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DISSERTATION

NO<sub>x</sub> AND N<sub>2</sub>O FLUXES IN AN UPLAND AGROECOSYSTEM  
OF THE NORTH CHINA PLAIN:  
FIELD MEASUREMENTS, BIOGEOCHEMICAL SIMULATION,  
AND CLIMATIC SENSITIVITY

Submitted by

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Graduate Degree Program in Ecology

In partial fulfillment of the requirements

For the Degree of Doctor of Philosophy

Colorado State University

Fort Collins, Colorado

Fall 2001

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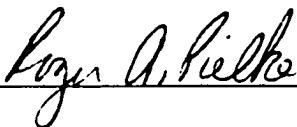
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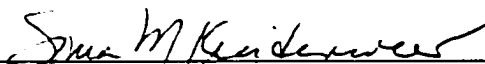
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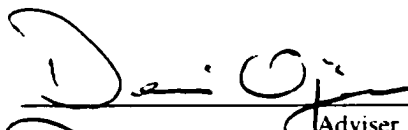
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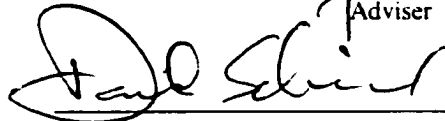
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## ABSTRACT OF DISSERTATION

### NO<sub>x</sub> AND N<sub>2</sub>O FLUXES IN AN UPLAND AGROECOSYSTEM OF THE NORTH CHINA PLAIN:

#### FIELD MEASUREMENTS, BIOGEOCHEMICAL SIMULATION, AND CLIMATIC SENSITIVITY

Chinese agriculture represents one of the most intensively managed and biogeochemically important ecosystems in the world. High fertilizer application rates and poor nutrient use efficiency by crops result in high nitrogen losses to the surrounding environment, with consequences to atmospheric composition, groundwater quality, public health, and ironically, agriculture itself. One loss mechanism, the gaseous production of NO<sub>x</sub> and N<sub>2</sub>O is examined here.

Flux measurements revealed seasonal emission factors of 1.24% and 0.22% of added nitrogen for NO<sub>x</sub> and N<sub>2</sub>O, respectively. An unequivocal relationship between the amount of added nitrogen and the magnitude of gaseous efflux was evident. A relationship to organic matter amendment, whose proportions have been steadily declining in China, was significant only for N<sub>2</sub>O. Relative seasonal fluxes were lower than those determined by other authors, possibly the result of particularly high ammonia volatilization under Chinese management regimes.

Mathematical simulations with the biogeochemical model DAYCENT adequately represented the temporal dynamic and peak size of measured fluxes. Ammonia volatilization levels were important considerations in comparing measured versus simulated trace gas fluxes. DAYCENT tended to underestimate the number of very small fluxes, however overall seasonal fluxes were similar for measured versus simulated fluxes.

In response to sensitivity to the climatic variables of temperature and precipitation, standard biogeochemical diagnostics including soil carbon, organic soil nitrogen, grain yield, net primary productivity, and actual evapotranspiration behave according to expectations. Emissions of NO and N<sub>2</sub>O, however, show a complex and nonlinear response, reflecting interactions and fluctuations within the many driving parameters of trace gas production.

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# CHAPTER 1

## INTRODUCTION

### Agricultural Nitrogen in the People's Republic of China

Globally, reactive nitrogen mobilization has more than doubled under the influence of anthropogenic activities (Holland et al., 1999). Fertilizer production, fossil fuel combustion, and legume cultivation are the primary drivers of this trend. As food and energy production are the proximal drivers of this phenomenon, Asia, and China in particular, with a dense population and rapidly developing economy is therefore a regional hotspot of reactive nitrogen mobilization and distribution (Galloway, 2000). The effects of this acceleration range from the microscopic to the global.

In 1990, 85% of the globally mobilized reactive nitrogen ( $N_R$ ) was created within agroecosystems, making agriculture the single largest contributor to biogeochemical nitrogen cycling (Galloway et al., 1995). China possesses 22% of the world's population and only 11% of the world's arable land (UNFAO). China's food demand will increase by ~1%/yr over the next two decades (Chameides et al., 1999), while urban development decreases the amount of arable land in that country at a similar rate (Lindert et al., 1996).

The increasing disproportionality of this situation results in an unprecedented intensity of land-use in order to ensure food security. Even so, yields have not been increasing as quickly as nitrogen application rates (Richter and Roelcke, 2000; Figure 1.1).

Rates of traditional nutrient inputs, including crop residues, human and animal wastes are decreasing proportionally, while synthetic nitrogen applications skyrocket nationally (Figure 1.1). China's synthetic nitrogen fertilizer consumption is the largest in the world, accounting for approximately 20 Tg of 80 Tg globally in 1990, and this proportion continues to increase. Traditional Chinese subsistence agriculture had a high degree of stability and sustainability while supporting high population densities (Guo and Bradshaw, 1993). Potential effects of these trends are unknown.

While regional fertilizer uptake efficiency averages 60% (Galloway, 2000), Zhang et al. (1992) measured only a 20-31% fertilizer recovery in the calcareous soils of the North China Plain. Roelcke and Richter (2000) report that 43-62% of added nitrogen in maize and 36-46% in winter wheat are lost from agricultural production in the Loess Plateau. Matsumoto et al. (1999) note an effect of crop and form of added N on uptake efficiency. The presence of organic matter seemed to exhibit a primary control on these secondary effects, as its addition has been shown to be effective at retaining nitrogen in the soil (Roelcke et al., 2000). A high degree of N-surpluses are noted in each of these systems.

Fertilization rates in the North China Plain typically exceed  $500 \text{ kg ha}^{-1} \text{ year}^{-1}$  (Zhang et al., 1996) in a double cropped, summer corn–winter wheat rotation. In an economic investigation, Roelcke et al. (1998) determined that at intermediate fertilization

rates yields were maximized and the cost of fertilizer inputs were substantially reduced. While this appears to be an optimal arrangement from both the microeconomic and environmental point of views, national averages still show increasing crop yields with increasing fertilizer inputs, and therefore, official policy still seeks to maximize production by maximizing fertilizer inputs.

Transfer of nutrients is laborious, and therefore, the majority of nitrogenous fertilizer inputs are near areas of high population density (Guo and Bradshaw, 1993). This creates a unique situation found in only a few regions in the world, which Chameides et al. (1994) have termed Metro-Agro-Plexes, where urban pollution issues impact agricultural production, and agrochemical pollution impacts the urban environment. Increasing evidence of nonpoint  $N_R$  pollution in air, water, and soils is mounting (Roelcke and Richter, 2000).

#### Atmospheric Effects of $NO_x$ and $N_2O$

Agricultural productivity and fertilizer applications in particular result in increasing atmospheric concentrations of chemically and radiatively active gases (Figure 1.2). In fact, 60% of anthropogenically generated reactive nitrogen ( $N_R$ ) is emitted directly or indirectly to the atmosphere (Galloway, 2000).  $NO_x$  and  $N_2O$  are of primary interest to this dissertation. As agriculture represents the largest contributor to accelerated nitrogen cycling in China, a short discussion on agriculture's role in the atmospheric composition of these gases is relevant. Each of these gases is an intermediate product in the processes of microbial nitrification and denitrification. Metabolic inefficiencies result in their release into the interstitial microenvironment

following production. However, under circumstances of scarcity, microbes may absorb NO in particular for use in their population-level nitrogen cycle. Absorption of these gases by soils may also occur as a result of simple diffusion processes. When the atmospheric concentration is greater in the atmosphere above the soil, a concentration gradient is produced and a net flux is observed into the soil, regardless of microbial utilization. This is not an uncommon scenario in urban agriculture, of which eastern China is exemplary.

Since 1950, global NO<sub>x</sub> emissions have quadrupled (Fenger, 1999). Chinese emissions of NO<sub>x</sub> are currently 12 Mt yr<sup>-1</sup> (Streets and Waldhoff, 2000), primarily the result of stationary energy production. Emissions are expected to double or triple in the next two decades (Horowitz and Jacob, 1999), driven by increasing consumption of transportation fuels and fertilizer. Chinese NO<sub>x</sub> emissions, although dwarfed by U.S. emissions, have a disproportionate impact on global atmospheric oxidizing capacity due to latitudinal proximity to the tropics (Horowitz and Jacob, 1999), thereby reducing the ability of the atmosphere to remove long-lived, radiatively active trace gases. NO<sub>x</sub> may contribute to regional atmospheric particulate loading. It is postulated that the reduction in radiative flux at the earth's surface resulting from this haze may reduce production of 70% of China's crops by 5-30% (Chameides et al., 1999). Its role in tropospheric ozone production (Horowitz and Jacob, 1999) may also reduce crop yields, as ozone is phytotoxic (Chameides et al., 1994). NO<sub>x</sub> contribution to acidification is minor compared with sulfur in most places, but stationary and mobile sources are expected to increase substantially (Seip et al., 1999). Over 1 million square kilometers in China already

subject to acidification are believed to be approaching their buffering limits, with the most sensitive areas being in the southeastern part of the country (Tao and Feng, 2000).

$\text{N}_2\text{O}$  is believed to be responsible for 5% of total radiative forcing (Li and Lin, 2000). It is a potent greenhouse gas, with a greenhouse warming potential 270 times that of  $\text{CO}_2$  over a century timescale. Its long lifetime ( $\tau = 120$  years) allows it to permeate the stratosphere, where it is responsible for some of the heterogeneous chemical reactions that result in the catalytic destruction of the ozone layer. The production of  $\text{N}_2\text{O}$  from Chinese soils has been estimated to be 0.282 Tg N for the year 1990 (Xing and Zhu, 2000). Xu et al. (2000) estimated that agriculture contributed 65% of the total  $\text{N}_2\text{O}$  production in 1995. They further estimate direct  $\text{N}_2\text{O}$  production from synthetic fertilizer in 1990 as 342.5 Gg N.

Ammonia ( $\text{NH}_3$ ) is not examined here, although it is believed to be the primary loss of added fertilizer nitrogen (Roelcke et al., 2000), with losses ranging from 51-66% within 21 days of addition. Xing and Zhu (2000) estimate that ammonia losses are equivalent to 11% of nationwide fertilizer applications.  $\text{NH}_3$  is volatilized at large rates from agricultural fertilizer applications. Together with dust and other basic minerals, ammonia gas acts to buffer acidic atmospheric emissions, resulting in negligible acid precipitation in northern China, despite the high magnitude of sulfur and nitrogen based acidic deposition precursors.

#### Effects on Aquatic Systems

Total nitrogen in Chinese waterways has increased markedly over the last several decades, displaying a strong correlation to fertilizer application rates in the Changjiang

(Yangtze River), Huanghe (Yellow River), and Zhujiang (Pearl River) drainages (Duan et al., 2000, Zhang et al., 1999, Chen et al., 2000). Runoff from these rivers represents only 3% of the total world riverine drainage, yet dissolved inorganic nitrogen (DIN) transport from the three rivers represented 12-23% of the total world transport (Duan et al., 2000). The tributaries here are characterized by intensive anthropogenic perturbation. From the upland agriculture of the north, leaching losses have been estimated at 0.5-4.2% of added nitrogen in fertilizer (Xing and Zhu, 2000). The application of chemical fertilizers in the Changjiang watershed has increased by 150% over the last two decades, where net primary productivity (NPP) is strongly phosphorus limited. As a result of crops' inability to use this additional nitrogen due to the superceding phosphorus limitation, large quantities of added N are lost through hydrological means.

Of the anthropogenically created  $N_R$ , 30% will be transported to oceans by waterways globally (Galloway et al. 1995). According to Zhang et al. (1999), changing land use and fertilization practices have caused a factor of five increase in the magnitude of nitrogen addition to ocean waters. The addition of anthropogenic N contributes to eutrophication of fresh and marine waters (Galloway, 2000).

### Effects on Public Health

While nitrogen pollution has been presented here as a threat to environmental health and sustained agricultural productivity, public health concerns relating to nitrogen pollution are numerous and often the most important factor where policy is concerned. For many such concerns, China is considered the quintessential epidemiological study. Yang (1999) demonstrated a relationship between the runoff from agrochemicals and

elevated genotoxicity of water supplies. High nitrate levels and total nitrogen content were the primary contributory factors relating to chromosomal damage potential in that study. In fact, toxicity at one site with particularly high levels of nitrogenous leachate was the statistically indistinguishable from the positive control for the study, 300 mg l<sup>-1</sup> mercuric chloride.

Yokokawa et al. (1999) investigated high-incidence areas for esophageal cancer in China. Concentrations of NO<sub>3</sub><sup>-</sup>-N in well water and well water consumption rate showed the strongest correlation to esophageal cancer occurrence. Zhou et al. (2000) further demonstrated that high rates of nitrate intake come from the vegetables cultivated under such intensive management scenarios. A more explicit link between nitrate contained in vegetables and esophageal cancer occurrence may become available in the future.

Air quality has a highly significant impact upon health and mortality through respiratory and coronary mechanisms. High particulate concentrations are strongly linked to increased mortality (Xu et al., 1994). Lung cancer is the primary cause of cancer death in some parts of China, and a significant relationship between air pollutants, including NO<sub>x</sub>, and mortality were observed in those areas. Other studies suggest that the development of respiratory function of children in Chinese urban areas is impeded due to the presence of pollution, including NO<sub>x</sub>, and that levels of respiratory irritation were elevated in these populations.

### Conclusions

The production of reactive nitrogen is an unavoidable byproduct of agricultural and economic activities. It contributes to degrading public health and may impede the

ability of agroecosystems to provide their fundamental food production services. China's contribution to global  $N_R$  creation is second only to that of the U.S. (Galloway et al., 1996), and is expected to increase substantially over the next several decades. Due to the primary role of agriculture in the release of  $N_R$  in China, it is important to quantify relevant fluxes from this sector.

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## Figure Captions

Figure 1.1. Chinese fertilizer use and grain yield. Synthetic fertilizer use has superceded organic nitrogen sources in recent decades. The marginal rate of return in grain yield seems to be diminishing with increased application rates. Adapted from Wang et al. (1996).

Figure 1.2. Nitrogen transformations and trace gas production. Inorganic soil nitrogen, present due to the mineralization of organic matter or the application of synthetic fertilizer fuels nitrification and denitrification activity. Metabolic inefficiencies in these processes result in the “leakage” of nitrogen-based trace gases into the atmosphere. Adapted from Firestone and Davidson (1989) and Wollast (1981).

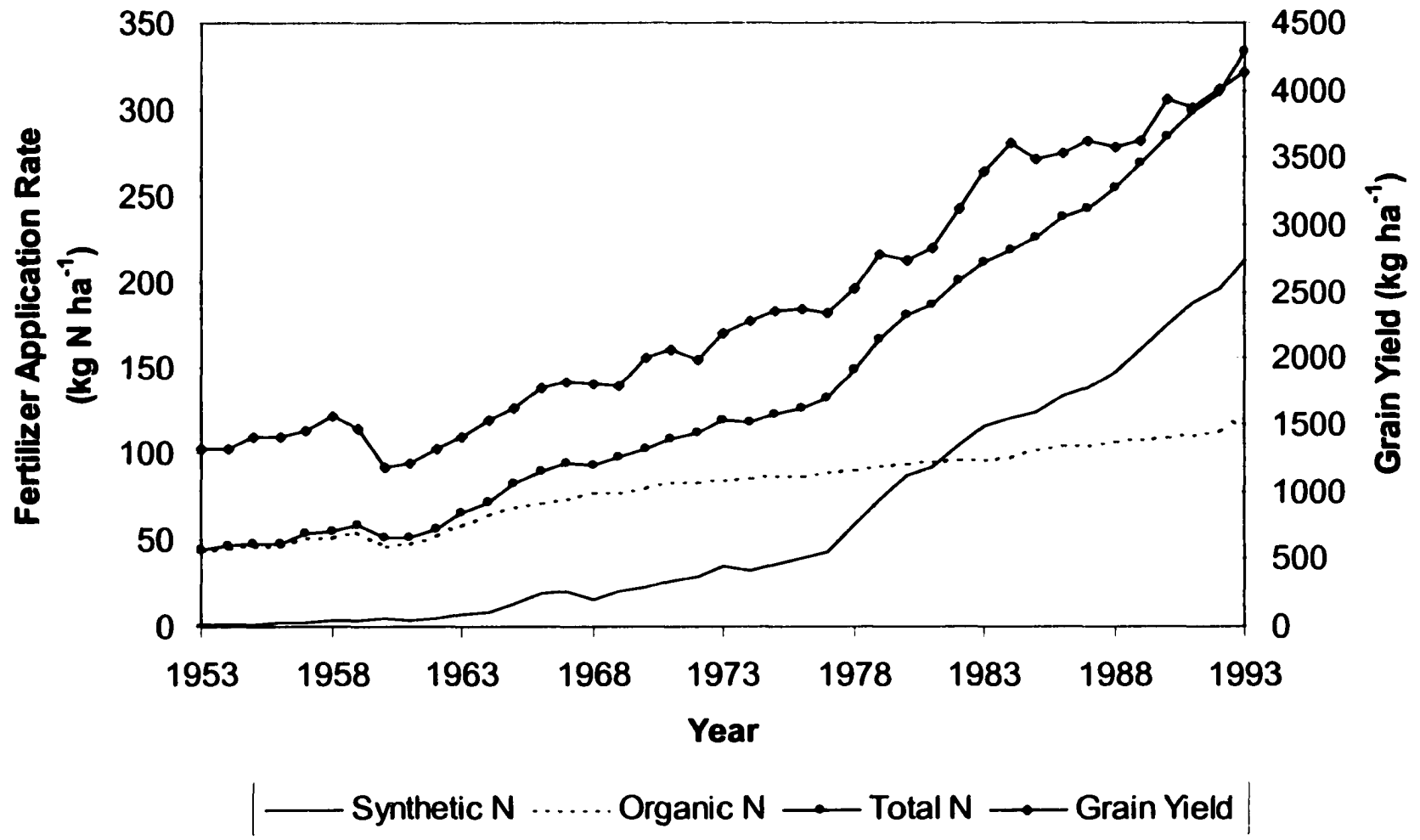


Figure 1.1 Fertilizer use and grain yield in the PRC.

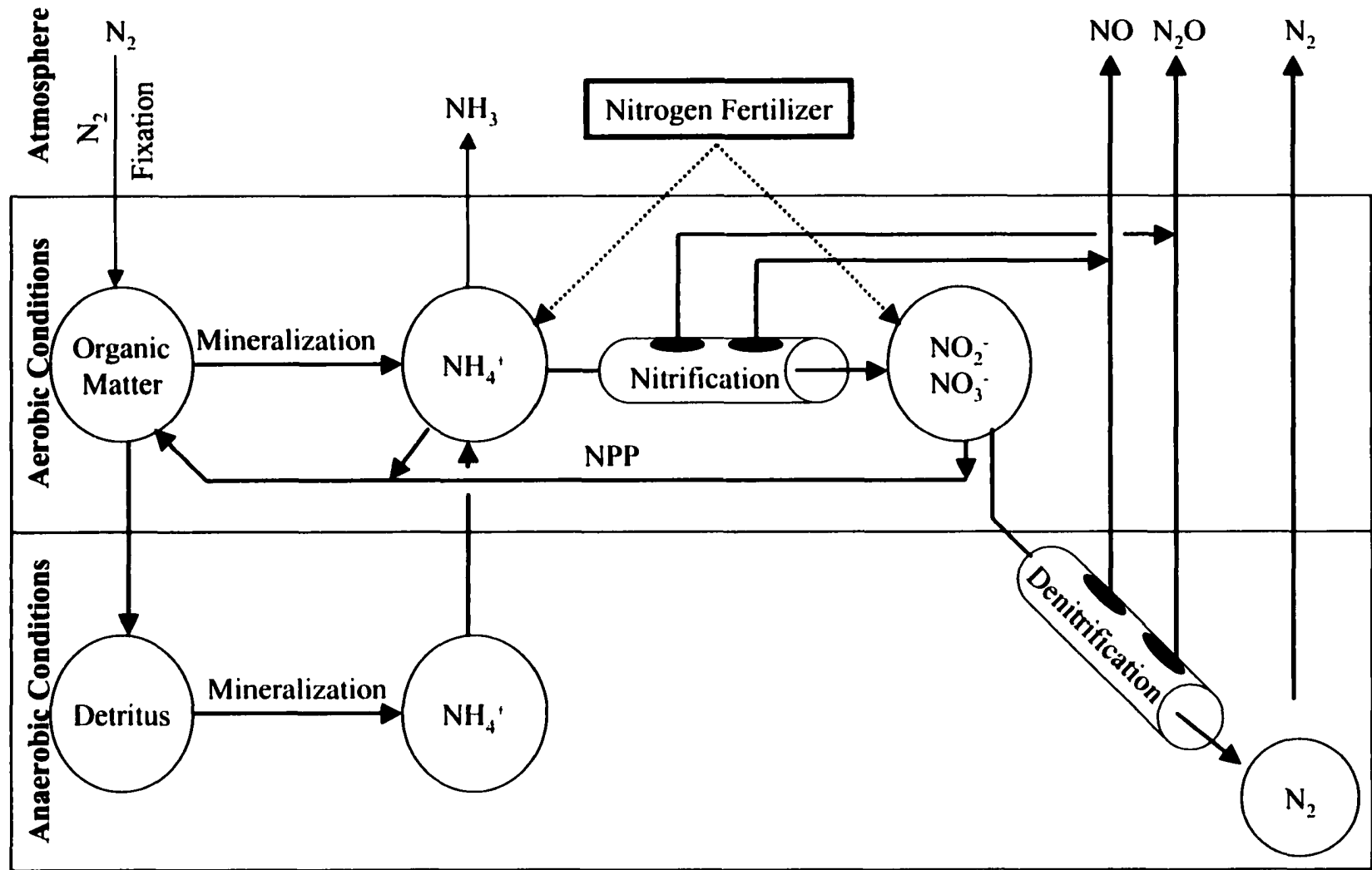


Figure 1.2 Schematic representation of trace gas production processes

## CHAPTER 2

### NO<sub>x</sub> and N<sub>2</sub>O Fluxes from Agricultural Soils on the North China Plain

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#### Abstract

Chinese agriculture represents one of the most intensively managed ecosystems in the world. Typical fertilization rates are several times those of the U.S., resulting in dramatically accelerated nitrogen cycling. In this study, we have examined NO and N<sub>2</sub>O exchange in the upland agricultural systems of northeastern China. Inorganic and organic fertilizer treatments were applied in order to evaluate their impact on the magnitude and proportion of trace gas emissions. Increasing inorganic fertilization rates showed a highly significant impact upon emissions of both NO and N<sub>2</sub>O. Organic matter amendment affected N<sub>2</sub>O but not NO fluxes. Overall losses of added nitrogen by NO and N<sub>2</sub>O emission averaged 1.24% and 0.22% respectively over the range of treatments in this study. Results from our field study indicate that Chinese agricultural systems represent a significant contribution to that nation's nitrogen budget.

## Introduction

The magnitude of global nitrogen cycling has more than doubled under anthropogenic influence (Holland et al., 1999). Among the most important results of accelerated nitrogen cycling are changes in atmospheric reactive trace gases. Although in developed countries reactive nitrogen (NR =  $\text{NH}_x$ ,  $\text{N}_x\text{O}_y$ ,  $\text{N}_{\text{ORGANIC}}$ ) creation is most frequently associated with the combustion of fossil fuels, this source accounts for only approximately 20 Tg NR  $\text{yr}^{-1}$  production globally. Far more important in magnitude and distribution is the agricultural source of NR, particularly that portion resulting from the consumption of synthetic nitrogen fertilizers. Fertilizers account for approximately 80 Tg NR production per year, well over half of the anthropogenic nitrogen budget. Inorganic nitrogen in soils is subject to chemical conversions by microbial nitrification and denitrification, causing the emissions of NO and  $\text{N}_2\text{O}$  (Firestone and Davidson, 1989). Skiba et al. (1997) estimate a 10 Tg NO-N soil source, 41% of which originates from agricultural soils (Yienger and Levy, 1995). IPCC (1995) estimates that cultivated soils are responsible for more than 60% of anthropogenic  $\text{N}_2\text{O}$  production globally. Chinese agriculture represents one of the most intensively managed and consequently influential ecosystems in the world. Typical fertilization rates are several times those of the U.S., resulting in dramatically accelerated nitrogen cycling. China's contribution to global nitrogen mobilization is currently second only to that of the U.S. Unlike the U.S.,

however, the rate of biogeochemical nitrogen cycling in China is expected to grow rapidly in the foreseeable future as a result of unprecedented fertilizer application rates (Galloway et al., 1996; Zhang, 1996). Of the 80 Tg NR mobilized by fertilizer annually, China is itself responsible for 20 Tg. According to the United Nations Food and Agriculture Organization (FAO) (<http://apps.fao.org/>), China has approximately 70% the arable land area of the U.S. and almost five times the population. Additionally, China's arable land is being irretrievably converted from agricultural uses (Lindert et al., 1996) as population continues to expand. This results in an intensity of land use rivaled only in comparably very small areas of the rest of the world. Fertilizer application rates routinely exceed  $500 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  (Zhang, 1996), several times those commonly applied or recommended in the U.S.

Not only is China a major contributor to global NR mobilization, its contribution is qualitatively unique and its temporal dynamics (Galloway et al., 1996) are very unlike those of the more extensively studied western countries upon which biogeochemical models and international assessments have been based. Fertilizer consumption in China is, and will remain, the major source of NR production in that country. China's already large contribution to the global NR budget is expected to double over the next 20 years. 80% of this increase will be the result of increased fertilizer applications (Galloway et al., 1996). China's shift from primarily organic fertilizer sources 40 years ago to synthetic fertilizers has had important consequences, including a 77.1% reduction in soil organic matter in upland agricultural soils (Cai 1996). Matson et al. (1996) have shown that management is the dominant control of trace gas losses. Consequently, any evaluation of

the global nitrogen cycle should consider China's unique characteristics.

To begin to address this situation, we are interested in the impact of fertilizer additions and organic matter amendment upon the magnitudes of NO and N<sub>2</sub>O fluxes under the extreme application rates and traditional land management practices in China.

### Methods

Our study was conducted at China Agricultural University, 39°57' north latitude, 116°18' east longitude, 16.5 km northwest of downtown Beijing. Soil pH averaged  $8.17 \pm 0.042$  over the top 30 cm, with initial organic matter values of  $0.870 \pm 0.19\%$  and nitrogen content of  $0.0719 \pm 0.023\%$ . Soil was a loam texture with a bulk density of  $1.32 \text{ g cm}^{-3}$ . Every attempt was made to simulate geographically typical management practices. This included two separate fertilization events over the course of the corn cropping cycle. The synthetic fertilizer applied was urea, and organic matter was a mixed farmyard manure containing 2.95% N by dry weight. First, at planting, a "base coat" fertilization was applied, consisting of all of the organic matter to be applied to that crop, and 50% of the synthetic nitrogen. The remainder of the synthetic nitrogen was applied 35 days following planting in what is termed the "top coat" application.

Studies were conducted over a 7-week period at the beginning of the corn portion of the crop rotation. Four replicates were maintained for each of the six treatments, consisting of three levels of urea addition (0, 150, and 300 kg N ha<sup>-1</sup> crop<sup>-1</sup>) and two levels of organic matter amendment (0, 3000 kg C ha<sup>-1</sup> crop<sup>-1</sup>). Plots were 4 m<sup>2</sup> each. NO<sub>x</sub> measurements were made and analyzed according to the method described in Williams and Davidson (1993) 2-5 times per week. A Unisearch model LMA-4 luminol-

based chemiluminescent nitrogen oxides detector was used over 5-minute measurement periods of the soil headspace gas in monitoring NO flux rates. N<sub>2</sub>O was monitored and analyses performed twice per week according to the method given in Hutchinson and Mosier (1981). Samples were taken three times over a 30-minute period and analyzed within 24 hours by GC-ECD.

Ambient and soil temperatures, soil moisture, and ammonium and nitrate concentrations were measured at depths of 0-10cm, 10-20 cm, and 20-30 cm each time gas monitoring occurred.

### Results and Discussion

Water filled pore space averaged 44.2% (SD 3.7) at the times samples were obtained. Average daily ambient temperature ranged from 14.4 to 29.7°C, and soil temperature averaged 23.3 ± 4.4°C over the sampling period. Soil ammonium and nitrate increases displayed in Figure 2.1 correspond to fertilization events.

Trace gas fluxes are shown in Figures 2.2 and 2.3. Flux values for NO<sub>x</sub> ranged from -107.7 ± 81 µg NO-N m<sup>-2</sup> h<sup>-1</sup> for the control plots to 1749 ± 1160 µg NO-N m<sup>-2</sup> h<sup>-1</sup> emissions for the highest N-treatment, with average values ranging from -6.84 ± 35 to 543.1 ± 506 µg NO-N m<sup>-2</sup> h<sup>-1</sup> respectively. Losses over the sampling period were determined by interpolation between sampling days to provide estimates of cumulative losses over the sampling period and may be found in the table in Figure 2.2. Losses for the highest three treatments, those most representative of typical Chinese agricultural practice, are compared with literature values in Table 2.1.a. The losses compare well with those obtained in agricultural systems in the southeastern United States (Thornton et

al., 1998; Thornton and Valente, 1996), but are quite low compared with values derived in other parts of the world (Veldkamp and Keller, 1997b; Matson et al., 1998; Jambert et al., 1997a) with comparable fertilization rates. Our emission factors (0.58 - 1.0% of added N lost as NO) are roughly comparable to that given by Veldkamp and Keller in their review (1997a) of 0.5% NO-N in temperate agriculture.

Figure 2.3 represents N<sub>2</sub>O emissions. Fluxes over the sampling period range from  $5.02 \pm 10 \mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$  for the control plot to  $359.5 \pm 33.9 \mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$  for the 300 kg N ha<sup>-1</sup> high organic matter treatment, with average fluxes ranging from  $10.2 \pm 3.3$  to  $123.3 \pm 103.2 \mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$ , respectively. Losses over the sampling period were again determined by interpolation between sampling days and summed to give cumulative losses over the sampling period, and may be found in the table in Figure 2.3. Losses for the highest three treatments are compared with literature values in Table 2.1.b. Our values (1.1 - 2.2% of added N lost as N<sub>2</sub>O) compare reasonably well to those found in the literature.

It should be noted that length of time over which measurements occur and the measurement frequency impact the observed magnitude of trace gas emission (Bouman, 1996). Additionally, in agricultural systems background emissions are often not negligible in their contribution to overall nitrogen fluxes. As our sampling period was shorter and sampling intervals sometimes less frequent than otherwise comparable studies, emissions from Chinese upland agricultural soils may be even higher than indicated here.

As expected, a highly significant positive relationship was found between

increasing urea application and NO<sub>x</sub> flux ( $p < 0.0001$  for both base and top coat fertilizations) and N<sub>2</sub>O emissions ( $p = 0.0007$  for base coat and  $p = 0.0431$  for top coat fertilization) by linear contrast analysis. No relationship between organic matter and NO<sub>x</sub> flux was evident. A significant relationship ( $p = 0.0625$ ) was discovered for the effect of organic matter addition upon N<sub>2</sub>O emission following the base coat fertilization event. This effect was transitory, however, and disappeared by the second (top coat) fertilization. Thornton et al. (1998) and Xing and Zhu (1997) each found significant differences in trace gas fluxes from organic and inorganic N-fertilization sources. Our results support this finding, but indicate further investigation of the temporal dynamic is warranted.

The period of elevated emissions following fertilization appears prolonged in this study compared with others (Skiba et al., 1992, Veldkamp and Keller, 1997b). In this study, elevated emissions are observed for close to 4 weeks following fertilization in the case of N<sub>2</sub>O, and 2 weeks in the case of NO, longer than the 1-2 week elevated response period determined in other studies. It is suggested that this temporal dynamic and possible causative factors be scrutinized in future studies.

### Conclusions

The relationship between fertilizer application rate and gaseous efflux is shown in Figure 2.4. The emission factor for NO was determined by linear regression to be  $1.24 \pm 0.22\%$  and for N<sub>2</sub>O  $0.22 \pm 0.07\%$  of added nitrogen. The proportion of NO is higher than the average in temperate agriculture estimated by Veldkamp and Keller (1997a) of 0.5%. The proportion lost as N<sub>2</sub>O is lower than the IPCC emission factor of 1.25% (Mosier et al., 1998). Although our data represent a small land area and a single land use, we

believe the differences in average emission factors should prompt further inquiry.

Because China represents such a large proportion of the world's fertilizer consumption and a unique range of application rates, further studies are recommended in order to determine appropriate emission factors for China, and their incorporation into larger scale examinations of anthropogenically induced trace gas emissions.

One reason for obtaining lower trace gas emission factors in China is the degree to which ammonia volatilization reduces the pool of soil nitrogen available for nitrification and denitrification, and consequently, reduces the potential for  $\text{NO}_x$  and  $\text{N}_2\text{O}$  releases. High soil pH and the manual incorporation of pellet-type, ammonia-based chemical fertilizers create ideal conditions for high rates of ammonia volatilization from Chinese soils. Much of this loss occurs from several hours to several days following application (Zhang et al., 1992), though Roelcke et al. (1996) discovered elevated volatilization as far removed as 13 days post-application. Xing and Zhu (2000) found nationwide  $\text{NH}_3\text{-N}$  volatilization rates to be 11% of applied nitrogen fertilizer, Zhang et al. (1992) determined a range of 12-32%, and the experiments of Roelcke et al. (1996) revealed losses approaching 60%.

Local conditions and management allow a diversity of circumstances that could easily perturb volatilization. Therefore, without having explicitly measured ammonia losses simultaneous with our other trace gas measurements, we have no way of determining where within this broad range of 11 – 60% our accumulated ammonia losses may have fallen. It stands to reason, however, that a significant proportion of the nitrogen added to the experimental soils was lost to ammonia volatilization before becoming

available for microbial conversion. The IPCC's (1996) approach to resolve this issue in the case of N<sub>2</sub>O is to reduce the levels of synthetic fertilizer applied by 10% and of organic fertilizers by 20%, so only 90% and 80% (respectively) of real nitrogen applications are accounted for in their emission estimates. Reducing application rates in calculations of emission factors would have the effect of increasing those factors. This approach was not taken here both because the 10% reduction offered by IPCC is at the lowest end of those estimates obtained specifically for China and would therefore be of limited utility, and because it does not seem to have been taken by those whose efforts precede ours, whose figures we wished to provide a direct comparison with. In large-scale biogeochemical assessments, however, it seems apparent that this effect is substantial enough that some accounting for ammonia losses must be attempted.

If the linear relationship for the calculation of emission factors holds, as other studies indicate it should (Skiba et al., 1992), then we may begin to evaluate the contribution of this land use to regional nitrogen budgets. In 1995 according to FAO (<http://apps.fao.org/>), 23 Mha of China's 125 Mha total arable land was under some kind of maize management regime. It is a reasonable assumption that 90% of this area (20 Mha) is double cropped with another grain. Fertilization rates in such systems are typically 300 kg N ha<sup>-1</sup> crop<sup>-1</sup>. If these estimates hold true, then over 12 Mt fertilizer-N would have been applied to systems comparable to those in this study. Our estimate would be consistent with reported agricultural statistics, given that upland agriculture accounts for half of the total agriculture in China, corn-wheat rotations compose 80% of this type of agriculture (Xing and Zhu, 1997), and China as a whole consumed over

23\*10<sup>6</sup> Mt fertilizer-N in 1995 (<http://apps.fao.org/>). If 1.25% of the 12 Mt N is emitted as NO<sub>x</sub> and 0.22% as N<sub>2</sub>O, corn-grain rotations may be responsible for the production of 1.54 \*10<sup>11</sup> g NO<sub>x</sub>-N yr<sup>-1</sup> and 2.71\*10<sup>10</sup> g N<sub>2</sub>O-N yr<sup>-1</sup>. Kato and Akimoto (1992) note that China is Asia's largest NO<sub>x</sub> producer, and estimate its 1987 contribution to be 7.37\*10<sup>12</sup> g yr<sup>-1</sup>. This figure does not appear to include the soil source of nitrogenous gases, therefore, the magnitude of NO<sub>x</sub> produced as a result of the intense cultivation of corn-grain rotations may be just over 2% of the non-soil NO<sub>x</sub> source in that country. World Bank estimates (Johnson et al., 1996) place China's 1990 N<sub>2</sub>O emissions at 0.26 Mt, 0.03 Mt the direct result of fertilizer applications. Our study finds emissions from upland corn-grain soils (covering 16.4% of the total arable land area) to be approximately 0.0271 Mt , similar to the World Bank's estimate of emissions for the whole country.

Our study indicates China's soil source of nitrogenous pollutant and climate-relevant gases is significant and driven in large part by agricultural fertilizer applications. China is responsible for a sizable portion of the global nitrogen budget, is unique in the management practices which lead to trace gas exchanges, and is not as well studied as other areas of the world, areas better accounted for in large-scale biogeochemical assessments; this study begins to help quantify nitrogenous fluxes in this increasingly important region.

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### Figure Captions

Figure 2.1. Average soil NH<sub>4</sub><sup>+</sup> (a) and NO<sub>3</sub><sup>-</sup> (b) in the top 10 cm during major phases of the crop cycle. Pre-fertilization concentrations are those preceding planting and the initial fertilization event; base coat concentrations are those for the two weeks immediately following the application of 50% of the synthetic fertilizer and all of the organic matter addition; the interfertilization period displays inorganic soil nitrogen for the following approximately three weeks; the top coat category refers to the time following the final application of the remaining 50% of the urea.

Figure 2.2. NO fluxes for the low (a) and high (b) organic matter treatments. Arrows indicate fertilization events. Pertinent fluxes are summarized in the accompanying table. Cumulative losses were calculated over the 49-day sampling period by interpolation. The seasonal loss reflects the proportion of added nitrogen lost as NO-N.

Figure 2.3.  $\text{N}_2\text{O}$  fluxes for the low (a) and high (b) organic matter treatments. Arrows indicate fertilization events. Pertinent fluxes are summarized in the accompanying table. Cumulative losses were calculated over the 49-day sampling period by interpolation. The seasonal loss reflects the proportion of added nitrogen lost as  $\text{N}_2\text{O-N}$ .

Figure 2.4.  $\text{NO-N}$  (a) and  $\text{N}_2\text{O-N}$  (b) losses as a function of fertilizer application rate. Error bars reflect one standard error. Intervals represent 95% confidence level.

Table 2.1.  $\text{NO-N}$  (a) and  $\text{N}_2\text{O-N}$  (b) flux rates are compared to other studies with comparable fertilization rates.

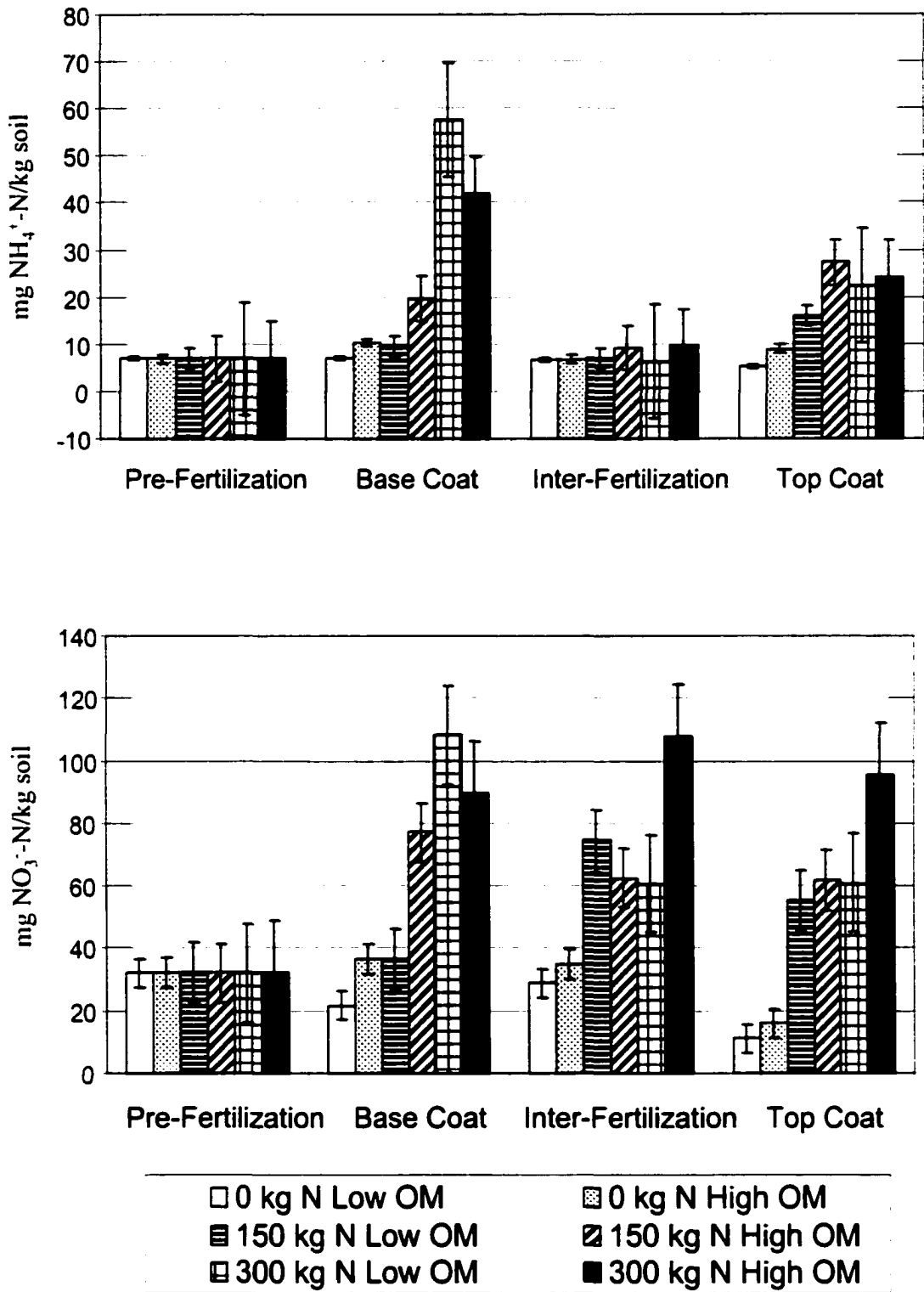
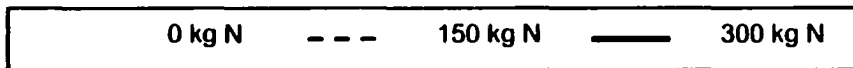
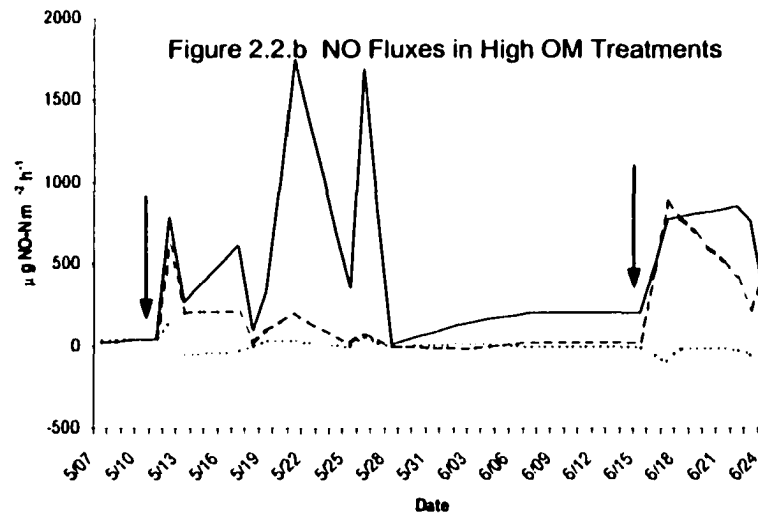
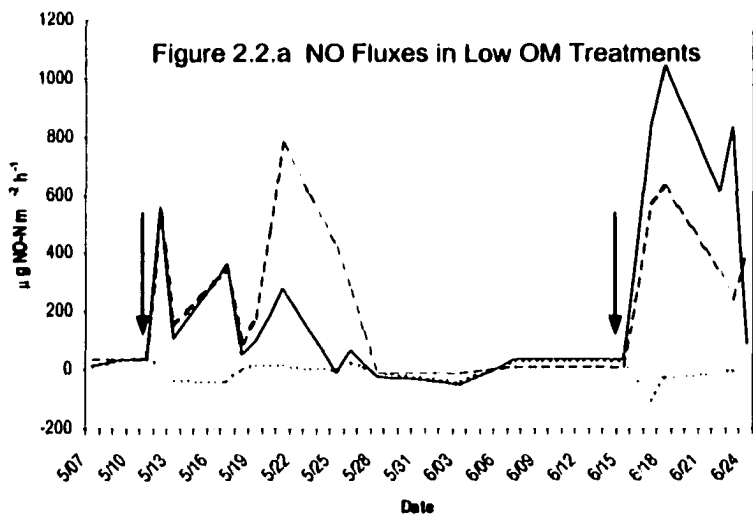
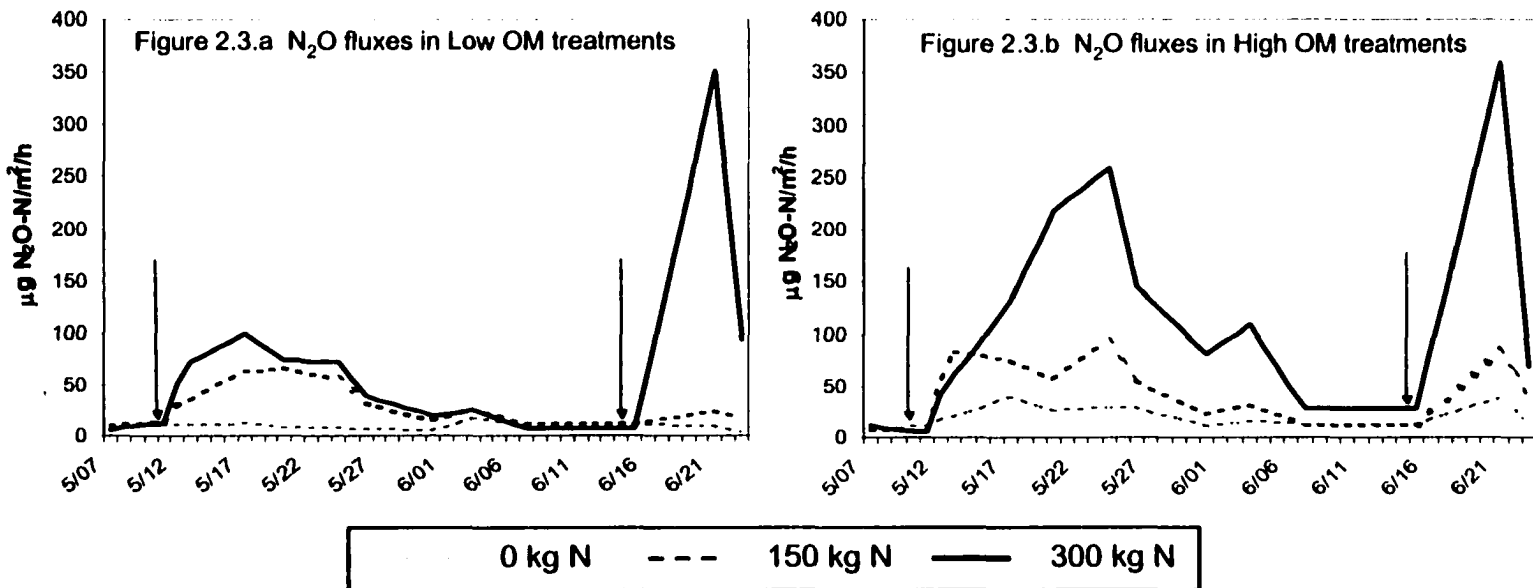


Figure 2.1 Soil NH<sub>4</sub><sup>+</sup> (a) and NO<sub>3</sub><sup>-</sup> (b).



$N_{\text{UREA}}$ (kg N ha <sup>-1</sup> )	OM	$N_{\text{TOTAL}}$ (kg N ha <sup>-1</sup> )	Fluxes (µg NO-N m <sup>-2</sup> h <sup>-1</sup> )			Cumulative Flux (kg N ha <sup>-1</sup> )	Seasonal Loss (%)
			Low	High	Average		
0	L	0	-108 (81)	44 (15)	-7 (35)	-0.016	n/a
0	H	88.5	-100 (8)	142 (96)	0.5 (55)	0.038	0.043
150	L	150	-10 (19)	776 (1020)	279 (234)	2.4	1.6
150	H	238.5	-17 (48)	786 (271)	239 (276)	1.9	0.78
300	L	300	-24 (45)	1046 (370)	275 (340)	2.3	0.75
300	H	388.5	9 (53)	1749 (1160)	543 (506)	5.2	1.3



N <sub>UREA</sub> (kg N ha <sup>-1</sup> )	OM	N <sub>TOTAL</sub> (kg N ha <sup>-1</sup> )	Fluxes (µg N <sub>2</sub> O-N m <sup>-2</sup> h <sup>-1</sup> )			Cumulative Flux (kg N ha <sup>-1</sup> )	Seasonal Loss (%)
			Low	High	Average		
0	L	0	5 (10)	17.4 (12.5)	10.2 (3.3)	0.12	n/a
0	H	88.5	11 (6)	40.3 (39.3)	22 (10.6)	0.12	0.14
150	L	150	10.5 (9.2)	65.8 (74.6)	30.8 (19)	0.19	0.13
150	H	238.5	6.6 (8.2)	93.6 (34.4)	47.4 (30.3)	0.35	0.15
300	L	300	6.7 (6.8)	352.3 (667)	72.8 (90.3)	0.60	0.20
300	H	388.5	6.1 (3.4)	359.5 (33.9)	123.3 (103.2)	1.2	0.30

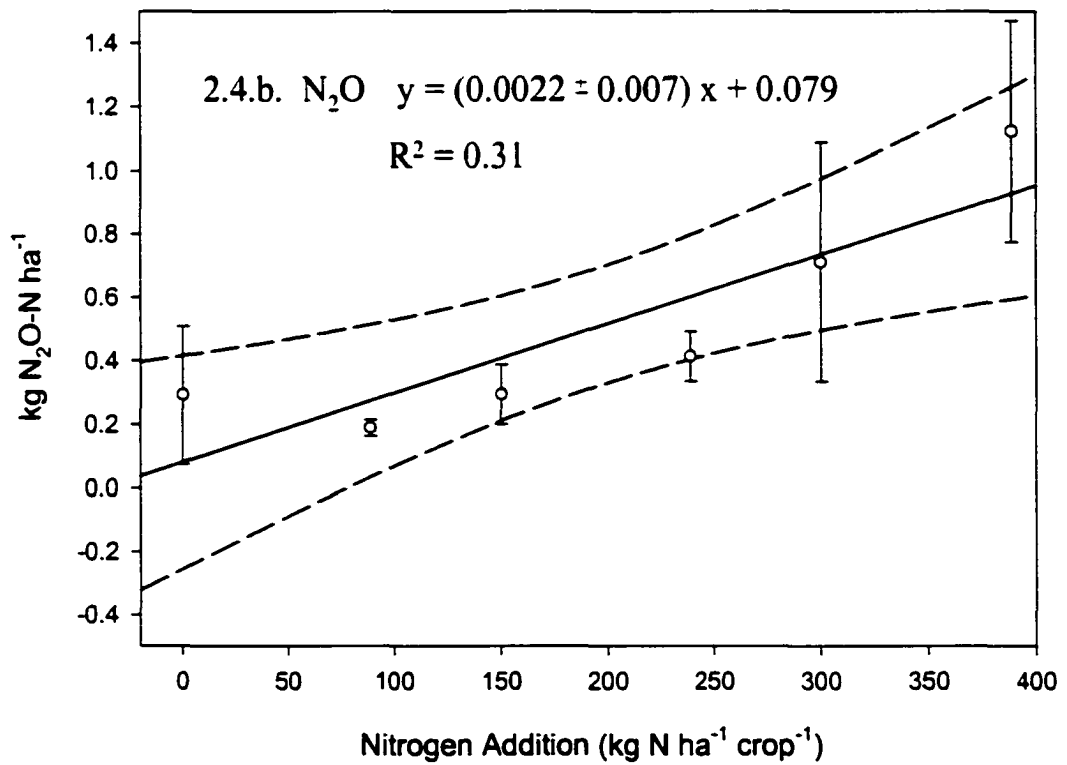
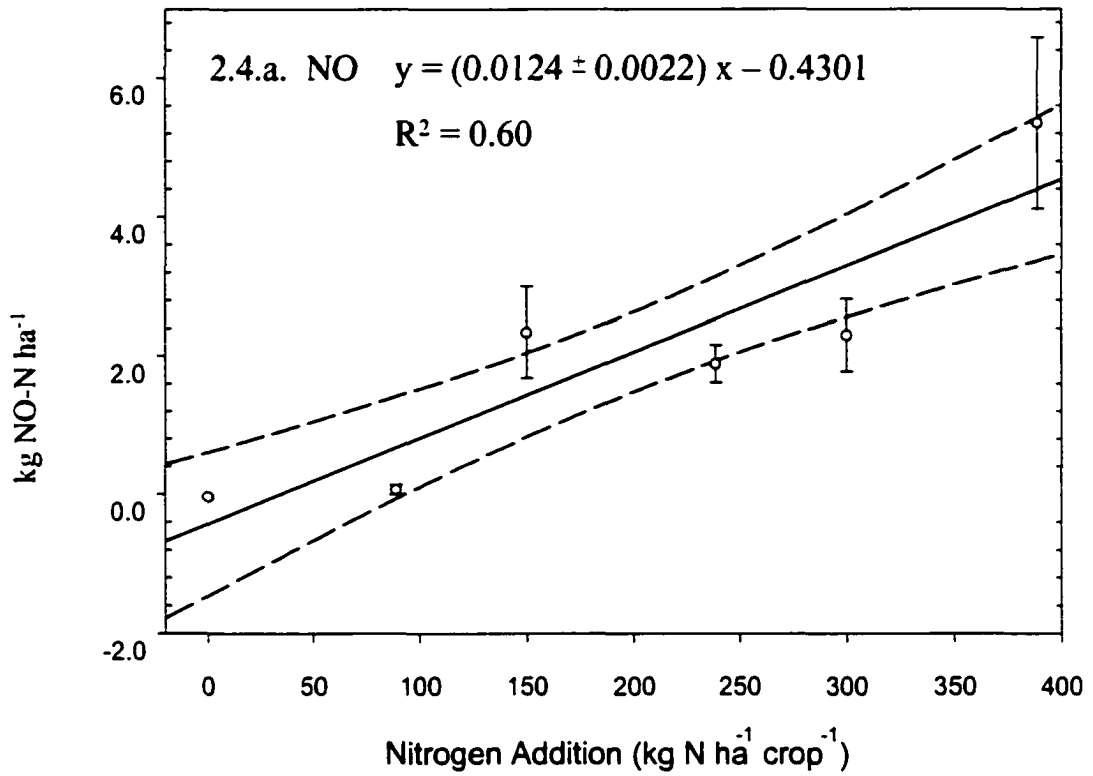


Table 2.1.a.

Study	N Application Rate (kg N ha <sup>-1</sup> )	Length of Study (days)	Average Loss ( $\mu\text{g NO-N m}^{-2} \text{ h}^{-1}$ )	Proportional Loss (%)	Loss Normalized To 1 Year (%)
Thornton and Valente, 1996	252	210	0.384	0.20	0.35
Thornton et al., 1998	336	365	0.700	0.36	0.36
This Study	238.5	49	23.9	0.078	0.58
This Study	300	49	27.5	0.075	0.56
This Study	388.5	49	54.3	0.13	1.0
Veldkamp and Keller, 1997b	360	365	441	5.4	5.4
Matson et al., 1998	250	150	3000-5000	2.64-4.52	6.4-11
Jambert et al., 1997a	280	365	3.07	11.3	11.3

Table 2.1.b.

Study	N Application Rate (kg N ha <sup>-1</sup> )	Length of Study (days)	Average Loss ( $\mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$ )	Proportional Loss (%)	Loss Normalized To 1 Year (%)
Thornton et al., 1998	336	365	88.5	0.73	0.73
Jambert et al., 1997b	230	365	179.2	1.1	1.1
This Study	238.5	49	47.4	0.15	1.1
This Study	300	49	72.8	0.20	1.5
Veldkamp and Keller, 1997b	360	365	92.9	2.1	2.1
This Study	388.5	49	123.3	0.30	2.2
Thornton and Valente, 1996	252	210	138.2	2.6	4.5
Matson et al., 1998	250	150	1000-6500	1.8-2.2	4.5-5.5

## CHAPTER 3

### Simulation of Nitrogen Trace Gas Flux Dynamics in an Upland Corn-Wheat Rotation of the North China Plain

#### Abstract

Chinese agriculture represents one of the most intensively managed ecosystems in the world. As a result, tools developed in the examination of other less densely populated and heavily fertilized areas must be evaluated under conditions more relevant to the world's most populous nation and largest consumer of synthetic fertilizer. It is the intent of this report to examine one such tool, the DAYCENT ecosystem model, in this context.

$\text{NO}_x$  and  $\text{N}_2\text{O}$  trace gas fluxes were simulated for a range of fertilization rates and organic amendments and compared with field measurements. Grain yield, total soil carbon, and total soil nitrogen compared well with experimental results. While the model simulates the temporal dynamics of the gaseous fluxes and reasonably approximates peak magnitude, it significantly overestimates seasonal trace gas emissions in this system. Over sensitivity to cultivation practices, unaccounted for ammonia volatilization, and the inability for soils to absorb gases in DAYCENT are believed to be responsible.

## Introduction

Chinese agriculture represents one of the world's most influential agroecosystems, consuming over one-quarter of the world's synthetic fertilizer production. Typical fertilization rates are ten times those of the U.S., resulting in dramatically accelerated nitrogen cycling in that nation. China's contribution to global nitrogen mobilization is currently second only to that of the U.S. Unlike the U.S., however, the rate of biogeochemical nitrogen cycling in China is expected to grow rapidly in the foreseeable future (Galloway et al., 1996; Zhang et al., 1996). Its contribution to global reactive nitrogen mobilization is expected to double within the next 20 years, overwhelmingly the result of increased fertilizer applications (Galloway et al., 1996). Inorganic nitrogen in soils is subject to chemical conversions by microbial nitrification and denitrification, causing the emissions of NO and N<sub>2</sub>O (Firestone and Davidson, 1989). It has been demonstrated that management provides the dominant control on trace gas emissions from agroecosystems (Matson et al., 1996). Any evaluation of large-scale nitrogen dynamics should consider China's unique characteristics. It is therefore imperative that a greater understanding of nitrogen cycling within agroecosystems of this region be achieved.

Many of the tools used to gain an understanding of biogeochemical control mechanisms are models which have evolved from far less intensively managed ecosystems (Parton et al., 1996). In a region as unique as that examined here, it is important that any tool be evaluated prior to claims of applicability or predictive value. This study is one attempt to evaluate the performance of one

such tool, the DAYCENT ecosystem model, against field observations of nitrogenous trace gas fluxes in an upland grain rotation in northeastern China.

The field data used for comparison are given in Chapter 2 of this dissertation. The site is under a typical management scheme of the Northern China Plain, a summer corn-winter wheat rotation. Characteristic fertilization rates are  $300 \text{ kg N ha}^{-1} \text{ crop}^{-1}$ , meaning annual fertilization exceeds  $500 \text{ kg N ha}^{-1}$  (Zhang et al., 1996).

### Methods

DAYCENT is a biogeochemical ecosystem model used to simulate the dynamics of carbon, nitrogen, and trace gas exchange between the atmosphere, soils, and vegetation (Del Grosso et al., 2000a). It is a daily time step model, based ultimately on the monthly time step model CENTURY (Parton et al., 1994). Among its other properties, DAYCENT explicitly simulates trace gas efflux. Production of NO and N<sub>2</sub>O in DAYCENT is accomplished by explicit mathematical representation of nitrification and denitrification transformation processes. The rates of trace gas production are proportional to nitrification and denitrification rates.

Nitrification rates in DAYCENT are controlled by [NH<sub>4</sub><sup>+</sup>], soil water, texture, temperature, and pH. Denitrification rates are controlled by heterotrophic respiration (a modeled parameter serving as a proxy for labile C availability), [NO<sub>3</sub><sup>-</sup>], and soil aeration (Del Grosso et al., 2000). Both the nitrification and denitrification submodels calculate N<sub>2</sub>O (Parton et al., 2000). From this, NO production is derived by applying an NO to N<sub>2</sub>O ratio function, followed by a

pulse multiplier to nitrification-derived  $\text{N}_2\text{O}$ . The  $\text{NO}:\text{N}_2\text{O}$  function assumes that as gas diffusivity decreases, a lower proportion of the total nitrogen-gas flux will be in the form of  $\text{NO}$ . The pulse multiplier is applied when moisture falls on a previously dry soil, and intended to reflect the substrate accumulation incurred during periods of water stress.

Weather data were derived for Beijing from several datasets (Tao et al., 1991, Kaiser et al., 1993). Weather for the field site itself was recorded for the same time period that field data were collected and into the generic weather file so that the simulation and the field data were appropriately aligned.

A 4000-year background run was completed to establish the initial operating parameters of the model. The model was then spun up for 73 years of increasingly intensive management, consistent with what is known about the evolution of Chinese agriculture (Lindert et al., 1996, Wang et al., 1996). This odd length was chosen because weather data were available for that time period and it was sufficient for initialization. The 74<sup>th</sup> year of DAYCENT output was used for comparison with empirically derived data. The first 42 years are a low intensity summer corn-winter wheat rotation. No synthetic fertilizers are utilized during this period, and organic matter is added at the rate of 250 grams per square meter per crop. Irrigation is maintained at 50% WFPS throughout the simulation, but soil moisture is allowed to vary with precipitation. Cultivation included manual plowing of soils at planting and weeding the following month. Synthetic fertilizer application is doubled each decade until current levels are reached 11 years prior to the time when measurements are compared with model output,

consistent with the known site history of the research farm at the field site. Treatments included three levels of urea fertilization (0, 150, and 300 kg N ha<sup>-1</sup> crop<sup>-1</sup>), and two levels of organic matter amendment (low and high) for each fertilization level. For each treatment, added N was reduced by 10% and by 60% to accommodate the possible range of nitrogen loss from ammonia volatilization (Roelcke et al. 1996)

### Results and Discussion

NO fluxes for the six treatments are shown in Figure 3.1. The prediction in Century of two major peaks within the corn season under conditions of no fertilization and no organic matter amendment (Fig. 3.1.a) is peculiar, and related to cultivation and irrigation in those months. Fluxes are overestimated in nonfertilized treatments (Figs. 3.1.a & 3.1.b). For those treatments receiving fertilization at 150 or 300 kg N ha<sup>-1</sup> crop<sup>-1</sup> (Figs. 3.1.c-f), DAYCENT captures the general temporal dynamic of the gaseous exchange. Flux magnitudes are similar to those predicted by the 60% NH<sub>3</sub>-N volatilization loss simulations.

Modeled and measured N<sub>2</sub>O fluxes are shown in Figure 3.2. In contrast to NO efflux, N<sub>2</sub>O shows no particular response to scheduled DAYCENT cultivation events in the nonfertilized treatments. Climatic parameters appear to drive N<sub>2</sub>O production in the absence of fertilization, as would be expected. As with NO, the appropriate temporal dynamics are represented by the model in the fertilized treatments. DAYCENT predicts N<sub>2</sub>O flux magnitudes most accurately when the higher-level (60%) NH<sub>3</sub>-N volatilization loss is assumed.

The frequency distribution in Figure 3.3 clearly shows DAYCENT's propensity for underpredicting a significant portion of the lowest-level fluxes for each gas.

Seasonal fluxes for each of these gases are shown in Figure 3.4 relative to the amount of added nitrogen (including that nitrogen contained within organic matter). Measurements for both gases appear more sensitive to nitrogen addition than model results. In both cases, results are more similar for the 60%  $\text{NH}_3\text{-N}$  volatilization loss simulations than the 10%.

### Conclusions

While its applicability to other agroecosystems has been demonstrated (Frolking et al., 1998), and its ability to accurately simulate basic soil biogeochemical properties has again been demonstrated here, its aptitude for the accurate representation of NO and  $\text{N}_2\text{O}$  fluxes in the intensively managed agricultural soils China proves more problematic. Several mechanisms working in concert are suggested.

First, it is obvious that ammonia volatilization plays an important role in trace gas efflux from these systems, effectively reducing the available soil nitrogen pool size prior to NO or  $\text{N}_2\text{O}$  production. This process is unaccounted for within DAYCENT's architecture, and must be manually implemented prior to initiating the simulation.

DAYCENT does not allow for soils to absorb gases from the atmosphere either through physical diffusion processes, or in the case of NO, through biologically facilitated uptake. It is possible this mechanism accounts for the

elevated baselines in the simulated results relative to the measured data. Field experiments were conducted in a heavily populated area where atmospheric concentrations of these gases were elevated (Streets and Waldhoff, 2000; Rasmussen et al., 1982), and as such are representative of the vast majority of agriculturally productive areas in China. The presence of these gases in the atmosphere above the soils would diminish the magnitude of the concentration gradient at the source of their microbial production, and consequently, reduce the efflux of these gases from the soil. A reasonable representation of diffusion kinetics would require a concerted model integration effort, and would involve the incorporation of a complex soil physics model such as that described by Grant and Pattey (1999).

Finally, another strong possibility in the case of NO emissions is the over sensitivity of DAYCENT to management events. Cultivation and irrigation produce a peak in simulated NO emissions when no fertilizer nitrogen has been added. That pulse is not evident in the field measurements.

Cumulative seasonal NO losses for field measurements ranged from 0.52 to 15.8%. DAYCENT's seasonal NO emission figures ranged from 15.2-43.9% for the low-end ammonia volatilization assumption, and from 5.9-15.6% for the 60% ammonia volatilization assumption, which has significant overlap with measurements. N<sub>2</sub>O emissions in the field ranged from 0.19-0.31%. For the simulation that assumed 10% ammonia-nitrogen volatilization, 0.57-1.23% losses were calculated, and for the simulation that assumed 60% volatilization, 0.14-

0.46% losses were calculated, encompassing the measured range. Seasonal estimates are then quite accurate.

The proximal drivers of nitrogenous trace gas production are globally consistent. However, the urban setting, management intensity, and chemical composition of applied fertilizer create unique conditions for Chinese agriculture. In order for that nation's contributions to be accurately accounted for, certain refinements in current representations of our understanding, exemplified in models such as DAYCENT, may be necessary. In particular, we suggest that ammonia volatilization and physical diffusion processes be taken into account, as they appear to be more important in the systems examined here than in previous investigations.

#### Acknowledgements

The authors wish to thank William Parton and Cindy Keough. This work was supported by NSF Cooperative Agreement Number ATM-9209181.

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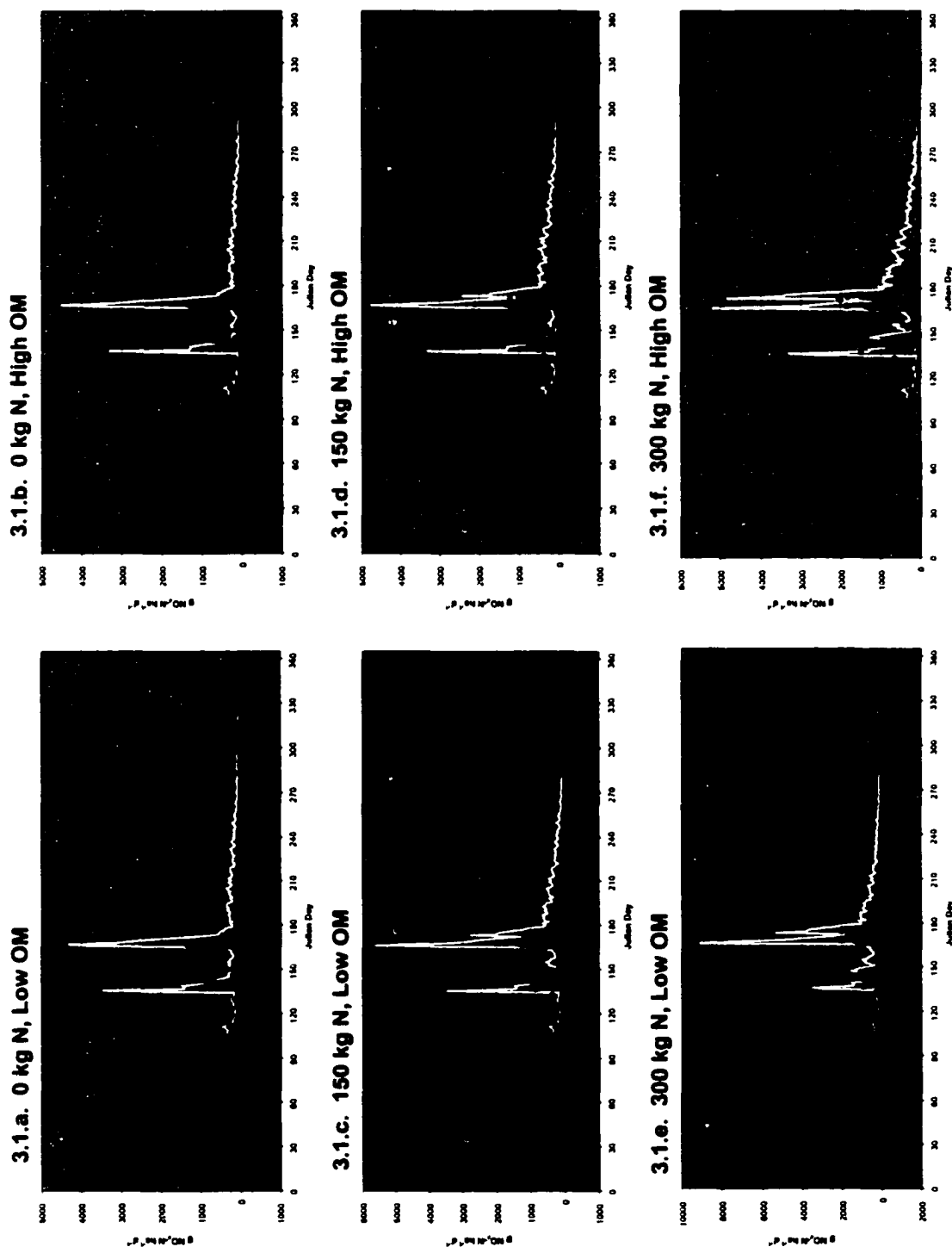
### Figure Captions

**Figure 3.1.** Comparison of NO fluxes for each of the six treatments from field measurements (black dots) and DAYCENT simulations (lines). Those simulations that account for a 10% reduction in available nitrogen are white. Those that account for a 60% reduction are black.

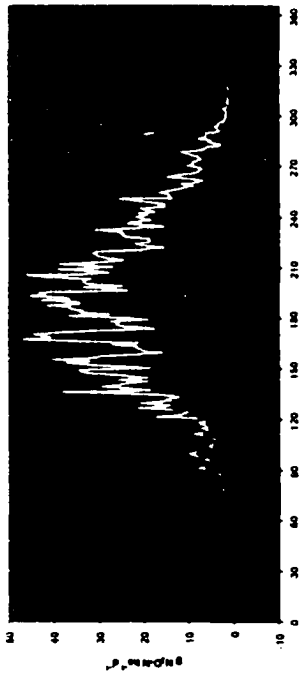
**Figure 3.2.** Comparison of N<sub>2</sub>O fluxes for each of the six treatments from field measurements (black dots) and DAYCENT simulations (lines). Those simulations that account for a 10% reduction in available nitrogen are white. Those that account for a 60% reduction are black.

**Figure 3.3.** Frequency distribution comparison between measured and modeled fluxes based on event size. Flux ranges are given in g N ha<sup>-1</sup> d<sup>-1</sup>. The NO distribution is given in figure a, while that for N<sub>2</sub>O is given in figure b.

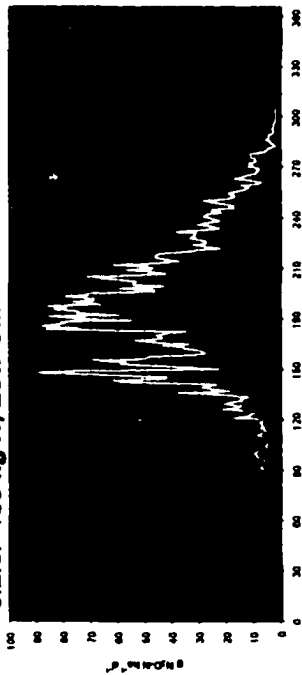
**Figure 3.4.** Seasonal NO (a) and N<sub>2</sub>O (b) efflux as a function of fertilizer-N (including organic-N) addition rates. Measured data are in black. DAYCENT simulations are white. The white dashed line with squares is the 10% N-reduction case. The solid white line with circles is the 60% N-reduction case.



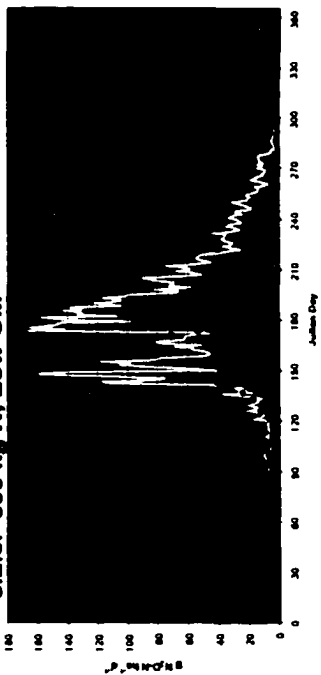
**3.2.a. 0 kg N, Low OM**



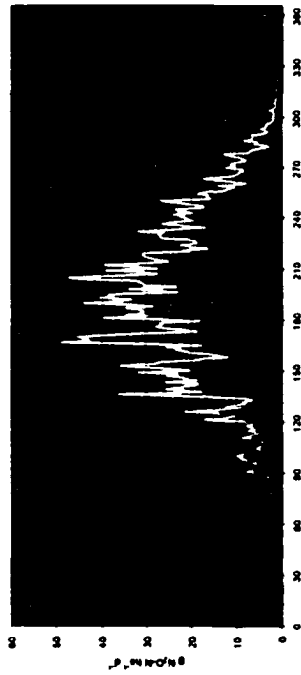
**3.2.c. 150 kg N, Low OM**



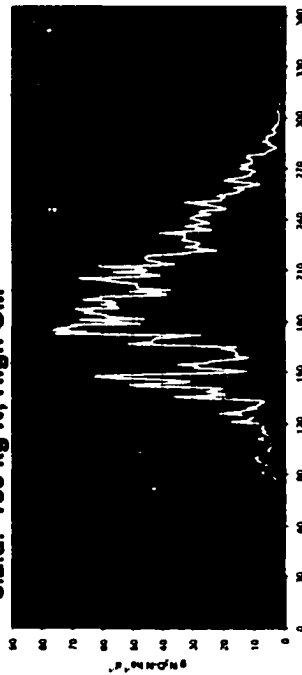
**3.2.e. 300 kg N, Low OM**



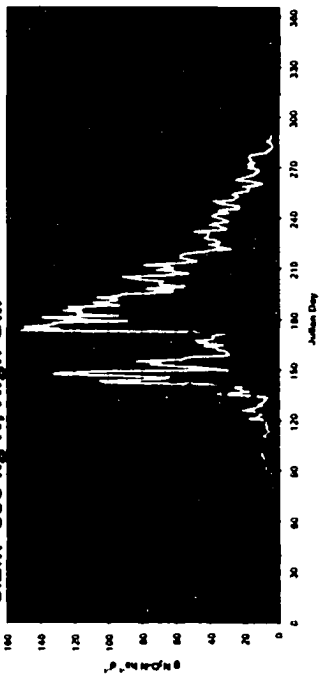
**3.2.b. 0 kg N, High OM**



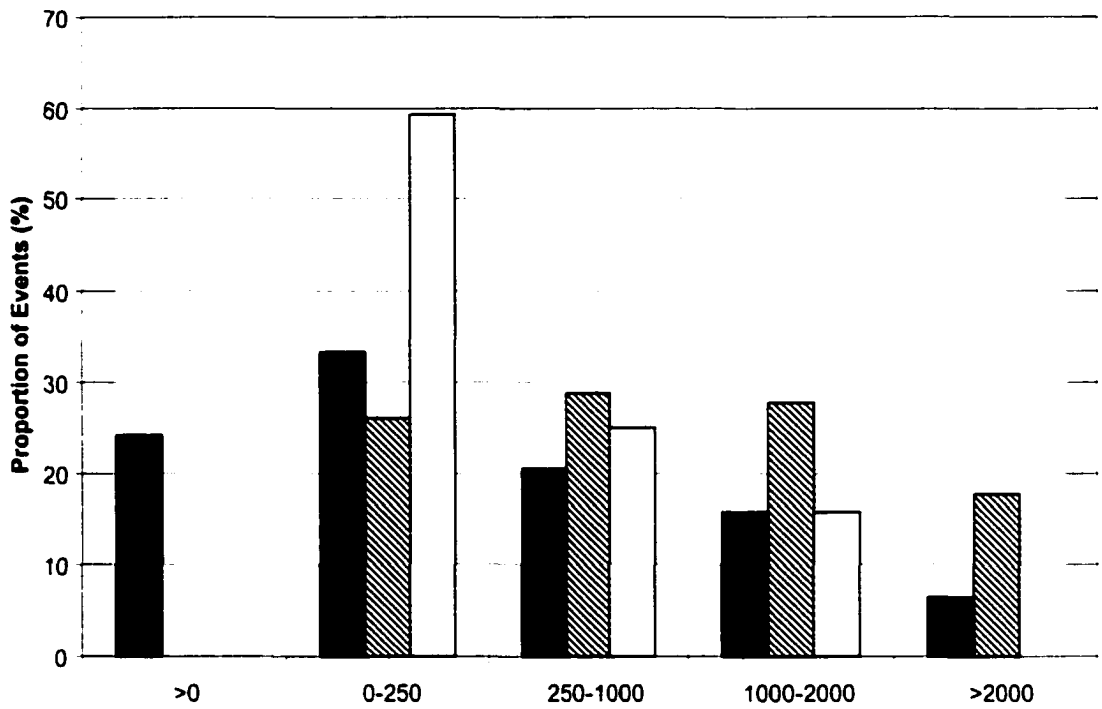
**3.2.d. 150 kg N, High OM**



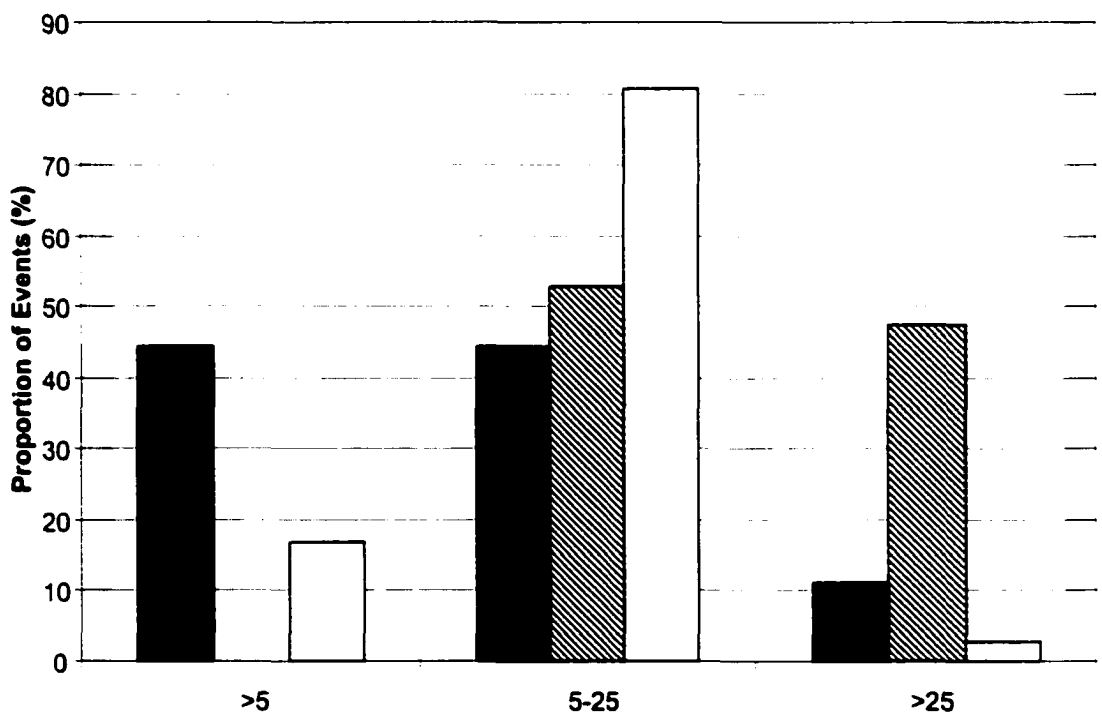
**3.2.f. 300 kg N, High OM**



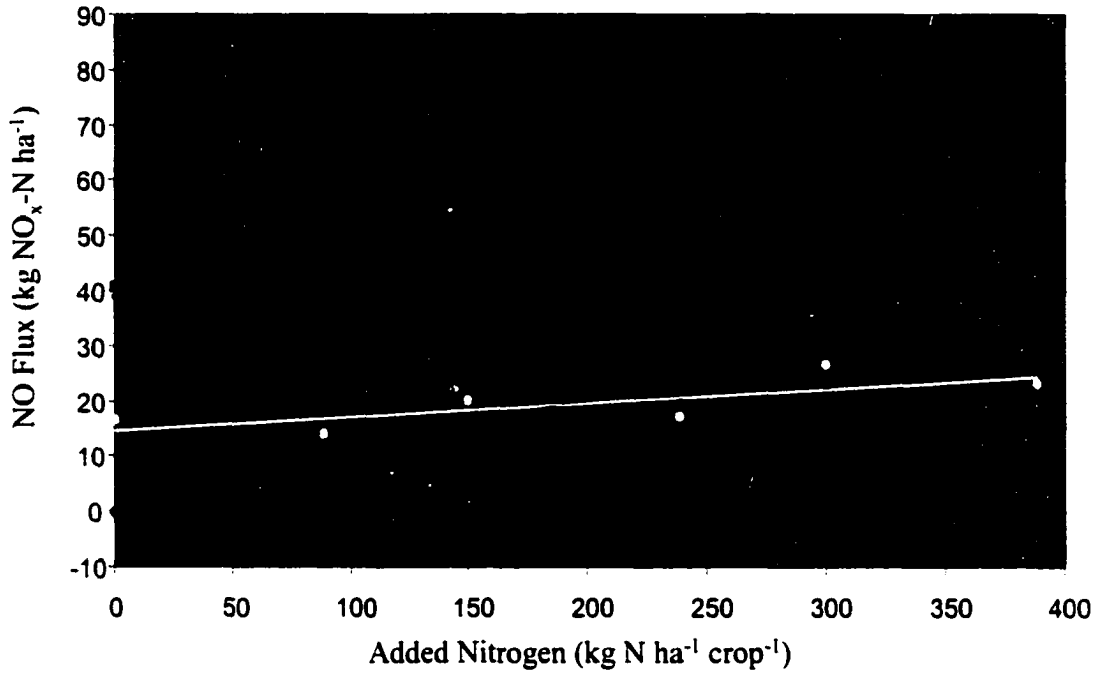
### 3.3.a. NO Error Distribution



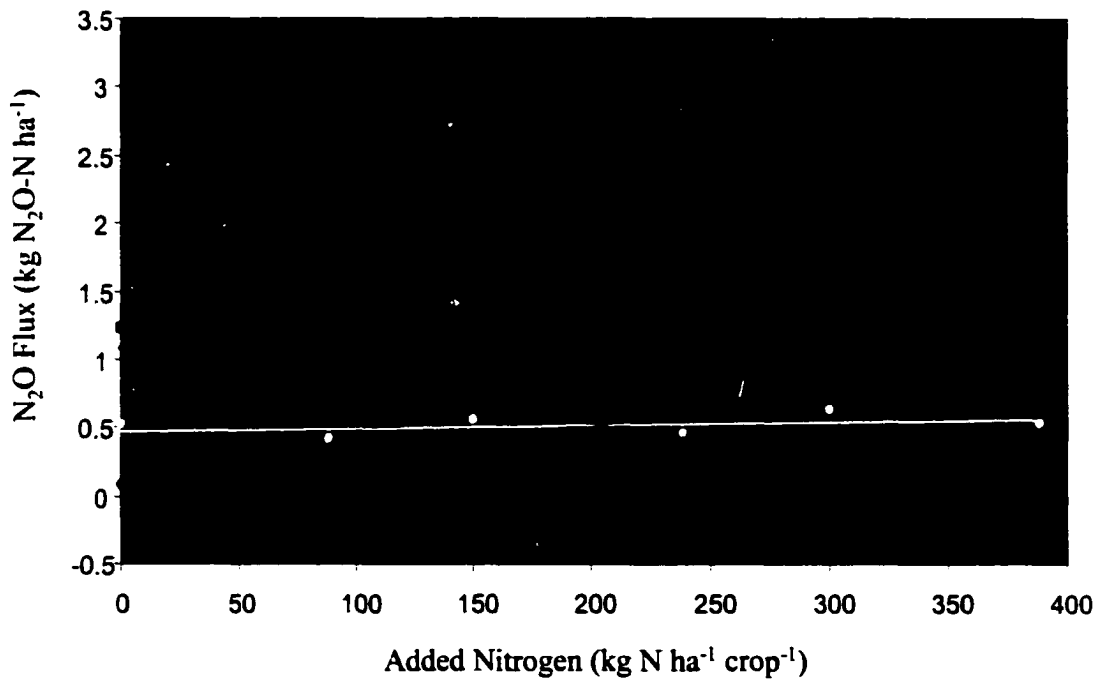
### 3.3.b. N<sub>2</sub>O Error Distribution



### 3.4.a. Seasonal NO flux as a function of added nitrogen



### 3.4.b. Seasonal N<sub>2</sub>O flux as a function of added nitrogen



## CHAPTER 4

### Climate Sensitivity of Nitrogenous Trace Gas Fluxes from Upland Chinese Agroecosystems

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#### Abstract

A sensitivity analysis was applied to determine changes to organic soil carbon and nitrogen, crop yield, net primary productivity, actual evaporation and transpiration, and NO and N<sub>2</sub>O emissions to altered temperature and precipitation regimes in an irrigated corn-wheat rotation common to northern China. The DAYCENT ecosystem model was used to calculate values for each of these dependent variables based on a range of simulated altered weather. Daily average maximum temperature, minimum temperature, and precipitation were calculated from available data (Li 1998), and arithmetically manipulated to yield conditions  $\pm 2^\circ$ ,  $4^\circ$ ,  $6^\circ$ ,  $8^\circ$ , and  $10^\circ\text{C}$  from average temperature, and  $\pm 20\%$ ,  $50\%$ , and  $100\%$  from average precipitation. Patterns of soil carbon and nitrogen showed an inverse relationship to temperature. Crop yield and productivity were maximal at  $+6^\circ\text{C}$  from average, regardless of precipitation levels. Evaporation and

transpiration increased with temperature. Response to precipitation was minimal for each of these variables, likely the result of irrigation-maintained soil moistures at relatively constant levels. NO and N<sub>2</sub>O fluxes were sensitive to both temperature and precipitation, and showed complex responses related to environmental variables.

### Introduction

China is a populous country with relatively little arable land per capita. As a result, it has developed high intensity management practices in order to maintain food security (Galloway et al., 1996; Wang and Lin, 1996). Climatic sensitivity of agricultural production in China is an important issue to which some scientific attention has been paid (Lin, 1996; Ohta et al., 1995; Smit and Cai, 1996; Thomas, 2000; Wang and Lin, 1996; Wang and Zhao, 1995; Zhan, 1994). Attempts have been made to gauge anticipated regional climatic shifts for this and other important regions resulting from global climate change (Lee et al., 2001; Hubbard and Flores-Mendoza, 1995; Jeton et al., 1999). They have, however, found considerable disagreement and uncertainty regarding continental and regional-scale projections. As a result, we have attempted to determine the sensitivity of several important agriculture-related biogeochemical variables to climatic variables in such a way that makes the results applicable to any potentially, generically altered climate.

The upland summer corn-winter wheat rotations of the North China Plain are representative of 80% of northern Chinese agricultural practices. In addition to its primary function of production, Chinese agriculture is an important contributor to global biogeochemical processes, second globally only to the United States in reactive nitrogen

mobilization (Galloway et al., 1996). Implications of climate sensitivities to some of these variables, particularly NO and N<sub>2</sub>O fluxes, are explored here.

### Methods

The DAYCENT ecosystem model has demonstrated accuracy in the simulation of important biogeochemical and agro-economic parameters for agricultural systems (Del Grosso et al., 2000 and 2001; Parton et al., 2000), including those examined here: soil organic carbon and nitrogen, production, yield, evaporation, transpiration, inorganic soil nitrogen, and gaseous NO and N<sub>2</sub>O fluxes. DAYCENT simulates biogeochemical fluxes between soils, vegetation, and the atmosphere based on ecosystem productivity and decompositional processes and their biophysical and management drivers (Parton et al., 1998). Three soil organic matter pools cycle at turnover rates from 6-12 months (active SOM), 1-5 decades (slow SOM), and 1000-5000 years (passive SOM). Physiological characteristics of vegetation (growth rate, tissue nutrient ratio requirements) alter soil biogeochemical processes through withdrawals required for production and decompositional inputs upon plant death, and are sensitive to biophysical drivers that alter growth. Management options, including fertilization, planting, harvesting, irrigation, weeding, and plowing, are implemented to represent the influence of typical agricultural activities. Nitrogen trace gas production (NO and N<sub>2</sub>O) is controlled by the explicit simulation of nitrification and denitrification processes, rates of which are determined by available inorganic soil nitrogen concentrations, labile organic carbon availability, soil moisture, temperature, pH, and texture. A “pulse multiplier” is applied in circumstances where soil moisture increases suddenly (due to precipitation or irrigation) on a soil that has been relatively dry for some time preceding the event. This

allows for greater emissions of NO than would be anticipated strictly from instantaneous soil moisture values.

The monthly version of the CENTURY model (Parton et al., 1994) was run for 4000 years until no drift in salient biogeochemical characteristics was evident. End values were used to initiate DAYCENT simulations.

The simulation protocol is generically representative of decadal-scale climatic variation. Daily weather data were available for five years during the 1990's (Li 1998). These data were averaged, and the means used to spin the model up for the period of 1918 through 1994. Weather conditions were steadily ramped toward their altered state each decade until the final decade of the simulation (that is, until 1989) when the desired weather was achieved and maintained. Temperature alterations of  $\pm 0^\circ$ ,  $2^\circ$ ,  $4^\circ$ ,  $6^\circ$ ,  $8^\circ$ , and  $10^\circ\text{C}$  from average, and precipitation alterations of  $\pm 0$ , 20, 50, and 100% of average, applied symmetrically throughout the year, were examined factorially for a total of 77 simulations. After the initial 1-2 years of the final decade (1990-1999), no drift was evident in soil carbon, nitrogen, or ecosystem productivity. Variables of interest were extracted for the final five years of the simulation (1995-1999) and averaged.

Increasing agricultural management intensity is apparent in this era of Chinese history and reflected in our simulations. Beginning in the 1960's, the application of chemical nitrogen fertilizers was initiated, and applications were increased through the 1980's. For the purposes of these simulations, organic matter amendments were maintained at a constant rate equivalent to  $3000 \text{ kg C ha}^{-1}$ . The C:N ratio of added organic matter was 15, reasonably representative of semi-decomposed, mixed (primarily bovine) farmyard manure. Synthetic nitrogen additions were increased over the period of

simulation to the level of  $300 \text{ kg N ha}^{-1} \text{ crop}^{-1}$  ( $600 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ), as these are typical of applications in this type of regional agroecosystem. Crops were irrigated to the equivalent of 50% water-filled pore space (WFPS), though variation in soil moisture occurred with precipitation events. Soils were tilled at crop planting (corn in May and winter wheat in October of each year), and weeding events which turned soil over but did not affect production occurred for two months following planting.

### Results and Discussion

Total soil organic carbon (Figure 4.1.a) and nitrogen (Figure 4.1.b) show strong temperature dependence, and a less obvious but still present precipitation dependence, as might be expected in an irrigated system. Lower temperatures (and to a lesser degree, lower precipitation) allow for slower decompositional processes, meaning that more organic carbon remains in the soils under these conditions. At the lowest temperature and precipitation levels examined here, total soil organic carbon is elevated by 27.3% above control levels. At the highest temperatures and precipitation levels, it is diminished by 32.7%. At the most reduced temperature and precipitation conditions, total organic nitrogen levels are increased by 21.7%; at the highest levels, the reduction is 27.5% of average condition nitrogen concentrations. Nitrogen's sensitivity to weather appears less than that of carbon, and the implied increase in soil C:N may indicate qualitative changes in cycling processes which merit further investigation. Within these general trends, variability in response is observable. This variability, though small relative to the size of the pools, represent substantial changes in the availability of important precursors to trace gas production.

Temperatures create the dominant sensitivity for crop yield (Figure 4.2.a), with maximal yield achieved at +6°C from the average under any of the precipitation regimes examined here. The maximum achieved at this temperature is 23.2% above control simulations, and yields are minimized at the lowest temperatures examined here, 68.3% below the control. Net primary productivity (Figure 4.2.b) shows a pattern similar to grain yield, optimized at 6°C with a 16.6% increase in NPP, and minimization within these experiments occurring at -10°C showing a reduction of 68.2%.

Inorganic soil nitrogen ( $N_i$ ) is displayed in Figure 4.3.a. This proximal control on trace gas flux is maximized near the lowest levels of temperature and precipitation (173% of average conditions) and minimized near the highest temperature manipulations (-43% of average). Evaporation and transpiration are summed in Figure 4.3.b as actual evapotranspiration. Temperature sensitivity is greater than that to changes in precipitation levels. Soil moisture is maintained relatively constant through irrigation, so precipitation changes do not exert a strong influence. Maximum AET is achieved at the greatest temperature and precipitation, and is elevated 71.2% above control. Minimal AET is -54.2% of control, and occurs at the most reduced temperature and precipitation levels.

NO and N<sub>2</sub>O emissions show a highly textured response across both temperature and precipitation continua (Figures 4.4.a and b). These variables prove the greatest challenge to interpretation, as they show complex responses and nonlinear sensitivities to multiple drivers. NO values range from +102.4% of average at -8°C and -100% precipitation, to -38.3% at -10°C and +100% precipitation. N<sub>2</sub>O emissions show a general decline under most weather deviations from average values, with several

anomalous spikes and dips within the dataset.  $\text{N}_2\text{O}$  fluxes range from +161.1% at  $-10^\circ\text{C}$  and  $-100\%$  precipitation, to  $-45.2\%$  at  $-4^\circ\text{C}$  and  $-50\%$  precipitation.

$\text{N}_i$  is among the most important and immediate drivers of  $\text{NO}$  and  $\text{N}_2\text{O}$  production.  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentrations are constantly changing, balancing supply (through direct fertilization or mineralization of organic matter) with demand (plant and microbial uptake) and loss mechanisms (volatilization and leaching), all of which are subject to a host of biophysical drivers. Figures 4.5.a and b show  $\text{N}_i$  as a function of the active soil organic nitrogen pool and NPP.  $\text{N}_i$  increases exponentially with organic nitrogen, and decreases linearly with increasing primary production. These simple relationships alone generate a complicated, if incomplete, picture.

As further explanation, there is notable variability within the generalized trends of Figures 4.1 through 4.3. This is to say that increasing precipitation across any single temperature scheme does not show monotonic responses in organic soil carbon or nitrogen, yield, production,  $\text{N}_i$ , evaporation or transpiration. These pools and fluxes are large, and what appears as small internal variation implies large changes to the states of trace gas production drivers. They additionally influence one another. It is not surprising that a subtle and complex response emerges.

It is with these considerations in mind that any individual point in Figures 4.4.a and b may be interpreted. To spare the reader an exhaustive and tedious explanation of over 150 individual results, a generalized interpretation is offered here. Figures provide sufficiently specific information that the reader may examine any individual point as s/he desires. At the lowest temperatures, a 70% reduction in NPP (Fig. 4.2.b) results in a significant  $\text{N}_i$  increase (Fig 4.3.b), leading to inflated  $\text{NO}$  and  $\text{N}_2\text{O}$  emissions. At average

temperatures, NO sits in a trough of higher emissions, while N<sub>2</sub>O emissions are near a maximum at average temperatures within our temperature/precipitation matrix. This is a result of differential partitioning between the two gases from subtle changes in soil moisture resulting from evaporation and transpiration (Fig 4.3.b). At higher AET, soils are more conducive to nitrification activity and hence, NO production at the expense of N<sub>2</sub>O.

### Conclusions

The use of averages for trace gas flux reporting is a crude tool, masking their highly episodic nature. Seasonality and sporadic events may have a big impact on these results. Nonetheless, we believe some useful principles may be demonstrated. Even an accurate knowledge of ecosystem state factors or climate parameters alone is insufficient to accurately predict trace gas production rates through simple conceptual models. Interacting and nonlinear intermediate pools, fluxes, feedbacks, and the timescales at which they operate must be considered (Schimel et al. 1996). For example, decreasing temperatures do not necessarily lead to diminished trace gas production when inorganic nitrogen has accumulated in the soil, both in reality and in a simulation framework such as that examined here.

### Acknowledgements

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#### Figure Captions

Figure 4.1. Change in organic soil carbon (a) and nitrogen (b) relative to control climatic conditions.

Figure 4.2. Change in crop yield (a) and NPP (b) relative to control climatic conditions.

Figure 4.3. Change in  $N_i$  (a) and AET (b) relative to control climatic conditions.

Figure 4.4. Change in NO (a) and  $N_2O$  (b) flux relative to control climatic conditions.

Figure 4.5.  $N_i$  as a function of SON (a) and NPP (b).

Figure 4.1.a SOC

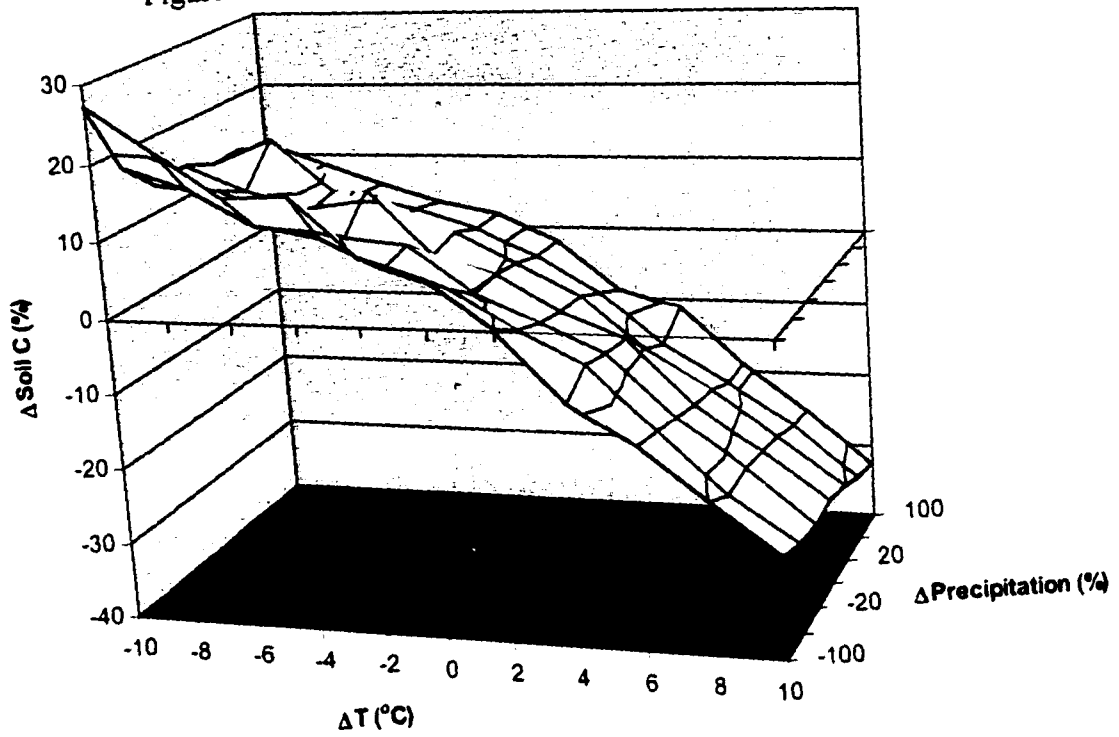


Figure 4.1.b SON

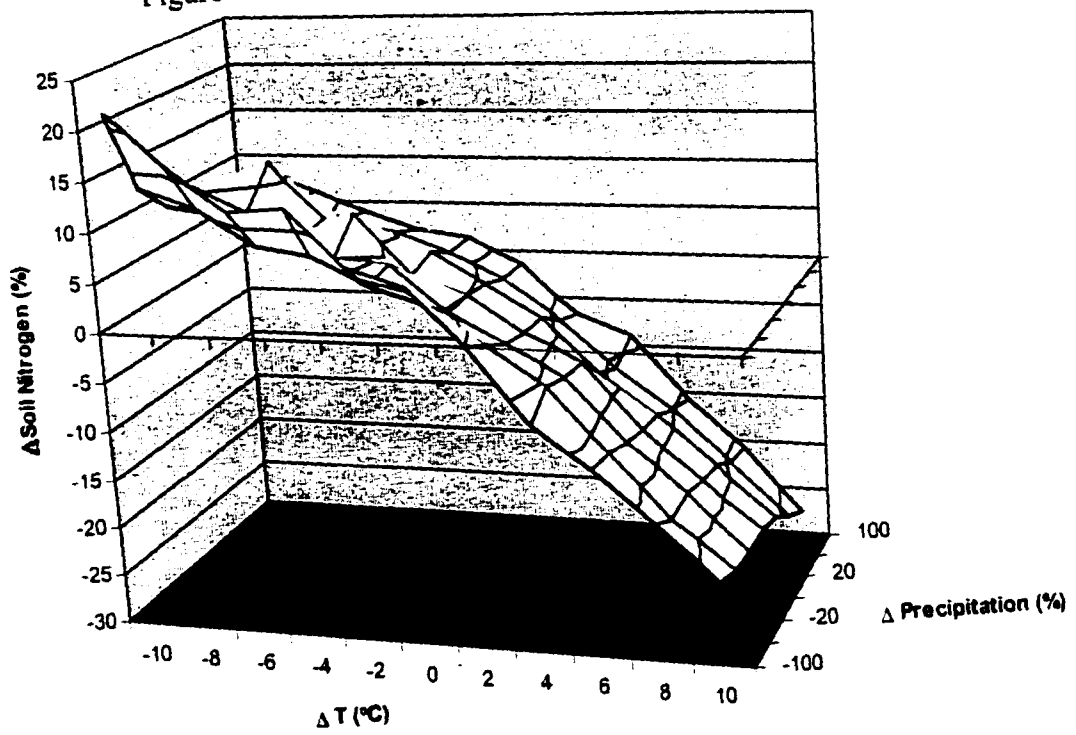


Figure 4.2.a Grain Yield

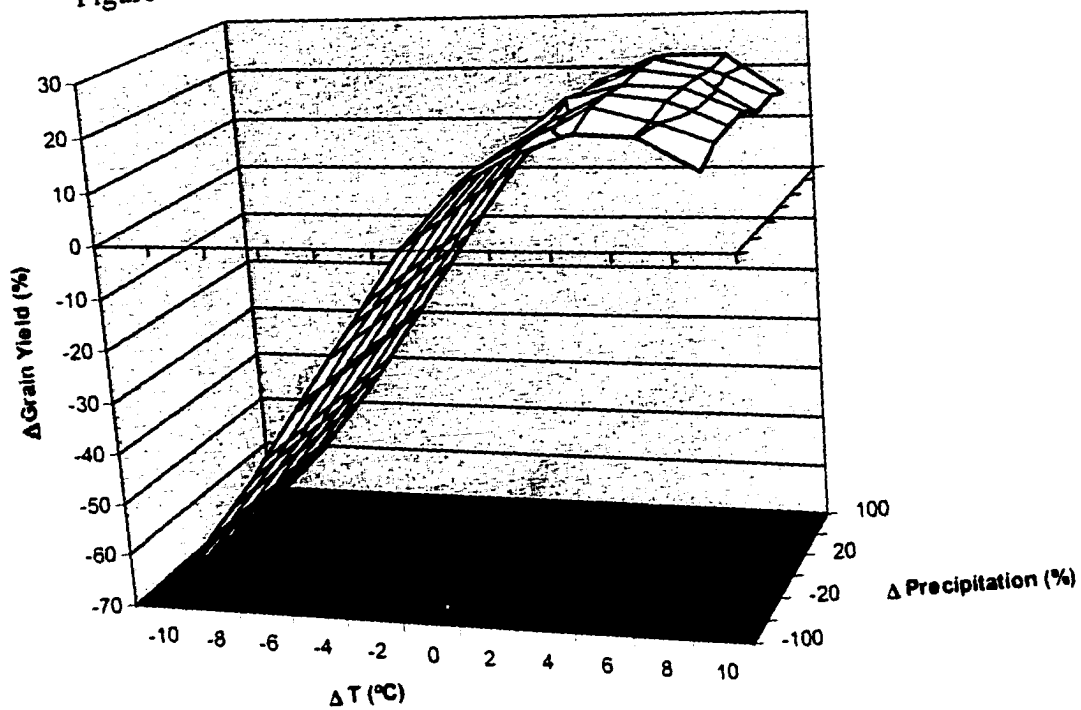


Figure 4.2.b NPP

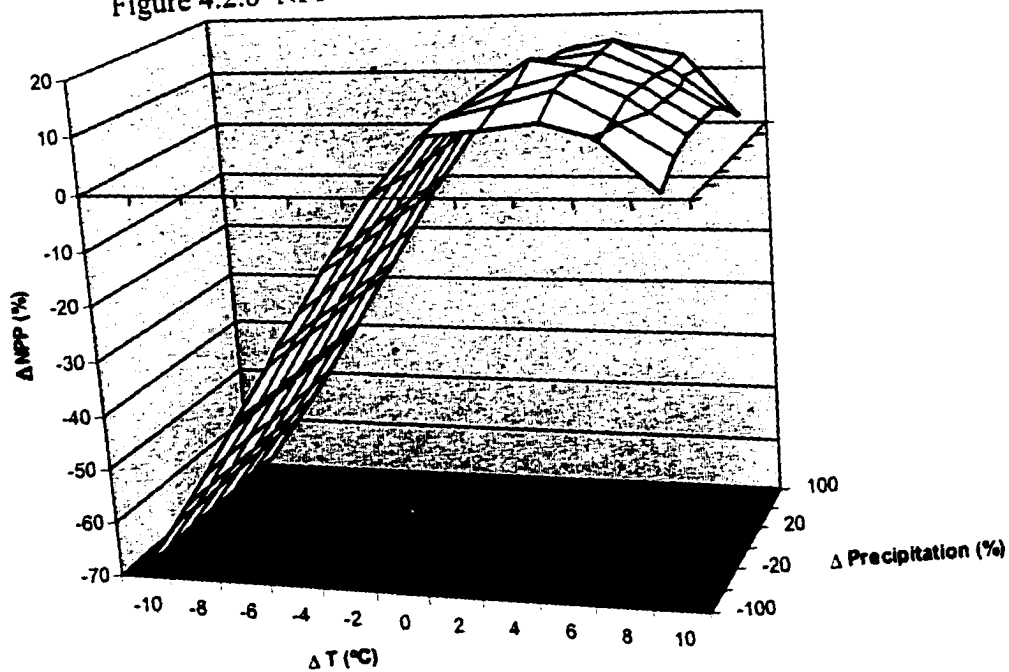


Figure 4.3.a  $N_i$

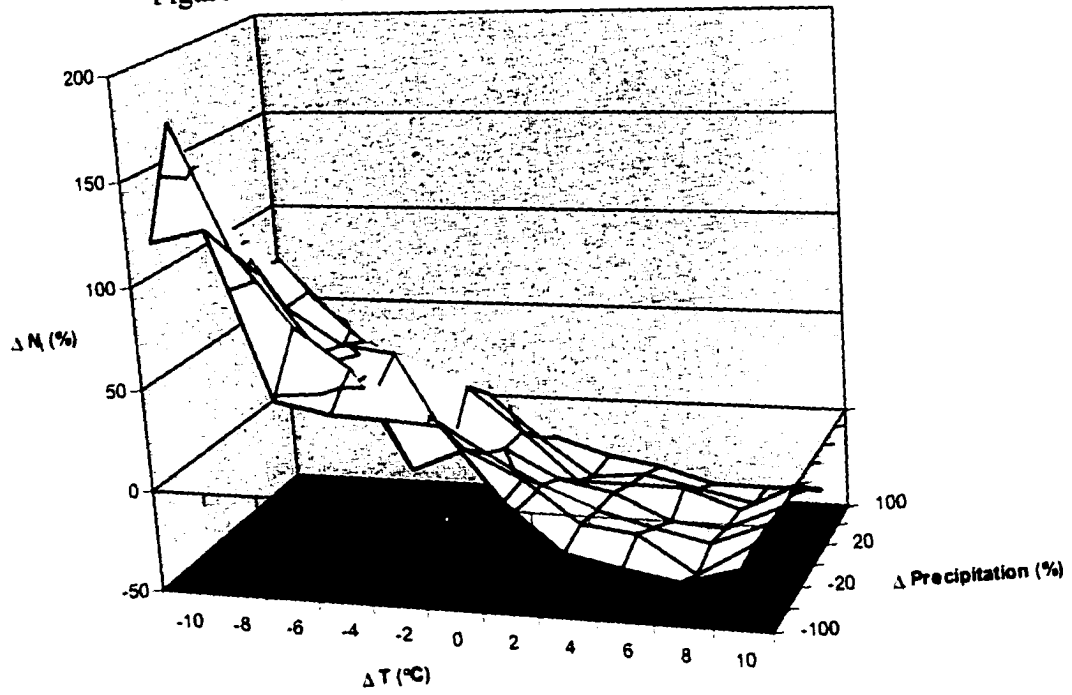


Figure 4.3.b AET

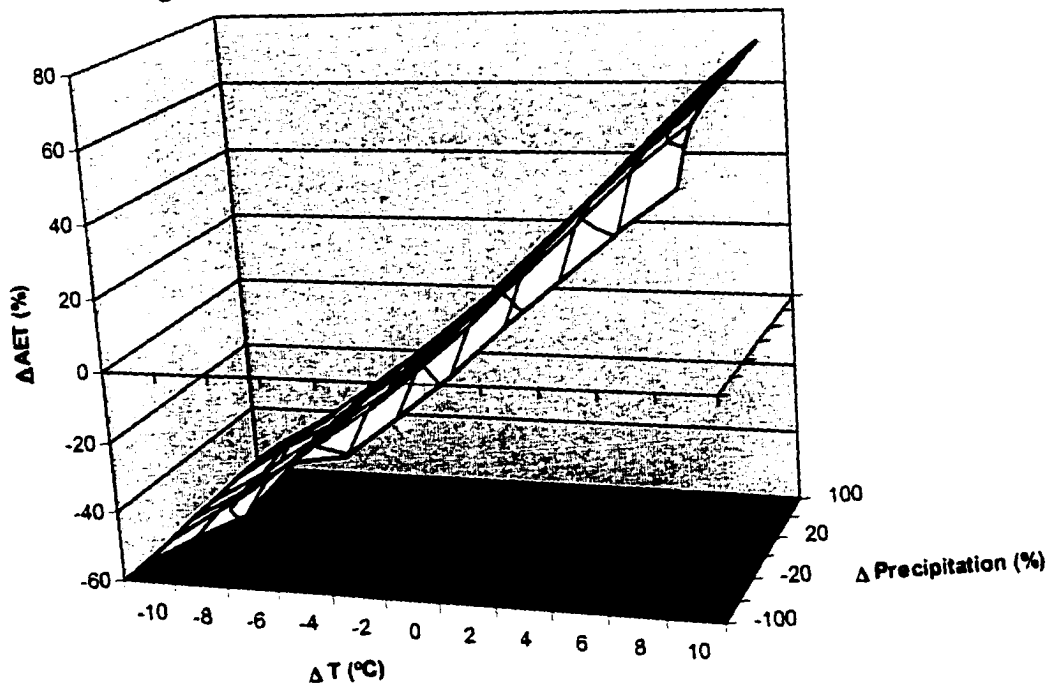


Figure 4.4.a NO flux

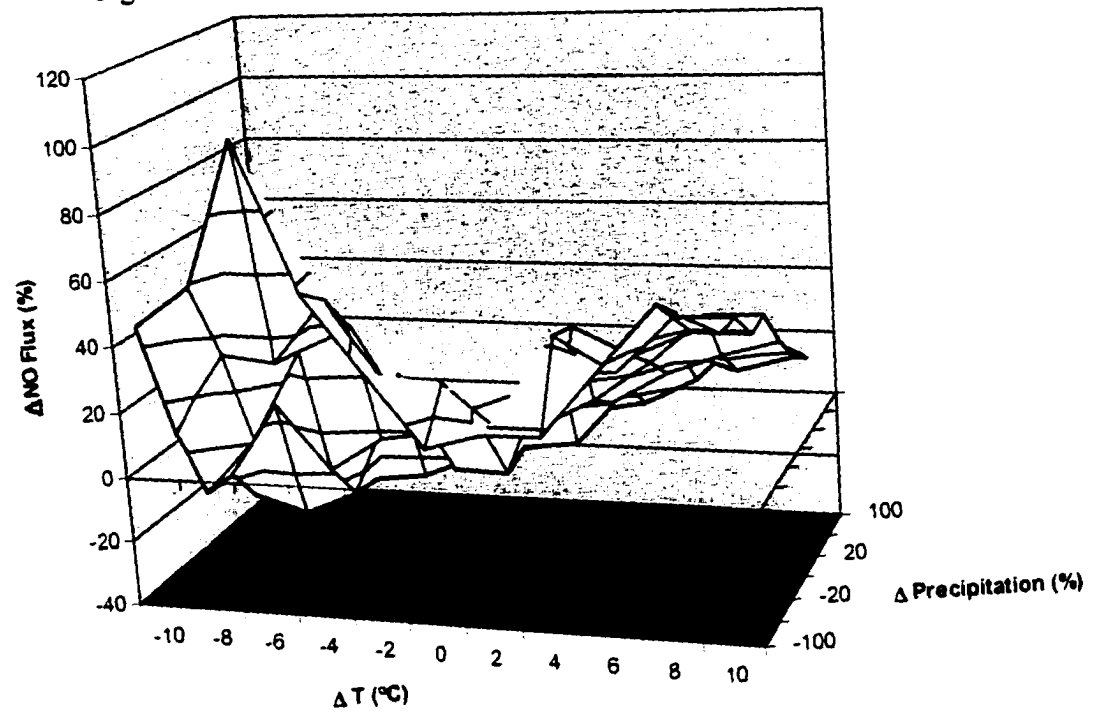


Figure 4.4.b N<sub>2</sub>O flux

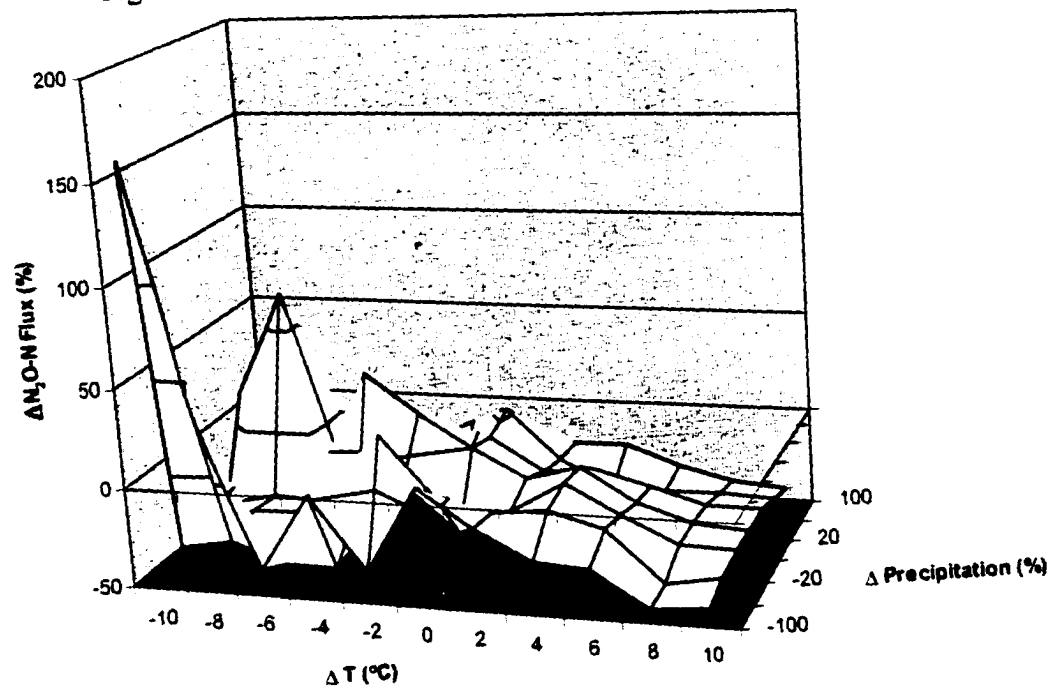


Figure 4.5.a  $N_i$  vs. SON

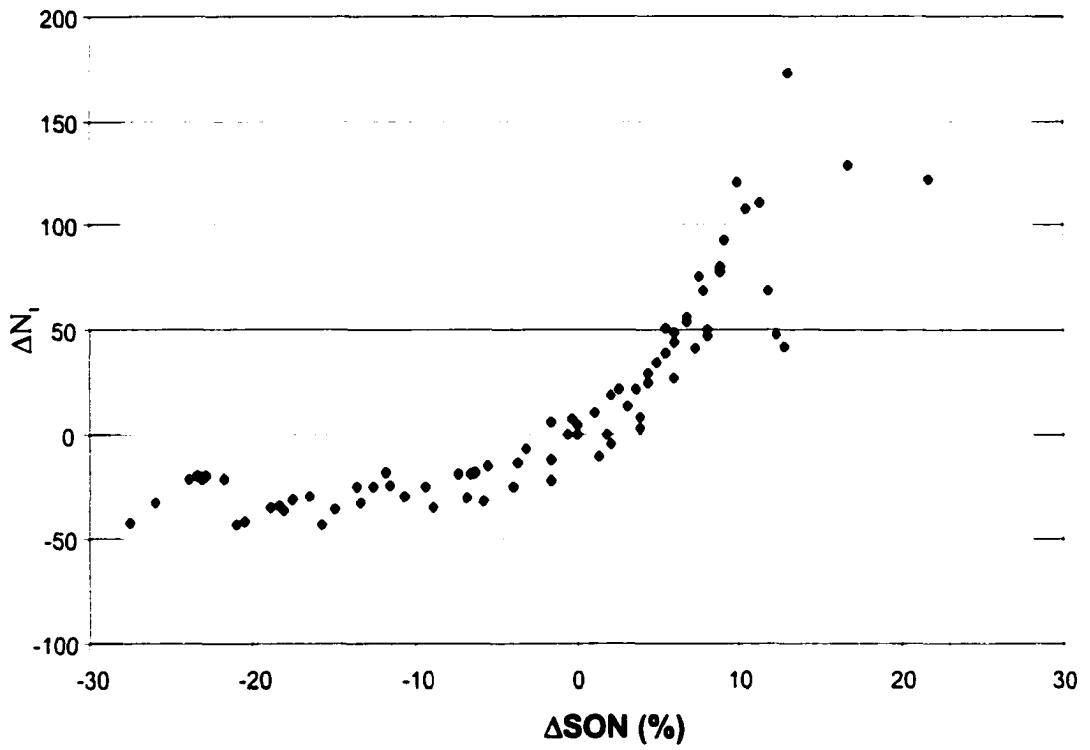
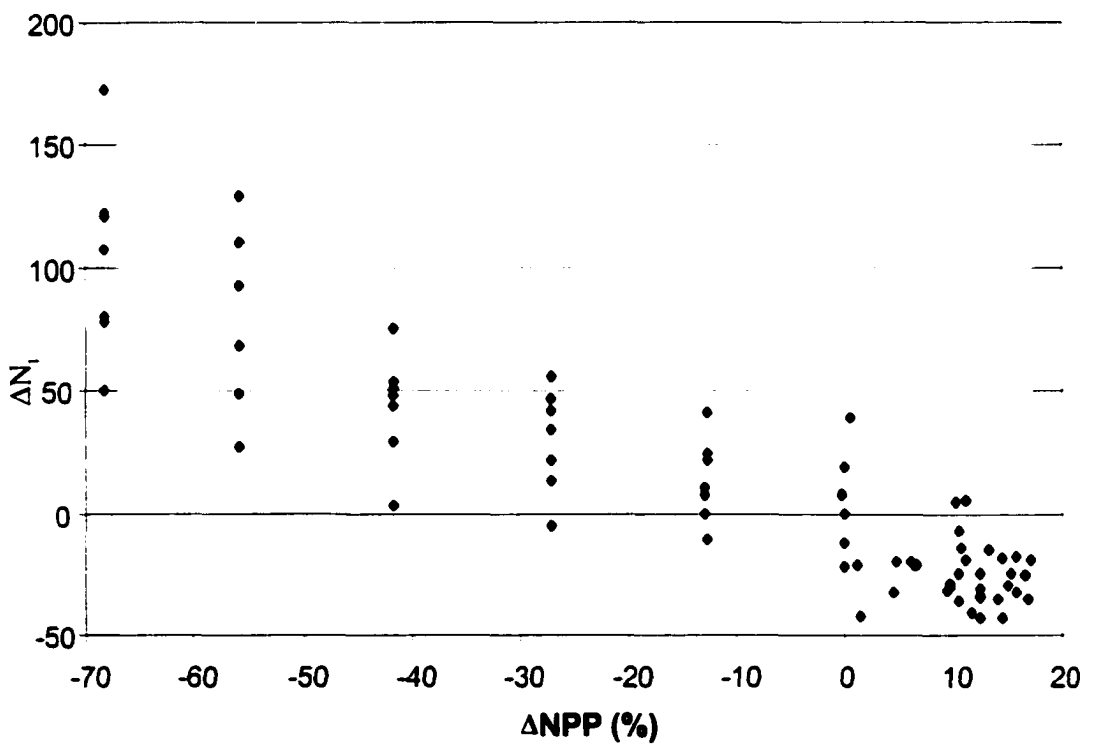


Figure 4.5.b  $N_i$  vs. NPP



## CHAPTER 5

### Conclusions

Reactive nitrogen in China is both copious and mobile. As most research endeavors do, this investigation has led to the generation of more questions than answers. Our field measurements, while certainly not to be regarded as the final authority on this matter, showed that less nitrogen was lost via  $\text{NO}_x$  and  $\text{N}_2\text{O}$  pathways than has been found in comparably fertilized agriculture. The extrapolation of an existing formal model of understanding, DAYCENT, also overestimated observed fluxes. Further investigation into these lower-than-expected fluxes is warranted. Although field measurements may never be considered ideal, we suggest several mechanisms which would operate in Chinese agroecosystems, which might not be accounted for in other studies or model representations.

Ammonia volatilization is likely the most important of these. This process operates on the timescale of days, and would effectively remove a substantial portion of the reactive nitrogen from the system before it may become incorporated within the microbial processes that would result in  $\text{NO}_x$  and  $\text{N}_2\text{O}$  releases. It is a particularly salient feature of Chinese agriculture due to the chemical composition of applied fertilizers in that country. Also, dampened fluxes may be an artifact of measurement timing. If atmospheric pollution levels in the Metro-Agro-Plex of Beijing follow a temporal dynamic similar to those observed in other urban areas, atmospheric  $\text{NO}_x$  concentrations

are higher during the day than at night, following a predictable diurnal cycle. The postulated higher atmospheric levels may then act to diminish the concentration gradient between the interstitial soil space where trace gases have been generated and the free atmosphere. In this scenario, although the gases have been created, they are simply not emitted to the atmosphere (or the monitoring device) at rates that reflect actual production.

While the general call for more research on a subject and better tools to examine it is often given, its need here is patent. China is the world's largest consumer of reactive nitrogen; agriculture is and will remain the most important sector into the foreseeable future, even under conditions of rapid economic development and industrialization. Through environmental contamination of the atmosphere, soils, and water, the effects of this nitrogen-based bounty have been noteworthy, both beneficial and, as is often more important in policy-making, detrimental. More measurements, and more specific model representations of Chinese agroecosystemic nitrogen fluxes are warranted.

The ability to create reactive substantial amounts of chemically reactive nitrogen from inert but plentiful atmospheric  $N_2$  has been important to the Chinese in its impacts on agricultural productivity. The importance of synthetic fertilizer to maintaining an adequately fed population cannot be overstated, particularly in the world's most populous country. Yet with advances in nutritional levels have come cancer, respiratory ailment, and increased mortality. And the question of whether food security may be maintained in the face of reduced arable land area and diminishing ecosystemic support, while often overstated by extremists, is worth asking. The Chinese ask it of themselves, as food

security issues consistently occupy a prominent position in the planning documents of the People's Republic.

To the rest of the world, Chinese nitrogen use translates through the atmosphere into changed atmospheric chemistry, acidification, and shifted global radiative balance. In the oceans it has meant eutrophication, changes in biodiversity, and fungal tides.

Although the importance of Chinese influence upon multiscale biogeochemistry has received recognition, a paucity of field measurements remains. At the time of submission of this dissertation, the author is aware of no internationally published agricultural-NO field measurements, and only a handful leaching experiments conducted in Chinese agroecosystems. While some N<sub>2</sub>O field studies are available, the number of model-based estimations of countrywide emissions is almost equivalent, creating considerable room for questions regarding verification methodology. While the drivers of agricultural nitrogen-based trace gas emissions are globally consistent, the environment in which they occur and the management to which they are subject are not.

China is unique, as any of its citizens will attest. The biogeochemical consequences of this realization are significant, and merit continued exploration.