

Nitrous oxide emissions from agricultural fields: Assessment, measurement and mitigation

A.R. Mosier¹, J.M. Duxbury², J.R. Freney³, O. Heinemeyer⁴ and K. Minami⁵

¹USDA/ARS, Fort Collins, CO 80522, USA*, ²Cornell University, Ithaca, NY, USA, ³CSIRO, Canberra, ACT, Australia, ⁴BFAL, Braunschweig, Germany and ⁵JIRCAS, Tsukuba, Japan

Key words: denitrification, nitrification, nitrification inhibitors, N₂O

Abstract

In this paper we discuss three topics concerning N₂O emissions from agricultural systems. First, we present an appraisal of N₂O emissions from agricultural soils (**Assessment**). Secondly, we discuss some recent efforts to improve N₂O flux estimates in agricultural fields (**Measurement**), and finally, we relate recent studies which use nitrification inhibitors to decrease N₂O emissions from N-fertilized fields (**Mitigation**).

To assess the global emission of N₂O from agricultural soils, the total flux should represent N₂O from all possible sources; native soil N, N from recent atmospheric deposition, past years fertilization, N from crop residues, N₂O from subsurface aquifers below the study area, and current N fertilization. Of these N sources only synthetic fertilizer and animal manures and the area of fields cropped with legumes have sufficient global data to estimate their input for N₂O production. The assessment of direct and indirect N₂O emissions we present was made by multiplying the amount of fertilizer N applied to agricultural lands by 2% and the area of land cropped to legumes by 4 kg N₂O-N ha⁻¹. No regard to method of N application, type of N, crop, climate or soil was given in these calculations, because the data are not available to include these variables in large scale assessments. Improved assessments should include these variables and should be used to drive process models for field, area, region and global scales.

Several N₂O flux measurement techniques have been used in recent field studies which utilize small and ultra-large chambers and micrometeorological along with new analytical techniques to measure N₂O fluxes. These studies reveal that it is not the measurement technique that is providing much of the uncertainty in N₂O flux values found in the literature but rather the diverse combinations of physical and biological factors which control gas fluxes. A careful comparison of published literature narrows the range of observed fluxes as noted in the section on assessment. An array of careful field studies which compare a series of crops, fertilizer sources, and management techniques in controlled parallel experiments throughout the calendar year are needed to improve flux estimates and decrease uncertainty in prediction capability.

There are a variety of management techniques which should conserve N and decrease the amount of N application needed to grow crops and to limit N₂O emissions. Using nitrification inhibitors is an option for decreasing fertilizer N use and additionally directly mitigating N₂O emissions. Case studies are presented which demonstrate the potential for using nitrification inhibitors to limit N₂O emissions from agricultural soils. Inhibitors may be selected for climatic conditions and type of cropping system as well as the type of nitrogen (solid mineral N, mineral N in solution, or organic waste materials) and applied with the fertilizers.

* FAX No: + 19704908213

Introduction

Nitrous oxide is an important atmospheric constituent because it is a long-lived greenhouse gas and it is also the major source of stratospheric NO (Cicerone, 1989). The atmospheric concentration of N₂O is about 310 ppbv, it is increasing at a rate of 0.6–0.9 ppbv yr⁻¹, and its lifetime is 166±16 years (Prinn et al., 1990). The global warming potential (GWP) of each molecule of N₂O is about 250 times greater than each molecule of CO₂. Nitrous oxide currently accounts for 2–4% of total GWP (Watson et al., 1992) and could contribute as much as 10% of GWP in the future (Cicerone, 1989). The only known significant removal mechanism for atmospheric N₂O is transport into the stratosphere where it is photolytically oxidized to NO which reacts with stratospheric ozone and absorbs harmful solar ultra violet radiation (Crutzen, 1981). It has been estimated that doubling the concentration of N₂O in the atmosphere would result in a 10% decrease in the ozone layer and this would increase the ultraviolet radiation reaching the earth by 20% (Crutzen and Ehhalt, 1977). This could result in increased skin cancer and other health problems (Lijinsky, 1977).

The concentration of N₂O in the atmosphere is increasing, because of biotic and anthropogenic activities (Andreae and Schimel, 1989; Rodhe, 1990). Previously it was estimated that about 1.5 Tg of N is injected directly into the atmosphere each year as N₂O as a result of fertilizer applications to agricultural ecosystems (CAST, 1992; Watson et al., 1992). This represented about 44% of the anthropogenic input and about 13% of the total input of N₂O to the atmosphere annually. These estimates (Watson et al., 1990, 1992) did not include N₂O production from other major N input sources; animal manures and biological N fixation. As we discuss later, these are important inputs to be considered in assessing global N₂O emission budgets and we include them in revised emission estimates presented below.

It is likely that N₂O production resulting from fertilizer and increased use of biological nitrogen fixation is underestimated because the effect of a N input is usually only partially traced through the environment (Duxbury et al., 1993). A complete accounting of fertilizer N, biologically fixed N, and N mineralized from soil organic matter is difficult to achieve, but is needed if we are to accurately assess the impact of increased use of N in agricultural ecosystems on terrestrial N₂O emissions. Since only about half of the fertilizer N added to a field is taken up by a crop and agricultur-

al soils are tending to lose N through time (CAST, 1992), about half of the N is eventually returned to the atmosphere through denitrification. Loss vectors from the field include nitrate leaching, erosion and gaseous emissions. The N removed from the field in the crop is fed to animals which generate manure. The manure is returned to cropland to fertilize a second crop and, in the process, about half of the N in the manure is volatilized as NH₃. Ammonia volatilization from agricultural systems is globally important (Isermann, 1993), but its impact on N₂O emissions has not been directly quantified.

Since about 70% of the N₂O emitted from the biosphere into the atmosphere is derived from soils (Bouwman, 1990) we assume that changes in N cycling in soil systems have influenced the increases in atmospheric N₂O during the past century and will help dictate future changes. In the past, land use conversion has caused major perturbations in soil N processes. Conversions of forests and grasslands to croplands accelerated C and N cycling and increased N₂O emissions from soil. Globally, land use conversion is important now only in tropical areas. Most of the conversions of forests and grasslands in the northern hemisphere occurred 50 to 200 years ago (Hammond, 1990). Continued growth in the atmospheric concentration of N₂O can be partly attributed to the increase in N input into the soil system. The increased input comes from atmospheric deposition [which ranges from about 0.5 g N m⁻² yr⁻¹ in the central US and other relatively pristine areas of the globe, to 6 g N m⁻² yr⁻¹ in western Europe (Andreae and Schimel, 1989)], N fertilization with mineral N sources or animal manures and biological N fixation. Nitrogen fertilizer use and biological N-fixation are projected to continue to increase during the next 100 years (Hammond, 1990). Much of this increase in N use is necessary to continue global food production to meet the needs of the rapidly expanding population, since crop production can be directly related to N-fertilizer use (World Development Report, 1992).

Soil production processes

Research during the past several decades provides an understanding of how N₂O is produced, factors that control its production, source/sink relationships and gas movement processes. However, even with this large amount of knowledge, we are not yet able to reliably predict the fate of a unit of N that is applied or deposited on a specific agricultural field. Studies of

emissions of N_2O from presumably 'similar' agricultural systems show highly variable results in both time and space. It is the complex interaction of the physical and biological processes involved that must be understood before appropriate predictive capability can be developed (Mosier, 1993).

N_2O is produced primarily from the microbial processes, nitrification and denitrification in soil. In well aerated, yet moist conditions, N_2O emissions from nitrification of ammonium based fertilizers can be substantial (Bremner and Blackmer, 1978; Duxbury and McConnaughey, 1986). Other work suggests that N_2O is a byproduct of nitrification (Yoshida and Alexander, 1970) through denitrification of nitrite by nitrifying organisms which denitrify nitrite under oxygen stress (Poth and Focht, 1985). In wet soils, where aeration is restricted, denitrification is generally the source of N_2O (Smith, 1990). Under these conditions both the rate of denitrification and the $N_2O/(N_2 + N_2O)$ ratio must be known to evaluate N_2O emissions through denitrification. According to Smith (1990), soil structure and water content, affecting the balance between diffusive escape of N_2O and its further reduction to N_2 are important in determining the proportions of the two gases.

Purpose of paper

In this paper we discuss three topics concerning N_2O emissions from agricultural systems. First we present a current appraisal of N_2O emissions from agricultural soils (**Assessment**). Secondly we discuss some recent efforts to improve N_2O flux estimates in agricultural fields (**Measurement**), and finally we relate some recent field studies which use nitrification inhibitors to decrease N_2O emissions from N-fertilized fields (**Mitigation**).

Assessment

The increase in N_2O emissions from agricultural soils during the past several decades has been related to the increase in N application to these soils (McElroy et al., 1977; Granli and Bockman, 1994). To assess N_2O emissions during a calendar year it is necessary to know the amount of N used as fertilizer on a global basis. Estimates of the total amount of N applied to agricultural soils as mineral N, animal waste (manure + urine) N and the area of harvested N-fixing crops are given in Table 1. The amount of mineral N con-

sumed in each of the seven regions is tabulated from information provided by FAO (1990a). The land area of harvested pulses and soybeans is also obtained from FAO (1990b). The amount of N from animal waste that is used to fertilize agricultural fields is not well known. We derived the estimates in Table 1 from calculations that were adapted from Safley et al. (1992) and Bouwman (1994a). We then estimated an amount of N for each region that may be used as fertilizer N. These numbers were based on estimates of animal distribution and management systems for each region and we do not consider the N estimates to be very reliable because of the lack of information.

Galbally et al. (1992) indicate that legumes may contribute to N_2O emission in a number of ways. Atmospheric N_2 fixed by the legumes can be nitrified and denitrified in the same way as fertilizer N, thus providing a source of N_2O . In addition, symbiotically living Rhizobia in root nodules are able to denitrify and produce N_2O (O'Hara and Daniel, 1985). Galbally et al. (1992) suggested an emission rate of $4 \text{ kg N ha}^{-1} \text{ y}^{-1}$ for improved pastures, and Duxbury et al. (1982) suggested that legumes can increase N_2O emissions by a factor of 2 to 3 compared to unfertilized fields.

In addition to including animal manure and N from biological N fixation with synthetic fertilizer N as total agricultural N sources for N_2O , we present below a revised method for calculating the contribution of N_2O from agricultural systems. Earlier estimates (OECD/OCDE, 1991) were generally based upon assessments derived from reviews of published N_2O emissions data (Bouwman, 1990; Eichner, 1990). More recently, Bouwman (1994a, b) reviewed the literature again and presented a more comprehensive assessment of N_2O emissions. He notes that loss of N_2O from agricultural soils may be presented in three ways: (1) the total loss of N_2O during the period covered by the measurements; (2) the difference between fertilized and control plots which is referred to as 'fertilizer induced N_2O loss' and (3) the total loss of N_2O calculated as a percentage of fertilizer N applied.

The total N_2O flux should represent N_2O from all possible sources; native soil N, N from recent atmospheric deposition, past years fertilization, N from crop residues (depending upon the C/N ratio of the residue this N could either be mineralized or immobilized), N_2O from subsurface aquifers below the study area, and current N fertilization. Because unfertilized control plots mostly represent the fertilization and cropping history of previous years, it is difficult to assess a proper control value for the recent fertilizer effects on

Table 1. Estimated nitrogen derived from synthetic fertilizers and animal wastes applied to agricultural lands and land area cropped with pulses and soybeans

Region	Fertilizer N applied (Tg)	Manure N produced (Tg)	N used as fertilizer (% of total)	Manure N used as fertilizer (Tg)	Harvested area of pulses + soybeans (ha × 10 ⁶)
Africa	2.1	20.9	50	10.5	12.8
Am. N and C	13.1	7.8	70	5.5	28.1
Am. S	1.7	21.9	50	11.0	23.5
Asia	37.3	37.4	70	26.2	48.5
Europe	13.6	12.3	90	11.1	4.0
Oceania	0.9	0.5	30	1.5	1.4
USSR ^a	8.7	10.1	90	9.1	6.6
Total	77.4	115.3		74.9	124.9

^a Former USSR.

N₂O loss. Even though we recognize that subtracting a control may underestimate the amount of N₂O directly derived from added fertilizer we use method (2) in our calculations to estimate the contribution of fertilization to N₂O emissions from agricultural soils.

We have discarded the concept suggested by Eichner (1990) of different amounts of N₂O evolving from fertilized soils according to N source. As noted in Mosier (1993), we consider soil management and cropping systems to impact N₂O emissions more than mineral N source. Limited data does, however, indicate that organic N sources such as animal manures and sewage sludge do induce larger N₂O emissions per unit of N added to the soil than does mineral N (Bouwman, 1990, 1994a, b). Because of the lack of adequate parallel experiments that cover the range of possibilities of mineral and organic N applications, we use a single conversion coefficient for all sources.

Bouwman (1994a) estimated the total emissions of N₂O from a regression equation: total annual direct field N₂O (kg N ha⁻¹) loss = 1 + 0.0125 × N-application. The value of 1 kg N₂O-N ha⁻¹ represents the background emission while the 0.0125 factor accounts for the contribution from fertilization. This estimate includes N sources from a variety of mineral and organic N-fertilizers and was based on long term data sets.

Conducting other analyses with the data tabulated by Bouwman (1994a) we arrived at similar N₂O conversion estimates. From the data listed, we selected data satisfying the following criteria: soils were cropped, measurements were made for more than 80

days, and 50 to < 500 kg fertilizer N⁻¹ha⁻¹ was added. Seventy of these studies included a nonfertilized control. The average 'fertilized induced N₂O flux' was 0.0124 kg N₂O-N kg⁻¹ N applied, with a standard error of 0.0016. The range of these data is 0 to 0.063 and the median is 0.009. Of these studies 1 found no 'fertilizer induced N₂O flux' while 28 studies found 0.001 to 0.004 kg N kg⁻¹ N, 10 cases found 0.004 to 0.008, 21 found 0.008 to 0.02, 8 found 0.02 to 0.036 and 2 were greater than 0.036.

Although these emission estimates are variable, the variability is lower than suggested in the OECD/OCDE (1991) calculation methodology. Experience in conducting field flux experiments tells us that much narrower constraints can be placed on the N₂O flux predictions. We expect that the Bouwman (1994a) estimate of 1.25% ± 1.0% of the applied N will encompass approximately 90% of the direct contributions of fertilization to N₂O emissions.

The indirect contribution of fertilizer N additions to N₂O emissions, apart from the fields where fertilizer N is applied, must also be considered in Agriculture's contribution to atmospheric N₂O. Based upon the discussions of Duxbury et al. (1993) and Mosier (1993) and the large amounts of N₂O frequently found in subsurface aquifers (Bowden and Bormann, 1986; Minami and Ohsawa, 1990; Ronen et al., 1988) we estimate that an additional 0.75% of N applications will eventually be evolved to the atmosphere as N₂O resulting from N leaching, runoff and NO_x and NH₃ volatilization.

Table 2. Estimates of direct and indirect emissions of N₂O produced by application of synthetic fertilizer N or animal waste N to agricultural soils or by growing legumes

Region	Estimated N ₂ O emitted from			Total estimate	Range of estimates
	Fertilizer N	Manure	N-Fixation		
	(Tg N ₂ O-N)				
Africa	0.04	0.21	0.05	0.30	0.15–0.45
Am. N and C	0.26	0.11	0.11	0.48	0.24–0.72
Am. S	0.03	0.22	0.09	0.34	0.17–0.51
Asia	0.75	0.52	0.19	1.46	0.73–2.19
Europe	0.27	0.22	0.02	0.51	0.26–0.77
Oceania	0.01	0.03	0.01	0.05	0.03–0.08
USSR ^a	0.17	0.18	0.03	0.3	0.19–0.57
Total	1.53	1.49	0.50	3.5	1.8–5.3

^a Former USSR.

The total direct and indirect N₂O-N emissions from application of mineral or organic N total approximately $2 \pm 1\%$ annually. This estimate is expected to encompass more than 90% of field situations. Nitrous oxide from biological N-fixation is calculated by multiplying the area of land used for growing pulses plus soybeans in each region by 4 kg N ha^{-1} (Duxbury et al., 1982; Galbally et al., 1992) (Table 2).

The N₂O emission estimates from Table 2 suggest that N₂O from fertilizer application to croplands is about equally proportioned between synthetic fertilizer and manure fertilizer sources. About 40% of the estimated N₂O production is from North and Central America, Europe and the former Soviet Union where about 20% of the world human population reside. Asian countries which hold about 55% of the global human population (World Development Report, 1992) contribute about 40% of the estimated annual N₂O production.

Improvements in local, regional and national N₂O emission assessments are needed to be more certain that these global emission estimates are realistic. Improving assessment methodologies may evolve in a series of steps that culminates in development of process based models which are coupled to land use, crop and soil data bases to provide geographically related information. With these models, if a relatively simple set of input information can be supplied on a country or region basis, then detailed emission calculations may be made. Because of the inherent spatial and temporal variability associated with N₂O production and emissions from soils, it appears that very simple approaches

may not provide realistic emission estimates (Mosier and Bouwman, 1993).

Measurement

Reducing uncertainty

A multitude of reviews on N₂O flux measurement methods have been published during the past 15 years (e.g. Baldocchi et al., 1988; Denmead, 1983, 1994; Desjardins and MacPherson, 1989; Fowler and Duyzer, 1989; Mosier, 1989). The reader is referred to some of the current reviews to gain historical and theoretical insight to gas flux measurement problems.

Nitrous oxide emissions from N-fertilized agricultural fields have been found to vary between 0.001 and 6.8% of the N applied to the field (Bouwman, 1990; Eichner, 1990). A portion of this variability in N₂O estimates, relative to the amount of fertilizer applied, has been attributed to spatial and temporal variability of the processes which produce N₂O in soil (Denmead, 1994). Since small chamber systems were used to collect most of these data, the data are assumed to be inherently flawed (Denmead, 1994). It is also assumed that by using flux measurement techniques which integrate over larger areas that the average N₂O flux value for a field will be more accurate and subject to less uncertainty. This assumption has recently driven the development of new techniques and funding for new research in many areas of the world. There is still little data from comparative field sites which discern whether or not the average N₂O flux made with cham-

bers in a field has any true value or if the variability noted in the literature reviews of Eichner (1990) and Bouwman (1990) is primarily from field factors such as crop, cultivation practices, former history of the field being studied, weather, irrigation practices or a host of other variables that regulate gas flux.

During the past two decades the need for detection systems which are rapid, sensitive and accurate has been expressed (Andreae and Schimel, 1989) and several N_2O measurement techniques have been proposed which permit using micrometeorological techniques to provide field scale spatial integration. Denmead (1983), Desjardins and MacPherson (1989), Fowler and Duyzer (1989) and Mosier (1990) discuss these possibilities and a variety of aspects as they relate to N_2O flux measurements. These techniques include N_2O detection by tunable diode laser (TDL) which permits eddy correlation or flux gradient micrometeorological flux measurements, Fourier transformed infrared (FTIR) spectrometry which can be used for flux gradient techniques or ultra-large chambers, and long path infrared analyzers for use in ultra-large chambers. Measurement techniques are now becoming available to permit making interfield comparisons without using small chamber techniques. These techniques are now being used in field studies and are presented as case studies to demonstrate some recent advances in N_2O measurement technology and to demonstrate recent efforts to compare the capabilities of flux techniques.

Case studies

Case 1. Stirling, Scotland, UK

Measurement of N_2O flux from a fertilized grassland using three different analytical techniques with the flux gradient micrometeorological technique (Hargreaves et al., 1994).

A level timothy grass (*Phleum pratense*) pasture about 0.08 m high on a clay soil with poor drainage was fertilized with ammonium nitrate (185 kg N ha^{-1}) on 3 April 1992 and N_2O emission rates were measured over the following three weeks. During this time the soil moisture content remained in the range of 40–50% on a dry weight basis and total soil mineral N content declined from about 200 to 80 mg N kg^{-1} (Clayton et al., 1994).

Gas chromatography. Gas samples were collected from 0.06, 0.23, 0.51, 1.05, and 1.99 m above the

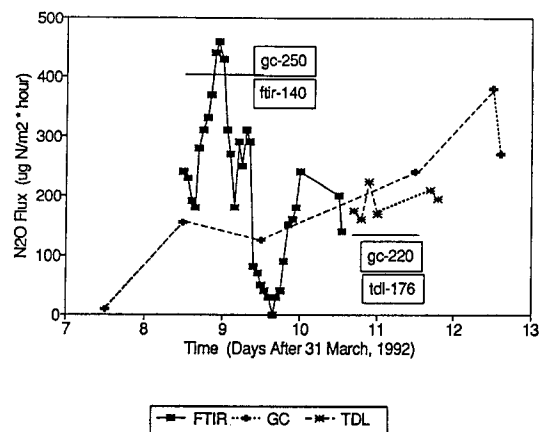


Figure 1. Nitrous oxide flux using three different N_2O detectors and the flux gradient micrometeorological technique at Stirling, Scotland, April 1992 (adapted from Hargreaves et al., 1994).

grass canopy during a 30-min period by filling 25-L Tedlar bags at the rate of 0.7 L min^{-1} . Aliquots of these samples were analyzed 10 to 15 times each by GC, using electron capture detection. Repeated analyses of the same sample increased analytical precision to 1.0 ppbv so that fluxes of $> 100 \text{ g ha}^{-1} \text{ d}^{-1}$ could be detected (Arah et al., 1994).

Tunable diode laser. The N_2O concentration gradient, 0.06 and 1.05 m above the grass canopy, was measured using a TDL (Hargreaves et al., 1994). This TDL employed a lead salt laser which rapidly scanned (1 kHz) across a single rotational-vibrational absorption line centered on $4.472 \mu\text{m}$. Ambient air was pumped through a multiple reflection white cell which provided an optical absorption path length of 38.7 m. Precision of 1 ppm in 1-min measurement periods were attained and 15 min averages were used for flux comparisons.

Fourier transformed infrared spectrometry. Galle et al. (1994) also used a FTIR to measure N_2O concentration differences at 0.06 and 1.05 m above the pasture canopy. Air was drawn from each height and pumped alternatively into a 25-L multiple reflection cell with an effective path length of 139 m. A differential spectrum was obtained by ratioing spectra from the two heights and 12 min averages of concentration differences between heights were obtained.

The three techniques provided generally similar estimates for field scale measurement of N_2O fluxes (Fig. 1). Hargreaves et al. (1994) concluded that 'the magnitude of the uncertainty of N_2O fluxes measured with the three techniques is fairly large because of the

small difference required to be measured against a large background concentration.'

Case 2. Lammefjorden, Denmark

Short-term comparison of N₂O fluxes measured by TDL eddy correlation, ultra-large chambers, and small chambers.

During 19–28 August 1993 another field comparison of analytical techniques was conducted in a high organic matter, silty clay soil where wheat (*Triticum aestivum* L.) had recently been harvested (Fowler et al., 1994; Smith et al., 1995).

Eddy correlation. Fowler and Duyzer (1989) describe the eddy correlation micrometeorological method for measuring gas fluxes. Eddy correlation measures the vertical transport of a gas past a point in the atmosphere. It is obtained by correlating the instantaneous vertical wind speed at a point with the instantaneous concentration of the gas. In the natural environment the eddies which are important in the transport process occur with frequencies of up to 5 or 10 Hz. The new TDL used by the ITE Edinburgh research group (Fowler et al., 1994) provides a fast response detector having sufficient sensitivity to perform eddy correlation measurements. Measurements were made almost continuously between 19 and 28 August 1993.

Ultra-large chamber and long path IR (Hawk) detector.

A large chamber was constructed from a series of plastic hoops covered with either tent fabric or polyethylene sheet to form a hemi-cylindrical chamber which was 2 m wide, about 30 m long and covered an area of about 60 m². The accumulation of N₂O released from the soil surface under the cover was measured with a long-path infrared absorption spectrometer tuned to an N₂O absorption band. The 'Hawk' gas monitor manufactured by Siemens Plessey¹ was used in these studies (Smith et al., 1994, 1995). This instrument can detect a N₂O concentration change of about 25 ppbv.

Small chambers. Small, closed chambers (IAEA, 1992; Smith et al., 1995) were arrayed along the assumed fetch of the eddy correlation technique and near the ultra-large chamber. The small chambers anchors were installed before the study was initiated

Table 3. Comparison of N₂O flux using small chambers (SC), ultra-large chamber with long path IR (ULC), and eddy correlation (EC) in a recently harvested wheat field in Lammefjorden, Denmark (Smith et al., 1995)

Date	Method		
	SC	ULC	EC
N ₂ O Flux ($\mu\text{g N m}^{-2} \text{h}^{-1}$)			
22 August	175	367	359
23/24 August	209	254	367
26/27 August	254	309	225

and each chamber covered 0.16 m². The concentration buildup within the chambers was measured by periodically withdrawing a gas sample from within the chamber and determining the quantity of N₂O by gas chromatography using an electron capture detector (Arah et al., 1994).

Table 3 shows the results of three comparisons on three occasions. The small chamber, ultra-large chamber and the eddy correlation technique provided flux measurements that were of similar variability to the three measurement techniques in Case 1 (Fig. 1). Smith et al. (1995) note that their previous experience indicates that similar flux measurements should be expected, provided that the area sampled by the chambers is representative of the micrometeorological fetch.

Case 3. Guelph, Ontario, Canada

Flux gradient technique using TDL. A sensitive, fast response N₂O analyzer, based on TDL absorption (IAEA, 1992) was used to make flux measurements using micrometeorological techniques. The TDL technique is based on infrared (IR) absorption spectrometry, whereby the extent of absorption depends upon path length, line strength and absorber concentration. The N₂O instrument has a total system noise of 1 ppb (v/v) based on a 30 minute sampling period, a resolution of 8 ppt (v/v) can be achieved. The maximum sampling rate is 10 Hz and data point averaging time is 0.1 s. This system is now commercially available from Campbell Scientific, Logan, Utah, USA¹.

The TDL system was used to measure N₂O fluxes utilizing the gradient-transport micrometeorological method (Wagner-Riddle et al., 1994) within four one ha adjacent fields at the Elora Research Station near Guelph, Ontario, Canada. The plots contained the following treatments: (1) bare fallow; (2) bare fallow fertilized with liquid cattle manure; (3) alfalfa (*Me-*

¹ Name of specific supplier of instrumentation does not constitute an endorsement by USDA/ARS or imply that other comparable instruments produced elsewhere are not suitable.

dicogo sativa L.) established in 1992 and (4) a mature stand of Kentucky bluegrass (*Poa pratensis* L.). Air samples were taken from two heights above each plot for one hour, six times each day. Flux measurements were begun before snow melt in March and continued through the remainder of 1993. Hourly flux measurements were averaged to provide a daily flux value for each site.

N₂O emissions from March to December totaled 3.5, 4.3, 3.2 and 0 kg N ha⁻¹ for bare fallow, manured bare fallow, alfalfa and bluegrass fields, respectively. Fluxes for the year were highest from the noncropped fields immediately following snow melt, when soil surface thawing occurred. This initial burst in emissions was not observed for the cropped plots, although the average fluxes were higher from March through April than the remainder of the year. Plowing the alfalfa field at the end of September resulted in large N₂O emissions, increasing the monthly average from 10.3 to 59.4 ng m⁻² s⁻¹ (or 0.17 kg N ha⁻¹ month⁻¹ and 1 kg N ha⁻¹ month⁻¹) (Wagner-Riddle et al., 1994).

These studies demonstrate that TDL can now provide micrometeorological measurement of N₂O fluxes on a routine basis. Particularly important in this demonstration is that the technology can be used to continuously monitor gas fluxes throughout the year. The studies also point out that year-round measurements are necessary because maximum fluxes are observed in different treatments during different times of the year. Such systems should be ideal to compare N₂O emissions from different management systems at the same time. Simultaneous measurement of different treatments on the field scale are required to determine if the uncertainty in N₂O emissions from agricultural fields under different management systems is as large as generally perceived (Eichner, 1990).

Methods comparisons

The comparisons of flux measurement techniques presented above in Cases 1 and 2 (Galle et al., 1994; Hargreaves et al., 1994; Smith et al., 1994, 1995) indicate that with appropriate experimental design and analyses the different methods provide essentially the same information concerning N₂O flux. According to Smith et al. (1995) the small chambers require a high labor requirement and the need for a large number of replicate measurements to overcome spatial variability. The ultra-large chambers average fluxes over areas of 2–3 orders of magnitude larger than conventional chambers and are useful where site character-

istics rule out micrometeorological methods. These ultra-large chambers are, however, cumbersome to set up and cannot be used in windy conditions. Overall, small chambers have been invaluable in establishing the effects of variables such as temperature, the supply of mineral N and soil water content on N₂O fluxes (Smith et al., 1995) and will probably remain the major flux measurement technique for many types of studies. Micrometeorological methods which supply 'real time' spatial integration of N₂O fluxes over areas of 0.1 to 1 km² should also provide the ability to interpret N₂O emissions in terms of short term environmental variables (Hargreaves et al., 1994).

Further interpretation of the field N₂O flux measurements discussed above indicates that the data collected thus far, primarily using chamber techniques, may after all, be reflective of the N₂O fluxes that occurred in the field. Utilization of techniques which provide spatial integration more readily may not necessarily change the interpretation of the numbers acquired. From this one may conclude that it is not the analytical technique that is providing the major uncertainty in N₂O flux values found in the literature but rather the diverse combinations of physical and biological factors which control gas fluxes. A careful comparison of published literature narrows the range of observed fluxes as noted in the section on assessment. An array of careful field studies which compare a series of crops, fertilizer sources, and management techniques in controlled parallel experiments are needed to improve flux estimates and decrease uncertainty in prediction capability using techniques which best fit the experimental design. Another point which is demonstrated clearly by the Guelph, Canada case study, is that studies must be conducted throughout the year and not just during the cropping period.

Mitigation

As noted in the above assessment section about 3 Tg of N₂O-N is emitted from agricultural soils that are fertilized with synthetic and manure N each year. This represents a small loss of the about 150 Tg of N (inorganic and organic) used as fertilizer world wide (Table 1), but does amount to approximately 20% of the annual global efflux of N₂O to the atmosphere.

The low efficiency of fertilizer N use in agricultural systems is primarily caused by the large losses of N from those systems in gaseous forms (Frenay and Simpson 1983; Hauck, 1984; Peoples et al., 1994) and

N_2O emission is directly linked to the loss processes. It is axiomatic then that any strategy which increases the efficiency of fertilizer N use will reduce emissions of N_2O , and this has been directly demonstrated for a number of strategies (Aulakh et al., 1984a, b; Bremner et al., 1981; Bremner and Blackmer, 1979; Bronson et al., 1992; Magalhaes et al., 1984; Minami et al., 1990). In general, N_2O emissions from mineral and organic N can be decreased by management practices which optimize the crop's natural ability to compete with processes whereby plant available N is lost from the soil-plant system (i.e. NH_3 volatilization, denitrification and leaching), and directly lowering the rate and duration of the loss processes (Doerge et al., 1991).

There are indirect contributions to N_2O emission through volatilization of NH_3 and emission of NO_x into the atmosphere, and its redistribution over the landscape through wet and dry deposition. Strategies to increase the overall efficiency of N are therefore necessary and some practices are noted in Table 4.

Although it is widely recognized that NH_3 losses from grazed pastures are a major source of atmospheric NH_3 (Freney et al., 1983; Schlesinger and Hartley, 1992), and loss by denitrification can be substantial from heavily fertilized grasslands in wet climates (e.g. up to $79 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, Jordan, 1989), most of the research effort has been devoted to reducing gaseous emissions from cropped soils rather than from pastures. Therefore, many of the strategies described in Table 4 which potentially can minimize gaseous emissions, deal primarily with cropping systems. Although most of the practices listed are assumed to decrease N_2O emissions there have been relatively few systematic studies which compare a variety of farming practices as to their ability to conserve N and limit N_2O emissions. A number of field studies have been conducted with nitrification inhibitors which demonstrate a high likelihood of decreased N_2O emissions when used.

Nitrification inhibitors

Since NH_3 or ammonium producing compounds are the main sources of fertilizer nitrogen (FAO, 1990a), maintenance of the applied nitrogen in the ammonium form should result in lowered emission of N_2O from cultivated soils. One mechanism of maintaining added N as ammonium is to add a nitrification inhibitor with the fertilizer (Broadbent et al., 1957; Bundy and Bremner, 1973; Sahrawat et al., 1987).

Numerous substances including pyridines, pyrimidines, mercapto-compounds, succinamides, acetylenes, thiazoles, triazoles, triazines and carbon disulfide have been tested for their ability to inhibit nitrification and several have been patented (Hauck, 1984). Unfortunately most of these compounds have limitations to their usefulness (Keeney, 1983). For example, the most commonly used nitrification inhibitor, nitrapyrin (2-chloro-6 (trichloromethyl)pyridine), is seldom effective because of sorption on soil colloids, hydrolysis to 6-chloropicolinic acid and loss by volatilization (Hoef, 1984).

It has been established in laboratory studies that acetylene is a potent inhibitor of nitrification (Bremner and Blackmer, 1979; Walter et al., 1979), but because it is a gas there are problems in introducing it into the soil in the field and maintaining it during the growing period at the concentration required to limit nitrification. This problem may be overcome by the use of calcium carbide coated with layers of wax and shellac to provide a slow-release source of acetylene (Banerjee and Mosier, 1989). Addition of wax-coated calcium carbide to the fertilized soil has reduced nitrification and increased yield, or recovery of N, in irrigated wheat (Freney et al., 1992), maize (Bronson et al., 1992) and cotton (Chen et al., 1994; Freney et al., 1993), and flooded rice (Banerjee et al., 1990; Bronson et al., 1994; Keerthisinghe et al., 1993).

Another way of overcoming the problem of applying gaseous acetylene is to use substituted acetylenes such as 2-ethynylpyridine or phenylacetylene which are liquids at ambient temperatures. These two compounds have proved to be effective inhibitors in laboratory studies (Crawford and Chalk, 1992; McCarty and Bremner, 1986, 1990) and the use of 2-ethynylpyridine in irrigated cotton has resulted in greatly increased recovery of applied N (Freney et al., 1993).

Using nitrification inhibitors does not always result in increased crop yields (Scharf and Alley, 1988), but a number of field studies indicate that nitrification inhibitors do limit N_2O emissions from ammonium based fertilizers (Aulakh et al., 1984b; Bremner and Blackmer, 1978; Bremner et al., 1981; Bronson et al., 1992; Magalhaes et al., 1984; Minami and Ohsawa, 1990). Several recent field tests continue to show that utilization of a variety of nitrification inhibitors does significantly limit N_2O emissions from the application of ammonium-based fertilizers. The following are three case studies from recent publications which illustrate this point.

Table 4. List of practices to improve fertilizer and manure N use efficiency in agriculture

-
- 1- Match N supply with crop demand
 - a) Use soil/plant testing to determine fertilizer N needs
 - b) Minimize fallow periods to limit mineral N accumulation
 - c) Optimize split application schemes
 - d) Match N application to reduced production goals in regions of crop over production

 - 2- Close N flow cycles
 - a) Integrate animal and crop production systems in terms of manure reuse and plant production
 - b) Maintain plant residue N on the production site

 - 3- Use advanced fertilization techniques
 - a) Controlled release fertilizers
 - b) Place fertilizers below the soil surface
 - c) Foliar application of fertilizers
 - d) Use nitrification inhibitors
 - e) Match fertilizer amount and type to seasonal precipitation

 - 4- Optimize tillage, irrigation and drainage
-

Table 5. Effect of nitrification inhibitors nitrapyrin and DCD on the emission of N₂O from ryegrass plots fertilized with ammonium sulfate, ammonium nitrate, or urea in an imperfectly drained clay loam soil (McTaggart et al., 1994) during the 1992 and 1993 growing seasons

Treatment	N ₂ O-N Emitted (g ha ⁻¹)	
	1992	1993
AS ^a	1100	500
AS + DCD ^b	500	250
AS + NP ^c	NA	250
Urea ^d	5000	2700
Urea + DCD ^e	2000	1000
Urea + NP ^f	NA	1500
AN ^g	3900	1500
AN + DCD ^b	2700	NA
Urea/AN/AN ⁱ	2900	NA

On 2 April, 9 June and 4 August 120 kg N ha⁻¹ of the respective fertilizers were applied, nitrification inhibitors were applied with the first fertilization and a second application of dicyandiamide (DCD) was made with the third fertilization.

^aAmmonium sulfate, ^bAmmonium sulfate + 12.5 kg DCD ha⁻¹, ^cAmmonium sulfate + 7.5 kg ha⁻¹ nitrapyrin, ^dUrea, ^eUrea + dicyandiamide, ^fUrea + nitrapyrin, ^gAmmonium nitrate, ^hAmmonium nitrate + DCD, ⁱFirst fertilization of urea and second and third with ammonium nitrate.

Case studies

Case 1. Scotland, UK

The effect of various N sources and nitrification inhibitors were quantified in a ryegrass (*Lolium* sp.)

Table 6. Effect of ECC, DCD and nitrapyrin on N₂O emissions from irrigated wheat and maize

Treatment	Wheat	Maize
	(g N ₂ O-N ha ⁻¹)	
Urea ^z	930 ^{ay}	1650 ^a
Urea + ECC ^z	510 ^b	480 ^c
Urea + DCD ^z	440 ^b	NA
No N Control	440 ^b	110 ^c
Urea + nitrapyrin ^z	NA	980 ^b

^zPrilled urea was banded between plant rows at the rate of 150 kg N ha⁻¹ at planting for winter wheat and 218 kg N ha⁻¹ for maize one month after planting. Nitrification inhibitors were applied with the urea, ECC (20 kg ha⁻¹ as calcium carbide) as solid material, DCD (15 kg ha⁻¹) in aqueous solution and nitrapyrin as an aqueous emulsion (0.5 L ha⁻¹).

^yNumbers within each column followed by the same letter are not significantly different at $p=0.05$.

field located near Edinburgh, Scotland in 1992 and 1993 (McTaggart et al., 1994). Nitrapyrin and DCD decreased N₂O emissions by 45 to 64% in plots fertilized with urea or ammonium sulfate (Table 5).

Case 2. Colorado, US

The effect of acetylene applied as encapsulated calcium carbide (ECC) (Banerjee and Mosier, 1989),

Table 7. Effect of ECC and nitrapyrin on soil nitrate content (0–30 cm soil depth) in a urea-fertilized maize field (Bronson and Mosier, 1993)

Time after fertilizing (weeks)	Treatment		
	Urea	Urea + ECC	Urea + NP
	Soil nitrate content (mg N kg ⁻¹)		
0	2	2	2
2	38	1	16
4	32	3	28
7	10	6	18

See Table 6 for treatment details.

Table 8. Effect of split application of ammonium sulfate and DCS on N₂O emission and nitrate leached from a carrot field (Minami, 1994)

Treatment	N ₂ O Emission (g N ha ⁻¹)	Nitrate leached (kg N ha ⁻¹)
AS (150 + 50) ^a	630	9.5
AS (200) ^b	360	11
AS (200 + DCS) ^c	260	6.8
No fertilizer control	200	5.2

^aA basal application of 150 kg N ha⁻¹ was made on 25 August and a 50 kg N ha⁻¹ top dressing was applied on 2 October, N₂O flux and nitrate leaching measurements were conducted until harvest on 21 December.

^bA basal application of 200 kg ammonium sulfate-N was made at planting.

^cIn addition to the basal application of ammonium sulfate 10 kg ha⁻¹ of DCS was applied.

DCD and nitrapyrin on N₂O emissions were tested in two field studies in Northeastern Colorado in irrigated maize (*Zea mays* L.) and winter wheat (Table 6) grown on clay loam and clay soils, respectively. Experimental details are described in Bronson and Mosier (1993). The amount of nitrate detected early in the maize growing season reflects the relative effects of ECC and nitrapyrin on nitrification and N₂O production (Table 7).

Case 3. Tsukuba, Japan

A study to quantify the effect of the nitrification inhibitor DCS (N-2,5-dichlorophenylsuccinamic acid) and split applications of ammonium sulfate on N₂O emissions was conducted in field lysimeters using carrot (*Daucus carota* L.) as a test crop (Minami, 1994). The soil at this site was a clay loam having a pH of 6.5. In this study either 200 or 150 kg N ha⁻¹ of ammonium sulfate was applied at planting. With plots fertilized with 200 kg N ha⁻¹, 10 kg ha⁻¹ of DCS was added with

the fertilizer. The addition of DCS markedly reduced N₂O emission and leaching of nitrate (Table 8).

These case studies clearly demonstrate the potential for using nitrification inhibitors to limit N₂O emissions from agricultural soils. Inhibitors may be selected for climatic conditions and type of cropping system as well as the type of nitrogen (solid mineral N, mineral N in solution, or organic waste materials) and applied with the fertilizers. Crop yield response is not always improved with nitrification inhibitors but a clear reduction in N₂O emissions is generally achieved. Case 1 and 3 also show that timing of fertilizer application and type of fertilizer can affect N₂O emissions. Where split fertilizer applications are possible application of ammonium based materials decrease N₂O emissions when denitrification seems the likely N₂O producing process and application of nitrate based fertilizers decrease N₂O emissions during the time when nitrification causes N₂O production (McTaggart et al., 1994).

Acknowledgements

We thank the following research groups for providing technical reports and preprints of manuscripts to provide the information for the case studies discussed above: Institute of Terrestrial Ecology at Midlothian, Scotland, UK under the direction of Dr David Fowler with specific help from Dr Ute Skiba; the Environmental Research Program in the Department of Land Resource Science in the University of Guelph, Guelph, Ontario, Canada under the direction of Dr George Thurtell with specific help from Dr Claudia Wagner-Riddle; and Soil Science Department, National College for Food, Land and Environmental Studies, Edinburgh, Scotland, UK, under the direction of Dr Keith Smith.

References

- Andreae M O and Schimel D S 1989 Exchange of Trace Gases Between Terrestrial Ecosystems and the Atmosphere. John Wiley and Sons, Chichester, UK.
- Arah J R M, Crichton I J, Smith K A, Clayton H and Skiba U 1994 Automated gas chromatographic analysis system for micrometeorological measurements of trace gas fluxes. *J. Geophys. Res.* 99, 16593–16598.
- Aulakh M S, Rennie D A and Paul E A 1984a Gaseous nitrogen losses from soils under zero-till as compared with conventional-till management systems. *J. Environ. Qual.* 13, 130–136.

- Aulakh M S, Rennie D A and Paul E A 1984b Acetylene and N-serve effects upon N_2O emissions from NH_4^+ and NO_3^- treated soils under aerobic and anaerobic conditions. *Soil Biol. Biochem.* 16, 351–356.
- Baldocchi E D, Hicks B B and Meyers T P 1988 Measuring biosphere-atmosphere exchanges of biologically related gases with micrometeorological methods. *Ecology* 69, 1331–1340.
- Banerjee N K and Mosier A R 1989 Coated calcium carbide as a nitrification inhibitor in upland and flooded soils. *J. Indian Soc. Soil Sci.* 37, 306–313.
- Banerjee N K, Mosier A R, Uppal K A and Goswami N N 1990 Use of encapsulated calcium carbide to reduce denitrification losses from urea-fertilized flooded rice. *Mitt. Dtsch. Bodenk. Ges.* 60, 245–248.
- Bouwman A F 1990 Exchange of greenhouse gases between terrestrial ecosystems and the atmosphere. *In Soils and the Greenhouse Effect*. Ed. A F Bouwman. pp 61–127. John Wiley and Sons, New York, USA.
- Bouwman A F 1994a Direct emission of nitrous oxide from agricultural soils. RIVM report No. 773004004. RIVM, Bilthoven, the Netherlands.
- Bouwman A F 1994b Estimated global source distribution of nitrous oxide. *In NIAES Series 2 - CH_4 and N_2O Global Emissions and Controls from Rice Fields and Other Agricultural and Industrial Sources*. Ed. K Minami, A Mosier and R Sass. pp 147–159. Yokendo Publishers, Tokyo, Japan.
- Bowden W B and Borman F H 1986 Transport and loss of nitrous oxide in soil water after forest clear-cutting. *Science* 233, 867–869.
- Bremner J M and Blackmer A M 1978 Nitrous oxide: Emissions from soils during nitrification of fertilizer nitrogen. *Science* 199, 295–296.
- Bremner J M and Blackmer A M 1979 Effects of acetylene and soil water content on emissions of nitrous oxide from soils. *Nature (London)* 280, 380–381.
- Bremner J M, Breitenbeck G A and Blackmer A M 1981 Effect of nitrapyrin on emission of nitrous oxide from soil fertilized with anhydrous ammonia. *Geophys. Res. Lett.* 8, 353–356.
- Broadbent F E, Tyler K B and Hill G N 1957 Nitrification of ammoniacal fertilizers in some California soils. *Hilgardia* 27, 247–267.
- Bronson K F, Mosier A R and Bishnoi S R 1992 Nitrous oxide emissions in irrigated corn as affected by encapsulated calcium carbide and nitrapyrin. *Soil Sci. Soc. Am. J.* 56, 161–165.
- Bronson K F and Mosier A R 1993 Nitrous oxide emissions and methane consumption in wheat and corn-cropped systems. *In Agricultural Ecosystem Effects on Trace Gases and Global Climate Change*. Eds. L A Harper, A R Mosier, J M Duxbury and D E Rolston. pp 133–144. ASA Special Pub. No. 55. Am. Soc. Agron., Madison, WI, USA.
- Bronson K F, Mosier A R, Bollich P K and Lindau C W 1994 Grain yield and ^{15}N uptake of drill-seeded rice as affected by coated calcium carbide. *IRRN* 19, 22.
- Bundy L G and Bremner J M 1973 Inhibition of nitrification in soils. *Soil Sci. Soc. Am. Proc.* 37, 396–398.
- CAST 1992 Preparing US Agriculture for Global Climate Change. Task Force Report. No. 119. P.E. Waggoner, Chair. Council for Agricultural Science and Technology. Ames, IA, USA. 96 p.
- Chen D L, Freney J R, Mosier A R and Chalk P M 1994 Reducing denitrification loss with nitrification inhibitors following presowing applications of urea to a cottonfield. *Aust. J. Exp. Agric.* 34, 75–83.
- Cicerone R J 1989 Analysis of sources and sinks of atmospheric nitrous oxide (N_2O). *J. Geophys. Res.* 94, 18265–18271.
- Clayton H, Arah J R M and Smith K A 1994 Measurement of nitrous oxide emissions from fertilized grassland using closed chambers. *J. Geophys. Res.* 99, 16599–16607.
- Crawford D M and Chalk P M 1992 Mineralization and immobilization of soil and fertilizer nitrogen with nitrification inhibitors and solvents. *Soil Biol. Biochem.* 24, 559–568.
- Crutzen P J 1981 Atmospheric chemical processes of the oxides of nitrogen including nitrous oxide. *In Denitrification, Nitrification and Atmospheric Nitrous Oxide*. Ed. C C Delwiche. pp 17–44. John Wiley and Sons, New York, USA.
- Crutzen P J and Ehhalt D H 1977 Effects of nitrogen fertilizers and combustion on the stratospheric ozone layer. *Ambio* 6, 112–117.
- Denmead O T 1983 Micrometeorological methods for measuring gaseous losses of nitrogen in the field. *In Gaseous Loss of Nitrogen from Plant-Soil Systems*. Eds. J R Freney and J R Simpson. pp 133–157. Martinus Nijhoff/Dr W Junk Publishers, The Hague, Netherlands.
- Denmead O T 1994 Measuring fluxes of CH_4 and N_2O between agricultural systems and the atmosphere. *In CH_4 and N_2O Global Emissions and Controls from Rice Fields and Other Agricultural and Industrial Sources*. Eds. K Minami, A Mosier and R Sass. pp 209–234. NIAES Series 2. Yokendo Publishers, Tokyo, Japan.
- Desjardins R L and MacPherson J I 1989 Aircraft-based measurements of trace gas fluxes. *In Exchange of Trace Gases Between Terrestrial Ecosystems and the Atmosphere*. Eds. M O Andreae and D S Schimel. pp 135–154. John Wiley and Sons, Chichester, UK.
- Doerge T A, Roth R L and Gardner B R 1991 Nitrogen Fertilizer Management in Arizona. College of Agriculture, University of Arizona, Tucson, USA.
- Duxbury J M, Bouldin D R, Terry R E and Tate R L III 1982 Emissions of nitrous oxide from soils. *Nature* 298, 462–464.
- Duxbury J M and McConnaughey P K 1986 Effect of fertilizer source on denitrification and nitrous oxide emissions in a maize field. *Soil Sci. Soc. Am. J.* 50, 644–648.
- Duxbury J M et al. 1993 Contributions of agroecosystems to global climate change. *In Agricultural Ecosystem Effects on Trace Gases and Global Climate Change*. Eds. L A Harper, A Mosier, J M Duxbury and D E Rolston. pp 1–18. ASA Special Pub. No. 55. Am. Soc. Agron. Inc., Madison, WI, USA.
- Eichner M J 1990 Nitrous oxide emissions from fertilized soils: Summary of available data. *J. Environ. Qual.* 19, 272–280.
- FAO 1990a Fertilizer Yearbook Volume 39. FAO statistics series No. 95. FAO, Rome, Italy.
- FAO 1990b Production Yearbook Volume 43. FAO statistics series no. 94. FAO, Rome, Italy.
- Fowler D, Skiba U, Hargreaves K J, Sheppard L J and Cape J N 1994 N_2O flux measurements from agricultural grasslands and natural soils using micrometeorological and chamber techniques. *TIGER TO 3064H6*.
- Fowler D and Duyzer J H 1989 Micrometeorological techniques for the measurement of trace gas exchange. *In Exchange of Trace Gases Between Terrestrial Ecosystems and the Atmosphere*. Eds. M O Andreae and D S Schimel. pp 189–208. John Wiley and Sons, Chichester, UK.
- Freney J R and Simpson J R 1983 Gaseous Loss of Nitrogen from Plant-Soil Systems. Martinus Nijhoff/Dr W Junk Publishers, The Hague, the Netherlands.
- Freney J R, Simpson J R and Denmead O T 1983 Volatilization of ammonia. *In Gaseous Loss of Nitrogen from Plant-Soil Systems*. Eds. J R Freney and J R Simpson. pp 1–32. Martinus Nijhoff/Dr W. Junk Publishers, The Hague, the Netherlands.
- Freney J R, Smith C J and Mosier A R 1992 Effect of a new nitrification inhibitor (wax coated calcium carbide) on transformations

- and recovery of fertilizer nitrogen by irrigated wheat. *Fert. Res.* 32, 1–11.
- Freney J R, Chen D L, Mosier A R, Rochester I J, Constable G A and Chalk P M 1993 Use of nitrification inhibitors to increase fertilizer nitrogen recovery and lint yield in irrigated cotton. *Fert. Res.* 34, 37–44.
- Galbally I E 1992 Biosphere-atmosphere exchange of trace gases over Australia. In *Australia's Renewable Resources: Sustainability and Global Change*. Eds. R M Gifford and M M Barson. pp 117–149. Bureau of Rural Resources, Canberra, Australia.
- Galle B, Klemetsson L and Griffith D W T 1994 Application of an micrometeorological method, an ultra-large chamber system, and conventional field chambers. *J. Geophys. Res.* 99, 16599–16608.
- Granli, T and Bockman O C 1994 Nitrous Oxide from Agriculture. *Norw. J. Agric. Sci. Suppl.* No. 12. 128 p.
- Hammond A L 1990 World Resources 1990-91. A report by the World Resources Institute. Oxford Univ. Press, Oxford, UK. 383 p.
- Hargreaves K J, Skiba U, Dowler D, Arah J, Wienhold F G, Klemetsson L and Galle B 1994 Measurement of nitrous oxide emission from fertilized grassland using micrometeorological techniques. *J. Geophys. Res.* 99, 16569–16574.
- Hauck R D 1984 Technological approaches to improving the efficiency of nitrogen fertilizer use by crop plants. In *Nitrogen in Crop Production*. Ed. R D Hauck. pp 551–560. Am. Soc. Agron., Madison, WI, USA.
- Hoefl R G 1984 Current status of nitrification inhibitor use in US agriculture. In *Nitrogen in Crop Production*. Ed. R D Hauck. pp 561–570. Am. Soc. Agron., Madison, WI, USA.
- IAEA 1992 Manual on measurement of methane and nitrous oxide emissions from agriculture. International Atomic Energy Agency. IAEA-TECHDOC-674. IAEA, Vienna, Austria. 91 p.
- Isermann K 1993 Territorial, Continental and Global Aspects of C, N, P and S Emissions from Agricultural Ecosystems. In *NATO Advanced Research Workshop (ARW) on Interactions of C, N, P and S Biochemical Cycles ASI Series*. pp 79–121. Springer-Verlag, Heidelberg, Germany.
- Jordan C 1989 The effect of fertilizer type and application rate on denitrification losses from cut grassland in Northern Ireland. *Fert. Res.* 19, 45–55.
- Keeney D R 1983 Factors affecting the persistence and bioactivity of nitrification inhibitors. In *Nitrification Inhibitors- Potentials and Limitations*. Eds. J J Meisinger, G W Randall and M L Vitosh. pp 33–46. Am. Soc. Agron., Madison, WI, USA.
- Keerthisinghe D G, Freney J R and Mosier A R 1993 Effect of wax-coated calcium carbide and nitrapyrin on nitrogen loss and methane emission from dry-seeded flooded rice. *Biol. Fertil. Soils* 16, 71–75.
- Lijinsky W 1977 How nitrosamines cause cancer. *New Sci.* 27, 216–217.
- Magalhaes A M T, Chalk P M and Strong W M 1984 Effect of nitrapyrin on nitrous oxide emission from fallow soils fertilized with anhydrous ammonia. *Fert. Res.* 5, 411–421.
- McCarty G W and Bremner J M 1986 Inhibition of nitrification in soil by acetylenic compounds. *Soil Sci. Soc. Am. J.* 50, 1198–1201.
- McCarty G W and Bremner J M 1990 Evaluation of 2-ethynylpyridine as a soil nitrification inhibitor. *Soil Sci. Soc. Am. J.* 54, 1017–1021.
- McElroy M P, Wofsy S C and Yung Y L 1977 The nitrogen cycle: Perturbations due to man and their impact on atmospheric N₂O and O₃. *Philos. Trans. R. Soc. (London) B.* 277, 159–181.
- McTaggart I, Clayton H and Smith K 1994 Nitrous oxide flux from fertilized grassland: Strategies for reducing emissions. In *Proceedings of the Symposium on Non-CO₂ Greenhouse Gases*. Maastricht, December 1993. pp 421–426. Kluwer, Dordrecht, the Netherlands.
- Minami K et al. 1990 Effect of nitrification inhibitors on emission of nitrous oxide from soils. *Trans. 14th Int. Congress Soil Sci.* 2, 267–272.
- Minami K and Ohsawa A 1990 Emission of nitrous oxide dissolved in drainage water from agricultural land. In *Soils and the Greenhouse Effect*. Ed. A F Bouwman. pp 503–509. John Wiley and Sons, New York, USA.
- Minami K 1994 Effect of nitrification inhibitors and slow-release fertilizer on emission of nitrous oxide from fertilized soils. In *CH₄ and N₂O Global Emissions and Controls from Rice Fields and Other Agricultural and Industrial Sources*. Eds. K Minami, A Mosier and R Sass. pp 187–196. NIAES Series 2. Yokendo Publishers, Tokyo, Japan.
- Mosier A R 1989 Chamber and isotope techniques. In *Exchange of Trace Gases Between Terrestrial Ecosystems and the Atmosphere*. Eds. M O Andreae and D S Schimel. pp 175–188. John Wiley and Sons, Chichester, UK.
- Mosier A R 1990 Gas flux measurement techniques with special reference to techniques suitable for measurements over large ecologically uniform areas. In *Soils and the Greenhouse Effect*. Ed. A F Bouwman. pp 289–302. John Wiley and Sons, Chichester, UK.
- Mosier A R 1993 Nitrous oxide emissions from agricultural soils. In *Methane and Nitrous Oxide: Methods in National Emission Inventories and Options for Control Proceedings*. Ed. A R van Amstel. pp 273–285. National Institute of Public Health and Environmental Protection, Bilthoven, The Netherlands.
- Mosier A R and Bouwman A F 1993 Working group report: Nitrous oxide emissions from agricultural soils. In *Methane and Nitrous Oxide: Methods in National Emission Inventories and Options for Control Proceedings*. Ed. A R van Amstel. pp 343–346. National Institute of Public Health and Environmental Protection, Bilthoven, The Netherlands.
- OECD/OCDE 1991 Estimation of Greenhouse Gas Emissions and Sinks. Final report from the OECD Experts Meeting. 18–21 Feb., 1991. Prepared for Intergovernmental Panel on Climate Change. Revised August, 1991. OECD, Paris, France.
- O'Hara G W and Daniel R M 1985 Rhizobial denitrification: a review. *Soil Biol. Biochem.* 17, 1–9.
- Peoples M B, Mosier A R and Freney J R 1994 Minimizing gaseous loss of nitrogen. In *Nitrogen Fertilization in the Environment*. Ed. P E Bacon. pp 565–602. Marcel Dekker Inc., New York.
- Poth M and Focht D D 1985 ¹⁵N kinetic analysis of N₂O production by *Nitrosomonas europae*: An examination of nitrifier denitrification. *Appl. Environ. Microbiol.* 49, 1134–1141.
- Prinn R D, Cunnold R, Rasmussen R, Simmonds P, Alyea F, Crawford A, Fraser P and Rosen R 1990 Atmospheric emissions and trends of nitrous oxide deduced from 10 years of ALE-GAGE data. *J. Geophys. Res.* 95, 18369–18385.
- Rodhe H 1990 A comparison of the contribution of various gases to the greenhouse effect. *Science (Washington)* 248, 1217–1219.
- Ronen D, Magaritz M and Almon E 1988 Contaminated aquifers are a forgotten component in the global N₂O budget. *Nature* 335, 57–59.
- Safley L M, Casada M E, Woodbury J N and Roos K F 1992 Global methane emissions from livestock and poultry manure. USEPA report 400/1-91/048. Office of Air and Radiation, Washington, DC, USA.
- Sahrawat K L, Keeney D R and Adams S S 1987 Ability of nitrapyrin, dicyandiamide and acetylene to retard nitrification in a mineral and an organic soil. *Plant and Soil* 101, 179–182.

- Scharf P C and Alley M M 1988 Nitrogen loss pathways and nitrogen loss inhibitors: a review. *Fert. Res.* 5, 109–125.
- Schlesinger W H and Hartley A E 1992 A global budget for atmospheric NH_3 . *Biogeochem.* 15, 191–211.
- Smith K A 1990 Greenhouse gas fluxes between land surfaces and the atmosphere. *Progr. Phys. Geography* 14, 349–372.
- Smith K A, Scott A, Galle B and Klemetsson L 1994 Use of a long-path infrared gas monitor for measurement of nitrous oxide flux from soil. *J. Geophys. Res.* 99, 16585–16592.
- Smith K A, Clayton H, McTaggart I P, Thomson P E, Arah J R M and Scott A 1995 The measurement of nitrous oxide emissions from soil using chambers. *Phil. Trans. R. Soc. London A. (In Press)*.
- Wagner-Riddle C, Thurtell G W, Kidd G E, King K M, Sweetman R, Beauchamp E G and Bergstrom D 1994 Efflux of trace greenhouse gases from agricultural sites into the atmosphere. Annual Report to the Ontario Ministry of Environment and Energy, Toronto, Canada.
- Walter H M, Keeney D E and Fillery I R 1979 Inhibition of nitrification by acetylene. *Soil Sci. Soc. Am. J.* 43, 195–196.
- Watson R T et al. 1990 Greenhouse gases and aerosols. *In Climate Change, the IPCC Scientific Assessment*. Ed. J T Houghton. pp 1–40. Cambridge Univ. Press, Cambridge, UK.
- Watson R T et al. 1992 Climate change 1992, The supplementary reports to the IPCC scientific assessment. *In Greenhouse Gases: Sources and Sinks*. Eds. J T Houghton, B A Callander and S K Varney. pp 25–46. Cambridge Univ. Press, Cambridge, UK.
- World Development Report 1992 Development and the Environment. Oxford Univ. Press, New York, NY, USA. 308 p.
- Yoshida T and Alexander M 1970 Nitrous oxide formation by *Nitrosomonas europaea* and heterotrophic microorganisms. *Soil Sci. Soc. Am. Proc.* 34, 880–882.

Section editor: R Merckx