the clustering of fertilization windows into three bands defined by latitude and the evaluation of 3-4 month windows of fertilizer-induced flux explicitly discounts finer scale spatio-temporal variation in fluxes. Nevertheless, these results present an important first evaluation of soil NO impacts on air quality in SSA using model parameterizations informed by measurements from agricultural soils in the region, which is one where agricultural N trace gas fluxes tend to differ substantially from global means\(\{\text{Hickman:2011iu}\}\). Currently, African agriculture is estimated to be responsible for just 6% of global anthropogenic N\(_2\)O emissions (biomass burning represents another 10%\(\{\text{Hickman:2011iu}\}\), and mitigation of N\(_2\)O from smallholder agriculture has been receiving increasing attention \(\{\text{Rosenstock:2013fr}\}\). NO emissions from smallholder agriculture are also thought to be small, but measurements are few, and given the
African Green Revolution, NO, and ozone

potential for NO emissions to lead to increases in regional ozone and the much higher
fluxes of NO than N$_2$O from this site, it is important to produce more accurate
characterizations of these fluxes across different climates and soils in areas where
agricultural intensification is expected, and to use these characterizations to produce
recommendations for environmentally sound intensification and mitigation of NO
emissions as necessary.

Methods

Experimental maize plots were established in January, 2011 in Yala, Kenya
(34.511 East, 0.1014 North, 1350 m above sea level, 1,750 mm annual rainfall). The site
was converted to agriculture in the 1960’s or 1970’s. Fields were left fallow from 1979-
1989 and from 1994-2007; 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 100g$^{-1}$. 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]).

Experimental design

Six levels of fertilizer treatment (0, 50, 75, 100, 150, and 200 kg N ha$^{-1}$) were
applied in a randomized complete block design (4 blocks, each block consisting of 6
African Green Revolution, NO, and ozone

258 plots, and each plot measuring 6 m x 3 m). Rows were spaced at 0.75 m intervals, and
259 plants were seeded by hand at 0.30 m intervals within rows following regional
260 recommendations, for a plant population of 44,444 plants ha$$^{-1}$$, or 80 plants per plot,
261 including two buffer rows along each plot edge. Kenya Seed Company hybrid maize
262 varieties were used (WH505 in 2011 and WH403 in 2012); 90% of farmers use hybrids
263 in the highland tropics and moist transitional zones of Kenya {Schroeder:2013wr}. Two
264 seeds were planted per hole at the start of the long rainy season on March 24, 2011 and
265 April 5, 2012, and thinned within two weeks of emergence. Maize was sown in the plots
266 without added fertilizer at the start of the short rainy season in October, 2011. The same
267 plots were used in 2011 and 2012.

268 A third of the fertilizer N was applied as diammonium phosphate (18% N) at
269 planting (March 24, 2011 and April 5, 2012) within 5 cm of each seed, and the remaining
270 2/3 was applied as urea (46% N) 5 weeks later (April 26, 2011 and May 7, 2012), within
271 5 cm of each maize stem. The field was weeded once during the week before the
272 topdressing application, and again several weeks later. Maize plants were harvested by
273 hand from within the buffered area of each plot the weeks of August 7, 2011 and August
274 20, 2012.

275

276 NO measurements

277 Sampling was conducted at least 5 times in weeks following fertilizer
278 applications, and at least weekly during the rest of the measurement period. To capture
279 fertilizer-induced fluxes, at planting each PVC chamber was centered over a planting
280 station, where it remained in place until the second fertilizer application. Just prior to the
second fertilizer application, each chamber was moved from its position over a plant to a position between between two maize plants within a row; the chambers then remained in place until the end of the measurement period. Each chamber covered soil fertilized at the rate determined for a single plant for a given treatment. In each block, an additional chamber was inserted over soil between maize rows in a randomly selected plot within each block 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), 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 equipped with a CrO$_3$ filter that converts all NO to NO$_2$ (Unisearch Associates LMA-3D, Concord, Ontario, Canada). Standard curves were conducted in the field using a standard gas with a known NO concentration (0.0992 ppm, Scott-Marin Co., Riverside, CA) 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 \cite{HALL:2008th}. The linear relationship between the LMA-3D detector readings (mV) and standard gas concentration (ppb) were used to calculate chamber NO$_x$ concentrations. Flux calculations accounted for. Ratios of NO:N$_2$O were calculated using the mean flux from each replicate chamber across days when both gases were measured. To avoid negative ratios, N$_2$O fluxes below zero were assumed to be 0.1 ng N$_2$O-N cm$^{-2}$ hr$^{-1}$.

Cumulative emissions were estimated by summing linearly interpolated daily emission rates. Estimates of field-scale emissions were calculated using a weighted
African Green Revolution, NO, and ozone

average of cumulative fluxes from chambers placed within rows and chambers placed between rows:

Cumulative field emissions\(_i\) = \(\sum_{j=1}^{j} 0.227(\text{chamber}_{ij}) + 0.773(\text{between-row chamber}_{j})/n\)

Where chamber\(_{ij}\) is the flux (g NO-N ha\(^{-1}\)) from the chamber placed in the \(i^{th}\) fertilizer treatment (or the control) and \(j^{th}\) block, between-row chamber\(_{j}\) is the flux (g NO-N ha\(^{-1}\)) from the chamber placed between rows in the \(j^{th}\) 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, a conservative estimate we believe may under-estimate the actual fertilizer-induced flux. Emission factors were calculated using the cumulative field-scale emission estimates. 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.

Emission factors were calculated using the cumulative field-scale emission estimates. 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. This assumption may overestimate the mean daily flux, though diurnal variation in N oxide...
Cumulative and daily $N_2O$ emission rates and emission factors

Cumulative emissions were estimated by summing linearly interpolated daily emission rates, which were then divided by the number of days between the first and final measurement and multiplied by 365 for an annual cumulative flux. Measurements planned for November and December 2012 could not be taken, so interpolated fluxes during that 112-day period are estimated from just the October 1 and January 21 measurements. Consequently, these two dates have a large influence on the interpolated $N_2O$ emission values, resulting in cumulative fluxes that may not accurately reflect the dynamics of $N_2O$ fluxes during the 112-day period. Two sets of annual estimates were calculated for 2012—one in which the interpolations between October 1 and January 21 were used in estimating annual fluxes, and one in which they were not. Since annual estimates for 2011 are based on a shorter measurement period, they are likely upper-bound estimates.

Estimates of field-scale emissions were calculated using a weighted average of cumulative fluxes from chambers placed within rows and chambers placed between rows. 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 any fertilizer-induced emissions of $N_2O$ from applications at planting had ended by the time the second fertilizer applications
African Green Revolution, NO, and ozone

were made. Emission factors were calculated using the cumulative field-scale emission estimates.

**Modeling**

Chambers were moved prior to the second fertilizer application from a position over a planting 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 issues with repeated measures of the same experimental unit and pseudoreplication, only the average daily flux for each replicate during each time period (before and after the second fertilizer application) was used as a response variable [e.g., {Hoben:2010ew}].

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

\[ Y_i = a + b_i \cdot N_i \]
\[ Y_i = a \cdot e^{(b_i \cdot N_i)} \]
\[ Y_i = a + b_i \cdot N_i + c_i \cdot N_i^2 \]
\[ Y_i = \frac{(a \cdot b_i \cdot e^{(d_i \cdot N_i)})}{(a + b_i \cdot (e^{(d_i \cdot N_i)})-1)} \]
\[ Y_i = a \text{ for } N < b; Y_i = c \text{ for } N > b \]
African Green Revolution, NO, and ozone

where \( Y_i \) is the average calculated daily trace N gas flux at the \( ith \) N fertilization rate, and

where \( a, b, \) and \( c \) are non-zero 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 at a resolution of 4° latitude by 5° longitude with 47 vertical layers and a

fully coupled Ozone-NOx-VOC-Aerosol chemistry mechanism {Park:2004wp}. The

model was run from June 2010 to December 2011, with 2010 as spin-up. The Berkeley-

Dalhousie Soil NOx Parameterization scheme was employed to simulate fertilizer-

induced NO emissions {Hudman:2012gf}.

One sensitivity model study was conducted corresponding to each fertilizer

application rate. The soil NO emission flux in the \( k^{th} \) sensitivity model run at a specific

grid box with longitude index \( i \) and latitude index \( j \) at time \( t \) is calculated as

\[
(E_k)_{i,j,t} = (E_0)_{i,j,t} + (M_k - M_0) \times (AGFRC)_{i,j} \times \frac{(E_0)_{i,j,t}}{(E_0)_{i,j}}
\]

where \( E_0 \) denotes control model soil NOx emission flux (without fertilizer application);

\( \overline{E}_0 \) represents mean soil NOx emission flux from model control runs for that grid cell,
averaged over the simulation period; \( M_k \) represents mean measured fertilizer-induced

NO emission flux (2011 and 2012) for a specific fertilizer application rate \( k \) and \( M_0 \) is
African Green Revolution, NO, and ozone

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.

Growing seasons in SSA vary primarily as a function of the movement of the
Inter-Tropical Convergence Zone, with planting dates and fertilizer applications
occurring during different times of year at different latitudes {Vrieling:2013ck}. Results
are presented for three latitudinal bands (6N-14N, 2S-6N, and 2S-36S), which broadly
map to different latitudinal bands of cropping seasons {Vrieling:2013ck}. As planting
and fertilizer application dates can vary inter-annually as well as among farms, results are
presented for the 3- or 4- month period in each band broadly representative of an early
growing season period (the period when elevated NO fluxes were observed in our field
study).

Frequentist Analysis

Frequentist analyses were conducted to provide traditional evaluations of
treatment differences, though the better fit of a non-linear model implies differences
between treatments. 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). Treatment was considered a fixed effect, and block a random
effect. 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
African Green Revolution, NO, and ozone

identify treatment differences. All analyses were conducted using the R programming language.

Figure 1. **NO fluxes following fertilization in 2011 and 2012.** Time series of daily precipitation (a & b) and NO flux for each treatment (c & d) during measurement periods in 2011 and 2012, and mean daily NO fluxes in 2011 (e) and 2012 (f) following the second fertilizer applications for each N input rate. In (c) and (d), arrows indicate dates of fertilizer application and error bars represent the standard error of the treatment means on each measurement date. In (e) and (f), the best-fitting models are presented, and error bars represent the standard error of the treatment means. Data are for fluxes from chambers placed within maize rows.

Figure 2: **Impact of fertilizer-induced NO flux on ozone concentrations.** Average surface ozone concentrations over SSA under a control simulation with no fertilizer-induced NO emissions (“Control”) during the early growing season in different latitudinal bands, and differences (“D”) in ozone concentrations between the control simulation and scenarios for fertilizer inputs of 50, 75, 100, 150, and 200 kg N ha$^{-1}$. Results are presented for months representative of the early growing season specific to each latitudinal range.
African Green Revolution, NO, and ozone

440
441
442 Figure 3. Mean daily NO flux as a function of mean yield for each N input rate in 2011 and 2012. Error bars represent the standard error of the treatment means.
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African Green Revolution, NO, and ozone

Table 1. Estimates of cumulative NO fluxes and emission factors.

<table>
<thead>
<tr>
<th>Treatment (kg N ha(^{-1}))</th>
<th>Cumulative NO(^*) (g NO-N ha(^{-1}))</th>
<th>Emission Factors(^†)</th>
<th>Field-scale cumulative NO(^†) (g NO-N ha(^{-1}))</th>
<th>Cumulative NO(^*) (g NO-N ha(^{-1}))</th>
<th>Emission Factors(^†)</th>
<th>Field-scale cumulative NO(^†) (g NO-N ha(^{-1}))</th>
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<tr>
<td>150</td>
<td>3300</td>
<td>0.47</td>
<td>970</td>
<td>1980</td>
<td>0.28</td>
<td>590</td>
</tr>
<tr>
<td>200</td>
<td>2950</td>
<td>0.31</td>
<td>890</td>
<td>2010</td>
<td>0.21</td>
<td>590</td>
</tr>
<tr>
<td>between-row</td>
<td>289</td>
<td>NA</td>
<td>NA</td>
<td>177</td>
<td>NA</td>
<td>N/A</td>
</tr>
</tbody>
</table>

\(^*\) 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 losses over the measurement period, 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.
African Green Revolution, NO, and ozone

Table 2. Model parameters, $R^2$, and corrected AIC values for models describing the mean $N_2O$ flux response to $N$ fertilization rate ($F$) for the 5-6 weeks following the second fertilizer application to maturity in 2011 (April 26 to xx 2011 and May 7 to xx 2012). Parameter estimation for the models was conducted using simulated annealing.

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter estimates</th>
<th>Corrected AIC</th>
<th>$R^2$</th>
<th>Parameter estimates</th>
<th>Corrected AIC</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear ($a + (b*F)$)</td>
<td>$a = 0.257$</td>
<td>218.13</td>
<td>0.64</td>
<td>$a = -4.71$</td>
<td>231.5</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td>$b = 0.415$</td>
<td></td>
<td></td>
<td>$b = 0.356$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exponential ($a<em>e^{(b</em>F)}$)</td>
<td>$a = 15.7$</td>
<td>222.3</td>
<td>0.58</td>
<td>$a = 10.4$</td>
<td>237.1</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>$b = 0.00844$</td>
<td></td>
<td></td>
<td>$b = 0.00944$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sigomoid $(a<em>b</em>e^{(c<em>F)})/((a+b</em>(e^{c*F})-1))$</td>
<td>$a = 83.3$</td>
<td>217.7</td>
<td>0.68</td>
<td>$a = 63.9$</td>
<td>229.5</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td>$b = 0.3.13$</td>
<td></td>
<td></td>
<td>$b = 0.0337$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$c = 0.0332$</td>
<td></td>
<td></td>
<td>$c = 0.0754$</td>
<td></td>
<td></td>
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<tr>
<td>Step</td>
<td>$a = 125$</td>
<td>218.5</td>
<td>0.67</td>
<td>$a = 125$</td>
<td>231.7</td>
<td>0.47</td>
</tr>
<tr>
<td>b for $F &lt; a$, c for $F &gt; a$</td>
<td>$b = 20.4$</td>
<td></td>
<td></td>
<td>$b = 12.4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$c = 78.9$</td>
<td></td>
<td></td>
<td>$c = 63.5$</td>
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<td></td>
</tr>
</tbody>
</table>
Table 3: **Impact of fertilizer-induced NO flux on the frequency of bad ozone days.**

The range of the number of days per month with afternoon (Local time 13:00-17:00) average surface ozone exceeding 40 ppbv over SSA for each region’s early growing season period under a control simulation with no fertilizer-induced NO emissions (“Control”), and the differences (“D”) in the number of over 40 ppbv afternoons for each month in scenarios with fertilizer inputs of 50, 75, 100, 150, and 200 kg N ha\(^{-1}\).

<table>
<thead>
<tr>
<th></th>
<th>6 – 14 N</th>
<th>2 S – 6 N</th>
<th>2 – 36 S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>JJA</td>
<td>MAM</td>
<td>NDJF</td>
</tr>
<tr>
<td>CONTROL</td>
<td>9-29</td>
<td>6-31</td>
<td>22-30</td>
</tr>
<tr>
<td>D50</td>
<td>0-2</td>
<td>0-2</td>
<td>0-1</td>
</tr>
<tr>
<td>D75</td>
<td>0-2</td>
<td>0-2</td>
<td>0-2</td>
</tr>
<tr>
<td>D100</td>
<td>0-2</td>
<td>0-2</td>
<td>0-3</td>
</tr>
<tr>
<td>D150</td>
<td>0-4</td>
<td>1-9</td>
<td>1-4</td>
</tr>
<tr>
<td>D200</td>
<td>0-4</td>
<td>1-8</td>
<td>1-4</td>
</tr>
</tbody>
</table>
Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

Acknowledgements We would like to thank Louis Verchot and ICRAF-Kisumu for the use of equipment and laboratory space. YH and SW acknowledge support from the U.S. EPA STAR program (grant #83518901).

Author Contributions JEH conceived, designed, and conducted field experiments, analyzed data, and wrote the paper. YH and SW designed and conducted modeling experiments, analyzed data, and edited the paper. CAP, WD, and PMG contributed to experimental design and edited the paper.

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Figure 1.
African Green Revolution, NO, and ozone

Figure 2
Figure 3.
African Green Revolution, NO, and ozone

516

517  {papers2_bibliography}