FERTILIZER NITROGEN SOURCE AND MANAGEMENT IMPACTS ON GREENHOUSE GAS EMISSIONS

D.T. Walters
University of Nebraska, Lincoln, Nebraska

Abstract

Agricultural soil management accounts for nearly 6.3% of all greenhouse gas emission in the U.S. Although fertilizer nitrogen is an essential component of nearly all agricultural systems, the addition of reactive N to soils and the emission of nitrous oxide (N_2O) via soil microbiological processes (nitrification and denitrification) makes U.S. agriculture the largest source (62%) of total U.S. N_2O emissions. Because N_2O is a potent greenhouse gas with a forcing potential more than 300 times greater than CO_2, total agricultural N_2O emissions comprise an estimated 1/3 of projected U.S. carbon sequestration potential in arable lands. Estimates of GHG emissions from agricultural activity are subject to a high level of uncertainty. Management controls over N_2O emissions are related to the size of substrate N pool and the addition of N in the presence of easily decomposable C. Existing data suggests that both rate and source of N application are key management areas in the regulation of total N_2O emissions. Anhydrous ammonia seems to show markedly higher (~4-fold) N_2O emissions than other fertilizer N forms. As the U.S. consumes 80% of the world's anhydrous ammonia, the trend toward increased urea and ammonium solution materials in the corn-belt should reduce the effective N_2O loading from fertilizer N use. Total N_2O emission data and is driven by formulated IPCC estimates which do not include the effect of N source but are based upon data highly influenced by emission data where anhydrous ammonia was used. Programs that encourage best-management-practices in prescribing N dosage to crops that insure an economic optimum return can also reduce total atmospheric N_2O load without resorting to punative regulation.

Introduction

Fertilizer nitrogen (FN) application to agricultural land comprises more than 50% of global reactive N attributed to human activity (Smil, 1999). Although the manufacture and application of N consumes considerable fossil fuel energy and contributed to agriculture's share of CO_2-C emissions, it is also responsible for enhanced primary productivity and net C-sequestration. When considering the impact of FN on greenhouse gas emissions (GHGE), attention has increasingly focused on the effect that management of FN has on the emission of nitrous oxide (N_2O). Nitrous oxide is a very potent GHG with a forcing potential about 300 times greater than CO_2. In addition to its effect on global warming, nitrogen oxides produced from photochemical reactions of N_2O in the stratosphere is involved in the destruction of ozone layer. Currently, the rate of increase in N_2O concentration in the atmosphere is +0.8 ppb yr^{-1}. The primary focus of this short paper will be to review the existing evidence regarding the effect of agricultural soil management and FN on N_2O emissions. A brief review of the contribution of agricultural N_2O to GHGE in the U.S. is also presented.

Processes that form N_2O in agricultural soils

Two primary microbiological processes contribute to N_2O emission in soils (Figure 1). The first is nitrification, a primarily chemautotrophic process whereby NH_4 is consumed and oxidized in a
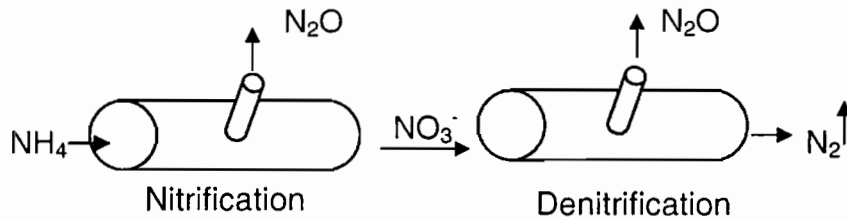

Figure 1. Schematic of the dominant processes contributing to N_2O production in soil. Adapted form Davidson, 1991. Figure courtesy of Dr. D. Ginting, UNL.

two step process. In the first step, NH_4^+ is oxidized to NO_2^- (*Nitrosommonas* are the best known autotrophs in this step). It is during this first step, that ammonium oxidizers can use NO_2^- as an alternative electron acceptor if O_2 is limiting and produce N_2O, a process known as nitrifier denitrification (Firestone and Davidson, 1989). In addition, NO_2^- can chemically decompose to N_2O under acidic conditions in a process known as chemodenitrification. Nitrite (NO_2^-) oxidizers do not produce N_2O. The second process is the more familiar anaerobic process whereby heterotrophic facultative anaerobes as well as certain fungi, in the absence of O_2, utilize NO_3^- as their primary electron acceptor during the decomposition of organic C and convert it to N_2. The process of conversion is stepwise: $NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$. Depending on environmental conditions, different products in this stepwise conversion may accumulate and be lost. In addition, the microbial diversity of denitrifying organisms is such that some may exhibit incomplete reduction to N_2 and favor greater emission of N_2O in the process. The N_2O/N_2 ratio is usually decreases as soil water content increases and available C but increases with higher soil NO_3^- concentrations (Weier et al., 1993). No general conclusions can be made regarding the degree of emission from either of these pathways as each is subject to different environmental and substrate requirements.

Contribution of agricultural N_2O emissions

U.S. agriculture contributes an estimated 6.3% of total U.S. GHGE with N_2O and methane (CH_4) as the primary GHG emitted by agricultural activities. Agricultural soil management activities are the largest source of U.S. N_2O emissions, accounting for 67% of total U.S. N_2O emissions (USEPA, 2005). USEPA estimates of agricultural emissions of N_2O in 2003 were 253.5 Tg CO_2 equivalents (1 Tg = 10^6 metric ton) (Table 1). This would be the equivalent of 69 x 10^6 Mg of C yr^{-1} or roughly 1/3 of the estimated annual U.S. potential for C-sequestration in arable lands (Metting, et al., 1998). Sources of N_2O emissions that are attributed to agricultural activity maybe categorized as either direct or indirect. *Direct* sources of N_2O emissions are associated with the application of fertilizers and manures, production of N_2-fixing crops, mineralization of crop residues and (to a lesser extent) the cultivation of histisols. *Indirect* N_2O emissions from the application of synthetic fertilizer to soil include: a.) atmospheric deposition of volatilized NH_3 and NO_x and b.) nitrogen leaching and runoff which both may enter surface waters and enhance N_2O production in these systems (IPCC, 1996).

Table 1. 1990 and 2003 EPA GHGE estimates for nitrous oxide emissions from agricultural soils. Values expressed in Tg CO_2 equivalents. (1 Tg = 10^6 metric ton). USEPA, 2005

	1990	2003
DIRECT	**140.4**	**155.3**
Agricultural Soils	100.1	114.8
Pasture, Range and Livestock Manure	40.2	40.5
INDIRECT	**112.6**	**98.2**
Volatilization and Atm. Deposition	15.6	16.5
Leaching and Runoff	97.1	81.8
TOTAL	**253.0**	**253.5**

Uncertainty in the measurement of soil N_2O emissions

It is beyond the scope of this paper to review all of the methodologies employed in the measurement of nitrous oxide emissions from soil. Excellent reviews of methods are available (Granli and Bøckman. 1994; Mosier and Klemedtsson, 1994). Needless to say, the amounts that are emitted per unit of area and time are very small and subject to extreme variation which is difficult to measure. Differences in methodologies, the extent of temporal measurement, treatments and site-specific edaphic properties also make it difficult to compare published data. The estimates provided by the Intergovernmental Panel on Climate Change (IPCC) suggest that, globally, cultivated soils contribute $0.03 - 3.0$ Tg N_2O-N yr^{-1}. The degree of uncertainty in agriculturally derived N_2O estimates are very high. Those published by the USEPA indicate a range of 82% above and below the 2003 emission estimate of 253. 5 Tg CO_2 Eq. with the greatest uncertainty in indirect emissions (Table 2).

Table 2. Quantitative uncertainty estimates for N_2O emissions from agricultural soil management in 2003. Values expressed in Tg CO_2 equivalents. (1 Tg = 10^6 metric ton). USEPA, 2005.

Source	2003 Emission Estimate (Tg CO$_2$ Eq.)	Uncertainty (%)	Uncertainty Range Relative to Emission Estimate (95 % confidence level) (Tg CO$_2$ Eq.)	
			Lower Bound	Upper Bound
Direct	155.3	64	55.9	254.7
Indirect	98.2	286	-182.5	379.1
TOTAL	253.5	82%	45.2	461.8

Management factors influencing N2O emissions

FN rate and residue inputs: It has generally been reported that N_2O emissions from native soils are lower than from fertilized cultivated lands. Estimates of the amount of N_2O emission from fertilized soils given in Table 1 are derived from the IPCC protocol that calculates direct N_2O emissions as a percentage (1.25%) of total FN inputs (IPCC, 1996). This tacitly assumes that there is a linear increase in N_2O emission regardless of the rate of application. This percentage is based upon the analysis of published literature on emissions from cropped land (Bouwman, 1994; Eichner, 1990; Mosier et al., 1998). The magnitude of emissions reported for different FN

rates can vary by several orders of magnitude which accounts for the high degree of uncertainty on direct emissions reported in Table 2. In a recent field study published by McSwiney and Robertson (2005) fertilized continuous corn was shown to maintain a relatively consistent linear increase in N_2O flux until FN rate exceeded that needed to achieve optimum yield. Beyond the yield threshhold, N_2O emissions more than doubled. They concluded that a set emission rate (such as the IPCC 1.25% factor) was appropriate only for FN rates below that needed for optimum yield. They concluded that N_2O flux in agricultural systems might be significantly reduced by proper management of FN to avoid excess beyond crop N requirement.

We have been monitoring trace gas emissions at our Mead, NE, Carbon Sequestration Sites. Nitrous oxide emissions are measured for the entire year on each of three quarter sections that are managed using best-management practices prescribed to local farmers. Table 3 shows the cumulative N_2O emissions for a 4-year period spanning 2001-2004 for three different cropping systems. Although total emissions are generally higher under the irrigated systems, emissions during the corn year as a percent of total N input have been greater in the corn-soybean rotation than under continuous corn and higher under rainfed than irrigated systems. We attribute this to the high productivity of irrigated maize and greater competition for inorganic N resources. There is much greater uncertainty in FN rate management in the rainfed system and much lower general productivity resulting a greater proportional emission percentage. Figure 2 shows the individual year N_2O emissions broken out into growing season and non-growing season (post harvest) periods.

Table 3. Cumulative N_2O emissions as a percent of applied FN for three systems: 1. Irrigated continuous corn, 2. Irrigated corn/soybean rotation, 3. rainfed corn soybean rotation. Univ. of NE, Carbon sequestration Program, Mead, NE. Values are the sum of 4-years of measurement. Data compiled courtesy of D. Ginting, UNL.

Site	System	Rotation[1]	Corn	Soybean	SE	FN[2]	% emission[3]
			-------kg N_2O-N ha^{-1}--------			kg N ha^{-1}	
1	Irrigated	C-C-C-C	16.9		1.31	946	1.78
2	Irrigated	C-S-C-S	9.2	7.2	2.79	410	2.24
3	Rainfed	C-S-C-S	7.8	5.6	1.42	224	3.48

[1] C = corn; S=soybean.

[2] FN applied to corn only

[3] % of FN as N_2O emission (corn year only), uncorrected for background N_2O

Note that in Figure 2, N_2O emissions are greater during the non-growing season following harvest of the soybean crop in the corn-soybean rotations. Previous laboratory incubations have shown that the C:N ratio of added organic N sources is negatively correlated with N_2O emissions and is directly related to available C (Bremner and Blackmer, 1981; Aulakh et al., 1991). A fraction of the EPA "direct" estimates given in Table 2 include N_2O emissions based upon the biomass and C:N ratio of various crops. Although, on average, N_2O emissions are lower for soybean than corn (Table 3), N_2O emissions during the 2004 growing season were similar to corn in 2001. These data illustrate that total emissions cannot be tied directly to FN rate and that considerable year-to-year variation exists in GHGE.
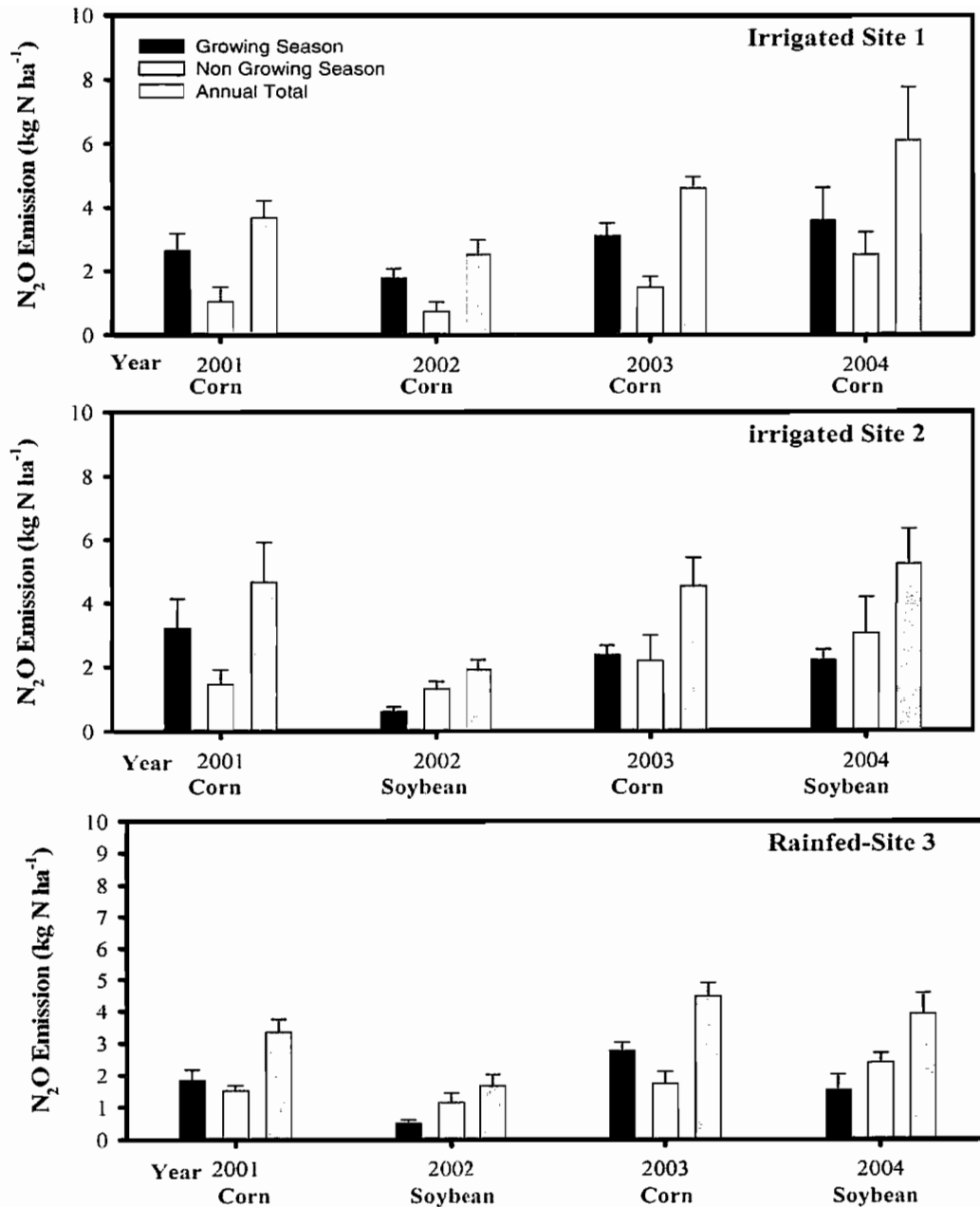
Figure 2. Annual (planting to planting) N2O emissions from an irrigated continuous corn, irrigated corn-soybean rotation and rainfed corn-soybean rotation. Mead, NE 2001-2004. Data compiled courtesy of Dr. D. Ginting, UNL.

FN form: A significant body of information has been compiled with regard to the effect of form of FN and N_2O emissions. In general, there is no single fertilizer type that results in greater N_2O emission with the exception of anhydrous ammonia. The majority of data on FN form has been collected from temperate soils. Table 4 shows a summary of data based on the compilation of data form numerous studies reported by Eichner, 1990 and Bøckman, 1994. The results indicate

that, with the exception of anhydrous ammonia, the % emission of N_2O is within the range of 0.1 to 2% which forms much of the basis for the IPCC guideline. The mechanism governing much higher N_2O emissions from anhydrous ammonia are not well understood. It has been suggested that the elevated pH in the injection zone results in a preferential inhibition of NO_3^- production and thus the buildup of NO_2^- increasing the substrate for ammonium oxidizers that might utilize NO_2^- as an alternative electron acceptor to O_2 (Focht and Verstraete, 1977).

Table 4. Median N_2O emission as percent of applied N as influenced by fertilizer form. (Eichner, 1990; Granli & Bøckman, 1994)

Source of FN	N_2O % of applied	Range of data %
Anhydrous ammonia	1.63	0.9 – 6.8
Ammonium Nitrate	0.40	0.04 – 1.7
Ammonium Sulfate (chloride)	0.15	0.02 – 1.7
Urea	0.11	0.01 – 0.6
Nitrate	0.05	0.01 – 1.8

Given the apparent enhanced effect of anhydrous ammonia on N_2O emissions, it is interesting to note the distribution of N sources that are consumed across the globe. Table 5 shows that, world-wide, only 5% of all FN sources in consumed as anhydrous ammonia, however, 80% of global anhydrous ammonia is consumed in the U.S. The implication here is that a significant reduction in N_2O emissions might be realized by simply changing the dominant source of fertilizer form anhydrous ammonia to liquids.

Table 5. Proportion of global and U.S. fertilizer N use by source. Source: IFADATA, 2000. Table courtesy of A. Dobermann, UNL.

	SOURCE	10^6 ton	%	% of Global
WORLD	Total N	83.0	100	
	Urea	39.6	48	
	Am. Nitrate	7.0	8	
	Anhydrous Am.	4.5	5	
	Liquid N	4.2	5	
	Other straight N	14.8	18	
	Compound N	12.9	16	
USA	Total N	11.3	100	14
	Urea	1.8	16	5
	Am. Nitrate	0.6	5	9
	Anhydrous Am.	3.6	32	80
	Liquid N	2.8	25	67
	Other straight N	0.3	3	2
	Compound N	2.2	19	17

Slow-release FN and nitrification inhibitors: Slow-release fertilizers are designed to provide inhibition to dissolution of product N over time to delay the release of FN and reduce the

probability of nitrification, denitrification or leaching when plant demand for N is low. There are few studies testing the effect of slow release fertilizers on N_2O losses in arable soils and more extensive work has been done in rice production systems. Minami (1994) compared N_2O losses from polyolefin-coated ammonium nitrate with uncoated ammonium sulfate and reported a 3 to 7-fold reduction in the emission of N_2O from arable soil. Other work comparing polyolefin-coated urea to uncoated urea showed a 35% reduction in N_2O emissions. Results are variable and the effectiveness of slow release products will depend on the rate of FN solubilization in relation to soil water content (Tsuruta, 1995).

Nitrification inhibitors such as nitrapyrin (2-chloro-6-(trichloromethyl)-pyidine) inhibit the oxidation of NH_4^+ and theoretically provide a means of reducing substrate for denitrification. A number of both laboratory and field studies have indicated that nitrapyrin will reduce the emission of N_2O but, of course, is only effective where the FN source is NH_4, urea or NH_3 (Bremner et al., 1981; Magalhaes et al., 1984). The utility of inhibitors like nitrpyrin in reducing N_2O emissions will be greatest with application of anhydrous ammonia because of the elevated N_2O potential of this FN form.

Summary

In the realm of GHGE and agriculture, N_2O emissions represent a significant portion of the total GHG loading attributable to agriculture. Although considerable attention has been paid to management and technology changes that might enhance soil C-sequestration, mitigation of agricultural N_2O flux may be the quickest way to reduce total GHG loading in production systems like corn that consume the lion's share of N in the U.S. corn-belt. Although N_2O measurement uncertainty is high, its forcing potential is great compared to CO_2 and management strategies are readily available to reduce total N_2O loading. Best-management practices that strive to increase FN-use-efficiency (FNUE) *and profitability* should also reduce both direct and indirect N_2O emission. The challenge we have as scientists is to assemble good quantitative evidence of the impact of BMP's on the mitigation of atmospheric N_2O load (vis. McSwiney and Robertson, 2005). The current IPCC inventory guidelines are based upon somewhat dated information and do not reflect the increases that have occurred in FNUE over the past several decades. We must also effectively transfer that information to policy makers.

References

Aulakh, M.S., J.W. Doran, D.T. Walters, A.R. Mosier and D.D. Francis. 1991. Crop residue type and placement effects on denitrification and mineralization. Soil Sci. Soc. Am. J. 55:1020-1025.

Bouwman, A.F. 1996Direct emissions of nitrous oxide from agricultural soils. Nutrient Cycling in Agroecosystems 46:53-70.

Bremner, J.M. and A.M. Blackmer, 1981. Terrestrial nitrification as a source of atmospheric nitrous oxide. Pp. 151-170 in C.C. Delwiche (ed.). Denitrification, nitrification and atmospheric N_2O. John Wiley & Sons Ltd., Chichester.

Bremner, J.M., G.A. Breitenbeck, and A.M. Blackmer. 1981. Effect of nitrapyrin on emission of nitrous oxide from soil fertilized with anhydrous ammonia. Geophys. Res. Lett. 8:353-356.

Davidson, E.A. 1991. Fluxes of nitrous oxide and nitric oxide from terrestrial ecosystems. pp.

219-235 in J.E. Rogers and W.B. Whitman (eds.). Microbial production and consumption of greenhouse gases: methane, nitrogen oxides and halomethanes, Amer. Soc. for Microbiology, Washington, D.C.

Eichner, M.J. 1990. Nitrous oxide emissions from fertilized soils: summary of available data. J. Environ. Qual. 19:272-280.

Firestone, M.K. and E.A. Davidson. 1989. Microbiological basis if NO and N_2O production and consumption in soil. pp 7-21. In M.O. Andreae and D.S. Schimel (eds.) Exchange of trace gases between terrestrial ecosystems and the atmosphere. John Wiley & Sons Ltd. Chichester.

Focht, D.D and W. Verstraete. 1977. Biochemical ecology of nitrification and denitrification. pp. 135-214. In M Alexander (ed.) Advances in Microbial Ecology. Vol.1. Plenum Press, NY, NY.

Granli, T. and O.C. Bøckman. 1994. Nitrous oxide from agriculture. Norwegian Journal of Agricultural Sciences, supplement 12:7-128. ISSN 0801-5341

IPCC. 1996. Module 4: Agriculture. In Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories. 1996, Intergovernmental Panel on Climate Change: Paris.

Magalhaes, A.M.T., P.M. Chalk and W.M. Strong. 1984. Effect of nitrpyrin in nitrous oxide emission from fallow soils fertilized with anhydrous ammonia. Fert. Res. 5:411-422.

Metting, F.B., J.L. Smith, J.S. Amthor. 1998. Science needs and new technologies for carbon sequestration. pp.1-34, In: N.J. Rosenberg (ed.), Carbon sequestration in soils: science, monitoring, and beyond. Proc. St. Michaels Workshop. Batelle, Columbus, OH

Minami, K. 1994. Effect of nitrification inhibitors and slow-release fertilizers on emissions of nitrous oxide from fertilized soils. pp. 187-196 In K. Minami, A. Mosier and R. Sass (eds.). CH_4 and N_2O: Global emissions and controls from rice fields and other agricultural and industrial sources. NIAES, Yokendo, Tokyo.

Mosier, A.R. and L. Klemedtsson. 1994. Measuring denitrification in the field. pp. 1047-1065 In: R.W. Weaver et al. (eds.) Methods of Soil Analysis Part 2 – Microbiological and Biochemical Properties. Soil Science Society of America book series; no. 5. Madison, Wisconsin, USA.

Mosier, A.R., Kroeze C., Nevison, C. (et al.) 1998. Closing the global N2O budget: nitrous oxide emissions and through the agricultural nitrogen cycle – OECD/IPCC/IEA phase II development of IPCC guidelines for national greenhouse gas inventor methodology. Nutrient Cycling in Agroecosystems 52:225-248.

McSwiney, C.P. and G.P. Robertson. 2005. Nonlinear response of N_2O flux to incremental fertilizer addition in a continuous maize (Zea mays L.) cropping system. Global Change Biology 11:1-8.

Smil, V. 1999. Nitrogen in crop production: an account of global flows. Glob. Biochem. Cycles. 13:647-662.

Tsuruta H, 1995. N_2O and NO emissions form fertilized soils, livestock waste and rice paddy fields. pp. 97-100 of the Proc. UK-Japan Workshop on controlling methane and the nitrogen cycle on farms. Silsoe, Beds. UK. March, 1995.

USEPA. 2005. Inventory of U.S. greenhouse gas emissions and sinks: 1990-2003. EPA 430-R-05-003.

Weier, K.L., J.W. Doran, J.F. Power, and D.T. Walters. 1993. Denitrification and the dinitrogen/nitrous oxide ratio as affected by soil water, available carbon and nitrate. Soil Sci. Soc. Am. J. 57:66-72.

PROCEEDINGS OF THE

THIRTY-FIFTH
NORTH CENTRAL
EXTENSION-INDUSTRY
SOIL FERTILITY CONFERENCE

Volume 21

November 16-17, 2005
Holiday Inn Airport
Des Moines, IA

Our cover: To world food security and agricultural production, the Haber-Bosch process has been the most economical means for fixation of nitrogen for fertilizer. Fritz Haber won the Nobel Prize for Chemistry in 1918 and Carl Bosch shared the prize in 1931.