

Global estimates of gaseous emissions of NH_3 , NO and N_2O from agricultural land

Plants take up only 50 percent of the nitrogen fertilizer applied to agricultural land. Part of this inefficiency is a result of emissions of ammonia (NH_3), nitrous oxide (N_2O) and nitric oxide (NO). Quantifying these emissions is important, both as part of an attempt to improve fertilizer use efficiency and because of their influence on ecosystems, atmospheric pollution and the so-called greenhouse effect. This report provides a comprehensive review of the literature about emissions of NH_3 , N_2O and NO , and examines the regulating factors, measurement techniques and models. It draws these data together and generates global emission estimates that can serve as a basis for further addressing the issues of efficiency and environmental impact.



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**Global estimates of
gaseous emissions of
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**INTERNATIONAL FERTILIZER INDUSTRY ASSOCIATION
FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS**

Rome, 2001

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Abstract

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This report describes global estimates of N₂O and NO emissions and NH₃ volatilization losses from fertilizer and manure application to fields used for crop production. Their quantification is important for assessing N fertilizer efficiency and their impact on atmospheric pollution and ecosystem acidification and eutrophication.

The report reviews the literature and examines the regulating factors (e.g. N application rate) and measurement techniques for N₂O and NO_x emissions and NH₃ volatilization. Using models, it generates global annual estimates: 3.5 million t of N₂O-N emission and 2.0 million t of NO-N emission from crop and grassland. Estimated by fertilizer type, the emissions *induced by fertilizers* amount to 0.9 and 0.5 Mt respectively or approximately 0.8 and 0.5 percent respectively of current nitrogen fertilizer input. An NH₃ loss of 14 percent of mineral fertilizer N use (higher in developing countries), while that from animal manure is 22 percent (60 percent from developed countries). The results for NH₃ volatilization agree with other inventories, though NH₃ volatilization from some fertilizers appears higher than previously thought.

The outcome of the model shows that the potential impact of fertilizer use regulations would be modest from a global emission perspective. The quantities involved, however, constitute a valuable plant nutrient source. Farmers' ability to curtail such losses will primarily relate to economic incentives, in particular in South and South East Asia.

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Acronyms

| | |
|--------|---|
| AA | Anhydrous ammonia including aqueous ammonia |
| ABC | Ammonium bicarbonate |
| ACI | Ammonium chloride |
| AF | Ammonium bicarbonate, ammonium chloride, ammonium sulphate |
| AP | Ammonium phosphate |
| AN | Ammonium nitrate |
| AS | Ammonium sulphate |
| b | Broadcast |
| bf | Broadcast and then flooded |
| bw | Broadcast in floodwater |
| bpi | Broadcast in floodwater at panicle initiation |
| CAN | Calcium ammonium nitrate and combinations of AN and CaCO ₃ |
| CEC | Cation exchange capacity |
| CN | Calcium nitrate |
| DAP | Diammonium phosphate |
| ECETOC | European Centre for Ecotoxicology and Toxicology |
| g | Gradient method |
| GIS | Geographical Information Systems |
| i | Incorporated |
| KCl | Potassium chloride |
| KN | Potassium nitrate |
| MAP | Monoammonium phosphate |
| Mix | Mix of various fertilizers |
| N | Nitrogen |
| NF | Calcium nitrate, potassium nitrate, sodium nitrate |

| | |
|------------------|--|
| NH ₃ | Ammonia |
| NO | Nitric oxide |
| NO ₂ | Nitrogen dioxide |
| NP | Ammonium phosphate and other NP fertilizers |
| N ₂ | Dinitrogen |
| N ₂ O | Nitrous oxide |
| O | Organic fertilizers |
| OS | Combinations of organic and mineral fertilizers |
| ppbv | Part per billion in volume |
| s | Fertilizer applied in solution |
| single | Single application |
| single/ps | Single application as part of split application scheme |
| split | Split application, aggregate |
| UAN | Urea-ammonium nitrate |
| UCN | Urea-calcium nitrate |
| UP | Urea phosphate |
| UU | Urea and urine |
| UUP | Urea-urea phosphate |

Chapter 1

Introduction

There is increasing concern about plant nutrient losses to the environment. Such losses arise through leaching to the groundwater and emissions to the atmosphere. Mineral fertilizer is one of the sources of plant nutrients used in crop production systems. Applied nutrients that crops fail to take up constitute both a financial loss to the farmer and a considerable economic loss at the national level. With the demand for food and fibres projected to increase, albeit at a decreasing pace, farmers will apply more fertilizer in the attempt to boost agricultural production. The implementation of mitigating measures will probably focus on those nutrient sources that are easiest to regulate, with mineral fertilizer use being a prime target.

Reconciling the goals of ensuring ample food supply, enabling adequate farm income and reducing the adverse environmental impact of increased fertilizer use requires the adoption of sound agricultural practices. The adoption of balanced fertilization would be one of the measures for achieving higher yields without incurring accelerated nitrogen losses to the environment.

In order to develop the measures and implementation programmes for fostering efficient mineral fertilizer use, it is necessary to quantify the nutrient losses involved. The magnitude provides a benchmark of the potential benefits at farm, national and global level. The effective implementation of such programmes should focus on regions where losses are largest.

This report generates global estimates of nitrous oxide (N_2O) and nitric oxide (NO) emissions and of ammonia (NH_3) volatilization losses. The analysis establishes the relative contribution of the sustained losses from the application of mineral fertilizers and animal manure to croplands and grasslands. The report also identifies the regions where such losses are primarily sustained.

The supply of nitrogen (N) for growth often constrains yields of crops and forage species. Although there are wide differences between various countries and regions, more than 50 percent of the world's major food crops,

sugar crops and some cash crops are routinely fertilized and high nitrogen fertilizer application rates are not uncommon. Moreover, fertilizer N is being increasingly applied to grasslands.

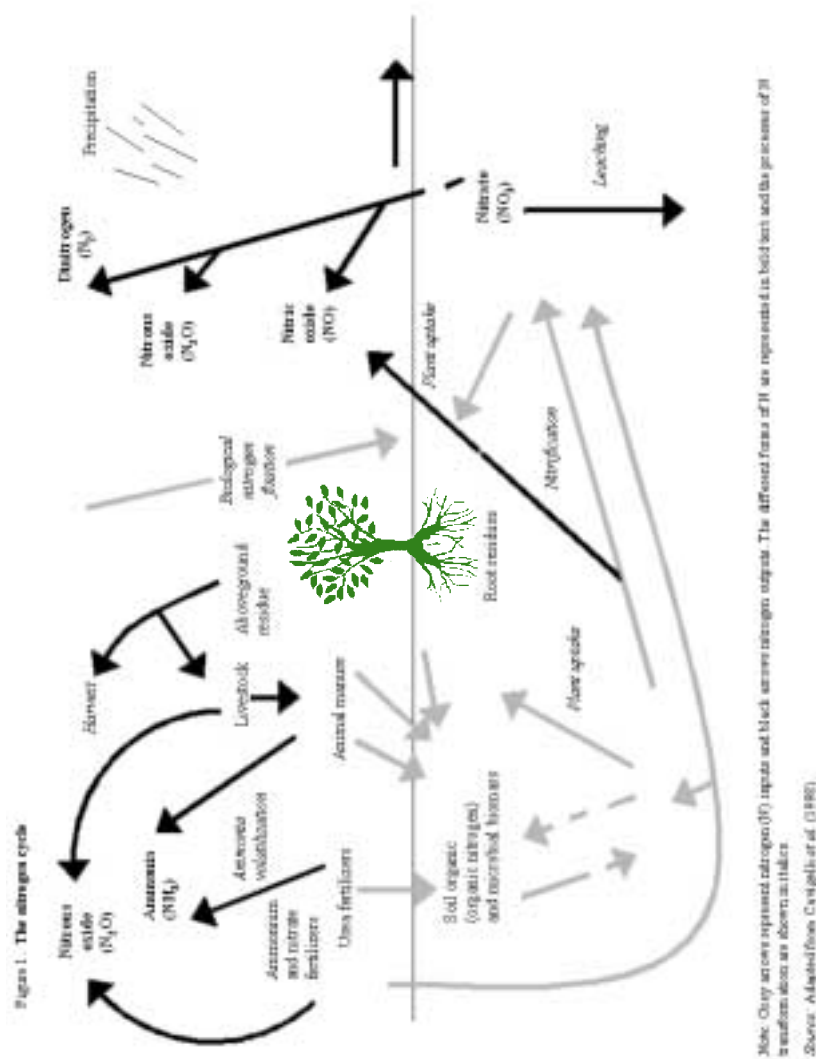
At present the global use of mineral fertilizers is 78 million t N per year, and farmers use large quantities of animal manure to fertilize crops and grasslands. The use of N fertilizer is expected to increase, particularly in developing countries, and the production of animal wastes may also continue to grow.

The use of N fertilizer by plants is rather inefficient. Plant uptake is commonly only 50 percent of the N applied. The major cause of this low N use efficiency is the loss of N from the plant-soil system via leaching, runoff, erosion, or by gaseous emissions. The relative importance of each of these pathways varies from site to site and from year to year. In climates where precipitation exceeds evapotranspiration or in irrigated fields leaching losses may be considerable. Water and wind erosion may occur in systems with bare fallow and in irrigation systems where water flows down the slopes from one field to another (e.g. wetland rice fields).

Gaseous loss of N is the dominant mechanism in many agricultural production systems. Loss processes include volatilization, nitrification and denitrification, resulting in the release of NH_3 , NO, N_2O and dinitrogen (N_2) to the atmosphere. The figure opposite illustrates the nitrogen cycle.

N_2O is one of the so-called greenhouse gases, constituting 6 percent of the anthropogenic greenhouse effect, and contributes to the depletion of stratospheric ozone. Neither the sources nor the causes of the increase in N_2O of 0.7 ppbv per year are well known. It is generally accepted that the most important source is natural soils, followed by emissions from the oceans (Table 1), although there is uncertainty regarding the distribution and magnitude of the sources themselves. Identified anthropogenic sources include: agricultural fields amended with N fertilizers, animal manure, aquifers, sewage, industry, automobiles, biomass burning, land clearing, and trash incineration. The contribution of agriculture to the global N_2O source is about 35 percent.

NO also plays an important role in atmospheric chemistry as it participates in regulating the oxidant balance of the atmosphere. In the atmosphere, NO oxidizes to nitrogen dioxide (NO_2). Re-deposition of NO_x (NO and NO_2 together) contributes to the acidification and eutrophication of ecosystems. The contribution of food production to the global NO emission may be about 10 percent (Table 1). The estimates for N_2O and NO emissions



from animal manure and mineral fertilizers are based on the so-called fertilizer induced emission. Therefore, they do not represent the total emission, as in their calculation the emission from unfertilized control plots is subtracted from that from the fertilized plot. The product of this report will be the total emission, which is more appropriate for global budget studies.

Food production is also a major source for NH₃, contributing more than 50 percent to the global emission. NH₃ is an important atmospheric pollutant with a wide variety of impacts. In the atmosphere, NH₃ neutralizes a large portion of the acids produced by oxides of sulphur and nitrogen. A large proportion of atmospheric aerosols, acting as cloud condensation nuclei, consists of sulphate neutralized to various degrees by ammonia. Deposition returns most of the NH₃ to the surface, where it may contribute to the acidification and eutrophication of ecosystems.

The effects of fertilizer application on the quantities of N₂O released from agricultural soil have been the subject for a number of reviews in recent years. Other similar studies have focused on NO. However, because of the extremely high spatial, temporal and interannual variability, considerable uncertainty persists in the estimates of N₂O emissions. The available data on NO emissions are more uncertain than those for N₂O as fewer studies have focused on NO, mainly because the measurements are intrinsically more demanding. There are many reviews of ammonia volatilization from flooded rice fields, N losses including ammonia volatilization from fertilizers in general, and ammonia losses from grazing systems. Various authors have estimated country emissions on the basis of their measurements. The ECETOC (1994) and Asman (1992) have compiled inventories of European NH₃ emissions.

Recent global estimates indicate that the global NH₃ loss from mineral N fertilizers is about 9 million t of NH₃-N, constituting more than 10 percent of global N fertilizer use (Table 1). However, the uncertainty in these estimates may be 50 percent.

A recent development is the use of simulation models to describe N₂O and NO fluxes. Models can form a firm basis for extrapolation by developing an understanding of the mechanisms that regulate processes and their spatial and temporal patterns. Models help to break down a system into its component parts and describe the behaviour of the system through their interaction. In general, trace gas flux models include descriptions of the processes responsible for the cycling of carbon or nitrogen and the fluxes associated with these processes. Various types of models exist, including empirical and process (or mechanistic) models.

TABLE 1.
Global sources of atmospheric NO_x, NH₃ and N₂O, 1990

| Source | NO _x | NH ₃ | N ₂ O |
|--|------------------|-----------------|-----------------------|
| | million t N/year | | |
| Anthropogenic sources | | | |
| Fossil fuel combustion including aircraft | 21.9 | 0.1 | 0.2 |
| Industrial processes | 1.5 | 0.2 | 0.3 |
| Animal manure application, direct emission | 0.7 | ~8 | 0.4 |
| Animal manure, emission from other animal waste management systems | — | ~13.6 | 2.1 |
| Animal manure application, indirect emission | — | — | 0.9 |
| Mineral fertilizer use, direct emission | 0.4 | 9.0 | 1.1 |
| Mineral fertilizer use, indirect emission | — | — | 0.5 |
| Leguminous crops | n.d. | n.d. | 0.1 |
| Cultivated histosols | n.d. | n.d. | 0.1 |
| Biomass burning including biofuel combustion | 7.7 | 5.9 | 0.7 |
| Crops and decomposition of crops | __ ^a | 3.6 | 0.4 |
| Human excreta | — | 2.6 | 0.2 |
| Coastal water | — | __ ^b | 1.9 |
| Atmospheric deposition | 0.3 | — | 0.6 |
| Natural sources | | | |
| Soils under natural vegetation | 13 | 2.4 | 6.6 |
| Oceans | — | 8.2 | 3.6 |
| Excreta of wild animals | — | 0.1 | 0.0 |
| Lightning | 12.2 | — | — |
| Tropospheric chemistry | 0.9 | — | 0.6 |
| Stratospheric chemistry | 0.7 | — | — |
| Total | 59 | 54 | 20^c |

n.d.: not determined

~ approximately

a. Other animal waste management systems include storage, grazing, etc.

b. NH₃ emissions from coastal water are included in the estimate for oceans.

c. This total is based on mass balance calculations of atmospheric N₂O. The sum of the individual source estimates exceeds the global source by about 30%.

Based on Bouwman et al. (1997), Davidson and Kinglerlee (1997), Lee et al. (1997), Mosier et al. (1998), Olivier et al. (1998), and Veldkamp and Keller (1997a).

An example of a global model describing processes of N₂O formation is an expanded version of the Carnegie-Ames-Stanford Biosphere model on a 1 resolution developed by Potter *et al.* (1996). This ecosystem model simulates nitrogen mineralization from net primary production, N uptake, litterfall and its decomposition. Fluxes of organic matter from litter and soil to microbial pools and from microbial pools back to soil pools occur in proportion to C assimilation rates so that prescribed C:N ratios for the various organic matter pools are maintained. The N₂O (and NO) fluxes are a fixed fraction of 2 percent of nitrogen mineralization. However, the uncertainty of the model is unknown as the output has not been validated against flux measurements.

Li and Aber (2000) and Li *et al.* (1992a, 1992b) developed a field-scale process model to simulate N₂O and NO_x fluxes from decomposition and denitrification in soils. The model simulated gas fluxes by using soil, climate and management data to drive three submodels (thermal-hydraulic, denitrification and decomposition). The management practices considered include tillage timing and intensity, fertilizer and manure application, irrigation (amount and timing), and crop type and rotation. Comparison of observed flux data with fluxes simulated by models including the field-scale process model reveal major differences in the simulated N gas fluxes from soils. A major problem in developing trace gas flux models is the proper statistical description of soil processes that operate in hot spots in field-scale models.

Large-scale patterns of soil gaseous emissions, when aggregated to prolonged (e.g. seasonal or annual) time scales, may have a strong element of predictability. This is because at such spatial and temporal scales integrated gas fluxes may be strongly related to average biophysical conditions. Therefore, if estimation of seasonal or annual emissions is the objective, the use of empirical relationships between gas fluxes and environmental and management conditions represents a suitable approach for bridging the gap between site and landscape scales.

Although the approaches to estimating N₂O and NO emissions and NH₃ volatilization losses are distinct, they are sufficiently similar to appear together in this document.

First, this report analyses the direct emissions of N₂O and NO from fertilized crops and grasslands. It does not consider indirect emissions from ground and surface water, or resulting nitrogen leached from agricultural soils. A review of measurement data from the literature forms the basis for calculating the estimates. An extrapolation exercise uses models for N₂O and NO emissions that include the major controlling factors. The basis for this is a

data set of measurements primarily from the reviewed literature. This report does not consider chemicals such as nitrification inhibitors as their use is still limited on the global scale. It also excludes experiments in grazed grasslands, as that system is not within the scope of this report. Furthermore, measurements of emissions from organic soils were excluded from the analysis. This report summarizes 896 measurements of N₂O emissions from 139 studies and 99 measurements for NO emissions from 29 studies.

The experiments represent a range of different techniques for measuring fluxes for different crops and uncropped systems, different soil types, climates, fertilizer types and N application rates, and methods and timing of fertilizer application. Table 2 lists the available information on the environmental conditions, soil properties and measurement techniques for each measurement provided in the literature reports and included in the data set.

The various research papers used different methods to determine soil pH, cation exchange capacity (CEC), carbon content, texture, etc. In addition, they sometimes reported temperature as air temperature, and in other cases as soil temperature. This report ignored these differences and used the reported values as such.

For NH₃ losses, the first objective of this report is to summarize the available literature on NH₃ volatilization from the application of mineral N fertilizers and animal manure to crops and grasslands in order to assess the factors that regulate NH₃ volatilization. A second objective is to describe the relationships found between regulating factors and NH₃ volatilization rates in an empirical summary model, and to use this model for a global-scale extrapolation on the basis of national fertilizer statistics and land-use data.

The data set of measurements (primarily from the reviewed literature) contains data for almost 1 900 individual measurements. Table 2 presents details of the available information on the environmental conditions, soil properties and measurement techniques for each measurement provided in the literature.

This report does not use data on the effect of controlled-release and stabilized fertilizers and chemical additives used to reduce NH₃ volatilization as their use also is still very limited on the global scale. In addition, the report does not include NH₃ losses from stored manure and plants.

The analysis of the complete set of literature data to assess relationships between the various regulating factors and N₂O and NO emission rates and NH₃ volatilization rates made use of Genstat 5 release 4.1 (PC/Windows NT).

TABLE 2.
Information collected for measurements

N₂O and NO emissions and denitrification

| | |
|-------------------------------|---|
| Data base label | N-rate |
| Reference | NH_4^+ -rate (for organic fertilizers) |
| Soil type | $\text{N}_2\text{O}/\text{NO}$ emission (kg N/ha) over measurement period |
| Texture/other soil properties | Denitrification (kg N/ha) over measurement period |
| Soil organic carbon content | Length of measurement period |
| Soil organic nitrogen content | Measurement technique |
| Soil drainage | Frequency of measurements |
| pH | $\text{N}_2\text{O}/\text{NO}$ emission (% of N application accounting for control) |
| Residues left in field | $\text{N}_2\text{O}/\text{NO}$ emission (% of N application) |
| Crop | Additional information (remarks) ^a |
| Fertilizer type | |
| Fertilizer application method | |

NH₃ volatilization rates in upland and flooded systems

| <i>Information for both upland and flooded systems</i> | | <i>Additional information for wetland rice systems</i> |
|--|---|--|
| Data base label | Fertilizer type | Floodwater pH |
| Reference | Fertilizer application method | Presence of azolla |
| Soil type | Fertilizer form | |
| Texture/other soil properties | N-rate | |
| Soil organic carbon content | NH_4^+ -rate (for organic fertilizers) | |
| Soil drainage | NH_3 volatilization loss (kg N/ha) | |
| pH | Length of measurement period | |
| CaCO_3 content | Measurement technique | |
| CEC | Frequency of measurements | |
| Mean temperature during measurements | NH_3 volatilization rate (% of N application accounting for control) | |
| Mean precipitation during measurements | NH_3 volatilization rate (% of N application) | |
| Flooding (if applicable) | Additional information (remarks) ^a | |
| Residues left in field | | |
| Crop | | |

a. Additional information on the measurement such as year/season of measurement, information on soil, crop or fertilizer management, the volume of air flowing through the forced draught chambers, specific characteristics of the fertilizer used, specific weather events important for explaining the measured volatilization rates.

Contrary to many studies using regression analysis, this report used the Residual Maximum Likelihood (REML) directive of Genstat for summarizing the data set and developing models relating gas emissions to controlling factors. REML is appropriate for analyzing unbalanced data sets with missing values. By assuming all factor classes to have an equal number of observations, REML balances the emission for factors not represented by the full range of environmental and management conditions.

Chapter 2 discusses the factors that regulate N_2O and NO_x emissions and NH_3 volatilization. Chapter 3 presents the different measurement techniques used in determining N_2O and NO_x emissions and NH_3 volatilization rates, as it is important to know the characteristics of each technique for the interpretation of flux estimates in comparison with those obtained with other techniques. Chapter 4 analyses the data collected for this study in order to determine the major regulating factors and their effect on N_2O and NO emissions and NH_3 losses. Chapter 5 extrapolates the results up to global estimates based on fertilizer statistics and geographic data for the regulating factors. Finally, Chapter 6 presents some conclusions.

Chapter 2

Regulating factors

FACTORS REGULATING NITROUS OXIDE AND NITRIC OXIDE EMISSION

General

Soils act as both sources and sinks of N_2O and NO . However, on the global scale the N_2O and NO emissions dominate the sink activity. The production and consumption of N_2O and NO in soils involves both biotic and abiotic processes. Numerous groups of micro-organisms contribute to the production and consumption of NO and N_2O , but biological nitrification and denitrification are the dominant processes involved.

Biological denitrification is the reduction of nitrate (NO_3^-) or nitrite (NO_2^-) to gaseous N oxides and molecular N_2 by essentially aerobic bacteria. Nitrification is the biological oxidation of ammonium (NH_4^+) to NO_2^- or NO_3^- under aerobic conditions. Under oxygen limited conditions nitrifiers can use NO_2^- as a terminal electron acceptor to avoid accumulation of the toxic NO_2^- , whereby N_2O and NO are produced.

The bacterial processes of denitrification and nitrification are the dominant sources of N_2O and NO in most systems. Only denitrification is recognized as a significant biological consumptive fate for N_2O and NO . The chemical decomposition of HNO_2 (or chemical denitrification), that is, the reduction of NO_2^- by chemical reductants under oxygen limited conditions and at low pH, can also produce N_2 , N_2O and NO . Chemical denitrification generally occurs when NO_2^- accumulates under oxygen limited conditions, which may occur when nitrification rates are high, e.g. after application of NH_4^+ -based mineral fertilizers or animal manure. This process may account for 15-20 percent of NO formation.

Plant uptake of NO and NO₂ is a further important biological process determining the exchange of NO_x at the Earth's surface. Some other abiotic processes may also produce and consume trace amounts of NO.

Controls of denitrification, nitrification and N oxide fluxes

The simplifying conceptual hole in the pipe model is useful in understanding the processes of NO, N₂O and N₂ emissions. In this model, gas production and exchange with the atmosphere depend on: (i) factors controlling the amount of N flowing through the pipe (that is those affecting denitrification and nitrification rates e.g. N availability and temperature); and (ii) the size of the holes in the pipe through which N gases leak. Factors controlling the partitioning of the reacting N species to NO, N₂O or more reduced or oxidized forms regulate the size, while the rate at which N moves through the pipes determines the importance of the leaks. In addition to soil and climate characteristics, agricultural management may also interfere with soil processes and thus influence N availability and the relative rates of N₂O and NO.

N availability

In agricultural soils N inputs from various sources determine the amount of N flowing through the pipe. N fertilizer, N inputs in agricultural soils, animal manure, crop residues, deposition and biological N fixation are strong stimulants of denitrification and associated N oxide fluxes.

The magnitude of NH₃ volatilization also determines the availability of N for nitrification and denitrification. Studies have found denitrification to be lower when NH₃ losses are high in both upland soils and wetland rice systems.

Nitrification and denitrification rates

Whether denitrification or nitrification dominates depends on many different factors. Nitrification is a relatively constant process across ecosystems, whereas denitrification rates are temporally and spatially variable. In most soils, availability of NH₄⁺ and oxygen are the most important factors controlling nitrification. The major controls on biological denitrification include the availability of organic carbon, oxygen and nitrate (NO₃⁻) or other N oxides.

Various studies have found high denitrification activity in hot spots created by decomposing organic matter which generates anaerobic microsites. This phenomenon may explain some of the high spatial variability of soil denitrification commonly observed.

N₂/N₂O ratios observed under different conditions in laboratory experiments were found extremely variable and dependent on the available C and NO₃⁻, and on the moisture content of the soil. The NO/N₂O emission ratio has been proposed as an indicator of the importance of nitrification and denitrification. Laboratory studies indicate that for nitrifiers the NO/N₂O ratio is close to unity while for denitrifiers this ratio is less than unity. As denitrification and nitrification often occur simultaneously, it is not possible to extrapolate these results to field conditions. However, even in field situations the NO/N₂O ratio may provide an indication of the dominant process responsible for NO emission.

Soil moisture and temperature

Soil moisture and temperature control soil processes at all levels by governing organic matter decomposition rates, denitrification and nitrification. Some studies have shown that emissions of NO increase with increasing soil temperatures. However, the relationship between temperature and NO fluxes is subject to considerable uncertainty with numerous exceptions in temperate and tropical systems where no clear relationship was found between temperature and NO fluxes. During denitrification the ratio of N₂O/N₂ generally increases with decreasing temperatures.

In systems where soil N temporarily accumulates due to wet-dry or freeze-thaw cycles, then early spring, winter and autumn in temperate climates may account for an important part of the annual N₂O emission from agricultural or any other land.

Soil-water content influences N₂O and NO_x emissions from all types of soil. In general, microbial activity peaks at 30-60 percent water-filled pore space. Nitrification and associated N₂O and NO_x production also show maximum activity at 30-60 percent water-filled pore space, while optimum conditions for denitrification may occur at 50-80 to 60-90 percent water-filled pore space.

The oxygen and moisture status and gas diffusion in agricultural soils depend on soil texture and drainage. Fine-textured soils have more capillary pores within aggregates than do sandy soils, and so hold soil water more tightly. As a result, anaerobic conditions may be more easily reached and maintained for longer periods within aggregates in fine-textured soils than in coarse-textured soils.

Wetting

The wetting of dry soils causes pulses in N mineralization, nitrification and NO and N₂O fluxes. The alternating drying and wetting of soils enhances the release of N₂O and NO from the soil to the atmosphere although peaks in N₂O production may decline with subsequent wetting events.

Soil pH

Soil pH has a marked effect on the products of denitrification. Denitrification rates are slower under acid than under slightly alkaline conditions, but the N₂O fraction may be larger at low soil pH, particularly with an adequate nitrate supply. This is commonly attributed to the sensitivity of N₂O reductase to proton activity. Emissions of N₂O and NO decrease with increasing pH in acid soils, and increase when the pH of alkaline soils decreases. Soil pH is a major factor in determining the mechanism of NO formation. In one study, in an alkaline loamy clay soil (pH 7.8) nitrification was the main source of NO, whereas in an acid sandy clay loam (pH 4.7) denitrification dominated the NO production.

Gas diffusion

Before escaping from the soil to the atmosphere the N gases diffuse through the soil pore system, where denitrifiers may consume NO and N₂O or plants may take up NO. In situations where high soil water content, impeded drainage, shallow groundwater, soil structure, soil compaction, fine soil texture or soil surface sealing limit gas diffusion, denitrification activity is high. However, such conditions greatly enhance the probability of denitrifiers re-consuming N₂O and NO. Soils close to saturation show high denitrification activity but low N₂O and NO emission. Under such conditions the oxygen supply is low and N₂O and NO diffusion is limited; in the absence of oxygen as an electron acceptor, denitrifiers consume more N₂O and NO than under more aerobic conditions. Under wet conditions N₂O uptake from the atmosphere may occur.

Agricultural management factors

Crop type

Nitrous oxide fluxes from flooded rice systems during the growing season are generally lower than those from rainfed fields. The cause of this may be the anaerobic conditions prevailing in wetland rice systems. However, aerobic conditions generally prevail during the fallow period after the rice crop,

allowing nitrification of NH₄⁺ mineralized from soil organic matter and residues of crops and aquatic biota. Observed N₂O emission from drained soils during the post-harvest fallow period is much higher than during the crop season.

Biological N fixation by leguminous crops, such as alfalfa, soybeans, pulses, and clovers, provides an important input of N in many agricultural systems. Although these crops generally receive no or only small N fertilizer inputs as a starter, studies have demonstrated that leguminous crops show emissions of N₂O that are of the same level as those of fertilized non-leguminous crops.

Fertilizer management

The type of fertilizer influences the magnitude of nitrification and denitrification. Furthermore, the type of fertilizer may influence the magnitude of NO and fluxes. For example, anhydrous ammonia (AA), which is generally injected, commonly shows higher losses than other fertilizers.

Total N gas production and in particular emission may increase with the N application rate. However, denitrification and production may be more closely related to the amount of unused N than to the total amount. Therefore, the timing of fertilizer application is an important factor. Any prolongation of the period when NH₄⁺-based fertilizers can undergo nitrification or NO₃⁻-based fertilizers undergo denitrification, without competition from plant uptake, is likely to increase emissions of NO and N₂O.

Under tropical conditions the potential for high and NO emission rates exists, but management plays an important role in determining the magnitude of the fluxes. In a study that adjusted N fertilizer inputs to plant demand, N₂O losses were low. Where fertilizer application is excessive, as in some cash crops such as banana, the N availability for nitrification and denitrification is high, and so the O₂ supply becomes the primary control of NO and N₂O emissions.

Fertilizer application mode and timing influence NH₃ volatilization and the efficiency of plant uptake, and hence the availability of N for nitrification and denitrification. Generally, emissions from subsurface applied or injected N fertilizers are higher than from broadcast mineral fertilizers and animal manure. Compared to broadcasting, subsurface applied N has resulted in higher N₂O but lower NO losses.

Soil and crop management

Inputs from crop residues in agricultural fields are important sources of C and N for nitrification and denitrification. In addition, the action of incorporation may also stimulate mineralization of soil organic matter. Some studies have observed higher denitrification activity and N₂O fluxes after retaining residues on the land compared to removing them. This effect may be related to the effect of residues on the soil surface on moisture conditions of the topmost soil layer. The incorporation of residues also causes accelerated NO emissions.

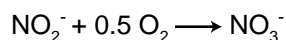
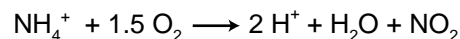
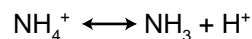
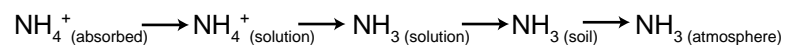
The effects of tillage on mineralization of soil organic matter are well established. Tillage may also affect the conditions for N₂O and NO emissions from soils. Some studies have observed higher N₂O losses for no-tillage systems compared to conventional tillage. This may be related to higher denitrification activity. However, N₂O losses from no-tillage systems may be lower than from tilled soils where fields have remained uncultivated for a number of years. Some studies report an increase in NO emission caused by ploughing in a temperate climate and under tropical conditions.

FACTORS REGULATING AMMONIA LOSS

General

Ammonia is formed constantly in soils because of the biological degradation of organic compounds and NH₄⁺ yielding mineral and organic fertilizers. As it is a gas, any NH₃ present in soils, water or fertilizers can volatilize to the atmosphere. However, NH₃ reacts with protons, metals and acidic compounds to form ions, compounds or complexes of varying stability. Ammonia has a strong affinity for water, and its reactions in water are fundamental to regulating the rate of loss.

After its application to the soil, the NH₄⁺ can remain on the exchange sites, nitrify to NO₃⁻, or decompose to NH₃, depending on soil and environmental conditions:



In fertilized fields the input of NH₄⁺ depends on: fertilizer type; the rate and mode of fertilizer application; soil moisture content, infiltration rate, and CEC; and urease activity (in the case of urea). The difference in NH₃ partial pressure between the ambient atmosphere and that in equilibrium with moist soil, floodwater, or the intercellular air space of plant leaves drives ammonia volatilization. The partial pressure of NH₃ in the soil is controlled by the rate of removal of ammonium or NH₃ in solution, or by displacing any of the equilibria in some other way. Wind speed (regulating the exchange between soil and air), temperature, and the pH of the soil solution or irrigation water are important regulating factors, as all three variables affect the partial pressure of NH₃.

Increasing temperature increases the relative proportion of NH₃ to NH₄⁺ present at a given pH, decreases the solubility of NH₃ in water, and increases the diffusion of NH₃ away from the air-water or air-soil interface.

In particular, the pH affects the equilibrium between NH₄⁺ and NH₃ so that the relative concentration of NH₃ increases from 0.1 percent to 1, 10 and 50 percent as the pH increases from 6 to ~7, ~8 and ~9, respectively. The volatilization process itself produces acidity. The nitrification process can reduce NH₃ volatilization in two ways: by decreasing NH₄⁺ availability; and by producing acidity.

Other variables influencing NH₃ volatilization include the pH buffer capacity and the CEC of the soil. The CEC is important as the negatively charged CEC absorbs the positively charged NH₄⁺. A major part of the soil's NH₃ holding capacity is attributable to soil organic matter.

Other factors include: the level of urease activity (in the case of urea application, or urine); the availability of moisture; soil texture; the nitrification rate; and the presence of plants or plant residues.

The presence of absorbed or added Ca and certain phosphate compounds may influence NH₃ losses in upland systems. The loss of NH₃ may be lower in the presence of Ca due to micro-environmental pH reduction, CaCO₃ formation or Ca-urea double salt formation. Certain acidic phosphate compounds, such as H₃PO₄, NH₄H₂PO₄ and Ca(H₂PO₄)₂ may precipitate the micro-environmental Ca and change the environment to favour increased NH₃. Both the formula (pH) and form of the phosphate added can influence reactions with Ca, and therefore NH₃ losses.

Flooded soils

Conditions in wetland rice systems require special attention. First, the measurement data in these systems suggest that NH_3 volatilization rates are often higher than in upland systems, and globally they may represent important losses. Second, the conditions in inundated systems with respect to NH_3 volatilization are different from those in upland systems.

In wetland rice systems, factors such as fertilizer type, rate, time and method of application, floodwater depth, and algal growth exert their influences through the primary variables (ammoniacal N concentration, the pH and temperature of floodwater, and wind speed).

The rate of NH_3 loss depends on the equilibrium vapour pressure of NH_3 in floodwater and on wind speed. Wind speed markedly affects NH_3 volatilization from floodwater. For example, data from Philippines field studies show a linear relationship between wind speed and NH_3 volatilization. This also explains why in some studies that used low or no air-exchange enclosure techniques or forced draught methods NH_3 loss rates were low even with high N application rates.

The vapour pressure of NH_3 in floodwater is a function of the ammoniacal N concentration, pH and temperature. The content of aqueous NH_3 in floodwater increases by about a factor of 10 per unit increase in pH in the pH range 7.5-9. A linear function at a given total ammoniacal N concentration best describes the dependency of aqueous NH_3 on temperature. Furthermore, water evaporation losses, which may be high under tropical conditions, will generally lead to increasing activity of NH_4^+ , thus influencing the chemical equilibria.

Processes that potentially affect the ammoniacal concentration of floodwater and indirectly the NH_3 loss include urease activity, cation exchange and N immobilization. Furthermore, assimilation of NH_4^+ by algae, weeds and rice plants can decrease the quantity of ammoniacal N. The competitiveness of rice plants for NH_4^+ varies with growth stage. One study found that plants contained negligible amounts of ^{15}N -labelled urea 1 week after broadcast and incorporated urea, and less than 10 percent of urea broadcast to floodwater 2-3 weeks after transplanting, and about 40 percent of the ^{15}N in urea applied at panicle initiation.

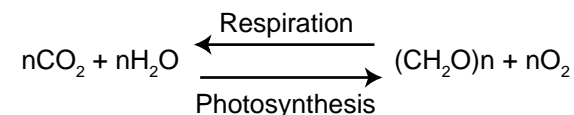
In sandy soils or soils with low CEC the fertilizer treatment may result in high ammoniacal concentrations in the floodwater, with large losses of applied N despite incorporation of the fertilizer.

In flooded rice fields the pH of floodwater appears to be synchronized with the cycles of photosynthesis and net respiration, i.e. the depletion and addition of CO_2 to the floodwater. Carbon dioxide in solution, as a product of the photosynthesis and respiratory balance of aquatic organisms, and occurring as undissociated carbonic acid, bicarbonate and carbonate ions is the buffering system that regulates the water pH. Water pH values of 9.5-10 can occur in shallow floodwater populated by aquatic biota under high solar radiation, rising during the day and dropping at night. Diurnal pH variations of 2-3 units are not uncommon where fertilizer N is broadcast in rice fields.

The correlation between water pH and the carbonic acid system in water is complex, but in its simplified form it can be characterized by the electroneutrality condition:

$$[\text{H}^+] = [\text{HCO}_3^-] = 2[\text{CO}_3^{2-}] + [\text{OH}^-]$$

and equilibrium activities: $-\log[\text{H}^+] = -\log[\text{HCO}_3^-] = 5.65$; $-\log[\text{CO}_2 \text{ aq.}] = -\log[\text{H}_2\text{CO}_3] = 5.0$ (as a non-volatile acid); $-\log[\text{H}_2\text{CO}_3] \sim 7.8$; $-\log[\text{CO}_3^{2-}] = 8.5$. In shallow-water systems found in flooded rice cultivation there is CO_2 exchange between the various submerged aquatic plant species and the water. The major organisms are algal forms, which develop quickly into a large biomass. The generalized reaction involving the plant biochemistry of CO_2 is as follows:



The photomineral process decreases the net activities of $[\text{CO}_2 \text{ aq.}] + [\text{H}_2\text{CO}_3]$ during favourable daylight periods, but when respiratory activity exceeds photosynthesis H_2CO_3 , acidity and the total concentration of dissolved carbonic acid increase. A number of complex relationships exist in the system, such as reactions of CO_2 with alkaline earth minerals, carbonates, and divalent cations. Factors that also affect water pH in flooded soil systems are: soil type, its electrical conductivity, and previous cropping history; soil management practices such as puddling; and the quality of the irrigation water.

Fertilizer management and the stage of crop development influence the magnitude of the diurnal fluctuation of the pH of floodwater, probably through their effect on the algal biomass. A strong increase in the maximum values of the floodwater pH occurs after urea application. Because phosphorous is also generally applied at this time, the algal biomass increases rapidly. In one study,

in some fields the floodwater pH did not increase as much due to the absence of algal growth, a fact attributed to the weather conditions during the rice crop at that location in China in that particular year. Diurnal variations in floodwater pH found at panicle initiation when the crop shades the floodwater are generally smaller than in early stages of the growing season.

As NH_3 volatilization produces acidity, alkalinity (primarily HCO_3^- in floodwater) must therefore be present to buffer the production of H^+ to sustain NH_3 volatilization. Where farmers use urea as a fertilizer, its hydrolysis is the major source of HCO_3^- . When ammonium sulphate (AS) is applied, the irrigation water is probably the major source of alkalinity. Even with low alkalinity in floodwater, evapotranspiration and repeated irrigation may cause a build up of alkalinity. Additional alkalinity may result from increased soil reduction at night coupled with CO_2 production.

Fertilizer management, through its influence on the concentration of ammoniacal N in the floodwater, has a pronounced effect on overall NH_3 loss. NH_3 losses are generally highest with applications of urea or ammonium sulphate fertilizer 2-3 weeks after transplanting the rice. Volatilization rates are much lower for ammonium sulphate and urea applications a few days before panicle initiation of the rice crop (commonly ~50-60 days after sowing), or at booting (~65-70 days after sowing). The reason is that the rice crop reduces wind speed and thus NH_3 exchange between the water surface and the air, the crop shades that floodwater and thus reduces algal growth. This causes lower pH levels and smaller amplitudes in the daily pH cycle than in fields with no or small rice plants.

The incorporation of urea to puddled soil, when done without standing floodwater, also reduces NH_3 losses. The cause of this reduction may be a better contact of the fertilizer with the soil and an associated increase in the reaction of the ammonium ions formed with the cation exchange sites and the immobilizing micro-organisms. Another possible cause may be a reduction of algal growth as a result of lower ammoniacal concentration of the floodwater. The incorporation of urea in the presence of floodwater was effective only in soils with a high CEC.

Chapter 3

Measurement techniques

An analysis of the literature reveals that many of techniques for measuring N₂O and NO emissions and NH₃ volatilization fall into two main categories: chamber (or enclosure) and micrometeorological techniques, although other techniques are available. A study by Lapitan *et al.* (1999) provides detailed information on the various measurement techniques and the concentration measurements. Table 3 provides a list of the various measurement techniques.

TABLE 3.
Measurement technique codes

| Code | Explanation |
|-----------------|--|
| c | Chamber technique, closed |
| cf | Chamber technique, forced draught |
| co | Soil core incubation method |
| cso | Chamber technique, semi-open chamber |
| g | Soil N ₂ /N ₂ O gradient method, based on gas concentration gradient in the soil profile |
| ioc | Indirect open measurement in air with comparison to plots with standard fluxes |
| m | Micrometeorological technique |
| m, ba | Bulk aerodynamic micrometeorological technique |
| m, fg | Flux gradient micrometeorological technique |
| m, mb | Mass balance micrometeorological technique |
| ¹⁵ N | ¹⁵ N isotope recovery |
| Nbal | N balance method, i.e. complete N balance of soil-crop system |
| Ndif | N-difference method, i.e. N input (t = 0) - Nsoil (t = t) for laboratory experiments with bare soil |
| ocb | Open and closed containers, where the difference in N content in soil + water is assumed equal to the NH ₃ loss |
| wt | Wind tunnel |

CHAMBER TECHNIQUES

Enclosure or chamber techniques involve the use of cuvettes, chambers or boxes placed over the bare soil surface or surfaces with low vegetation cover. There is little uniformity in design of the enclosures used, but they can be described in their variation from being completely sealed (closed) to the atmosphere, to open on two ends with some means of varying wind speed over the measurement surface (forced draught) to simulate that found in the field. The current types of chambers vary in basal sampling area from <1 m² to 5.76 m² to 64 m². Larger cover boxes integrate spatial variability and the number of replications per plot can be reduced.

Concentration measurements in chamber techniques are generally made with a gas chromatograph-electron capture detector for N₂O, and chemiluminescence detection techniques for NO. NH₃ volatilization is determined by chemical trapping, followed by elution of the NH₃ with distilled water and measurement of its concentration. Various types of NH₃ traps and analytical techniques have been used.

Closed chambers (c) include those with no forced or enhanced circulation in which emitted gases are allowed to accumulate or with closed-loop chambers where gases are circulated. The N₂O or NO gas flux from closed chambers can be calculated by periodically collecting gas samples from the chamber and measuring the change in concentration of gas with time during the period of linear concentration change. Ammonia volatilization is determined from the NH₃ accumulated in the chemical trap.

Advantages of the closed chamber include: (i) small fluxes can be measured; (ii) chambers are cheap, simple to construct, install and remove, and no extra equipment requiring electrical supply is needed; (iii) the disturbance of the site is limited due to the short time during which the chamber is in place for each flux measurement.

Disadvantages of closed chambers are:

1. Concentrations in the chamber can build up to levels where they inhibit the normal emission rate. This problem can be limited by using short collection periods;
2. Closed chambers alter the atmospheric pressure fluctuations normally found at the soil surface. Such fluctuations can cause a pumping action on the surface, hence a closed chamber may underestimate the flux that would have occurred in its absence;

3. The soil may be disturbed by the action of placing the cover. This problem can be limited by installing collars in the soil that are normally open to the atmosphere; the chambers are sealed to the collars;
4. Differences may occur in rainfall, temperature and moisture between the chamber and the field.

Forced-draught chambers are coupled to the atmosphere via an air inlet through which outside air is continuously drawn into the cover and forced to flow over the enclosed soil surface. The N₂O or NO gas flux from the soil surface can be calculated from concentration difference, flow rate, and area covered. NH₃ volatilization is determined by chemical trapping of NH₃ in the outgoing airflow. Often the NH₃ is extracted from the air before it enters the chamber, which may lead to over-estimation of the estimated NH₃ volatilization rate. For NH₃, the forced-draught technique is most appropriate for comparisons of N sources, N rates, and various management practices, provided that the airflow does not limit NH₃ exchange. Generally forced draught enclosures aim at determining the maximum NH₃ loss.

The main advantage of forced-draught chambers is that they maintain environmental conditions close to those of the uncovered field. Forced-draught chambers are therefore more applicable for continuous long-term monitoring of gas flux, provided that moisture conditions inside and outside the chamber remain the same.

Forced-draught chambers are sensitive to pressure deficits inside the chamber caused by the forced airflow which may cause artificially high fluxes. This problem can be overcome by ensuring that the size of the inlet is large compared to the size of the outlet. Another problem is that this technique assumes equilibrium flux between soil atmosphere and chamber atmosphere gas concentration. However, the estimated fluxes may be erroneous during the period of equilibration.

A general disadvantage of the use of any type of chamber is that they disrupt the soil and environmental conditions (wind speed, temperature, rainfall, formation of dew). The alteration of soil and environmental factors can be minimized by covering the treated area only for short periods during the measurement, allowing normal conditions to exist between the measurements.

Temporal and spatial variability are major problems in making estimates of gas fluxes observed based on chamber measurements. For example, in a field study using small chambers it was estimated that 350 measurements are required to estimate the N₂O emission within 10% of the true mean for a 3 m by 30 m plot. As noted above, larger chambers integrate spatial variability and

the number of replications per plot can be reduced. The influence of sampling frequencies was investigated by many authors. For example, reducing the frequency from high to daily sampling could result in a calculated mean flux from any chamber that can vary by as much as 20%, even though the calculated mean would be within 10% of the mean from the intensive measurements. Automated chamber measurements of N₂O flux have become more common recently in response to the recognition of the high temporal variability in the emissions.

Many studies based on chamber techniques have neglected the influence of plants. Often plants are omitted because they are difficult to include in the gas collection system. Plants affect nutrient availability, soil moisture, soil atmosphere and temperature. In addition, plants may play a role in the transport of gases.

A variant of the enclosure technique is the open-sided chamber or plastic cover (cso) to pattern the rate of air exchange of the wind speed outside the chamber. A disadvantage of this technique is that these half-open systems may permit the escape of NH₃ from the chamber.

In a further attempt to minimize differences between enclosures and the field, wind tunnel enclosures (wt) were developed which minimize the disturbance of the natural conditions. In these wind tunnels the airflow through the tunnel can be adjusted to the wind speed outside the tunnel. However, conditions within tunnels may still differ from actual conditions (e.g., rainfall and formation of dew). This problem may be solved partially by frequently moving the tunnel.

MICROMETEOROLOGICAL TECHNIQUES

Micrometeorological techniques that use analyses of the atmospheric concentration of the gas and meteorological measurements such as wind speed, wet- and dry-bulb air temperatures, net radiation, and heat fluxes do not disturb the environmental conditions. These techniques are used for determining field-scale fluxes, and include eddy correlation, energy balance, aerodynamic and mass balance techniques.

The first three micrometeorological techniques require flux measurements over large areas of uniformly treated crop, with fetches between 150 and 200 m. This is necessary to ensure that fluxes measured at some height above the surface, say 1 or 2 m, represent fluxes from the surface itself. Fluxes are constant with height over vertical distances above the surface of only about 1/100 of the fetch.

Eddy correlation methods use high frequency measurements (typically 10 samples per second) of vertical wind speed w and atmospheric gas concentration c at a point above the surface. The mean vertical flux density of the gas F over sampling periods long enough to encompass all the significant transporting eddies (usually 15 to 30 minutes) is given by:

$$F = \overline{wc}$$

where the overbar denotes a time mean.

Energy balance and aerodynamic techniques both rely on the following expression to calculate gas fluxes:

$$F = K \frac{dc}{dz}$$

where K is the eddy diffusivity of the gas in air and z the height above a crop, soil or floodwater surface at which measurements of c are undertaken. It is necessary to measure c at heights within the constant flux layer. The magnitude of the diffusivity in air varies with height, atmospheric conditions and the aerodynamic roughness of the surface.

Energy balance methods require measurements of vertical gradients of temperature and humidity in the air above the surface to provide estimates of K . Aerodynamic methods require measurements of the vertical profiles of wind velocity and temperature to estimate K . Using a modified aerodynamic method suitable for flooded systems it is possible to calculate the gas flux from measurements of wind speed at one height above the surface and the gaseous concentrations in the floodwater and the air at the reference height.

The mass balance or integrated horizontal flux method is for use on experimental plots with fetches ranging between 20 and 50 m. Based on the conservation of mass, the general method equates the horizontal flux of gas across a face of unit width on the downwind edge of a designated area with the surface emission or absorption of the gas along a strip of similar width upwind. The horizontal flux density at any height is the product of horizontal wind speed u and gas concentration C_g . The total horizontal flux is obtained by integrating that product over the depth of the modified layer Z , which is about 1/10 of the fetch X in neutral conditions, but usually less than that in unstable conditions and more in stable conditions. The average surface flux density is:

$$F = (1/X) \int_0^Z u(C_g - C_b) dz$$

where C_b is the upwind, background concentration and the overbar denotes a time average.

If the wind direction is other than normal to the plot, it is necessary to allow for the effects of wind direction on the fetch. However, it is possible to avoid this by working with a circular plot and measuring the integrated horizontal flux at the plot centre. Regardless of compass direction, the wind will always blow towards the centre and X will always be the plot radius. If the experimental plot is square or rectangular, it will be necessary to measure the horizontal fluxes over the two upwind and the two downwind edges as well as the wind direction.

A major limitation of the mass balance technique is its high labour requirement. However, there is a simpler, less laborious method based on the mass balance technique. In this case estimates of gas fluxes derive from analyses of \bar{u} and \bar{c} made at a single height at which the normalized horizontal flux, $\bar{u}c/F$, has almost the same value in any atmospheric stability regime. To use the simplified mass balance micrometeorological technique, it is necessary to satisfy two requirements: the treated plots should be small (20-50 m radius), and located within a larger plot of uniform crop surface so that the wind profiles are equilibrium ones. However, the technique is not appropriate for fields with well-established canopies as single measurements will not be adequate to predict the strongly modified wind and concentration profiles.

For NH_3 all micrometeorological methods determine atmospheric gas concentrations by chemical trapping, followed by elution of the NH_3 with distilled water and measurement of its concentration. The literature on micrometeorological studies records various types of NH_3 traps and analytical techniques. Many studies of N_2O and NO emissions have used micrometeorological methods. Micrometeorological techniques employed for measuring N_2O and NO fluxes are similar to those used for estimating NH_3 fluxes. However, the concentration measurements are more difficult and require specialised instrumentation such as tuneable diode laser trace gas analysers or Fourier transform infrared spectroscopy for N_2O concentrations, and chemiluminescence detection techniques for NO .

INDIRECT OPEN MEASUREMENT TECHNIQUE

The indirect open measurement technique (ioc) relies on a comparison between sources of known and unknown NH_3 volatilization. A network of point sources in a plastic tubing system on the surface releases ammonia at a

known rate from a standard plot. Samplers with acid traps measure the ammonia in the air over the standard and the manured plots. The advantages of this technique over others, such as wind tunnels, are its limited technical requirements and the unaltered climatic conditions.

^{15}N , N BALANCE AND N DIFFERENCE METHODS

N balance techniques determine the difference of N applied and that remaining in soil and crop after some time. A simplification of a complete N balance is the N difference method for uncropped soils to determine the difference between the N applied + the N remaining in control treatments, and the N remaining in the treated plots or samples. The loss of N from the system is commonly attributed to NH_3 volatilization, while the role of other pathways of N loss, such as denitrification and leaching, is ignored. As in most cases this method has been applied to flooded systems amended with urea and NH_4^+ -yielding fertilizers, denitrification has been assumed to be negligible during the time period considered.

^{15}N balance techniques can analyse the fate of the applied ^{15}N labelled N fertilizer in soil and crop (and floodwater). Measurements of NH_3 loss with, for example, micrometeorological methods in conjunction with ^{15}N techniques have been used to estimate the denitrification loss. This is possible if runoff and leaching losses are also known or if these loss pathways are preventable.

Because environmental as well as chemical and biological factors affect NH_3 volatilization from fertilized soils, it is advisable to determine NH_3 volatilization using techniques that cause no or minimum disturbance to the field environment. The micrometeorological and ^{15}N balance approaches both meet this requirement. However, ^{15}N balance techniques produce estimates of total N loss. Hence, for determining NH_3 loss and denitrification, a combination of ^{15}N balance and micrometeorological techniques is the most appropriate approach.

Chapter 4 Measurements

NITROUS OXIDE, DENITRIFICATION AND NITRIC OXIDE MEASUREMENTS

Fertilizer induced emissions

Like natural soils, unfertilized agricultural fields show emissions of NO and N_2O . A prerequisite for such emissions is the availability of N , which is determined primarily by the mineralization of soil organic matter and N deposition. Mineralization rates depend on the history of land use (i.e. previous crop, residue management and fertilization).

To estimate the anthropogenic effect on emissions many authors have used the concept of the fertilizer induced emission (i.e. the emission from the fertilized plot minus that of the control plot expressed as a percentage of the N applied). In this concept, the emission from the control plot is assumed to be equivalent to the natural or background emission.

Tables 4 and 5 present the calculations of fertilizer induced emission for different fertilizer types irrespective of the length of the measurement period, climate and soil conditions. Not all measurements included control plots, hence the number of measurements for the fertilizer induced emission is smaller than that for the total N_2O or NO emission.

Nitrous oxide

The measurements in the data set from the literature since 1995 have not changed significantly from earlier results found using a subset of the present data set except for the high mean values for nitrate-based fertilizers and the high maximum values for ammonium sulphate and urea (Table 4). These results stem from one experiment in Costa Rica, with extremely high emissions. The authors of these measurements speculated that emissions in the tropics may exceed those in temperate regions as a result of the temperature

and moisture conditions which are prone to high N₂O losses. However, the high maximum values in the data set for injected anhydrous ammonia were from measurements in a temperate climate: 7.3 percent and 6.8 percent.

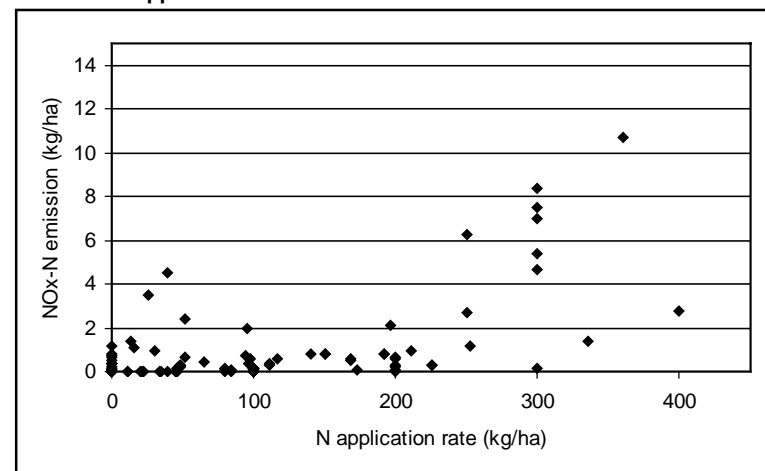
The mean and median values for the fertilizer induced emission for various fertilizer types (Table 4) show important differences, indicating that the emission rates are not normally distributed.

TABLE 4.
Fertilizer induced N₂O emission, % calculated directly from the data set

| Fertilizer type | Mean | Median | Standard deviation | No. measurements | Max. | Min. |
|-----------------|------|--------|--------------------|------------------|------|------|
| AA | 2.0 | 1.4 | 2.2 | 26 | 7.3 | 0.0 |
| ACI | 0.1 | 0.1 | 0.1 | 9 | 0.4 | 0.0 |
| AN | 1.7 | 1.0 | 1.8 | 50 | 7.1 | 0.0 |
| AS | 0.8 | 0.2 | 2.4 | 22 | 11.4 | 0.0 |
| CAN | 1.2 | 0.7 | 1.5 | 40 | 8.3 | 0.0 |
| CN | 1.5 | 0.4 | 3.5 | 11 | 12.0 | 0.0 |
| KN | 2.4 | 0.1 | 4.4 | 12 | 12.5 | 0.0 |
| Mix | 1.0 | 0.7 | 1.0 | 8 | 2.4 | 0.1 |
| AP | 1.4 | 0.8 | 1.8 | 11 | 6.3 | 0.3 |
| O | 0.6 | 0.3 | 0.7 | 45 | 3.3 | 0.0 |
| OS | 2.4 | 1.9 | 1.8 | 25 | 6.8 | 0.2 |
| Urea | 1.1 | 0.3 | 2.7 | 48 | 14.7 | 0.0 |
| UAN | 1.0 | 0.5 | 2.0 | 34 | 10.8 | 0.0 |

Bouwman (1996) concluded that the length of the measurement period strongly influences the fertilizer induced N₂O emission. The N input from fertilizer appears to have an effect that lasts longer than the crop growing season. Figure 2 presents the relation between fertilizer N application rate and the measured N₂O emission for the measurements with a measurement period equal to or longer than one year present in the data set. Contrary to the results of Bouwman (1996), Figure 2 shows that there is no clear relation between N application rate and annual emission.

FIGURE 2.
Fertilizer N application and nitrous oxide emission



Nitric oxide

The data on fertilizer induced NO emissions from fertilized fields also show important differences between the mean and median values (Table 5). The median values for the fertilizer induced NO emission are lower than those for N₂O, with typical values of 0.1-0.4 percent, with the exception of the data for ammonium nitrate (AN) and ammonium sulphate. The high values for ammonium nitrate stem from one publication, while those for ammonium sulphate are from three measurements.

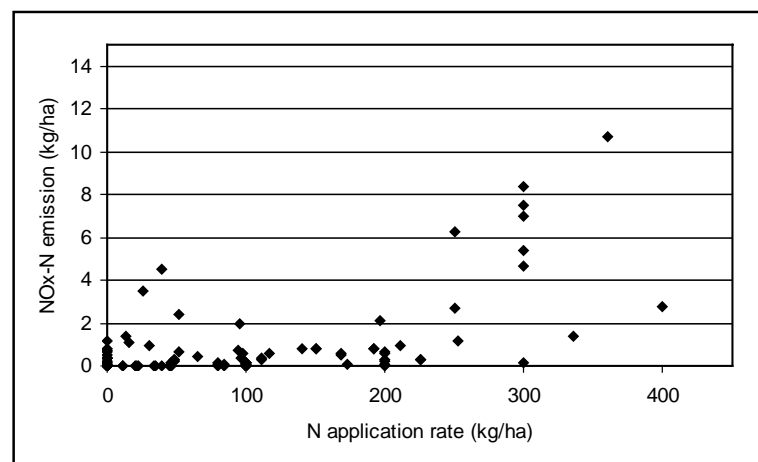
TABLE 5.
Fertilizer induced NO emission (%) and the NO/N₂O ratio, calculated directly from the data set

| | Mean | Median | Standard | No. | Max. | Min. | NO/N ₂ O | Standard | No. |
|-----------------|------|--------|----------|-----|------|------|---------------------|----------|-----|
| ACI | 0.1 | 0.1 | 0.3 | 8 | 1 | 0 | n.d. | n.d. | 0 |
| AN | 3.8 | 0.3 | 5.6 | 10 | 13 | 0 | 0.6 | 0.8 | 9 |
| AS | 3.5 | 3.2 | 1.1 | 3 | 5 | 3 | 5.7 | 1.5 | 2 |
| CAN | 0.2 | 0.4 | 0.3 | 8 | 0 | 0 | 1.1 | 1.1 | 6 |
| NO ₃ | 0.3 | 0.1 | 0.5 | 7 | 2 | 0 | n.d. | n.d. | 0 |
| O | 0.0 | 0.0 | 0.1 | 4 | 0 | 0 | 0.4 | 0.1 | 4 |
| Urea | 0.9 | 0.2 | 1.2 | 9 | 3 | 0 | 0.5 | 0.6 | 10 |

Hutchinson and Brams (1992) observed high NO:N₂O ratios in a Mediterranean climate. Harrison *et al.* (1995) observed the high values for calcium ammonium nitrate (CAN) at Rothamsted, the United Kingdom. However, the number of measurements is small, and the high standard deviation of the NO:N₂O ratio suggests that the uncertainty is high.

Figure 3 presents the relationship between N fertilizer application rate and NO emission from all the studies in the data set. It indicates that there is no clear relationship between N application rate and NO emission. This contrasts with Veldkamp and Keller (1997a) who concluded that 0.5 percent of the N applied as fertilizer is lost as NO (on the basis of a subset of the data used in this report).

FIGURE 3.
Relation between fertilizer N application and nitric oxide emission



Analysis of regulating factors of nitrous oxide and nitric oxide emissions

The above discussion indicates that it is not possible to use simple relationships between fertilizer N application rates and emissions. The reason for the lack of correlation is that the data set includes measurements from a variety of locations with differing climate, soil, crop and management conditions. This calls for a different approach whereby the data set is summarized based on the factors that regulate N₂O and NO emissions.

Data handling

The factors selected for the data summary include: climate, crop type, fertilizer type, application rate, mode and timing of application, soil organic C and N content, soil pH, soil texture and drainage, measurement technique, frequency of measurements and length of the measurement period. The analysis did not include organic soils.

TABLE 6.
Climate codes

| Code | Climate type |
|-------|-----------------------------|
| Clim1 | Temperate continental |
| Clim2 | Temperate oceanic |
| Clim3 | Subtropical, summer rains |
| Clim4 | Subtropical, winter rains |
| Clim5 | Tropical, warm humid |
| Clim6 | Tropical, warm seasonal dry |
| Clim7 | Cool tropics |
| Clim8 | Boreal |

Based on Fresco *et al.* (1998) using criteria of the FAO Agro-Ecological Zones approach (de Pauw *et al.*, 1996).

Table 6 presents the classification used for climate. The description of the differences in soil conditions uses functional groupings based on: soil texture, drainage, soil organic C and N content, and soil reaction (pH) (Table 16, Annex 2). Crops were grouped into five crop types: grass, grass-clover mixtures, wetland rice, legumes and other crops. Table 16 also shows the groupings for fertilizer types, application rate, and mode and for timing of fertilizer application (excluding measurements with grazing and fertilizer type CAN with grazing, and organic soil texture).

Table 3 summarizes the different measurement techniques in the data set. The classes used for the length of the measurement period were: <120, 120-180, 180-240, 240-300 and >300 days. The groupings for frequency of measurement were: more than one measurement per day, one per day, one every 2-3 days, one every 3-7 days, less than one per week. Many studies have used variable measurement frequencies, with measurements that are more intensive shortly after fertilization and lower frequencies when emission rates dropped to background levels. In such cases, we selected the highest frequency. The groupings for the NO measurement data are different because of scarcity of data (Table 16).

On the basis of the classification for the different factors, the data set was summarized by calculating for each factor class: mean, median, balanced mean and balanced median values of the measured emission of N₂O and NO.

Balanced mean values indicate unbalanced features of mean values. They were calculated with the residual maximum likelihood procedure. The balanced median indicates unbalanced features and extreme values present in the median. Balanced median values were calculated with the residual maximum likelihood procedure using log-transformed emissions. Log-transformation reduces the influence of extreme values. Back-transformation yields a balanced mean value for the emission.

Subsequently, the most important factors in the data set explaining log-transformed N₂O and NO emissions were selected. The residual maximum likelihood procedure was done with research paper as a random effect, using the WALD statistic to select the most important factors ($P < 0.005$). For the selected factors with significant influence on the N₂O emission residual maximum likelihood models were developed to predict emissions of N₂O and NO. The formulation for the emission models for N₂O and NO is:

$$\ln(\text{Emission}) = \sum_n^1 \text{Factor class } (n)$$

with *Emission* expressed as N in kg/ha. Back-transformation of the result of this equation yields the emission. Table 7 presents the different class values of the model terms.

TABLE 7.
Values of constants and factor classes in the models for N₂O and NO

| Model term | Class/value | | | | | |
|--|---------------|---------------|---------------|---------------|-------------|------------|
| N₂O model | | | | | | |
| Constant | -0.414 | | | | | |
| Fertilizer type* N application rate interaction^a | | | | | | |
| | AA | AF | AN | CAN | NF | Mix |
| | 0.0056 | 0.0051 | 0.0061 | 0.0037 | 0.0034 | 0.0065 |
| | NP | O | OS | UU | UAN | |
| | 0.0039 | 0.0021 | 0.0042 | 0.0051 | 0.0053 | |
| Crop type | | | | | | |
| | Other | Grass | Clover | Legume | Rice | |
| | 0.000 | -1.268 | -1.242 | -0.023 | -2.536 | |
| Soil texture | | | | | | |
| | Coarse | Medium | Fine | | | |
| | -0.008 | -0.472 | 0.000 | | | |

| | | | | | | |
|--|-----------------|----------------|------------------|------------------|------------------|------------|
| Soil organic C content (%) | | | | | | |
| | <1.0 | 1.0-3.0 | 3.0-6.0 | >6.0 | | |
| | 0.000 | 0.140 | 0.580 | 1.045 | | |
| Soil drainage | | | | | | |
| | Poor | Good | | | | |
| | 0.000 | -0.420 | | | | |
| Soil pH | | | | | | |
| | <5.5 | 5.5-7.3 | >7.3 | | | |
| | 0.000 | 0.109 | -0.352 | | | |
| Climate^b | | | | | | |
| | Temp. | Trop. | | | | |
| | 0.000 | 0.824 | | | | |
| Length of measurement period (days) | | | | | | |
| | <120 | 120-180 | 180-240 | 240-300 | >300 | |
| | 0.000 | 0.004 | 0.487 | 0.657 | 0.825 | |
| Frequency of measurements | | | | | | |
| | >1m/d | 1m/d | 1m./2-3 d | 1m./3-7 d | <1m./w | |
| | 0.000 | 0.125 | 1.639 | 0.825 | 0.788 | |
| NO model | | | | | | |
| Constant | -1.527 | | | | | |
| Fertilizer type* N application rate interaction^a | | | | | | |
| | AA | AF | AN | CAN | NF | Mix |
| | 0.0051 | 0.0056 | 0.0040 | 0.0062 | 0.0054 | 0.0078 |
| | NP | O | OS | UU | UAN | |
| | 0.0055 | 0.0016 | 0.0055 | 0.0061 | 0.0004 | |
| Soil organic C content (%) | | | | | | |
| | <3.0 | >3.0 | | | | |
| | 0.000 | 2.571 | | | | |
| Soil drainage | | | | | | |
| | Poor | Good | | | | |
| | 0.000 | 0.946 | | | | |

a. The values presented are multiplied with the N application rate under consideration. The values presented here were used to estimate emissions for the fertilizer types distinguished by IFA (1999). For ammonium sulphate, ammonium chloride and ammonium bicarbonate, the values for AF were used; for NKN, that for NF; for urea, that for UU; for nitrogen solutions (Ns), that for Mix; for ammonium phosphates, compound NP and NPK N fertilizers, those for NP.

b. Temp: temperate climates, including temperate oceanic and continental, cool tropical, boreal and polar/alpine. Trop: tropical climates, include subtropics winter rains, subtropics summer rains, tropics, warm humid, and tropics warm seasonal dry.

Data interpretation for nitrous oxide emissions

Although Table 16 presents the mean, median, balanced mean and balanced median values for the measured N₂O emissions for all systems for all the factors under consideration, the discussion here concentrates on the balanced median values.

The balanced median values for N application rate are nearly constant emissions below 100 kg N/ha, and emissions increase along with the N application at rates exceeding 100 kg N/ha. Mean and median values show a similar pattern, except for rates of 1-50 kg N/ha which show higher values than the 50-100 kg N/ha class. The trend is highest at rates exceeding 250 kg N/ha.

The balanced median for Clim1 exceeds that for Clim2, reflecting the observed winter emissions which are higher for Clim1 than for Clim2. The balanced median for subtropical climates exceeds that for Clim1 by 94 percent, and that for Clim2 by 127 percent. The balanced median value for N₂O emission in Clim5 exceeds that for Clim1 by 37 percent and that for Clim2 by 60 percent. Results for Clim6, Clim7 and Clim8 are more uncertain than for the other climate types due to the limited number of measurements.

For soil organic C content and soil N content the balanced median values indicate increasing N₂O emission along with increasing C and N content. The difference in the balanced median value between soils with >3-6 percent soil organic C and those with <1 percent is 38 percent, while the balanced median for soils with organic C content >6 percent exceeds those with <1 percent organic C by 113 percent. For soil N content the balanced median value for soils with 0.15-0.3 percent N exceeds that for 0.05-0.15 percent N by 38 percent. The number of observations in the other classes is limited and the calculated values are less certain.

The balanced median value for fine soil texture exceeds that for coarse texture by 8 percent and that for medium soil texture by 59 percent. The balanced median value for soil drainage exceeds that from well-drained soils by 35 percent. The balanced median value is highest for soils with intermediate soil pH (5.5-7.3) exceeding those for soils with pH < 5.5 by 7 percent and those with pH >7.7 by 49 percent.

The highest balanced median values are for mixed fertilizers, anhydrous ammonia and OS, respectively, while those for the NO₃⁻-based and NP fertilizers (NF and NP) are lowest. The differences between highest and lowest values are 103-109 percent. The high values for anhydrous ammonia and OS and low values for NF are consistent with earlier studies.

The difference between broadcasting and incorporation is small. Broadcasting at panicle initiation (bpi) in wetland rice cultivation leads to a reduction in N₂O emissions compared to broadcasting 2-3 weeks after transplanting by 23 percent, reflecting more efficient plant N uptake. The balanced median values for split applications exceed those for single applications only slightly.

The balanced median values are highest for leguminous crops, followed by other crops, grass, wetland rice and grass-clover mixtures. The balanced median value for other crops exceeds that for grass by 121 percent, and that for rice by more than a factor of 7. The balanced median value for leguminous crops exceeds that for the other crops class by 37 percent. Lower emissions for grass than for other crops may result from more efficient N uptake by grass as a result of longer growing periods, particularly in temperate climates.

The differences in balanced median values between the micrometeorological technique and open and closed chamber methods are 46 and 23 percent, respectively, while the balanced median value for the gradient technique is highest and that for the open chamber technique lowest. In most cases there is an increase of measured N₂O along with the length of the measurement period. The balanced median value for measurements covering more than 300 days exceeds that for periods of 240-300, 180-240 and <180 days by 54, 72 and 172 percent, respectively. Many measurements cover at most a half year (<180 days), and yield only part of the annual emission and probably only part of the fertilizer effect. In general, high-frequency measurements show the lowest balanced median values, with the highest values at intermediate frequency (1 measurement in 2-3 days).

In summary, the results of the data summary agree with the literature. Regarding the factors determining the N availability, the results show that: (i) there is a strong increase of N₂O emissions along with N application rates; (ii) warm climates show higher N₂O emissions than temperate climates; and (iii) fertile soils with high organic C and N contents show higher emissions than less fertile soils.

Regarding factors influencing the N₂O:N₂ ratio, fine soil texture, restricted drainage, and neutral to slightly acidic soil reaction are conditions that favour N₂O production and emission. Furthermore, emissions from grasslands are lower than for crops. With respect to measurement techniques, the results indicate that longer measurement periods yield more of the fertilization effect on N₂O emissions. This finding confirms the conclusions of an earlier study. Finally, intensive measurements (>1 per day) yield lower

emissions than less intensive measurements, which is in agreement with other studies.

The following factors had a significant influence ($P < 0.005$): N application rate per fertilizer type, climate type, soil organic C, soil texture, drainage, pH, crop type, length of experiment and frequency of measurements. The most important factors are the interactions between the N application rate and the fertilizer type and the crop type.

All the factors with significant influence on emissions were included in a REML model (see equation in the section on data handling). The values of the model terms are presented in Table 7. To calculate the full annual N_2O emission with this model the class >300 days for length of the measurement period was used, while emission estimates based on frequencies of more than one measurement per day were considered to be more reliable than measurements with lower frequencies.

Data interpretation for nitric oxide emissions

Table 17 (Annex 2) presents the calculated values for the mean, median, balanced mean and balanced median for the measured emissions. The balanced median values show a consistent increase in emissions with increasing N application rate, which is in line with generally observed trends in the literature. The balanced median values are highest for Clim3, and the balanced median value for Clim5 is 10 percent higher than that for Clim1, while it is 9 percent lower than that for Clim2. The balanced median value for Clim3 exceeds that for Clim1 by more than a factor of 5, and those for Clim2 and Clim5 by more than a factor of 4.

The balanced median value for soils with a soil organic C content of >3 percent exceeds that for soil with <3 percent by a factor of 5, which is in agreement with the results for N_2O emissions. Contrary to the results for N_2O for soil texture, the balanced median value for NO emission for coarse soil texture exceeds that for medium texture by 160 percent and that for fine texture by 148 percent.

Except for the median values, all values for well drained soils exceed those for poorly drained soils, a reflection of the fact that high NO emission requires aerobic conditions. Soil pH has a marked effect on NO emissions, with higher balanced median values for low pH soils ($pH < 5.5$) compared with soils with $pH > 5.5$; a finding in agreement with the literature.

The fertilizer types that are well represented in the data set include the NH_4^+ -yielding fertilizers, AN, NO_3^- -yielding fertilizers, urea and urine. In

this group of fertilizer types the highest balanced median values are for AN, exceeding those for AF, NF and UU by 75, 17 and 26 percent, respectively.

The balanced median value for broadcasting exceeds that for incorporation by more than a factor of 5 and that for application in solution by 124 percent. For timing of fertilizer application, comparisons between the different classes are difficult due to uncertainty in the values for split application schemes.

The balanced median values for other crops exceed those for grass and leguminous crops by 85 and 176 percent, respectively. The data for wetland rice are too scarce for drawing any conclusions.

The balanced median value for open chambers exceeds that for closed chambers by 24 percent. Most measurements covered less than 120 days, with lower balanced median values than for measurements covering >120 days. This suggests that also for NO the measurement period may be important when assessing measurements from literature. However, although the data available for measurement periods of >300 days are scarce, the results suggest that the effect of N application on NO emissions is less long-lasting than for N_2O . High-frequency measurements (>1 measurement per day) of NO emission show lower balanced median values than measurements with lower frequencies. This pattern is in general agreement with the results for N_2O .

In summary, for the factors that determine N availability, the data indicate that NO emissions increase along with N application rates, and that warm climates and fertile soils with high C contents favour NO emission. For factors influencing the relative rate of NO emission, the data show that NO emissions are highest for coarse textured and neutral soils. Longer measurement periods yield higher emissions than short measurement periods although this effect is less certain than for N_2O due to the smaller number of measurement data. As with N_2O , high-frequency measurements yield lower emission estimates than lower frequencies. All these findings agree with the general understanding of the controls of NO fluxes.

The factors that exert a significant influence on NO emissions are: N application rate per fertilizer type, soil organic C content and drainage. The influence of climate is not significant. NO emissions appear to be much more concentrated in the crop growing season than N_2O . During the growing season, climatic conditions differ less between climate types than during other periods such as winter, spring and autumn.

SUMMARY OF AMMONIA VOLATILIZATION MEASUREMENTS

Rather than presenting the complete data set, this section summarizes the data for the major fertilizer types for upland and flooded systems.

Upland systems

Anhydrous ammonia

The analysis of the literature found only a few measurements for anhydrous ammonia, an indication that NH_3 volatilization from this fertilizer is low. This is probably related to the mode of application (usually injection), and volatilization losses may occur when the injector does not penetrate deep enough, or when the soil is either too wet or too dry. Moreover, the spacing between the lines of injection influences the NH_3 loss, with higher losses associated with close spacing. This is related to the anhydrous ammonia concentration per unit volume of soil, which is higher with close spacing.

Ammonium bicarbonate

Few data are available for ammonium bicarbonate (ABC). An NH_3 volatilization rate of 21 percent was measured with the enclosure technique without forced draught. Laboratory measurements with the forced draught technique in calcareous loess soils indicate NH_3 volatilization rates of more than 30 percent, in some cases up to 70 percent.

Ammonium nitrate

Measurements with the mass balance technique presented by Jarvis *et al.* (1989a) indicate an NH_3 volatilization rate of 6 percent. However, these measurements refer to grazed grassland, and it is not clear whether the loss is attributable to the fertilizer alone, as part may have been the result of animal excretion in the field. The data indicate that NH_3 volatilization rates are 0-2 percent at low pH, while for soils with high pH and low CEC the loss may exceed 60 percent.

Ammonium sulphate

Few micrometeorological measurements are available for trash-covered soils in sugar cane fields. NH_3 volatilization rates were 0-2 percent for ammonium sulphate, which is much lower than observed in some experiments using other techniques. NH_3 volatilization rates of up to 90 percent of the applied N have been reported using forced draught systems for calcareous soils.

Calcium ammonium nitrate

Forced draught techniques in laboratory measurements with both slightly acid, neutral and slightly alkaline soils resulted in NH_3 volatilization rates of up to 6 percent, while field measurements with forced draught techniques showed much lower NH_3 volatilization rates. Measurements with wind tunnels on slightly acid soils also showed low NH_3 volatilization rates.

Calcium nitrate

Although not an NH_4^+ -based fertilizer, calcium nitrate (CN) has enabled comparisons with other fertilizer types. The difference between the N applied as fertilizer and the N recovered in the crop used as a proxy for NH_3 volatilization loss resulted in low to negligible volatilization rates.

Diammonium phosphate

Both the forced draught technique and the N balance method for broadcast diammonium phosphate (DAP) show that NH_3 volatilization rates are highly variable, ranging from 2 percent to over 50 percent. Laboratory experiments for soils with high pH reported the highest NH_3 volatilization rates. The N balance method with high pH soils also resulted in high NH_3 volatilization rates (up to 35 percent). The incorporation of DAP resulted in lower NH_3 volatilization rates of about 10 percent, about half of the rate observed for broadcast DAP on alkaline soils.

Monoammonium phosphate

The forced draught measurements reviewed in the data set yielded NH_3 volatilization rates from broadcast monoammonium phosphate (MAP) ranging between 2 and 35 percent on soils ranging from slightly acid to alkaline. The N balance method showed lower NH_3 losses (8 percent) for broadcast MAP than for DAP on high pH soils. Incorporated MAP showed NH_3 volatilization rates of 2 percent.

Urea

Measurements of NH_3 losses from urea fertilizer show a coherent pattern. Results from closed systems, forced draught, micrometeorological and wind tunnel measurements indicate that NH_3 volatilization rates range from 15-20 percent of the applied nitrogen for broadcast fertilizer. For incorporated urea, the NH_3 volatilization rates are between 5 and 15 percent.

Urea ammonium nitrate

Volatilization rates of NH_3 from broadcast urea-ammonium nitrate (UAN) measured with micrometeorological techniques were close to 15 percent, with a range of 8 to 18 percent. However, soil pH values were not reported. NH_3 volatilization rates measured with the forced draught technique ranged from negligible amounts to almost 45 percent in a field experiment with broadcast UAN on a heavy textured vertisol. High NH_3 volatilization rates were also observed with the N difference method on neutral to slightly acidic soils.

Flooded systems

Ammonium bicarbonate

The data from micrometeorological methods show that NH_3 volatilization rates from ABC may reach 40 percent. The values obtained for Chinese paddy fields were lower, due to the low pH of the floodwater. However, where NH_3 volatilization rates were low, the total loss of N from ABC was still high as a result of denitrification. The method of application did not influence markedly the NH_3 volatilization in the measurements. For ABC, there were only measurements based on micrometeorological techniques.

Ammonium sulphate

The one micrometeorological measurement available for broadcast ammonium sulphate indicates that up to 40 percent of ammonium sulphate-N may volatilize. Volatilization of NH_3 from ammonium sulphate broadcast at panicle initiation may amount to 10 percent, and about 5 percent from incorporated ammonium sulphate applied at transplanting. The seasonal loss of NH_3 from ammonium sulphate incorporated at transplanting and broadcast at panicle initiation was about 5 percent in the Philippines. Enclosure-based measurements show a similar pattern, with NH_3 losses varying between negligible amounts and 20-30 percent for broadcast ammonium sulphate, and between insignificant loss and 6-10 percent for incorporated ammonium sulphate. The measurements with open and closed bottles show high NH_3 volatilization rates from floodwater with a pH of 9-10, and markedly lower from floodwater with a pH <9.5.

Urea

Micrometeorological techniques used in flooded rice fields fertilized with urea applied at transplanting of rice show a clear difference in NH_3 volatilization rate between broadcast urea (26 percent; range 0-56 percent) and incorporated

urea (21 percent; range 0-43 percent). Urea applied at panicle initiation gives lower volatilization rates of 7 percent (1-15 percent). Forced draught techniques show NH_3 volatilization rates of 17 percent for broadcast urea, and higher values of 20 percent for incorporated urea. ^{15}N techniques give somewhat higher NH_3 volatilization rates of 28 percent (5-60 percent). Incorporation of urea in the puddled soil before permanent flooding results in NH_3 losses of close to 10 percent (0-16 percent).

Summary of regulating factors of ammonia volatilization

Data handling

The analysis of the complete set of literature data to assess relationships between the various regulating factors and NH_3 volatilization rates made use of Genstat 5 release 4.1 (PC/Windows NT).

The regulating factors considered consisted of: type of measurement (field or laboratory), measurement technique, soil pH, CEC, and organic carbon content, temperature during measurements, fertilizer type, method of application, N application rate, and type of crop. The analysis did not consider factors for which data were scant. Nor did it consider factors related (indirectly) to weather conditions, such as rainfall during the period of measurements, wind speed, algal growth and associated floodwater pH. This is because it is not possible to use weather conditions for making predictions. Finally, the analysis also excluded studies concerning the use of chemicals such as algicides, urease and nitrification inhibitors. Hence, the analysis involved 1 667 individual measurements (out of a total of 1 900), from 148 different studies.

Table 8 presents the various factor groupings and their classifications. For crop type, the analysis assumed that in upland systems fertilizer is applied at seeding, hence the soil surface is bare. Field and laboratory experiments with non-flooded bare soil were therefore included in this group. The classification of pH values in Table 8 derived from the fact that careful analysis of the data suggested a non-linear relation between soil pH and NH_3 volatilization rates. Moreover, such a classification would make the relationships compatible with the classifications used in the global data bases of soil properties. The analysis did not consider floodwater pH (an important factor in flooded systems) as it is not possible to use this factor in extrapolations.

TABLE 8.
NH₃ volatilization rates for various factors

| Factor | Est. ^a | Class/type/value | | | | | | | |
|------------------------------|-------------------|------------------|----------------|--------------|------------|-----------------------|---------------|----------------|--------------|
| Measurement location | | | | | | | | | |
| | Field | Lab. | | | | | | | |
| M | 0.159 | 0.235 | | | | | | | |
| BM | 0.054 | 0.089 | | | | | | | |
| WR | 101 | 47 | | | | | | | |
| Measurement technique | | | | | | | | | |
| | c | cf | cso | ioc | m | ¹⁵N | Nbal | ocb | wt |
| M | 0.114 | 0.203 | 0.140 | 0.445 | 0.164 | 0.400 | 0.289 | 0.260 | 0.175 |
| BM | 0.049 | 0.047 | 0.044 | 0.113 | 0.066 | 0.116 | 0.082 | 0.089 | 0.057 |
| WR | 13 | 56 | 16 | 1 | 40 | 2 | 5 | 1 | 15 |
| Crop | | | | | | | | | |
| | Upland | Grass | Flooded | | | | | | |
| M | 0.197 | 0.159 | 0.174 | | | | | | |
| BM | 0.068 | 0.070 | 0.070 | | | | | | |
| WR | 77 | 33 | 38 | | | | | | |
| Fertilizer type | | | | | | | | | |
| | AS | Urea | AN | CAN | AA | Nsol. | CN | ABC | UAN |
| M | 0.187 | 0.210 | 0.081 | 0.022 | 0.001 | 0.044 | 0.005 | 0.152 | 0.124 |
| BM | 0.112 | 0.140 | 0.048 | 0.022 | 0.029 | 0.034 | 0.010 | 0.130 | 0.105 |
| WR | 12 | 74 | 4 | 2 | 1 | 0 | 0 | 3 | 5 |
| | MAP | DAP | U+DAP | U+MAP | UP | UUP | Manure | Grazing | Urine |
| M | 0.094 | 0.138 | 0.194 | 0.057 | 0.089 | 0.170 | 0.212 | 0.058 | 0.147 |
| BM | 0.025 | 0.089 | 0.122 | 0.036 | 0.054 | 0.111 | 0.160 | 0.038 | 0.142 |
| WR | 0 | 3 | 1 | 1 | 1 | 1 | 18 | 3 | 6 |
| | AN+gra. | Uc | U+KCl | U+Ca | UCN | U+FYM | | | |
| M | 0.280 | 0.134 | 0.177 | 0.264 | 0.062 | 0.143 | | | |
| BM | 0.204 | 0.093 | 0.099 | 0.154 | 0.045 | 0.095 | | | |
| WR | 1 | 4 | 2 | 2 | 1 | 2 | | | |
| Application mode | | | | | | | | | |
| | b;b/w | i | s | bf;if | bpi | NR | | | |
| M | 0.203 | 0.138 | 0.179 | 0.119 | 0.059 | 0.116 | | | |
| BM | 0.103 | 0.051 | 0.086 | 0.053 | 0.050 | 0.092 | | | |

| | | | | | | | |
|--------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|-----------|
| WR | 94 | 20 | 22 | 6 | 2 | 6 | |
| N application (kg N/ha) | | | | | | | |
| | <50 | 50-100 | 100-150 | 150-200 | 200-250 | >250 | NR |
| M | 0.134 | 0.193 | 0.170 | 0.158 | 0.190 | 0.174 | 0.278 |
| BM | 0.060 | 0.074 | 0.071 | 0.060 | 0.070 | 0.079 | 0.072 |
| WR | 13 | 58 | 24 | 17 | 11 | 18 | 8 |
| Temperature (°C) | | | | | | | |
| | <20 | >20 | NR | | | | |
| M | 0.178 | 0.212 | 0.176 | | | | |
| BM | 0.069 | 0.071 | 0.068 | | | | |
| WR | 37 | 26 | 85 | | | | |
| Soil pH | | | | | | | |
| | <5.5 | 5.5-7.3 | 7.3-8.5 | >8.5 | NR | | |
| M | 0.153 | 0.174 | 0.215 | 0.221 | 0.188 | | |
| BM | 0.051 | 0.057 | 0.079 | 0.092 | 0.075 | | |
| WR | 22 | 66 | 32 | 2 | 25 | | |
| Soil CEC (cmol/kg) | | | | | | | |
| | <16 | 16-24 | 24-32 | >32 | NR | | |
| M | 0.190 | 0.187 | 0.183 | 0.175 | 0.180 | | |
| BM | 0.079 | 0.075 | 0.083 | 0.050 | 0.065 | | |
| WR | 30 | 24 | 12 | 12 | 70 | | |
| Soil organic C (%) | | | | | | | |
| | <1% | 1-2.5% | 2.5-5% | >5% | NR | | |
| M | 0.208 | 0.164 | 0.183 | 0.163 | 0.187 | | |
| BM | 0.070 | 0.059 | 0.074 | 0.085 | 0.062 | | |
| WR | 25 | 42 | 13 | 6 | 61 | | |
| Soil texture | | | | | | | |
| | Coarse | Medium | Fine | Organic | NR | | |
| M | 0.164 | 0.207 | 0.188 | 0.026 | 0.145 | | |
| BM | 0.085 | 0.116 | 0.096 | 0.025 | 0.068 | | |
| WR | 30 | 63 | 29 | 1 | 25 | | |

NR, not reported.

a. M, mean; BM, balanced weighted median; WR, weight representation. M and BM are expressed as a fraction of the fertilizer N applied.

The soil texture classification in Table 8 consists of three broad groupings: coarse (including sand, loamy sand, sandy loam, loam, silty loam and silt), medium (sandy clay loam, clay loam and silty clay loam) and fine (sandy clay, silty clay and clay).

The next step was to make a summary of the data by determining straightforward mean values (M) for the NH₃ volatilization rate for each class of all the regulating factors (Table 8). Because values from one source are probably not independent, each data source received an equal weighting to calculate these means. Weighting has no systematic influence on the result in the case of independent values. However, by weighting, only 148 degrees of freedom remain instead of the 1 667 of the full data set. The weight representation (WR) given for each factor class (Table 8) depends on the number of studies reporting NH₃ volatilization rates for this factor class and the number of NH₃ volatilization rates reported in each study. As the data set includes results of 148 different studies, the maximum value of WR is 148. Where, for example, a factor class occurs with nine others in only one study the weight representation is 0.1.

Next, all NH₃ volatilization rates were log transformed. This reduced the influence of outliers, particularly the extremely high NH₃ loss rates in the data set. The residual distribution of the log-transformed NH₃ volatilization rates is closer to a normal distribution, and back-transformation results in an estimate of the median value for the NH₃ volatilization rate estimated rather than the mean. Effects or differences between factor classes were shown and studied by determining balanced weighted medians (BM) for the NH₃ loss rate for each factor class, eliminating the influence of the other factors considered. Table 8 presents the back-transformed values for the balanced weighted medians. The analysis did not study the effects of specific combinations of different factors on NH₃ volatilization rates (interaction effects) because: (i) analysing the data set for all such combinations is difficult given the number of factors and classes; and, (ii) a priori knowledge of such combinations was not available.

The next stage was to develop a linear regression model (summary model) for log-transformed weighted values of NH₃ volatilization rates, and to use it to calculate global NH₃ volatilization losses. For predicting NH₃ volatilization rates, it is advisable to perform the regression on the basis of the data used in the extrapolation. However, for laboratory measurements this is not possible. Furthermore, the resolution of 0.5 x0.5 in the maps used gives a generalized representation of environmental and management conditions on the landscape scale. Such a resolution is therefore not suitable for use in combination with local field measurements.

Data interpretation for ammonia volatilization

The results for the means and balanced weighted medians indicate that there is a clear difference between measurements carried out in the field and laboratory studies (Table 8). Various factors may account for this, including the measurement technique (generally forced draught enclosures aimed at determining the maximum NH₃ loss), though also the environmental conditions in the laboratory may favour NH₃ losses. Finally, in most cases (except in greenhouse studies) the soils in the enclosures were uncropped, which may also favour NH₃ loss.

The measurement technique used to determine NH₃ losses is also very important. The mean and balanced median values were high for ¹⁵N-based measurements and indirect open measurement (ioc). The mean value for the forced draught technique (cfd) is higher than that for micrometeorological techniques (m), while the balanced medians show the reverse order. The estimates for both techniques derive from a large number of observations in the data base, providing a much firmer basis than the data available for the other techniques.

The influence of the type of crop is less important than the location or measurement technique used (Table 8). The mean for grass is 20 percent lower than that for upland crops, and 10 percent lower than that for flooded systems. The mean values confirm the expectation that NH₃ volatilization rates are generally lower in grasslands than in croplands, but the balanced medians show almost no difference.

However, the effect of the type of fertilizer applied on the NH₃ loss is, as expected from the literature review, very important. The mean values and balanced medians are in broad agreement with expert judgements. One exception is anhydrous ammonia where the mode of application is not accounted for. The effect of the type of fertilizer applied on the NH₃ volatilization is, as expected, very important. Differences between fertilizer types occur both in the mean and balanced median, with the highest values for AN applied to grazing land, then for manure, and urea, and the lowest values for CN and anhydrous ammonia.

Broadcasting and application of fertilizer in liquid form have similar balanced medians. Incorporation leads to an important reduction of 50 percent in comparison with broadcasting. In rice systems the application of fertilizer before inundation (bf; i/f) and application at panicle initiation (bpi) has much lower balanced median values than application to the flooded field (b; bw). The reduction of NH₃ volatilization that is achievable by application at panicle

initiation compared to broadcasting at transplanting is 50 percent, which is in agreement with the literature review. In contrast to the application mode, the application rate exerts no clear influence on NH_3 loss rates.

The results for soil properties agree, to varying degrees, with the expectations based on studies in the literature. The balanced medians for soil $\text{pH} > 8.5$ exceed those for the pH range of 5.5 to 7.3 by 61 percent, and those for $\text{pH} \in 5.5$ by 80 percent. The balanced medians for soil pH in the range of 7.3 to 8.5 exceed those for the range of 5.5 to 7.3 by 39 percent and those for $\text{pH} \in 5.5$ by 55 percent.

The effect of soil CEC is somewhat less clear than that of soil pH . The mean values for the different CEC classes show a consistent pattern, with lower NH_3 volatilization in soils with high CEC than for low CEC. The balanced medians are 40 percent lower for $\text{CEC} > 32$ cmol/kg than for soils with $\text{CEC} < 32$ cmol/kg. However, in the balanced medians the relationship between NH_3 volatilization rates and CEC for soils with $\text{CEC} < 32$ cmol/kg has disappeared.

The influence of soil organic carbon content is not clear. Both the mean and balanced median values are higher for the lowest soil organic carbon class than for the second lowest. The number of observations is small in the classes 3 and 4, and estimates are therefore less reliable than for classes 1 and 2.

The influence of soil texture is not clear, with high means and balanced medians for the NH_3 volatilization rate for medium textured topsoils, and lower values for both fine and coarse textured soils.

Regression

The next stage was to study the combined effects of the different factors using regression analysis. From the set of factors selected for the above data summary, the regression concerned only those that had a clear influence on NH_3 volatilization, except for weather-related factors and the measurement technique and location factors.

It was necessary to exclude weather-related factors a priori from the regression as lack of data prevents their use in extrapolations. The different measurement techniques and locations evidenced clear differences between both the means and balanced medians. However, their exclusion depended on the fact that it is not possible to use measurement techniques for predictions as the a priori knowledge for judging their accuracy is lacking, while the data set used cannot provide a sufficient basis for explaining the influence of the

measurement location. Therefore, the regression yields an average value for NH_3 volatilization rates applying to all measurement techniques and locations included in the data set.

The N application rate, soil organic carbon content and soil texture show no consistent relationship with NH_3 volatilization rates and were therefore not used in the regression. The absence of a relationship may be due to the fact that soil organic carbon and texture are the main determinants of soil CEC. Therefore, the influence of soil C and texture on NH_3 volatilization rates is assumed to be included in the CEC factor.

The factors selected for the regression included: crop type, fertilizer type and application mode, temperature, soil pH , and CEC. Table 9 presents the fitted parameters for the different factor classes of the resulting summary model. The factor values are log-transformed. The calculation for the NH_3 loss rate is: $\exp(\text{factor value crop type} + \text{fertilizer type} + \text{application mode} + \text{soil pH} + \text{soil CEC} + \text{climate})$. For example, for grass fertilized with urea by broadcasting (b) on a soil with a $\text{pH } 5.5 < \text{pH} < 7.3$, a $\text{CEC of } 16 < \text{CEC} < 24$, in a temperate climate the NH_3 volatilization rate is: $\exp(-0.158 + 0.666 - 1.305 - 0.933 + 0.012 - 0.402) = \exp(-2.120) = 0.120$. Hence, the loss as a fraction of urea-N application is 0.120.

The variance accounted for by the model is about 30 percent. This means that individual NH_3 volatilization values from research papers differ, on average, about 15 percent less from the means calculated by the model than from their common mean. Hence, the summary model is not suitable for calculating NH_3 volatilization rates from measurements in individual research papers for specific sites. The model calculates median NH_3 volatilization rates, which are of more interest when the working scale is that of landscapes rather than point measurements done under site-specific conditions.

TABLE 9.**Factor values in the linear regression model**

| Crop type | | Fertilizer type^a | |
|------------------------------|--------|------------------------------------|--------|
| Upland crops | -0.045 | AS | 0.429 |
| Grass | -0.158 | Urea | 0.666 |
| Flooded crops | 0 | AN | -0.35 |
| | | CAN | -1.064 |
| | | AA | -1.151 |
| | | Nsol. ^a | -0.748 |
| | | CN | -1.585 |
| | | ABC | 0.387 |
| | | UAN | 0 |
| | | MAP | -0.622 |
| | | DAP | 0.182 |
| | | U+DAP | 0.803 |
| | | U+MAP | -0.48 |
| | | UP | -0.25 |
| | | UUP | 0.45 |
| | | O | 0.995 |
| | | Grazing | -0.378 |
| | | Urine | 0.747 |
| | | AN+grazing | 1.229 |
| | | Uc | 0.25 |
| | | U+KCl | 0.469 |
| | | U+Ca/Mg | 0.753 |
| | | UCN | -0.43 |
| | | U+FYM | 0.385 |
| Method of application | | | |
| b | -1.305 | | |
| i | -1.895 | | |
| s | -1.292 | | |
| bf;i/f | -1.844 | | |
| bpi | -2.465 | | |
| Soil pH | | | |
| pH≤5.5 | -1.072 | | |
| 5.5<pH≤7.3 | -0.933 | | |
| 7.3<pH≤8.5 | -0.608 | | |
| pH>8.5 | 0 | | |
| Soil CEC | | | |
| CEC≤16 | 0.088 | | |
| 16<CEC≤24 | 0.012 | | |
| 24<CEC≤32 | 0.163 | | |
| CEC>32 | 0 | | |
| Climate | | | |
| Temperate climate | -0.402 | | |
| Tropical climate | 0 | | |

a. The factor value for ammonium phosphates is calculated on the basis of the global composition of 80% DAP and 20% MAP; for compound NK (mainly KNO₃) the value for CN is used; factor values for the other compound fertilizers are based on the various compound NP and NPK fertilizers in the data set of measurements; for N solutions the data collected for all N fertilizers applied in solution used.

Chapter 5

Global estimates

DATA ON LAND USE, FERTILIZER MANAGEMENT AND ENVIRONMENT

The land cover/use distribution data for areas of grassland, rice and other crops came from Zuidema *et al.* (1994). This global database derives from maps of natural vegetation and climate in combination with statistical information from FAO (2000). As the resolution is 0.5°, there are errors in the gridded data for small countries. For example, the total land area of a small country may not be represented by the 0.5° grid cells. Such problems occur often with islands or coastal areas.

The data on grassland management are extremely scant. However, in order to extrapolate NH_3 volatilization from fertilizer and manure application, it is necessary to know the location of more or less intensively used grasslands. This process involved some simple assumptions with three types of grassland being defined: (i) intensively used grasslands, receiving only inputs from animal manure, and defined as grassland located within arable areas; (ii) fertilized grasslands, receiving nutrient inputs from mineral fertilizers as reported by IFA/IFDC/FAO (1999) in addition to animal manure (these grasslands are located within intensively used grasslands); (iii) extensive grasslands consisting of the remaining grasslands given by Zuidema *et al.* (1994) were not considered as they are grazed and deliberate application of fertilizers or manure was assumed to be negligible.

For most countries, the intensively used grasslands are in those cells where arable land makes up at least one third of the area. It was necessary to make many exceptions in order to match the areas with those of IFA/IFDC/FAO (1999).

For wetland rice fields, the N fertilizer use per hectare values are from IFA/IFDC/FAO (1999), with some exceptions. The N fertilizer use for the other, dryland crops was calculated as the difference between total N fertilizer

use from IFA (1999) and the sum of the N used in wetland rice and grasslands from IFA/IFDC/FAO (1999), with exceptions for some countries.

The quantity of animal manure N available for fertilizing crops and grasslands was calculated from total excretion by excluding the excretion during grazing, use of animal manure as fuel and NH_3 losses during storage of animal manure. Half the animal excreta available as fertilizer were assumed to be used in croplands and the other half in grasslands. For some countries, it was necessary to adjust the percentage of the manure applied on grasslands in order to avoid excessive application rates. Thus, the assumed maximum N application rate was 200 kg/ha for industrialized countries, and 50 kg/ha for developing countries; this affects the availability for crops. Manure application rates for wetland rice and upland crops were assumed to be equal.

Ammonia volatilisation rates are linear with respect to the N application rate. However, the models for N_2O and NO emissions show a non-linear response of emissions to N application rates. Therefore, for N_2O and NO the average country application rates used for ammonia would not give a correct estimation of emissions. To account for the fact that not all agricultural fields receive fertilizer, IFA/IFDC/FAO (1999) data on mineral fertilizer N application rates and the percentage of each crop actually receiving fertilizer N were used to calculate the mean application rate for upland crops for the area actually fertilized. These data are available for 49 countries, including some with 100 percent of the fields fertilized. The analysis included data for 38 developing countries and made the assumption that a fraction of the fields receive fertilizer in order to determine apparent total N use per country. For other developing countries, N application rates were assumed equal to calculated rates for Central America, South America, Asia and Africa. There are no statistics on the use of animal manure in croplands and grasslands. Estimates for regions within countries may be available, but sometimes they do not correspond to official statistics or are outdated. The paucity of data makes it necessary to generalize. Therefore, for animal manure applied on croplands the same minimum N rates were used. For manure applied to grasslands N application rates of 50 percent of those for upland crops were assumed to reflect lower application rates in grasslands relative to crops.

In addition to the land use data, the 0.5° resolution information on soil pH, CEC, organic C content, soil texture and soil drainage came from Batjes (1997), and a map of climate types with 0.5° resolution from Fresco *et al.* (1998). For NH_3 this climate database was not used as it is difficult to estimate the temperature at the time of fertilizer application (generally the beginning of the growing season). Therefore, for extrapolating the NH_3 volatilization rates,

the assumption was that the temperature at fertilizer application is $>20^\circ\text{C}$ between 40°N and 40°S , and $<20^\circ\text{C}$ at other latitudes.

A number of additional assumptions had to be made. Measurements of N_2O and NO emissions during the crop season when the rice fields are inundated dominate the data set. Therefore, in the extrapolation of N_2O emissions from rice, for rice the model parameters for 'other crops' were used to account for the emissions during the post-harvest period.

Fertilizer management, which had a significant effect on NH_3 volatilization rates, is the least known aspect in the extrapolation. Although much is known at local and national level, it is difficult to generalize such information in a global inventory. Much of the fertilizer applied to rice in Southeast Asia is either broadcast directly onto flooded soil 14-21 days after transplanting or broadcast directly onto flooded soil after transplanting. Broadcasting is also common in grasslands.

Therefore, the general assumption about fertilizer application was that of a basal application by broadcasting. Exceptions included anhydrous ammonia (estimates based on incorporation), and fertilizer solutions (liquid). Animal manure used in rice cultivation was assumed to be incorporated. If incorporation of fertilizers is a more common practice, the estimates of NH_3 loss would require adjustment downwards.

It is difficult to quantify uncertainties associated with scaling. Uncertainties in fertilizer use stem primarily from the grouping of different N fertilizer types into one category. The data on fertilizer use by crops have a varying degree of reliability; data are more complete and probably more certain in industrialized countries than in developing countries. However, there are no statistics on fertilizer management. The extrapolation included assumptions on the mode of application of fertilizers and manure. Although application rates vary between crops and farmers within countries, the spatial distribution of fertilizer application rates is not well known. Moreover, it is not known if certain fertilizer types are preferentially used for specific crops or grasslands.

The distribution of arable lands is well known, but data on the distribution and the management of grasslands are uncertain. Although information is available on the use of mineral fertilizers in grasslands, the application of animal manure in grasslands is based on a global estimate. For different world regions and individual countries, the application of animal manure is highly uncertain.

Animal populations are well known, although the season in which censuses are made does cause some uncertainty. The uncertainty in the data on animal populations is probably <10 percent. Most of the uncertainty in the NH₃ volatilization rate for animal manure stems from the assumptions on N excretion and waste management. For developing countries, in particular, there are no reliable data on waste management practices and on the use of animal manure in grasslands and arable lands. Therefore, uncertainty is probably highest for tropical countries and lowest for western Europe.

EXTRAPOLATION FOR NITROUS OXIDE AND NITRIC OXIDE

The simple models for N₂O and NO discussed in Chapter 4 were used in a GIS with the geographic information and the assumptions on fertilizer management discussed above.

The combined resulting figures from Tables 10 and 11 yield a global annual N₂O-N emission (about 3.5 million t) and NO-N emissions (about 2.0 million t). Some 34 percent of the global annual N₂O-N emission from cropped fields of 3.2 million t stems from developed countries and 66 percent from developing countries. The global emission from cropped fields is 3.3 percent of the N fertilizer input (3.3 percent in developed countries and 3.4 percent in developing countries). The annual NO-N emission from fertilized crops amounts to about 1.5 million t, 44 percent from developed and 56 percent from developing countries. This is 2.0 percent of the N input for developed countries and 1.4 percent for developing countries.

The annual N₂O-N emission from fertilized grasslands amounts to about 0.3 million t (58 percent from developed countries and 42 percent from developing countries), and that of NO-N to about 0.5 million t (68 percent stemming from developed and 32 percent from developing countries) (Table 11).

The fertilizer induced N₂O emissions were calculated as the total emission minus that of unfertilized fields (all other conditions equal to the fertilized plot), expressed as a percentage of the N input (Table 12). The results indicate important differences between fertilizer types. The global annual fertilizer induced N₂O-N emission is about 0.9 million t, or 0.8 percent of the N input, lower than the 1.25 percent estimated by Bouwman (1996). The highest fertilizer induced emission rates are for urea and other straight N fertilizers (primarily ABC used in China), and the lowest for organic fertilizers.

TABLE 10.
N₂O and NO emission estimates from N fertilizer and animal manure application on crops, 1995

| Region ^a | Area 000 000 ha | Fertilizer N | Animal manure | N ₂ O-N emission 000 t | NO-N emission |
|---------------------|--------------------|-----------------|------------------|---|------------------|
| Canada | 46 | 1 576 | 207 | 67 | 103 |
| United States | 190 | 11 150 | 1 583 | 316 | 167 |
| Central America | 40 | 1 424 | 351 | 106 | 31 |
| South America | 111 | 2 283 | 1 052 | 260 | 102 |
| North Africa | 22 | 1 203 | 36 | 53 | 24 |
| Western Africa | 75 | 156 | 140 | 171 | 41 |
| Eastern Africa | 41 | 109 | 148 | 78 | 31 |
| Southern Africa | 42 | 480 | 79 | 72 | 24 |
| OECD Europe | 90 | 6 416 | 3 408 | 233 | 131 |
| Eastern Europe | 48 | 1 834 | 757 | 70 | 35 |
| Former Soviet Union | 230 | 1 870 | 2 392 | 262 | 182 |
| Near East | 58 | 2 376 | 180 | 83 | 45 |
| South Asia | 206 | 12 941 | 3 816 | 614 | 186 |
| East Asia | 95 | 24 345 | 5 150 | 397 | 269 |
| Southeast Asia | 87 | 4 216 | 941 | 247 | 85 |
| Oceania | 49 | 651 | 63 | 109 | 29 |
| Japan | 4 | 436 | 361 | 12 | 11 |
| World | 1 436 | 73 467 | 20 664 | 3 150 | 1 498 |

a. World regions from Kreileman et al. (1998).

The global annual fertilizer induced emission for NO-N is about 0.6 million t, or 0.5 percent of the N input (Table 12), which is in agreement with the estimate of 0.5 percent by Veldkamp and Keller (1997a). The highest fertilizer induced emission rates of 0.8 percent are for compound NK-N and other straight nitrogen fertilizers (primarily ABC used in China). The lowest fertilizer induced emission rates are calculated for organic fertilizers (0.4%).

The calculation of a median estimate involved the use of log-transformed emissions and balancing. The result is a best estimate of the emission for a specific combination of factor classes. With the residual maximum likelihood

TABLE 11.
N₂O and NO emission from N fertilizer and animal manure application on grasslands, 1995

| Region ^a | Area 000 000 ha | Fertilizer N | Animal manure N 000 t | N ₂ O-N emission 000 t | NO-N emission |
|---------------------|--------------------|-----------------|-----------------------------|---|------------------|
| Canada | 20 | 0 | 207 | 7 | 40 |
| United States | 84 | 0 | 1 583 | 31 | 50 |
| Central America | 22 | 25 | 351 | 15 | 14 |
| South America | 59 | 12 | 1 051 | 34 | 44 |
| North Africa | 10 | 0 | 34 | 5 | 6 |
| Western Africa | 48 | 0 | 137 | 30 | 26 |
| Eastern Africa | 26 | 0 | 148 | 13 | 17 |
| Southern Africa | 24 | 31 | 78 | 13 | 14 |
| OECD Europe | 50 | 3 074 | 3 085 | 56 | 85 |
| Eastern Europe | 18 | 210 | 737 | 8 | 13 |
| Former Soviet Union | 177 | 760 | 2 389 | 58 | 115 |
| Near East | 13 | 17 | 167 | 5 | 10 |
| South Asia | 10 | 0 | 425 | 6 | 5 |
| East Asia | 29 | 0 | 1 404 | 9 | 15 |
| Southeast Asia | 15 | 0 | 477 | 8 | 11 |
| Oceania | 20 | 175 | 52 | 29 | 40 |
| Japan | 0 | 27 | 59 | 1 | 1 |
| World | 625 | 4 331 | 12 386 | 329 | 507 |

a. World regions from Kreileman et al. (1998).

procedure it is not possible to produce an estimate of the standard error of the model estimate of emissions. Therefore, the standard errors were calculated for a range of combinations of the factors considered for a weighted multiple regression model for N₂O. The multiple regression used only those records in the data set that have values for all factors (353 measurements). The variance explained by this model is 50 percent, and the overall uncertainty ranges from about -40 percent to +70 percent based on twice the standard error accounting for 95 percent of the data. The uncertainty of the residual maximum likelihood model is probably less than that of the weighted multiple regression because the residual maximum likelihood procedure considered more measurements

TABLE 12.
Global N use and fertilizer induced N₂O and NO emission estimates by fertilizer type

| Fertilizer type ^a | Global N use (million t/year) | N ₂ O-N loss ^b (%) | NO-N loss (%) |
|--|----------------------------------|---|------------------|
| Ammonium sulphate | 2.4 | 1.0 | 0.6 |
| Urea | 34.4 | 1.1 | 0.6 |
| Ammonium nitrate | 7.5 | 0.9 | 0.5 |
| Calcium ammonium nitrate | 3.6 | 0.6 | 0.6 |
| Ammonia, direct application | 4.6 | 0.8 | 0.5 |
| Nitrogen solutions | 4.0 | 0.9 | 0.6 |
| Other straight nitrogen fertilizers ^c | 10.1 | 1.0 | 0.8 |
| Ammonium phosphates | 4.1 | 0.8 | 0.6 |
| Other compound NP-N | 1.7 | 0.8 | 0.5 |
| Compound NK-N | 0.0 | 0.8 | 0.8 |
| Compound NPK-N | 6.1 | 0.7 | 0.5 |
| Total mineral fertilizers | 78.5 | 1.0 | 0.6 |
| Organic fertilizers | 33.0 | 0.6 | 0.4 |
| Total mineral and organic fertilizers | 111.6 | 0.8 | 0.5 |

a. Estimates for fertilizer types are based on areas where only mineral fertilizers are applied (using the factor values for individual fertilizer types), areas where organic and mineral fertilizers are applied in combination (using the factor value for these combinations) and areas where organic fertilizers are used (using factor value for organic fertilizers).

b. Possible uptake of NO by plant leaves has not yet been accounted for. This uptake may be particularly important in grasslands and perennial crops.

c. Most (90%) of the other straight N fertilizers are used in China, predominantly (95%) in the form of ammonium bicarbonate. The remainder is mainly ammonium chloride. For both fertilizers the factor value for ammonium sulphate was used.

(846 for N₂O). For NO, the number of degrees of freedom after weighting is too small to derive a model that resembles the residual maximum likelihood model, and it is therefore difficult to estimate the uncertainty of the model.

The models for N₂O and NO are non-linear with respect to the N application rate. Although estimates for the areas actually fertilized were used, the heterogeneity in N application rates may still influence the model results.

The associated error in the extrapolated emission estimates is acceptable when compared to other uncertainties in the global extrapolation. The models are not suitable for predicting emissions from measurements in individual research papers for specific sites. However, the mean emission rates for factor class combinations are of more interest for extrapolation to landscape conditions than individual measurements.

EXTRAPOLATION FOR AMMONIA

The summary model (Chapter 4) was used to calculate regional and global volatilization losses. This extrapolation exercise combined various sources of statistical data and geographical information. Tables 13 and 14 summarize the results of the extrapolation. The global ammonia loss from mineral fertilizers of 11 million t N/year (14 percent of mineral fertilizer N use) estimated in this report is in close agreement with Bouwman *et al.* (1997). The results indicate that NH₃ volatilization rates in developing countries exceed those in developed countries by a factor of 4.3.

The global NH₃ loss from the annual use of 11.8 million t of mineral fertilizer N in wetland rice cultivation amounts to 2.3 million t N/year, or 20 percent of the N application. Most of this loss occurs in developing countries (97 percent). In upland crops, 14 percent of the 61.7 million t of mineral fertilizer N is lost as NH₃, with higher loss rates in developing countries (18 percent) than in developed countries (8 percent). In grasslands, the annual global use of mineral fertilizer N is 4.3 million t N, with estimated loss rates of 13 percent for developing countries and 6 percent for developed countries. Nearly 100 percent of mineral N fertilizer use in grasslands is in developed countries.

The global NH₃ loss from the annual use of 12.4 million t N in animal manure in grasslands amounts to 2.7 million t N/year, of which about 60 percent stems from developed countries. The NH₃ volatilization rate from animal manure is 22 percent of the N application (20 percent in developed countries and 25 percent in developing countries). In upland crops, 26 percent of the 17.4 million t N from animal manure is lost as NH₃, with higher loss rates in developing countries (29 percent) than in developed countries (22 percent). This higher rate for developing countries is due to high temperatures and the dominance of the use of urea, ABC and ammonium sulphate in wetland rice cultivation. The volume of animal manure applied annually to upland crops is 8.6 million t N in developed countries and 8.8 million t N in developing countries. In wetland rice systems, the estimated annual use of N

from animal manure is 3.3 million t N, mainly in developing countries. As incorporation is assumed to be prevalent in rice cultivation, the NH₃ volatilization rates are lower than for upland crops (17 percent in developing countries and 16 percent in developed countries).

TABLE 13.
NH₃ volatilization loss estimates from mineral N application on fertilized grasslands, upland crops and wetland rice by region, 1995

| Region ^a | Fertilized grasslands | | | Upland crops | | | Wetland rice | | |
|---------------------|-------------------------|---------------------|---------------------------------------|-------------------------|---------------------|---------------------------------------|-------------------------|---------------------|---------------------------------------|
| | Area (million ha) | N use (000 t) | NH ₃ -N loss (000 t) | Area (million ha) | N use (000 t) | NH ₃ -N loss (000 t) | Area (million ha) | N use (000 t) | NH ₃ -N loss (000 t) |
| Canada | 0 | 0 | 0 | 46 | 1 576 | 140 | 0 | 0 | 0 |
| United States | 0 | 0 | 0 | 189 | 10 982 | 787 | 1 | 168 | 15 |
| Central America | 1 | 25 | 3 | 40 | 1 392 | 215 | 0 | 32 | 5 |
| South America | 1 | 12 | 1 | 109 | 2 049 | 348 | 3 | 234 | 43 |
| North Africa | 0 | 0 | 0 | 21 | 1 126 | 214 | 1 | 78 | 16 |
| Western Africa | 0 | 0 | 0 | 73 | 130 | 19 | 1 | 26 | 4 |
| Eastern Africa | 0 | 0 | 0 | 40 | 109 | 17 | 1 | 1 | 0 |
| Southern Africa | 3 | 31 | 3 | 42 | 477 | 51 | 0 | 3 | 0 |
| OECD Europe | 37 | 3 074 | 156 | 90 | 6 384 | 448 | 0 | 32 | 3 |
| Eastern Europe | 3 | 210 | 13 | 48 | 1 834 | 123 | 0 | 1 | 0 |
| Form. Soviet Union | 33 | 760 | 59 | 229 | 1 856 | 157 | 1 | 14 | 1 |
| Near East | 4 | 17 | 3 | 57 | 2 305 | 422 | 1 | 71 | 18 |
| South Asia | 0 | 0 | 0 | 162 | 8 295 | 1 827 | 44 | 4 646 | 1 030 |
| East Asia | 0 | 0 | 0 | 69 | 19 855 | 3 318 | 26 | 4 490 | 829 |
| Southeast Asia | 0 | 0 | 0 | 52 | 2 405 | 421 | 35 | 1 811 | 335 |
| Oceania | 20 | 175 | 23 | 49 | 639 | 108 | 0 | 12 | 2 |
| Japan | 0 | 27 | 4 | 2 | 265 | 36 | 2 | 171 | 24 |
| Total | 103 | 4 331 | 265 | 1 319 | 61 678 | 8 650 | 117 | 11 788 | 2 327 |

a. Regions designated for global change research as defined by Kreileman *et al.* (1998).

TABLE 14.
NH₃ volatilization loss estimates from animal manure application on intensively used grasslands, upland crops and wetland rice by region, 1995

| Region ^a | Fertilized grasslands | | | Upland crops | | | Wetland rice | | |
|---------------------|-------------------------|---------------------|---------------------------------------|-------------------------|---------------------|---------------------------------------|-------------------------|---------------------|---------------------------------------|
| | Area (million ha) | N use (000 t) | NH ₃ -N loss (000 t) | Area (million ha) | N use (000 t) | NH ₃ -N loss (000 t) | Area (million ha) | N use (000 t) | NH ₃ -N loss (000 t) |
| Canada | 20 | 207 | 41 | 46 | 207 | 45 | 0 | 0 | 0 |
| United States | 84 | 1 583 | 366 | 189 | 1 573 | 394 | 1 | 10 | 2 |
| Central America | 22 | 351 | 92 | 40 | 349 | 105 | 0 | 3 | 0 |
| South America | 59 | 1 051 | 271 | 109 | 1 020 | 291 | 3 | 32 | 5 |
| North Africa | 10 | 34 | 11 | 21 | 33 | 12 | 1 | 3 | 1 |
| Western Africa | 48 | 137 | 35 | 73 | 137 | 39 | 1 | 3 | 1 |
| Eastern Africa | 26 | 148 | 40 | 40 | 143 | 43 | 1 | 6 | 1 |
| Southern Africa | 24 | 78 | 20 | 42 | 78 | 23 | 0 | 2 | 0 |
| OECD Europe | 50 | 3 085 | 561 | 90 | 3 402 | 684 | 0 | 7 | 1 |
| Eastern Europe | 18 | 737 | 130 | 48 | 757 | 149 | 0 | 0 | 0 |
| Form. Soviet Union | 177 | 2 389 | 511 | 229 | 2 378 | 555 | 1 | 15 | 2 |
| Near East | 13 | 167 | 53 | 57 | 177 | 64 | 1 | 2 | 1 |
| South Asia | 10 | 425 | 114 | 162 | 2 850 | 917 | 44 | 965 | 175 |
| East Asia | 29 | 1 404 | 324 | 69 | 3 500 | 953 | 26 | 1 650 | 276 |
| Southeast Asia | 15 | 477 | 114 | 52 | 544 | 147 | 35 | 396 | 62 |
| Oceania | 20 | 52 | 14 | 49 | 63 | 19 | 0 | 0 | 0 |
| Japan | 0 | 59 | 16 | 2 | 186 | 51 | 2 | 175 | 28 |
| Total | 625 | 12 386 | 2 712 | 1 319 | 17 396 | 4 492 | 117 | 3 270 | 555 |

a. Regions designated for global change research as defined by Kreileman et al. (1998)

Table 15 compares the global mean NH₃ volatilization rates for the fertilizer types (IFA, 1999) based on the summary regression model with other inventories from the literature. The results are in agreement with the ECETOC (1994) and Bouwman *et al.* (1997) estimates, except for ammonium sulphate and the compound fertilizers including MAP and DAP. The data collected in this report for ammonium sulphate are based on 176 measurements from a great number of different research papers and from different sites with different conditions. Hence, the results can be considered to be representative for actual conditions in the field.

The NH₃ volatilization rates found for phosphorous containing fertilizers are higher than values presented by ECETOC (1994) and Bouwman *et al.*

TABLE 15.
NH₃ volatilization loss rates for mineral fertilizer category and for animal manure, 1995

| Fertilizer category | Use million t | NH ₃ volatilization loss | | | Comparative values | |
|----------------------------------|------------------|-------------------------------------|-----------|------------|--|-----------------------|
| | | Total million t | Mean % | Range % | Bouwman <i>et al.</i> , (1997) % | ECETOC (1994) % |
| Ammonium sulphate | 2.4 | 0.4 | 16 | 12-20 | 8 | 5-15 |
| Urea | 34.4 | 7.3 | 21 | 18-26 | 15-25 | 10-20 |
| Ammonium nitrate | 7.5 | 0.5 | 6 | 5-9 | 2 | 1-3 |
| Calcium ammonium nitrate | 3.6 | 0.1 | 3 | 2-4 | 2 | 1-3 |
| Ammonia, direct application | 4.6 | 0.1 | 2 | 1-3 | 4 | 4 |
| Nitrogen solutions | 4.0 | 0.2 | 5 | 2-11 | 2.5 | - |
| Other straight nitrogen | 10.1 | 1.5 | 15 | 10-22 | 20-30 | - |
| Ammonium phosphates ^a | 4.1 | 0.5 | 11 | 5-25 | 2-5 | 5 |
| Other compound NP-N ^b | 1.7 | 0.2 | 11 | 6-19 | - | - |
| Compound NK-N ^c | 0.0 | 0.0 | 2 | 1-5 | - | - |
| Compound NPK-N ^b | 6.1 | 0.5 | 9 | 5-16 | 2-4 | 1-5 |
| Total mineral fertilizers | 78.5 | 11.2 | 14 | 10-19 | - | - |
| Animal manure | 33.0 | 7.8 | 23 | 19-29 | 20 | 20 |

a. Results for AP are based on the global estimated mix of 80% DAP and 20% MAP.

b. The results for other NP-N and NPK-N are the mean of the estimates for all P containing N fertilizers present in the data set.

c. The estimate for NK-N (mainly NO₃⁻-based fertilizer) is based on CN.

(1997). This may be due to the influence of phosphate which may change the environment to favour increased NH_3 loss by precipitating Ca. Both the formula (pH) and form of the phosphate added can influence the reaction with Ca, and therefore NH_3 losses. It is not certain what the composition is of the fertilizer categories NP-N and NPK-N. In this report the volatilization rate for these compound fertilizers was based on data for all NP fertilizers present in the data base; the NH_3 volatilization rate for ammonium phosphate (AP) is based on the results for MAP and DAP (Tables 9 and 15).

Uncertainties in the results of the extrapolation stem from uncertainties in the summary model as such and uncertainties caused by scaling errors. The range of NH_3 volatilization rates for the various fertilizers was calculated using the standard errors of the regression. The standard errors depended on the combination of factor classes selected, but appeared to be very similar for individual fertilizer types across crop types, climate and soil conditions. Therefore, the range of volatilization rates was calculated for a number of combinations of factor classes for each crop type and fertilizer type. This was done on the basis of twice the standard errors to include 95 percent of the observations. The average deviation from the model results in Table 15 was applied to the estimated global NH_3 volatilization loss for each fertilizer category. The resulting range in the estimates for the global NH_3 volatilization loss from all fertilizers is 10-19 percent for all mineral fertilizers and 19-29 percent for animal manure. The range for some individual fertilizers is much wider, depending on the number of representations in the data set (Table 15). The calculated ranges do not account for the omissions in the summary model or for scaling errors.

Because the fertilizer application rate was found not to influence the NH_3 volatilization rate, NH_3 losses could be scaled up based on average country fertilizer and manure application rates. Hence, it is recognized that there are errors in the spatial distribution of the mix of fertilizers and their application rates, and their combination with soil conditions. However, for the 0.5 resolution used, this error is acceptable.

Chapter 6

Conclusions

NITROUS OXIDE AND NITRIC OXIDE EMISSIONS

The major factors controlling N_2O emissions include those that regulate N availability, i.e. N application rate, climate and soil C content. The N application rate determines directly N availability. Soil C content is a proxy for soil fertility, while climate influences the speed of soil processes and plant / microbe competition through temperature and moisture. It is apparent from studies in the tropics that plant uptake can exceed microbe competition, therefore denitrification rates can be relatively low even in warm, moist conditions.

Factors influencing the relative rate of N_2O compared to total denitrification loss are soil texture, drainage and pH. Fine soil texture, poor drainage and neutral to slightly acidic soil reaction are conditions that favour N_2O emission. Management factors that influence N_2O emission are crop type (with N_2O emission increasing in the order: grass, non-leguminous annual crops, leguminous crops) and type of fertilizer (with the highest values being for anhydrous ammonia and mixtures of mineral and organic fertilizers).

The major factors regulating NO emission are: N application rate, fertilizer type, soil organic C content and soil drainage. Similar to N_2O , NO emissions increase with N application rate and soil C content. However, contrary to N_2O , NO emissions from well drained exceed those from poorly drained soils. The factors relating to climate and length of measurement period do not have a significant influence on NO emissions.

Measurement techniques are very important in assessing gas flux measurements. Closed and open chamber techniques yield about equal emission estimates for N_2O and NO . However, other techniques yield markedly different emission estimates, particularly for N_2O . The data show that N_2O emission estimates in agricultural fields should be based on

measurements with a frequency of at least one measurement per day in periods with high emission rates (e.g., periods following fertilizer application or rainfall events) and with lower frequencies in periods with low emission rates, extended over periods of at least one year. For NO shorter measurement periods may yield most of the effect of N fertilization because the factor relating to the length of measurement period does not have a significant influence on NO emissions. Hence, N fertilization may have a more long-lasting effect on N₂O than on NO emissions.

The estimated global annual N₂O-N and NO-N emissions from crop and grassland amount to 3.5 million t of N₂O-N emission and 2.0 million t of NO-N emission. The fertilizer induced emissions for N₂O and NO amount to 0.8 and 0.5 percent, respectively. The global estimates presented in Chapter 4 account for the major controls of N₂O and NO emissions at the landscape-scale from arable land and grassland.

AMMONIA VOLATILIZATION

Although it includes a large number of measurements from the literature, the data set is probably not a fair representation of environmental and management conditions found in the real world. This is because in many cases the measurements were carried out under conditions or in places prone to high N gas losses. Therefore, the report adopted a statistical approach in an attempt to avoid this problem of lack of representativeness.

The comparison of straightforward means and the balanced medians resulted in the selection of the most important regulators of NH₃ volatilization. The results are in good agreement with European and global inventories of NH₃ volatilization from fertilizers, except for ammonium sulphate, ABC and the different compound NP fertilizers. The data in this report indicate that these fertilizers are more prone to NH₃ volatilization than previously thought.

Although the nitrogen fertilizer statistics used may be reliable, the analysis presented in this report involves many uncertainties (Chapter 3). Moreover, the timing and mode of fertilizer application have a strong influence on NH₃ volatilization loss. The greatest uncertainty stems from underrepresentation in the data set of measurements of NH₃ volatilization rates in tropical cropping systems.

Finally, the regression model developed in the report is a representation of the literature data available. Many factors that are known to be crucial controls of NH₃ volatilization, e.g. wind speed, and floodwater pH in flooded

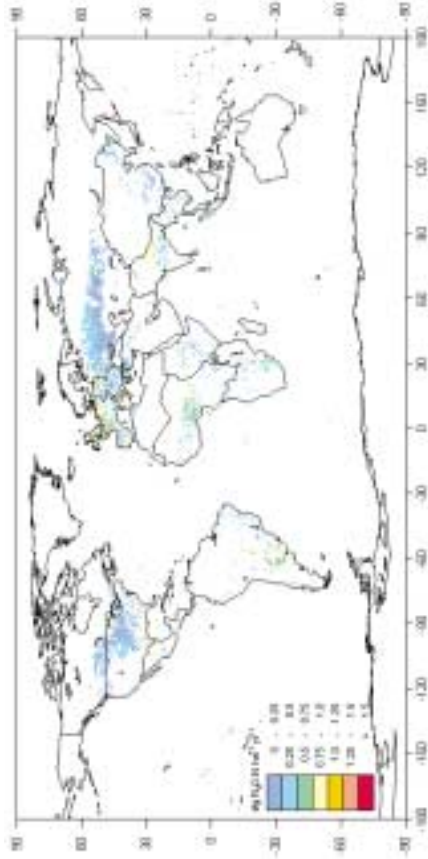
systems, could not be included in the regression model. This is because such data are simply not available on the global scale. Therefore, it is difficult to indicate the uncertainty in the prediction of NH₃ losses.

Perhaps the major uncertainty is in the omission of the effect of rainfall on NH₃ volatilization. In practice, farmers apply fertilizers in periods just after rainfall events, or in periods during which they expect rainfall. The omission of rainfall events may lead to a systematic overestimation of NH₃ volatilization losses. However, it is difficult to estimate the uncertainty caused by this omission.

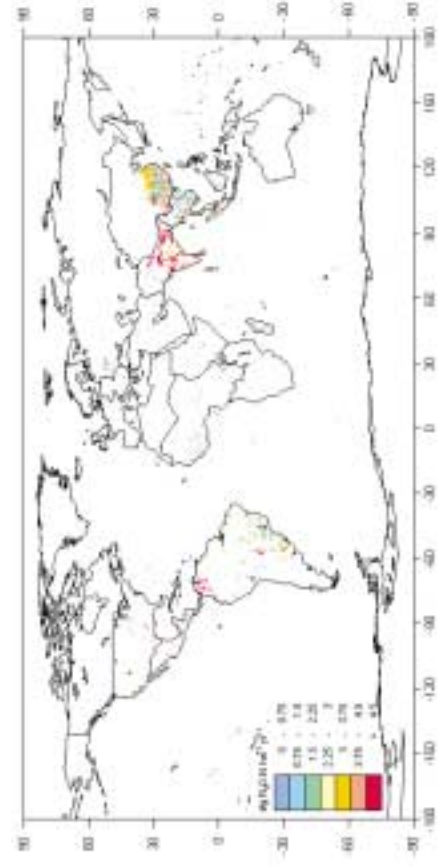
The uncertainty of the results of the summary model is about ±30 percent. The uncertainty for individual fertilizer types depends on the number of measurements available. On a grid cell basis the uncertainty is probably greater because the allocation of arable lands and grasslands is based on statistics combined with land cover maps and land suitability. In particular the allocation of the intensively used grasslands and fertilized grasslands was based on very simple assumptions.

The outcome of the model shows that the potential impact of fertilizer use regulations would be modest from a global emission perspective. The quantities involved, however, constitute a valuable plant nutrient source. Farmers' ability to curtail such losses will primarily relate to economic incentives, in particular in South and South East Asia.

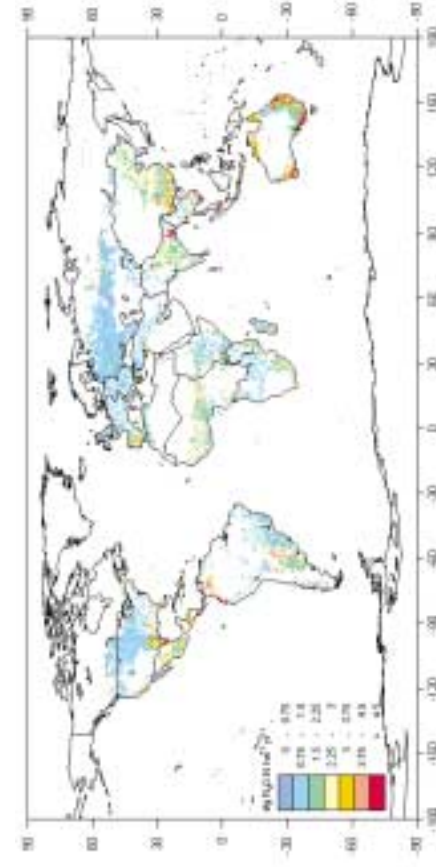
Annex 1 Maps



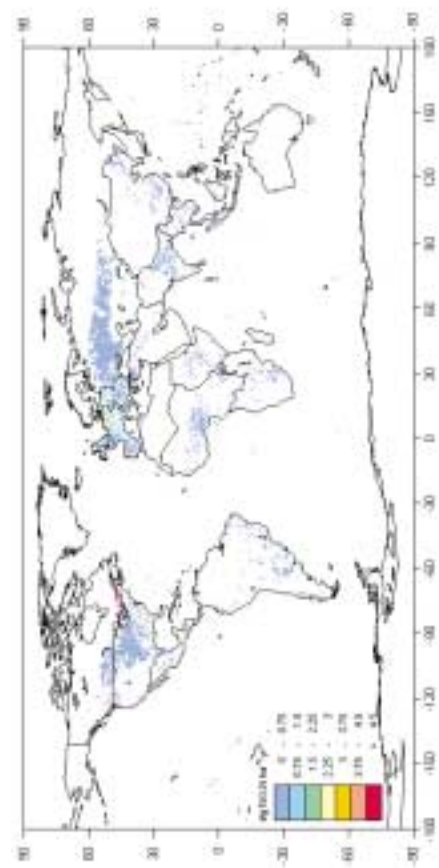
Map 1: Emission of N_2O from grasslands where mineral fertilizers and animal manure were applied. Emissions represent the emissions per year, accounting for country specific cropping intensities.



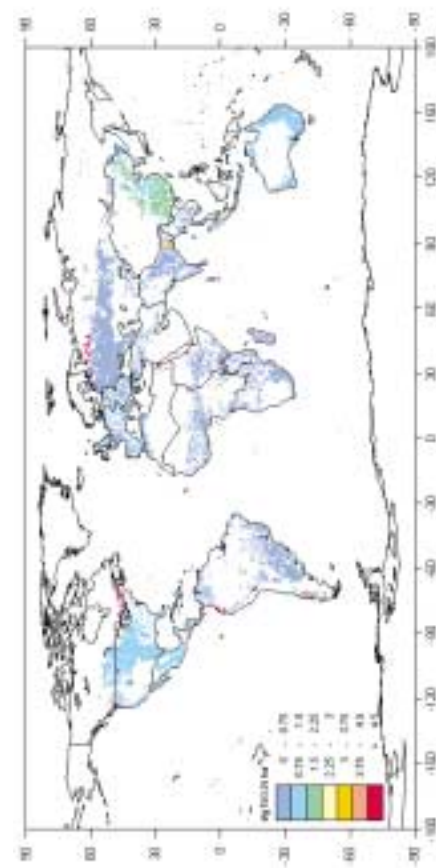
Map 2: Emission of N₂O from wetland rice where mineral fertilizers and animal manure were applied. Emissions represent the emissions per year, accounting for country specific cropping intensities.



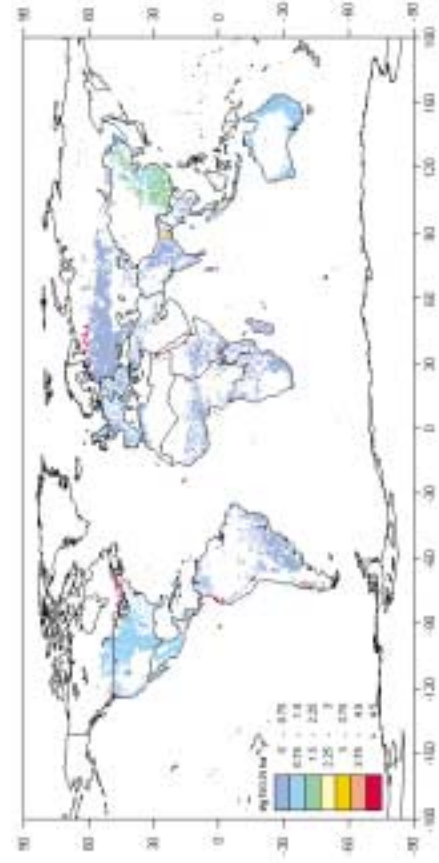
Map 3: Emission of N₂O from upland crops where mineral fertilizers and animal manure were applied. Emissions represent the emissions per year, accounting for country specific cropping intensities.



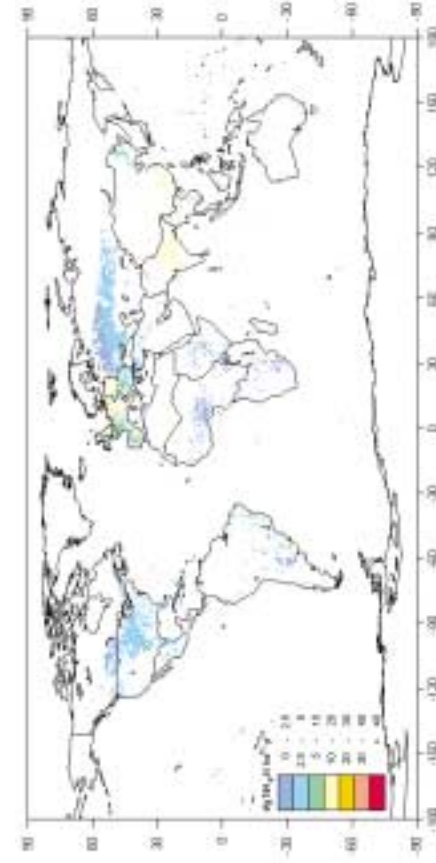
Map 4: Emission of NO from grasslands where mineral fertilizers and animal manure were applied. Emissions represent the emissions per year, accounting for country specific cropping intensities.



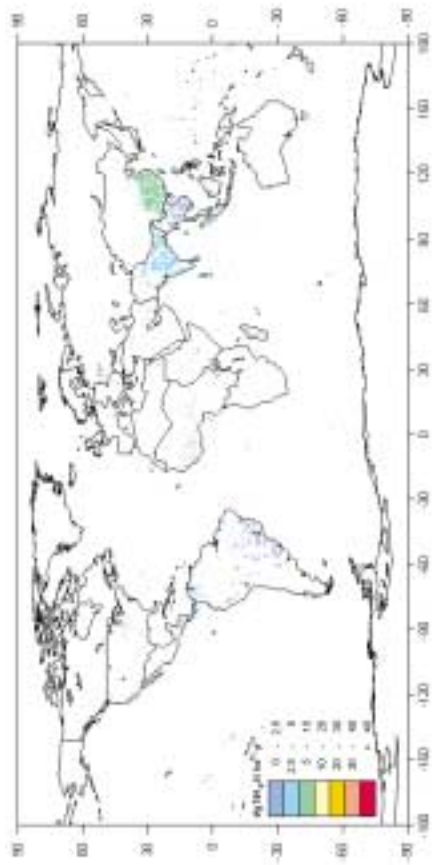
Map 5: Emission of NO from wetland rice where mineral fertilizers and animal manure were applied. Emissions represent the emissions per year, accounting for country specific cropping intensities.



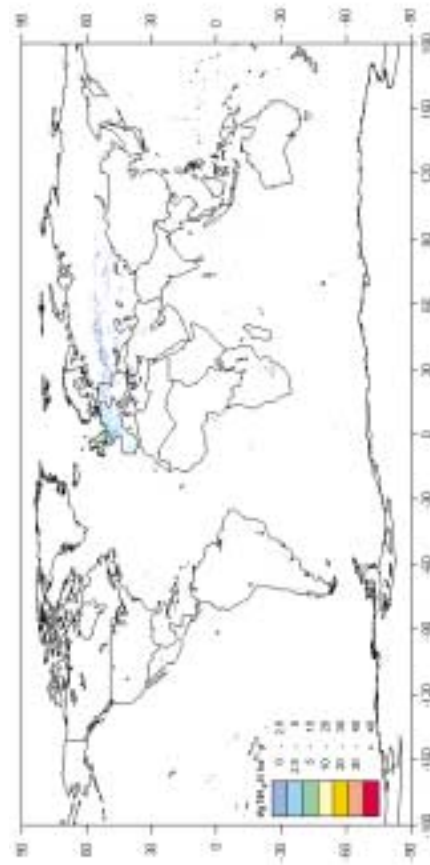
Map 6: Emission of NO from upland crops where mineral fertilizers and animal manure were applied. Emissions represent the emissions per year, accounting for country specific cropping intensities.



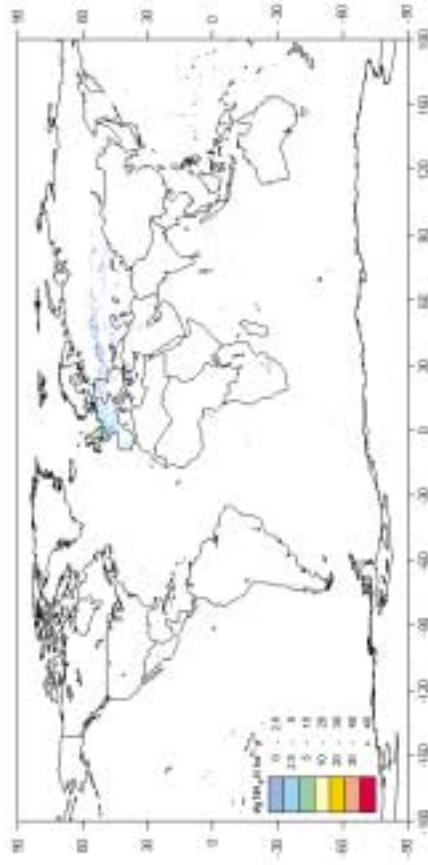
Map 7: Estimated annual emission of NH₃ for 1995 from animal manure applied to grasslands.



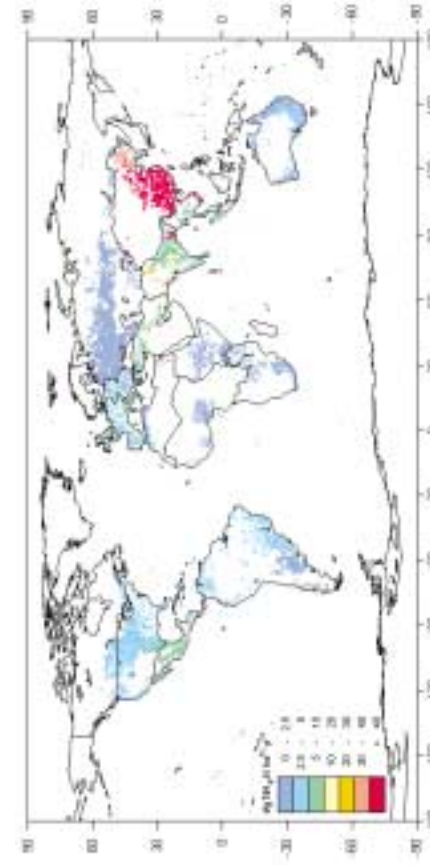
Map 8: Estimated annual emission of NH_3 for 1995 from animal manure applied to wetland rice.



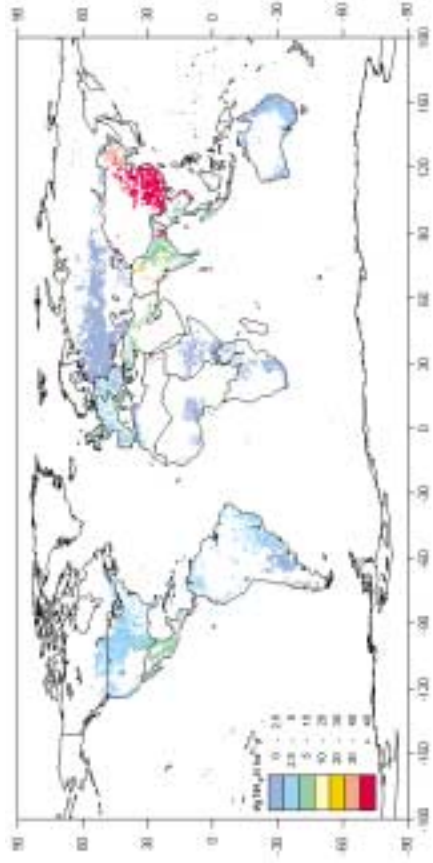
Map 9: Estimated annual emission of NH_3 for 1995 from animal manure applied to upland crops.



Map 10: Estimated annual emission of NH_3 for 1995 from mineral fertilizers applied to grasslands. The emission is an annual estimate. High values may be caused by high cropping intensities, such as in China, while low values may be the result of low cropping intensities. The emission rates per ha of harvested land may thus differ from those presented here.



Map 11: Estimated annual emission of NH_3 for 1995 from mineral fertilizers applied to wetland rice. The emission is an annual estimate. High values may be caused by high cropping intensities, such as in China, while low values may be the result of low cropping intensities. The emission rates per ha of harvested land may thus differ from those presented here.



Map 12: Estimated annual emission of NH_3 for 1995 from mineral fertilizers applied to upland crops. The emission is an annual estimate. High values may be caused by high cropping intensities, such as in China, while low values may be the result of low cropping intensities. The emission rates per ha of harvested land may thus differ from those presented here.

Annex 2 Tables

TABLE 16.
N₂O emissions from the data set (kg N₂O-N/year/ha)

| N application rate (kg/ha) | 0 | 1-50 | 50-100 | 100-150 | 150-200 | 200-250 | >250 | |
|-----------------------------------|-----------------|------------------|-----------------|----------------|----------------|----------------|----------------|--------------|
| No. observations | 206 | 33 | 184 | 113 | 98 | 56 | 156 | |
| Mean | 1.1 | 1.6 | 1.5 | 1.9 | 2.4 | 3.3 | 6.8 | |
| Median | 0.6 | 1.2 | 0.7 | 1.2 | 1.2 | 1.4 | 4.1 | |
| Balanced mean | 0.5 | 1.8 | 1.8 | 2.0 | 2.3 | 3.1 | 5.4 | |
| Balanced median | 0.5 | 1.0 | 1.0 | 1.2 | 1.4 | 1.9 | 3.5 | |
| Climate type | Clim1 | Clim2 | Clim3 | Clim4 | Clim5 | Clim6 | Clim7 | Clim8 |
| No. observations | 253 | 389 | 50 | 61 | 77 | 8 | 6 | 2 |
| Mean | 2.2 | 2.5 | 4.2 | 5.7 | 2.1 | 0.2 | 1.2 | 4.0 |
| Median | 1.0 | 1.3 | 0.8 | 1.8 | 0.9 | 0.2 | 1.1 | 4.0 |
| Balanced mean | 1.8 | 1.2 | 4.3 | 4.5 | 1.8 | 0.6 | 2.4 | 3.5 |
| Balanced median | 0.9 | 0.8 | 2.0 | 1.7 | 1.3 | 0.5 | 0.7 | 1.2 |
| Soil organic C content (%) | <1.0 | 1.0-3.0 | 3.0-6.0 | >6 | | | | |
| No. observations | 92 | 353 | 126 | 18 | | | | |
| Mean | 1.3 | 2.0 | 2.7 | 5.0 | | | | |
| Median | 0.8 | 1.0 | 1.5 | 1.6 | | | | |
| Balanced mean | 2.0 | 1.6 | 2.1 | 4.4 | | | | |
| Balanced median | 0.8 | 0.7 | 1.1 | 1.8 | | | | |
| Soil N content (%) | <0.05 | 0.05-0.15 | 0.15-0.3 | >0.3 | | | | |
| No. observations | 2 | 71 | 228 | 29 | | | | |
| Mean | 3.0 | 1.6 | 2.3 | 4.2 | | | | |
| Median | 3.0 | 1.0 | 1.2 | 2.3 | | | | |
| Balanced mean | 2.3 | 2.2 | 3.3 | 2.3 | | | | |
| Balanced median | 0.7 | 1.0 | 1.4 | 1.2 | | | | |

| Soil texture class | Coarse | Medium | Fine | Soil drainage | Poor | Good |
|------------------------------------|----------------|------------------|----------------|----------------------|-------------|-------------|
| No. observations | 447 | 147 | 134 | No. observations | 193 | 460 |
| Mean | 2.8 | 2.6 | 1.9 | Mean | 2.8 | 2.6 |
| Median | 1.2 | 1.3 | 0.9 | Median | 1.4 | 1.1 |
| Balanced mean | 2.3 | 2.1 | 3.1 | Balanced mean | 2.6 | 2.4 |
| Balanced median | 1.2 | 0.8 | 1.3 | Balanced median | 1.2 | 0.9 |
| Soil pH | <5.5 | 5.5-7.3 | >7.3 | | | |
| No. observations | 93 | 359 | 109 | | | |
| Mean | 2.8 | 2.3 | 2.0 | | | |
| Median | 1.0 | 1.1 | 0.7 | | | |
| Balanced mean | 2.9 | 3.3 | 1.3 | | | |
| Balanced median | 1.2 | 1.2 | 0.8 | | | |
| Fertilizer type | AA | AF | AN | CAN | NF | Mix |
| No. observations | 38 | 59 | 117 | 61 | 53 | 25 |
| Mean | 4.4 | 0.6 | 3.0 | 2.3 | 2.6 | 3.4 |
| Median | 2.7 | 0.4 | 1.4 | 1.7 | 0.7 | 2.2 |
| Balanced mean | 4.9 | 1.9 | 3.2 | 2.0 | 2.5 | 3.3 |
| Balanced median | 1.4 | 1.1 | 1.2 | 1.0 | 0.7 | 1.8 |
| Fertilizer type | NP | O | OS | UUR | UAN | |
| No. observations | 16 | 74 | 41 | 98 | 37 | |
| Mean | 3.8 | 4.7 | 5.9 | 1.9 | 3.2 | |
| Median | 3.0 | 1.0 | 4.2 | 0.7 | 2.7 | |
| Balanced mean | 1.7 | 3.1 | 3.5 | 2.2 | 3.3 | |
| Balanced median | 0.7 | 1.2 | 1.4 | 1.2 | 0.9 | |
| Fertilizer application mode | b | bpi | i | s | | |
| No. observations | 163 | 4 | 162 | 122 | | |
| Mean | 3.4 | 0.8 | 2.7 | 2.4 | | |
| Median | 1.3 | 0.7 | 1.2 | 1.4 | | |
| Balanced mean | 2.8 | 2.6 | 2.7 | 2.3 | | |
| Balanced median | 1.3 | 1.0 | 1.2 | 1.0 | | |
| Timing of application | Single | Single/ps | Split | | | |
| No. observations | 337 | 153 | 104 | | | |
| Mean | 2.5 | 4.2 | 3.3 | | | |
| Median | 1.0 | 2.2 | 1.6 | | | |
| Balanced mean | 3.0 | 2.1 | 2.4 | | | |
| Balanced median | 1.2 | 1.2 | 1.5 | | | |

| Crop type | Grass | Grass+ clover | Legume | Rice | Other |
|--|-----------------|----------------------|------------------|------------------|------------------|
| No. observations | 177 | 16 | 36 | 61 | 512 |
| Mean | 3.3 | 1.1 | 1.3 | 0.7 | 2.9 |
| Median | 1.4 | 0.9 | 1.1 | 0.5 | 1.3 |
| Balanced mean | 2.7 | 1.2 | 3.6 | 1.9 | 3.2 |
| Balanced median | 1.0 | 0.8 | 2.9 | 0.3 | 2.1 |
| Measurement technique | c | co | g | m | cf |
| No. observations | 766 | 15 | 7 | 32 | 25 |
| Mean | 2.5 | 1.7 | 4.5 | 1.7 | 8.8 |
| Median | 1.1 | 1.2 | 3.6 | 1.3 | 3.3 |
| Balanced mean | 2.7 | 1.5 | 2.1 | 2.8 | 4.1 |
| Balanced median | 0.9 | 0.7 | 2.6 | 1.1 | 0.8 |
| Experiment length (days) | <120 | 120-180 | 180-240 | 240-300 | >300 |
| No. observations | 343 | 132 | 42 | 34 | 277 |
| Mean | 1.4 | 2.3 | 2.1 | 2.6 | 4.5 |
| Median | 0.5 | 1.2 | 1.2 | 1.3 | 2.3 |
| Balanced mean | 2.0 | 1.9 | 2.1 | 2.4 | 4.2 |
| Balanced median | 0.7 | 0.7 | 1.1 | 1.2 | 1.9 |
| Measurement frequency¹ | >1m/d | 1m/d | 1m./2-3 d | 1m./3-7 d | <1m./w |
| No. observations | 140 | 286 | 78 | 262 | 46 |
| Mean | 1.5 | 2.9 | 2.6 | 2.8 | 4.5 |
| Median | 0.8 | 1.1 | 1.1 | 1.3 | 2.0 |
| Balanced mean | 2.1 | 3.1 | 3.1 | 3.2 | 2.7 |
| Balanced median | 1.0 | 0.9 | 1.9 | 1.3 | 1.4 |

Reprinted from Bouwman et al., 2001b

1. For the classes of measurements frequency of one or more than one per day, generally these high frequencies are used in periods following fertilizer application or rainfall events, with lower frequencies in periods with low emission rates.

TABLE 17.
NO emissions from the data set (kg NO-N/year/ha)

| N application rate (kg/ha) | 0.0 | 1-100 | 100-200 | >200 | | | | | |
|-----------------------------------|----------------|----------------|----------------|----------------|--------------|--------------|--------------|--------------|--|
| No. observations | 21 | 45 | 16 | 17 | | | | | |
| Mean | 0.3 | 0.5 | 0.5 | 5.4 | | | | | |
| Median | 0.1 | 0.1 | 0.6 | 2.8 | | | | | |
| Balanced mean | 1.7 | 2.4 | 2.5 | 4.3 | | | | | |
| Balanced median | 0.2 | 0.8 | 1.0 | 1.7 | | | | | |
| Climate type | Clim1 | Clim2 | Clim3 | Clim4 | Clim5 | Clim6 | Clim7 | Clim8 | |
| No. observations | 19 | 34 | 18 | 0 | 18 | 10 | 0 | 0 | |
| Mean | 1.1 | 1.1 | 1.0 | - | 2.7 | 0.1 | - | - | |
| Median | 0.6 | 0.1 | 0.6 | - | 0.8 | 0.1 | - | - | |
| Balanced mean | -3.5 | 1.8 | 1.9 | - | 0.4 | 1.2 | - | - | |
| Balanced median | 0.3 | 0.4 | 1.6 | - | 0.3 | 0.9 | - | - | |
| Soil organic C content (%) | <3.0 | >3.0 | | | | | | | |
| No. observations | 47 | 8 | | | | | | | |
| Mean | 0.5 | 4.5 | | | | | | | |
| Median | 0.1 | 0.4 | | | | | | | |
| Balanced mean | 0.2 | 0.5 | | | | | | | |
| Balanced median | 0.3 | 1.3 | | | | | | | |
| Soil Texture class | Coarse | Medium | Fine | | | | | | |
| No. observations | 71 | 13 | 5 | | | | | | |
| Mean | 1.5 | 0.4 | 0.0 | | | | | | |
| Median | 0.2 | 0.2 | 0.0 | | | | | | |
| Balanced mean | 0.3 | 0.4 | 0.4 | | | | | | |
| Balanced median | 1.1 | 0.4 | 0.4 | | | | | | |
| Soil drainage | Poor | Well | | | | | | | |
| No. observations | 7 | 60 | | | | | | | |
| Mean | 0.5 | 1.8 | | | | | | | |
| Median | 0.5 | 0.4 | | | | | | | |
| Balanced mean | -0.4 | 1.1 | | | | | | | |
| Balanced median | 0.4 | 0.8 | | | | | | | |
| Soil pH | <5.5 | >5.5 | | | | | | | |
| No. observations | 23 | 53 | | | | | | | |

| Mean | 1.7 | 0.3 | | | | |
|---|---------------|---------------------|---------------|-------------|--------------|------------|
| Median | 0.1 | 0.1 | | | | |
| Balanced mean | 0.6 | 0.1 | | | | |
| Balanced median | 0.8 | 0.4 | | | | |
| Fertilizer type | AA | AF | AN | CAN | NF | Mix |
| No. observations | 2 | 14 | 17 | 5 | 15 | 1 |
| Mean | 16.3 | 1.1 | 1.7 | 0.5 | 0.5 | 6.3 |
| Median | 16.3 | 0.2 | 0.4 | 0.4 | 0.1 | 6.3 |
| Balanced mean | 1.1 | 0.3 | -0.2 | -1.1 | 0.1 | 4.3 |
| Balanced median | 0.5 | 0.4 | 0.6 | 0.2 | 0.5 | 2.0 |
| Fertilizer type | NP | O | OS | UUR | UAN | |
| No. observations | 0 | 3 | 0 | 19 | 1 | |
| Mean | - | 0.6 | - | 1.3 | 1.0 | |
| Median | - | 0.5 | - | 0.0 | 1.0 | |
| Balanced mean | - | -0.4 | - | 0.7 | -0.5 | |
| Balanced median | - | 0.2 | - | 0.5 | 4.2 | |
| Fertilizer application mode | b | bpi | i | s | | |
| No. observations | 27 | 0 | 8 | 33 | | |
| Mean | 1.1 | - | 5.5 | 0.1 | | |
| Median | 0.8 | - | 0.4 | 0.0 | | |
| Balanced mean | 1.4 | - | -1.1 | -0.3 | | |
| Balanced median | 1.0 | - | 0.2 | 0.5 | | |
| Timing of fertilizer application | Single | Single/ps | Split | | | |
| No. observations | 28 | 3 | 6 | | | |
| Mean | 1.7 | 3.1 | 0.7 | | | |
| Median | 0.1 | 2.7 | 0.8 | | | |
| Balanced mean | 1.8 | -0.8 | -1.3 | | | |
| Balanced median | 0.5 | 1.0 | 0.5 | | | |
| Crop type | Grass | Grass-clover | Legume | Rice | Other | |
| No. observations | 23 | 0 | 16 | 2 | 51 | |
| Mean | 1.9 | - | 0.7 | 1.4 | 1.3 | |
| Median | 0.7 | - | 0.1 | 1.4 | 0.1 | |
| Balanced mean | 1.0 | - | 1.7 | -3.5 | 2.3 | |

| | | | | | |
|---|------------------|----------------|------------------|------------------|------------------|
| Balanced median | 0.6 | - | 0.4 | 0.4 | 1.1 |
| Measurement technique | c | cf | | | |
| No. observations | 30 | 69 | | | |
| Mean | 0.5 | 1.6 | | | |
| Median | 0.5 | 0.1 | | | |
| Balanced mean | 0.3 | 0.4 | | | |
| Balanced median | 0.5 | 0.6 | | | |
| Length of experiment (days) | <120 | >120 | | | |
| No. observations | 64 | 35 | | | |
| Mean | 0.4 | 3.0 | | | |
| Median | 0.1 | 0.8 | | | |
| Balanced mean | -1.2 | 1.9 | | | |
| Balanced median | 0.3 | 1.1 | | | |
| Measurement frequency ¹ | >1m./d | 1m./d | 1m./2-3 d | 1m./3-7 d | <1m./w |
| No. observations | 51 | 20 | 8 | 10 | 2 |
| Mean | 0.2 | 2.9 | 4.6 | 0.9 | 0.7 |
| Median | 0.1 | 1.1 | 0.4 | 0.7 | 0.7 |
| Balanced mean | -1.0 | 1.2 | 7.1 | -2.0 | -1.6 |
| Balanced median | 0.2 | 1.0 | 1.0 | 0.9 | 1.2 |

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1. For the classes of measurements frequency of one or more than one per day, generally these high frequencies are used in periods following fertilizer application or rainfall events, with lower frequencies in periods with low emission rates.

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