AP42 Section:	9.2.1
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Emission Factor Documentation for AP-42
Section 9.2.1

Fertilizer Application

Draft Report

For U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Emission Factor and Inventory Group
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NOTICE

This document is a preliminary draft. It has not been formally released by the U. S. Environmental Protection Agency and should not at this stage be construed to represent Agency policy. It is being circulated for comments on its technical merit and policy implications.

PREFACE

This report was prepared by Midwest Research Institute (MRI) for the Office of Air Quality Planning and Standards (OAQPS), U. S. Environmental Protection Agency (EPA), under Contract No. 68-D2-0159, Work Assignment No. 4604-04 and Purchase Order No. 8D-1933-NANX. Mr. Dallas Safriet was the requester of the work.

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Fertilizer Application

1. INTRODUCTION

The document *Compilation of Air Pollutant Emission Factors* (AP-42) has been published by the U. S. Environmental Protection Agency (EPA) since 1972. Supplements to AP-42 have been routinely published to add new emission source categories and to update existing emission factors. AP-42 is routinely updated by EPA to respond to new emission factor needs of EPA, State and local air pollution control programs, and industry.

An emission factor is a representative value that attempts to relate the quantity of a pollutant released to the atmosphere with an activity associated with the release of that pollutant. Emission factors usually are expressed as the weight of pollutant divided by the unit weight, volume, distance, or duration of the activity that emits the pollutant. The emission factors presented in AP-42 may be appropriate to use in a number of situations, such as making source-specific emission estimates for areawide inventories for dispersion modeling, developing control strategies, screening sources for compliance purposes, establishing operating permit fees, and making permit applicability determinations. The purpose of this report is to provide background information from test reports and other information to support preparation of AP-42 Section 9.2.1, Fertilizer Application.

This background report consists of five sections. Section 1 includes the introduction to the report. Section 2 gives a description of fertilizer application. It includes a characterization of the industry, a description of the different methods of application, a characterization of emission sources and pollutants emitted, and a description of the technology used to control emissions resulting from these sources. Section 3 is a review of emission data collection and emission measurement procedures. It describes the literature search, the screening of emission data reports, and the quality rating system for both emission data and emission factors. Section 4 details how the new AP-42 section was developed. It includes the review of specific data sets and a description of how candidate emission factors were developed. Section 5 presents the AP-42 Section 9.2.1, Fertilizer Application. Appendices A through P include references, supporting documentation, and calculations used to determine the emission factors.

2. INDUSTRY DESCRIPTION

This section includes a brief discussion of chemical fertilizer consumption in the United States and the basic application methods used for fertilizer in gaseous, fluid, or solid form. Particulate and gaseous air emissions generated during the application of chemical fertilizers are discussed in relationship to naturally occurring soil-based biological/chemical reactions, other biological activities, fertilizer application variables, soil conditions, and climate.

2.1 INDUSTRY CHARACTERIZATION[1-5]

Fertilizer production industries include manufacturers of fertilizer plant food (SIC 2871), nitrogen and organic fertilizers (SIC 2873), phosphate, potash, and other fertilizers (SIC 2874), and pesticides and other agricultural chemicals (SIC 2879). Fertilizers are distributed through agricultural supply retailers, farmer cooperatives, and custom fertilizer dealers. There are an estimated 13,000 retail fertilizer businesses providing bulk blended, fluid-mix, and bagged fertilizers. Application is performed by farmers and by fertilizer dealers using specialized application equipment.

Demand for fertilizer has seen moderate growth in recent years. Growth in production was approximately 6 percent between 1993 and 1994. Of the total 45.1 million megagrams (Mg) (49.6 million tons) sold in 1994, 51.7 percent was dry bulk fertilizer, 40.7 percent was fluid fertilizer, and 7.6 percent was dry bagged fertilizer. Total usage in 1994 was:

- Dry bulk fertilizers, 23.3 million Mg (25.6 million tons)
- Fluid fertilizers (including anhydrous ammonia), 18.4 million Mg (20.2 million tons)
- Dry bagged fertilizers, 3.5 million Mg (3.8 million tons)

Consumption data for the top 10 states in agricultural single and multiple nutrient fertilizer consumption as of June 30, 1994 are presented in Table 2-1. These 10 states account for approximately 53 percent of agricultural fertilizer sales in the United States.

Once the fertilizer has been sold, fertilizer is applied by various means to crop producing fields. Uncontrolled emissions are generated by the application process (immediate emissions) as well as by the soil reactions with the fertilizer (latent emissions). These uncontrolled emissions are affected by the method of application and the chemical and biological reactions within the soil. Immediate emissions include ammonia (NH_3), particulate matter (PM), and the volatilized fertilizer. Latent emissions may include NH_3, nitrous oxide (N_2O), NO_x ($NO + NO_2$), sulfur dioxide (SO_2), PM, and the volatilized fertilizers. No data exist for the volatilized fertilizer, SO_2, and PM emissions. Gaseous emissions from phosphorus containing fertilizer application are expected to be low as compared to the gaseous emissions from nitrogen containing and sulfur containing fertilizers.

Recent scientific papers discussing the biological mechanisms for NO_x emissions from the soil have cited evidence to show that essentially all (over 90 percent) NO_x emissions are in the form of NO and little, if any, are in the form of NO_2. The formation of NO_2 occurs through the rapid oxidation of the NO by ozone present in the soil or the air immediately above the soil surface. There is no evidence to conclude that appreciable quantities of NO_2 are formed directly in the soil.

2.2 METHODS OF APPLICATION[4,6,7]

Although many types of fertilizers are manufactured, the basic application methods depend on whether the fertilizer is in gaseous, fluid, or solid form. Methods for application of each of these three forms of fertilizer are discussed below.

2.2.1 Application of Gaseous Fertilizers

Anhydrous NH_3 is the only fertilizer that is a gas at room temperature (with compression and cooling, it becomes a liquid that is about 60 percent as dense as water). Approximately 8.3 million Mg (9.1 million tons) of anhydrous NH_3 are produced annually. Of that amount, approximately 5.2 million Mg (5.7 million tons) are applied to croplands; the remainder is used to manufacture other nitrogen fertilizers. Anhydrous NH_3 is the most economical form of nitrogen available to the farmer. It is readily absorbed in water up to concentrations of 30 percent to 40 percent by weight, depending on the temperature. Anhydrous NH_3 is the most concentrated nitrogen fertilizer available, with 82 percent nitrogen. Because NH_3 can be dissolved in water (aqua ammonia), it can be applied directly to soil or indirectly through irrigation systems. However, the primary application method is via direct soil injection of anhydrous NH_3 as described below.

Anhydrous NH_3 is stored as a liquid under pressure and is applied by injection into the soil. The liquified NH_3 quickly vaporizes into a gas, but is captured by soil components including water, clay, and other minerals. The equipment used generally consists of a vehicle (usually a tractor); a pressurized tank mounted on a trailer and filled with anhydrous NH_3; a metering system; and a distribution manifold with applicator knives and tube holders. Critical components of the injection system are the metering assembly and the tube holder.

The metering system consists of a control board, usually located in the cab of the vehicle, a connection to the speedometer of the vehicle, and an NH_3 meter located near the tank. This meter may consist of a variable orifice meter or a piston pump. With a variable orifice meter system, the rate of application is determined by the speed of the tractor, the swath width, and the size of the orifice. With the piston pump system, the rate of application is determined by the piston stroke length. Several metering systems currently in use include a feedback loop to verify movement of the vehicle with a ground movement sensor. Figure 2-1 is a schematic drawing of a simplified NH_3 metering system. The metering system is designed so that it is activated only when the vehicle is moving.

The NH_3 application system generally consists of an exit line from the pressurized tank (nurse tank) to the manifold, which feed the applicator tubes located immediately behind the applicator knives in the tilling trailer. Each knife and tube assembly can be placed at a depth ranging from 10 to 25 centimeters (cm) (4 to 10 inches [in.]) below the surface of the soil. Figure 2-2 shows one example of a simplified trailer used to apply anhydrous NH_3 and fluid fertilizers. Frequently, an application of a second fertilizer occurs simultaneously using a depth setting of 10 cm (4 in). Figure 2-3 shows four of the possible placements of applicator knives and injection tube(s) for both single and dual application. The spacing between application rows is between 30 and 45 cm (12 and 18 in), depending on the tilling trailer.

The amount of fertilizer to be applied is calibrated prior to use, based on the size of the nozzle orifices and the characteristics of the pumping system, which vary by manufacturer. After the nozzles are installed, the application of fertilizer can be calibrated based on the change of pressure within the tank and the flow control setting.

2.2.2 Application of Fluid Fertilizers

Fluid fertilizers include liquid solutions, suspensions, and slurries. Liquid solution fertilizers contain water-soluble nutrients at high concentrations, usually prepared as a mixture of nitrogen, phosphorus, and potassium (NPK) components; they are also known as liquid mixed fertilizers. Suspension fertilizers are fluid mixtures of solid and liquid materials in which the solids do not settle rapidly and can be redispersed readily with agitation to give a uniform mixture. Slurry fertilizers are fluid mixtures of solid and liquid materials in which the solids settle rapidly in the absence of agitation to form a firm layer that is difficult to resuspend. Examples of slurries include precipitation of fluid fertilizers resulting from storage for prolonged periods of very cold weather, application of elemental sulfur, and mixing of ammonium nitrate and potassium chloride to saturation leading to salting out of potassium nitrate.

The three general application methods for fluid fertilizers are aerial, irrigation, and ground application. Occasionally, aerial application of fertilizers, which is more expensive than ground application is used because it is quicker or because wet soil precludes tractor use. Irrigation application is used in areas like the southwest that make extensive use of irrigation in crop production. Irrigation application can apply fertilizers at a frequent, diluted rate. Because use of aerial and irrigation techniques are less common than ground applications and because emission data are unavailable for those two methods, the discussion below focuses on ground application.

Four different methods of ground application are used: broadcast, band, row, and deep banding (injection).

- In the broadcast application, fluid fertilizers are broadcast by high flotation applicators. High flotation applicators usually have up to 20 nozzles equally spaced and positioned several feet above the ground (see diagram in Figure 2-4). Broadcast application occurs at high speeds with accurately metered application rates.

- In band application, the height of the nozzles is reduced and the band width of the resultant spray is narrowed so the fluid fertilizers can be applied between rows of growing crops. Figure 2-5 shows a typical band application.

- In row application, which usually occurs at the time of planting, fluid or dry fertilizer is applied in a row near the planted seed. The distance from the fertilizer row to the seed row is dependent on the amount of fertilizer, the type of fertilizer, and the crop.

- The deep banding or injection technique is similar to that used for anhydrous ammonia. This technique is also referred to as root zone application.

The equipment used for broadcast, band, and row application of fertilizers consists of the ground vehicle, a liquid tank with fluid fertilizer, a metering system, and a distribution manifold with spray nozzles. The metering system, manifold, and the calibration system are the same as described for gaseous fertilizers in Section 2.2.1. The optional port for liquid fertilizer is shown in Figure 2-1. The metering system (not shown) is similar to that for anhydrous ammonia, except that the pressure valve is replaced with a tank volume controller, and the piston pump is usually a centrifugal pump.

The major differences in the distribution manifolds for gaseous and fluid fertilizers are the size of booms and the types of spray nozzles. The manifolds are usually composed of two 6- to 20-meter (m) (20 to 65-foot [ft]) booms with nozzles set on 51- to 152-cm (20-in to 60-in.) centers with no more than 20 nozzles. Several varieties of nozzles can be used depending on the application method. By varying the type and height of the nozzles and the flow rate, fluid fertilizer can be applied in overlapping coverage for broadcast application or in discrete bands for band/row application.

The ground equipment used for deep band application of fertilizers is the same as described in Section 2.2.1. Typically, a phosphate fertilizer and ammonia are banded together in a "dual application" method.

2.2.3 Application of Solid Fertilizers

Solid fertilizers can be applied using a broadcast technique by aircraft or by high flotation applicator. Because no emission data were found for aerial application, the discussion focuses on high flotation application. Note however, that irrespective of application method, solid fertilizers are frequently mixed with herbicides in order to reduce the expense of a second application.

The equipment for broadcast application of solid fertilizers by high flotation applicator consists of the vehicle, a hopper containing solid fertilizer, a metering system, and the distribution manifold. The metering and calibration systems are generally the same as those described in Section 2.2.1 for gaseous fertilizer application. Centrifugal and boomed spreaders are used to broadcast solid fertilizers.

A centrifugal spreader is composed of one or two spinning disks which broadcast fertilizer in 12- to 15-m (39- to 50-ft) swaths. Figure 2-6 shows an example of a centrifugal spreader with a double spinner applicator. A spread pattern calibration is an essential part of applicator maintenance. Possible adjustments include positioning the spinner blades, positioning where the fertilizer drops on the spinner blades, changing the spinner speed, and changing the fertilizer particle size.

Two types of boomed spreaders are available and both look similar to the fluid fertilizer broadcast system shown in Figure 2-4. One type moves fertilizer by an auger through the boom and can supply up to 4 nozzles. Another moves fertilizer with high velocity air to as many as 20 nozzles. Each nozzle has a deflector to distribute the fertilizer. Nozzles can spread fertilizer in an arc pattern from 0.15 m to 3.7 m (0.5 to 12 ft) in diameter.

2.3 EMISSIONS[7-14]

Both PM and gaseous air emissions are generated as a result of the application of chemical fertilizers. Emissions may occur during application, shortly after application, and for extended periods following application.

2.3.1 Emission Mechanisms

Emissions from the application of fertilizer generally are attributed to four different mechanisms: (1) soil reactions with the applied fertilizer generating increased gaseous emissions including NO_x, N_2O, NH_3, and SO_2; (2) volatilization of the fertilizer immediately behind the vehicle generating gaseous emissions of NH_3 and the fertilizer itself, (3) soil disturbance generating PM emissions where soil particles and other materials in the soil become airborne, and (4) volatilization of the fertilizer immediately above the solid fertilizer trailer generating gaseous emissions of NH_3 and other fertilizers. Emissions attributed to the first mechanism are often called latent emissions, while those attributed to the other three mechanisms are called immediate emissions. The specific emission points associated with these mechanisms are illustrated in Figures 2-7a through 2-7e for gaseous fertilizer application, ground application of fluid fertilizers, irrigation application of fluid fertilizers, ground application of solid fertilizers, and aerial application of fluid and solid fertilizers, respectively.

Emissions that result from the reactions between the soil and the applied fertilizer are believed to be higher than emissions that result from the other three mechanisms. Consequently, most of the data available on emissions from fertilizer application are estimates of emissions from soil-fertilizer reactions.

2.3.2 Particulate Matter

Particulate matter emissions of solid fertilizer compounds are primarily generated along with wind-blown dust during broadcast application. Constituents of gaseous, fluid, or solid fertilizers and manure (or their reaction products) attached to soil particles may also become airborne much later as a result of soil disturbances caused by wind (i.e., wind erosion) or mechanical operations (e.g., tilling). These emissions are associated with mechanism (3) in Section 2.3.1.

Particulate matter emissions from fertilizers or manures have not been characterized in the literature. However, heavy elements listed as Hazardous Air Pollutants (HAP's) in the 1990 Clean Air Act Amendments have been identified in soils treated with various types of fertilizers. Table 2-2 provides a summary of data obtained from a variety of investigators and compiled by Kabata-Pendias and Pendias for trace elements in fertilizer-treated soil. A number of these elements are listed HAP's.

2.3.3 Gaseous Air Emissions[5-18,21-23]

Gaseous air emissions from fertilizer application can occur either immediately, as a result of the volatilization of the fertilizer itself, or after a period of time, as a result of the biological/chemical transformation of the fertilizer and subsequent release of gases to the atmosphere. The transformation products are generally oxidized forms of either nitrogen, sulfur, or phosphorus. Data on emissions related to the application of micronutrients, which are trace elements such as boron, chlorine, copper, iron manganese, sodium, molydenum and zinc that are essential for plant growth, are insufficient to permit an analysis, so they are not discussed.

Because emissions from fertilizer application are generated via the four primary mechanisms stated in Section 2.3.1 and because emission rates associated with each of these four mechanisms are affected by a variety of physical, chemical, and biological processes, characterizing emission rates for a particular application scenario or time period is complicated. The subsections below present an overview of five classes of factors that are described in the literature as affecting emissions. These five broad classes are biological and chemical reactions in the soil; other biological activities; soil conditions; climate; and nutrient management (the form, placement, and timing of fertilizer application).

Because of the complexity of the emission mechanisms and the interaction of many of the factors, data are insufficient to estimate the magnitude of the effects of most of the factors. Consequently, the discussion below presents a comprehensive but qualitative review of the information on emission mechanisms contained in the literature. While quantitative data are not available for most factors, the data collected at a number of sites generally show consistent effects of substantial magnitude for two factors--soil moisture content and temperature. For most fertilizers, it is believed that emissions increase significantly as moisture contents are raised via rainfall or irrigation. Also, emissions are directly related to ambient temperatures. Hourly emission rates exhibit diurnal patterns that follow temperature patterns, and emissions are higher during summer months. The effects of both temperature and moisture are interrelated with other biological and chemical factors discussed below.

2.3.3.1 Biological and Chemical Reactions Affecting Air Emissions from Fertilizer. Naturally occurring biological and chemical reactions in the soil that affect air emissions from fertilizer application are primarily related to either the nitrogen cycle (Figure 2-8) or the sulfur cycle (Figure 2-9), depending on the type of fertilizer applied. These reactions generate four gases (N_2O, NO, NO_2, and SO_2) that can have an adverse effect on air quality when their concentrations are higher than can be maintained in the soil by the natural equilibrium between the soil and air. Both the nitrogen and sulfur cycles are part of a complex overall equilibrium between inorganic and organic solids, air, water, and microorganisms. When one or more of these reactions is affected, the entire equilibrium is also affected. Biological and chemical reactions are associated with mechanism (1) discussed in Section 2.3.1.

Biological Reactions: For several elements, notably carbon, nitrogen, and sulfur, microbial reactions almost totally determine the soil reaction rates. Biochemical and microbial reactions are primarily catalytic processes affected by soil mineral composition, climate, gas exchange with the atmosphere, and energy from photosynthesis. Three gases (NH_3, N_2O, and hydrogen sulfide [H_2S]) that are precursors to the gases noted above are generated from three separate biological processes: nitrogen fixation, denitrification, and the hydrogen sulfide reaction. A brief summary of these processes and the factors that affect them follow.

Nitrogen fixation — Nitrogen fixation is a process that reduces elemental nitrogen (N_2) from the atmosphere to NH_3 through a series of reactions catalyzed by soil microflora (see Figure 2-8). Factors that affect nitrogen fixation include the presence and type of organotropic bacteria, the presence or absence of air (or oxygen) in the soil matrix as related to the bacteria, the photosynthetic capability of bacteria and algae, and the absence of hydrogen gas. Additional information may be found in References 8, 9, 17, and 23.

Denitrification/nitrification — Denitrification is a process that reduces nitrates to nitrogen in one or more reaction steps. One reaction produces N_2O. The reverse process, which is called nitrification, starts with either NH_3 or N_2 and oxidizes it to nitrates through a series of reactions. Different microflora and molecular oxygen (O_2) are required for nitrification. Factors that affect nitrification and denitrification include the microflora, level of oxygen in the soil, the moisture content of the soil, the temperature, and the available food energy sources for the microbes. Available information indicates that both nitrification and denitrification contribute to soil nitrogen compound emissions. Additional information may be found in References 5, 6, 11, 12, 13, 17, and 23.

Hydrogen sulfide — Under anaerobic conditions, sulfates are reduced to H_2S. Factors that increase the generation of hydrogen sulfide include flooding, presence of sulfur reducing bacteria, and the absence of oxygen. Additional information may be found in References 11, 14, 15, 17, and 23.

Chemical Reactions: The chemical reactions of fertilizers with soil are usually a series of reactions that occur under conditions closely related to those affecting the presence of microflora. This section summarizes the factors that affect emissions as they are related to the fertilizer. Three specific processes are discussed: NH_3 volatilization, reduction of nitrates, and reduction of sulfates.

Ammonia Volatilization — Ammonium is normally stored in soil as a complex with carbonate ions or sulfate ions and is readily absorbed by plant roots. Ammonia volatilizes more readily when the soil lacks these anions. Ammonia volatilization also increases with flooding, high soil pH, the presence of high levels of calcium, and high or elevated temperatures. Flooding mobilizes the NH_3 and carries it to the surface where it is readily volatilized into the atmosphere. Soils with high pH (basic soils) react with ammonium ions to generate water and NH_3 gas. Calcium forms insoluble precipitates with sulfates and carbonates, thus reducing the anions available for complexing with ammonium ions. Ammonia emissions also increase with temperature. Under drying conditions, especially with increasing wind speed, soils with high moisture content enhance NH_3 volatilization, especially with urea-containing materials.

Reduction of Nitrates — Generally, nitrate is a soluble anion found in the soil solution and is readily absorbed by plant roots. However, these nitrate compounds can undergo reduction reactions to produce less soluble oxides of nitrogen and increase emissions of NO_x. The magnitude and rate of nitrate reduction in soils is increased with increasing quantities of decomposable organic matter, soil moisture content (decreasing soil aeration), soil pH, soil temperature, and soil nitrate content.

Reduction of Sulfates — Sulfates are loosely bound to the soil as salts and are readily absorbed by plant roots. However, chemical reduction of these sulfates to SO_2 or H_2S act to increase sulfur-related emissions. Factors that increase sulfur-related emissions by increasing the rate of these reduction reactions include flooding, the presence of key minerals and other anions, the concentration of sulfate ions, the type of clay and clay content in the soil, and the type and quantity of soil organic matter. In general, the presence of more tightly bound anions within the soil increases sulfur-related emissions because of the reduced concentration of available cations.

2.3.3.2 Other Biological Activities. Because most emissions from fertilizer application are related to the ecological and chemical reactions related to the sulfur and nitrogen cycles, any biological factor that influences these biological and chemical reactions can influence the quantity and rate of gaseous emissions. Three factors may result from mechanism (1) in Section 2.3.1. For example, earthworms and other soil organisms can provide channels through the soil that enhance water and nutrient transport, which in turn effect nitrification and denitrification reactions. Other biological factors that affect emissions can be related to soil microorganisms, surface plants, and animal activity at the site.

Microorganisms compete effectively with plants for available nitrogen and other nutrients. Without the application of certain nutrients, especially nitrogen, plant growth can be severely reduced because of microbial competition for nitrogen. In addition, any factor that reduces plant yield potential (pests, diseases, water and nutrient stress, and many others) will reduce recovery of applied nitrogen and may potentially increase gaseous emission of nitrogen. When the supply of nitrates is high, the presence of growing plants can enhance denitrification because the population of denitrifier microorganisms is greater than in root-free soil.

The presence of animals in grassland ecosystems enhances gaseous losses of nitrogen through volatilization and denitrification of nitrogen in urine. These losses can be greater than those observed for urea with similar nitrogen content applied to the pasture.

2.3.3.3 Soil Conditions.[4,6] Physical and chemical conditions of soil, including pH, texture, moisture content, and temperature, will affect air emissions from fertilizer application. Fine, well-aggregated soils are generally well-suited for optimum plant growth and nutrient use, and thus reduce the potential for gaseous emissions. Poorly aggregated soils with genetic or management-related hardpans (compacted soil layers) reduce root penetration and water movement and may enhance gaseous emissions. Variations in soil properties between or within fields used to quantify gaseous emissions is one reason for wide variation in many of the test results (up to 50 percent relative standard deviation [RSD]). Soil conditions are associated with emission mechanisms (1) and (3) in Section 2.3.1.

Moisture content of the soil is an important factor in emissions generation. As soil moisture content approaches saturation, the rate of denitrification greatly increases. Fluctuating soil moisture content, by frequent irrigation or rainfall, also enhances gaseous nitrogen emissions. When soil moisture is above the maximum moisture content (the point at which the voids between soil grains are filled with water), air emissions may be reduced because ammonium and nitrate in the soil solution are diluted and also may be transported into the ground and/or surface water systems.

Because they affect biological and chemical reaction rates, soil chemical conditions also affect gaseous emissions. Important chemical properties include the soil solution pH, the cation exchange capacity (CEC) of the soil, and the concentration of nutrients in the soil that potentially could be released to the atmosphere through numerous biological and chemical reactions. The CEC is defined as the capacity of the soil to adsorb or hold cations (Ca^{+2}, Mg^{+2}, Al^{+3}, K^+, Na^+, NH_4^+). Soils with a high CEC will adsorb more NH_4^+ and, thus, exhibit lower NH_3 volatilization potential than soils with a low CEC. Basic soils generally increase the release of nitrogen as NH_3 and nitrogen oxides (NO_x) (including NO and NO_2), and N_2O, and convert all other nutrients to less soluble forms. Acidic soils (<5.0-5.5 pH) reduce NO_x emissions, but also may reduce plant growth due to aluminum toxicity.

2.2.2.4 Climate. Climatic conditions that affect emission rates through their influence on biological and chemical reaction rates include moisture, temperature and wind speed. Climatic conditions can impact all four of the emission mechanisms cited in Section 2.3.1. Conditions that reduce oxygen content of the soil (increasing soil moisture, temperature changes, etc.) generally increase the emission of gas to the atmosphere above normal background levels. Even in well-aerated soils, denitrification still occurs in anaerobic microsites within soil aggregates. During short periods of saturation of the surface soil following rainfall or irrigation, the rate of denitrification greatly increases until drainage occurs and an aerated condition returns. Nitrogen and other soluble nutrients can subsequently be removed with the drainage water. Volatilization losses of nitrogen generally are enhanced when wet soils are subject to drying conditions. Increasing wind velocity enhances volatilization and under flooded conditions also increases denitrification. Ammonium volatilization increases as soil temperature rises, emissions generally increase throughout the day relative to an increase in soil temperature. Also, daily peak emissions will increase throughout the summer season as compared to the other three seasons. Denitrification also increases with rising temperature. Additional information may be found in References 7 and 23.

2.3.3.5 Nutrient Management (Form, Placement, and Timing of Fertilizer Application). In addition to influencing the quantity of nutrient absorbed or used by the plant, the nutrient source and the rate, method, and time of application can influence the magnitude and rate of gaseous emissions of the nutrient. Nutrient management can impact all four of the emission mechanisms cited in Section 2.3.1. It is important to recognize that any source of nitrate or ammonium nitrogen in the soil can participate in biological or chemical reactions that result in the formation of nitrogen gases. For example, nitrogen mineralized from manure or legume residues can be emitted to the atmosphere by the same reactions involved with gaseous emissions from nitrogen.

Compared to other nitrogen sources, NH_3 volatilization is usually greater with urea or urea-containing fertilizers (e.g., urea, ammonium nitrate) and manures. Ammonia loss with anhydrous NH_3 is usually not significant because this source must be injected 10 to 25 cm (4 to 10 in.) below the soil surface. Generally, only small quantities of NH_3 are volatilized from ammonium-containing fertilizers (diammonium phosphate, monoammonium phosphate, ammonium sulfate, and ammonium nitrate). However, NH_3 volatilization can be significant with surface broadcast applications of diammonium phosphate and ammonium sulfate on calcareous or high pH soils. When these two fertilizers are applied to high pH soils, formation of calcium sulfate or calcium phosphate reaction products occurs, which increases the ammonium concentration in the soil solution and ultimately, the ammonium volatilization potential.

Generally, increasing the application rate increases the potential for gaseous emission and leaching of nitrogen. Therefore, identifying the correct nitrogen rate for optimum production will maximize the quantity of applied nitrogen recovered by the plant and minimize the potential environmental impact of nitrogen use. Again, this phenomenon holds for fertilizer, manure, and legume nitrogen sources (see section 2.4 for details).

Compared to surface broadcast-applied nitrogen, any nitrogen containing fertilizer or manure that is applied to the subsurface will reduce the quantity of nitrogen emitted to the atmosphere. However, gaseous emissions related to volatilization and denitrification still occur regardless of placement. In high pH soils and/or in zero tillage and reduced tillage systems (where crop residue covers the soil surface) on soils of any pH, subsurface placement of nitrogen fertilizer will enhance nitrogen recovery by the crop and reduce the potential for gaseous emissions. Surface broadcast nitrogen is usually incorporated into the soil with tillage shortly after application. Incorporation of nitrogen fertilizers will generally reduce potential gaseous emissions (especially with urea-containing sources) compared to not incorporating the nitrogen fertilizer or manure; however, with or without incorporation, nitrogen emissions are generally higher with surface broadcast nitrogen than with subsurface applications because broadcasting maximizes the quantity of soil in contact with the nitrogen.

2.4 EMISSION CONTROL TECHNOLOGY[14,20,21,24-27]

The review of the literature provided no information on control measures or on fertilizer management practices that are being used explicitly to reduce emissions of nitrogen and sulfur compounds from fertilizer application. Furthermore, because the processes that generate emissions from fertilizer application are so complex and depend on a number of soil and climatic properties via complex relationships that have not been characterized quantitatively, the emission reduction potential of alternative management practices cannot be quantified at this time. However, the best form of emission control identified to date is through appropriate "nutrient management." Here, nutrient management is defined as the form, placement, and timing of the fertilizer application relative to the crops' need for fertilizer. Again, no quantitative information is available on specific management practices, but the paragraphs below describe general approaches as they are described in the literature.

Appropriate nutrient management requires not only appropriate quantities of fertilizer but also timing of the application. Maximizing the quantity of nitrogen recovered by the plant requires that the nitrogen be applied as close to the time of maximum nitrogen demand as is possible. Therefore, split applications (part of the nitrogen is applied before planting and part is applied during an early crop growth stage) will maximize crop recovery and minimize gaseous emissions of the applied nitrogen. Since gaseous emissions can increase with increasing temperature, nitrogen application at cooler times during the year or during the day will reduce the potential for gaseous nitrogen loss.

Because a substantial quantity of emissions from fertilizer applications is related to the denitrification process, management techniques that reduce denitrification potential also will increase nitrogen utilization and decrease emissions. Additives to fertilizer nitrogen sources that reduce or inhibit nitrification or urea hydrolysis (N-Serve, DCD, and others) may reduce the potential for gaseous nitrogen emissions. Use of encapsulated calcium carbide (ECC) has been shown to be effective in the inhibition of nitrification and the reduction of N_2O and N_2 emissions from irrigated corn and wheat fields as well as flooded rice fields. It was not effective for dry land wheat fields. Details on these studies can be found in References 24, 25, and 26. Encapsulation of the fertilizer nitrogen also may significantly reduce emission losses. Considerable more research is required to identify the most effective inhibitors.

Currently, uniform nitrogen recommendations are provided for a crop grown on a given field, and nitrogen is applied at a uniform rate over the entire field. Since crop yield potential varies spatially over a field, varied nitrogen application rates would also increase nitrogen utilization. However, the technologies that facilitate variable nitrogen application to improve nitrogen use efficiency and minimize the environmental impact of nitrogen use are not generally available at this time.

Nitrogen management technologies that include placement, timing, and identification of the correct nitrogen rate are currently available through cooperative extension service or can be found in Reference 27, "Fertilizer Nitrogen Management," and References 14, 20, and 21. If these technologies are utilized to elevate the recovery of applied nitrogen by plants, the environmental release of nitrogen compounds from fertilizer application could be reduced.

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TABLE 2-1. TOP 10 STATES IN AGRICULTURAL FERTILIZER CONSUMPTION IN 1994[a]

	State	Volume consumed (million Mg)	Volume consumed (million tons)
1.	Illinois	3.7	4.1
2.	Texas	3.2	3.5
3.	Iowa	3.0	3.3
4.	Indiana	2.4	2.6
5.	California	2.4	2.6
6.	Ohio	2.1	2.3
7.	Nebraska	2.1	2.3
8.	Minnesota	1.9	2.1
9.	Florida	1.6	1.8
10.	Kansas	1.5	1.7

[a]Source: Reference 5. As of June 30, 1994.

TABLE 2-2. AGRICULTURAL SOURCES OF TRACE ELEMENT CONTAMINATION IN SOILS[a]

Element	Sewage sludges	Phosphate fertilizers	Nitrogen fertilizers	Manure
As[b]	2-26	2-1,200	2.2-120	3-25
B	15-1,000	5-115	-	0.3-0.6
Ba	150-4,000	200	-	270
Be[b]	4-13	-	-	-
Br	20-165	3-5	185-716	16-41
Cd[b]	2-1,500	0.1-170	0.05-8.5	0.3-0.8
Ce	20	20	-	-
Co[b]	2-260	1-12	5.4-12	0.3-24
Cr[b]	20-40,600	66-245	3.2-19	5.2-55
Cu	50-3,300	1-300	<1-15	2-60
F	2-740	8,500-38,000	-	7
Ge	1-10	-	-	19
Hg[b]	0.1-55	0.01-1.2	0.3-2.9	0.09-0.2
In	-	-	-	1.4
Mn[b]	60-3,900	40-2,000	-	30-550
Mo	1-40	0.1-60	1-7	0.05-3
Ni[b]	16-5,300	7-38	7-34	7.8-30
Pb[b]	50-3,000	7-225	2-27	6.6-15
Rb	4-95	5	-	0.06
Sc	0.5-7	7-36	-	5
Se[b]	2-9	0.5-25	-	2.4
Sn	40-700	3-19	1.4-16.0	3.8
Sr	40-360	25-500	-	80
Te	-	20-23	-	0.2
U	-	30-300	-	-
V	20-400	2-1,600	-	-
Zn	700-49,000	50-1,450	1-42	15-250
Zr	5-90	50	-	5.5

Source: Reference 8.

[a] Parts per million dry weight (µg/g). Summarized in reference 8.
[b] Listed as Hazardous Air Pollutant in 1990 Clean Air Act Amendments.

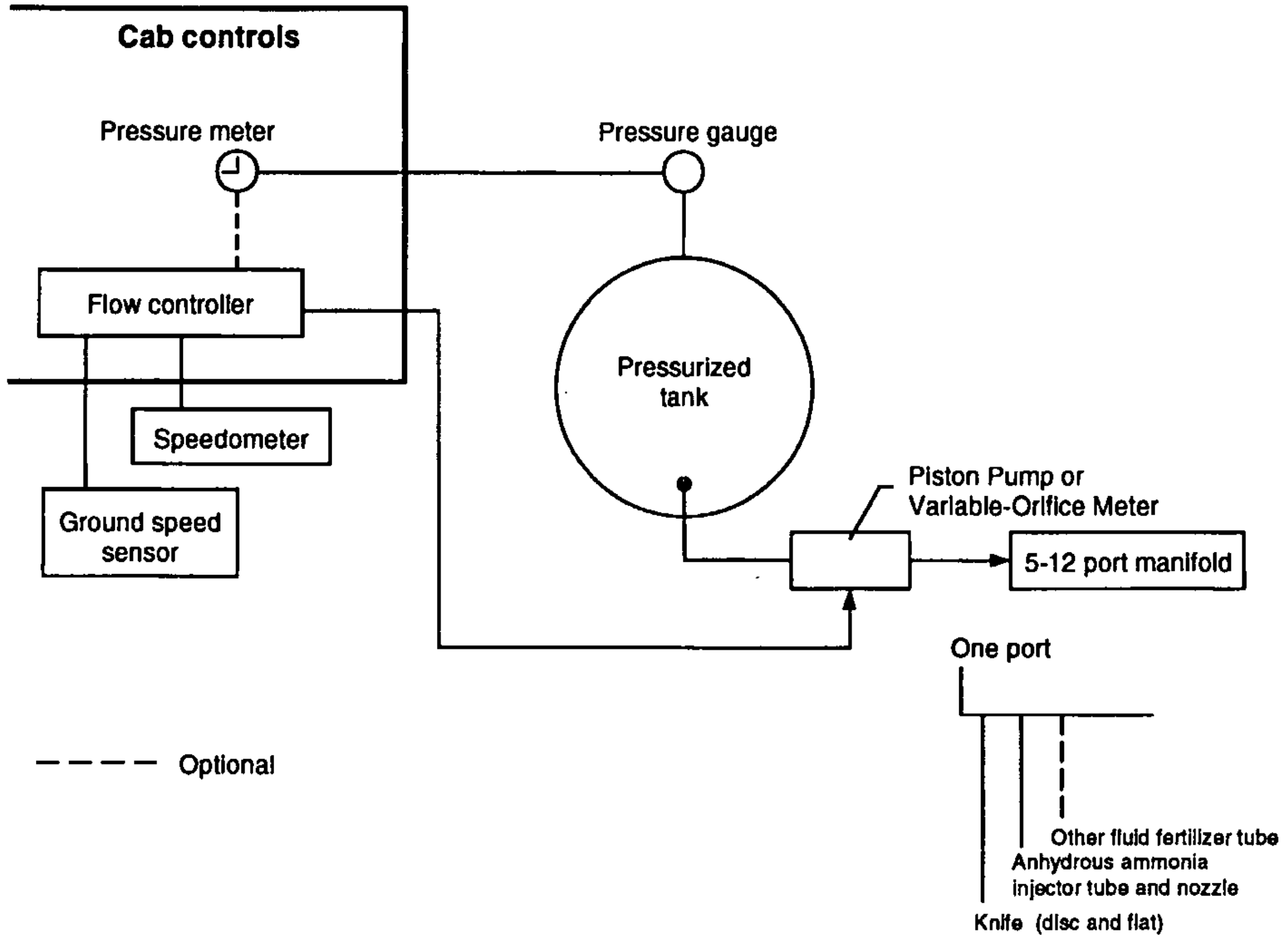


Figure 2-1. Diagram of a typical metering system for anhydrous ammonia application.

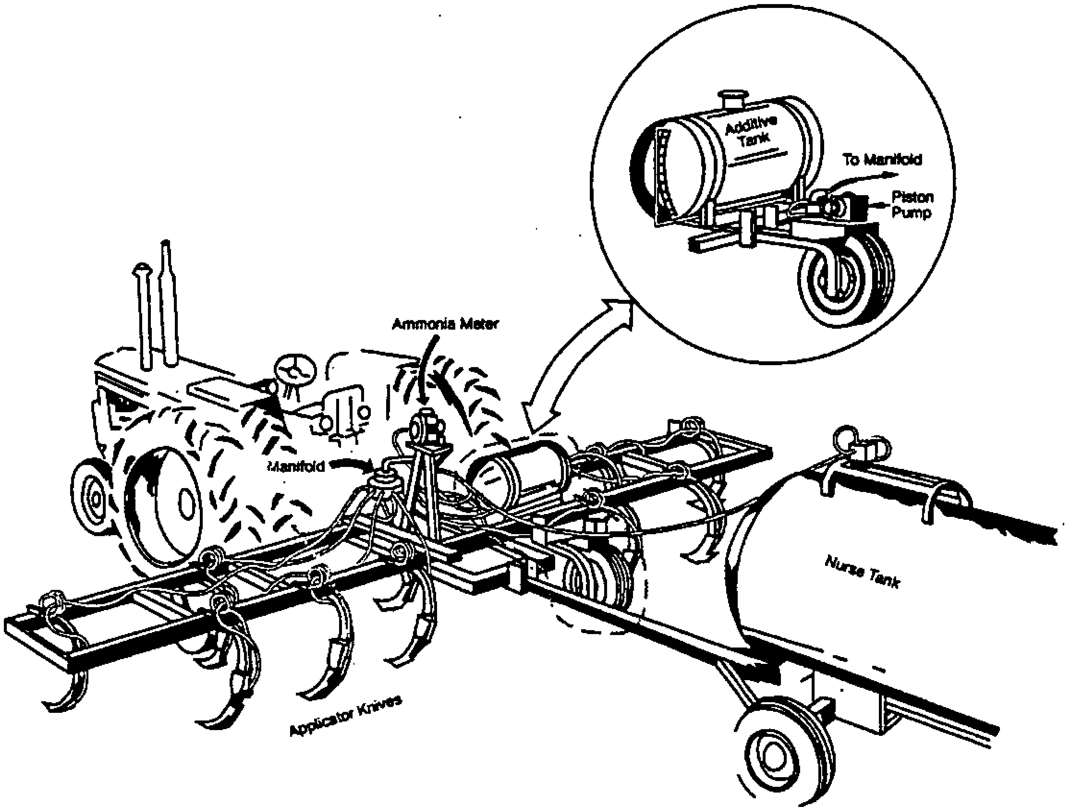


Figure 2-2. Typical trailer for application of anhydrous ammonia and fluid fertilizers.

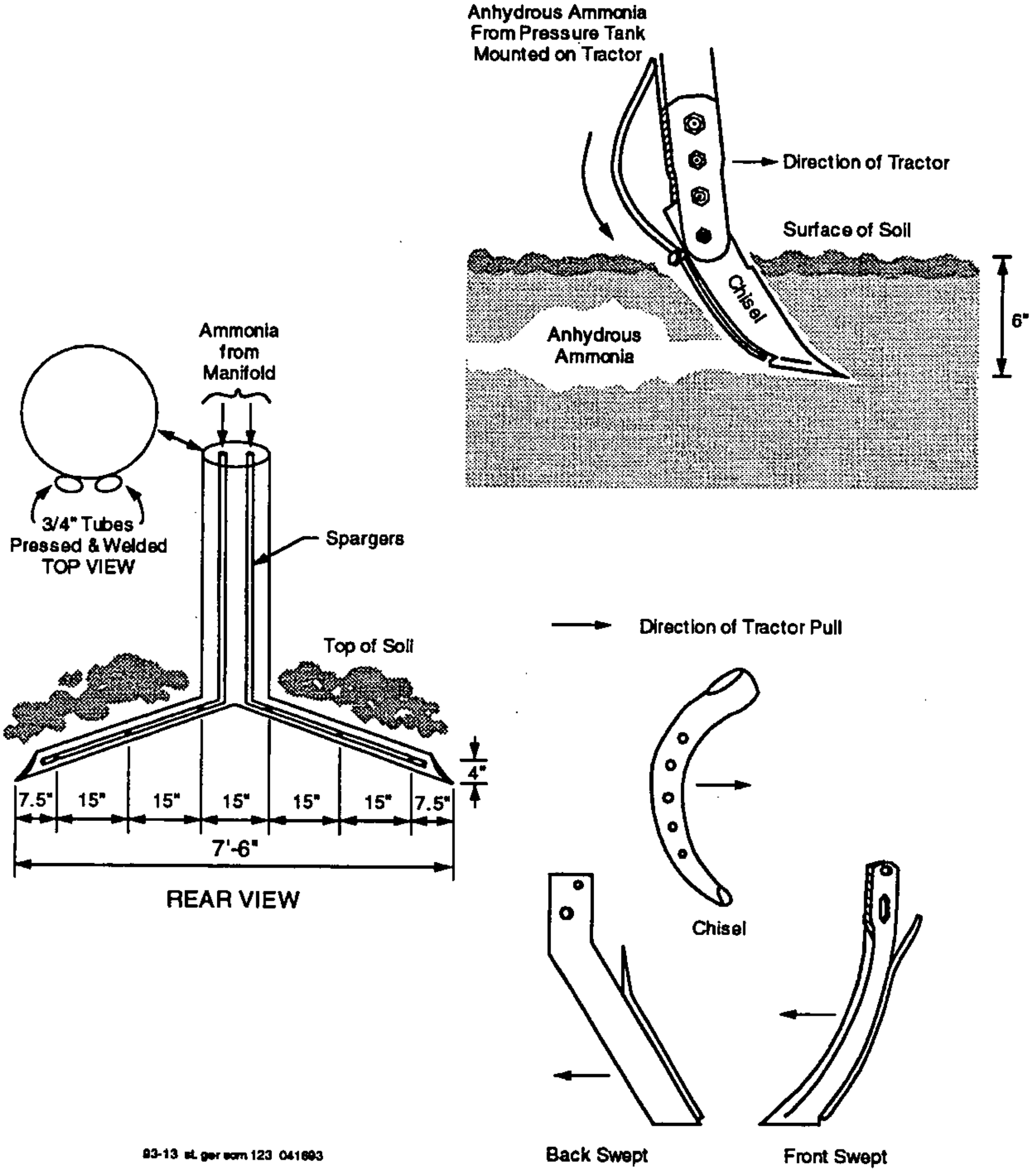
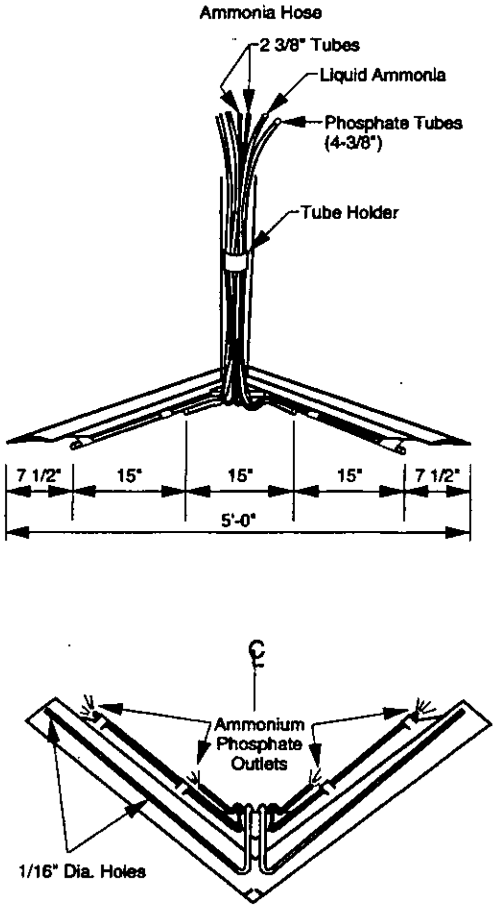
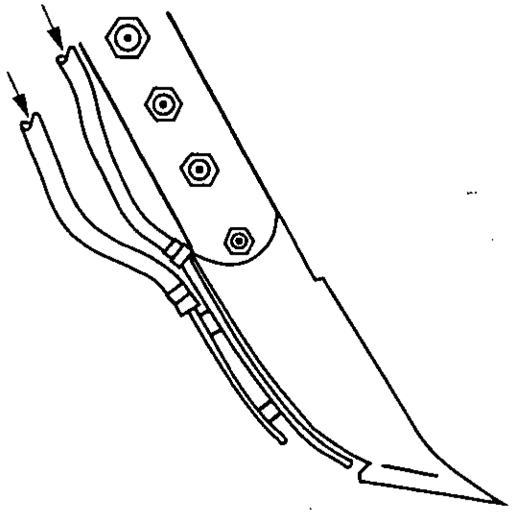


Figure 2-3. Typical tilling blades with injection tube.



View Underneath V-Blades Showing Location of Tubes

V-blade equipped with ammonia sparger and liquid phosphate injection assembly



Dual application knife with ammonia and phosphate tubes separated

Figure 2-3. (continued)

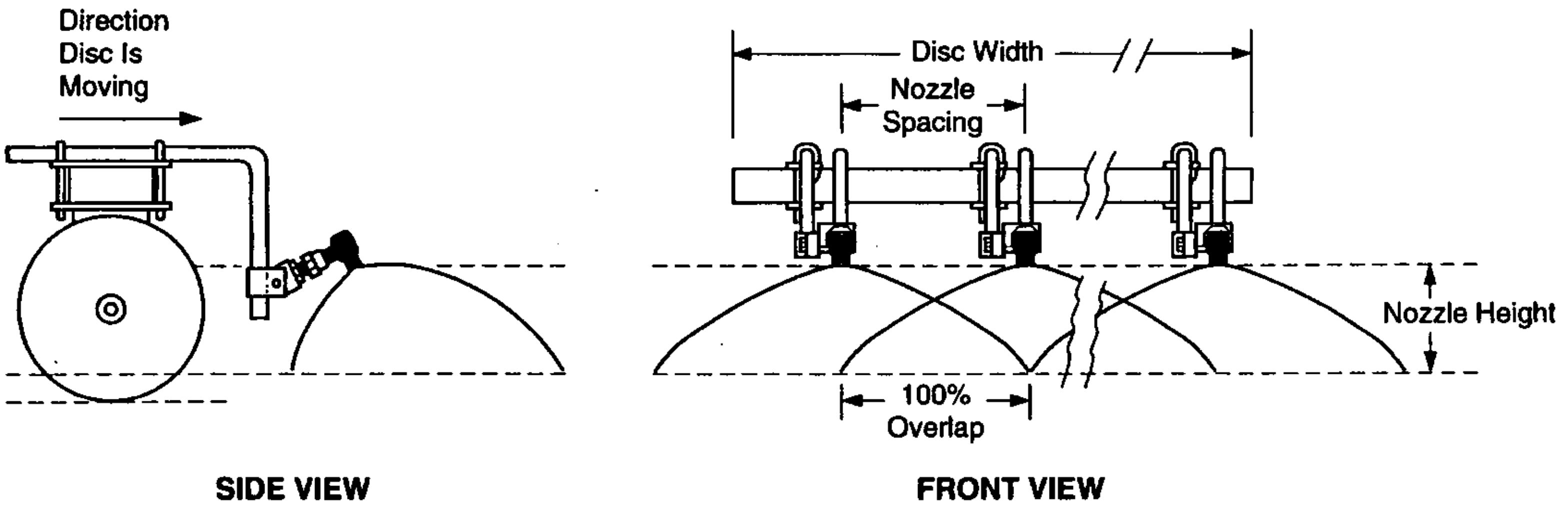


Figure 2-4. Side view and front view of a typical spray nozzle system used for broadcast application of fluid fertilizers.

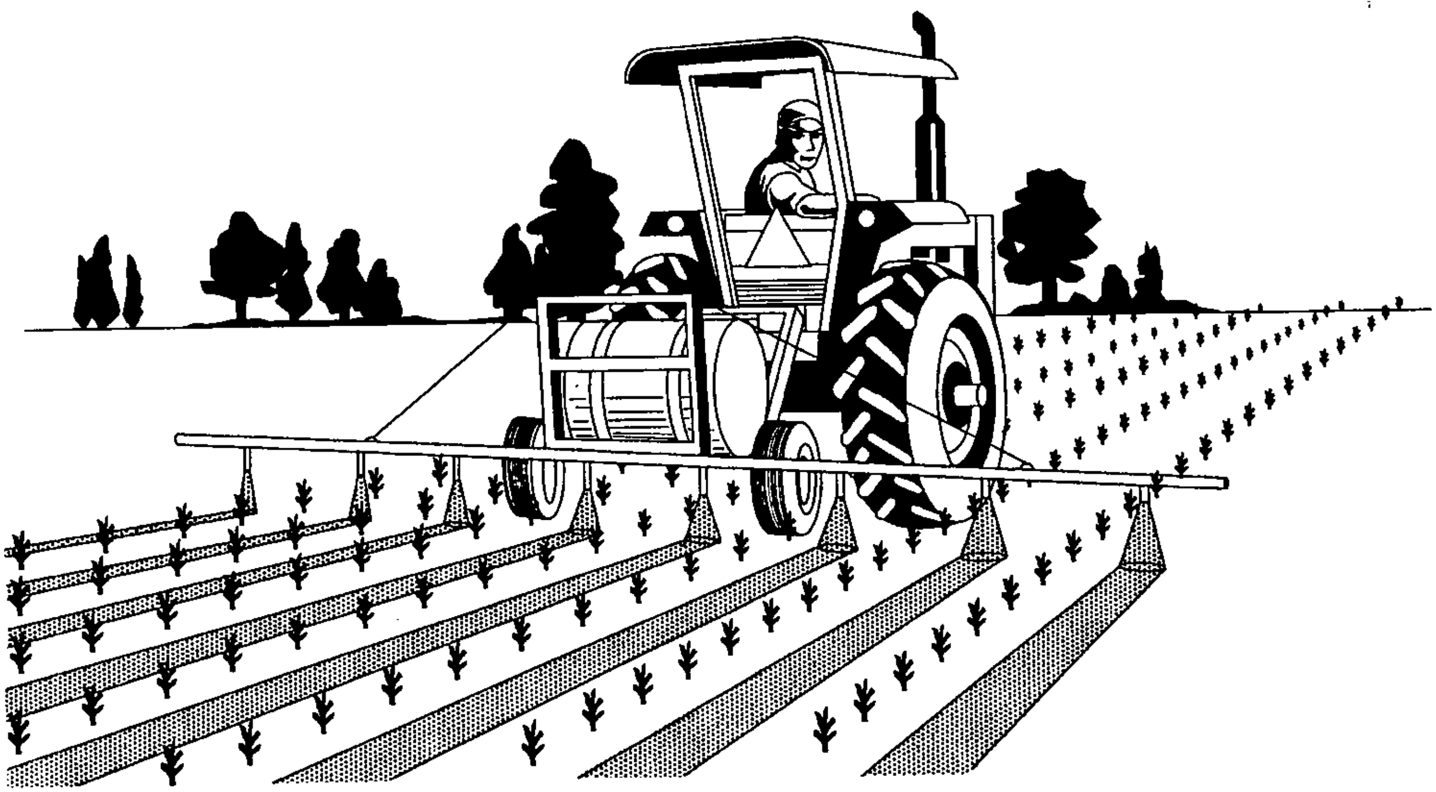


Figure 2-5. Typical "banding" application for fluid fertilizers.

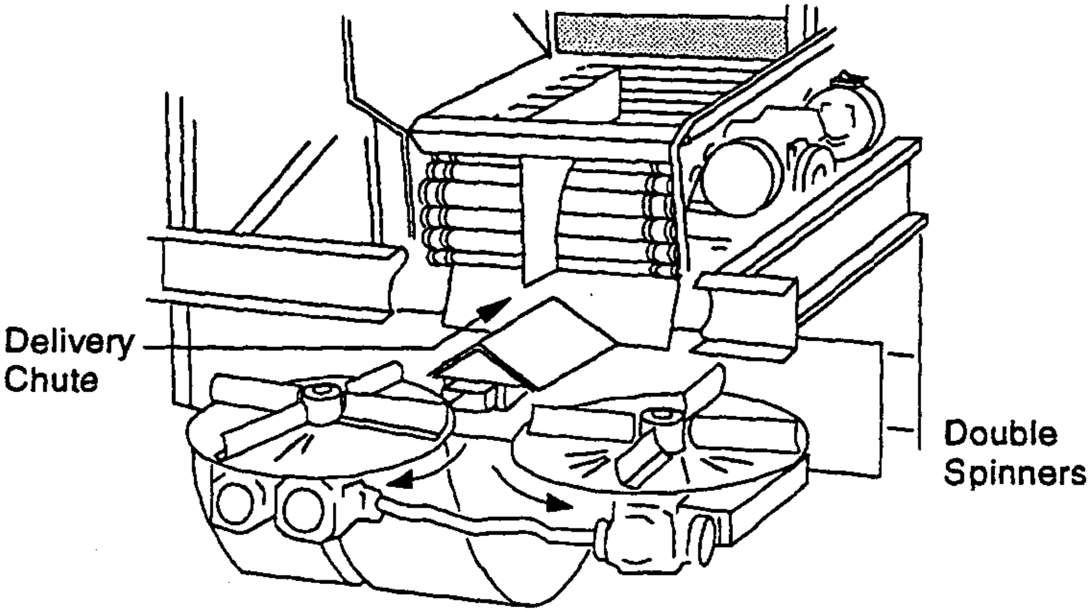


Figure 2-6. Centrifugal spreader for solid fertilizers.

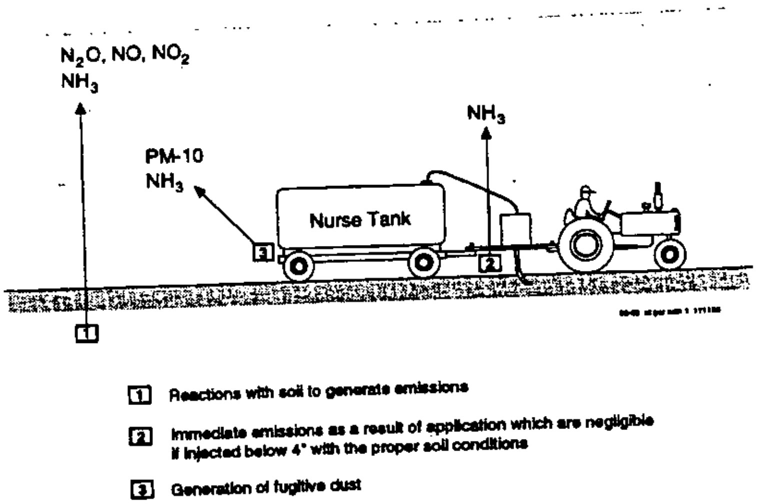


Figure 2-7a. Emission points for gaseous fertilizers.

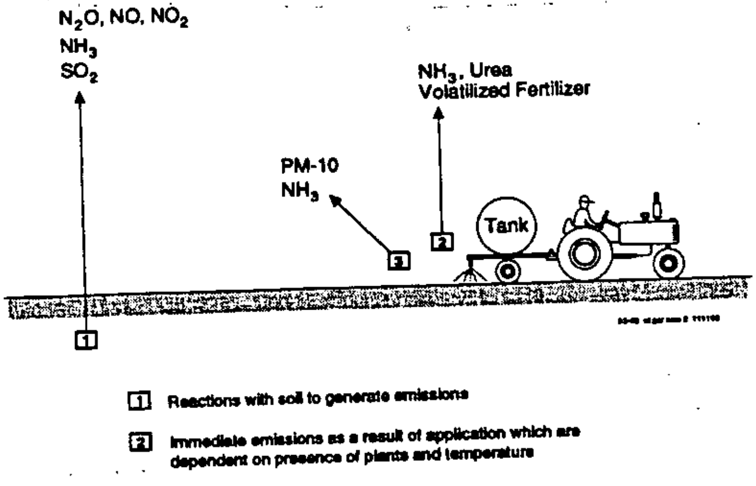


Figure 7b. Emission points for ground application of fluid fertilizers.

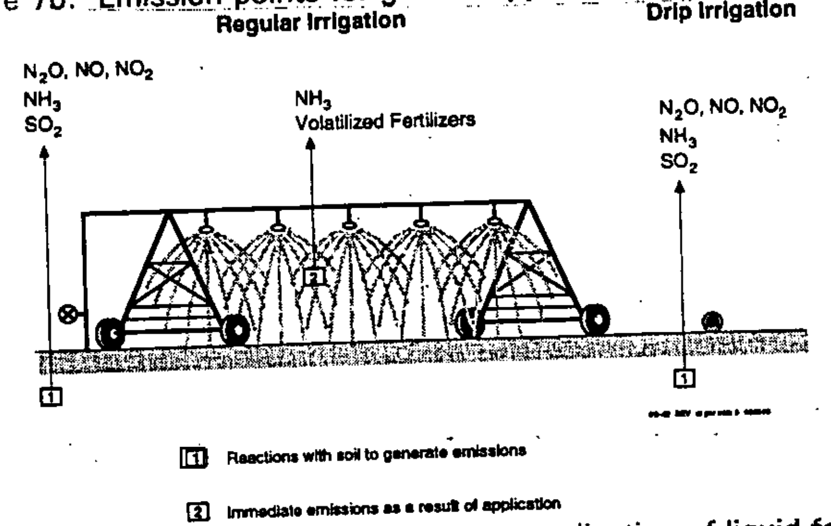
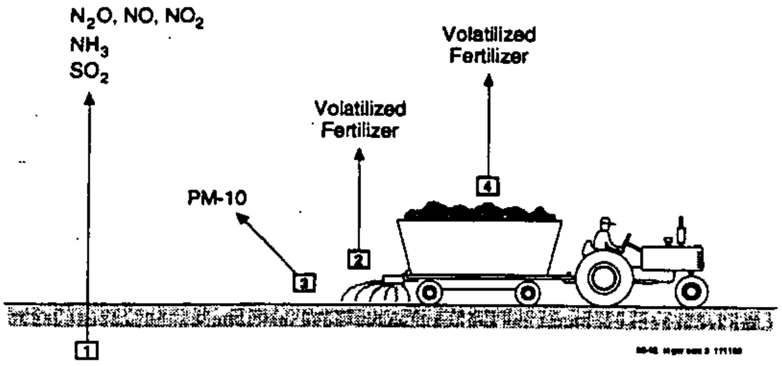


Figure 2-7c. Emission points for irrigation application of liquid fertilizers.



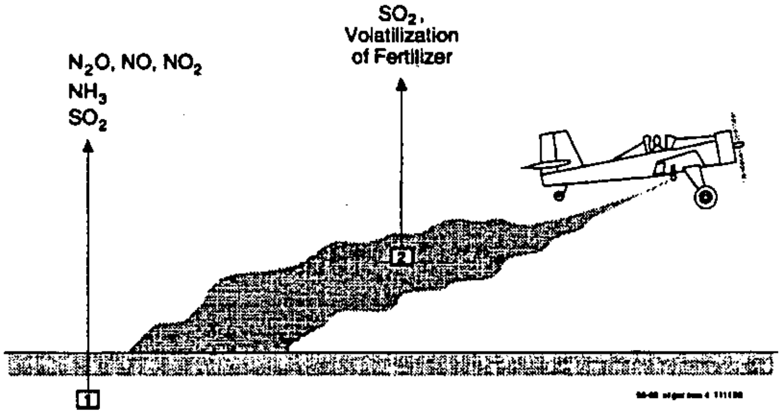
1 Reactions with soil to generate emissions

2 Immediate emission due to broadcasting the fertilizer. Believed to be negligible.

3 Generation of fugitive dust

4 Immediate emission due to volatilization of fertilizer. Believed to be negligible.

Figure 2-7d. Emission points for ground application of solid fertilizers.



1 Reactions with soil to generate emissions

2 Volatilization of fertilizer. Immediate emissions believed to be much higher than ground application.

Figure 2-7e. Emission points for aerial application of fluid and solid fertilizers.

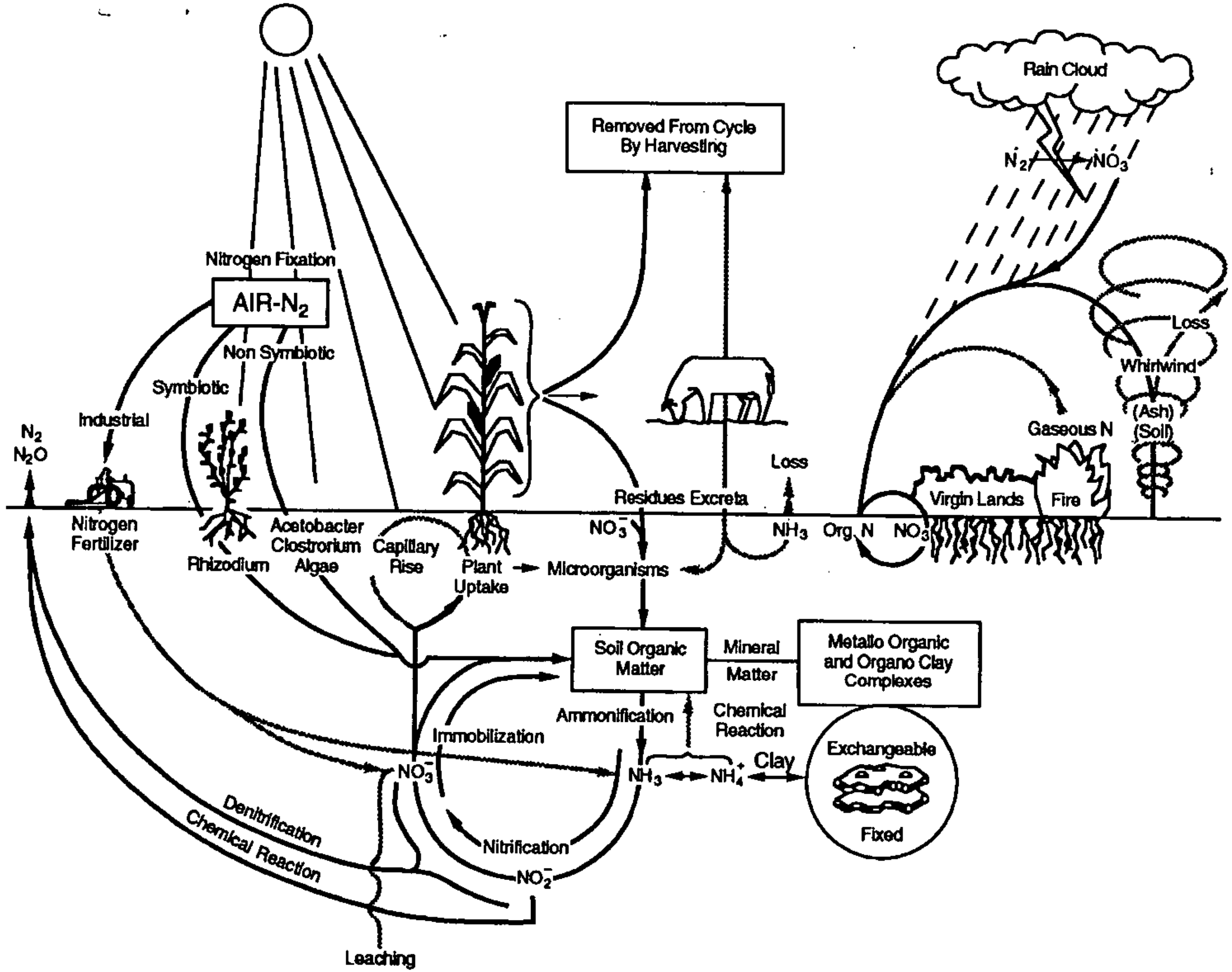


Figure 2-8. Nitrogen cycle.

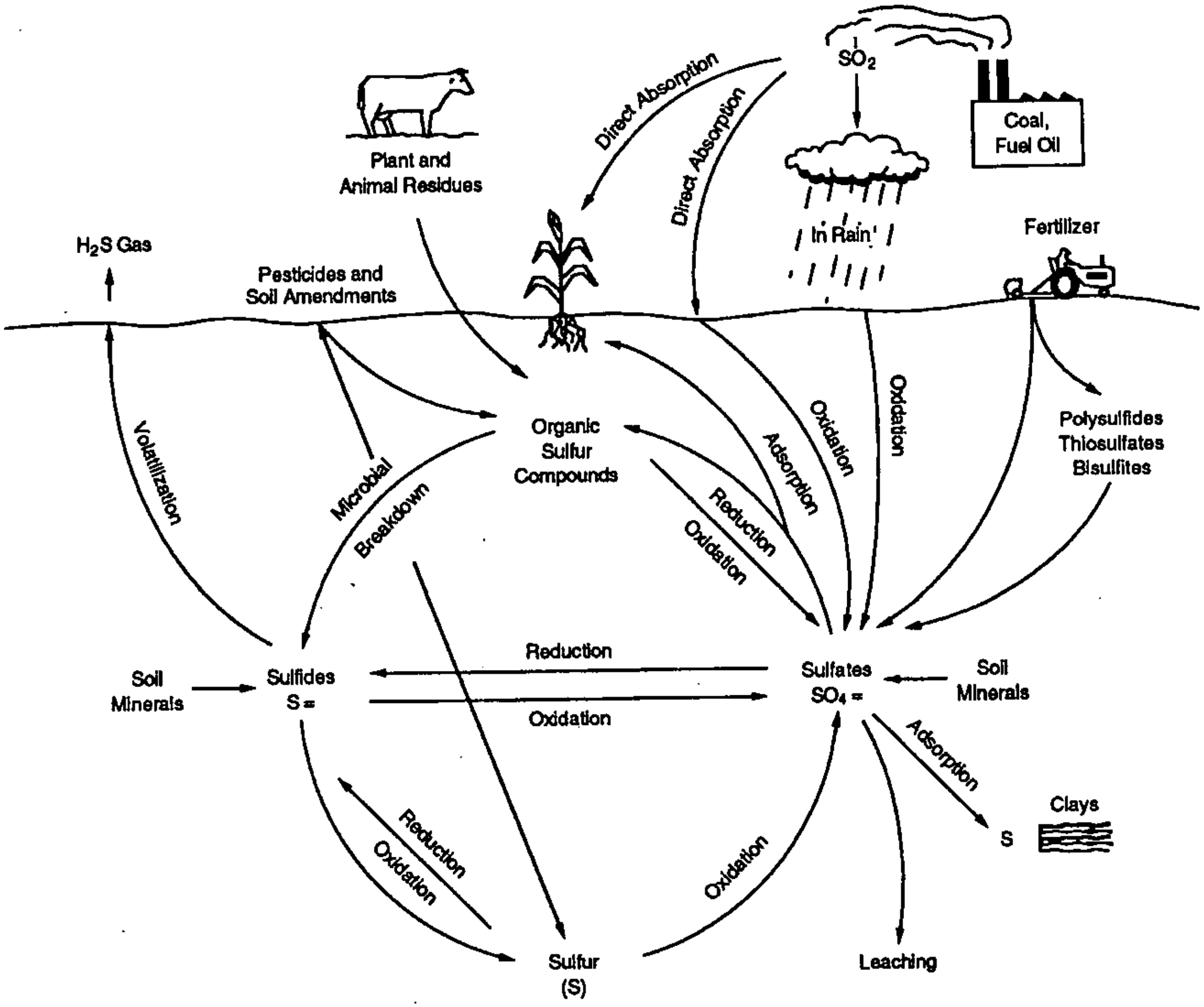


Figure 2-9. Sulfur cycle.

3. GENERAL DATA REVIEW AND ANALYSIS PROCEDURES

This section describes the literature search to collect emissions data and the EPA quality rating systems applied to data and to any emissions factors developed from those data.

3.1 LITERATURE SEARCH AND SCREENING[1-3]

A literature search was performed to collect pertinent emission data for operations associated with fertilizer application. This search included documents obtained from EPA's Office of Air Quality Planning and Standards (OAQPS), the AP-42 background files, the Crosswalk/Air Toxic Emission Factor Data Base Management System (XATEF), the VOC/PM Speciation Data Base Management System (SPECIATE), and the Air CHIEF CD-ROM. In addition, a comprehensive search of the Agricola Data Base (1/92-3/97) was performed.

Information on the application processes, including types of fertilizers, annual production, and usage was obtained from the *Fertilizer Use by Class*, *Today's Retail Fertilizer Industry*, and other sources. The Aerometric Information Retrieval System (AIRS) data base also was searched for data on the types of fertilizers and estimated annual emissions of criteria pollutants.

A number of sources of information were investigated specifically for emission test reports and data. A search of the Test Method Storage and Retrieval (TSAR) data base was conducted to identify any test reports for fertilizer application. The EPA library was searched for additional test reports. Publications lists from the Office of Research and Development (ORD) were searched for reports on emissions from fertilizer application. In addition, representative trade associations, including the International Fertilizer Development Center in Muscle Shoals, Alabama, and the National Fertilizer and Environmental Research Center in Muscle Shoals, Alabama, were contacted for assistance in obtaining information about the industry and emissions.

During the review of each document, the following criteria were used to determine the acceptability of reference documents for emission factor development:

1. The report must be a primary reference:

a. Source testing must be from a referenced study that does not reiterate information from previous studies.
b. The document must constitute the original source of test data.

2. The referenced study must contain test results based on more than one test run.

3. The report must contain sufficient data to evaluate the testing procedures and source operating conditions.

3.2 DATA QUALITY RATING SYSTEM[1]

Based on OAQPS guidelines, the following data are always excluded from consideration in developing AP-42 emission factors:

1. Test series averages reported in units that cannot be converted to the selected reporting units;
2. Test series representing incompatible test methods; and
3. Test series in which the production and control processes are not clearly identified and described.

If there is no reason to exclude a particular data set, data are assigned a quality rating based on an A to D scale specified by OAQPS as follows:

A—This rating requires that multiple tests be performed on the same source using sound methodology and reported in enough detail for adequate validation. Tests do not necessarily have to conform to the methodology specified by EPA reference test methods, although such methods are used as guides.

B—This rating is given to tests performed by a generally sound methodology but lacking enough detail for adequate validation.

C—This rating is given to tests that are based on an untested or new methodology or that lack a significant amount of background data.

D—This rating is given to tests that are based on a generally unacceptable method but may provide an order-of-magnitude value for the source.

The following are the OAQPS criteria used to evaluate source test reports for sound methodology and adequate detail:

1. Source operation. The manner in which the source was operated should be well documented in the report, and the source should be operating within typical parameters during the test.

2. Sampling procedures. The sampling procedures should conform to a generally accepted methodology. If actual procedures deviate from accepted methods, the deviations must be well documented. When this occurs, an evaluation should be made of how such alternative procedures could influence the test results.

3. Sampling and process data. Adequate sampling and process data should be documented in the report. Many variations can occur without warning during testing and sometimes without being noticed. Such variations can induce wide deviations in sampling results. If a large spread between test results

cannot be explained by information contained in the test report, the data are suspect and are given a lower rating.

4. Analysis and calculations. The test reports should contain original raw data sheets. The nomenclature and equations used are compared to those specified by EPA (if any) to establish equivalency. The depth of review of the calculations is dictated by the reviewer's confidence in the ability and conscientiousness of the tester, which in turn is based on factors such as consistency of results and completeness of other areas of the test report.

3.3 EMISSION FACTOR QUALITY RATING SYSTEM[1]

The quality of the emission factors developed from analysis of the test data be rated using the following general criteria:

A—Excellent: Developed from A- and B-rated source test data taken from many randomly chosen facilities in the industry population. The source category is specific enough so that variability within the source category population may be minimized.

B—Above average: Developed only from A- or B-rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industries. The source category is specific enough so that variability within the source category population may be minimized.

C—Average: Developed only from A-, B- and/or C-rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industry. In addition, the source category is specific enough so that variability within the source category population may be minimized.

D—Below average: The emission factor was developed only from A-, B-, and/or C-rated test data from a small number of facilities, and there is reason to suspect that these facilities do not represent a random sample of the industry. There also may be evidence of variability within the source category population. Limitations on the use of the emission factor are noted in the emission factor table.

E—Poor: The emission factor was developed from C- and D-rated test data, and there is reason to suspect that the facilities tested do not represent a random sample of the industry. There also may be evidence of variability within the source category population. Limitations on the use of these factors are footnoted.

The use of these criteria is somewhat subjective and depends to an extent upon the individual reviewer. Details of the rating of each candidate emission factor are provided in Section 4.

3.4 EMISSION TESTING METHODS FOR FERTILIZER APPLICATION[4-16]

3.4.1 Sampling Methods[4-10]

Sampling methods used to determine atmospheric emissions from fertilizer application include the collection of soil grab samples and three types of air samples— air grab samples, "static" air samples, and "flux" air samples. The soil grab sample technique, which has not changed significantly over the years, involves using a scoop, auger, or bottle to collect a sample of soil for analysis. The three techniques used for the collection of air samples are discussed below.

3.4.1.1 Air Grab Sample Collection. Several techniques using bottles or flasks and several types of bags or balloons are used to obtain air grab samples. The containers are evacuated and then filled to a known volume based on the evacuation method. Reactive chemicals are placed in some containers for specific pollutants. The reactive chemicals preserve the pollutant for analysis at a later date or give qualitative information at the testing site.

3.4.1.2 Static Air Sample Collection. Downwind air samples collected at known heights above ground (see Figure 3-1) are called static air samples. As indicated by the arrows in Figure 3-1, the applicator moves in alternate directions up and down the field perpendicular to the wind direction. The pollutant concentration at different heights and the wind speed at those heights are determined from data collected at the sensor mast. Under the assumption that the flux from the field surface is equal to the horizontal flux normal to the vertical plane at the downwind edge of field, the total mean flux across a cross sectional vertical area of unit width is calculated as:

$$\overline{Q} = \int_{o}^{z} \overline{u}(z)\ \overline{c}(z)\ dz$$

where:

$\overline{Q}$ = the total time average flux across a unit width of the vertical plane at the field edge

$\overline{u}(z)$ = average wind speed at height z

$\overline{c}(z)$ = average pollutant concentration at height z

Z = height of the curve layer affected by the emissions

In practice, $\overline{Q}$, is obtained by numerical integration of the vertical profiles of wind speed and concentrations are obtained from the sensor mast. Note that under the assumptions listed above, $\overline{Q}$ is also equal to the total pollutant flux from a unit width of field surface.

Techniques for collecting static air samples have not changed over the years, except that the sorbents have been refined for lower detection limits and fewer interferences. The two types of static sample collection methods that are available—adsorption and absorption—are briefly discussed below.

For sample collection by adsorption, a desiccant tube, a sample tube containing a porous, solid sorbent specific to the pollutant being collected, and a calibrated vacuum pump are used. The pump pulls air through the sample tube at a known rate for the required length of time. This type of collection is very efficient until the adsorbent is near capacity. The available adsorbents are generally not pollutant-specific, however, and the presence of other compounds may interfere with the measurement of concentrations of specific pollutants.

For sample collection by absorption, a fritted tube, which is immersed into a reactive solution specific to the pollutant of interest, and a vacuum pump are used. Additional components may include impingers, packed columns, countercurrent scrubbers, and atomizing scrubbers. Again, the pump pulls the air sample through both the fritted tube and the liquid or hygroscopic solid for collection. The absorbent is then analyzed in the laboratory, usually within 1 week of collection.

3.4.1.3 Flux Air Sample Collection.[8,9] Air samples collected over a known area of soil or cropland for a specific period of time are called flux air samples. This type of sample is usually collected several times over a period of up to a year after initiation of the study. The results are then compared against both the background (i.e., unfertilized soil) and the peak emissions after application of the fertilizer. Flux air sample measurements allow scientists to determine the effects of both immediate and latent emissions from the application of fertilizers. The various flux air sampling systems are the most widely used of the three sampling procedures and are currently accepted as the techniques that provide the most reliable emission estimates.

A number of different flux chambers are used by investigators. All of these resemble the "isolation flux chamber" developed by Kienbusch et al. for determination of volatilized organic compounds at hazardous waste sites. Figure 3-2 is a diagram of the original sample collection apparatus used for flux sampling of fertilizer emissions as described by Hansen et al. Within the last 10 years, collection methods for flux air samples have improved greatly. These improved methods minimize the soil perturbations in the collection of samples, maximize the mixing of air within the containment, and achieve better calibration determinations.

The most common sample collection apparatus (Figure 3-3) includes a canopy (or "flux chamber") that is laid gently on the surface of the soil. The canopy includes a skirt around the perimeter, a removable lid with two ports, and a fan. The skirt is attached to the soil to prevent the canopy from being lifted due to sudden gusts of wind. The removable lid allows the soil to react with the environment with minimal disturbances when it is not being tested. Calibration of the canopy is performed using one port in the lid for the addition of a known gas while simultaneously collecting air samples. A small fan mixes the air within the canopy so that uniform and reproducible samples may be collected. Additional features may include a collar around the canopy to allow for a better seal with the soil and a white styrofoam cover to prevent rapid heating of the test area.

Air samples can be collected from a flux chamber using either of two basic techniques: static (closed) air sampling or dynamic (open) air sampling. In static air sampling, a known volume of air is manually extracted from the headspace of the chamber using a syringe or evacuated container every 10 to 15 minutes over a 1-hour period. The samples extracted from the chamber are analyzed in the laboratory using various standard techniques (e.g., gas chromatography) to determine pollutant concentrations. Typically the sampling periods are short enough that these concentrations increase linearly with time. This linear increase, coupled with the volume of the flux chamber are used to estimate pollutant flux from the surface enclosed by the chamber. In dynamic flux sampling, a flow of filtered ambient air is continuously passed through the chamber for a specified period of time. The pollutants contained in the chamber are flushed from the headspace by the clean airflow, which is directed to one or more types of instruments for subsequent sampling and analysis of pollutant concentration. The concentrations and exhaust rates are used to calculate pollutant flux from the surface under the chamber. This technique is most applicable to the use of continuous analyzers that provide on-line data in the field.

3.4.2 Analytical Methods[4,6,7,9,15,16]

Analytical methods traditionally used for the determination of air emissions from fertilizer application have included those needed for measurement of soil properties, measurement of chemicals within the soil, the qualitative analysis of air pollutants, and the quantitative analysis of air pollutants. These methods may be performed in the field or in the laboratory, depending on acceptable holding times of the collected samples. This section summarizes the determinations and analytical methods pertinent to the collection of air samples for fertilizer-related pollutants for the four groups of measurements defined above.

3.4.2.1 Measurements of Soil Properties. Typical soil properties that are measured as part of the test protocol include the temperature, pH, texture, and moisture content. The temperature of the soil is measured using a calibrated thermometer, usually placed at a depth of 25 to 50 mm (1 to 2 in.) below the surface of the soil. The pH is measured using either pH paper or a pH meter. The texture is usually noted relative to the county soil surveys for the area or as previously characterized.

Two different measures of soil moisture content that may be used are percent of surface moisture content and maximum moisture volume. To measure percent of surface moisture content, a known weight of sample is dried overnight in an oven at 110°C (230°F). This technique removes all water, except that which is captured within the clay matrix. The noted difference in weight is directly related to the soil surface percent moisture within the soil sample. To measure maximum moisture volume, a known weight of sample is gravity-filtered to determine if the soil is already saturated. If so, the volume of water is measured and recorded. Then, water is added to a known weight of sample until it is saturated to determine the saturation point.

3.4.2.2 Measurements of Chemicals Within the Soil.[12] Frequently, it is important to know the concentration of either a pollutant or related compounds in the soil during the collection of air samples. The analytical method generally used involves extraction of the soil sample with 2 molar potassium chloride (M KCl) (10 mg/g of soil). Analysis of the extract for NH_3, NO_2, and NO is performed by steam-distillation of ammonium, addition of ball-milled Devarda alloy for the reduction of nitrate and nitrite to ammonium, and the addition of sulfamic acid for the destruction of nitrite. The concentration of ammonium is determined by appropriate titration. This method allows the sample to be stored for long periods of time before analysis by first adding 2M KCl to the soil sample, filtering the supernatant, and storing the filtrate at 4°C (39.2°F).

3.4.2.2 Qualitative Analysis of Air Pollutants.[13] Occasionally, it is important to know the general magnitude of pollutant concentrations in the field. Colorimetric methods are used to qualitatively determine the concentration of a specific pollutant above a certain minimum. Typically, the colorimetric methods use a buffered dye to determine a change in pH or the presence of a basic gas such as NH_3. The field method used for qualitative determinations of NH_3 is briefly described.

The method uses a neutral indicator-gypsum suspension sprayed on the cross section of the NH_3 band of a soil column that is exposed by making a vertical cut across the band with a spade. The indicator-gypsum suspension is prepared by titrating 1 g of phenol red with 28 mL of 0.1 normal sodium hydroxide (N NaOH), diluting to 1 L with water, adding 300 g of finely divided calcium sulfate ($CaSO_4{\bullet}2H_2O$) powder, and adjusting the color of the indicator to orange.

3.4.2.3 Quantitative Analysis of Air Pollutants.[11,13,14] The quantitative analyses of pollutant compounds generally use accepted procedures or American Society for Testing and Materials (ASTM) methods. These analyses include routine calibration of the systems, verification of the standards, and calibration over a known concentration range for the pollutant. Table 3-1 summarizes the analytical methods used for each pollutant. Descriptions of the methods can be found in the references that are cited.

Other analytical methods also used are described in references 4 and 16.

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8. M. R. Kienbusch et al., "The Development of an Operations Protocol for Emission Isolation Flux Chamber Measurements on Soil Surfaces," Paper 86-20.1, 79th Annual Meeting of the Air Pollution Control Association, Minneapolis, MN, June 1986.

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15. L. B. Fenn and D. E. Kissel, "Ammonia volatilization from surface applications of ammonia compounds on calcareous soils. II. Effects of temperature and rate of ammonium nitrogen application," *Soil Science Society of American Proceedings*, 38:606-610, 1974.

16. D. H. Lenschow and B. B. Hicks (eds.), *Global Tropospheric Chemistry*, National Center for Atmospheric Research, Boulder, CO, May 1989.

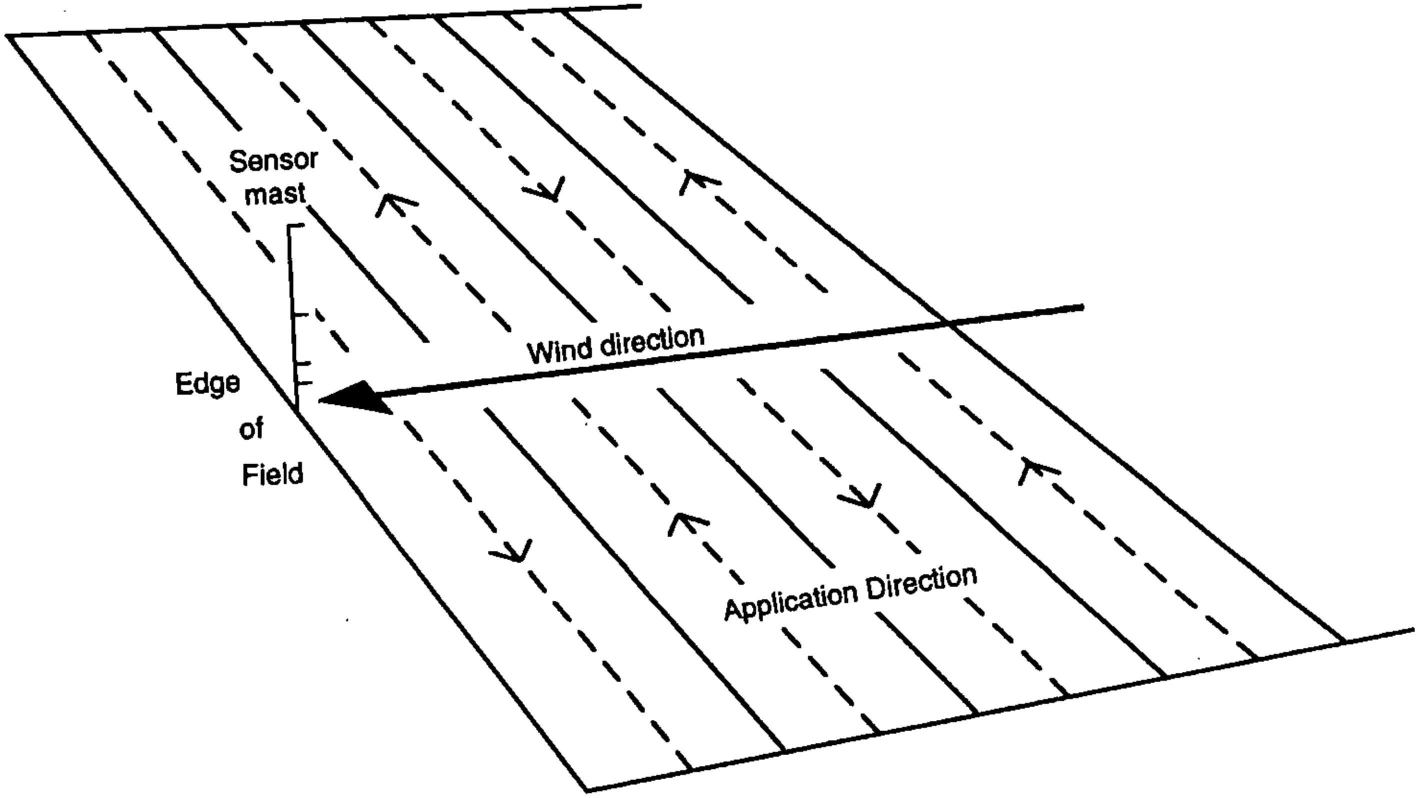

Figure 3-1. Diagram of static air sample collection.

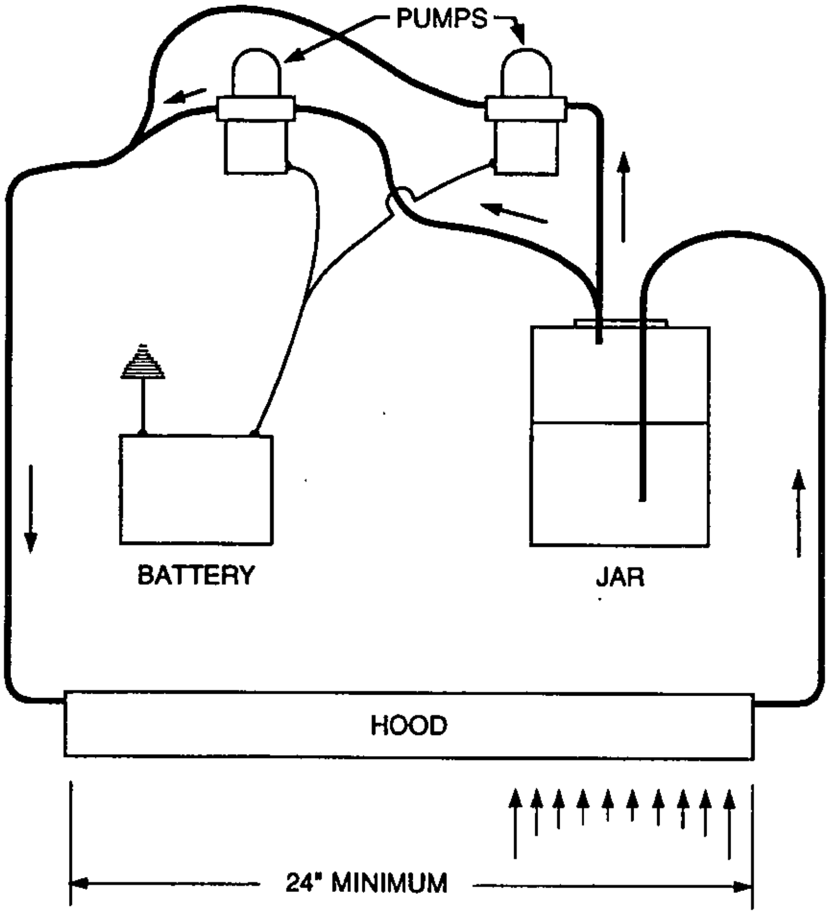

Figure 3-2. Diagram of the original flux chamber sample collection apparatus.

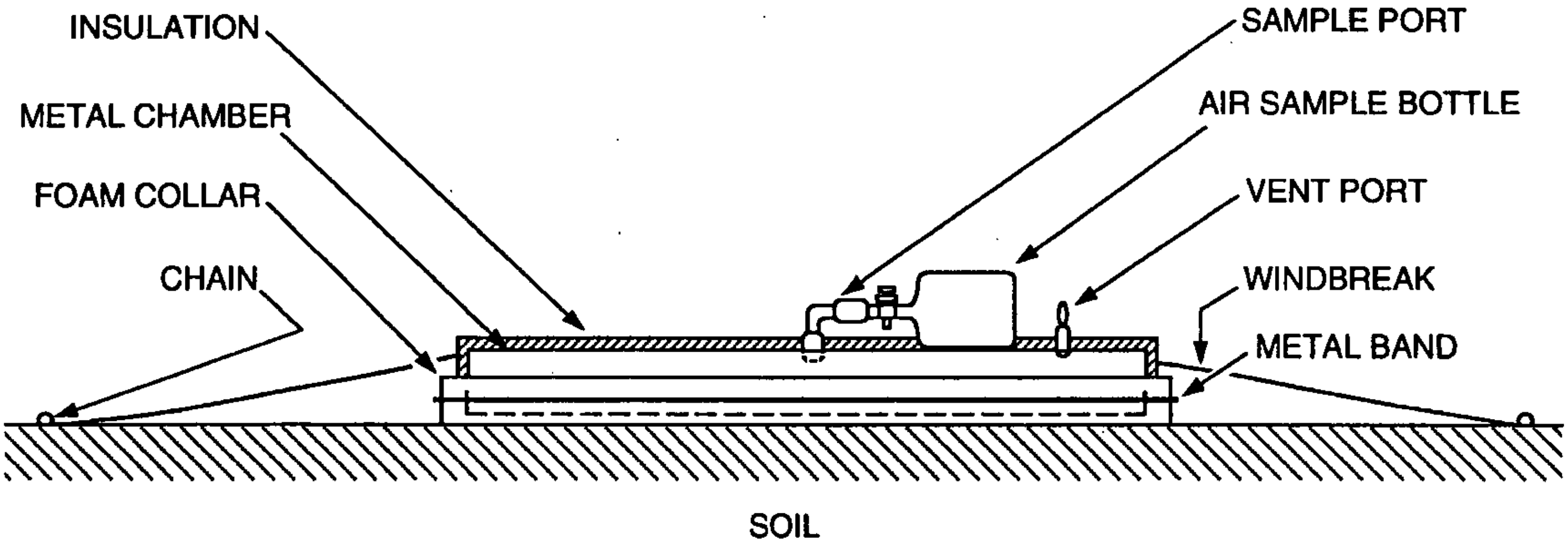

Figure 3-3. Typical canopy for sample collection (i.e., "flux chamber").[8]

TABLE 3-1. QUANTITATIVE ANALYTICAL METHODS FOR AIR EMISSIONS

Pollutant	Fertilizers	Methods	Reference No.
NH_3	Liquid NH_3	ASTM D1426	11
NH_3	Liquid NH_3	Absorption	12
NH_3	Liquid NH_3	Soil extract	11
N_2O	Nitrogen-containing	GC/Xenon	13
NO	Nitrogen-containing	Absorption	4
NO_2	Nitrogen-containing	Absorption	4
NO_2, NO	Nitrogen-containing	Luminax NO_2	10

4. AP-42 SECTION DEVELOPMENT

This section describes the test data and methodology used to develop air emission factors for the application of fertilizer. Fertilizer application is a new section in Chapter 9 of AP-42. Because it is new, several references were reviewed for background information on the processes by which fertilizer is applied and used to promote plant growth. The section narrative was prepared from this review and from comments provided by industry representatives.

4.1 REVIEW OF SPECIFIC DATA SETS

An initial literature search yielded 37 documents that were collected and reviewed during the background study for this AP-42 section. Of these, 14 contained data useful in the development of candidate emission factors for fertilizer application. These 14 documents are summarized in this background document. A subsequent literature search yielded 24 additional documents that were collected and reviewed. Three of these documents contain sufficient data for use in developing emission factors. These three documents are summarized in this background document. Those documents not summarized in this section are listed in Table 4-1 along with the reasons for their rejection.

No emission test reports were located in the literature search. All of the documents reviewed were technical papers published by academic investigators in refereed (peer reviewed) journals. Most of these articles relate to the estimation of nitrogenous greenhouse gases in the global environment and were not specifically intended for emission factor development. In addition, many articles summarized data generated from nontypical fertilizer compounds. The articles do not generally provide extensive detail on test protocols, raw data collected, procedures used to ensure data quality, and similar information necessary to assess the experimental data. For this reason, a B rating was the highest rating given to the data contained in any of the references described below.

4.1.1 Reference 1

Reference 1 is a technical paper published by Canadian investigators in 1991, which summarizes flux measurements of N_2O and NO_x on four barren fields located in Ontario. Limited analyses of the NO_x emissions indicated that they were primarily NO rather than NO_2. Each field was treated with 33 percent granular ammonium nitrate (NH_4NO_3) at application rates of a 100 kg per hectare (kg/ha) (89 lb per acre [lb/ac]), 200 kg/ha (178 lb/ac), and 300 kg/ha (267 lb/ac) by dry broadcasting. These same sites had been treated in a similar fashion for the past 19 years, except the amount of fertilizer applied varied over the years.

Sampling of N_2O and NO_x emissions was performed using a flux chamber five to eight times each day between the hours of 10 a.m. and 6 p.m. during the period from April to September. Concentrations of N_2O and NO_x in air samples from the chamber were determined by two separate methods. In the case of N_2O, headspace samples were extracted from the chamber using evacuated tubes, which were later analyzed by a gas chromatograph equipped with an electron capture detector (GC/ECD) and Porapak Q column. Nitrogen oxide flux measurements were taken by passing filtered air through the chamber. The filtered air was analyzed on a continuous basis using a commercial chemiluminescent analyzer. Soil parameters monitored during the program included temperature, moisture, nitrate, and ammonium. The majority of the N_2O emissions occurred within about 60 days of application. Emission factors were developed for emissions of N_2O and NO from dry application of NH_4NO_3. Although the emitted NO is likely to be converted quickly to NO_2 in the atmosphere, the NO_x emissions were estimated as NO. Recent publications have stated that most, if not all, of the NO_x emissions from soils are in the form of NO, which is rapidly oxidized to NO_2 by the ozone in the soil or air above the soil; see Reference 39.

Reference 1 reported original experimental results. The measurements were conducted using a nonstandard but acceptable methodology, and adequate documentation was provided to assess data quality. Therefore, a rating of C was assigned to the test data contained in Reference 1. A copy of the paper is provided in Appendix A, along with applicable emission factor calculations.

4.1.2 Reference 2

Reference 2 is a technical paper that summarizes the results of flux measurements for two barren fields planted with maize. Manure, which was used as the basic nitrogen fertilizer, was fortified with either NH_4NO_3 or with a combination of NH_4NO_3 and urea. The fertilizer mix was dry broadcast at an application rate of 181 kg N/ha (161 lb N/ac) for the ammonium nitrate fortified manure and 237 kg N/ha (211 lb N/ac) for manure fortified with ammonium nitrate and urea. The material was immediately incorporated into the soil at the time of application.

Triplicate measurements of the N_2O emitted from the soil were conducted using a closed flux chamber over a period of 330 days. Headspace air samples were collected from the chamber using plastic syringes. The air samples were later analyzed using GC/ECD to determine the concentration of nitrous oxide. Soil grab samples were collected and analyzed for moisture, pH, and texture. Soil temperature and precipitation also were monitored as part of the study. Emission factors were developed for N_2O emissions from the dry application of a mixture of manure and NH_4NO_3 and from the application of a mixture of manure, NH_4NO_3, and urea.

As was the case with Reference 1 above, this paper reported only experimental data. The measurements were conducted using a generally accepted methodology that was adequately documented. The data contained in Reference 2 were, therefore, assigned a rating of C. A copy of Reference 2 is provided in Appendix B, along with applicable emission factor calculations performed using the data provided in the document.

4.1.3 Reference 3

Reference 3 is a technical paper of a study conducted at two sites in Sweden that were treated with calcium nitrate ($Ca(NO_3)_2$), a nontypical fertilizer. Fertilizer application rates of 120 kg N/ha (107 lb N/ac) (barley) and 200 kg N/ha (178 lb N/ac) (grass) were used at the two test sites. Two additional, unfertilized sites (barley and lucerne) were used as experimental controls. All four sites had soil of the same general type. The method used for application of the fertilizer was not specified.

Replicate air sampling was conducted using a flux chamber installed over the soil surface at each site over a period of 2 to 10 min. A commercial chemiluminescent analyzer was used to analyze the air sample extracted from the chamber for NO. Data on soil moisture, pH, texture, and temperature were collected during the study and reported in the paper.

Although the data were reasonably well presented, certain key information (e.g., method of fertilizer application) was missing. For this reason, a rating of D was assigned to the experimental data reported in Reference 3. A complete copy of the reference is provided in Appendix C, which also includes emission factor calculations performed using the experimental data. An emission factor was developed for NO emissions from the application (unspecified method) of $Ca(NO_3)_2$. However, because the application method was not specified, this emission factor was not incorporated into Section 9.2.1 of AP-42.

4.1.4 Reference 4

Reference 4 is a technical paper that reports the results of air and soil sampling at two forested locations (Sorentorp and Jardass) in Sweden. At each location, six individual test sites were selected: two fertilized, two watered only, and two untreated. For the fertilized sites, either fluid $Ca(NO_3)_2$ or fluid sodium nitrate ($NaNO_3$) was spray-applied to the moss-covered soil (grey-brown podsolic) at a rate of 46.4 kg N/ha (41.3 lb N/ac) and 11.2 kg N/ha (9.98 lb N/ac), respectively.

Duplicate measurements were made during each sampling period using a flux chamber. The concentration of NO was determined shortly after installation of the chamber using a continuous chemiluminescent analyzer. A total of 82 separate measurements (35 at Sorentorp and 47 at Jardass) were taken after application of the fertilizer on 12 different test plots over a period of 340 h. Soil parameters reported included pH, texture, and selected cation concentrations (by wet chemistry).

Since reference 4 is the original publication of the experimental data, it was considered in the development of candidate emission factors. The tests were performed using a generally accepted but nonstandard methodology. Documentation of the results was lacking and little information was provided about instrument calibration and maintenance. For these reasons, a rating of D was assigned to the test data. A copy of the reference is provided in Appendix D, along with appropriate emission factor calculations. Emission factors were developed for NO emissions from spray application of $Ca(NO_3)_2$ and $NaNO_3$.

4.1.5 Reference 5

Reference 5 is a technical paper that summarizes the results of emission testing at multiple test plots (sites) at two different locations (Mainz, Germany, and Seville, Spain). At the first location (Mainz), seven plots were tested for NO/NO_2: two unfertilized sites with barren soil, one barren site fertilized with ammonium chloride (NH_4Cl), one barren site fertilized with $NaNO_3$, one barren site fertilized with ammonium nitrate (NH_4NO_3), one unfertilized site covered with grass, and one grass-covered site fertilized with ammonium chloride (NH_4Cl). For the second test location (Seville), six different plots were evaluated for fluxes of NO/NO_2: one unfertilized site with barren soil, two barren sites fertilized with NH_4NO_3, one barren site fertilized with $NaNO_3$, one barren site fertilized with urea; and one barren site fertilized with NH_4Cl. At the Seville location, three additional plots were used to determine fluxes of N_2O: one unfertilized site with barren soil, one barren site fertilized with NH_4NO_3, and one barren site fertilized with urea. All fertilizers were applied as a fluid spray at a rate of 100 kg N/ha (89.1 lb N/ac).

Duplicate measurements were made using a flux chamber over a 15- to 18-day study period at each test site. A continuous chemiluminescent analyzer was used to determine the concentration of NO and NO_2. Semicontinuous N_2O measurements were also obtained using a gas chromatograph equipped with a gas sampling loop. At the Mainz location, sampling was conducted between 8 a.m. and 6 p.m., and 1 to 3 flux measurements were obtained each day at all seven plots. For the Seville location, NO and NO_2 flux rates were determined 5 to 8 times per day between 6 a.m. and 11 p.m. at each of the plots. Soil grab samples were collected and analyzed for pH, texture, and moisture content. Rainfall and soil temperature were also measured during the study. Emission factors were developed for NO, NO_2, and N_2O emissions from spray application of NH_4NO_3, urea, NH_4Cl, and $NaNO_3$.

Reference 5 reported original data and thus was suitable to use for emission factor development. The tests were conducted using an accepted methodology and instrumental detection limits and accuracy determinations were specified in the text. However, certain key information was lacking with respect to the measurement method used for N_2O as well as details on the fertilizer application. Also, information was lacking on actual emission calculation procedures. For these reasons, a rating of D was assigned to the data contained in Reference 5. A copy of the paper is reproduced in Appendix E, which also contains calculations performed using the experimental data.

4.1.6 Reference 6

Reference 6 is a technical paper that is a companion study to reference 5. In reference 6, five different plots were tested for fluxes of N_2O at one location near Seville, Spain. Two plots were covered with Bermuda grass; the other three plots were located on cultivated land, which remained unplanted until the beginning of the study. One plot of each type remained unfertilized and was the experimental control. The remaining Bermuda grass plot received a 55 percent liquid solution of NH_4NO_3, which was spray-applied. The two fertilized plots on the cultivated land were treated with either urea or NH_4NO_3, which was applied as a liquid solution. The application rate of all fertilizers was 100 kg N/ha (89.1 lb N/ac).

A flux chamber was used to determine N_2O emission rates over a 31-day period. The flux chamber was installed over the soil surface, and the pollutant concentration was determined by the same semiautomatic sampling and analysis technique described above for reference 5. Using this method, eight individual data points were generated each day per plot for the grass-covered plots. For the three cultivated plots, six individual measurements were made each day on each plot. Emission factors were developed for N_2O emissions from spray application of urea and NH_4NO_3.

Reference 6, like Reference 5, is the first publication of original data collected during the study. The tests were conducted using an accepted method, but documentation for both analysis method and results was somewhat limited. For this reason, a rating of D was assigned to the test results reported in Reference 6. A copy of the paper, as well as applicable hand calculations, is included in Appendix F.

4.1.7 References 7 and 8

References 7 and 8 are original publications of a study conducted at a single site located in Narrabri, New South Wales. In this study, 130 kg N/ha (116 lb N/ac) of anhydrous NH_3 was injected into a bare, moist clay soil at a depth of 12 cm. The fertilizer was applied 12 bands at a time and was spaced 0.5 m (20 in.) apart.

"Static" air samples (Figure 3-1) were collected downwind of the site at sampling heights of 0.31, 0.74, 1.24, and 2.24 m (1.02, 2.43, 4.07, and 7.35 ft). Bubblers containing 5 mL of 2 percent phosphoric acid were used to collected the samples, which were later analyzed for NH_3 content. Samples were initially collected during every applicator pass, but later samples were collected every two or four passes. The average sampling time per pass was 17 min. In addition, soil samples were collected and analyzed for total nitrogen (Kjeldahl), bulk density, and moisture content. Wind speed and air temperature were determined at each measurement height. An emission factor was developed for fugitive NH_3 emissions from anhydrous NH_3 application.

References 7 and 8 are the first publication of original data, and the tests were performed using a reasonable test protocol. Appropriate QA procedures appear to have been applied and results were well documented. For these reasons, a rating of B was assigned to the test data. Copies of both papers are provided in Appendix G, along with applicable emission factor calculations.

4.1.8 Reference 9

Reference 9 is a technical paper that summarizes the results of a study conducted at the Iowa State University Agronomy Research Center near Ames, Iowa. Ammonium sulfate [$(NH_4)_2SO_4$], urea, and $Ca(NO_3)_2$ were applied to 72 different plots of cultivated land at application rates of 125 kg N/ha (111 lb N/ac) or 250 kg N/ha (223 lb N/ac). The emissions of N_2O from these plots were compared to 12 unfertilized plots at the same location. The fertilizers were spray-applied to rototilled barren soil in seven duplicate treatments and were then immediately tilled into the soil.

Nitrous oxide emission rates were determined over a period of 96 days using a closed flux chamber installed over the soil surface. Multiple grab samples were extracted from the chamber headspace over 10-min measurement periods. The samples were later analyzed by gas chromatography using xenon as an internal standard. Soil parameters determined during the study included temperature (at 7.5 cm [2.95 in.]), moisture content, field capacity, and exchangeable ammonium and nitrate content. Emission factors were developed for N_2O emissions from spray application of $Ca(NO_3)_2$, urea, and $(NH_4)_2$ SO_4.

Reference 9 is the first publication of the original data from the experimental program. The tests were performed using a generally accepted method and reasonable documentation was provided on the sampling and analysis conducted in the study. For these reasons, a rating of B was given to the data provided in Reference 9. A copy of the publication is provided in Appendix H, along with applicable emission factor equations.

4.1.9 Reference 10

Reference 10 is a technical paper summarizing the results of a 2-year study conducted at two sites (Harrow and Woodslee) in Ontario, Canada. At the Harrow site, NH_4NO_3 was applied once a year during the study period to multiple test plots by dry broadcasting at application rates of 0, 112, 224, and 336 kg N/ha (100, 200, and 300 lb N/ac). At the Woodslee location, five different plots were sampled during the first year of the study. Four plots were treated with either potassium nitrate (KNO_3) or urea at application rates of 168 kg N/ha (150 lb N/ac) or 336 kg N/ha (300 lb N/ac), and the fifth plot was left unfertilized. During the second year at Woodslee, plots of the same soil type were treated with NH_4NO_3 at application rates of 112, 224, and 336 kg N/ha (100, 200, and 300 lb N/ac), respectively. One unfertilized plot also was used as the experimental control during the second year of testing. All sampling sites were planted with corn during the study.

Triplicate sampling was conducted over a period of up to 1 year using a flux chamber. The chambers were installed between the rows of corn with the edges of the chamber inserted 5 to 10 cm (1.97 to 3.94 in.) into the soil. Three samples were collected from the chamber headspace every 30 min using evacuated Pyrex tubes. The tube samples were analyzed for N_2O using GC/ECD with a Porapak Q column. Soil moisture content also was determined in the study. Emission factors were developed for N_2O emissions from dry application of urea, NH_4NO_3, and KNO_3.

Reference 10 is the first publication of original experimental data. The tests were conducted using a generally accepted method, and better than average documentation was provided on calibration of the analytical instrument. The lack of continuity in fertilizer type and application at the Woodslee location between the 2 years of the study made data comparison difficult. For these reasons, a rating of C was assigned to the data contained in Reference 10. A copy of Reference 10, along with applicable emission factor calculations, is provided in Appendix I.

4.1.10 Reference 11

Reference 11 is a technical paper that summarizes a study conducted at a site in Canada. Urea was applied to a Kentucky bluegrass/red fescue sod mowed to a height of 7.5 cm (2.95 in.). The fertilizer was dry-broadcast at a rate of 100 kg N/ha (89.1 lb N/ac) in a circular area of 0.405 ha (1.0 ac) for test purposes.

Static air sampling was conducted in the center of the test plot using a single mast on which "gas collector flasks" and anemometers were mounted at heights of 10, 50, 100, and 150 cm (3.94, 19.7, 39.4, and 59.1 in.). Two-hour samples were collected by continuously passing air through 500-mL glass tubes containing glass beads and a 3 percent solution of H_3PO_4. The concentration of NH_4^+ in the absorbing solution was measured colorimetrically using a Technicon Autoanalyzer procedure. Using an atmospheric dispersion calculation, the total mass flux of NH_3 from the site was determined from the measurements. An emission factor was developed for NH_3 emissions from dry application of urea.

Because Reference 11 is the first publication of original experimental data, it was considered in the analysis. The tests, however, were conducted using a generally unproven test method, and the information in the reference was poorly documented with few details provided on test conditions, analytical results, and so forth. Therefore, a rating of D was assigned to the data contained in Reference 11. A copy of the document, along with appropriate emission factor calculations, has been provided in Appendix J.

4.1.11 Reference 12

Reference 12 is a technical paper that presents the results of a sampling program conducted at a site located in New York State. Anhydrous NH_3 was applied to a depth of 10 to 20 cm (4 to 8 in.) in loam soil at rates of 95.4 to 293 kg N/ha (85 to 261 lb N/acre). Ammonia loss was determined both behind the applicator knife as well as outside of the knife path.

To determine the loss of NH_3, a simple flux chamber system, consisting of an inverted pan inserted into the soil, was used. Air was passed through the chamber in a dynamic manner and was directed to an acid absorption tower containing dilute sulfuric acid. Up to 20 different chambers were operated simultaneously for a period of about 6 h for sample collection. The amount of NH_3 collected by the acid in the absorption tower was determined by titrating with standardized NaOH. In addition, one pan was placed immediately above the applicator blade, and air was pulled through an absorption tower at the rate of 3 ℓ/min. This system provided an estimate of the fugitive emissions during application, while the other pans provided a measure of immediate emissions.

Reference 12 is the first publication of the experimental results obtained in the study. The test method used was somewhat crude, but it was reflective of measurement technology available when the sampling was conducted. Therefore, a rating of D was assigned to the data contained in Reference 12. A copy of the paper, accompanied by applicable hand calculations, is provided in Appendix K.

4.1.12 Reference 13

Reference 13 is a technical paper that studies the influence of plant residues (chopped wheat straw) on denitrification rates in conventional tilled (CT) and zero tilled (ZT) soils using hard red spring wheat as the test crop. Flux measurements and cumulative gaseous N_2O-N losses from the study plot in Saskatchewan were measured using the acetylene inhibition technique. Four plots were prepared for each of the two tilled soils: one was a control, one had straw treatment only, one had fertilizer only, and one had fertilizer plus straw. For plots receiving fertilizer, an aqueous solution of ammonium sulfate [$(NH_4)_2SO_4$] at a level of 100 kg of N per hectare (kgN/ha) was applied using a back-pack sprayer.

Samples were obtained from each test plot during the test period (June 5 to September 4, 1981) by removing three pairs of undisturbed soil cores from each treatment every week. The major N_2O emissions for fertilized ZT and CT plots occurred during June following a heavy mid-June rainfall. Emissions of N_2O were much higher for the ZT plots than the CT plots during this period.

Reference 13 is the first publication of the original data. Tests were performed using a relatively new method for measurement; reference was provided to an earlier publication for the method but analytical procedure and calibration data were lacking for the current study. For these reasons, a rating of D was assigned to the test data. A copy of the reference is provided in Appendix L along with appropriate emission factor calculations. Emission factors were developed for N_2O emissions from spray application of $(NH_4)_2SO_4$.

4.1.13 Reference 14

This reference is a technical paper that reports the results of a study on the influence of soil compaction and fertilization on methane uptake and N_2O emissions from an easily compacted soil in the humid climate of western Norway. The experiment was a split-plot design with two replicates, soil compaction on main plots and fertilization on small subplots. Flux measurements were obtained using soil cover chambers placed at random within each field plot. Fertilizer treatments were: NPK fertilizer (18-3-15) at an application rate of 140 kg NH_4NO_3-N/ha and two cattle slurries (CS) equivalent to 189 kg N/ha and 81 kg N/ha. Dry fertilizer was spread by hand and the CS fertilizers were diluted with water and spread by can with a spreading plate. Soil compaction was done with a double rear-wheel tractor. The crops were green fodder with rape, barley, peas, vetch, and rye grass.

Gas fluxes at the soil surface were measured by removing gas samples through rubber stoppers in the top of the soil cover chambers and storing the samples in evacuated glass vials. Fluxes were estimated by the increase in concentration during the first 3 hours after placement. Within 14 days of sampling, the samples were analyzed by gas chromatography using one of three detectors, depending on N_2O concentration or presence of CH_4 or CO_2. The areas under the flux curves were used to estimate the accumulated N_2O emissions and methane uptake during the experiment. Reference 14 is the first publication of the original data. The tests were performed using a generally accepted analysis method and reasonable documentation was provided for the sampling method. A rating of C was assigned to the test data. A copy of the reference is provided in Appendix M along with emission factor calculations.

4.1.14 Reference 39

Reference 39 is a technical paper that presents measurements of NO and N_2O emissions from fertilized Bermuda grass plots located in a subtropical region of southern Texas. The measurements were taken during the 1989 growing season (May 24 through July 26). Ammonium sulfate $(NH_4)_2SO_4$ was applied at a rate of 52 kg N/ha (46 lb/ac) in an intensive cultural management scheme. The management scheme consisted of harvest and fertilization cycles repeated every 9 weeks. The application method was not specifically discussed, but the text indicates that the fertilizer was a solid and was probably broadcast. Selected soil and climatic data was recorded and presented in the paper.

The experiment to determine N_2O emissions utilized a vented, cylindrical soil cover mounted on top of a ring driven 5 cm into the soil. Each cover was constructed of polyvinyl chloride pipe, insulated with polyurethane foam and covered with a reflective aluminized polyester film to reduce heating of the soil. The experiment to determine NO emission used a similar cover equipped with an air circulator. Air was collected using polypropylene syringes equipped with nylon stopcocks. Collected samples were analyzed within 12 hours using a gas chromatograph equipped with an electron capture detector. The experimental method was designed to maximize consistency and allowed slightly enhanced NO emissions due to the clipping and removal of grass.

Reference 39 reported the results of original experimental data. The measurements were conducted using acceptable methods and adequate documentation was provided to evaluate data quality. The data are assigned a C rating. A copy of Reference 39 is provided in Appendix N, with applicable emission factor calculations performed using the data provided in Table 2 of the article.

4.1.15 Reference 41

Reference 41 is a technical paper that presents NO and N_2O emissions from a fertilized no-till corn site at the West Agricultural Experiment Station in Jackson, Tennessee. The data were collected between April 27 and November 30, 1993 (210 d). Corn was planted on April 21 in 76 cm rows on four replicated plots. The application method was not discussed. However, based on comparisons within the article to other articles that document emissions from dry broadcast application, the application method for this study is assumed to be dry broadcast application. Soil data were recorded and presented in the article.

A static-chamber technique was utilized to collect emissions data. The chambers were constructed of an aluminum frame driven 20 cm into the ground. The frame was enclosed with an aluminum cover equipped with sampling ports. Air samples were withdrawn at 3-minute intervals using a gas correlation instrument. Gross emission rates were obtained using measured data in conjunction with mass balances. The experimental method included process steps to ensure the reliability of data.

Reference 41 reported original experimental results. The experimental and analytical methods were acceptable. Adequate documentation was provided to evaluate the data quality. However, the application method was not discussed. The data were assigned a C rating. A copy of Reference 41 is provided in Appendix O, with an applicable emission factor calculations performed using the data provided in Table 2 of the article.

4.1.16 Reference 43

Reference 43 is a technical paper that summarizes the results of N_2O emissions from different cropping systems and aerated, nitrifying, and denitrifying tanks of a municipal waste water treatment plant. Data pertaining to the tanks at the municipal waste water treatment plant were not considered. The experiments were implemented at the Experimental Station of the Institute for Agronomy and Plant Breeding, Justus Liebig University, Germany. Average soil and climatic data were recorded and presented in the paper.

The experimental site consisted of 8 x 10 m plots. The sites were established in 1982 and ammonium nitrate (assumed dry broadcast application) was applied at rates of 80 kg N/ha (71 lb/ac) and 120 kg N/ha (107 lb/ac) on independent experimental plots. The N_2O emission fluxes were determined as described by Scwartz et al. (1994), but without flushing the soil sample with C_2H_2. Open chambers with a steel base and a removable lid were placed 5 cm into the soil between the rows. Samples were collected in three molecular sieve traps during 4h/d periods with the chamber lids installed. The chamber lids were removed at other times to prevent microclimate changes within the testing environment.

Reference 43 reported original experimental data. The measurements were conducted using acceptable methods and adequate documentation was provided to evaluate data quality. As a result, the data are assigned a C rating. A copy of Reference 43 is provided in Appendix P, with applicable emission factor calculations performed using the data provided in the text on page 257 of the article.

4.2 DEVELOPMENT OF CANDIDATE EMISSION FACTORS

As discussed in Section 2.3, emissions of gaseous air pollutants associated with the application of nitrogen fertilizers may be "immediate," generated during or shortly after application, and/or "latent," occurring days or weeks after application. Candidate emission factors for both emission types were developed as discussed below.

4.2.1 Analysis of Experimental Data

No comprehensive emission test reports were found in the literature search. Technical papers published in refereed journals were used for emission factor development. All the data in these technical papers were generated for the purpose of determining global budgets of nitrogenous greenhouse gases and not for emission factor purposes. Inconsistent and nonstandardized sampling and analytical methods were used, and testing was conducted over vastly different time periods, from a few hours or days to months or even years. For this reason, analysis of the data was difficult and resulted in generally low ratings being assigned to the emission factors.

To derive the candidate emission factors for fertilizer application, individual emission factors were hand calculated for each test series from the experimental data (see Appendices A to M). All emission factors were normalized on the basis of equivalent nitrogen applied, regardless of fertilizer type. The emission factors obtained from each reference were tabulated according to type of emission (i.e., immediate or latent) and type of pollutant, and the arithmetic mean and standard deviation were calculated for the data in each pollutant category.

The arithmetic mean of the individual emission factors in each pollutant category was calculated, as appropriate, by summing the emission factors derived from each test data set and dividing the sum by the total number of factors.

The standard deviation of the average emission factors was calculated using the general expression:

$$s = \left[\frac{\sum x_i^2 - \frac{(\sum x_i)^2}{n}}{n-1} \right]^{0.5} \tag{4-1}$$

where: s = standard deviation
n = number of individual emission factors
x_i = emission factors derived from each test data set

The candidate emission factors developed by the above method are provided in Tables 4-2 and 4-3 for immediate and latent pollutant emissions, respectively. Except in the case of latent N_2O, the candidate emission factors shown in these tables were obtained by averaging all data sets in each pollutant category.

In Reference 5, emission data were presented for soil emissions of NO and NO_2. Recent scientific papers discussing the biological mechanisms for NO_x emissions from the soil have cited evidence to show that essentially all (over 90 percent) NO_x emissions are in the form of NO and little, if any, are in the form of NO_2. There is no evidence to conclude that appreciable quantities of NO_2 are emitted directly from the soil. The formation of NO_2 occurs through the rapid oxidation of the NO by ozone present in the soil or the air above the soil (Reference 39). The authors in Reference 5 state that their measurements clearly indicate the establishment of NO and NO_2 equilibrium mixing ratios. The NO_2 data reported in Reference 5 are included in Table 4-3. However, because of the differing viewpoints concerning soil emissions of NO_2, these data are not used to develop candidate emission factors later in this section and were not included in the AP-42 section.

As shown in Tables 4-2 and 4-3, the data used to derive the candidate emission factors are highly variable and typically range over several orders of magnitude. Also, the data are usually of limited quantity and of poor quality, which is reflected in the E rating assigned to the candidate emission factors. For this reason, appropriate footnotes are provided to explain the derivation and applicability of each emission factor determined in the analysis. Also, some of the average emission factors should be interpreted cautiously as noted in the paragraphs below.

The immediate emissions of NH_3 generated by the application of anhydrous NH_3 (Table 4-2) are quite low compared to the latent emissions of the same pollutant from the application of urea (Table 4-3). A substantial reduction in NH_3 emissions has been realized by the use of newer, subsurface injection methods in comparison to older techniques employing surface application. Second, the magnitude of the latent NH_3 emissions for solid, ammonia-containing fertilizers, such as urea, is highly affected by soil properties and biota population. Therefore, the candidate emission factor developed subsequently may not be indicative of the generation of this pollutant from other general soil types.

Another factor to note relates to the time period over which the latent emissions were generated and measured. Table 4-3 shows that widely varying time periods were monitored to determine the total mass emission factors in each study. From the references reviewed, it was determined that the majority of the emissions are created during a relatively limited period of time with lower emission rates occurring in the preceding and succeeding periods. The location of this maximum emission period on the temporal scale after application varies substantially as a function of fertilizer and application type, soil conditions, meteorology, and climatology. Furthermore, release rates show substantial diurnal variation, probably as a function of temperature. Thus, the temporal distribution of latent emissions is not well defined, and the usefulness of the factors for short-term emission estimates is questionable.

Finally, since all emission estimates were expressed in terms of equivalent nitrogen applied, appropriate calculations may be required to convert application rates to a common format for use with the emission factors shown in Tables 4-2 and 4-3. Table 4-4 provides the equivalent nitrogen content of several commonly used chemical fertilizers. It should be noted that the nitrogen content of a fertilizer is usually specified by the manufacturer on the container. If combinations of fertilizers are used, the overall nitrogen equivalent can be calculated by proportional multiplication of the individual factors provided in Table 4-4 based on the composition of the mixture.

4.2.2 Candidate Emission Factors

Using data from the references described in Section 4.1 of this report, candidate emission factors were compiled for inclusion in AP-42 for the application of anhydrous NH_3, urea, NH_4NO_3, $CA(NO_3)_2$, $NaNO_3$, NH_4Cl, and $(NH_4)_2SO_4$ fertilizers. An emission factor also was developed for the application of a mixture of fertilizers in which nitrogen is the primary component. These emission factors are summarized in Table 4-5. Candidate emission factors are presented for immediate, latent, and fugitive NH_3; latent NO; and latent N_2O. Latent NO_2 emissions are not included in the table because scientific evidence cited in recent technical papers do not support the soil emission of NO_2 but rather the oxidation of NO to NO_2. All of these emission factors are rated E because they are based on a combination of B-, C-, and D-rated data.

4.2.2.1 Ammonia (NH_3). Two emission factors were developed for NH_3 emissions from application of anhydrous NH_3. An emission factor for fugitive emissions directly off the application was obtained from the average of the 4 tests from Reference 12 shown in Table 4-2. The emission factor for immediate volatilization over a 1 to 3 hour period was obtained by averaging the factors of 22.4 lb/ton from References 7 and 8 and 2.30 lb/ton from Reference 12. The emission factor for latent NH_3 emissions from broadcast application of solid urea fertilizer is based on two tests documented in Reference 11.

4.2.2.2 Nitric Oxide (NO). The emission factor for latent NO emissions from broadcast application of fluid urea fertilizer is based on a single test documented in Reference 5, and the emission factor for latent NO emissions from broadcast application of fluid NH_4NO_3 fertilizer is based on the average of two tests documented in Reference 5. The emission factor for latent NO emissions from the application of fluid $Ca(NO_3)_2$ is based on two tests documented in Reference 4, and the emission factor for latent NO emissions from the application of fluid $NaNO_3$ is based on the average of a test documented in Reference 4 and the average of two tests documented in Reference 5. The emission factor for latent NO emissions from the application of fluid NH_4Cl is based on two tests documented in Reference 5 (a third test conducted on a grass-covered test plot was not used). The emission factor for latent NO emissions from broadcast application of solid NH_4NO_3 fertilizer is based on a test documented in Reference 1 and the average of two tests documented in Reference 41. The emission factor for latent NO emissions from broadcast application of solid $(NH_4)_2SO_4$ is based on a single test documented in Reference 39. All values in Table 4-5 were taken directly from appropriate averages in Table 4-3.

4.2.2.3 Nitrous Oxide (N_2O). The emission factor for latent N_2O emissions from broadcast application of fluid urea fertilizer was developed from one test documented in Reference 5 (11.5 lb/ton), one test documented in Reference 6 (11.3 lb/ton), and two tests documented in Reference 9 (7.96 lb/ton). The emission factor for latent N_2O emissions from broadcast application of fluid NH_4NO_3 fertilizer was developed from one test documented in Reference 5 (2.52 lb/ton) and the average of two tests documented in Reference 6 (3.62 lb/ton). The emission factor for latent N_2O emissions from application of fluid $Ca(NO_3)_2$ is based on two tests documented in Reference 9 (1.7 lb/ton). Two emission factors (one for standard tilling and one for a zero-till plot), both based on single tests documented in Reference 13, are presented for latent N_2O emissions from the application of fluid $(NH_4)_2SO_4$. The emission factor for latent N_2O emissions from broadcast application of solid NH_4NO_3 fertilizer was developed from one test documented in Reference 1 (333 lb/ton), one test documented in Reference 14 (212 lb/ton), the average of two tests documented in Reference 41 (56.2 lb/ton), and the average of three tests documented in Reference 43 (45.8 lb/ton). Two emission factors for latent N_2O emissions from broadcast application of a mixture of nitrogen-based fertilizers were developed. An emission factor from a mixture that does not include manure was developed from one test documented in Reference 10, and an emission factor from a mixture that does include manure was developed from the average of two tests documented in Reference 2.

The emission factor for latent N_2O emissions from application of solid $(NH_4)_2SO_4$ is based on a single test documented in Reference 39 (12.1 lb/ton).

As noted in Table 4-5, total mass emission factors tend to increase, at least partially, with oxidation number. This appears to be reasonable from a mechanistic viewpoint, taking into consideration the expected production of primary emissions in the soil matrix and their interaction with the atmosphere at the interface (see Figures 2-8 and 2-9).

There is substantial variability in the emissions data both from within sites and between different sites and the overall quality of the data is poor. Because of this, the emission factors in Table 4-5 provide only relatively crude estimates of the emissions resulting from the application of nitrogenous fertilizers, and should be used with caution. No attempt should be made to infer that there is any significant difference in emissions between fertilizer types or that any degree of emission control could result from the use of different types of fertilizers. Additional testing under controlled conditions using a standardized procedure would be required to improve the quality of the emission factors shown in Table 4-5.

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TABLE 4-1. DOCUMENTS REJECTED FOR EMISSION FACTOR DEVELOPMENT

Ref. No.	Reason for rejection
5	Secondary paper; no new air emission data presented; all secondary data simply presented as percentage loss
16	Combustion effects study; no process data from which to calculate emission factor because fertilizer not applied
17	Study of the effect of soil properties on denitrification; no process data to convert emission rates to emission factors
18	Excellent emission flux data, but no information presented on application rates
19	Study of the effects of soil properties and climatic conditions on NO and NO_2 flux rates with excellent flux data; no fertilizer application data to allow emission factor calculation
20	Laboratory studies of basic mechanisms; no data on actual field applications, and no application rates for laboratory studies
21	Laboratory study of the effects application technique on NH_3 volatilization rates; no field application data
22	Nonrepresentative sampling conditions make flux rate estimates unreliable
23	Limited data presented on application rates, but data on fertilizers and application methods insufficient to develop reliable emission factors
24	Reliable flux data and limited application rate data, but data on application methods and fertilizers insufficient to develop reliable emission factors
25	Secondary study of the sulfur cycle; no original emission test data
26	Secondary study of the sulfur soil cycle; no emission test data
27	Review study on the nitrogen cycle; no emission test data
28	Summary report on available information on the nitrogen cycle as of 1976; general global emission estimates presented, but no emission test data provided
29	Laboratory study of denitrification process; no actual field application data
30	A study of NO_x emissions from three land use types during summer and fall testing; detailed descriptions of new flux chamber and flux data were given but no identification of fertilizer type was provided
31	A greenhouse study of nitrous oxide and nitric oxide emissions with and without the addition of a nitrification inhibitor; no actual field application data
32	Study of factors controlling emissions in cool temperate climates; emission flux data presented but no sampling time intervals or description of application methods
33	Study of a wide range of fertilizer application rates, soil textures, grazed and ungrazed sites, soil moisture, and soil temperature on denitrification patterns; no data presented for fertilizer types or application methods and only general analytical methods provided
34	Reports flux data for nitrogen plus nitrous oxide combined but no separate data, no accumulation data, and no time duration data
35	Study of effects of lime on reducing nitrous oxide emissions from a beech forest; N_2O emissions unreliable because control plot had been fertilized for each of previous 5 years and no application methods given
36	Laboratory study of farmyard manure application; no actual field application data
37	A review article on NO_x and N_2O emissions from soil. Presents summaries of NO and N_2O emission flux data for several land use categories but no data on application rates or accumulated emissions.
38	Sampling began months after the fertilizer application. Study was performed to compare test methods, not to quantify emissions from fertilizer application.
40	Application of both solid and fluid fertilizer; report does not specify how much of each fertilizer was used
42	Unspecified application method
44	Time period not specified and total emissions not provided
45	Methane emissions from a flooded rice field; not applicable
46	No original data presented
47	Emissions not related to fertilizer application
48	Methane emissions from a rice field; not applicable

TABLE 4-1. (continued)

Ref. No.	Reason for rejection
49	No original test data presented
50	Global estimates; no original test data presented
51	No original test data presented
52	Methane emissions from fertilizer storage; not applicable
53	Methane emissions from manure not applied as a fertilizer
54	No original test data presented
55	No original test data presented
56	Total amount of fertilizer applied not specified
57	Global estimates; not presented by application method
58	Study on NH_3 inhibitors; soil losses measured, but actual air emissions were not measured
59	Emissions from fertilizer and livestock waste; cannot determine contribution from individual sources
60	No original test data presented
61	No original test data presented

TABLE 4-2. SUMMARY OF TEST DATA FOR IMMEDIATE EMISSIONS FROM THE APPLICATION OF ANHYDROUS AMMONIA

Emission Factor Rating: E

Pollutant[a]	Ref. No.	Type of fertilizer applied	Application rate, kg N/ha[b]	Total mass emission factor[c]		Data quality rating	Emission generation period, h[d]	Average emission factor[e]	
				g pollutant/ kg N applied	lb pollutant/ ton N applied			g pollutant/ kg N applied (s)	lb pollutant/ ton N applied (s)
NH_3	7, 8[f]	ℓ-NH_3[g]	107	11.2[h]	22.4[h]	B	2	11.2	22.4
	12[h]	ℓ-NH_3[g]	227	<1.21	<2.42	D	6	1.15 (0.89)[i]	2.30 (1.8)
			214	<1.21	<2.42		6		
			292	1.82	3.65		6		
			95	<1.21	<2.42		6		
			95	<1.21	<2.42		6		
			272	2.67	5.35		9		
	12[j]	ℓ-NH_3[g]	288	0.012	0.024		3.3	0.203 (0.27)	0.405 (0.54)
			251	0.072	0.146		6.6		
			293	0.606	1.21		3.3		
			293	0.12	0.24		3.3		

[a] NH_3 = Vapor-phase ammonia volatilized after application of anhydrous ammonia.

[b] Amount of equivalent N added to the soil. 1 kg N/ha = 1.21 kg NH_3/ha; 1 ha = 10^4 m^2 = 2.471 acres.

[c] Total emissions to the atmosphere regardless of time period, expressed in terms of total nitrogen applied to the soil. 1 g/kg N = 2 lb/ton N. See appropriate appendix containing reference and hand calculations.

[d] Time period over which the emissions were measured.

[e] Arithmetic mean of total mass emission factors. Standard deviation (s) shown in parentheses.

[f] Emissions over 2 hour period after applications.

[g] Liquid anhydrous ammonia injected as a gas into the soil at a depth of at least 10 cm (4 in.).

[h] Emissions over 6 to 9 hour period after application.

[i] Mean values were calculated using half of the detection limit for those runs below detection.

[j] Fugitive emissions released immediately behind the blade.

TABLE 4-3. SUMMARY OF TEST DATA FOR LATENT EMISSIONS FROM THE APPLICATION OF NITROGEN FERTILIZERS

Pollutant gas[a]	Ref. No.	Type of applic.[b]	Type of fertilizer applied[c]	Application rate, kg N/ha[d]	Total mass emission factor[e]		Data quality rating	Emission generation period, days[f]	Average emission factor[g]	
					g pollutant/ kg N applied	lb pollutant/ ton N applied			g pollutant/ kg N applied (s)	lb pollutant/ ton N applied (s)
NH_3	11	DRY	Urea	100	183	366	D	8	132 (72)	264 (144)
					81.1	162		5		
NO	1	DRY	NH_4NO_3	11.5; 23.1; 34.6[h]	236	472	C	160	236	472
	3	NS	$Ca(NO_3)_2$	200[j]	4.28[j]	8.56[j]	D	365	4.28	8.56
	4	SPR	$Ca(NO_3)_2$	46.4	6.56	13.1	D	14.2 (340 h)	3.8 (3.9)	7.6 (7.8)
				46.4	1.04	2.08		3.1 (75 h)		
			$NaNO_3$	11.2	3.20	6.40		1.9 (45 h)	3.20	6.40
	5	SPR	$NaNO_3$	100	0.738	1.48	D	18	1.88 (1.6)	3.76 (32)
			$NaNO_3$	100	3.02	30.4		30		
			NH_4Cl	100	32.5	65.1		18	29.4 (4.3)	58.4 (8.6)
			NH_4Cl	100	26.4	52.8		30		
			NH_4Cl[k]	100	11.9	23.9		18	11.9	23.8
			NH_4NO_3	100	13.5	27.0		18	14.4 (1.2)	28.7 (2.1)
			NH_4NO_3	100	15.2	30.4		30		
			Urea[k]	100	69.7	139		30	69.7	139
	39	DRY	$(NH_4)_2SO_4$	52	69.2	138	C	63	69.2	138
	41	DRY	NH_4NO_3	140	1.36	2.72	C	210	1.67 (0.44)	3.34 (0.88)
				252	1.98	3.96				
NO_2	5	SPR	$NaNO_3$	100	2.37	4.74	D	18	3.47 (1.5)	6.93 (3.1)
			$NaNO_3$	100	4.56	9.12		30		
			NH_4Cl	100	38.9	77.8		18	29.4 (13.5)	58.7 (27.1)
			NH_4Cl	100	19.8	39.5		30		
			NH_4Cl[k]	100	4.08[m]	8.16[m]		18	4.08	8.16
			NH_4NO_3	100	21.0	42.0		18	19.3 (2.4)	38.7 (4.7)
			NH_4NO_3	100	17.6	35.3		30		
			Urea[k]	100	71.9	144		30	71.9	144

TABLE 4-3. (continued)

Pollutant gas[a]	Ref. No.	Type of applic.[b]	Type of fertilizer applied[c]	Application rate, kg N/ha[d]	Total mass emission factor[e]		Data quality rating	Emission generation period, days[f]	Average emission factor[g]	
					g pollutant/ kg N applied	lb pollutant/ ton N applied			g pollutant/ kg N applied (s)	lb pollutant/ ton N applied (s)
N_2O	1	DRY	NH_4NO_3	11.5; 23.1; 34.6[h]	167	333	C	130	167	333
	2	DRY	Manure + NH_4NO_3	181	56.6	113	C	330	56.6	113
			Manure + NH_4NO_3 + Urea	237	64.5	129		330	64.5	129
	5	SPR	NH_4NO_3	100	1.25	2.52	D	30	1.25	2.52
			Urea	100	5.77	11.5		30	5.77	11.5
	6	SPR	Urea	100	5.66	11.3	D	30	5.66	11.3
			NH_4NO_3 NH_4NO_3	100 100	1.26 2.36	2.52 4.72		30 10	1.81 (0.79)	3.62 (1.5)
	9	SPR	$Ca(NO_3)_2$	125 250	1.31 0.352	2.61 0.704	C	96 96	0.83 (0.68)	1.66 (1.4)
			Urea	125 250	4.35 3.61	8.70 7.22		96 96	3.98 (0.52)	7.96 (1.05)
			$(NH_4)_2SO_4$	125 250	5.71 3.56	11.4 7.12		96 96	4.64 (1.5)	9.27 (3.0)
	10	DRY	Urea; NH_4NO_3; KNO_3	112; 224; 336[n]	7.86	15.7	D	80	7.86	15.7
	13	SPR	$(NH_4)_2SO_4$	100 100[p]	33.9 146	67.8 292	D	92 92	33.9 146	67.8 292
	14	DRY SPR	NH_4NO_3 Manure	140 81 189	106 73.7 49.9	212 147.4 99.8	C	27 27 27	106 61.8	212 124
	39	DRY	$(NH_4)_2SO_4$	52	6.04	12.1	C	63	6.04	12.1
	41	DRY	NH_4NO_3	140 252	30.2 26.0	60.4 52.1	C	210	28.1 (3.0)	56.2 (6.0)

TABLE 4-3. (continued)

Pollutant gas[a]	Ref. No.	Type of applic.[b]	Type of fertilizer applied[c]	Application rate, kg N/ha[d]	Total mass emission factor[e]		Data quality rating	Emission generation period, days[f]	Average emission factor[g]	
					g pollutant/ kg N applied	lb pollutant/ ton N applied			g pollutant/ kg N applied (s)	lb pollutant/ ton N applied (s)
	43	DRY	NH_4NO_3	80	17.7	35.4	C	ND	22.9 (7.4)	45.8 (15)
				120	19.6	39.2				
				120	31.4	62.8				

[a] NH_3 = Vapor-phase ammonia; NO = nitric oxide; NO_2 = nitrogen dioxide; and N_2O = nitrous oxide.

[b] Method of fertilizer application: INJ = injection; SPR = liquid spray; DRY = dry broadcasting; NS = not specified.

[c] $Ca(NO_3)_2$ = calcium nitrate; $NaNO_3$ = sodium nitrate; NH_4NO_3 = ammonium nitrate; NH_4Cl = ammonium chloride; and $(NH_4)_2SO_4$ = ammonium sulfate.

[d] Amount of equivalent N added to the soil. 1 kg N/ha = 1.21 kg NH_3/ha = 2.14 kg urea/ha = 8.13 kg $(NH_4)_2SO_4$/ha = 7.30 kg $Ca(NO_3)_2$/ha = 2.86 kg NH_4NO_3/ha = 3.72 kg NH_4Cl = 6.06 kg $NaNO_3$/ha. 1 ha = 10^4 m^2 = 2.471 acres; 1 kg = 1,000 g = 2.2 lb.

[e] Total mass emissions to the atmosphere regardless of time period, expressed in terms of total nitrogen applied to the soil. 1 g/kg N = 2 lb/ton N. From appropriate appendix containing reference and hand calculations.

[f] Time period over which the emissions were measured.

[g] Arithmetic mean of data shown in columns 6 and 7. Standard deviation(s) shown in parentheses.

[h] Emissions are proportionally the same for all application rates between 11.5 and 34.6 kg N/ha.

[j] Calculated from the overall totals provided in the reference document.

[k] Grass-covered test plot.

[m] Plot acted as a nitrogen sink at a rate of - 205 g NO_2/ha.

[n] Emissions are proportionally the same for all application rates and fertilizer types.

[p] Zero - till plot.

TABLE 4-4. EQUIVALENT NITROGEN CONTENTS OF COMMON CHEMICAL FERTILIZERS[a]

Type of fertilizer	Chemical formula	Nitrogen content[b] (weight percent)	Equivalent nitrogen content, lb fertilizer per lb N[c]
Anhydrous ammonia	NH_3	82.3	1.2
Urea	$CO(NH_2)_2$	46.7	2.1
Ammonium nitrate	NH_4NO_3	35.0	2.9
Ammonium sulfate	$(NH_4)_2SO_4$	21.2	4.7
Ammonium chloride	NH_4Cl	26.2	3.8

[a] Equivalents for pure chemicals.

[b] Nitrogen content (weight percent) = $\frac{\text{atomic weight of nitrogen}}{\text{molecular weight of fertilizer}} * 100\%$

e.g., for ammonia: $\text{wt\%} = \frac{14}{17} * 100\% = 82.3\%$

To determine the pounds of nitrogen per ton of fertilizer, multiply the nitrogen content (weight percent) times the tons of fertilizer. Then convert tons to pounds by multiplying by 2,000.

e.g., for one ton of urea:

1 ton x 46.7 x 1/100 = 0.467 tons of nitrogen
0.467 tons x 2,000 lb/ton = 934 lb of nitrogent/ton of urea

For fluid fertilizers, the weight of the solvent should not be included in calculating the weight of the fertilizer.

[c] Amount of fertilizer (lb) to produce 1 lb equivalent nitrogen application. To convert pounds of nitrogen to pounds of fertilizer, multiply pounds of nitrogen by the equivalent nitrogen content.

e.g., 934 lb N x 1.2 lb ammonia/lb N = 1,121 lb ammonia

TABLE 4-5. SUMMARY OF EMISSION FACTORS FOR FERTILIZER APPLICATION
Emission Factor Ratings: E

Application/fertilizer	PM-10	NH_3	NO	N_2O
Gaseous fertilizer:				
• Injection				
-- Anhydrous ammonia	NA	12[a] 0.41[b]	ND	ND
Fluid fertilizer:				
• Injection or deep band				
-- Aqueous ammonia	NA	ND	ND	ND
-- Urea	NA	ND	ND	ND
-- Ammonium nitrate	NA	ND	ND	ND
-- Nitrogen mixtures[c]	NA	ND	ND	ND
• Band, row, and broadcast application[d]				
-- Urea	ND	ND	140[e]	10[f]
-- Ammonium nitrate	ND	ND	29[e]	3.0[g]
-- Nitrogen mixtures[c]	ND	ND	ND	ND
-- Calcium nitrate	ND	NA	7.6[h]	1.7[j]
-- Sodium nitrate	ND	NA	5.1[k]	ND
-- Ammonium chloride	ND	ND	58[e]	ND
-- Ammonium sulfate	ND	ND	ND	39[m] 290[n]
• Aerial				
• Irrigation				
Solid fertilizer:				
• Broadcast application[d]				
-- Urea	ND	260[p]	ND	ND
-- Ammonium nitrate	ND	ND	240[q]	160[r]
-- Nitrogen mixtures[c]	ND	ND	ND	
-- without manure				16[s]
-- with manure				120[t]
-- Ammonium sulfate	ND	ND	140[u]	12[u]

ND = No data available.
NA = Not applicable.
All emission factors in terms of pounds of pollutant per ton of nitrogen in fertilizer applied (lb pollutant/T N applied).

[a] References 7, 8, 12. Volatilization immediately (1-3 hrs) after application (source No.2 on Figure 2-7a). To convert from lb/ton to kg/Mg, multiply by 0.5.
[b] Reference 12. Fugitive emissions (6 to 9 hr) after application (source No. 3 on Figure 2-7a).
[c] Fertilizer mixtures in which nitrogen is the predominant component.
[d] Latent emissions from soil reactions.
[e] Reference 5.
[f] References 5, 6, 9.

TABLE 4-5. (continued)

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[g] References 5, 6.
[h] Reference 4.
[j] Reference 9.
[k] References 4, 5.
[m] References 9, 13. Conventional till plots.
[n] Reference 13. Zero-till plot.
[p] Reference 11.
[q] References 1, 41.
[r] References 1, 14, 41, 43.
[s] Reference 10.
[t] Reference 2. Mixture of feedlot cattle manure and added nitrogen source (ammonium nitrate, urea).
[u] Reference 39.

5. PROPOSED AP-42 SECTION 9.2.1

A proposed AP-42 section for fertilizer application is presented on the following pages as it would appear in the *document.*

DRAFT

This is preliminary material, in draft form, for purposes of review. This material must not be quoted, cited, or in any other way considered or used as final work.

9.2.1 Fertilizer Application

9.2.1.1 General[1-4]

The role of fertilizers in the agriculture industry is to supply essential plant nutrients to improve crop production. There are 16 essential elements or nutrients necessary for plant growth, three of which (carbon, hydrogen, and oxygen) are supplied from the atmosphere or water. The other 13 elements (nitrogen, phosphorus, potassium, calcium, magnesium, sulfur, copper, zinc, boron, manganese, iron, chlorine, and molybdenum) are principally supplied through the soil medium. Concentrations of some of these elements are limited in most soils and must be supplemented by fertilizers.

Fertilizers are produced by the following types of industries: fertilizer plant foods; nitrogen and organic fertilizers; and phosphate potash and other fertilizers. Fertilizers are distributed through agricultural supply retailers, farmers' cooperatives, and fertilizer dealers. Application is performed by farmers and by fertilizer dealers using specialized application equipment.

9.2.1.2 Process Description[3-6]

Fertilizer application is based on the physical form of the fertilizer, i. e., a gaseous, fluid, or solid form.

Gaseous Fertilizer -

Anhydrous ammonia, which supplies nitrogen, is the only gaseous fertilizer used. Farmers usually hire trained specialists to apply the 5.7 million tons of ammonia used annually in the United States. Anhydrous ammonia is typically stored in a liquid form, most commonly under pressure, and to a lesser degree, under refrigeration. Anhydrous liquified ammonia is applied by subsurface injection. The ammonia quickly vaporizes, but is captured by several components in the soil including water, clay, and other minerals.

The equipment for the injection of anhydrous ammonia consists of a vehicle (tractor), a pressurized tank containing anhydrous ammonia, a metering system, manifolds, and injection knives. The critical components of the injection system are the metering assembly and injection knives. The meter assembly controls release of the fertilizer in direct proportion to the speed of the vehicle. Generally, the depth settings for injection are from 4 to 10 inches (10 to 25 centimeters) below the surface, depending on soil type, soil conditions, and spacing of injection knives. Figure 9.2.1-1 shows a simplified trailer used to apply anhydrous ammonia and liquid fertilizers.

Fluid Fertilizer -

Fluid fertilizers are typically classified as either solutions or suspensions. Solution fertilizers are free of solid particles. Suspension fertilizers are two-phase fertilizers in which solid particles are maintained in suspension in the aqueous phase.

The equipment for surface spraying of fertilizers consists of the vehicle, a tank holding the fluid, a metering system, manifolds, and spray nozzles. The manifolds are mounted inside long booms (20 to 40 feet) having no more than 20 nozzles. Fluid fertilizers are most commonly sprayed onto the surface of freshly tilled soils. Figure 9.2.1-2 shows a side view and rear view of a typical spray nozzle system. By varying the height of the nozzles above the ground and the flow of the fluid fertilizer, the applicator can apply the fertilizer in discreet bands (band and row) or as overlapping coverage (broadcast).

Solid Fertilizers — In the United States, solid fertilizers are typically either straight nitrogen fertilizers (urea or ammonium nitrate) or mixed fertilizers containing nitrogen and phosphate, potassium, and other nutrients. The equipment for broadcast application of fertilizers consists of the vehicle, a dry hopper containing solid fertilizer, a metering system, and either fan-type spreaders or boomed spreaders. The flow is controlled by a sprocket-driven belt that feeds the dry fertilizer into the spreader. The application rate is dependent on the position of the spinner blades, the position where the fertilizer drops on the spinner blades, the spinner speed, and the particle size of the fertilizer. Figure 9.2.1-3 shows an example of a centrifugal spreader.

9.2.1.3 Emission And Controls[3,5-8]

Both particulate matter (PM) and gaseous air emissions are generated from the application of nutrients as fertilizers or manures. Emissions from the storage and application of animal wastes and green manures are not considered in this section; see Section 9.4.1, Cattle Feedlots; 9.4.2 Swine Feedlots; 9.4.3, Poultry Houses; and 9.4.4 Dairy Farms. For emissions from the production of commercial dry manure fertilizers, see Section 9.5.4, Manure Processing. Emissions may be immediate (occurring during or shortly after application), and latent (occurring days or weeks following application). Four possible sources of uncontrolled emissions have been observed with the process of fertilizer application. These sources are (1) soil reactions with the applied fertilizer generating increased gaseous emissions including NO, N_2O, NH_3, and SO_2, (2) volatilization of the fertilizer immediately behind the vehicle generating gaseous emissions *including* NH_3 *and the fertilizer itself,* (3) *soil disturbance creating* PM emissions with constituents that become airborne, and (4) volatilization of the fertilizer immediately above the solid fertilizer trailer, generating gaseous emissions including NH_3 and the fertilizer. Figure 9.2.1-4 shows these sources for emissions.

Recent scientific papers discussing the biological mechanisms for NO_x emissions from the soil have cited evidence to show that essentially all (over 90 percent) NO_x emissions are in the form of NO and little, if any, are in the form of NO_2. The formation of NO_2 occurs through the rapid oxidation of the NO by ozone present in the soil or the air immediately above the soil surface. There is no evidence to conclude that appreciable quantities of NO_2 are formed directly in the soil.

Wind-blown dust is created immediately during the application of dry fertilizers and later from disturbances caused by mechanical operations (e. g., tilling) and/or wind erosion. Gaseous air emissions can be generated after application by the immediate volatilization of gaseous fertilizers (i. e., anhydrous ammonia) or after some period of time by the chemical/biological transformation of nitrogen (N) added as fertilizers or manures to the soil. Table 9.2.1-1 provides equivalent nitrogen contents of common chemical fertilizers.

Emission factors are not presently available for PM. A number of heavy elements listed as Hazardous Air Pollutants in the 1990 Clean Air Act Amendments have been identified in soils treated with phosphate, nitrogen, and manure fertilizers, and could become airborne with fugitive dust. These elements are: cadmium, mercury, nickel, selenium, chromium, manganese, lead, and cobalt. Some of these elements also occur naturally in some soils. Research is needed to quantify fertilizer and manure contributions to airborne heavy metals.

At present, only gaseous air emission factors have been developed for nitrogen fertilizers. These emission factors, which are shown in Table 9.2.1-2, are based on equivalent nitrogen applied to the soil. Note that the studies that were used to develop these emission factors indicate that emissions can exhibit substantial temporal and spatial variability. Factors that affect this variability include soil type and composition, soil properties such as moisture content and pH, and ambient temperature. These factors result in wide differences in emissions from site-to-site as well as day-to-day variations and diurnal emission variation at a given site. *Consequently, the emissions factors shown in* Table 9.2.1-2 should be used with caution because data from the 15 studies used to develop them were extremely variable. The variability is partly due to variances in soils, temperatures, and precipitation between sites, and is also partly due to differences in experimental procedures.

It should not be inferred from these data that any degree of emission control could result from the use of different types of fertilizers. To date, the best form of emission control is through "nutrient management." In other words, the form, placement, and timing of the fertilizer relative to the need of the fertilizer is the best available control of the uncontrolled emissions of fertilizer application.

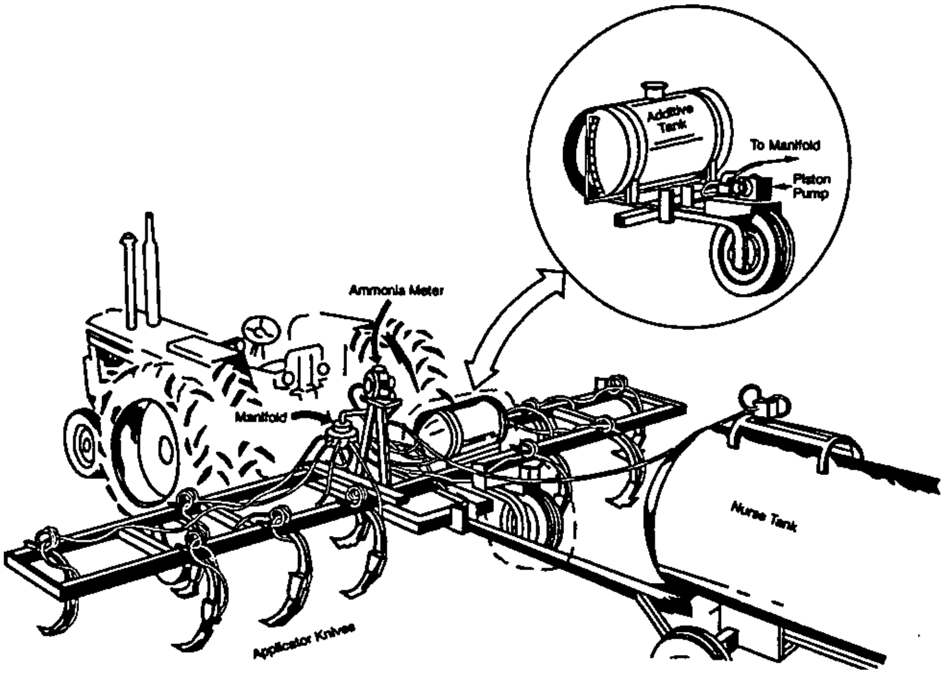


Figure 9.2.1-1. Typical trailer for application of anhydrous ammonia and fluid fertilizers.

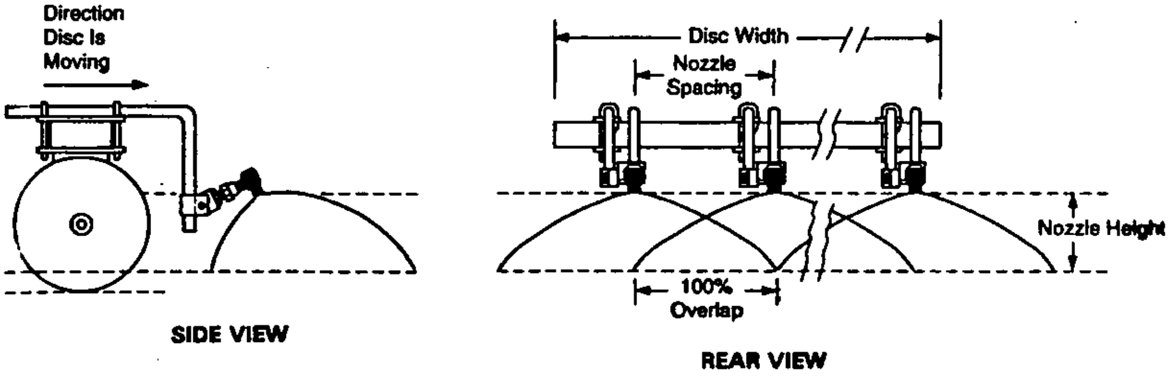


Figure 9.2.1-2. Side view and rear view of a typical spray nozzle system used for application of fluid fertilizers.

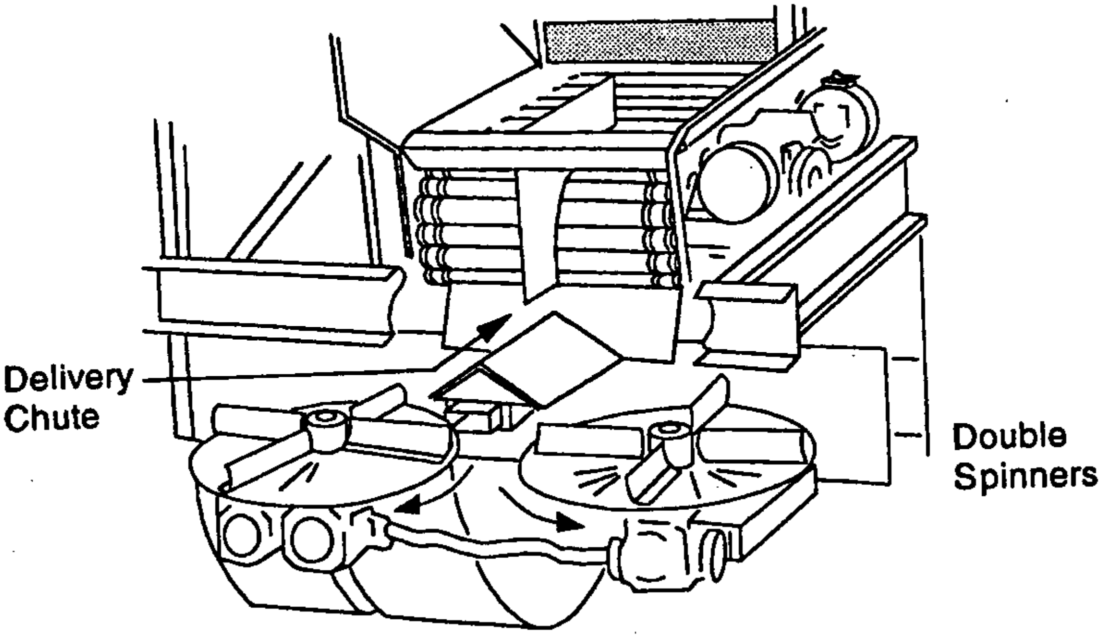
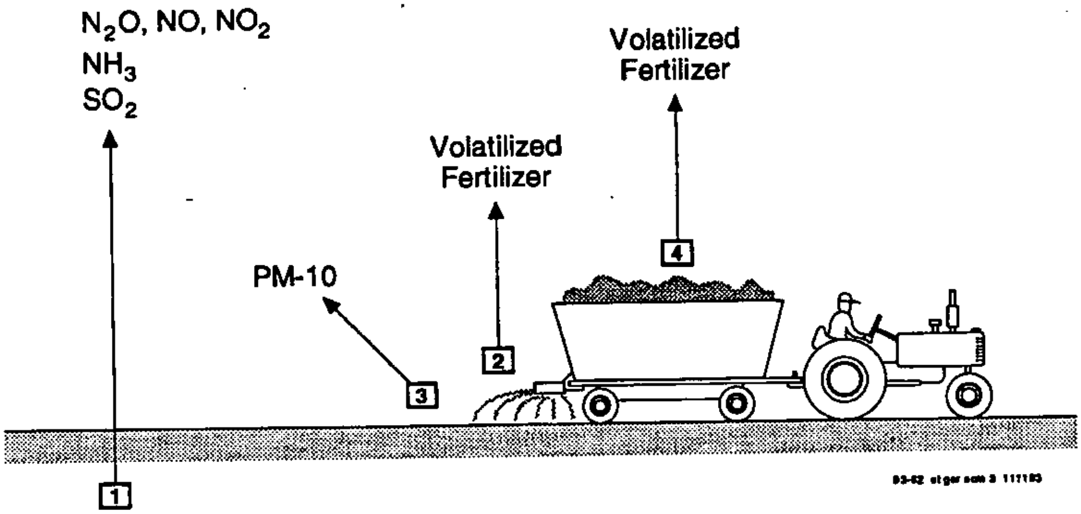


Figure 9.2.1-3. Example of centrifugal spreader.



1 Reactions with soil to generate emissions

2 Immediate emission due to broadcasting the fertilizer. Believed to be negligible.

3 Generation of fugitive dust

4 Immediate emission due to volatilization of fertilizer. Believed to be negligible.

Figure 9.2.1-4. Emission sources from fertilizer application.

Draft Table 9.2.1-1 EQUIVALENT NITROGEN CONTENT OF COMMON CHEMICAL FERTILIZERS[a]

Type of fertilizer	Chemical formula	Nitrogen content[b] (weight percent)	Equivalent nitrogen content, lb fertilizer per lb N[c]
Anhydrous ammonia	NH_3	82.3	1.2
Urea	$CO(NH_2)_2$	46.7	2.1
Ammonium nitrate	NH_4NO_3	35.0	2.9
Ammonium sulfate	$(NH_4)_2SO_4$	21.2	4.7
Ammonium chloride	NH_4Cl	26.2	3.8

[a] Equivalents for pure chemicals.

[b] $$\text{Nitrogen content (weight percent)} = \frac{\text{atomic weight of nitrogen}}{\text{molecular weight of fertilizer}} * 100\%$$

$$\text{e.g., for ammonia: wt\%} = \frac{14}{17} * 100\% = 82.3\%$$

To determine the pounds of nitrogen per ton of fertilizer, multiply the nitrogen content (weight percent) times the tons of fertilizer. Then convert tons to pounds by multiplying by 2000.

e.g., for one ton of urea:

$$1 \text{ ton} \times 46.7 \times \frac{1}{100} = 0.467 \text{ tons of nitrogen}$$

0.467 tons x 2,000 lb/ton = 934 lb of nitrogen/ton of urea

For fliud fertilizers, the weight of the solvent should <u>not</u> be included in calculating the weight of the fertilizer.

[c] Amount of fertilizer (lb) to produce 1 lb equivalent nitrogen application. To convert pounds of nitrogen to pounds of fertilizer, multiply pounds of nitrogen by the equivalent nitrogen content.

$$\text{e.g.: } 934 \text{ lb N} \times \frac{1.2 \text{ lb ammonia}}{\text{lb N}} = 1{,}121 \text{ lb ammonia}$$

Draft Table 9.2.1-2 SUMMARY OF EMISSION FACTORS FOR FERTILIZER APPLICATION[a]

EMISSION FACTOR RATING: E

Fertilizer/application	PM-10	NH_3	NO	N_2O
Gaseous fertilizer:				
• Injection				
-- Anhydrous ammonia	NA	12[b] 0.41[c]	ND	ND
Fluid fertilizer:				
• Injection or deep band				
-- Aqueous ammonia	NA	ND	ND	ND
-- Urea	NA	ND	ND	ND
-- Ammonium nitrate	NA	ND	ND	ND
-- Nitrogen mixtures[d]	NA	ND	ND	ND
• Band, row, and broadcast application[e]				
-- Urea	ND	ND	140[f]	10[g]
-- Ammonium nitrate	ND	ND	29[f]	3.0[h]
-- Nitrogen mixtures[d]	ND	ND	ND	ND
-- Calcium nitrate	ND	NA	7.6[j]	1.7[k]
-- Sodium nitrate	ND	NA	5.1[m]	ND
-- Ammonium chloride	ND	ND	58[f]	ND
-- Ammonium sulfate	ND	ND	ND	39[n] 290[p]
• Aerial				
• Irrigation				
Solid fertilizer:				
• Broadcast application[e]				
-- Urea	ND	260[q]	ND	ND
-- Ammonium nitrate	ND	ND	240[r]	160[s]
-- Nitrogen mixtures[d]	ND	ND	ND	
-- without manure				16[t]
-- with manure				120[u]
-- Ammonium sulfate	ND	ND	140[v]	12[v]

[a] ND = no data available. NA = not applicable. All emission factors in terms of pounds of pollutant per ton of nitrogen in fertilizer applied (lb pollutant/ton N applied). To convert from lb/ton to kg/Mg, multiply by 0.5.

[b] References 13-14, 18. Volatilization immediately (1-3 hr) after application.

Draft Table 9.2.1-2 (cont'd)

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[c] Reference 18. Fugitive emissions (6 to 9 hours).

[d] Fertilizer mixtures in which nitrogen is the predominant component.

[e] Latent emissions from soil reactions.

[f] Reference 11.

[g] References 11-12,15.

[h] References 11-12.

[j] Reference 23.

[k] Reference 15.

[m] References 11,23.

[n] References 15,24. Conventional till plots.

[p] Reference 24. Zero-till plot.

[q] Reference 17.

[r] References 9,21.

[s] References 9,19,21-22.

[t] Reference 16.

[u] Reference 10. Mixture of feedlot cattle manure and added nitrogen source (ammonium nitrate, urea).

[v] Reference 20.

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APPENDIX A

REFERENCE 1 AND ASSOCIATED HAND CALCULATIONS

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Printed in Great Britain.

0004-6981/91 $3.00+0.00
Pergamon Press plc

THE PRODUCTION OF ATMOSPHERIC NO_x AND N_2O FROM A FERTILIZED AGRICULTURAL SOIL

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Abstract—The source strength of atmospheric trace gases from rural or remote locations must be quantified in order to assess the effect of such inputs on the background tropospheric chemistry. To assess the importance of biological production of NO_x and N_2O from fertilized agricultural soil, enclosure techniques have been used to determine the emission fluxes of NO_x and N_2O at a site in Southern Ontario, Canada. NO_x fluxes on the unfertilized soil range from 1.5 to 41.6 $\mu g(NO)\,m^{-2}\,h^{-1}$. The corresponding N_2O fluxes are 0–61.8 $\mu g(N_2O)\,m^{-2}\,h^{-1}$. For the most highly fertilized soil NO_x fluxes range from 3.1 to 583 $\mu g(NO)\,m^{-2}\,h^{-1}$ and the N_2O fluxes from 0 to 446 $\mu g(N_2O)\,m^{-2}\,h^{-1}$. The fluxes increase linearly with fertilizer application, with 11% of the nitrogen in the fertilizer converted to NO_x and 5% to N_2O. The emission rates were studied as functions of the soil parameters temperature, moisture, ammonium, nitrate and pH, to attempt to understand better the production mechanisms, although a model for the process could not be developed. In rural areas away from transportation corridors the increased NO_x emission from fertilized soil may dominate local oxidant production but is not significant on the Province-wide scale.

Key word index: Flux chamber, NO_x emissions, N_2O emissions, fertilizer loss, soil, agriculture, oxidants.

1. INTRODUCTION

The oxides of nitrogen are important species in the cycling of nitrogen through the atmosphere and are involved in both radiative and chemical processes.

Nitrous oxide (N_2O) is important in climate control as it is a greenhouse gas absorbing in two bands where the atmosphere and Earth emit, namely at 7.78 μm and 17.0 μm. Its present concentration of slightly over 300 ppbv contributes ~1 K to the greenhouse warmed mean surface temperature (Kuhn, 1985). Since N_2O has a long tropospheric lifetime (150 years) it can diffuse into the stratosphere where, through reaction with excited oxygen atoms, it produces nitric oxide (NO). Reaction with the nitric oxide so produced is the major removal process for ozone in the stratosphere (WMO, 1985). The concentration of N_2O has been observed to be increasing at about 0.2% per year (WMO, 1985). This can be expected to result in an increase in surface temperature via greenhouse warming and a decrease in stratospheric ozone by increasing the rate of odd nitrogen catalysed ozone destruction.

The nitrogen oxides NO and NO_2 (collectively known as NO_x) control the oxidative capacity of the troposphere. At high concentrations the photolysis of NO_2 results in the net production of ozone which in turn produces hydroxyl radicals which are believed to initiate most atmospheric oxidation processes. However, at low NO_x levels the reaction of NO with oxidants can lead to the net destruction of ozone (Chameides *et al*., 1987). The threshold for ozone production is an NO concentration between 10 and 30 pptv. The post industrial revolution increase in ozone (Volz and Kley, 1988) has been attributed to man's input of NO_x to the atmosphere. This increase can produce deleterious effects on human and vegetative health. It will also contribute to greenhouse warming (Ramanathan *et al*., 1985).

Prior to the industrial revolution the atmospheric concentration of these gases over land masses was likely dominated by biological processes. The onset of industrialization certainly increased the NO_x production to the point where today fossil fuel combustion is the major NO_x source (NAS, 1984). The N_2O situation is not as clear. Direct production from combustion is generally thought to be small but production from biomass burning may be significant. Since combustion sources are generally localized, biological production of N_2O and NO_x is still significant away from major urban and industrial centres. However, biological production does not mean pre-industrial production. Man is having an indirect effect on the nitrogen budget by chemical conversion of atmospheric nitrogen into ammonium nitrate, the bulk of which is used as fertilizer. Any of this nitrogen released into the atmosphere as NO_x or N_2O represents a significant incremental source of these trace gases. This could be especially important in the rural areas of the western world where there is a high usage of inorganic fertilizer.

There have been several studies of the emission rates of these trace gases in the laboratory and in the field. Johansson and Galbally (1984), Levine *et al*. (1984) and McKenney *et al*. (1984), have carried out laboratory studies on the aerobic nitrification and anaerobic denitrification processes capable of producing NO_x and N_2O. Field measurements of NO_x emissions have been undertaken by Anderson and Levine (1987), Galbally and Roy (1978), Johansson (1984), Johansson and Granat (1984), Parrish *et al.* (1987), Slemr and Seiler (1984) and Williams *et al.* (1987). Field measurements of N_2O emissions have been made by Anderson and Levine (1987, 1988), Bremner *et al.* (1980), Cates and Keeney (1987), Duxbury *et al.* (1982), McKenney *et al.* (1980), Mosier and Hutchinson (1982) and Slemr *et al.* (1984).

The purpose of this work is to focus on the importance of agricultural fertilizer as a source of atmospheric nitrogen species. This was done by measuring the fluxes of NO_x and N_2O from an agricultural soil under controlled fertilizer applications.

2. EXPERIMENTAL

2.1. *Site*

Emission fluxes of NO_x and N_2O were measured from an experimental field at Agriculture Canada's Harrow Research Station in South Western Ontario, between 19 April and 29 September 1988. The soil was a grey brown Fox fine sandy loam with an approximate composition of 78% sand, 9% silt and 12% clay. The organic matter content was between 1.5% and 2%. The field has been under continuous cultivation for about 100 years. The four plots used in this study have been treated identically for the last 19 years except for the amount of fertilizer each received. Ammonium nitrate fertilizer has been applied to each of the four plots for each of these 19 years as follows: the first, no fertilizer; the second, $100\ \mathrm{kg\ ha^{-1}}$; the third, $200\ \mathrm{kg\ ha^{-1}}$; and the fourth, $300\ \mathrm{kg\ ha^{-1}}$. Note that the fertilizer was 33% NH_4NO_3 and the remainder was crushed limestone filler. For convenience these plots will be referred to as Plots 0, 100, 200 and 300, respectively. Although the field was sown with beans, all measurements were made on bare soil. This was done to separate the soil emission process from the plant uptake of nitrogen. The latter process has been studied separately and there are many estimates of deposition velocities and surface resistances (McRae and Russell, 1984). As a result the fluxes determined here may well overestimate the net emission of nitrogen in cases where there is significant plant uptake of atmospheric nitrogen in the plant canopy.

2.2. *Methodology*

Emission fluxes were measured using enclosure techniques. For N_2O a static chamber was used and the increase in the N_2O concentration in the headspace used to determine the flux. As NO_x is more reactive, a dynamic chamber was used. In this, clean air was passed through the chamber and the NO_x concentration in the air leaving the chamber was used to determine the flux.

The N_2O flux chambers were aluminium cylinders, 25 cm high and 17 cm in diameter, with removable plexiglass lids. Two cylinders per plot were placed approximately 5 cm into the soil at the start of experiment and left in place, where possible, to minimize the perturbation to the soil. For a measurement the lid, which contained a stirrer and a syringe needle, was placed onto the cylinder. A 25 ml sample of the headspace gas was withdrawn immediately by piercing a rubber septum of a pre-evacuated tube with the needle on the lid. Similar samples were taken at regular intervals over the next hour. In all but the largest emission measurements, the increase in N_2O concentration in this period was generally less than a 25% increase on the ambient level which gave good precision in the flux determination but which was not expected to influence the emission process. The needle was left open to the atmosphere to ensure there was no pressure gradient between the chamber and the ambient atmosphere. The samples were analysed for N_2O within 36 h with an HP5880A series Gas Chromatograph using a Porapac Q column and a Nickel 63 electron capture detector. A least squares fit of the N_2O concentration against time was converted to an emission flux from a knowledge of the headspace volume and the cross-sectional area of the chamber. Initially up to eight samples per hour were taken but as confidence in the technique grew this was reduced to five. Measurements were usually made between 10 a.m. and 6 p.m. and in this time it was possible to make one N_2O flux determination at each of two canisters on each of the four plots, for a total of eight flux determinations per day.

The NO_x flux measurements apparatus is shown in Fig. 1. The system is designed around the chamber which is a $27\ \ell$ plexiglass cube open at the bottom and lined on all five sides with FEP Type L fluorocarbon film. A stainless steel fan was used to circulate the air within the chamber. This chamber was sealed to a stainless steel frame set approximately 5 cm into the ground. Two frames were set into each plot and left undisturbed throughout most of the measurement period. The chamber was placed on one of these frames when a measurement was taken. Ambient air was scrubbed of NO_x and ozone using activated charcoal and pumped into the chamber at a rate of $4.0–4.5\ \ell\ \mathrm{min}^{-1}$, thus the residence time for air in the chamber (τ) was 6–7 min. Approximately

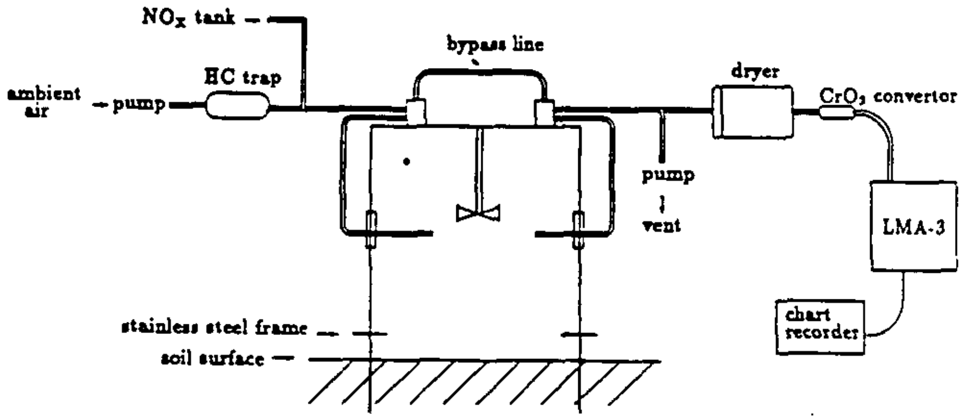

Fig. 1. Dynamic chamber equipment used for the field measurement of NO_x emission fluxes.

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2 *l* min^{-1} of the air leaving the chamber was analysed for NO, using an LMA-3 commercial NO_2 analyser preceded by a CrO_3 based NO to NO_2 converter (Drummond *et al.*, 1989). After approximately 10–20 min the NO_x concentration reached a steady level and the NO_x flux was determined from the total mass of NO in the chamber (*m*), and the area of soil exposed (*A*) using

$$NO_x \text{ flux} = m\,\tau^{-1}A^{-1}.$$

The time the soil was covered was kept as short as possible to minimize the perturbations of the chamber on the soil and was never more than 45 min. Pressure gradients between the chamber and ambient air were prevented by a 0.2 cm hole in the chamber and on sunny days heating of the chamber was minimized by shading with an umbrella. In this way the air temperature inside the chamber was kept within a degree or two of the ambient temperature, and because of the short time the chamber was in place the soil temperature was not measurably different inside or outside of the chamber.

Prior to this experiment the chamber had been evaluated in the laboratory, and on both grass and bare soil sites on the grounds of York University. By placing a Teflon sheet on the bottom of the chamber and adding ambient concentrations of NO and NO_2 it was found that above -10°C the walls of the chamber did not absorb either NO or NO_2, below this temperature NO_2 absorption was observed. Zero air was used to improve the precision of the measurement by removing the fluctuating ambient NO_x levels and to prevent ozone oxidation of the emitted NO to the more readily deposited NO_2. Flux determinations were found to independent of the residence times (τ) between 3.5 and 13 min. This is consistent with the inert nature of the chamber and the lack of uptake of the emitted gases. In general, the concentrations of NO_x measured in the chamber were between 1 and 40 ppbv.

On several occasions the NO to NO_2 converter was removed so the NO_2 flux could be determined. It was always less than 2% of the total NO_x flux showing the emitted gas to be NO. On a typical field day NO_x fluxes were determined two or three times for each of the eight frames.

In conjunction with each emission flux measurement a number of supporting measurements were made. Soil temperature was measured with a mercury thermometer inserted 2 cm into the soil. Moisture, nitrate, ammonium and pH were measured in soil samples taken from next to the chambers. The soil moisture was determined gravimetrically by the weight loss on drying at 105°C for 24 h. Ammonium was measured by extracting the soil with 0.05 M K_2SO_4 and quantified using an Orion ammonium electrode (Orion, 1987). Nitrate was extracted in a similar manner and also measured as ammonium following reduction by $TiCl_3$ (Orion, 1987). Soil pH was determined by extracting the soil with de-ionized water and measuring the pH of the extract with a pH electrode.

*Method

3. RESULTS AND DISCUSSION

3.1. *Flux and soil parameter measurements*

Figures 2 and 3 show the soil ammonium and nitrate plotted against the day of the measurement. Prior to the fertilizer application on day 116, the levels on the fertilized plots are low indicating that little if any of the previous year's nutrients remain. The exceedingly low values on days 113 and 115 are due to the field being ploughed and the nutrient poor soil from below being brought to the surface. Since the fertilizer is applied as granules, it takes several days for the nutrient levels to rise after the application of the fertilizer. The soil ammonium appears to peak some 20–30 days after the fertilizer is applied. Only Plot 300 retains any significant amount of the applied ammonium past day 180. This may be due to a lower soil pH which may have either inhibited the microbial nitrification or plant growth and the subsequent uptake of ammonium. The nitrate appears to peak about 80 days after application, this is due in part to the continued production from ammonium. A striking feature of Figs 2 and 3, which to some extent masks the gross features, is the nutrient decrease for days 159 and 160. Prior to these measurements the field was irrigated with 2.5–5 cm of water. This exceeded the field capacity of the soil and so leached the nutrients from the upper level to the lower soil levels. The subsequent increase is due to the movement of nutrient rich water from below being brought to the surface by capillary action as the soil dried. The effect is less pronounced with ammonium as it has a higher exchange capacity

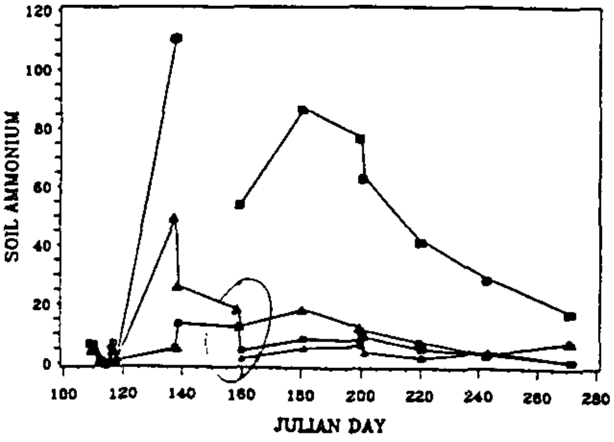

Fig. 2. Soil ammonium, in ppm, vs date for Plot 0 (open triangles), Plot 100 (open squares), Plot 200 (filled triangles) and Plot 300 (filled squares).

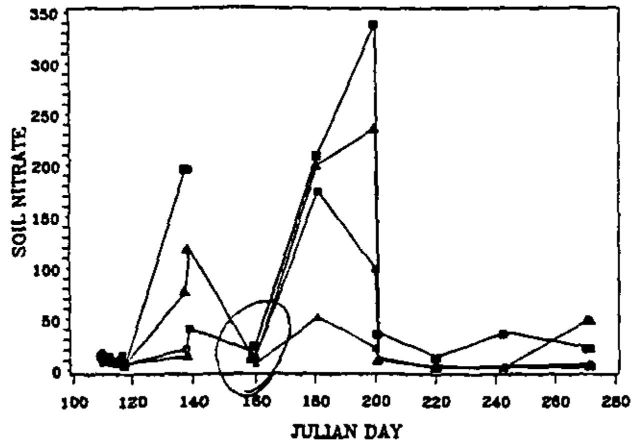

Fig. 3. Soil nitrate, in ppm, vs date for Plot 0 (open triangles), Plot 100 (open squares), Plot 200 (filled triangles) and Plot 300 (filled squares).

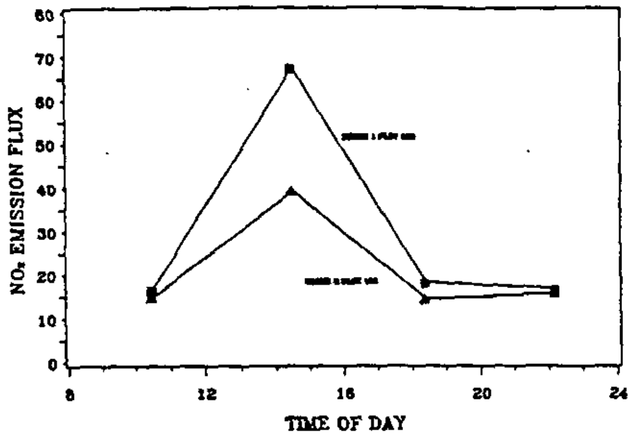

Fig. 4. Diurnal variation of the emission flux of NO_x from two frames on Plot 100 on day 243.

so is less easily leached from the soil. The maximum in the Plot 0 soil nitrate at day 180 could be due to the movement of nitrate rich water from one of the adjacent fertilized plots or to nitrogen fixation by the bean crop. The nutrient levels drop as the growing season progresses although heavy rain during the night of day 200 gives rise to an accentuated rate of removal between days 200 and 201.

Figure 4 shows a typical day of NO_x emission measurements. Four measurements were made on each of the two frames over a 10-h period. The variations in soil moisture and temperature are shown in Fig. 5. The first point to note is that there is substantial NO_x emission 2 h after sunset, showing that the process producing the NO_x is not sunlight dependent. The night-time emissions are lower than the midday values but are the same as the morning values where the soil temperature was comparable. It appears therefore that the diurnal variation in NO_x emission is a consequence of temperature variations. The other major feature is the variation in emission rate within what is expected to be a homogeneous plot. For example, there is almost a factor of two difference in some of the simultaneous NO_x emission measurements. The two frames were only 2.5 m apart and no closer than 3 m to the boundary of the plot. Since the field has been so carefully tended there is no reason to predict any variation between the sites. We must conclude that in spite of man's attempt to homogenize the soil there is a great deal of variation within it. This degree of variation has been seen elsewhere but never under such controlled conditions.

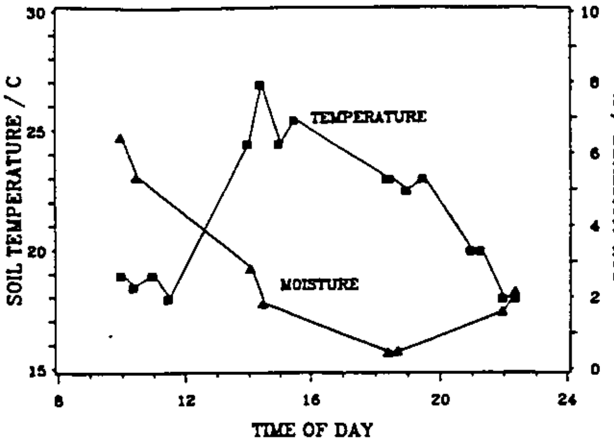

Fig. 5. Soil temperature (squares) and soil moisture (triangles) for Plot 100 on the same day as for Fig. 4.

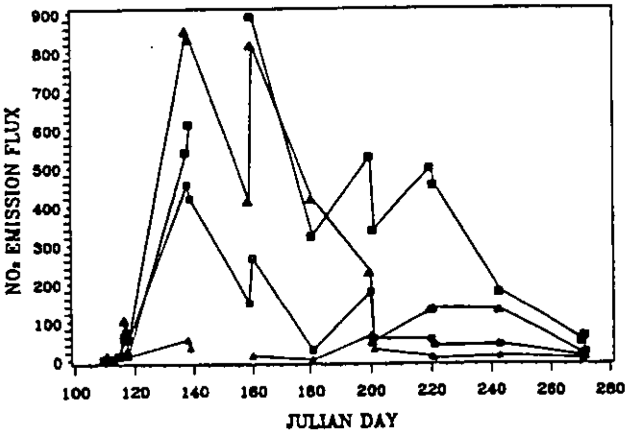

Fig. 6. NO_x emission flux in $\mu g(NO)\,m^{-2}\,h^{-1}$ vs date for Plot 0 (open triangles), Plot 100 (open squares), Plot 200 (filled triangles) and Plot 300 (filled squares).

This variation makes it difficult to make detailed measurements on the soil. A large number of measurements are needed to determine trends and true averages.

Figures 6 and 7 show the fluxes of NO_x and N_2O determined during this study. Each point is the average of measurements from both frames on each plot. The emission flux measurements showed huge variations throughout the measurement period. For Plot 0 the NO_x emission ranged from 1.5 to 41.6 $\mu g(NO)\,m^{-2}\,h^{-1}$ whereas for Plot 300 the range was from 3.1 to 583 $\mu g(NO)\,m^{-2}\,h^{-1}$. A similar variation was noted for N_2O where the flux for Plot 0 ranged from 0 to 61.8 $\mu g(N_2O)\,m^{-2}\,h^{-1}$ and for Plot 300 from 0 to 446 $\mu g(N_2O)\,m^{-2}\,h^{-1}$. There is a clear seasonal cycle in the emission fluxes which seem to follow the nutrient levels, but there are marked day-to-day variations.

The emissions from the fertilized plots rose above that of Plot 0 simultaneously with the increase in soil nitrate and ammonium between days 116 and 138. The emissions appear to peak around day 160, about 40 days after the application of the fertilizer.

The N_2O emission dropped back to the Plot 0 level by day 180. This is not consistent with the soil nitrate measurements which are still high from days 180 to 200. There is some correlation with ammonium in the time scale for removal, but on Plot 300 there is little emission late in the season, even in the presence of elevated ammonium. A plot of emission flux against soil nutrients (ammonium and nitrate) gave no further insight into the process.

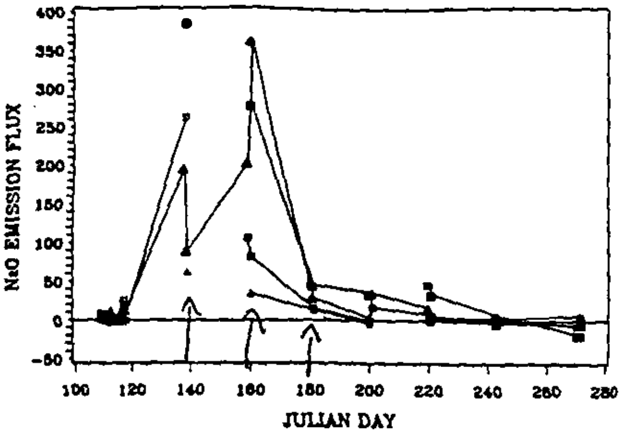

Fig. 7. N_2O emission flux in μg (N_2O) $m^{-2} h^{-1}$ vs date for Plot 0 (open triangles), Plot 100 (open squares), Plot 200 (filled triangles) and Plot 300 (filled squares).

The NO_x emissions persisted throughout the growing season with discernible emissions past day 240, 120 days after fertilizer application. This behaviour appears to correlate better with soil ammonium than nitrate, especially in the response to the irrigation on day 159 and the persistence of NO_x emissions on Plot 300. This would suggest that the NO_x is a product of biological nitrification consistent with the observations of Anderson and Levine (1987). However this correlation does not hold up to detailed analysis. Again a plot of emission against soil nutrients gave no additional information.

Although the emissions seem most closely related to the nutrient levels, the day to day variation is substantial and must be related to the more variable parameters of temperature and soil moisture, along with agricultural practice. The variability of the emissions between days 110 and 118 are largely due to the soil being ploughed three times so that most of the microbes, which live in the top 2–3 cm of soil, were buried about 15–20cm. The microbe population then took several days to regenerate in the surface layer. There is little variation in either N_2O or NO_x emissions between days 138 and 139 consistent with similar temperatures and no rain on those days. The major discrepancy occurred for the NO_x emission on days 159 and 160. As noted above heavy irrigation lowered the nutrients on these days. NO_x fluxes were measured for all four plots on day 160 but only for plots 100 and 200 on day 159. These two measurements show a substantial decrease in NO_x emission but it had returned to apparently more typical levels by the next day. In this case the drying of the field, and the associated movement of nutrients, appears to dominate the NO_x emissions. Plot 200 showed an increased N_2O emission on day 160 but otherwise the effect of the irrigation was minimal for N_2O. By the next measurement on day 180 the N_2O emissions had dropped to pre-fertilization levels and little day to day variation was observed subsequently. The NO_x levels at day 180 appear depressed by the hot dry conditions but recover by day 200. They are suppressed again by rain that night. There is some evidence for a small increase in N_2O emission on day 200 due to the moister soil conditions. The NO_x emission had recovered again by day 220 and showed a steady decrease to the end of the growing season.

3.2. *Comparison with previous studies*

As with previous studies, particularly those on agricultural soils, a wide range of emission fluxes were obtained with the values for the most fertilized plot among the highest reported.

Tables 1 and 2 present the results of NO_x and N_2O flux measurements on fertilized agricultural soils. While the values reported here are somewhat higher than most they are not remarkably so. The measurements were made on research soil subjected to abnormally high fertilizer applications, so higher emissions would be expected from these fields than those under regular cultivation. It must also be remembered that these measurements were made on bare soil and may overestimate the actual net nitrogen emission to the atmosphere.

3.3. *Discussion of the flux variation*

Examination of these data shows, as have a number of studies, that the emissions are dependent on soil nutrients (ammonium and nitrate), temperature, soil moisture and agricultural practice. We now describe our attempts to quantify these dependencies to obtain a model for the emission flux in terms of the readily measureable soil parameters.

Table 1. NO_x emission fluxes from fertilized agricultural soils

Ground character	NO_x Flux $\mu g(NO)\,m^{-2}\,h^{-1}$	Reference
Corn field	20–860	Williams *et al.* (1988)
Wheat field	1.3–6.2	Williams *et al.* (1988)
Corn field	21–241	Anderson and Levine (1987)
Soy field	2.5–33.8	Anderson and Levine (1987)
Arable field	0.4–223	Johansson and Granat (1984)
Experimental field	1.5–583	This study

Table 2. N_2O emission fluxes from fertilized agricultural soils

Ground character	N_2O flux $\mu g(N_2O)\,m^{-2}\,h^{-1}$	Reference
Arable field	228–1712	Blackmer *et al.* (1982)
Arable field	34–367	Bremner *et al.* (1980)
Arable field	35–482	Anderson and Levine (1987)
Corn field	411–594	Cates and Keeney (1987)
Cropped field	868 (average)	Mosier and Hutchinson (1982)
Experimental field	0–446	This study

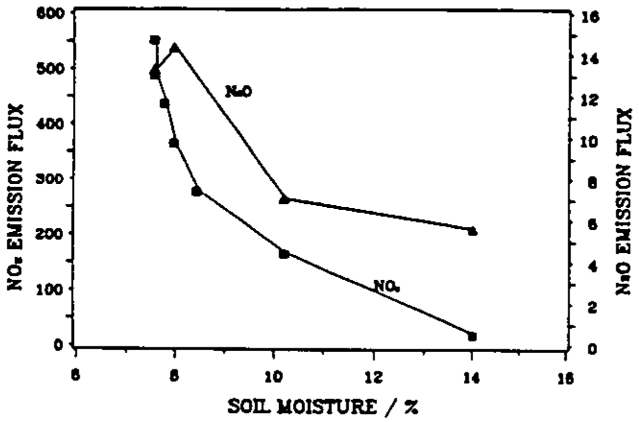

Fig. 8. NO_x (squares) and N_2O (triangles) emission fluxes in $\mu g(NO$ or $N_2O)$ $m^{-2}\,h^{-1}$ vs soil moisture (%) for Plot 200 on day 182.

An experiment to investigate the soil moisture dependence was performed on day 182 when 1.5–2.0 cm of water was applied. This brought the soil close to field capacity, about 14% soil moisture, but did not exceed it as on day 159. Measurements commenced immediately after the irrigation ceased. The NO_x emission flux was less than 5%, and the N_2O flux less than 20% of the previous day's values. As the soil dried the fluxes increased to values consistent with those obtained in the period before irrigation. The variation of the fluxes with soil moisture are given in Fig. 8. The steady increase in the NO_x emission rate with decreasing soil moisture is consistent with the depression of an aerobic process by the high water content of the soil. This is the same conclusion drawn in section 3.1 on the basis of the ammonium dependence of the emission flux. The N_2O emission appears to be limited by a physical process as evidenced by the sharp increase in flux below 10% soil moisture. Davidson and Firestone (1988) have shown that, for N_2O emission, diffusion through the soil pore spaces is important. Thus it appears likely that in this case the anaerobic production of N_2O continued even at the high soil moisture levels but the emission was physically controlled by the presence of water in the soil pores. This effect has been observed previously by several groups including Slemr and Seiler (1984) and Grundmann *et al.* (1988). The NO_x flux results were found to be best fitted by a ln(flux) dependence on soil moisture, but a simple analytical expression for N_2O flux was not possible.

There is a wide temperature range from which a temperature dependence can be determined. The temperature dependence is best described by an activation energy type expression, i.e.

$$\ln(\text{flux}) = \ln(A) - E_a/RT_s.$$

Here A is a constant, T_s the soil temperature, R the gas constant and E_a the activation energy. However, when E_a was so determined it was found to be plot dependent. This was due, in part, to the simultaneous variation of soil nitrogen and temperature. The nutrients were greatest when the temperatures were the highest, thus we were fitting some nitrogen dependence as well. Restricting the determination of E_a to the latter half of the season where the nitrogen variation was small produced a more consistent result of 108 $\pm 20\ \text{kJ mol}^{-1}$. This is similar to the values of 65–83 kJ mol^{-1} obtained by Johansson and Granat (1984), 44–103 kJ mol^{-1} by Slemr and Seiler (1984) and $97 \pm 11\ \text{kJ mol}^{-1}$ by Williams *et al.* (1988).

Using this dependence on moisture and temperature, and assuming a linear dependence of the flux rates on ammonium, nitrate and pH, we attempted to develop a model for the emission flux in terms of these parameters. The results of this exercise were disappointing. Within a single plot or for a limited time period the model was able to simulate the fluxes satisfactorally. However for the data set as a whole the model was unsatisfactory indicating this simple model to be incomplete. For example the soil moisture dependence appears to change with nutrient level. A multiple regression model cannot be used for this kind of non-linear system and we have insufficient data for a more detailed model. The relationships we have described apply well to the system as it was studied, but extrapolation to different moisture and nutrient conditions is not possible.

3.4. *Total* NO_x *and* N_2O *released*

By integrating the data in Figs 6 and 7 we can determine a total seasonal release of NO_x and N_2O. Figure 9 gives the total emission for each plot as a function of the applied fertilizer. There appears to be a simple linear relationship between the emission flux and the applied fertilizer. From these data an average of 5.3% of the nitrogen applied as fertilizer (NH_4 or NO_3) is released to the atmosphere as N_2O and 11% as NO_x.

As the area in which these measurements were made is a major population area, the anthropogenic emissions of NO_x are well quantified. Thus using the results of this study with anthropogenic emissions does allow the assessment of the importance of biological input into the atmosphere. For a $5 \times 5\ \text{km}^2$ area centred on the city of Windsor, the annual anthropogenic NO_x emission is 732.8 tonnes (MOE, 1985). The average for the same area of agricultural land in southwestern Ontario, off the transit corridor, is only 15 tonnes. Assuming an equivalent of $150\ \text{kg ha}^{-1}$ of NH_4NO_3 fertilizer is applied to the agricultural land in this area then the annual biogenic emission is 14.5 tonnes for the same $5 \times 5\ \text{km}^2$ area. Thus in a rural area the biological emission is comparable to the anthropogenic emission.

On a province wide basis only 3.9% of Ontario is under cultivation for cereal, legume or vegetable production. Using the same assumptions, as above, yields an Ontario biological NO_x production of 14 kilotonnes per year. The comparable anthropogenic emissions are 329 kilotonnes for vehicular emissions, 178 kilotonnes from point sources and 78 kilotonnes from other sources (MOE, 1985). Thus on the larger scale anthropogenic NO_x emissions are dominant.

$\frac{100\,kg}{ha} \times \frac{1\,ha}{10{,}000\,m^2} \times \frac{1000\,g}{kg} = \frac{10\,g}{m^2}$

$33\% = \frac{3.3\,g}{m^2}$

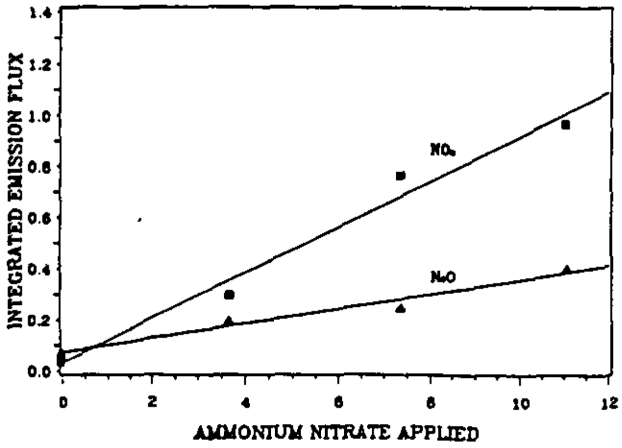

Fig. 9. Total seasonal emission of NO_x (squares) and N_2O (triangles) vs the amount of fertilizer applied (g ammonium nitrate m^{-2}).

This exercise shows how carefully these agricultural data must be used. Near a major urban centre the agricultural component is insignificant, as is the total provincial wide contribution. However, away from major anthropogenic centres and for cases where transport from such centres is small, the agricultural contribution is significant.

4. CONCLUSIONS

A study of the emissions of NO_x and N_2O from a field with controlled fertilizer applications has been performed. The fluxes of these gases to the atmosphere are strongly related to the nutrient levels, the moisture and the temperature within the soil. Attempts to develop a model for the fluxes in terms of these parameters were unsuccessful. Over the course of a full growing season approximately 11% of the nitrogen supplied to the field as ammonium nitrate fertilizer was converted to NO_x and 5% to N_2O. In rural areas away from major transportation routes the NO_x emission from fertilized soils may be comparable to the anthropogenic NO_x production and so may dominate the local oxidant chemistry. However, for the Province of Ontario as a whole the increased NO_x emission as a result of fertilizer usage is small.

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JSK 9/20/92

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From Section 3.4, p. 1968: (DEN)

Average Emission Rates = 5.3% N fertilizer as N_2O / 11% N fertilizer as NO_x (as $NO_{\cancel{2}}$) JWL 2/7/95 (regardless of applic. rate)

Applic. Rates: 100, 200, & 300 kg/ha of 33% NH_4NO_3

$$100\ \frac{\text{kg fert}}{\text{ha}} \times 0.33\ \frac{\text{kg } NH_4NO_3}{\text{kg fert}} \times \frac{28\ \text{kg N}}{80\ \text{kg } NH_4NO_3} = 11.5\ \frac{\text{kg N}}{\text{ha}}$$

$$200\ \frac{\text{kg fert}}{\text{ha}} \times 0.33\ \frac{\text{kg } NH_4NO_3}{\text{kg fert}} \times \frac{28\ \text{kg N}}{80\ \text{kg } NH_4NO_3} = 23.1\ \frac{\text{kg N}}{\text{ha}}$$

$$300\ \frac{\text{kg fert}}{\text{ha}} \times 0.33\ \frac{\text{kg } NH_4NO_3}{\text{kg fert}} \times \frac{28\ \text{kg N}}{80\ \text{kg } NH_4NO_3} = 34.6\ \frac{\text{kg N}}{\text{ha}}$$

N_2O Emissions – Same for all applic. rates!

$$= 11.5\ \frac{\text{kg N fert}}{\text{ha}} \times \frac{5.3\ \text{kg N}}{100\ \text{kg N fert}} \times \frac{44\ \text{kg } N_2O}{14\ \text{kg N}} \times \frac{10^3\ \text{gm}}{\text{kg}} \times \frac{1\ \text{ha}}{11.5\ \text{kg N fert}}$$

$$= 166.6\ \frac{\text{gm } N_2O}{\text{kg N fert}}$$

From Fig 7, p. 1966 – Emissions from Day 110 to 240

$$\therefore\ 166.6\ \frac{\text{gm } N_2O}{\text{kg N fert}} \times \frac{1}{130\ \text{days}} = 1.28\ \frac{\text{gm } N_2O}{\text{kg N} \cdot \text{day}}$$

NO_2 Emissions – Same for all applic. rates!

$$11.5\ \frac{\text{kg N fert}}{\text{ha}} \times \frac{11\ \text{kg N}}{100\ \text{kg N fert}} \times \frac{\overset{30\ \text{kg NO}}{\cancel{46\ \text{kg } NO_2}}}{14\ \text{kg N}} \times \frac{10^3\ \text{gm}}{\text{kg}} \times \frac{1\ \text{ha}}{11.5\ \text{kg N fert}} = \cancel{\frac{361.4\ \text{g } NO_2}{\text{kg N}}}$$

JWL 2/7/95

$\uparrow$

JWL 2/7/95 $\frac{235.7\ \text{g NO}}{\text{kg N}}$

②

From Fig. 6, p. 1965 – Emissions from Day 110 to 270

$$\therefore \overset{235.7}{\cancel{361.4}}\ \frac{\text{gm NO}_x}{\text{kg N}} \times \frac{1}{160\text{ days}} = \cancel{2.26\ \frac{\text{gm NO}_x}{\text{kg N}\cdot\text{day}}}$$

$$\uparrow\ \frac{1.47\text{ g NO}}{\text{kg N}\cdot\text{day}}$$

gml
2/7/95

ok
mws
9/20/95

APPENDIX B

REFERENCE 2 AND ASSOCIATED HAND CALCULATIONS

Nitrous Oxide Production throughout the Year from Fertilized and Manured Maize Fields[1]

R. L. CATES, JR. AND D. R. KEENEY[2]

ABSTRACT

Two field sites on a loam soil were established to monitor N_2O concentration in the soil atmosphere and rate of emission from the soil surface. The sites were cropped to maize (*Zea mays* L.) and managed at two high-N levels (181 or 237 kg N ha^{-1}). Both sites received 168 kg N ha^{-1} as feedlot cattle (*Bos taurus*) manure (preplant-incorporated) and 13 kg N ha^{-1} as NH_4NO_3 fertilizer in the row at planting. One site (Site B) received additional soil-incorporated N (56 kg N ha^{-1}) as urea. Fluctuations in N_2O emissions from the two sites were temporally similar, and differed only in magnitude with Site A (no additional fertilizer), emitting about 3.6 kg N_2O-N ha^{-1} yr^{-1} and Site B about 5.2 kg N_2O–N ha^{-1} yr^{-1} or about 2% of the N applied. Most of the N_2O was emitted between mid-June and the end of July when the soil was warm and NH_4^+-N was present, and at spring thaw (late March the following year) when soils were cold and near water-saturated. High N_2O emissions during the growing season occurred following precipitation events, and hence were associated with high soil water and probably with the initiation of soil drying. Nitrous oxide production was continuous during winter months, presumably a result of denitrification. The N_2O concentration in the profile of the frozen soil increased to high levels (nearly 2000 μL L^{-1} N_2O at Site B) before spring thaw. At thaw, nearly 330 d after application of the N amendments, an apparent physical release period occurred and N_2O flux was far higher (about 50 g N_2O-N ha^{-1} d^{-1}) than at most times during the growing season.

Additional index words: *Zea mays* L., Nitrification, Denitrification, Cold soils, Soil atmospheres, Profile nitrous oxide, Ozone layer.

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Nitrous oxide (N_2O) has been implicated in the destruction of stratospheric ozone (Crutzen, 1981), which protects the biosphere from harmful levels of ultraviolet radiation. The gas may also contribute to the "greenhouse" effect (Yung et al., 1976; Joyce, 1985) expected to result from increasing atmospheric CO_2 levels.

The use of N fertilizer can result in dramatic increases in N_2O emissions from soils. Annual losses of N as N_2O from fertilizer-amended soils may be as high as 40 kg ha^{-1} (Ryden and Lund, 1980a), whereas annual emissions from unfertilized soils are usually < 1 to 2 kg N ha^{-1} (Colbourn and Dowdell, 1984; Sahrawat and Keeney, 1986). Losses as N_2O from anhydrous NH_3 fertilized soils can represent as much as 7% of the applied N (Bremner et al., 1981).

Production of N_2O by soils had been viewed as evidence of denitrification, but it is now accepted that N_2O is also emitted during nitrification (Bremner and Blackmer, 1978, 1981; Blackmer et al., 1980; Goodroad and Keeney, 1984b; Duxbury and McConnaughey, 1986; Sahrawat and Keeney, 1986). Although it has been assumed that most N_2O is evolved during the growing season subsequent to application of N fertilizer, there is now evidence that N_2O emissions during thaw may be as high as at any other time of the year (Bremner et al., 1980; Goodroad and Keeney, 1984c, 1985). Even though the mechanisms of production and release have not been elucidated, denitrification may be the principal source of that N_2O. The significance of high N_2O emissions at thaw in relation to time of fertilizer application is not yet established, but could be one reason for the low efficiency of fall-applied fertilizer N.

We monitored N_2O emissions for 330 d and N_2O concentration in the soil atmosphere during winter and spring in two maize (*Zea mays* L.) fields managed at two N levels (181 or 237 kg N ha^{-1}). The study was conducted to provide information relating to factors controlling temporal fluctuations in N_2O emission and production rate, and the relationship of N_2O concentration in the soil profile to N_2O emission rate.

Sites

Two sites for monitoring N_2O production were established in May 1981 on a Kidder loam soil (fine-loamy, mixed, mesic Typic Hapludalf). The field in which the sites were established had been in maize since 1978 and alfalfa (*Medicago sativa* L.) for several years prior to 1978. Some characteristics of the surface (0–15 cm) soil were: water pH 6.7; organic C 1.2 g kg^{-1}; cation exchange capacity, 13 $mmol_c$ kg^{-1}; bulk density, 1.29 Mg m^{-3}. Feedlot cattle (*Bos taurus*) manure (ca. 33.6 Mg ha^{-1}; 750 g kg^{-1} H_2O; 168 kg N ha^{-1}) was incorporated into the top 20 cm of soil at both sites, along with residue from the previous year's maize crop, just prior to maize planting (2 May). Both sites received an additional 13 kg N ha^{-1} as NH_4NO_3 in-row at planting, but only one of the sites (Site B) received additional N fertilizer (56 kg N ha^{-1}) as urea. The fertilizer urea was broadcast and immediately incorporated in the soil on 4 May. Thus the total N added as fertilizer and manure was 181 kg N ha^{-1} or 237 kg N ha^{-1} at Sites A and B, respectively. Soil test results indicated that P and K levels were not limiting for maize growth. Broadcast herbicides Bladex (2-{[4-chloro-6-(ethylamino)-*s*-triazin1-yl]amino}-2-methylpropionitrite) and Lasso [2-chloro-2′-6′-diethyl-*N*-(methoxymethyl)-acetanilide] were applied on the soil surface at both sites on 12 May. Furadan [2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate] insecticide was surface-applied in bands at planting.

Nitrous Oxide Monitoring

Nitrous oxide flux from the soil surface was measured using a closed-chamber technique (Goodroad and Keeney, 1984a). The chambers were open, rectangular, steel frames with a 2.5-cm flange on the top to provide a sealing surface. Surface area was 100 cm^2. Chambers (three replicates per site) were pushed into the soil approximately 7.5 cm so that the height remaining above the soil surface was 2.5 cm. At each site, one of the replicates was placed in-row, the other two between-row. Chambers were left in place once established. At sampling, chambers were enclosed with 1-cm thick plywood covers that had been coated

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with epoxy paint and fitted with high-density polyvinyl foam and a central septum. Samples of the enclosed atmosphere were withdrawn by syringe at 0, 10, and 20 min. Air samples were contained in plastic syringes until analyzed. Sampling was conducted between 1000 and 1400 h at 7-d to 30-d intervals dependent on anticipated N_2O emission activity.

Soil atmosphere samples were estimated by use of sampling probes constructed of 2.5 cm (i.d.) polyvinylchloride pipe (Goodroad and Keeney, 1985). The probes were fitted with a 20-mL diffusion chamber at the lower end. A capillary tube led from the diffusion chamber to the top of the probe to allow for withdrawal of some of the chamber atmosphere by syringe. Three replicate probes were placed at each of three depths (10, 20, and 30 cm) in-row and between-row at each site. Additionally, three replicate probes were placed at 90 cm between-row at Site B.

Soil temperature measurements were made in duplicate at 1, 10, 20, and 30 cm using soil moisture-temperature cells (Soil Test, Inc., Evanston, IL) that measure temperature directly. Precipitation data were obtained from climatological stations located in the proximity of the experimental site.

The concentration of N_2O in air samples was determined with a Perkin-Elmer Sigma 3 gas chromatograph (Perkin Elmer Corp., Norwalk, CT) equipped with a ^{63}Ni electron capture detector (Mosier and Mack, 1980; Goodroad and Keeney, 1984a) interfaced to a Perkin-Elmer Sigma 10B controller. The relationship between area of N_2O peaks and concentration (v/v) was determined by standard curves developed from appropriate dilutions of a known concentration standard. Time between sampling and analysis was never greater than 24 h.

Nitrous oxide flux was calculated by the equation:

$$F = (k/T)(V/A)(\Delta c/\Delta t)$$

where F is the N_2O flux (g N_2O-N ha^{-1} d^{-1}), k is a unit conversion factor (3.41 g N K m^2 L^{-1} ha^{-1}) for calculation of N_2O emission, T is the mean air temperature (K) corresponding to each date of sampling, V is the volume of air within the chamber (2.5 L), A is area of soil within the chamber (0.1 m^2), and $\Delta c/\Delta t$ is the rate of change in the concentration of N_2O in the air within the chamber (μL L^{-1} N_2O d^{-1}).

Coefficients of variation (CV, %) among replicate flux or depth data on a given sampling date were calculated as an indication of spatial variability at each site. Duncan's multiple range test ($P \leq 0.10$) was used to compare N_2O data from each site across sampling dates and/or depths, where applicable.

RESULTS AND DISCUSSION

May to December Nitrous Oxide Flux

One of the three chambers at each site included the soil surface area designated as in-row (the zone immediately adjacent to the maize row in which banded fertilizer was placed at time of planting); the other two were placed between-row. All data presented are averages of the three chambers; we did not distinguish N_2O flux from in-row and between-row surface areas. Between May and December, the two sites had flux patterns that were temporally similar and differed only in magnitude (Fig. 1). The higher flux of N_2O from Site B than from Site A is presumed to be due to the additional urea N (56 kg ha^{-1}) applied at Site B. Most of the N_2O that was produced at the sites was released between mid-June and the end of July (Julian Day, JD, 160 to 204) during which time surface soil temperatures were warm (within the range 17 to 26 °C at 1 cm soil depth) and the concentration of soil NH_4^+-N in the top 15 cm of soil was relatively high (20 to 75 kg ha^{-1}).

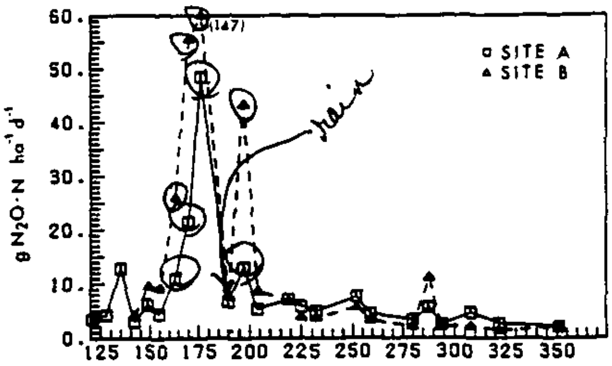

Fig. 1. Nitrous oxide flux from Sites A and B, May through December. Coefficients of variation (%) varied between 1 and 120.

The first N_2O peak (15 May, JD 135) at Site A (first sampling at Site B was 22 May, JD 142) corresponded with a dramatic increase in soil temperature. Surface soil temperature (1-cm depth) increased from 11 °C (8 May, JD 128) at 24 °C (15 May, JD 135). The soil stayed at about this temperature all summer. May was a very dry month, whereas June and August were wet (Table 1).

Broadcast herbicides (Bladex and Lasso) were applied to the maize field on 12 May (JD 132). Bremner at al. (1981) observed a small peak in N_2O emission after herbicide application. Some of the N_2O flux at Site A on 15 May may be attributed to this herbicide effect. For the remainder of the growing season, temporal fluctuations in N_2O flux over time at both sites were closely related to wetting and drying cycles. The peak emission rates during 12 June (JD 163) through 4 July (JD 185) occurred after rains (Table 1). Focht (1974) described a model for N_2O evolution that appears to fit the maximum-minimum relationship to soil water observed. The model predicts that N_2O flux would be low when the soil was saturated. Following a rain, N_2O would increase as the soil began to dry out (peak emission would occur when 12% of the pores were aerated) and then decrease. Fluctuations in N_2O production rate in response to wetting and drying have been also observed (e.g., Ryden and Lund, 1980b; Goodroad and Keeney, 1984b).

The manure applied at the sites was a major source of N for N_2O production. Duxbury et al. (1981) found that more N_2O was evolved from a maize field soil tested at

Table 1. Weekly precipitation at the sites, May through November (prior to soil freeze).

Month/day	Julian day	Precipitation
		mm
1 May–4 June	121–155	18
5 June–2 July	156–183	113
3 July–6 Aug.	184–210	132
7 Aug.–3 Sept.	219–246	167
4 Sept.–1 Oct.	247–274	59
2 Oct.–5 Nov.	275–309	61
6 Nov.–3 Dec.	310–330	34

the same N rates with manure than one that was sidedressed with liquid N fertilizer. Christiansen (1983) reported eightfold more N_2O from a manured than a fertilized grassland, and Goodroad et al. (1984) found the highest N_2O emission rates from manure-amended compared to fertilized or sludged-treated soils. Additionally, as a source of organic C, manure and residue from the 1980 maize crop would contribute to higher denitrification rates (when conditions were appropriate) and, in turn, greater N_2O production (Rolston et al., 1978; Goodroad et al., 1984; Linn and Doran, 1984).

The addition of urea to Site B resulted in a substantial increase in N_2O emissions, particularly in June. While N_2O flux from arable soils can be expected to increase with rate of fertilizer N (Bremner and Blackmer, 1978; Mosier et al., 1982; Breitenbeck and Bremner, 1986b), the form of fertilizer N can have a marked effect on the magnitude of the flux at similar N levels. Generally it has been shown that anhydrous ammonia, in particular, will result in more fertilizer-N loss as N_2O than urea (Breitenbeck et al., 1980; Bremner et al., 1981; Breitenbeck and Bremner, 1986a). Ammonium oxidizers are largely responsible for the high N_2O emission rates in arable soils (Christianson et al., 1979; Breitenbeck et al., 1980; Blackmer et al., 1980; Goodraod and Keeney, 1984b). In recent work, Duxbury and McConnaughey (1986) showed that the N flux from a urea-fertilized maize field was equally divided between dentrification and nitrification of liberated NH_4^+ over an 85-d growing period.

Average daily N_2O flux measured in our research over the 1981 sampling period (1 May to 17 December) was approximately 8 and 12 g N_2O-N ha^{-1} at Site A and Site B, respectively. In comparison, a minimum tillage maize field near Madison, WI, was sampled for N_2O emission rates over 2 years' growing seasons. This field was fertilized with 200 kg N ha^{-1} (as NH_4NO_3) both years. Average daily N_2O flux was approximately 2 g N_2O-N ha^{-1} d^{-1} in the first year and 30 g N_2O-N ha^{-1} d^{-1} in the second year (Goodroad et al., 1984). Wide yearly deviations in measured N_2O emissions appear to be related to precipitation patterns and perhaps to spacing of sampling times relative to precipitation events.

Differences in N_2O concentration with soil depth (10, 20, and 30 cm) were generally not significant ($P \leq 0.10$) due to high spatial variability. Spatial variability was usually greatest (CVs 90 to 100%) when N_2O concentrations in the soil atmosphere profile were high. This indicates localized areas of N_2O production and/or limited diffusivity of the gas due perhaps to high soil water content. Low CVs (10% or less) among replicates were often associated with low N_2O concentrations in the soil profile.

Temporal fluctuations in N_2O concentration in the soil profile were similar at both sites and for the in-row and between-row locations. Concentrations were generally highest from mid-June through the end of July (JD 165 to 204) when the soil was warm and soil NH_4^+-N was relatively high. Short-term fluctuations were related to soil wetting and drying cycles. Peak N_2O concentrations were associated with high soil water content. This observation is in agreement with findings of Goodroad and Keeney (1985). Soil N_2O sampling intensity was insufficient to establish whether maximum concentrations actually occurred at the same time as maximum soil water or after the soil began to dry. Based on the precipitation record, it would appear that most of the N_2O is produced after rainfall events and commencement of soil drying. Others have also noted that continuously wet soils where nitrification is limited and/or denitrification proceeds rapidly to N_2 emit little N_2O (Sahrawat and Keeney, 1986).

The amount of N_2O in the soil profile over the sampling period differed with site and proximity to the maize row. The highest N_2O concentrations were measured where N application rate was highest, i.e., in-row greater than between-row at each site, Site B greater than Site A. The differences were most pronounced at times of peak N_2O concentrations (JD 170, 176, 197, 252, and 288). Although only 13 kg N ha^{-1} additional N was placed in-row at planting, the effect of this N on local N_2O production was substantial. Nevertheless, given the relatively small surface area affected by the in-row treatment, the additional N_2O produced in that zone would not be expected to be a major contributor to the overall N_2O flux from the maize field. Higher N_2O concentration between-row as compared to in-row at Site A on 8 May (JD 128) could not be explained by a difference in soil water content but may be the result of an earlier initiation of nitrification of fertilizer N between-row. Differences in soil moisture in-row vs. between-row were not significant, although the in-row soil profile tended to be slightly drier in mid to late growing season (9 July, JD 190 to 28 August, JD 240), presumably due to more intensive plant uptake of available water in that zone.

Fluctuations in soil profile N_2O were closely reflected in the temporal pattern of N_2O evolution (Fig. 1) from the soil surface (high N_2O concentrations associated with high N_2O flux) with the exception of the possible herbicide-induced N_2O flux on 15 May (JD 135).

By early November (JD 305), the soil atmosphere N_2O concentration was uniformly low (ca. 1 to 3 μL N_2O L^{-1}) in the surface 30 cm at both sites. The soil profile over that depth froze later in early December and remained frozen throughout the winter.

January to March Nitrous Oxide Flux and Soil Profile Concentration

The two sites were monitored from January through initial soil thawing in late March (Table 2). Failure of the electron capture detector on the gas chromatograph forced us to terminate the experiment after 25 March. Nitrous oxide flux and concentration data and soil temperatures over this period are summarized in Table 2. There were no significant ($P = 0.10$) differences in N_2O concentration with soil depth because of the high spatial variability encountered.

The concentration of N_2O in the soil atmosphere was low in January through mid-February, but was greater than the previous November. Flux from both sites was

Table 2. Nitrous oxide flux and N_2O concentration in the soil atmosphere, late January through initial thaw in mid-March.

			N_2O flux or profile concentration†					
Sampling		Soil temp.‡	Site A			Site B		
Date	Depth		Flux	Profile BR	Profile IR	Flux	Profile BR	Profile IR
	cm	°C	g N ha^{-1} d^{-1}	μL N_2O L^{-1}		g N ha^{-1} d^{-1}	μL N_2O L^{-1}	
26 Jan.	0	−1	7(26)b§			9(57)b		
	10	−1		8(19)b	9b		<1b	11(15)b
	20	−1		8(18)c	11(74)c		4(15)b	10(30)b
	30	−1		9(30)c	8b		7(65)b	9(22)b
	90	–					13b	
18 Feb.	0	0	13(34)b			16(75)b		
	10	0		6(72)b	11(29)b		2(76)b	15(61)b
	20	0		11(90)c	11(16)c		7(75)b	12(50)b
	30	0		1c	9(26)b		7(85)b	12(28)b
	90	–					9b	
24 Feb.	0	1	35(99)ab			15(32)b		
	10	1		83(54)b	135(48)ab		49(35)b	306(58)ab
	20	0		64(60)b	102(5)b		191(118)ab	140(92)b
	30	1		59(34)b	82(74)ab		76(83)b	94(62)a
	90	–					15b	
11 Mar.	0	0	17(32)b			29(44)b		
	10	0		156(98)b	157(6)ab		24(34)a	352(64)ab
	20	0		82(33)b	123(65)ab		163(118)b	272(32)b
	30	0		97b	118(36)a		147(27)b	147(14)a
	90	–					111(14)a	
18 Mar.	0	2	9(29)b			23(71)b		
	10	1		213(65)a	310(82)a		1900(92)a	459(84)a
	20	1		174(31)a	207(9)a		1700(138)a	1700(114)a
	30	1		177a	138(45)a		279(73)a	98(41)a
	90	–					98(19)a	
25 Mar.¶	0	4	47(12)a			49(40)a		
	10	1						
	20	1						
	30	1						

† BR, between-row; IR, in-row. Figures in parentheses are coefficients of variation in percent.

‡ Soil temperature data applicable to both sites; surface temperature (indicated as the 0-cm depth) was actually measured just below the soil surface (ca. 1 cm).

§ Flux values at a given site followed by the same letter are not significnatly different at the 10% probability level. Profile data compared at a given depth and site across sampling dates followed by the same letter are not significantly different.

¶ No profile N_2O data taken.

greater on 18 February than had been measured since the previous summer (16 July, JD 197), even though the surface soil (0 to 15 cm) was still frozen. Six days later (24 February), the profile N_2O concentration had increased considerably. The soil had partially thawed by then and the emission rate at Site A was much higher than previously observed even during the past spring-summer. This phenomenon has been observed elsewhere (Bremner et al., 1980; Goodroad and Keeney, 1984c, 1985; Goodroad et al., 1984).

The surface soil was again frozen on 11 March but the profile N_2O concentration continued to increase. By 18 March extremely high profile N_2O concentrations were measured at both sites. Concentrations of ca. 1700 to 1900 μL N_2O L^{-1} had accumulated in the surface 20 cm at Site B. The lower N_2O concentrations at 30 cm, and particularly at 90 cm at Site B between-row indicate that N_2O was probably being produced near the soil surface and then was subsequently trapped and held. Soil temperature remained above freezing after 18 March and on 25 March high N_2O emission rates were measured at both sites. Presumably soil profile N_2O concentrations declined precipitously as the release of the over-winter build-up occurred concurrent with soil thawing (Goodroad and Keeney, 1985). The N_2O flux from Site A at the end of March was as high as at any time during the previous growing season.

We cannot be certain of the mechanism(s) involved in the high N_2O production, release, or both, during the spring freeze-thaw period. Possible explanations (Goodroad and Keeney, 1984c) include: (i) rapid nitrification-denitrification at the soil surface (at low temperatures nitrous oxide reductase activity is suppressed, and almost all the gaseous N is released as N_2O; Keeney et al., 1979; Sahrawat and Keeney, 1986); (ii) nitrification, denitrification, or both below the frozen soil, leading to N_2O accumulation, with release on thawing; or (iii) N_2O production deep in the profile, including the saturated zone, with release on thawing.

It is interesting to note that there was still an effect of N applied the previous May on N_2O production during winter-early spring. Whereas flux from the two sites were comparable, higher soil profile N_2O concentrations were generally measured at Site B compared to Site A. In addition, in-row soil N_2O concentrations were higher than between-row concentrations except early in the sampling period at Site A and on 18 March at Site B. It is conceivable that emission as N_2O during thaw could represent a significant and undesirable N loss mechanism from residual fertilizer N, particularly if the N_2O is from denitrification. This observation should be evaluated further.

Cumulative Losses of Nitrous Oxide

Cumulative annual N_2O losses from the sites monitored in this study were ca. 3.6 and 5.2 kg N_2O-N ha^{-1} at Site A and Site B, respectively. In comparison, the cumulative annual N_2O loss from an adjacent unfertilized, but grazed Kentucky bluegrass (*Poa pratensis* L.) pasture, which we monitored over the same sampling period (Cates and Keeney, 1987), was 0.34 kg N_2O-N ha^{-1}, about 15 times less than from Site B. The annual loss of N as N_2O represented 2% of the applied N at both maize sites. Mosier et al. (1986) reported a similar fraction of N from $(NH_4)_2SO_4$ lost as N_2O-N from an irrigated maize field in Colorado. The percentage of applied N lost as N_2O in other studies has varied from nil (Colbourn and Dowdell, 1984) to near 7% (Bremner et al., 1981).

ACKNOWLEDGMENTS

The assistance of Mr. Phillip Speth for sampling and analysis, and of Mr. Richard Cates, Sr. for the use of the land where sites were located is gratefully acknowledged.

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PROJECT DEVELOPMENT SKETCH
TITLE Reference 7; Cates, et al.: J. Environ Qual 16(4), 1987
PROJECT NO. 6500-35 DRAWN ______ APPR. TSK DATE 9/19/92

From Abstract:

∗ Site A: Applic rate = 181 kg N/ha (manure + NH_4NO_3)
Emission rate = 3.6 kg N/ha·yr
Background = 0.34 kg N/ha·yr (p. 447, Cum. Losses)

$$\therefore (3.6-0.34)\frac{\cancel{kg\ N}}{\cancel{ha}\cdot yr} \times \frac{44\ \cancel{kg}\ N_2O}{14\ \cancel{kg\ N}} \times \frac{10^3\ gm}{1\ \cancel{kg}} \times \frac{\cancel{1\ ha}}{181\ kg\ N\ fert.} = \boxed{56.6\ \frac{gm\ N_2O}{kg\ N\cdot yr}}$$

$$56.6\ \frac{gm\ N_2O}{kg\ N\cdot \cancel{yr}} \times \frac{1\ \cancel{yr}}{330\ days} = 0.171\ \frac{gm\ N_2O}{kg\ N\cdot day}$$

∗ Site B: Applic. rate = 237 kg N/ha (manure + NH_4NO_3 + urea)
Emission rate = 5.2 kg N/ha·yr
Background = 0.34 kg N/ha·yr

$$\therefore (5.2-0.34)\frac{kg\ N}{ha\cdot yr} \times \frac{44\ kg\ N_2O}{14\ kg\ N} \times \frac{10^3\ gm}{1\ kg} \times \frac{1\ ha}{237\ kg\ N\ fert} = \boxed{64.5\ \frac{gm\ N_2O}{kg\ N\cdot yr}}$$

$$64.5\ \frac{gm\ N_2O}{kg\ N\cdot yr} \times \frac{1\ yr}{330\ days} = 0.195\ \frac{gm\ N_2O}{kg\ N\cdot day}$$

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APPENDIX C

REFERENCE 3 AND ASSOCIATED HAND CALCULATIONS

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Emission of nitric oxide from arable land

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(Manuscript received June 13; in final form October, 11, 1983)

ABSTRACT

The flux of NO between arable land and atmosphere has been measured with a chamber technique. The net flux from the soil to the atmosphere varied from less than 0.1 up to 62 ng NO–N m^{-2} s^{-1} for a fertilized area (200 kg N ha^{-1} as calcium nitrate) and up to 17 ng NO–N m^{-2} s^{-1} for an unfertilized area. The emission was high in the summer when the temperature was high and the soil was dry and decreased to low values when the soil surface was thoroughly wetted by rain. Previously reported findings of equilibrium concentrations of NO (compensation point) have been verified. These concentrations ranged from 2 to more than 75 ppbv. At the rural site where the measurements were made, the atmospheric NO concentration was always below this compensation point and there was consequently a net emission of NO from the soil. Nitrogen gases, measured as the difference between NO and NO_x (including NO_2 and possibly also HNO_3 and PAN), were found to be absorbed on soil and vegetation. The absorption of NO_x was generally smaller than the emission of NO.

The areal variability within an area of 100 m^2 was found to be moderate with a standard deviation of 25%, somewhat higher on recently fertilized soil (between 50 and 80%). The temperature dependence of NO emission could be described with an activation energy of 65 to 83 kJ mol^{-1} (Q_{10} between 2.7 and 3.6). A more rapid increase of production than that predicted by the temperature increase was observed in morning hours. This is tentatively explained to be caused by nutrient dynamics in the soil.

The yearly emission is estimated to be about 0.6 kg NO–N ha^{-1} and 0.2 kg NO–N ha^{-1} for the fertilized and unfertilized areas, respectively. During the vegetation period, NO emission from highly fertilized areas might be of some importance when compared with anthropogenic emission from combustion within Sweden.

1. Introduction

From the atmospheric chemist's point of view, emission of NO from soil is a source of odd nitrogen for the atmosphere that has to be added to other more well-known sources when estimating atmospheric N budgets. For the soil system, NO emissions represent a loss of N. Our knowledge about the chemical and biological processes leading to NO losses is poor, although it is known that NO can be produced both during nitrification (Lipschultz et al., 1981), and denitrification (Firestone et al., 1979; McKenney et al., 1982). Lipschultz et al. (1981) found that nitrifying bacteria (*Nitrosomonas europaea*) produced NO and N_2O in molar ratios ranging from 2.8 to 7.8 at 0.5% O_2. The ratio decreased as the oxygen concentration increased to give a value of about 1.1 at 20% O_2. These authors also showed that the NO production was insignificant when the respiratory system of the bacteria was inhibited by $HgCl_2$. Studying a Brookstone clay column undergoing anaerobic denitrification, McKenney et al. (1982) reported production of NO and N_2O in molar ratios ranging from 2.0 to 2.5.

NO can also be produced by chemical decomposition of NO_2^-. In the measurements by McKenney et al. (1982) it was found that up to 45% of the NO produced during denitrification came from decomposition of NO_2^-. Since no laboratory experiment has been conducted so far at conditions which closely simulate those in the field,

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* Contribution No. 495.

there is an obvious need to verify findings by field experiments. It is of particular importance to estimate the magnitude of the flux and its variation in time and space as a function of identifiable environmental variables.

To our knowledge, only three papers have reported on field measurements of NO_x emissions from soils. Kim (1973) measured emission from soil beneath three stands of vegetation (pine, oak and sod). A plastic hood containing petri dishes with a solution of sodium hydroxide to absorb NO_2 was placed on the ground. The average values for the stands of pine, oak and sod were 0.21, 0.12 and 0.19 kg NO_2 ha^{-1} $week^{-1}$, respectively (corresponding to 10.6, 6.0 and 9.6 ng NO_2–N m^{-2} s^{-1}). Galbally and Roy (1978) measured emissions of NO_x from grazed and ungrazed areas using a chamber technique. A box was placed on the ground and the increase in concentration during the first few minutes was followed. The average emission of NO for ungrazed and grazed pastures was observed to be 1.6 and 3.5 ng NO–N m^{-2} s^{-1}, respectively. In later measurements on grazed pasture NO emission ranging from 1 to 50 ng NO–N m^{-2} s^{-1} were found (Galbally and Roy, 1981).

The measurements of NO/NO_x emission presented below, form part of an integrated research effort to study the biogeochemical nitrogen cycle of arable land. Efforts have been made to measure simultaneously emissions of N_2O, NO, NO_x and NH_3 from several plots with different treatment. In this paper we will mainly deal with the NO measurements and in a later paper compare the fluxes of several gaseous N compounds to and from the field. For a detailed description of the project with its many subprojects, including the results from measurements of NO_x emissions during 1981, the reader is referred to Rosswall (1982).

2. Experimental site

The measurements were performed in an agricultural field at Kjettslinge, approximately 40 km north of Uppsala, Sweden (Steen et al., 1984). The main part of the experimental field consists of four cropping systems:

1. Barley with no addition of N fertilizer (hereafter called B0);
2. Barley with an annual addition of 120 kg N ha^{-1} (calcium nitrate) (B120);
3. Grass ley with an annual addition of 200 kg N ha^{-1} (calcium nitrate) (GR200);
4. Lucerne with no addition of N fertilizer (LU).

Each cropping system has four replicates, each plot measuring 40 × 14 m. The soil consists of three distinct layers:

(i) top soil (plough layer), a sandy loam (mean thickness 27 cm);
(ii) a fine sand layer (very varying thickness, from 0 to 50 cm, mean 15 cm);
(iii) a clay layer.

The top soil consists of 15–20% clay, 4% carbon and has a pH of 6.0–6.5. As a median for the top soil of the four cropping systems during the growing season, the NH_4^+–N and NO_3^-–N contents was about 7.5 and 6.7 kg N ha^{-1}, respectively. The NO_2^- concentration was less than 0.05 kg N ha^{-1}.

3. Instruments and methods

We have used a "chamber" technique, similar to that used by Galbally and Roy (1978). A box is placed on the ground and the air is mixed with a fan to reduce the transfer resistance between soil and atmosphere. The flux is calculated either from measured changes in concentration in an air stream passing through the chamber at steady state (open system), or from the gradual increase in concentration, in an almost closed chamber (later referred to as closed system). This appears to be the only practically possible method, as methods using a micrometeorological approach are invalidated by the structure of the experimental field which consists of several small plots of different treatment.

Cylindrical chambers of three different sizes have been used. The volume of the chambers was 5, 30 and 110 litres and the covered area 0.03, 0.20 and 0.20 m^2, respectively. Generally the smaller chambers were used during measurements in the open system and the large one (110 litres) for measurements in the closed system. The chambers had a sharp bottom edge and were inserted a few centimetres into the soil to prevent movement of air into or out of the chamber. The chambers were teflon-lined and the air was well stirred with a paddle (30 cm diameter, approximately 250 rpm) driven by an external motor (80 W) mounted on

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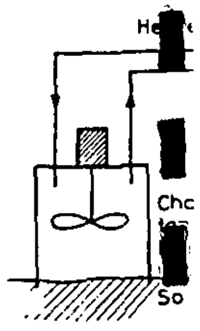

Fig. 1. Schemati

the top of the chamber. In the open system ambient air was pumped to the chamber and the concentration of NO, NO_x and O_3 was measured (Fig. 1). The majority of the air was then pumped from the chamber to the analytical instruments. The sampling and delivery tubes were teflon (about 15 m long), and in order to avoid condensation of water they were heated and insulated. Absorption in tubes and pumps was small and without consequence for the flux determinations. When measurements were made in the open system, the residence time could be varied between 2 and 25 minutes. Deliberate leaks ensured that the pressure difference between chamber and atmosphere was small, in fact it was below detection, less than 0.2 mm H_2O measured with a tilting water manometer. In the "closed" system, throughflow was limited to that required for the gas analysers (about 1.5 l min^{-1}). The air in the chamber was then replaced by outside air through the leaks. The NO concentration gradually built up and usually reached an equilibrium value in about 30 minutes. In this system both NO and O_3 were measured.

The NO analyser was a Thermo Electron series 14 modified according to Delany et al. (1982). The sensitivity of the instrument was ±0.2 ppbv. A change in the NO concentration in the chamber of 0.2 ppbv during 10 minutes (closed system) corresponds to an NO emission of 0.1 ng NO–N m^{-2} s^{-1}. The NO_x concentration was determined after conversion to NO in a heated molybdenum converter. Not only NO_2 but also substances like HNO_2, HNO_3, alkyl nitrites, alkyl nitrates and PAN (peroxylacetyl nitrate) are known to be converted to NO by this treatment (Winer et al., 1974). NO calibration was performed using a cylinder containing 1.02 ± 0.05 ppmv NO in N_2. A permeation tube system was used for NO_2 calibration. O_3 was measured with a continuous chemiluminescent analyser.

The analyses of N_2O and CO_2 were made with GC and infrared absorption respectively and performed by Leif Klemendtsson and Bo Svensson, Swedish University of Agricultural Sciences, Uppsala. The NH_3 determinations mentioned in this report were made by collection of oxalic acid impregnated pyrex tubes for subsequent chemical analysis (Ferm, 1979). These analyses were made by M. Ferm, Swedish Water and Air Pollution Research Institute, Gothenburg.

4. Results and discussion

4.1 *Chamber technique*

The air in the chamber was mixed with a moving "paddle". This makes the chamber air homogenous and facilitates the measurements. Air turbulence above the soil (occurring both naturally and in the chamber) can significantly increase the exchange of gases between soil and atmosphere (Kimball and Lemon, 1971). The maximum windspeed in the chamber was less than 2 m s^{-1}. In a set of measurements of NO emission on the same area with the air in the chamber unstirred, it was found that the emission then decreased to between 30 and 70% of the flux in the stirred chamber.

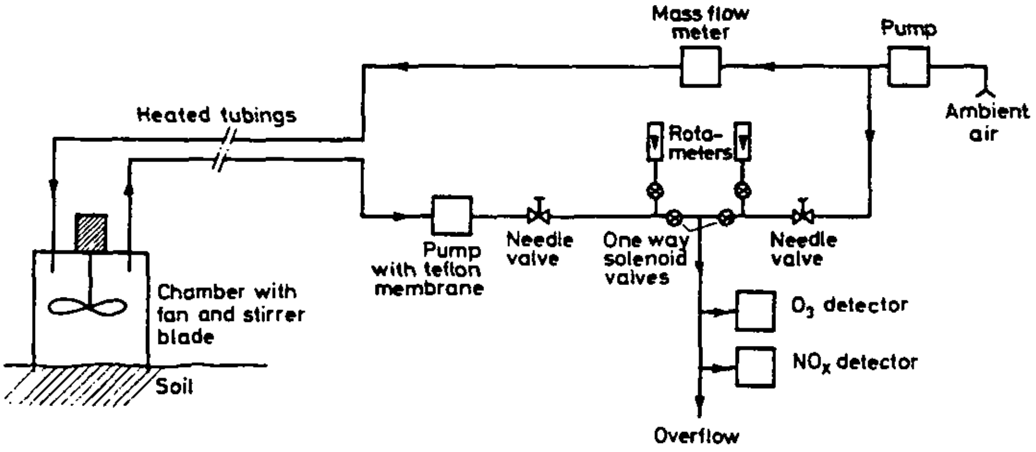

Fig. 1. Schematic diagram of the sampling system.

Comparison of measurements of the NO emission using the open and closed system is shown in Table 1. The measurements were made over the same area, at similar times, and the chamber stirring was identical. We attribute the smaller emission rates in the open system to increased concentration of NO in the chamber and disturbance of the natural environment in the soil. We believe that for these measurements, the closed system is the most reliable, with the chamber covering the soil for only 2 to 10 minutes depending on the emission rate. With this technique it is possible to compare the emission rate from several areas in a very short time.

Similar comparisons of fluxes of N_2O derived from measurements with closed and open systems were performed by Denmead (1979). In his system the chamber covered the soil for approximately 3 hours and was removed for 34 minutes between each measurement. The fluxes as observed from measurements in the closed system were about 30% higher than the fluxes measured in the open system, and thus, were similar to our results for NO. However, Denmead explains this difference by disturbance of the N_2O concentration profile in the soil when the closed system was used and insufficient time for the soil profile to readjust between the measurements. Therefore, he concluded that the closed system overestimated the flux.

4.2 *Production of NO—existence of an equilibrium concentration (compensation point)*

Fig. 2 shows the increase in NO concentration in the closed chamber, immediately after chamber installation. The increase in concentration during the first few minutes is used to estimate the flux of NO from the undisturbed soil. After 10 to 30 minutes, depending on the emission rate, a steady state is reached. This behaviour can be simulated by an expression of the type:

$$c = c^* (1 - e^{-kt})$$

where c^* is an equilibrium concentration in the chamber and k a parameter which depends both on the transfer resistance in soil and air and on losses in the chamber due to withdrawal of air and absorption on the chamber walls. This expression is easily derived from an assumption of an equilibrium concentration in the soil. The same expression can also be obtained from other hypotheses on production and consumption of NO in the soil. The relation is useful when discussing influence of dilution and absorption on the change in NO concentration in the chamber. In our experiments

Table 1. *Comparisons of measurements using the open and closed systems on the same area (times in parentheses correspond to the time when measurements in the open system were started)*

Date	Time	Plot	System used Open = O Closed = C	Soil surface temp. (°C)	Residence time in chamber (min)	Emission rate (ng NO–N $m^{-2} s^{-1}$)	Ratio of emission rate Closed system / Open system
Apr. 22	20^{02}	LU	C	6.5	—	2.68	1.5
	21^{40} (20^{10})		O	4.9	21	1.84	
Apr. 23	19^{02}	LU	C	9.7	—	5.50	2.0
	20^{40} (19^{10})		O	9.5	21	2.80	
Apr. 28*	8^{14}	LU	C	6.3	—	1.17	1.0
	7^{47} (19^{10})†		O	6.1	1.8	1.13	
July 1	9^{28}	GR 200	C	11.7	—	2.13	1.6
	10^{18} (9^{40})		O	12.7	8.2	1.36	
July 1	10^{50}	GR 200	C	13.0	—	2.83	2.1
	11^{33} (11^{02})		O	14.2	22	1.36	2.3
	11^{47}		C	14.5	—	3.19	

* Different chambers were used. 110 and 5 l in the closed and open system respectively.

† The measurements in the open system were started on April 27.

GR = grass ley; LU = lucerne.

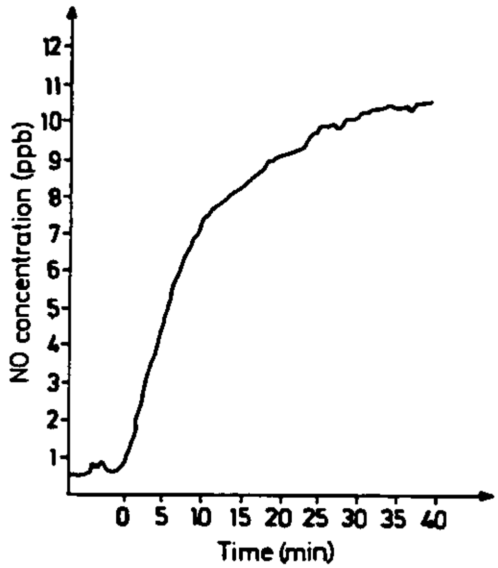

Fig. 2. Example of a typical measurement of NO emission rate (closed system) showing the increase in NO concentration in the chamber air when the chamber is placed on the soil surface (=0 minutes).

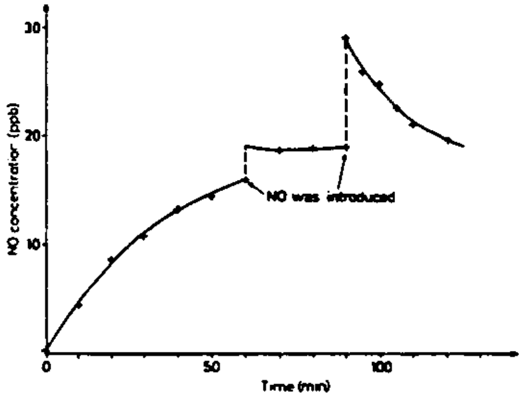

Fig. 3. NO concentration in the chamber air (closed system). NO was introduced by a rapid injection from a cylinder. Curves fitted by hand.

the rate constant k varied between 0.02 and 0.09 min^{-1}. Of this, 0.014 min^{-1} is accounted for by withdrawal of air for the O_3 and NO_x detectors.

In an experiment shown in Fig. 3, the NO concentration in the chamber was increased above the equilibrium concentration by rapid injection of NO. The concentration of NO decreased to reach equilibrium concentration. The rate of removal of NO corresponded in this particular case to $k =$ 0·07 min^{-1}. Thus, the withdrawal of air can in some cases affect the measured equilibrium concentration to some degree, but is, in most cases, of little importance compared to other removal mechanisms.

There are several possible explanations for the decrease in net emission of NO during an experiment.

1. There is an equilibrium NO concentration in the soil and the driving force for NO emission decreases as NO concentration in the chamber increases.
2. The production of NO in the soil is counteracted by a deposition which increases as NO concentration in the chamber increases.
3. Losses of NO due to uncontrolled exchange with the atmosphere and/or absorption of NO on the chamber walls.

We can exclude the last explanation based on measurements of changes in NO concentration in the chamber when this was placed on a teflon film instead of on the ground. Experimental data satisfy both the first and second hypothesis.

Neither the flux estimates nor the magnitude of the equilibrium concentrations were affected by O_3 as the O_3 concentration in the chamber air decreased to less than 2 ppbv immediately after the chamber was installed over the soil.

From measurements under different conditions (temperature, soil, moisture, vegetation cover and NO_3^- content) equilibrium concentrations ranging from 2 to more than 75 ppbv were observed. The concentrations in the ambient air were generally less than 1 ppbv and consequently there was always an upward flux of NO. The existence of an equilibrium concentration for NO was first reported by Galbally and Roy (1978). In later measurements on a grazed pasture, equilibrium concentrations ranging from 3 to 150 ppbv were observed (Galbally, pers. comm.).

Efforts to compare the fluxes of NO, N_2O and CO_2 and NH_3 have been made. The measurements of the concentrations of these gases were made simultaneously in the same chamber. N_2O, CO_2 and NO were measured using the closed system and it was found that an equilibrium concentration was established, not only for NO but also for the two other gases. Results from the measurements are shown in Fig. 4. Both the equilibrium concentration and the flux of N_2O were almost two orders of magnitude higher than that for NO. It

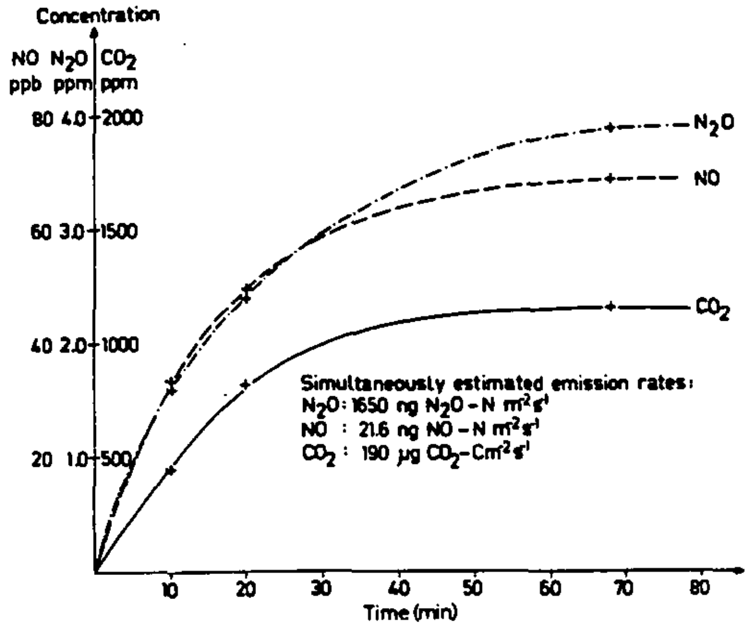

Fig. 4. Simultaneous measurements of the concentration of NO, N_2O and CO_2 in the same chamber (closed system).

Table 2. *Comparison of NO and NH_3 emissions in the same chamber during the same period using an open system (April 1982)*

Day and time from–to	Plot	Emission (ng N m^{-2} s^{-1}) of NO*	NH₃	Range of soil temp. (°C)
20 20^{40}–21 08^{30}	LU	0.84	1.53	−0.1–+3.9
21 11^{20}–21 13^{20}	LU	1.76	9.5	7.0–10.0
21 21^{00}–22 09^{00}	LU	0.96	0.57	0.1–3.9
22 13^{15}–22 15^{40}	LU	2.30	3.5	10.5–11.2
22 20^{40}–23 08^{40}	LU	1.7	0.78	1.2–5.9
23 11^{40}–23 12^{50}	B 120†	0.61	1.23	5.6–6.8
23 13^{30}–23 14^{35}	GR 200†	0.22	0.84	8.8–9.0
23 20^{40}–27 11^{50}	LU	2.98	2.52	3.0–12.2

* Average of hourly data.

† Fertilized in May 1981.

LU = lucerne; B = barley; GR = grass ley.

should be pointed out that this measurement was made on an area recently fertilized with NO_3^- and glucose.

Similar conditions apply for the measurements of NH_3. Table 2 shows simultaneous measurements of NH_3 and NO emissions using the open system. The NH_3 concentration in the chamber was actually an equilibrium concentration indicating that the actual emission is higher (Ferm, pers. comm.). A direct comparison with NH_3 emission is therefore uncertain, but indicates that the fluxes were always in the same order of magnitude. As each measurement of the NH_3 concentration took at least one hour, it was not possible to use the closed system for the NH_3 measurements.

4.3 *Emission and deposition of NO_2*

On several occasions, NO_x was measured in addition to NO. The concentration difference between NO_x and NO indicates the presence of

NO_2 and, possibly, also some other nitrogen-containing trace gases (see discussion under Instruments and methods), and we will in this section denote the difference between NO_x and NO as NO_2. All measurements of the flux of NO_2 were made using the open system. With this method it is important to remove O_3 in the air entering the chamber in order to know if NO_2 is emitted from the soil or just formed as a product of the oxidation (with O_3) of NO. This was done on some occasions by putting an active carbon filter on the air intake and results from these measurements are shown in Table 3.

When NO_2 in the air entering the chamber was high (>2 ppbv) there was an uptake of NO_2 in the chamber. On occasions when the concentration was low, measurements indicate that there might be an emission of NO_2 of less than 10% of the NO emission.

In one experiment the concentration of NO_2 in the air entering the chamber was increased by addition of NO_2 from a permeation tube (April 22 at 3.05 p.m. in Table 3). Then the flux of NO_2 changed sign, from emission to uptake in the chamber. As the concentrations of NO_2 at the site of measurements were low, there was almost always a net production of NO_x in the chamber. In earlier measurements of NO_x emissions (reported in Rosswall, 1982), the flux of NO_2 was up to 50% of the NO flux. Later measurements of the concentration of O_3 at the inlet and outlet of the chamber have shown that oxidation of NO to NO_2 by O_3 might explain these high productions of NO_2 in the chamber. These results should be compared with those reported by Galbally and Roy (1978) who found NO_2 fluxes which were less than 3% of the NO flux on grazed and ungrazed pastures.

4.4 *Areal variability*

When the chamber was placed on exactly the same area several times in succession and removed for short periods (1–2 minutes) in between, the estimated rate varied slightly with a standard deviation of between 9 and 16% of the mean value. Fig. 5.1 shows the results from three measurements on the same place, within about 15 minutes, on both lucerne and grass ley. The emission rate has been normalized by division by the median value in each set of observations. These measurements indicate the expected precision of a point measure. When the emission rate was measured a few metres apart (close in time) the variation was higher—see Figs 5.2–5.5. Furthermore, the variation in the fertilized areas (GR 200 and B 120) was significantly higher than in the non-fertilized areas. This areal variation may be explained by an inhomogeneous distribution of both nutrients and microbiological activity. In the case of a recently fertilized area, the uneven distribution of fertilizer pellets certainly adds to the variability in NO emission rates. As an example, the emission from recently fertilized grass ley (Fig. 5.2b) varied from 4.5 to 62 ng NO–N m^{-2} s^{-1} within an area of 14 × 8 metres.

Areal variability in NO emission on grazed pasture in Australia gave a factor of 35 on an area of 300 m^2 (Galbally, pers. comm.). It is possible that the comparatively low spatial variability observed at Kjettslinge is due to more homogenous soil conditions than is the case with the grazed pasture in Australia.

Much larger areal variability has been found for N_2O production in the Kjettslinge soil (Klemendtsson, pers. comm.). N_2O emission is determined by taking soil cores of 10 cm diameter and measuring the production in the laboratory under standardized conditions. One reason for the larger variability in estimated N_2O emission could, therefore, be the smaller area used for the measurements, but other factors might also be of importance. Large areal variability for N_2O emissions has earlier been reported in the literature. Thus, Bremner and Blackmer (1980) found that N_2O emission rates from a "seemingly uniform area" of 100 m^2 varied from values corresponding to between 48 and 457 ng N_2O–N m^{-2} s^{-1} with a standard deviation of about 50%.

4.5. *Temperature dependence*

Fig. 6 shows the diurnal variation of the NO emission rate on all four treatments together with soil surface temperature (at about 3 cm depth). A plot of the logarithm of the net NO emission rate versus the inverse of absolute temperature is shown in Fig. 7. This figure indicates an interesting anomaly, in that the emission rate increases more rapidly than could be predicted from the increase in soil temperature during the morning hours (dashed arrows in Fig. 7). One possible explanation is that the roots of the plants exude organic substances during these morning hours just as the sun rises and when the soil has not yet been warmed up

Table 3. *Simultaneous measurements of NO and NO_2* using the open system*

			Concentrations (ppbv)				Flux (ng N m^{-2} s^{-1})		Temp. (°C) soil surface
			NO		NO_2†				
Plot	Date	Time	Inlet	Outlet	Inlet	Outlet	NO	NO_2	
LU	Apr. 21	11^{19}	0.72	7.1	3.7	1.9	1.5	−0.43	10.3
		11^{50}	1.0	8.0	3.3	2.1	1.7	−0.31	11.5
		12^{20}	0.8	8.4	3.9	2.5	1.8	−0.33	12.0
		13^{20}	1.1	8.9	4.9	2.5	1.9	−0.58	10.0
LU	Apr. 22‡	13^{15}	0.72	10.6	1.2	2.1	2.4	0.23	10.8
		14^{00}	0.60	11.0	1.3	1.8	2.5	0.11	10.5
		14^{40}	0.60	11.8	1.6	2.5	2.7	0.21	11.0
		15^{05}§	2.7	12.1	4.0	2.2	2.3	−0.44	11.0
		15^{40}§	1.9	12.7	4.2	2.2	2.6	−0.43	11.2
LU	Apr. 22‡	21^{40}	0.4	7.9	1.2	1.6	1.8	0.10	4.9
		22^{40}	0.2	8.2	1.3	1.3	1.9	0.03	4.0
		23^{40}	0.4	8.2	1.2	1.5	1.9	0.07	3.2
		00^{40}	0.3	8.2	1.3	1.5	1.9	0.05	2.8
		01^{40}	0.2	7.9	1.2	1.3	1.8	0.02	2.3
		02^{40}	0.2	7.2	1.1	1.3	1.7	0.05	2.0
		03^{40}	0.4	6.7	1.0	1.3	1.5	0.07	1.8
		04^{40}	0.3	6.3	1.1	1.4	1.5	0.07	1.5
		05^{40}	0.4	6.4	1.0	1.3	1.5	0.07	1.2
		06^{40}	0.5	7.0	1.2	1.4	1.6	0.05	2.0
		07^{40}	0.6	7.1	1.2	1.7	1.6	0.12	2.5
		08^{40}	0.7	7.9	1.3	1.7	1.7	0.10	4.1
B 120	Apr. 23‡	11^{20}	0.84	2.5	1.7	2.2	0.64	0.12	5.6
		12^{02}	0.72	2.5	1.8	2.0	0.61	0.06	6.0
		12^{50}	0.60	2.4	1.8	2.0	0.58	0.05	6.8
LU	Apr. 23	20^{40}	1.4	12.8	5.6	2.6	2.8	−0.72	9.5
		21^{40}	1.2	13.0	5.8	2.7	2.9	−0.74	9.0
		22^{40}	1.6	13.0	5.5	2.7	2.8	−0.67	8.2
		23^{40}	1.2	12.3	6.7	2.9	2.7	−0.91	8.0
		00^{40}	1.2	12.4	5.4	2.8	2.7	−0.62	7.8
		01^{40}	1.2	12.2	4.6	2.8	2.7	−0.43	7.6
		03^{40}	1.0	12.1	4.2	2.7	2.7	−0.36	7.1
		05^{40}	0.84	12.5	4.0	2.6	2.8	−0.33	6.9
		07^{40}	1.5	13.1	3.9	2.5	2.8	−0.33	6.8
		09^{40}	1.1	13.3	4.5	2.7	3.0	−0.45	7.0
		11^{40}	0.54	11.5	2.7	2.9	2.7	−0.05	7.8
		13^{40}	0.60	12.7	2.5	2.9	2.9	0.10	9.1
		15^{40}	0.48	10.3	2.3	3.2	2.4	0.22	10.0
		17^{40}	0.60	12.4	2.3	3.2	2.9	0.22	10.9
		19^{40}	0.42	12.8	2.3	3.1	3.0	0.19	10.5
LU	Apr. 27	19^{10}	0.5	3.0	3.3	4.1	2.1	0.67	10.8
		20^{10}	0.7	3.2	4.6	3.6	2.1	−0.84	9.4
		21^{10}	0.8	3.1	5.8	4.4	1.9	−1.2	8.6
		22^{10}	0.5	2.6	3.1	2.9	1.8	−0.17	8.1
		23^{10}	0.5	2.6	3.4	2.8	1.8	−0.50	7.2
		00^{10}	0.6	2.8	4.2	2.7	1.8	−1.3	7.2
		01^{10}	0.6	2.7	3.7	2.4	1.8	−1.1	6.3
		02^{10}	0.5	2.6	3.3	2.4	1.8	−0.76	6.1
		03^{10}	0.5	2.5	3.0	2.3	1.7	−0.59	6.0
		04^{10}	0.5	2.4	3.2	2.3	1.6	−0.76	6.0
		05^{30}	0.6	2.6	3.2	2.1	1.7	−0.92	5.8
		06^{10}	0.7	2.8	4.0	2.3	1.8	−1.4	5.8
		07^{10}	0.9	3.0	4.8	2.6	1.8	−1.8	6.0

Temp. (°C) soil surface
10.3
11.5
12.0
10.0
10.8
10.5
11.0
11.0
11.2
4.9
4.0
3.2
2.8
2.3
2.0
1.8
1.5
1.2
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9.4
8.6
8.1
7.2
7.2
6.3
6.1
6.0
6.0
5.8
5.8
6.0

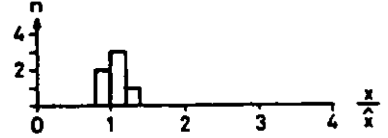
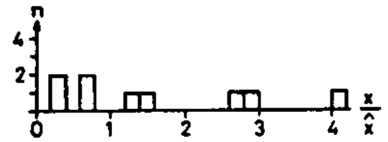
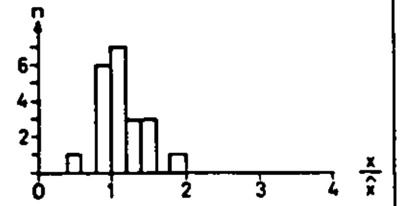
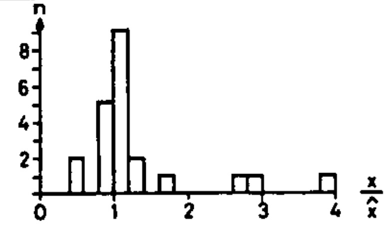
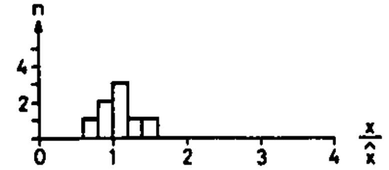
Plot	Number of measurements (n)	NO emission (mean value) (ng N m^{-2} s^{-1})	Standard deviation (% of mean)	Frequency distribution (normalized to median value, $\hat{x}$)
1. LU GR 200	a 3 b 3	1.4 0.38	9 16	
2. GR 200	a 3 b 6	0.45 23.5	60 89	
3. LU	a 5 b 7 c 4 d 5	2.0 1.9 0.37 3.1	33 20 30 18	
4. B 120	a 8 b 4 c 5 d 5	1.6 0.38 1.9 35.3	66 68 29 26	
5. B 0	a 5 b 3	12.0 2.3	21 26	

Fig. 5. NO emission variability. Set 1: Consecutive measurements at exactly the same place. Sets 2–5: Measurements at different places within the plot. Within each subset (i.e., 2a, 2b, etc.) measurements were close in time. GR 200: fertilized grass ley; B 0: unfertilized barley; B 120: fertilized barley; LU: lucerne.

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* Might also include alkyl-nitrates, -nitrites, HNO_2, HNO_3 and PAN (peroxyacetylnitrate).

† The absolute values of the concentrations of NO_2 might be 0.5 ppbv too high due to offset of the NO_2 zero signal.

‡ Periods when O_3 was removed from the air entering the chamber.

§ Addition of NO_2 to the air entering the chamber.

LU = lucerne; B = barley.

(Rosswall, personal communication). These compounds can then be utilized by the denitrifying bacteria which will start to reduce NO_3^- and, subsequently, NO will be produced more rapidly than the soil temperature will predict. This explanation is consistent with the fact that this phenomenon is most obvious in the fertilized soils where the NO_3^- content is higher. Measurements of NO emission in Australia on grazed pastures did not show any temperature dependence (0 to 25 °C) (Galbally, personal communication). This fact indicates that different processes are involved in the production of NO at the two experimental fields.

From the slope in Fig. 7 the activation energy can be calculated and is given in Table 4 together

Table 4. *Activation energy and Q_{10} values for NO production (cf. Fig. 7). Q_{10} is the change of emission rate between 10 and 20 °C*

Plot	Activation energy (kJ mole^{-1})	Q_{10}
Barley (*B 120*)	83	3.6
Grass ley (GR 200)	83	3.6
Barley (B 0)	79	3.5
Lucerne (LU)	65	2.7

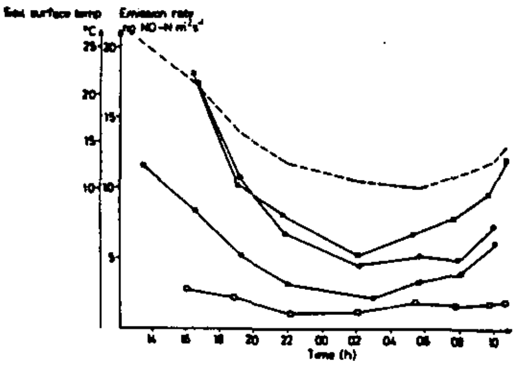

Fig. 6. Diurnal variation of NO emission rate on four cropping systems. Fertilized barley (×) and grass ley (O), unfertilized barley (★) and lucerne (□). Dashed line is soil surface temperature.

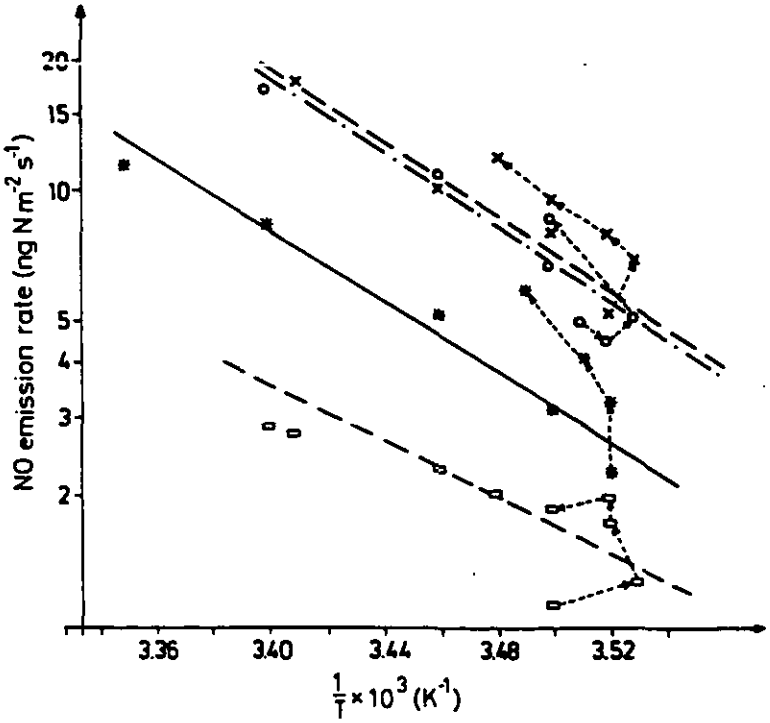

Fig. 7. Temperature dependence of NO emission rate (data from Fig. 6) on: fertilized barley (×), fertilized grass ley (O), unfertilized barley (★) and lucerne (□). Dashed arrows combine points in the morning hours in Fig. 6.

with Q_{10} values (changes in emission rate between 10 and 20 °C). These values (65–83 kJ mole^{-1}; Q_{10} = 2.7–3.6) can be compared with those found for N_2O production in an anaerobic soil which were in the range 77–83 kJ mole^{-1} (Q_{10} = 3.1–3.4) (McKenney et al., 1980), and $Q_{10} = 2.8$ which was found in a field investigation of N_2O emission from a grass-sword (Denmead et al., 1979). A strong temperature dependence of NO production in soil during anaerobic conditions has also been observed (McKenney et al., 1982).

4.6. *The effect of soil water content*

The many measurements of NO emission in the Kjettslinge field have shown that NO emission is lowest from thoroughly wetted soil. This was shown by the measurements before and after rain events both in 1981 and 1982 and after artificial watering of the soil. However, we have not been able to find a simple relation between the emission rate of NO and soil moisture content (with due consideration of for instance the effect of temperature). As an example, the emission was normalized with regard to temperature (to 20°) and compared to soil moisture content (obtained either from weight loss or from tensiometers), but no relation was found. The following measurements further indicate that the relation between NO emission and soil water content far from saturation is very complex. After a modest rain which came after a period of drought, the NO emission increased for a period of half a day. After that the NO emission decreased to low values in response to very heavy rainfall.

4.7. *Production versus soil depth*

There are several indications that the NO production occurs in the uppermost layer of the soil (the first few centimetres). These include:

1. The emission rate responded to rapid changes in surface temperature. For example, there was a much better relation between NO emission rate and chamber air temperature than with soil temperature at, say, 10 or 15 cm depth
2. The NO emission rate decreased, even when only enough water is added to moisten the upper few centimetres of the soil.
3. In one experiment, the NO emission from the soil was measured before and after 5 cm of top soil was removed. The NO emission immediately after removal was about one-fifth of the value before removal.
4. The calculation of the diffusion rate of NO in the soil suggests that an equilibrium concentration is already reached at a depth of only a few centimetres. The calculations are not very precise, and the results vary with the variations in compensation point and production rate from day to day. However, they indicate that only a very shallow layer is responsible for NO emission. This finding is of importance for the interpretation and parameterization of the flux in future experiments. Similar conditions may also occur for the production of N_2O, judging from vertical concentration gradients in the soil (Seiler and Conrad, 1981), although it appears to be generally believed that a layer of several tens of centimetres is responsible for the measured flux of N_2O from the soil.

4.8. *Effect of vegetation*

We have also observed an interesting influence of vegetation on the emission rate. Fig. 8 shows the

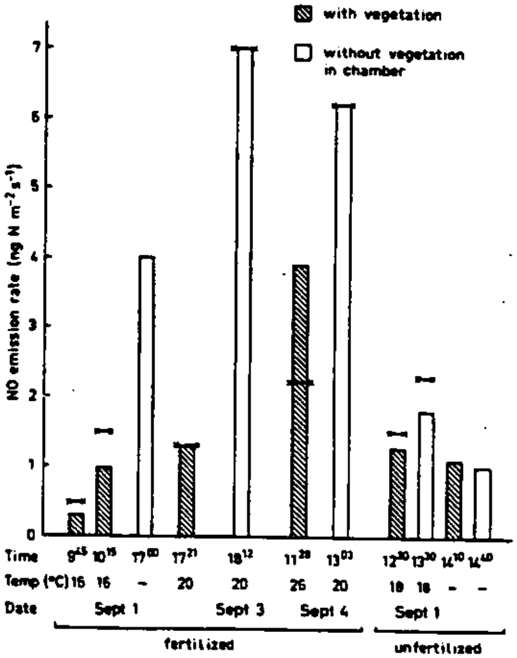

Fig. 8. Comparison of NO emission rate with and without vegetation (barley plants) in the chamber. The plants were cut before the measurements; from 60–80 cm to approx. 5 cm. ×—×, value if normalized to 20 °C according to the temperature dependence in Fig. 7.

flux of NO from the B 120 plot with and without vegetation, and B0 with and without vegetation normalized to the same temperature with the aid of the temperature dependence in Fig. 7. The results could be interpreted basically in two ways:

(i) that NO is deposited on vegetation;

(ii) that vegetation to some extent prevents the vertical mixing, and a higher NO concentration builds up near or slightly below the soil surface which, as we have discussed earlier, will give a reduced net emission rate of NO.

4.9. *Yearly losses to the atmosphere*

From present knowledge, we cannot give a very accurate estimate of the yearly emission of NO_x from the measured areas. Table 5 summarizes measurements made during 1982 and in September 1981. Although the time distribution is not very even, we think that they give a fairly good estimate of temporal variation during the vegetation period, with the highest emission rates in June and comparatively low in spring and autumn.

In order to obtain an approximate estimate of the emission for a whole year, we used the measurements so far available, considered emission rates during day and night and during periods with different soil temperatures, assumed zero emission during winter and calculated a weight average value for the year. We then arrived at an estimated emission of 0.6 kg N ha^{-1} a^{-1} from fertilized grass ley and 0.2 kg N ha^{-1} a^{-1} from unfertilized barley.

This can be compared with the yearly deposition of nitrogen compounds from the atmosphere. Wet deposition is measured in the area to be about 4 kg N ha^{-1} a^{-1} (1.7 kg NO_3^-–N ha^{-1} a^{-1}, 1.9 kg NH_4^+–N ha^{-1} a^{-1} and 0.7 kg organic N ha^{-1} a^{-1}). Dry deposition of particulate matter contributes less than 0.3 kg N ha^{-1} a^{-1} as estimated from particulate nitrate concentration, particle size distribution and a dry deposition velocity as a function of particle size. These deposition fluxes are typical for areas affected by the large anthropogenic emissions in Europe.

As a comparison, the average NO emission from

Table 5. *Summary of the measurements of NO emission (closed system) during 1982*

Plot	Month	Number of measurements	Range of emission rates (ng N m^{-2} s^{-1})	Soil temperature (range) (°C)	
Barley (B0)	Apr.	5	0.29–2.99	4.9–6.1	
	May	3	1.20–2.23	9.8–11.0	
	June	40	0.46–17.0	10.7–25.5	
	July	22	0.66–2.08	11.5–28.6	
	Sept.*	4	1.0–1.8	18.0	
Lucerne (LU)	Apr.	26	0.31–5.50	5.0–11.9	
	May	2	0.82–1.95	nm	
	June	14	1.03–4.1	10.7–21.8	
Barley (B 120)	Apr.	28	0.15–5.66	2.9–13.0	
	May†	8	0.96–4.38	7.3–10.7	— Bkg +
	June	23	0.99–52.8	10.6–25.5	←
	July	1	3.24	13.9	
	Sept.*	7	0.3–7.0	16–26	
Grass ley (GR 200)	Apr.	6	0.1–1.29	7.2–10.1	Bkg Bkg +
	May†	1	0.45	10.0	—
	June‡	15	1.86–61.6	10.7–25	←
	July	3	1.36–3.19	11.7–14.5	—
	Sept.*	1	1.7	21.0	

* Measurements performed in 1981.
† Fertilization 120 kg NO_3^-–N ha^{-1}.
‡ Fertilization 80 kg NO_3^-–N ha^{-1}.
nm = not measured.

grazed and ungrazed pastures in Australia was 3.5 and 1.6 ng N m^{-2} s^{-1} which corresponds numerically to 1.1 and 0.5 kg N ha^{-1} a^{-1}, respectively (Galbally and Roy, 1978).

We can conclude that the losses of NO from agricultural soils appear to be of little importance for the soil nitrogen budget. On the other hand, the emission might be an important source of atmospheric NO_x. For example, if our experimental site is representative for all Sweden's agricultural land, the emission during the growing season is about 10% of the emission from anthropogenic combustion sources within the country. Continuing investigations of processes leading to NO and NO_x emission from arable land (and other soils) are, therefore, of considerable interest both from the point of view of atmospheric chemistry and for a better understanding of soil nitrogen processes.

5. Acknowledgements

We greatly appreciate the work of Leif Bäcklin who built most of the equipment necessary for the measurements and modified commercial analytical instruments to obtain necessary performance. We would like to thank Thomas Rosswall for encouragement and support during our participation in the project "Ecology of arable land" as well as for many fruitful discussions both during the field measurements and during preparation of this paper. We would also like to thank Leif Klemendtsen and Bo Svensson for stimulating cooperation during the field experiments and data interpretation.

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MRI-18

MIDWEST RESEARCH INSTITUTE

PROJECT DEVELOPMENT SKETCH

TITLE Reference 9. C. Johansson Tellus 36B

PROJECT NO. 6500-3513 DRAWN Mlewey APPR. DATE 9-17-92

1. Pollutant: $\boxed{NO}$

2. Fertilizer: $CaNO_3$

3. Rates: $\boxed{120 \text{ kg N/ha} \quad , \; 200 \text{ kg N/ha}}$

4. Emissions

text: bkg = 0.2 kg N/ha yr on p. 36
200 = 0.6 kg N/ha yr on p. 36

Convert kg N/ha yr to g NO/ha day, and subtract bkg

$$\frac{0.6 \text{ kg N}}{\text{ha yr}} - \frac{0.2 \text{ kg N}}{\text{ha yr}} = \frac{0.4 \text{ kg N}}{\text{ha yr}} \quad \text{from 200 kg N/ha fertilizer}$$

$$\frac{0.4 \text{ kg N}}{\text{ha yr}} \times \frac{\text{yr}}{365 \text{ day}} \times \frac{1000 \text{ g N}}{1 \text{ kg N}} \times \frac{30 \text{ g NO}}{14 \text{ g N}} = 2.35 \frac{\text{g NO}}{\text{ha day}}$$

Calculate EF_{day}

$$EF_{day} = \frac{2.35 \text{ g NO/ha day}}{200 \text{ kg N/ha}} = \boxed{0.0117 \text{ g NO/kg N day}}$$

Calculate EF_{total}, assume total = 1 yr equivalent

$$EF_{total} = \frac{0.4 \text{ kg N/ha} \times \frac{1000 \text{ g N}}{\text{kg N}} \times \frac{30 \text{ g NO}}{14 \text{ g N}}}{200 \text{ kg N/ha}} = \boxed{4.28 \frac{\text{g NO}}{\text{kg N}}}$$

APPENDIX D

REFERENCE 4 AND ASSOCIATED HAND CALCULATIONS

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Field Measurements of Emission of Nitric Oxide from Fertilized and Unfertilized Forest Soils in Sweden

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Abstract. Application of nitrate fertilizers on two types of forest soils led to a marked increase in the NO emission rate indicating a large potential for NO production in these soils. The largest fluxes on the fertilized plots were up to 60 ng NO–N m^{-2} s^{-1}. About 0.35% of the applied nitrogen was lost as NO within about 14 days after fertilization. The fluxes from the unfertilized forest soils were in the range 0.1 to 0.8 ng NO–N m^{-2} s^{-1} with a median value of 0.3 ng NO–N m^{-2} s^{-1}. If this value, obtained during June and August to September, is representative for the growing season (150 days), it corresponds to an annual emission of 0.04 kg NO–N ha^{-1}. This is about 30% of the value obtained for an unfertilized agricultural soil. Because of the large areas occupied by forests in Sweden the flux of NO from forest soils represents a significant contribution to the total flux of NO from soils in Sweden.

Earlier observations of equilibrium concentrations for NO have been verified. These were found to range from 0.2 to 2 ppbv for an unfertilized forest soil and up to 170 ppbv for a fertilized soil. At the rural site in Sweden where these measurements were performed the ambient concentrations where found to be less than this equilibrium concentration, and consequently there was generally a net emission of NO.

There are still large uncertainties about the global flux of NO from soils. Using direct measurements on three different types of ecosystems and estimates based on a qualitative discussion for the remaining land areas, a global natural source for NO of the order of 1 Tg N a^{-1} was obtained. If 0.35% of the total annual production of fertilizer nitrogen is lost as NO, fertilization of soils may contribute with 20% to the natural flux from soils.

Key words. Nitric oxide, emission, forest soils, fertilized, unfertilized.

1. Introduction

Production of nitric oxide (NO) in soils represents an important source of NO_x in the lower atmosphere (Galbally and Roy, 1978; Galbally *et al.*, 1980: Logan *et al.*, 1981). In order to achieve an estimate of the global flux of NO from the ground, field measurements on different types of soils are needed. Earlier measurements have been performed in different ecosystems: forests (Kim, 1973), pastures (Galbally and Roy, 1978) and arable land (Johansson and Granat, 1984). In these measurements NO emissions ranging from less than 0.1 ng NO–N m^{-2} s^{-1} up to 70 ng NO–N m^{-2} s^{-1} have been observed.

Some progress has been made in the investigation of how environmental factors such as soil temperature, soil moisture and nitrate content in the soil affect the NO emission *in situ* (Galbally and Roy, 1978; Johansson and Granat, 1984). It has been shown that NO emission is higher on grazed or fertilized soils than on ungrazed or unfertilized soils. Our earlier measurements on arable land (Johansson and Granat, 1984) have shown that for the vegetation period the NO emission was three times higher on the fertilized area (200 kg N ha^{-1}) than on the unfertilized area. A rough estimate showed that approximately 0.2% of the applied nitrate nitrogen ($Ca(NO_3)_2$) was lost as NO.

Recent laboratory studies using gas flow through soil columns, where the NO loss is maximized, have shown that as much as 30 to 40% of the NO_3^-–N may be lost as NO within less than 20 hours under anaerobic conditions (McKenney *et al.*, 1982; Johansson and Galbally, 1984). Earlier laboratory studies report nitrogen losses in the range 1 to 5.3% of the applied nitrogen after the addition of ammonium or urea fertilizers (Steen and Stojanovic, 1971; Bundy and Bremner, 1974; Keeney *et al.*, 1970; Marshall and Debell, 1980).

This paper presents field measurements of fertilizer-induced NO emission. The flux of NO from both unfertilized and from freshly fertilized forest soils was measured at two different sites.

2. Experimental Sites and Method

The measurements were made in two different forests, at Sörentorp, 10 km north of Stockholm, and at Jädraås, 220 km northeast of Stockholm. The characteristics of the sites and the concentrations of ammonium (NH_4^+), nitrate (NO_3^-) and nitrite (NO_2^-) in the surface (upper 2 cm) of the soil are given in Table I.

The site at Jädraås is a 20- to 25-year-old stand of Scots pine (Pinus sylvestris) at the Swedish Coniferous Forest Project site, Invantjärnsheden. The ground vegetation is of a dry to very dry dwarf shrub type. The soil is an iron podzol on sandy sediments. Further characteristics regarding vegetation cover, nutrient status of the soil and climatic data are given in Axelsson and Bråkenhielm (1980). The site at Sörentorp is a rather open park-

Table I. Characteristics of the two sites

Site	Vegetation	Soil type and texture (10 cm depth)	pH	NH_4^+	NO_3^-	NO_2^-
				(mg N/100 g dry soil)		
Sörentorp	Scots pine mixed with Norway spruce, silver birch and aspen. Undergrowth of grasses and herbs	Grey-brown podzolic soil. 15% clay, 76% silt, 9% sand	4.5	3.0	<0.01	0.015
Jädraås	Scots pine heath on sand. Undergrowth of dwarf shrubs and lichens	Iron podzol. 2% clay, 43% silt, 46% sand	4.0	1.6	<0.01	0.094

like forest dominated by Scots pine mixed with Norway spruce, silver birch and aspen. The stand is approximately 75–80 years old. Undergrowth consists mainly of grasses, some herbs and small shrubs. The ground surface is covered with a carpet of mosses. The soil is an intermediate type between podzol and brown earth and could be characterized as grey-brown podzolic soil.

The flux measurements were made using the chamber technique described in Johansson and Granat (1984). With this method a chamber is placed over the surface and the increase in the concentration of NO during the first few minutes is monitored. The emission rate is calculated from the increase in NO concentration right after the chamber is installed over the soil. The chamber was an aluminium cylinder with the inside walls lined with a teflon film. The air in the chamber was stirred with a stainless steel stirrer blade. The volume of the chamber was 110 l and the covered area 0.5 m^2. An area of approximately 25 m^2 was selected at each site. Within this area six aluminium frames were inserted approximately 5 cm into the soil. The air inside the box was sealed with a rubber collar attached to the frames and the chamber. Two plots were fertilized, two treated with just water and two plots were untreated. Each plot was 1 m^2 and contained one aluminium frame (each 0.5 m^2). At Jädraås the frames were placed on plots covered with *Cladonia* lichens, and at Sörentorp they covered plots with grasses and mosses. Soil surface temperature was measured a few meters beside the flux measurements at about 2 cm depth. In the first and second fertilization calcium nitrate ($Ca(NO_3)_2$) was applied (4.64 g NO_3^-–N m^{-2}), and in the third sodium nitrate ($NaNO_3$) was applied (1.12 g NO_3^-–N m^{-2}). The $Ca(NO_3)_2$ fertilizer contained 14.5% NO_3^-–N and 1% NH_4^+–N; thus the $Ca(NO_3)_2$ fertilized plots also received 0.32 g NH_4^+–N m^{-2}. The fertilizers were dissolved in water, and 10 l m^{-2} was added.

Nitric oxide was analyzed with a modified chemiluminescent NO detector. Calibration was made using cylinders containing 1.02±0.05 ppmv (10^{-6} v/v) and 50.5 ± 1.0 ppmv NO. The sensitivity was ±0.10 ppbv (10^{-9} v/v). The least detectable flux when the chamber was allowed to cover the soil for 10 min was ~0.07 ng NO–N m^{-2} s^{-1}. The mechanical and chemical analyses of the soil were made at the National Laboratory for Agricultural Chemistry, Uppsala, Sweden. Levels of NO_3^- and NO_2^- were determined by an automated colorimetric method (Technicon, 1973). In this procedure NO_3^- was first reduced to NO_2^- with a copper-cadmium reductor column. Ammonium was analyzed using the indophenol blue method.

3. Results and Discussion

When the chamber was placed on the same plot several times in succession and removed for short periods (1–2 min) in between, the estimated rate varied slightly with a standard deviation of less than 6% of the mean value (Table II).

Table III gives the results of the emission measurements on the unfertilized plots at Sörentorp and Jädraås. The fluxes at the two different sites were similar in magnitude. All fluxes were in the range 0.10 to 0.76 ng NO–N m^{-2} s^{-1}, and the median value of all data (82 measurements on 12 different plots) was 0.29 ng NO–N m^{-2} s^{-1}. The mag-

Table II. Successive measurements of NO emission on the same plot

Local time	Soil surface temperature (°C)	NO emission (ng NO–N m^{-2} s^{-1})	Average	Standard dev.
0943	15.8	3.17	3.42	0.19
0947	15.6	3.48		
0951	16.0	3.63		
0945	15.5	4.99	5.14	0.12
0949	15.9	5.14		
0954	16.1	5.29		
1544	11.4	6.29	6.52	0.21
1549	11.4	6.48		
1554	11.4	6.99		
1558	11.4	6.48		
1603	11.4	6.29		
1608	11.4	6.76		
1614	11.5	6.38		
1619	11.5	6.57		
1625	11.5	6.38		
1630	11.5	6.57		

nitude of these emissions is smaller than earlier reported measurements on forest soils (Kim, 1973) and pastures (Galbally and Roy, 1978). It is about 30% of the value obtained previously for an unfertilized agricultural soil (Johansson and Granat, 1984).

On the freshly fertilized plots the emission increased dramatically, indicating a large potential for NO production in these soils. Figures 1, 2 and 3 show the temporal change in NO emission together with soil surface temperature on the three fertilized areas, the first at Sörentorp and the second and third at Jädraås. The duplicate plots showed very similar development of maximum fluxes and subsequent temporal decrease of emission. The emissions from the controls (watered plots) were generally in the range of the

Table III. Summary of the measurements performed on the unfertilized plots at Sörentorp (June) and Jädraås (August and September)

Site	No. of measurements	Soil surface temperature (range, °C)	NO emission (ng NO–N m^{-2} s^{-1})		
			Range	Median	Standard dev.
Sörentorp	35	11.3–22.5	0.10–0.76	0.35	0.15[a]
Jädraås	47	9.0–17.3	0.10–0.56	0.23	0.04[b]
All	82	9.0–22.5	0.10–0.76	0.29	0.09

[a] Average value on 5 plots.
[b] Average value on 4 plots.

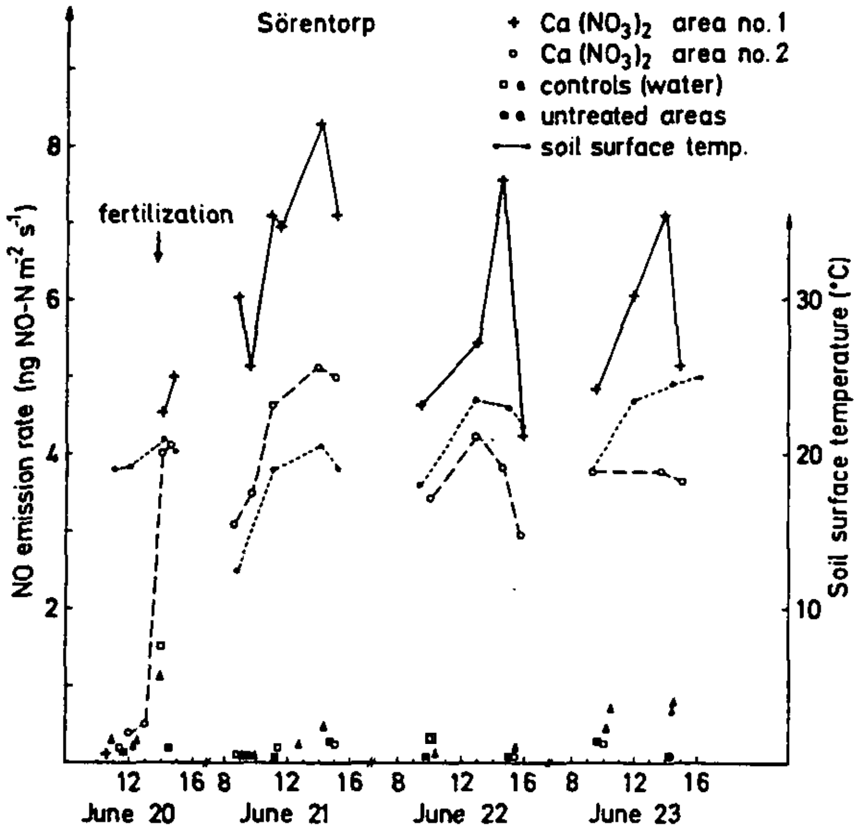


Fig. 1. Temporal change of the NO emission rate after calcium nitrate fertilization at Sörentorp (4.64 g NO_3^-–N m^{-2} was applied).

emissions from the untreated plots. Only immediately after the soil was watered in the first experiment did the emission increase slightly; it returned to the background values in a short period of time (cf. Figure 1). The NO emission was observed to increase within only 10 min after fertilization. The maximum fluxes were observed after about 20 h. As is shown in Figures 1 and 3 the NO fluxes were still above the control and untreated plots when the measurements were interrupted, indicating that the fertilizer-induced NO production continued.

Figures 1 and 2 show a strong dependecy of the NO emission rate on the temperature at the soil surface. This is in agreement with what has been found earlier for arable land (Johansson and Granat, 1984). On the unfertilized plots, where the emission was much lower, the covariation with temperature was not so evident. The soil surface temperature ranges were 11.3–22.5°C and 9–17.3°C at Sörentorp and Jädraås, respectively.

The magnitude of fertilizer-induced emission was quite different at the two sites. Comparing fluxes at similar temperaures, the maximum values at Jädraås amounted to

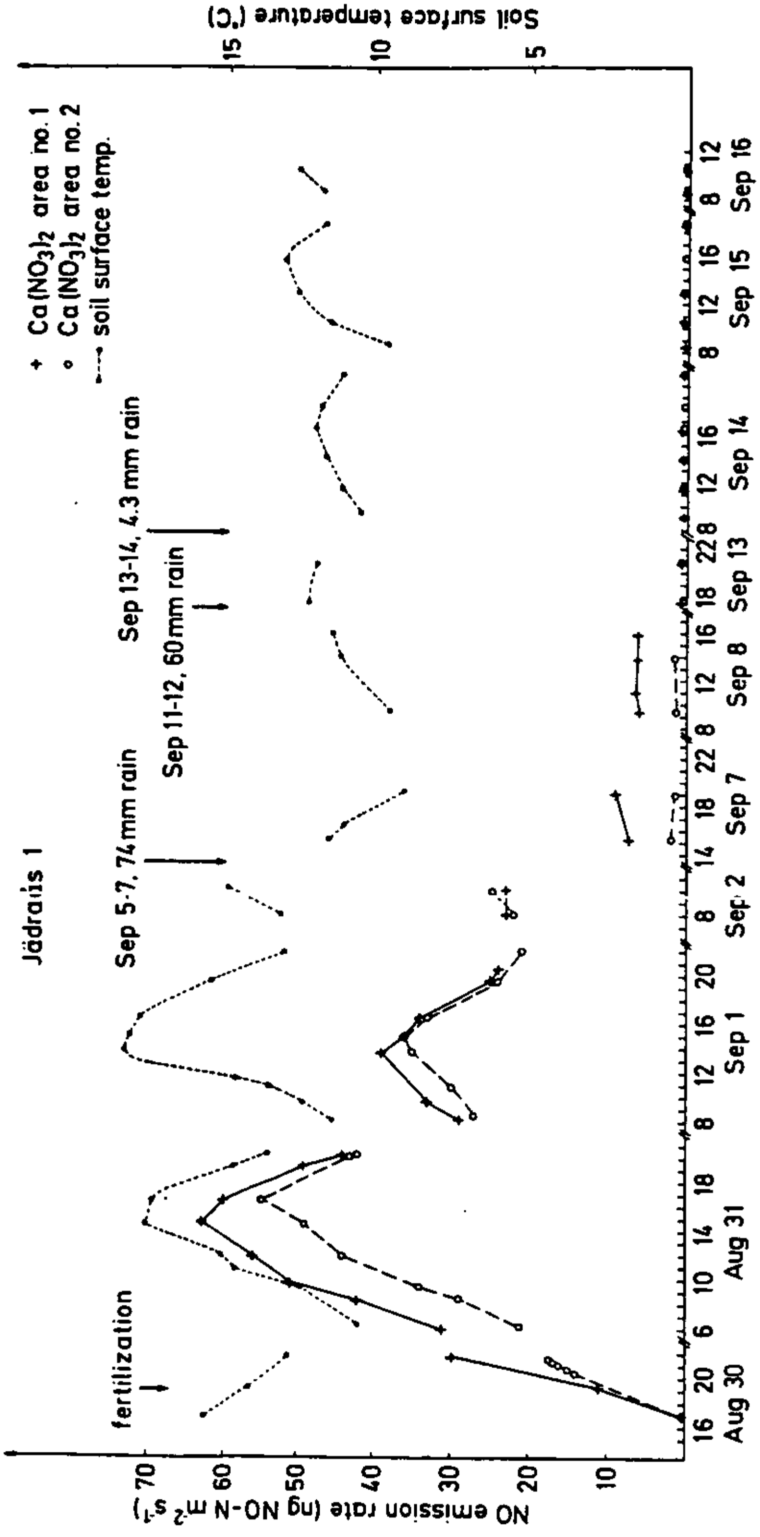


Fig. 2. Temporal change of theNO emission rate after calcium nitrate fertilization at Jädraås (4.64 g NO_3^-–N m^{-2} was applied).

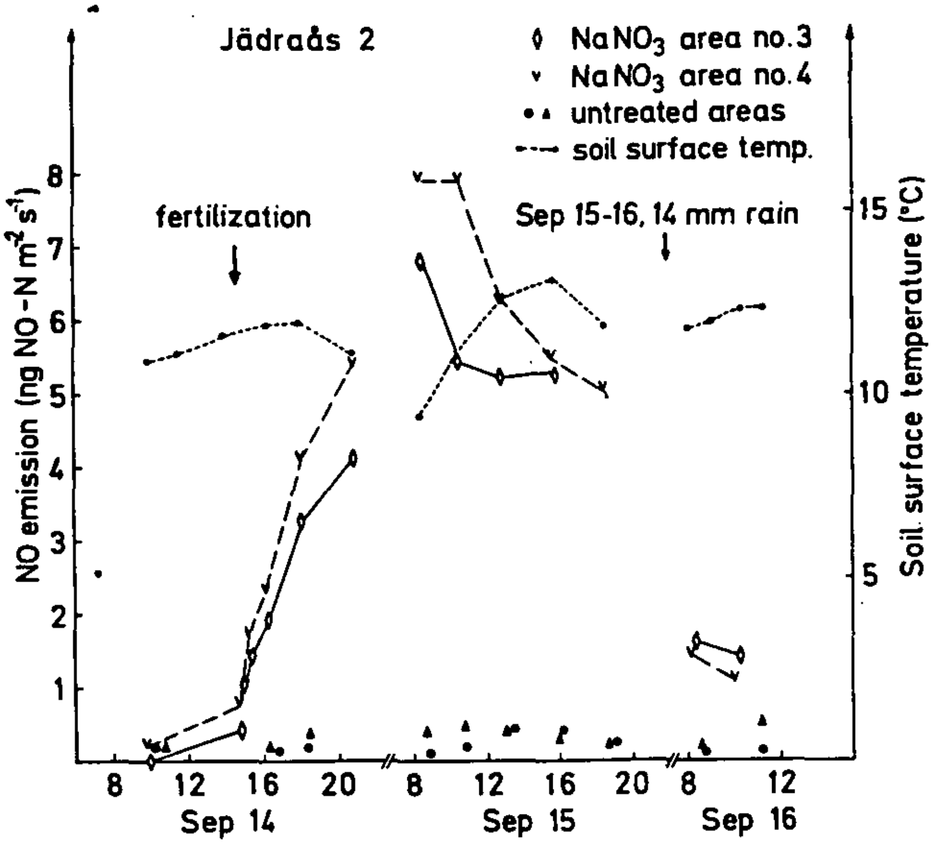


Fig. 3. Temporal change of the NO emission rate after sodium nitrate fertilization at Jädraås (1.12 g NO_3^-–N m^{-2} was applied).

about 40 ng NO–N m^{-2} s^{-1} (Figure 2), whereas the maximum fluxes at Sörentorp were only about 6 ng NO–N m^{-2} s^{-1} (Figure 1). This difference may be attributed to both different soils and different types of vegetation covering the soils.

Emission rates and loss of nitrogen as NO were both lower on the $NaNO_3$ fertilized plots than on the $Ca(NO_3)_2$ fertilized plots at the same site (Figures 2 and 3, Table VI). As the $NaNO_3$ fertilized plots received 1.12 g NO_3^-–N and the $Ca(NO_3)_2$ fertilized plots 4.64 g NO_3^-–N, this indicates that the NO production was highly dependent on the amount of NO_3^- applied. Comparing the emission rates at equal temperatures (Figures 2 and 3), the emission rate from the calcium $Ca(NO_3)_2$ fertilized plots was approximately 7 times higher than the emission rate from the $NaNO_3$ fertilized plots.

As has been pointed out, the $Ca(NO_3)_2$ fertilized plots received 0.32 g NH_4^+–N m^{-2}. Earlier laboratory studies have indicated that the NO production in soils under aerobic conditions is independent of the NH_4^+ concentration (Johansson and Galbally, 1984). In addition, field measurements on different plots on an agricultural soil fertilized with equal amounts of NH_4^+ –N or NO_3^- –N showed higher NO emissions from the NO_3^-

Table IV. Ammonium, nitrate and nitrite concentrations in the surface soil at Sörentorp. Fertilization with $Ca(NO_3)_2$ was performed June 20

Date	Treatment	Plot No.	NH_4^+	NO_3^-	NO_2^-
			(mg N/100 g dry soil)		
June 16	Untreated	1	2.5	<0.01	0.017
		2	1.9	<0.01	0.015
		3	4.0	<0.01	0.019
		4	4.7	<0.01	0.015
		5	1.8	<0.01	0.011
June 21	Fertilized	1	5.5	6.1	0.027
		2	4.5	2.2	0.052
	Watered	5	2.8	<0.01	0.019

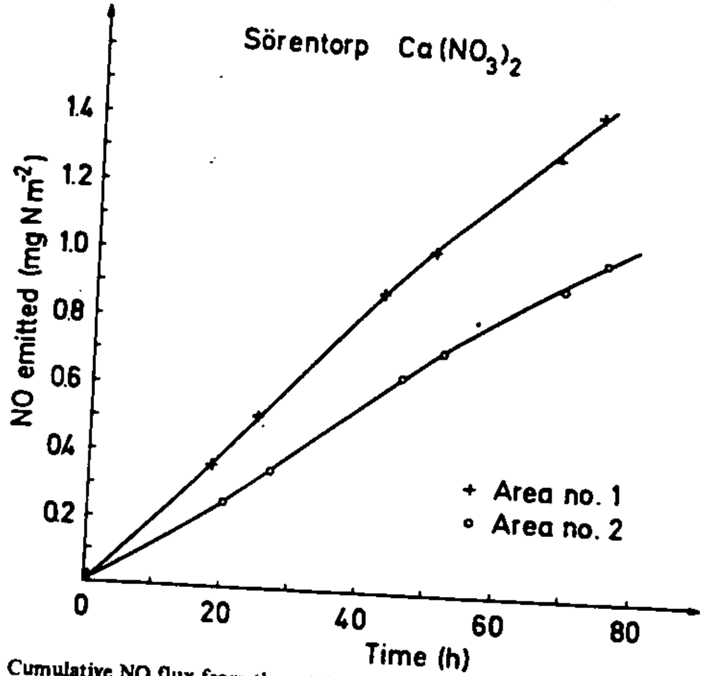
fertilized plots. Thus, it seems improbable that the small amount of NH_4^+ present in the $Ca(NO_3)_2$ fertilizer could have generated such a large difference between the $Ca(NO_3)_2$ and $NaNO_3$ fertilized plots. Although the soil has a low water-retaining capacity, it might have been caused by different soil moistures, since the $NaNO_3$ fertilizer was added after a period with two heavy rainfalls (cf. Figure 2).

The NO_2^- contents of the soils at Jädraås and Sörentorp were very low. After the addition of $Ca(NO_3)_2$ fertilizer, the NO_2^- concentration increased at both sites, although the increase was much larger at Jädraås (Tables IV and V). The highest NO_2^- concentrations were observed at Jädraås 14 days after $Ca(NO_3)_2$ fertilization. At that time the observed NO fluxes had returned to background values. This seems to indicate that the NO production in this soil was not the result of NO_2^- decomposition.

In Figures 4, 5 and 6 the cumulative fluxes are plotted versus time. The losses of NO_3^-–N as NO are given in Table VI. The differences in the cumulative fluxes from the

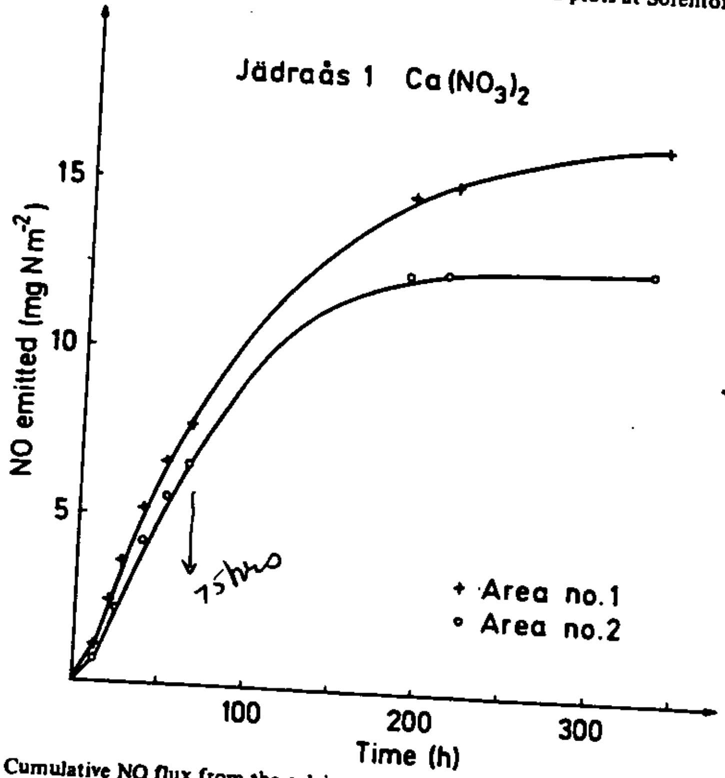
Table V. Ammonium, nitrate and nitrite concentrations in the surface soil at Jädraås. Fertilization with $Ca(NO_3)_2$ was performed August 30

Date	Treatment	Plot No.	NH_4^+	NO_3^-	NO_2^-
			(mg N/100 g dry soil)		
Aug. 31	Untreated	5	0.17	<0.01	0.036
	Watered	3	2.0	<0.01	0.087
		4	0.49	<0.01	0.061
	Fertilized	1	5.9	26	0.32
		2	1.5	8.4	0.15
Sept. 14	Untreated	5	3.0	<0.01	0.15
	Fertilized	1	6.5	0.22	0.57
		2	1.3	<0.10	0.24



match Table VI

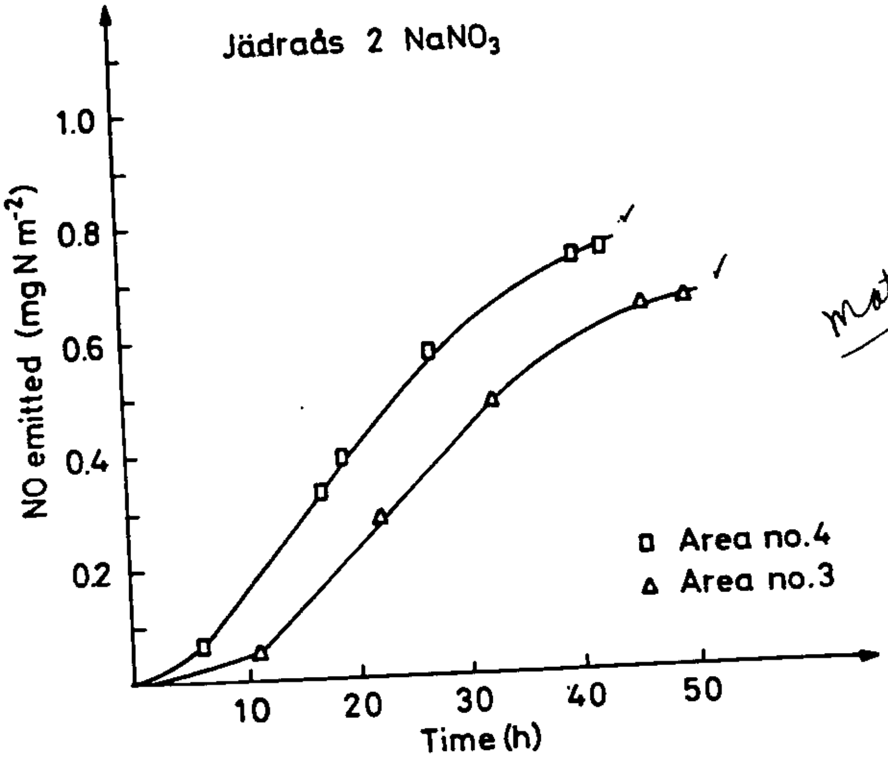
Fig. 4. Cumulative NO flux from the calcium nitrate fertilized plots at Sörentorp.



75hrs

match table VI

Fig. 5. Cumulative NO flux from the calcium nitrate fertilized plots at Jädraås.



match table VI

Fig. 6. Cumulative NO flux from the sodium nitrate fertilized plots at Jädraås.

duplicate plots were within 37% of the average value. The resultant losses of nitrogen as NO from the $Ca(NO_3)_2$ fertilized plots at Sörentorp were smaller by a factor of 6 than the losses from the $Ca(NO_3)_2$ fertilized plots at Jädraås (Table VI).

In the second fertilization the NO flux from the fertilized plots was down in the same range as the flux from the unfertilized plots after about 14 days (Figure 2). The subsequent soil analyses showed very low NO_3^- concentrations, indicating that the decrease in NO flux was the result of exhaustion of the available nitrate (Table V). In this experiment 0.35% of the applied NO_3^- was lost as NO (Table VI). This can be compared with the estimate of the corresponding value for an agricultural soil, which was 0.2% (Johansson and Granat, 1984), and with the observations on N_2O losses, which are between 0.01 and 2% (Conrad *et al.*, 1983), suggesting that the fluxes of NO and N_2O are about equally important for losses of nitrogen from soils.

Equilibrium concentrations, i.e., the concentration at which the uptake of NO balances production, were in the range 0.2 to 2 ppbv on the unfertilized plots. When the concentration in the chamber was increased above the equilibrium concentration, NO was found to be absorbed on the soil and vegetation. Only on four occasions at Sörentorp did the ambient NO level exceed the equilibrium concentration so that a net uptake of NO was observed. The average ambient concentrations observed during the measurements at

Table VI. Cumulative NO fluxes from the fertilized plots. On the $Ca(NO_3)_2$ fertilized plots 4.64 g NO_3^-–N was applied; on the $NaNO_3$ fertilized plots 1.12 g NO_3^-–N was applied

Site	Fertilizer	Plot No.	NO emitted (mg N m^{-2})[a]		
			45 hours	75 hours	340 hours
Sörentorp	$Ca(NO_3)_2$	1	0.92 (0.020)	1.4 (0.031)	–
	$Ca(NO_3)_2$	2	0.63 (0.014)	1.0 (0.022)	–
Jädraås 1	$Ca(NO_3)_2$	1	6.9 (0.15)	8.3 (0.18)	16.4 (0.35)
	$Ca(NO_3)_2$	2	4.9 (0.11)	7.1 (0.15)	12.7 (0.27)
Jädraås 2	$NaNO_3$	3	0.74 (0.066)	–	–
	$NaNO_3$	4	0.65 (0.058)	–	–

[a] The figures in parentheses indicate the fertilizer-induced emission of NO in percent of NO_3^-–N applied.

Sörentorp and Jädraås were 0.48 ± 0.38 ppbv (87 measurements) and 0.10 ± 0.10 ppbv (82 measurements), respectively. The average concentrations at Sörentorp are influenced by the city of Stockholm, whereas those observed at Jädraås are more representative of NO concentrations at a rural site in Sweden. At Jädraås there was always a net emission of NO. The equilibrium concentration was observed to be dependent on the emission rate. On the fertilized plots, where the emission was much higher, equilibrium concentrations up to 170 ppbv was observed. These results are similar to those observed earlier for arable land (Johansson and Granat, 1984).

4. Speculation on Global NO Fluxes

Söderlund and Svensson (1976) estimated the average global flux of NO_x from soils from a mass balance calculation. The value obtained as a residual source was 21–89 Tg N a^{-1}. (a = annum). Galbally and Roy (1978) estimated the global flux of NO based on their measurements on pastures in Austria to be of the order of 10 Tg N a^{-1}. Lipschulz *et al.* (1981) measured production of NO and N_2O by pure cultures of nitrifying bacteria. A ratio of about 1:5 between NO and N_2O production was observed. Based on this value and an estimate of the global source of N_2O, they arrived at a global flux for NO of 15 N a^{-1}. These three estimates have been used in papers dealing with the global nitrogen budget (Söderlund, 1980; Logan *et al.*, 1981; Ehhalt and Drummond, 1982; Sanhueza, 1982; Söderlund and Rosswall, 1982; Crutzen, 1983).

With more direct field measurements available, it is of interest to attempt a new estimate of the global flux of NO. Table VII summarizes measurements made on three different ecosystems together with estimated values for the remaining land area.

For cultivated land the emissions reported in Johansson and Granat (1984) on unfertilized agricultural land were used. The measurements on pastures in Australia by Galbally and Roy (1978) were taken as representative for temperate grasslands. For

Table VII. Ecosystem type and respective estimated fluxes of NO. The respective areas are taken from Bolin *et al.* (1979)

Ecosystem type	Based on	Area (10^{-12} m^2)	Length of season (days)	Yearly flux range	median (mg N m^{-2})	Global flux range (Tg N a^{-1})	median
Cultivated land	Johansson and Granat, 1984	16	200	2–86	20	0.03–1.4	0.3
Temperate grass-lands	Galbally and Roy, 1978	2.4	200	28–60	43	0.07–0.14	0.10
Temperate forests, mixed forests, taigas	This paper	26	200	2–14	5	0.05–0.36	0.13
Tropical seasonal and rain forests	Estimated	16	300	1–50	15	0.01–0.80	0.24
Savannas and tundras	Estimated	26	200	1–20	5	0.03–0.52	0.13
Total		86				0.2–3.2	0.9

temperate forests, mixed forests and taiga the emissions on the unfertilized forest soils obtained in this paper were used. To the knowledge of the author, there are no measurements of NO production in tropical soils, deserts, tundras or savannas. Data on nitrification and denitrification are also very scanty. In tropical soils, where nitrification occurs at high temperatures and where pH is generally fairly low, chemical decomposition of NO_2^- formed by nitrification might be an important pathway for NO loss (Laudelout, *et al.*, 1977). Likewise for savannas, which consist of aerated, well drained acid soils, self-decomposition of NO_2^- and subsequent emission of NO has been suggested as a process for loss of nitrogen (Pereira, 1982). The NO emission rates from these areas are assumed to be lower than the emission from cultivated land. The release of NO from deserts was assumed to be zero. All the NO fluxes given in Table VII are of course very uncertain since they are based on only three sets of measurements which have been extrapolated to very large areas.

The global flux obtained here, 0.2 to 3 Tg N a^{-1} and a median value of ~1 Tg a^{-1}, is appreciably lower than earlier estimates. The median value is less than 10% of the estimates reported earlier and about 5% of the anthropogenic emission by combustion of fossil fuels, which is around 20 Tg N a^{-1} (Söderlund and Svensson, 1976). According to Table VII the global flux from cultivated land represents about 30% of the total release of NO from soils. Given the annual production of nitrogen fertilizers, 55 Tg N (FAO, 1979), and the maximal estimated loss of fertilizer nitrogen (0.35%) obtained in this paper, the resultant contribution of 0.19 Tg N a^{-1} to the global natural NO flux is about 20% of the median global flux. With increased demands for land used in agriculture and global use of artificial nitrogen fertilizers this source of NO_x in the atmosphere is expected to increase.

Acknowledgements

I would like to thank Leif Bäcklin for technical assistance during the measurements and Dr Lennart Granat and Professor Henning Rodhe for encouragement and constructive suggestions during the measurements and preparation of this paper. Thanks are due to Andreas Richter for cooperation and many stimulating discussions during the field measurements. I am also indebted to Erik Troeng at the Swedish Conferous Forest Project site for support and help during the visit at Jädraås and to Bo Eknert (Department of Physical Geography, University of Stockholm), who characterized the vegetation and soil at Sörentorp. This work received financial support from the National Swedish Environment Protection Board under contract No. 53 150 53–8.

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Index

MIDWEST RESEARCH INSTITUTE
PROJECT DEVELOPMENT SKETCH

MRI-18

TITLE Reference 10. C. Johansson J. Atmos. Chem (1) (4 pgs)

PROJECT NO. 6500-3513 DRAWN MMurray APPR. DATE 9-17-92

1. Pollutant : NO

2. Fertilizer :
   - $CaNO_3$ 46.4 kg N/ha 2 sites
   - $NaNO_3$ 11.2 kg N/ha
   - spray

3. Emissions

Convert $\frac{ng\ N}{m^2\ sec}$ to $\frac{g\ NO}{ha\ day}$

(a) Emissions = $\frac{ng\ N}{m^2\ sec} \times \frac{10^4\ m^2}{ha} \times \frac{8.64 \times 10^4\ sec}{day} \times \frac{g\ N}{10^9\ ng\ N} \times \frac{30\ g\ NO}{14\ g\ N}$

Conversion factor = $\cancel{1.85}\ 1.00\ \frac{ng\ N}{m^2\ sec} \Longrightarrow 1.85\ \frac{g\ NO}{ha\ day}$

(b) EF_{day} = $\frac{\text{Emissions (g NO/ha day)}}{\text{rate (kg N/ha}}$

(c) EF = ~~EF day x days~~ $\frac{\text{Emissions (g NO/ha day)}}{\text{applied rate (kg N/ha)}}$

4. Background emissions for both sites, Table III, all median (±30% RSD) (82 tests)

Bkg Emissions = $\frac{0.29\ ng\ N}{m^2\ sec} \times 1.85 = 0.536\ \frac{g\ NO}{ha\ \cancel{kg\ N}\ day}$

MIDWEST RESEARCH INSTITUTE
PROJECT DEVELOPMENT SKETCH

TITLE Ref. 10 (pg 2 of 4)

PROJECT NO. 6500-3500 DRAWN mlwy APPR. DATE 9-17-92

Jardrass 1 - $CaNO_3$ Table VI , 340hrs (2 plots)

$$\bar{x} = \frac{16.4 + 12.7}{2} \frac{\cancel{mg\ N}}{\cancel{m^2}} \times \frac{10^4\ \cancel{m^2}}{ha} \times \frac{1\ \cancel{g\ N}}{10^3\ \cancel{mg\ N}} \times \frac{30\ g\ NO}{14\ \cancel{g\ N}}$$

$$\bar{x} = \frac{311.8\ g\ NO}{g\ ha} \quad \text{for } 340\text{hrs}$$

$$\bar{x} = \frac{311.8\ g\ NO}{ha \cdot 340hrs} \times \frac{24hrs}{day} = \frac{22.0\ g\ NO}{ha\ day}$$

$$\text{Corr Emissions} = \bar{x} - Bkg = \frac{22.0\ g\ NO}{ha\ day} - \frac{0.536\ g\ NO}{ha\ day} = \frac{21.47\ g\ NO}{ha\ day}.$$

Since emissions leveled off at 340 hrs, then total emissions due to the fertilizer are equivalent to 340hrs

$$\text{Emissions}_{total} = \frac{21.47\ g\ NO}{ha\ day} \times \frac{340hr \cdot day}{24hr} = 304 \frac{g\ NO}{ha}$$

$$EF_{total} = \frac{304\ g\ NO/ha}{46.4\ kg\ N/ha} = \boxed{6.56 \frac{g\ NO}{kg\ N}}$$

$$EF_{day} = \frac{21.47\ g\ NO/ha\ day}{46.4\ kg\ N/ha} = \boxed{0.463 \frac{g\ NO}{kg\ N\ day}}$$

Note approximately half of emissions were released at 75hrs

MRI-18

MIDWEST RESEARCH INSTITUTE

PROJECT DEVELOPMENT SKETCH

TITLE Ref 10 (pg 3 of 4)

PROJECT NO. 6500-3513 DRAWN Meues APPR. DATE 9-17-92

Sorentarp $CaNO_3$ Table VI, $\boxed{75 \text{ hrs} \times 2}$ (2 plots)

$$\bar{x} = \frac{1.4 + 1.0}{2} \frac{\text{mg N}}{\text{m}^2} \times \frac{10^4 \text{ m}^2}{\text{ha}} \times \frac{1 \text{ g N}}{10^3 \text{ mg N}} \times \frac{30 \text{ g NO}}{14 \text{ g N}}$$

$$\bar{x} = 25.71 \frac{\text{g NO}}{\text{ha}} \text{ for 75 hrs}$$

$$\bar{x} = \frac{25.71 \text{ g NO}}{\text{ha} \cdot 75 \text{ hrs}} \times \frac{24 \text{ hrs}}{1 \text{ day}} = 8.23 \frac{\text{g NO}}{\text{ha day}}$$

$$\text{Corr. Emissions}_{\text{day}} = \bar{x} - \text{Bkg} = 8.23 - 0.536 \frac{\text{g NO}}{\text{ha day}} = 7.69 \frac{\text{g NO}}{\text{ha day}}$$

$$EF_{\text{day}} = \frac{7.69 \text{ g NO/ha day}}{46.4 \text{ kg N/ha}} = \boxed{0.166 \frac{\text{g NO}}{\text{kg N day}}}$$

Assume at 75 ~~days~~ hrs ≅ ½ of total emissions like at Jeardas, then

$$\text{Emissions total} = \frac{7.69 \text{ g NO}}{\text{ha day}} \times \frac{75 \text{ hr day}}{24 \text{ hr}} \times 2 = 48 \frac{\text{g NO}}{\text{ha}}$$

$$EF = \frac{48 \text{ g NO/ha}}{46.4 \text{ kg N/ha}} = \boxed{1.036 \frac{\text{g NO}}{\text{kg N}}}$$

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MIDWEST RESEARCH INSTITUTE

PROJECT DEVELOPMENT SKETCH

TITLE Ref 10 (pg 4 of 4)

PROJECT NO. 2500-3513 DRAWN Mewey APPR. DATE 9-21-92

Jordaas 2 $CaNO_3$, Table III, 45 hours for comparison (Jordaas 1)
$NaNO_3$, Table VI, 45 hrs for emissions

$CaNO_3$ Total average emissions for 45 hrs

$$\bar{X}_{CaNO_3} \quad \frac{5.9\ mg\ N}{m^2} \times \frac{10^4\ m^2}{ha} \times \frac{1\ g\ N}{10^3\ mg\ N} \times \frac{30\ g\ NO}{14\ g\ N} = \frac{126.4\ g\ NO}{ha} \text{ for 45 hrs}$$

$NaNO_3$ Total average emission for 45 hrs

$$\bar{X}_{NaNO_3} = \frac{\overset{0.695}{\cancel{0.78}}\ mg\ N}{m^2} \times \frac{10^4\ m^2}{ha} \times \frac{1\ g\ N}{10^3\ mg\ N} \times \frac{30\ g\ NO}{14\ g\ N} = \frac{14.89\ g\ NO}{ha} \text{ for 45 hours}$$

Determimine relative emissions of $NaNO_3$ to $CaNO_3$

$$\frac{\bar{X}_{NaNO_3}}{\bar{X}_{CaNO_3}} \times 100\% = \frac{14.89\ g\ NO/ha}{126.4\ g\ NO/ha} \times 100\% = 11.8\%$$

Calculate corrected daily emission for $NaNO_3$ ~~and emission factor (EF)~~

$$\frac{14.89\ g\ NO}{ha \cdot 45\ hr} \times \frac{24\ hr}{day} = \frac{7.94\ g\ NO}{ha\ day}$$

Use average bkg (#A) = 0.536 g NO /~~kg~~ ha day

$$EF = \frac{\frac{7.94\ g\ NO}{ha\ day} - \frac{0.536\ g\ NO}{ha\ day}}{11.2\ kg\ N/ha} = \frac{7.40\ g\ NO/ha\ day}{11.2\ kg\ N/ha} = \boxed{0.661 \frac{g\ NO}{kg\ N\ day}}$$

If $NaNO_3$ - 11.8% of $CaNO_3$ total emission then the total NO emissions from $NaNO_3$ would equal 35.9 g NO/ha for 340 hrs

$$\underset{\text{(from Jordaas 1)}}{304\ g\ NO/ha} \times 0.118 = 35.9\ g\ NO/ha\ NaNO_3$$

$$\therefore \quad EF_{total} = \frac{35.9\ g\ NO/ha}{11.2\ kg\ N/ha} = \boxed{\frac{3.2\ g\ NO}{kg\ N}} \text{ @ 340 hrs}$$

APPENDIX E

REFERENCE 5 AND ASSOCIATED HAND CALCULATIONS

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Journal of Atmospheric Chemistry 2 (1984), 1–24. 0167–7764/84/0021–0001$03.60

Field Measurements of NO and NO$_2$ Emissions from Fertilized and Unfertilized Soils

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(Received: 1 December 1983; in revised form: 23 July 1984)

Abstract. Field measurements of NO and NO$_2$ emissions from soils have been performed in Finthen near Mainz (F.R.G.) and in Utrera near Seville (Spain). The applied method employed a flow box coupled with a chemiluminescent NO$_x$ detector allowing the determination of minimum flux rates of 2 μg N m^{-2} h^{-1} for NO and 3 μg m^{-2} h^{-1} for NO$_2$.

The NO and NO$_2$ flux rates were found to be strongly dependent on soil surface temperatures and showed strong daily variations with maximum values during the early afternoon and minimum values during the early morning. Between the daily variation patterns of NO and NO$_2$, there was a time lag of about 2 h which seem to be due to the different physico-chemical properties of NO and NO$_2$. The apparent activation energy of NO emission calculated from the Arrhenius equation ranged between 44 and 103 kJ per mole. The NO and NO$_2$ emission rates were positively correlated with soil moisture in the upper soil layer.

The measurements carried out in August in Finthen clearly indicate the establishment of NO and NO$_2$ equilibrium mixing ratios which appeared to be on the order of 20 ppbv for NO and 10 ppbv for NO$_2$. The soil acted as a net sink for ambient air NO and NO$_2$ mixing ratios higher than the equilibrium values and a net source for NO and NO$_2$ mixing ratios lower than the equilibrium values. This behaviour as well as the observation of equilibrium mixing ratios clearly indicate that NO and NO$_2$ are formed and destroyed concurrently in the soil.

Average flux rates measured on bare unfertilized soils were about 10 μg N m^{-2} h^{-1} for NO$_2$ and 8 μg N m^{-2} h^{-1} for NO. The NO and NO$_2$ flux rates were significantly reduced on plant covered soil plots. In some cases, the flux rates of both gases became negative indicating that the vegetation may act as a sink for atmospheric NO and NO$_2$.

Application of mineral fertilizers increased the NO and NO$_2$ emission rates. Highest emission rates were observed for urea followed by NH$_4$Cl, NH$_4$NO$_3$ and NaNO$_3$. The fertilizer loss rates ranged from 0.1% for NaNO$_3$ to 5.4% for urea. Vegetation cover substantially reduced the fertilizer loss rate.

The total NO$_x$ emission from soil is estimated to be 11 Tg N yr^{-1}. This figure is an upper limit and includes the emission of 7 Tg N yr^{-1} from natural unfertilized soils, 2 Tg N yr^{-1} from fertilized soils as well as 2 Tg N yr^{-1} from animal excreta. Despite its speculative character, this estimation indicates that NO$_x$ emission by soil is important for tropospheric chemistry especially in remote areas where the NO$_x$ production by other sources is comparatively small.

Key words. NO, NO$_2$, soil, decomposition, production, global budget, mineral fertilizer.

1. Introduction

Nitrogen oxides play a key role in the atmospheric photochemistry (Crutzen, 1981). Nitrogen monoxide and nitrogen dioxide act as catalysts in various reaction chains and thereby strongly influence the concentration and distribution of tropospheric O$_3$ and OH radicals. Consequently, they have a strong impact on the distribution and abundance of many carbon, sulphur and halogen compounds in the atmosphere. Thus, knowledge of the atmospheric cycle of nitrogen oxides is of primary importance for an understanding of atmospheric chemistry.

Nitrogen monoxide and nitrogen dioxide are emitted into the atmosphere by a number of anthropogenic processes, such as combustion of fossil fuels and biomass burning. In addition, NO and NO_2 are formed by lightning, atmospheric conversion of ammonia, and by biological processes in soils. The global NO_x source strength ($NO_x = NO + NO_2$) has been estimated repeatedly by several authors with figures varying between 20 and 80 Tg N yr^{-1} (Böttger *et al.*, 1980; Ehhalt and Drummond, 1982; Hahn and Crutzen, 1982; Crutzen, 1983; Logan, 1983). In all these estimates, the source strength of NO and NO_2 from soil is the most uncertain.

It is known from laboratory experiments that NO and NO_2 are formed by biological processes. Nitrogen monoxide has been proved to be an obligatory intermediate in the denitrification process (John and Hollocher, 1977; Firestone *et al.*, 1979). More recently, Lipschultz *et al.* (1981) reported that NO is also produced by soil nitrifying bacteria (*Nitrosomas europaea*) and McKenney *et al.* (1982) found the NO production from anaerobic denitrification in soil to be significant. In addition to the biological NO and NO_2 formation, both gases may also be produced by the chemical decomposition of nitrite (Nelson and Bremner, 1970; Smith and Chalk, 1979, 1980a, 1980b) which is known to be an intermediate of denitrification and nitrification (Payne, 1981; Bremner and Blackmer, 1981). Although all these measurements have been performed in the laboratory and may not be applicable to natural conditions, they clearly indicate that soil may provide a significant source of the global NO and NO_2 budget.

Field measurements of the NO_x emission processes are very rare. The first data were published by Makarov (1969) who found a mean NO_2 emission rate of 0.01 g N m^{-2} $week^{-1}$ from a nonfertilized soil over the entire vegetation period. In addition, his experiments with mineral fertilizers showed that 0.2% of the applied nitrogen was lost as NO_2 to the atmosphere demonstrating that the increased application of mineral fertilizer may have an effect on the atmospheric NO_x budget. Kim (1973) found NO_2 emission rates of about 0.02 g N m^{-2} $week^{-1}$ on the forest soil in July 1971. In contrast, the NO_2 emissions measured in May and June were below the detection limit of his technique. The possible emission of NO could not be observed since both authors used wet chemical absorption techniques insensitive to NO (Cheng and Bremner, 1965). The only data on NO emission were reported by Galbally and Roy (1978) who found values on the order of 0.1 g N m^{-2} yr^{-1} from nonfertilized grazed and ungrazed grassland. All these data clearly show that NO_x is actually formed in soils under natural conditions and is emitted into the atmosphere. However, the present data base on the NO_x flux rates at the soil/atmosphere interface is too limited to derive a reliable estimate of the global NO_x emissions from soils.

To provide a better data base, we have performed field measurements of the NO_x flux from fertilized and unfertilized soils into the atmosphere. Measurements were carried out on two different types of soils in two different climatic zones. NO and NO_2 fluxes obtained on bare and plant covered soils are reported and discussed. The data n understanding

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show that the production of NO_x in soils plays an important role in the atmospheric NO_x cycle.

2. Methodology

Measurements of the NO and NO_2 flux rates at the soil/atmosphere interface have been performed using the flow box method described in detail by Slemr *et al.* (1984). Figure 1 shows the schematic of the experimental set-up consisting of the flow box, a pump and the NO_x detector. The flow box (length = 40 cm, width = 22.5 cm, height = 20 cm) was set on a stainless steel frame which was inserted 20 cm deep into the soil to prevent exchange of the enclosed and free atmosphere. The interception between the box and the frame was sealed with boiled distilled water. The pump provided a constant flow of ambient air through the box with flow rates of up to 45 l (STP) min^{-1}. Pressure differences between the box and the atmosphere causing a convective flux of NO and NO_2 from the soil into the box were avoided by supplying the box with a large inlet opening (i.d. = 50 mm). The opening was shielded by a glass plate fixed about 20 mm in front of the inlet to minimize the influence of changing wind speed and direction on the pressure inside the box and consequently a convective NO and NO_2 flux at the soil/atmosphere interface.

The flux P of NO or NO_2 at the soil/atmosphere interface expressed in $\mu g\ N\ m^{-2}\ h^{-1}$ was determined from the mass balance of the box by

$$P = \frac{V \times N}{A \times M}\,(m_0 - m_1)$$

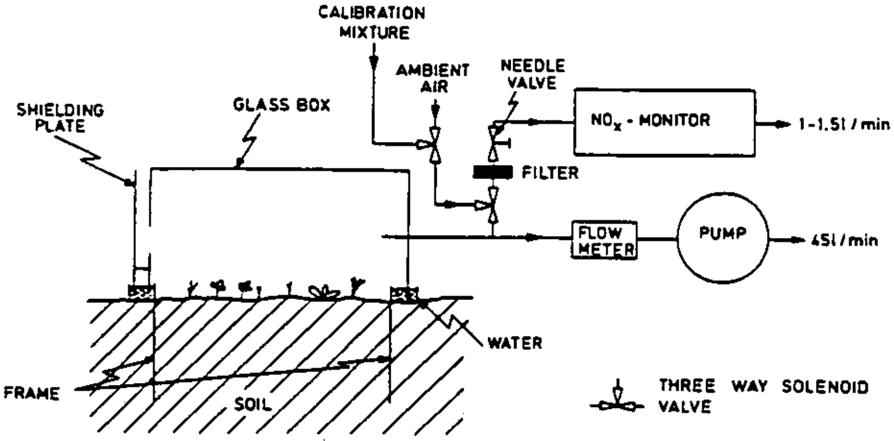

Fig. 1. Schematic of the experimental set-up used for the measurements of the NO and NO_2 flux rates at the soil/atmosphere interface.

where V is the mass flow rate of ambient air through the box in l (STP) h^{-1}, A is the soil surface area enclosed by the box (about 0.075 m^2), N is the atomic weight of nitrogen, M is the molar volume, m_0 is the NO or NO_2 mixing ratio (ppbv) at the inlet of the box (ambient air) and m_1 is the NO or NO_2 mixing ratio (ppbv) at the outlet of the box. The NO and NO_2 mixing ratios at the inlet and outlet of the box were measured with a commercial chemiluminescent detector (Thermo-Electron 14 B) modified according to Delany *et al.* (1982). The detection limit of the NO_x detector was 100 pptv and the accuracy at typical mixing ratios of NO and NO_2 of less than a few ppbv were in the range of ±4%. NO_2 was determined by conversion of NO_x into NO by a molybdenum converter heated to 400°C and subtracting the original NO signal of the air stream. Since the molybdenum converter reduces not only NO_2 but also HNO_3, PAN, N_2O_5, alkyl nitrites and alkyl nitrates (Winer *et al.*, 1974; Delany *et al.*, 1982), the difference between the NO_x and NO signals may not only be due to NO_2 but may also include other nitrogen compounds. There is evidence that the nitrogen compounds listed do not contribute significantly to the total odd nitrogen in soil air so that the difference between NO_x and NO may be almost exclusively due to NO_2. Therefore, we will denote the measured difference between NO_x and NO as NO_2. The NO_x detector was repeatedly calibrated using a standard of 1 ppmv in N_2 provided by Messer Griesheim (Frankfurt, Germany).

The NO_x instrument was installed in a small trailer located next to the experimental field and connected with the box using Teflon-tubes (about 5 m long, inside diameter = 4 mm). Absorption or desorption processes in the tube were not observed. The lower detection limit of the NO and NO_2 flux rates were determined to be 2 $\mu g\ m^{-2}\ h^{-1}$ and 3 $\mu g\ m^{-2}\ h^{-1}$, respectively. The whole system was operated automatically providing a data point for the NO and NO_2 flux rates once every 6 min.

The soil moisture was determined by a standard gravimetric method on samples taken from the uppermost 5 cm soil layer. The values are given in percent of wet weight. Soil surface temperatures were measured at a depth of 10 mm using mercury thermometers or thermocouples. In Utrera, the method recommended by Taylor and Jackson (1965) was applied for the measurement of the soil temperature. This method uses a thermocouple attached to the 100 × 100 mm large, 1.5 mm thick copper plate covered by a soil layer of 10 mm. Soil moisture and temperature were both measured in a separate plot which was treated the same way as the plots measured.

Nitrous oxide fluxes were measured concurrently by an automatically operating semicontinuous closed-static method described by Conrad *et al.* (1983). The soil was covered for at most 1 h and subsequently exposed to natural conditions for several hours before beginning a new experiment.

Each experimental station consisted of several plots. The frames surrounding the plots were inserted into the soil about a week before starting the experiment and remained in the soil during the whole measuring period. Prior to fertilization, the NO and NO_2 fluxes were determined on all plots, and only plots showing comparable fluxes were taken for further measurements. Each plot was covered by the glass box only during the measurement period required (12 min) in order to obtain two consecutive data points

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for the NO and NO$_2$ flux rates. During the rest of the time, the plots remained uncovered and exposed to natural environmental conditions.

For determination of the fertilizer loss rates, the plots were treated with fertilizer dissolved in 0.5 l distilled water. The control plots were also irrigated with the same amount of distilled water. The amount of mineral fertilizer applied corresponded to an application rate of 100 kg N ha^{-1}. The fertilizer loss rates were calculated by

$$L = \frac{P_F - P_C}{R} \times 100\ (\%)$$

where P_F and P_C are the flux rates observed at the fertilized and control plot, respectively, integrated over the entire measuring period and R is the amount of fertilizer nitrogen.

3. Field Stations

The measurements were performed in Finthen near Mainz in July and August 1982 and at the BASF experimental station in Utrera near Seville, Spain in September and October 1982. Relevant details on the soils studied are listed in Table I.

Table I. Characteristics of soil

Location	Soil type	pH (0.1 N KCl)	CaCO$_3$ (% wJ)	org. C (% wJ)	Size fractions (%)		
					Clay (2 μm)	Silt (2–20 μm)	Sand (20–2000 μm)
Finthen, Mainz	loess	7.4	2.0	0.8	20	21	59
Utrera, Seville	loamy sand	7.4	–	0.5	7	4	89

In Finthen, the experiments were carried out on a meadow which had never been used for agricultural purposes and had always remained unfertilized. The grass was cut twice a year. For measurements on bare soil, part of the meadow was ploughed one week before starting the experiments. The ploughing depth was about 30 cm. Measurements were performed on seven plots with two plots in the meadow and five in the ploughed area. One of the plots in the meadow was fertilized with NH$_4$Cl whereas the other remained undisturbed, acting as control. Two of the five plots with bare soil remained unfertilized, the others were fertilized with NaNO$_3$, NH$_4$NO$_3$ and NH$_4$Cl, respectively. Measurements were performed discontinuously between 8 a.m. and 6 p.m. During this period, 1 to 3 individual flux rates per plot and day were obtained. The experimental field in Utrera consisted of nine plots, six of which were used for measurements of NO$_x$ fluxes and the rest for measurements of the N$_2$O emission rates. All plots were without vegetation cover. From the six plots used for the NO$_x$ measurements, one remained unfertilized, two were fertilized with NH_4NO_3 and three were fertilized with $NaNO_3$, NH_4Cl and urea, respectively. The N_2O measurements were carried out on one unfertilized plot and on two plots fertilized with NH_4NO_3 and urea, respectively. All plots were fertilized on 9 September and irrigated on 16 and 20 September (precipitation rate of 7 mm each), on 24 September (3.5 mm) and on 1 October (10 mm). In addition, 10 mm of rain fell on 25 September. The NO and NO_x flux rates were determined 5 to 8 times per day and plot. The frequency of the measurements on urea treated plots was doubled to ensure more detailed information on the NO_x flux rate. The data were obtained between 6 a.m. and 11 p.m. thus covering two-thirds of the day and including the periods with minimum and maximum daily temperatures of surface soil.

The experimental station in Utrera is used in conjunction with agricultural experiments with fertilizers and insecticides and the history of each field has been carefully recorded for many years. The field selected for our experiments was used for cultivation of field beans in 1980 and for soy beans in 1981. The soy beans were ploughed under in September 1981. Since that time, the field has not been used for cultivation purposes. The field was harrowed on 2 September 1982, one week before starting our experiments. In the course of the last two years, the field was fertilized several times: on 11 November 1980 with 26 kg N ha^{-1}; on 30 April 1981 with 75 kg N ha^{-1}; on 4 June 1981 with 65 kg N ha^{-1} (all applied as NH_4NO_3) and on 8 November 1981 with 120 kg P ha^{-1}, and 240 kg N ha^{-1}. Insecticides have not been applied since June 1981.

4. Results

Table II summarizes the NO/NO_2 flux rates measured at 16 individual plots located within the experimental field in Utrera covering an area of 10 m^2. Data show significant

Table II. NO and NO_2 flux rates from different plots in Utrera on 7 September 1982

Plot number	Local time	Soil temperature (°C)	NO flux (μg N m^{-2} h^{-1})	NO_2 flux (μg N m^{-2} h^{-1})
1	11.50	35,4	10	4
2	12.02	36,4	8	21
3	12.14	37,0	12	19
4	12.28	38,6	12	18
5	12.40	40,5	17	17
6	12.52	42,1	18	16
7	13.04	45,1	30	28
8	14.10	50,5	3	44
9	14.22	50,5	44	62
10	14.34	52,0	372	877
11	15.20	53,2	732	1397
12	15.32	53,2	27	23
13	15.44	53,4	27	23
14	15.56	53,4	16	25
15	16.08	53,2	22	37
16	16.20	53,2	14	4

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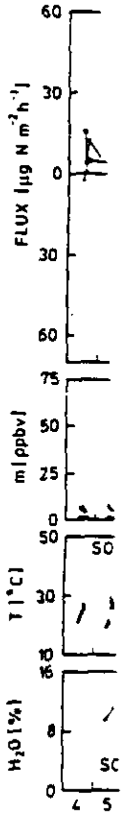

Fig. 2. Temporal va
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NO_2 flux (μg N m^{-2} h^{-1})
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spatial variation of the NO/NO_2 flux rates with values of 8-732 μg NO–N m^{-2} h^{-1} and 4–1397 μg NO_2–N m^{-2} h^{-1}. Measurements were carried out on a single day at different times so that part of the variations may be due to changes of soil temperature or soil moisture, etc. which have a significant influence on the absolute figure of the individual NO/NO_2 flux rates. The extremely high NO/NO_2 fluxes from plot No. 10 and 11, however, indicate that 'hot spots' with higher production of NO and NO_2 and thus high flux rates of NO and NO_2 from the soil into the atmosphere may exist. The observed spatial variation of NO and NO_2 flux rates may be explained by the soil inhomogeneity, e.g., of the distribution of organic soil matter.

In addition, the NO and NO_2 fluxes show significant temporal variations. Typical examples are given in Figures 2, 3a and 3b for NO and NO_2 measurements carried out in Finthen and Utrera on nonfertilized soils and in Figures 7a and 7b for NO and NO_2

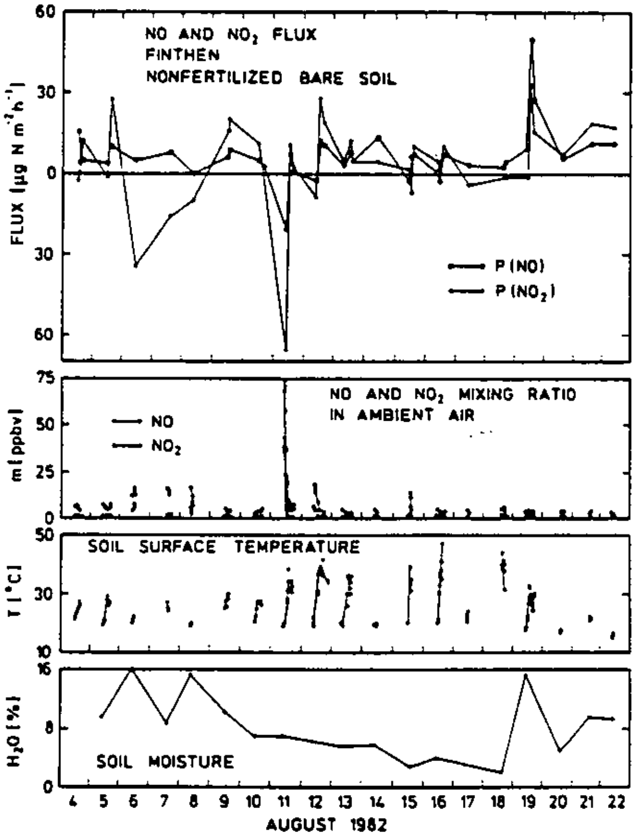

Fig. 2. Temporal variation of the NO and NO_2 flux rates measured in Finthen on nonfertilized soils without vegetation. Lower part of the figure shows the temporal variation of NO and NO_2 mixing ratios in ambient air as well as the variation of soil surface temperature and soil moisture.

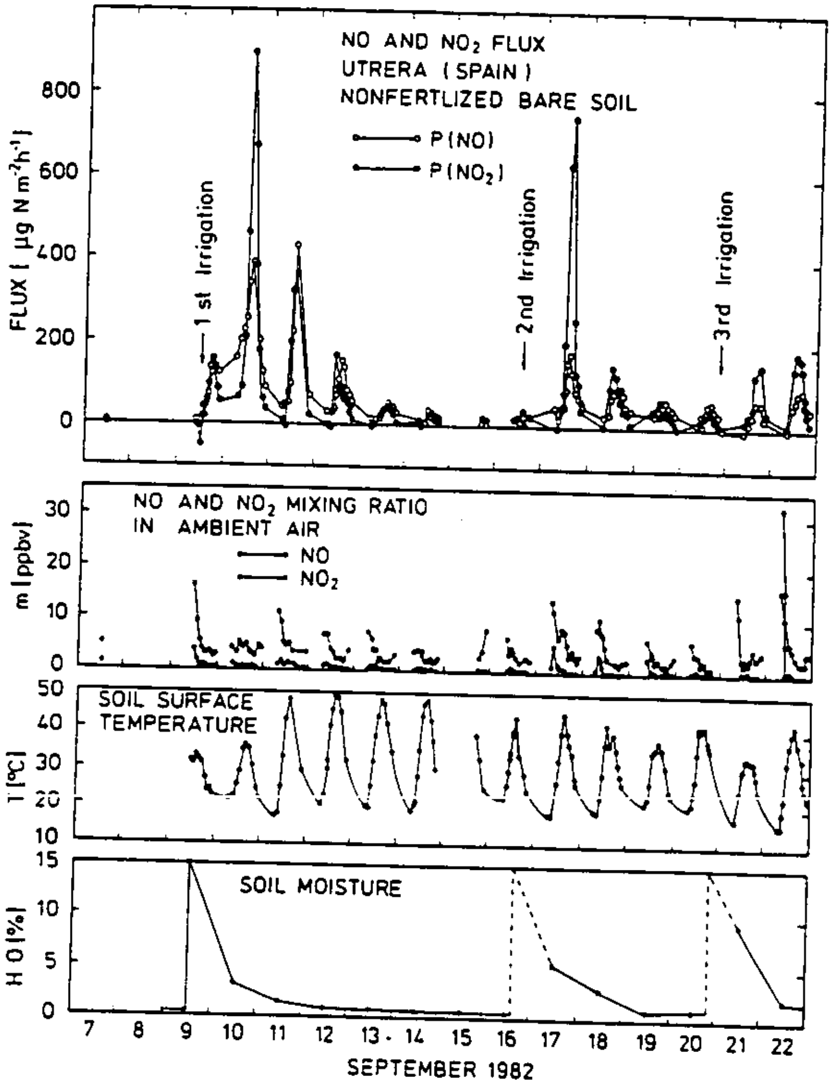

Fig. 3a. Variation of the NO and NO$_2$ flux rates measured in Utrera on nonfertilized soils without vegetation. The lower part of the figure shows the temporal variation of NO and NO$_2$ mixing ratios in ambient air as well as the variation of soil surface temperature and soil moisture.

measurements in Utrera on fertilized soils. In Finthen, the flux rates ranged between −21 and 51 µg N m^{-2} h^{-1} for NO and −66 and 33 µg N m^{-2} h^{-1} for NO$_2$. The corresponding figures for unfertilized soils in Utrera were −8 to 385 µg N m^{-2} h^{-1} for NO and −54 to 893 µg N m^{-2} h^{-1} for NO$_2$.

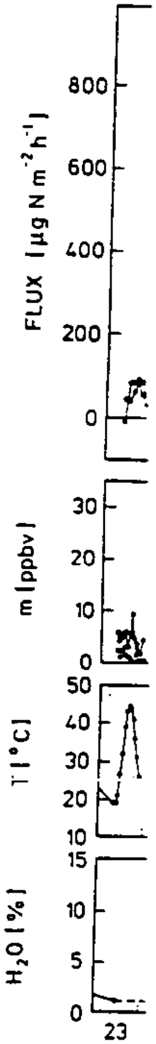

Fig. 3b. Continuation

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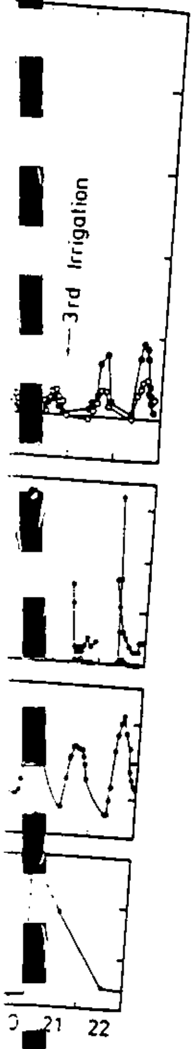

soils without
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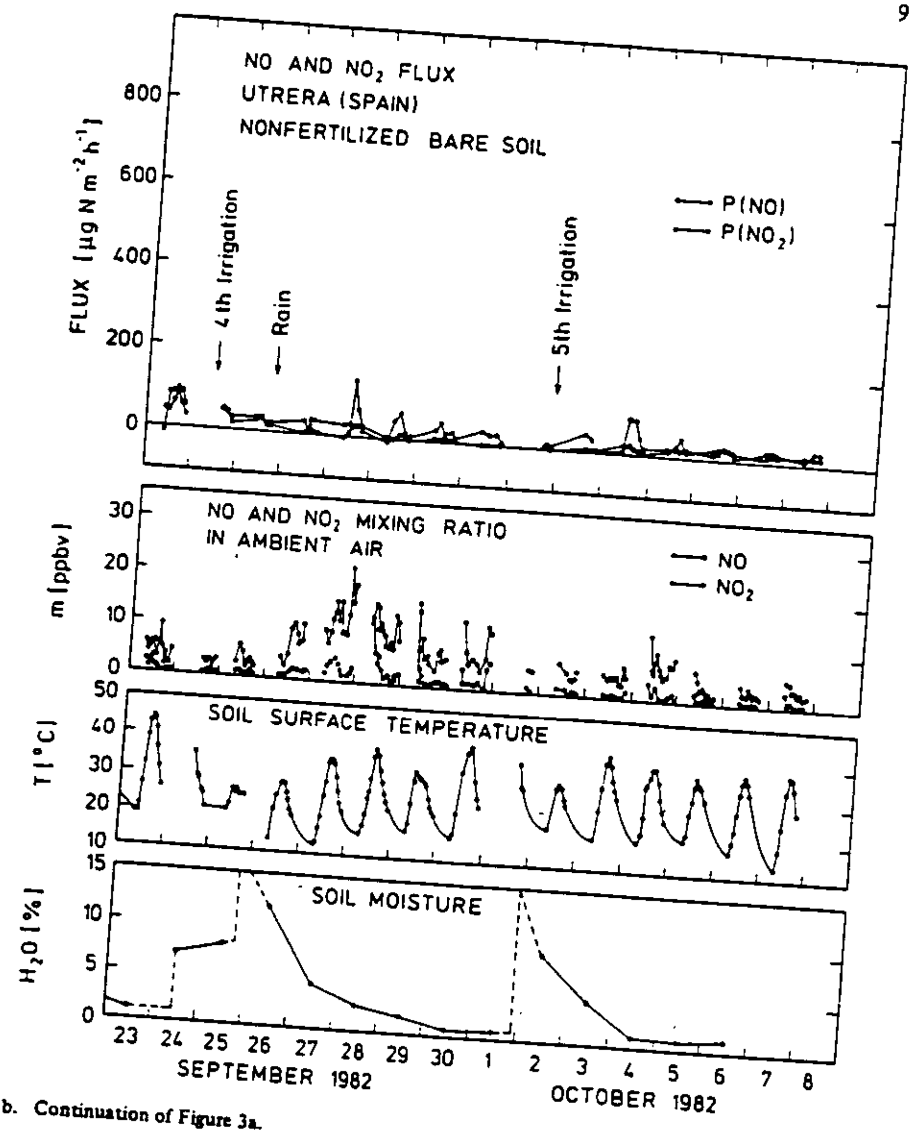

Fig. 3b. Continuation of Figure 3a.

In fertilized soils, maximum NO and NO_2 mixing ratios even reached values of 8000 and 6000 $\mu g\ N\ m^{-2}\ h^{-1}$, respectively. Negative flux rates, which means uptake of NO and NO_2 by soil, were always accompanied by high NO and NO_2 mixing ratios in ambient air. An excellent example is provided by the data observed in Finthen on 1 August. On this day, the NO and NO_2 mixing ratios in air reached values larger than 40 ppb and the fluxes of NO and NO_2 were -20 and -66 μg N m^{-2} h^{-1}, respectively.

In contrast, the soil is always a source of NO and NO_2 at very low NO and NO_2 mixing ratios. The compensation point or equilibrium mixing ratios, i.e., the mixing ratio at which the NO and NO_2 destruction equals the NO and NO_2 production is in the order of 20 ppbv for NO and 10 ppbv for NO_2 under the conditions existing in Finthen during August 1982. The absolute values of the equilibrium mixing ratios are dependent on several parameters, such as soil temperature, moisture, and organic carbon content and, therefore, should show large variations between the individual type of soil and climate.

The dependency of the size and direction of the NO and NO_2 fluxes at the soil surface on the NO and NO_2 mixing ratios in ambient air as well as the existence of equilibrium NO and NO_2 mixing ratios clearly indicate that NO and NO_2 are produced and destroyed concurrently in the soil or at the soil surface. Consequently, the measured NO and NO_2 flux rates represent net fluxes. Equilibrium mixing ratios have already been reported for other trace gases such as CO, H_2 and N_2O (Seiler, 1978; Seiler and Conrad, 1981).

The NO and NO_2 flux rates showed pronounced daily variations both on unfertilized and fertilized plots (see, e.g., Figures 3a, 3b, 4, 6a, 6b). The NO flux rates were positively correlated with the soil temperature with maximum values at about 7 a.m. The apparent activation energy calculated from the Arrhenius equation ranged between 44 and 103 kJ per mole. Interestingly, the NO_2 flux rates from soil did not correlate with soil temperature but correlate with the solar radiation. Maximum NO_2 flux rates were observed at 1 p.m. at minimum zenith angle (European summer time) and thus were about 2 h ahead of the maximum NO flux rates. This phase shift indicates that NO and NO_2 are

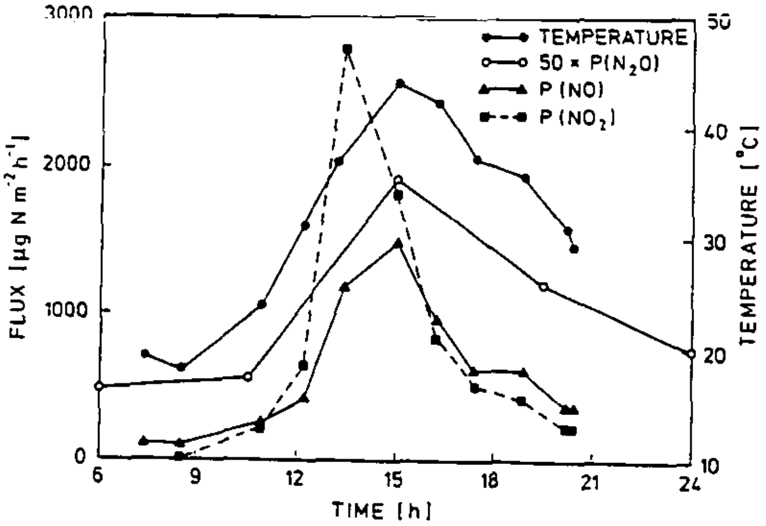

Fig. 4. Daily variation of the NO, NO_2 and N_2O flux rates and the soil surface temperature measured in Utrera.

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very likely produced by different processes. Possible NO_2 production by chemical conversion of NO in the presence of O_3 appears to be insignificant in view of the large phase shift (2 h) between the NO and NO_2 flux rates and the positive correlation between NO_2 flux rates and solar irradiation. This argument is in agreement with the observation of high NO_2 flux rates in the absence of O_3 in the flow box. Thus, we believe that NO_2 is also produced by biological or abiological processes in the soil. Because of the correlation between NO_2 flux rates and irradiation, the processes are active in the uppermost soil layers or at the soil surface. The time lag between NO flux rates and irradiation, on the other hand, indicates that NO formation occurs at depths deeper than 1 cm. It is worth mentioning that the N_2O flux from soil also exhibited a diurnal pattern (Slemr *et al.*, 1984) which agrees very well with the NO flux rates but is out of phase if compared with the NO_2 flux rates (Figure 4).

The NO and NO_2 flux rates were strongly dependent on the soil moisture. At soil moistures below 1%, the NO flux rates in unfertilized soils (on the order of 8—44 μg N m^{-2} h^{-1}) increased by a factor of about 10 after the soil moisture had been increased by artificial irrigation to values of about 15% (Figure 3a). Similarly, the amplitude of the daily NO flux rate variations increased dramatically after irrigation and declined with decreasing soil moisture. After 6 days, the soil moisture reached the 1% level and the NO flux rates approached the values initially measured before irrigation. Repeated artificial irrigation indicated that the effect of increasing soil moisture on the NO flux decreased with increasing number of irrigations and was no longer observed after the fourth irrigation (Figure 3b). There was generally a delay of approximately one day between irrigation and maximum NO flux which may be due to the fact that the soil pores in the uppermost soil layers were filled with water during irrigation so that the diffusivity within the uppermost soil layer and thus the exchange rate between soil and atmosphere were reduced. A similar but more pronounced relationship was observed between the NO_2 flux rates and soil moisture, with values of about 20 μg N m^{-2} h^{-1} at low soil moistures and up to 900 μg N m^{-2} h^{-1} after irrigation. Nitrogen dioxide fluxes also appear to respond much more rapidly to the change of the soil moisture than the NO flux which again supports the assumption that NO and NO_2 production occur at different depths with the NO_2 production at the uppermost soil layers. Similar dependence of the NO and NO_2 flux rates on soil moisture has also been observed on fertilized soils (Figures 6, 7).

The influence of vegetation on the NO and NO_2 fluxes from the soil into the atmosphere is illustrated in Figure 5. The measurements were carried out in Finthen in August 1982 on a soil plot with bare soil and a soil plot covered by dense grass vegetation. Both plots were fertilized with ammonium chloride at a rate of approximately 100 kg N ha^{-1}. Measurements on these two plots were performed within time intervals of 30 to 40 min for which the meteorological conditions can be assumed to be constant. Nevertheless, the NO flux rates obtained at these two plots show significant differences with low NO flux rates from grass covered soils. Even larger differences are observed for the NO_2 flux rate. In this case, the NO_2 sometimes showed negative values on plant covered soils which means uptake of NO_2 and emission rates up to 1500 μg N m^{-2} h^{-1} from unvegetated

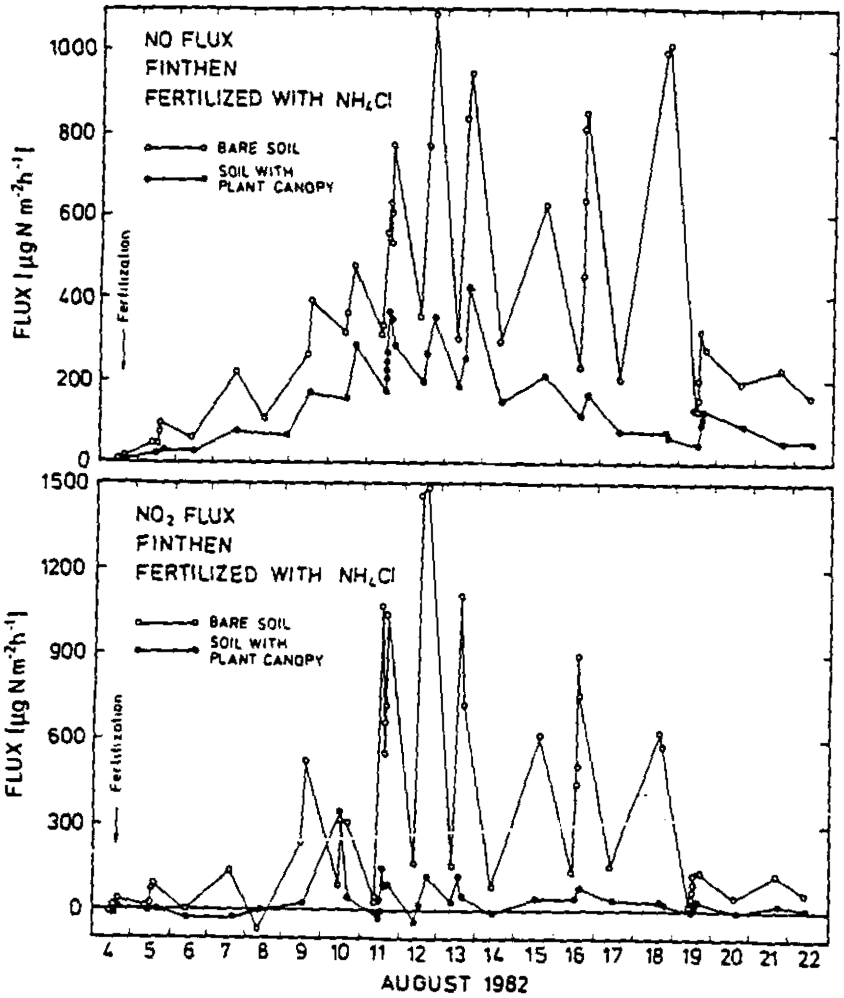

Fig. 5. Influence of vegetation cover on the flux rates of NO and NO$_2$. Data were obtained from measurements in Finthen on soil plots fertilized with NH$_4$Cl.

soil. The reduction of NO and NO$_2$ fluxes by vegetation may reflect the reduction of mean soil temperature from 26.2 to 23.8°C due to the shading of the soil surface by vegetation. The reduction might also result from the different content of organic soil matter and from an actual uptake of NO and particularly NO$_2$ at the leaf surface.

The influence of mineral fertilizer application on the NO and NO$_2$ flux rates has been studied in Finthen and Utrera. Measurements were carried out only on those plots which showed similar NO and NO$_2$ flux rates prior to fertilization. The results of fertilization using NH$_4$Cl at a rate of 100 kg N ha^{-1} on a planted and unplanted plot in Finthen are

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Table III. Integrated

Plot	Fertili
bare	none
bare	none
bare	NaNO$_3$
bare	NH$_4$NC
bare	NH$_4$Cl
grass	none
grass	NH$_4$Cl

shown in Figure 5. The NO flux rates from the fertilized plot increased after fertilization to maximum values of 1100 μg N m^{-2} h^{-1} on 12 August and then declined approaching the initial values after 16 to 20 days. Similar time patterns with maximum values of almost 1500 μg N m^{-2} h^{-1} were observed for the NO_2 flux rates. In the same period, the NO and NO_2 flux rates from the unfertilized plot shown in Figure 2 did not exceed 51 and 33 μg N m^{-2} h^{-1}, respectively. The variations of NO and NO_2 fluxes are partially due to variations of the soil temperature and the strong fluctuations of the NO and NO_2 mixing ratios in ambient air typical for air masses near a big city. Heavy rainfall on the 19 August (Figure 2) caused an increase in the NO and NO_2 flux rates although it was not of great significance when compared with the overall variation of the NO and NO_2 flux rates after fertilization.

Somewhat different results were obtained from the experiments carried out on hot dry soil in Utrera, Spain. Under these conditions, the NO and NO_2 fluxes increased much more rapidly with time, reaching first maximum values 1 to 2 days after fertilization and approaching the original values after 5 days (see Figures 6 and 7). Moreover, additional irrigation without fertilizer caused another increase of the NO and NO_2 flux rates from the soil (Figures 6a, 7a). Surprisingly, the highest flux rates of NO and NO_2 were found after the first repeated irrigation when fertilized with $NaNO_3$, NH_4NO_3 and NH_4Cl. When using urea as fertilizer, the maximum flux rates did not occur until the second irrigation (see Figure 7a). After four irrigation cycles – which means after 8 October – the NO and NO_2 fluxes were no longer elevated compared to the unfertilized soils. The delay of the NO/NO_2 maximum for urea fertilization may be explained by the fact that urea must first be converted into ammonia NH_3 (Mulvaney and Bremner, 1981) before nitrification can take place.

The total fluxes of NO and NO_2 integrated over the entire observation period in Finthen and Utrera are summarized in Tables III and IV, respectively. Table IV also includes the flux rates of N_2O measured simultaneously and reported by Slemr *et al.* (1984). It is obvious from these tables that the NO and NO_2 flux rates are strongly dependent on the type of mineral fertilizer. Relatively low flux rates were observed on soil plots fertilized with $NaNO_3$ where the NO and NO_2 emission integrated over the observation period in Utrera reached values of 39 and 37 mg N m^{-2}, respectively which

Table III. Integrated NO and NO_2 emission rates measured in Finthen between 4 and 22 August 1982

Plot	Fertilizer	$\Sigma P(NO)$ (mg N m^{-2}) 18 day	$\Sigma P(NO_2)$ (mg N m^{-2})	% applied fertilizer nitrogen loss as		
				NO	NO_2	Total
bare	none	2.57 *	0.46 *	–	–	–
bare	none	3.52 *	0.09 *	–	–	–
bare	$NaNO_3$	6.49	7.48	0.04	0.07	0.11
bare	NH_4NO_3	66.07	64.15	0.63	0.64	1.27
bare	NH_4Cl	154.91	118.64	1.52	1.18	2.70
grass	none	−0.72 *	−6.23 *	–	–	–
grass	NH_4Cl	55.04	6.18	0.56	0.13	0.69

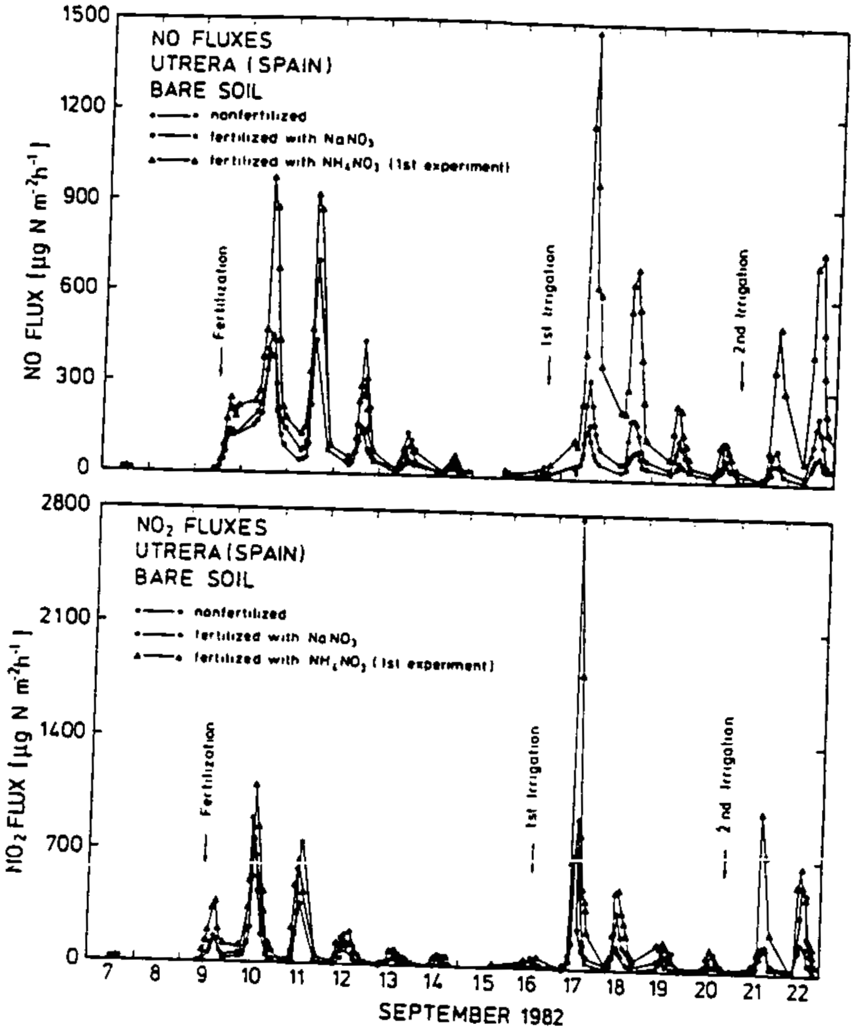

Fig. 6a. NO and NO_2 flux rates measured in Utrera on unfertilized soil plots and soil plots fertilized with $NaNO_3$ and NH_4NO_3. All Plots were artificially irrigated on 16 and 20 September with a precipitation rate of 7 mm H_2O.

are only slightly higher than the corresponding values of 24 and 23 mg N m^{-2} observed from unfertilized soil plots on the same field (Table IV). Considerably higher NO and NO_2 flux rates were found on plots fertilized with NH_4NO_3 and NH_4Cl with values of 100–150 mg N m^{-2} for NO and 80–83 mg N m^{-2} for NO_2. The highest emission rates, 350 mg N m^{-2} for NO and 240 mg N m^{-2} for NO_2 were observed from plots fertilized with urea exceeding the corresponding emission rates on unfertilized soils by more than

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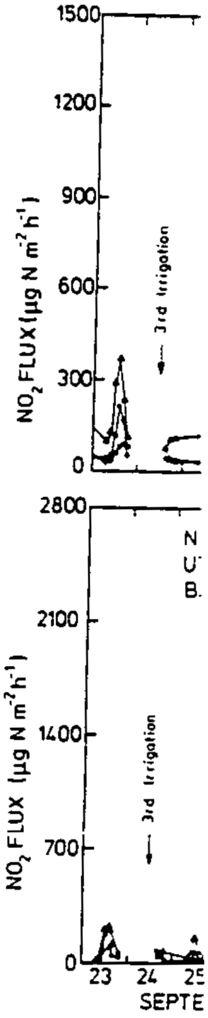

Fig. 6b. Continuation of Figu
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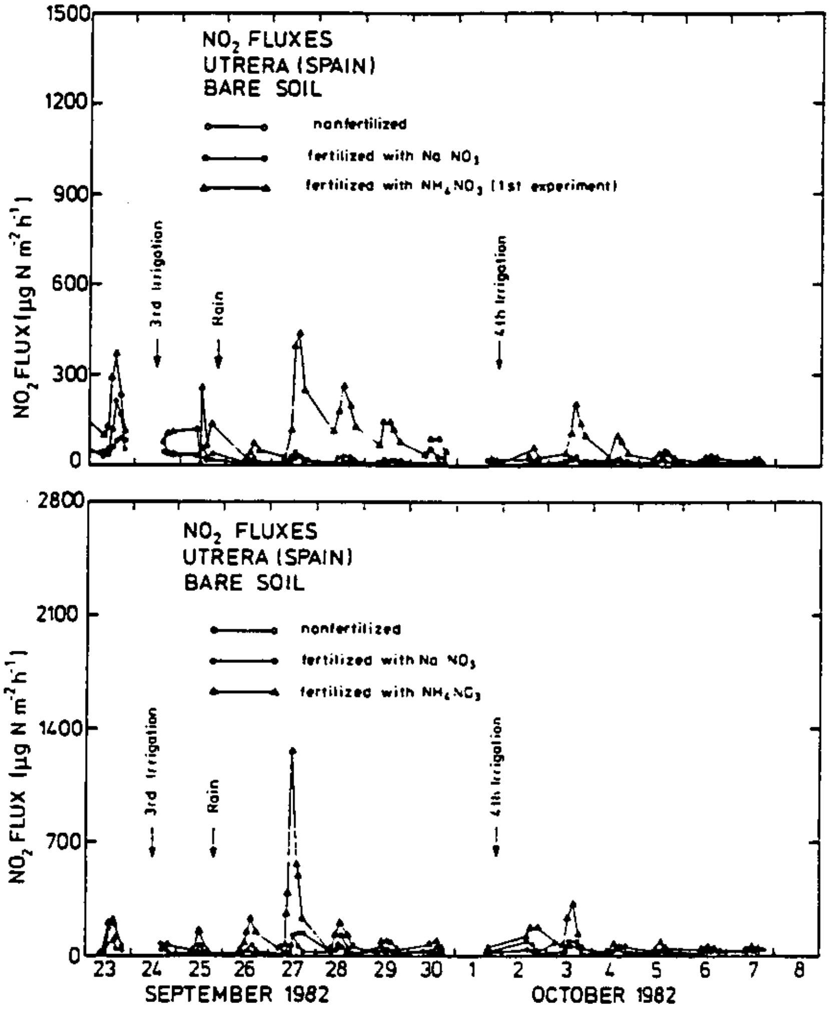

Fig. 6b. Continuation of Figure 6a. All plots were irrigated on 24 September and 1 October with a precipitation rate of 3.5 and 10 mm H$_2$O.

a factor of 10 (Table IV). A similar dependence of the NO and NO$_2$ emission on the type of mineral fertilizer has been found in Finthen. Interestingly, the absolute values of the integrated NO and NO$_2$ emission measured in Utrera and Finthen on soil plots fertilized with the individual types of mineral fertilizers agree reasonably well despite the large differences in soil moisture and temperature.

It is noteworthy that measurements of the N$_2$O emission from fertilized soils showed

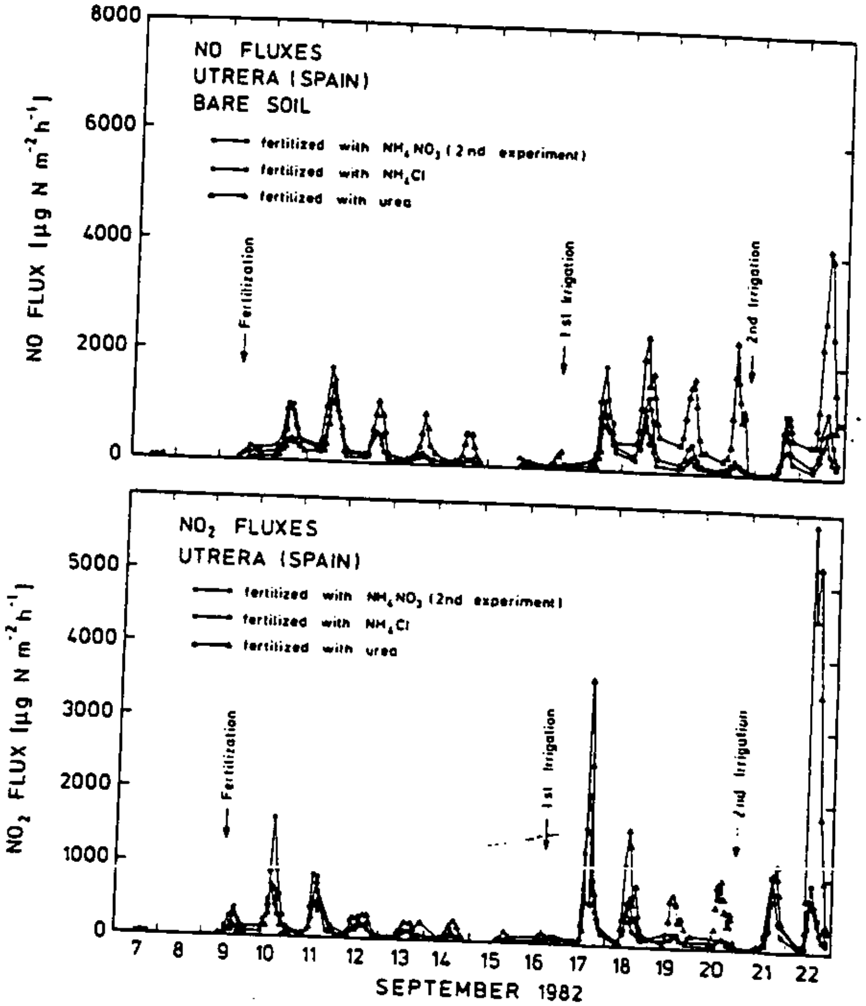

Fig. 7a. Influence of fertilization with NH_4NO_3, NH_4Cl and urea on the NO and NO_2 flux rates measured in Utrera on soils without vegetation.

the same dependence on type of mineral fertilizer observed for the NO and NO_2 emission (Conrad *et al.*, 1983), with considerably lower flux rates (see, e.g., Table IV). The higher NO and NO_2 emission from soils fertilized with ammonium fertilizer indicates that nitrification is much more efficient in producing nitrogen oxides than the denitrification. However, the possibility of additional NO_x production by denitrification of nitrite formed by nitrification (Schmidt, 1982) cannot be ruled out. The total NO flux was significantly reduced from the plant covered, NH_4Cl fertilized plot with a value of 55 mg NO—N m^{-2}

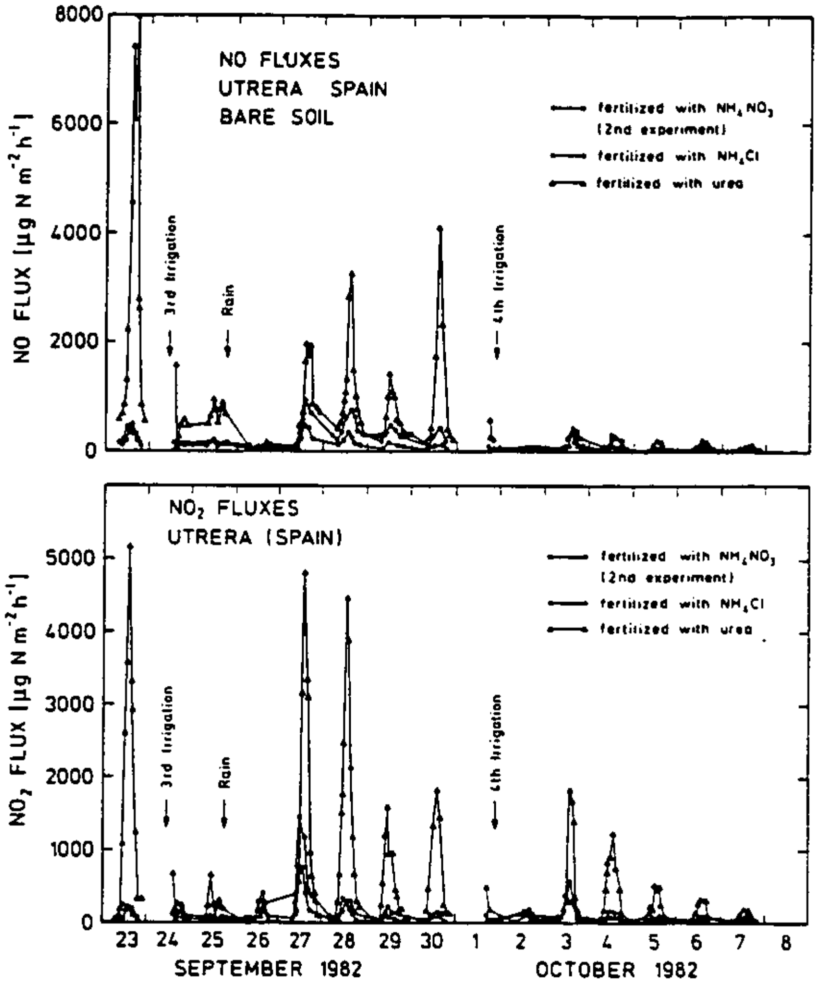

Fig. 7b. Continuation of Figure 7a.

compared to 155 mg m^{-2} from the bare soil plot (Table III). Even more pronounced is the difference between the total NO_2 fluxes of 6 and 119 mg NO_2–N m^{-2}, respectively.

The loss rates of mineral fertilizer N as NO_x ($NO + NO_2$) expressed in percent of applied mineral fertilizer N vary between 0.11% for $NaNO_3$ and 5.4% for urea (see Tables III and IV). Despite the different climate and soil conditions, the loss rates obtained from measurements in Finthen and Utrera agree reasonably well and thus may be assumed to be representative of global conditions as a first approximation.

Table IV. Integrated NO, NO_2 and N_2O emission rates measured in Utrera, 9 September - 10 October, bare soil

Fertilizer	$\Sigma P(NO)$ (mg N m^{-2})	$\Sigma P(NO_2)$ (mg N m^{-2})	$\Sigma P(N_2O)$ (mg N m^{-2})	% applied fertilizer loss as			
				NO	NO_2	N_2O	Total
none	24.37	23.26	8.62	..		.	–
$NaNO_3$	38.45	37.12	–	0.14	0.14	–	0.28
NH_4NO_3	88.42	74.54	12.60	0.64	0.51	0.04	1.19
NH_4NO_3	101.81	79.43		0.77	0.56		1.37
NH_4Cl	147.66	83.40	–	1.23	0.60	–	1.83
urea	349.72	242.10	26.97	3.25	2.19	0.18	5.62

5. Discussion

The measurements carried out in Finthen and Utrera clearly demonstrate that soil, both fertilized and unfertilized, acts as a source for NO which confirms earlier results published by Galbally and Roy (1978). In addition, the measurements indicate that other nitrogeneous species, most likely NO_2, must be produced in the soil which are emitted into the atmosphere. The flux rates of both nitrogeneous species are quite comparable and are strongly dependent on the soil moisture as well as on the vegetation cover. Whereas the NO flux rates are positively correlated with soil temperature measured at a depth of 10 mm, the NO_2 flux rates correlate with the irradiation intensity.

The similar behaviour of the NO and N_2O flux rates strongly suggests that NO is produced by biological processes, most likely during denitrification and nitrification. This assumption is supported by laboratory measurements carried out by Nelson and Bremner (1970), John and Hollocher (1977), Smith and Chalk (1979, 1980a, 1980b), Lipschultz *et al.* (1981) and McKenney *et al.* (1982) who found NO to be one of the general products of nitrification and denitrification. Because of the positive correlation of the NO flux rate and soil temperature at a depth of 10 mm, the production of NO may occur predominantly in the upper soil layer.

NO_2 fluxes presented in this work were calculated as the difference between the NO_x and NO fluxes. The ambiguity of this ascription caused by the nonselective conversion of nitrogen species on molybdenum converter has already been mentioned. However, there are several reasons to believe that NO_2 is the major compound. First of all, high NO_2 flux rates were also measured by Makarov *et al.* (1963; 1969) and Kim (1973) using chemical techniques which were NO_2 specific (Cheng and Bremner, 1965). Furthermore, the NO_2 fluxes measured in this work, were found to be dependent on the difference of NO_x and NO mixing ratios in ambient air which generally is predominantly due to NO_2 (Kelly *et al.*, 1979); Shetter *et al.*, 1983). Finally, the differences between the NO and NO_2 flux patterns discussed later are compatible with the physicochemical properties of NO_2. However, although all this evidence suggests that NO_2 is the predominant species responsible for the difference between NO_x and NO fluxes, the existence of minor fluxes of other nitrogeneous species such as. e.g.. methyl nitrite cannot be definitely eliminated.

The pattern of NO$_2$ flux rates indicates that the processes responsible for NO$_2$ emission are located in the uppermost soil layer or at the soil surface. Although NO$_2$ may also be produced in deeper soil layers, its solubility in water with subsequent conversion to NO$_2^-$ and NO$_3^-$ (Lee and Schwartz. 1981). its reactivity towards organic soil matter such as humic acids (Lee and Schartz. 1981) and its efficient absorption by the soil (Prather *et al*.. 1973) would effectively preclude its transport to the soil surface. NO. on the contrary. is much less soluble in water (Stephen and Stephen. 1963) and is not absorbed by the soil as effectively as NO$_2$ (Wesely *et al*.. 1982: Hill. 1971: Judeikis and Wren. 1980: Böttger *et al*.. 1980: Sehmel. 1980).

The process responsible for the emission of NO$_2$ from the soil is not known. The current biochemical models of nitrification and denitrification do not show NO$_2$ as a gaseous intermediate (Focht and Verstraete. 1977: Knowles. 1981: Firesteon. 1982: Garber and Hollocher. 1982: Schmidt. 1982) so that NO$_2$ might be produced by an abiological process. One possibility is the chemical decomposition of nitrite (Nelson and Bremner. 1970: Smith and Chalk. 1979. 1980a. 1980b). by

$$2\,HNO_2 \rightarrow NO + NO_2 + H_2O$$

Since nitrite is an obligate intermediate in the nitrification and denitrification. the chemical formation of NO$_2$ may be a common source of NO$_2$ in soils. Another possibility for NO$_2$ formation is the catalytic oxidation of NO to NO$_2$ proposed by Nelson and Bremner. (1970) and Prather and Miyamoto (1974). The existence of these two NO$_2$ production processes would suggest a strong link between the NO and NO$_2$ emissions which. however. was not observed. This indicates that other NO$_2$ sources in soil. e.g.. by microbial activities. may exist. It is possible that NO$_2$ production in microbial studies has not been observed because NO$_2$ is effectively absorbed in the water media and therefore has not been detected in the gaseous phase.

Interesting is the observation of NO/NO$_2$ equilibrium values which indicate the existence of production and destruction processes occurring simultaneously in the soil or at the soil surface. The absolute value of equilibrium mixing ratios is dependent on several parameters. such as soil moisture. soil temperature. type of soil. fertilizer. etc. and varies between less than 1 ppbv and a few ppbv. In some cases. particularly in Finthen in the vicinity of large cities. the ambient NO and NO$_2$ mixing ratios exceeded the equilibrium values so that during these time periods the soil acted as a net sink of atmospheric NO and NO$_2$. Such situations may only occur in polluted areas so that uptake of atmospheric NO and NO$_2$ on the soil surface may be restricted to heavily populated and industrialized areas. NO and NO$_2$ uptake by soils has also been reported by Judeikis and Wren (1978). Hill (1971). Prather *et al*. (1973) and Prather and Miyamoto (1974).

Neglecting the results obtained during periods with highly polluted air. the average flux rates of NO and NO$_2$ measured on bare unfertilized soils in Finthen were approximately 10 μg N m^{-2} h^{-1} for NO$_2$ and 8 μg N m^{-2} h^{-1} for NO. In contrast. the results obtained on dry hot soils in Utrera show extremely high NO and NO$_2$ fluxes after the first irrigation which subsequently decreased with further irrigation, finally reaching mean values of 10 μg N m^{-2} h^{-1} for NO and for NO_2 comparable to those found in Finthen. This pattern agrees with the observations made by Dommergues (1977) on Moroccan soils showing that rain rapidly revived the nitrification activities after a long period of dryness. Furthermore, Patten *et al.* (1980) reported that drying of soil increased markedly the capacity of denitrification of nitrate. Therefore, it appears that because of the dry soil conditions and consequently low microbial activity, nitrients may have accumulated which then initiates very effective microbial processes shortly after the soil moisture exceeds a critical value.

The NO flux rates agree reasonably well with 2.2–26 μg N m^{-2} h^{-1} found by Galbally and Roy (1978) on grassland in Australia. In contrast, the NO_2 flux rates observed in our experiments are much lower than the figures of 26–105 μg N m^{-2} h^{-1} as reported by Makarov (1969) and 66–150 μg N m^{-2} h^{-1} as reported by Kim (1979). The different values may reflect the natural variability of the NO_2 emission from different ecosystems. Possibly, the higher NO_2 emissions found by those authors are due to artifacts caused by the applied sampling technique or oxidation of NO to NO_2 in the closed chamber.

The strong impact of plant cover on the NO and NO_2 flux rates may partially be due to the reduced soil temperature and higher soil moisture content causing lower production rates and favouring a higher uptake of NO_2 on the moist soil surfaces. In addition, NO and NO_2 might be metabolized by the plants (Rogers and Campbell, 1979) so that part of the NO and NO_2 emitted at the soil surface does not pass the plant canopy reducing the flux of these gases into the atmosphere. Furthermore, the root system providing easily available organic carbon to the soil may influence the microbial activity and thus the production and destruction rate of NO and NO_2 in the soil.

All experiments clearly demonstrate that the application of mineral fertilizer enhances the flux rates of NO and NO_2 from the soil into the atmosphere. The NO_x flux rates strongly depend on the oxidation state of the mineral fertilizer added. Highest flux rates were observed from soils fertilized with ammonium fertilizer suggesting that an oxidation process, e.g., nitrification, is the likely source of NO_x while denitrification seems to be less important. The fertilizer derived NO and NO_2 flux rates correspond to loss rates of 0.04 and 0.07% for $NaNO_3$ and 3.3 and 2.2% for urea, respectively, and thus exceed those found for N_2O (see, e.g., Conrad *et al.*, 1983). From production data of individual types of fertilizer (FAO, 1982) and assuming the figures observed to be representative for global conditions, the average fertilizer loss rates as NO and NO_2 are on the order of 1.6% for NO and 1.1% for NO_2.

In view of the large demand for a rough estimate of global NO/NO_2, the flux rates from these admittedly very limited *in-situ* measurements may be extrapolated to the global NO_x cycle. The figures calculated for the NO and NO_2 fluxes from natural and fertilized soils are summarized in Table V together with information on NO_x production by other processes reported by Crutzen (1983) and Ehhalt and Drummond (1982). The estimate of 1.7 Tg NO_x–N yr^{-1} derived from the application of mineral fertilizer is based on an average loss rate of 1.6% for NO and 1.1% for NO_2 as well as a global nitrogen fertilizer production of 60 Tg N yr^{-1} for 1980. This estimate might be an upper

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Table V. Estimates of NO_x soil source strength and total emission (in Tg N yr^{-1})

	This work	Crutzen (1983)	Ehhalt and Drummond (1982)
(A) from mineral fertilizers	<1.7		
(B) from unfertilized soils	7		
(C) from animal excreta	<2		
Total soil source strength	<11	1–15	1–10
Fossil fuel burning		12–20	8–19
Biomass burning		10–40	6–16
Lightning		1–10	2–8
Total NO_x		24–85	17–53

limit for fertilizer derived NO_x flux since part of the mineral fertilizer is applied to plant covered fields so that part of the NO_x emitted from the soils may be taken up by plants.

The figure of 7 Tg NO_x–N yr^{-1} estimated for the flux of NO_x from natural unfertilized soils is based on the assumption that the NO_x flux rates measured on unfertilized bare soils in Finthen and Utrera are representative only for approximately half of the total land surface and that the other half does not act as a source of NO_x because of vegetation cover. The given estimate takes also into account that due to the strong temperature dependence, the NO_x flux should show significant seasonal variations. As a first approximation, it is assumed that the NO_x flux from land areas north and south of 30° latitude does not contribute to the atmospheric NO_x cycle for a period of 6 months per year. Polar regions are not considered to be active with respect to the NO and NO_2 production.

Additional NO_x may be emitted from the soil by the production of animal excreta – mainly urea – whose degradation causes an enhanced NO_x production as shown by the experiment in Utrera using urea fertilizer. The total production of urea by animals is estimated by Böttger *et al.* (1980) to be approximately 40 Tg urea N yr^{-1} which may result in an NO_x flux of about 2 TG NO_x–N yr^{-1}. This figure might be overestimated since part of the urea is emitted in vegetated areas which may reduce the NO_x emission from the soil into the atmosphere.

Summarizing the individual NO_x sources, we obtain an upper limit of the total NO_x emission from soils into the atmosphere of about 11 Tg NO_x–N yr^{-1}. This figure is certainly far from definite. Additional measurements over extended periods of time and in other climatic regions are urgently needed to verify the figure given above. It is noteworthy, however, that the flux of 11 Tg NO_x–N yr^{-1} as estimated in this paper agrees reasonably well with theoretical estimates (5.5 Tg N yr^{-1} given by Ehhalt and Drummond, 1982) and is also within the range of 1–15 Tg N yr^{-1} as reported by Crutzen (1983).

Compared to the other major sources of NO_x compiled in Table V, the flux of NO_x into the atmosphere contributes substantially to the global NO_x cycle. The influence of NO_x flux from the soil becomes even more important if one takes into account that the NO_x production by combustion of fossil fuel representing predominant sources of atmospheric NO_x is restricted to relatively small areas and because of its short residence time, NO_x will not be transported over long distances. Thus, in remote continental areas, the NO_x flux from the soil may be the dominant NO_x source and therefore will significantly influence the atmospheric chemistry.

Acknowledgements

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MIDWEST RESEARCH INSTITUTE
PROJECT DEVELOPMENT SKETCH MRI-18

TITLE Ref 11, R. Slemr et al J. Atmos Chem (2)
5 pgs

PROJECT NO. 6500 - 3513 DRAWN mwuse APPR. DATE 9-21-92

1. Rate $\boxed{100\ \text{kg N/ha}}$

2. Pollutants $\boxed{NO}$ $\boxed{N_2O}$ $\boxed{NO_2}$

3. Fertilizers : spray
   - Urea
   - $NaNO_3$
   - NH_4NO_3
   - NH_4Cl

4. Emissions $\boxed{NO}$ Table 3 and Table 4

Calculate bkg emissions for bare ground (Table 3)

$$b1 = \frac{2.57\ \text{mg N}}{\text{m}^2} \times \frac{10^4\ \text{m}^2}{\text{ha}} \times \frac{\text{g N}}{10^3\ \text{mg N}} \times \frac{30\ \text{g NO}}{14\ \text{g N}} = \frac{55.1\ \text{g NO}}{\text{ha}}$$

$$b2 = \frac{3.52\ \text{mg N}}{\text{m}^2} \times \frac{10^4\ \text{m}^2}{\text{ha}} \times \frac{\text{g N}}{10^3\ \text{mg N}} \times \frac{30\ \text{g NO}}{14\ \text{g N}} = \frac{75.4\ \text{g NO}}{\text{ha}}$$

$$\text{Bkg }1 = \bar{x}_b = \frac{55.1\frac{\text{g NO}}{\text{ha}} + 75.4\frac{\text{g NO}}{\text{ha}}}{2} = 65.3\ \text{g NO/ha}$$

Calculate bkg emissions for grass (Table 3)

$$\text{Bkg }2 = g = \frac{-0.72\ \text{mg N}}{\text{m}^2} \times \frac{10^4\ \text{m}^2}{\text{ha}} \times \frac{\text{g N}}{10^3\ \text{mg N}} \times \frac{30\ \text{g NO}}{14\ \text{g N}} = -15.4\frac{\text{g NO}}{\text{ha}}$$

Calculate bkg emission for bare ground (Table 4)

$$\text{Bkg }3 = b_3 = \frac{24.37\ \text{mg N}}{\text{m}^2} \times \frac{10^4\ \text{m}^2}{\text{ha}} \times \frac{\text{g N}}{10^3\ \text{mg N}} \times \frac{30\ \text{g NO}}{14\ \text{g N}} = 522.2\frac{\text{g NO}}{\text{ha}}$$

MRI-18

MIDWEST RESEARCH INSTITUTE
PROJECT DEVELOPMENT SKETCH

TITLE Ref 11 (pg 2 of 5)

PROJECT NO. DRAWN Murray APPR. DATE 9-21-92

Calculate the emission, emission factor (EF), and daily EF.

$$\Sigma \text{ flux} = 1 \frac{\text{mg N}}{\text{m}^2} \times \frac{10^4 \text{ m}^2}{\text{ha}} \times \frac{\text{g N}}{10^3 \text{ mg N}} \times \frac{30 \text{ g NO}}{14 \text{ g N}} = 21.4 \frac{\text{g NO}}{\text{ha}}$$

$$EF = \frac{\Sigma \text{ flux} - \text{bkg}}{\text{applied rate}}$$

$$EF_{day} = \frac{EF}{\# \text{ days}}$$

ex: bare $NaNO_3$ = 6.49 mg N/m² w/ bkg 1

$$\Sigma \text{ flux} = \frac{6.49 \text{ mg N}}{\text{m}^2} \times \frac{10^4 \text{ m}^2}{\text{ha}} \times \frac{\text{g N}}{10^3 \text{ mg N}} \times \frac{30 \text{ g NO}}{14 \text{ g N}} = 139.1 \frac{\text{g NO}}{\text{ha}}$$

$$EF = \frac{139.1 \text{ g NO/ha} - 65.3 \text{ g NO/ha}}{100 \text{ kg N}} = \boxed{0.738 \text{ g NO/kg N}}$$

$$EF_{day} = \frac{0.738 \text{ g NO/kg N}}{18 \text{ day}} = \boxed{0.041 \text{ g NO/kg N day}}$$

Table 11-1 NO Emissions

Plot	Fertilizer	Σ flux g NO/ha	EF	# days	EF_{day}	source
bare	$NaNO_3$	134.1	0.738	18	0.041	Table 3
bare	NH_4NO_3	1416	13.51	18	0.751	↓
bare	NH_4Cl	3320	32.54	18	1.808	↓
grass	NH_4Cl	1179	11.95	18	0.664	↓
bare	$NaNO_3$	823.9	3.017	30	0.1006	Table 4
bare	NH_4NO_3	* 2038	15.2	30	0.506	↓
bare	NH_4Cl	3164	26.42	30	0.881	↓
bare	Urea	7494	69.72	30	2.324	↓

* = average of two tests

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PROJECT DEVELOPMENT SKETCH

TITLE Ref 11 (pg 3 of 5)

PROJECT NO. ______ DRAWN Mwz APPR. ______ DATE 9-21-92

5. Emissions N_2O Table ~~Trend~~ # IV

Repeat same calculations as in step 4 except use $\frac{44\,g\,N_2O}{14\,g\,N}$ as the conversion from nitrogen to pollutant

~~example~~ Bare NH_4NO_3 – background

$$Bkg = \frac{8.62\ mg\,N}{m^2} \times \frac{10^4\,m^2}{ha} \times \frac{g\,N}{10^3\,mg\,N} \times \frac{44\,g\,N_2O}{14\,g\,N} = 270.9\ \frac{g\,N_2O}{ha}$$

(average of two tests)

$$NH_4NO_3 = \frac{12.60\ mg\,N}{m^2} \times \frac{10^4\,m^2}{ha} \times \frac{g\,N}{10^3\,mg\,N} \times \frac{44\,g\,N_2O}{14\,g\,N} = 396\ \frac{g\,N_2O}{ha}$$

$$EF = \frac{396\ g\,N_2O/ha - 270.9\ g\,N_2O/ha}{100\ kg\,N/ha} = \boxed{1.251\ g\,N_2O/kg\,N}$$

$$EF_{day} = \frac{1.251\ g\,N_2O/kg\,N}{30\ day} = \boxed{0.0417\ g\,N_2O/kg\,N\cdot day}$$

Bare urea

$$Bkg = 270.9\ g\,N_2O/ha$$

$$Urea = \frac{26.97\ mg\,N}{m^2} \times \frac{10^4\,m^2}{ha} \times \frac{g\,N}{10^3\,mg\,N} \times \frac{44\,g\,N_2O}{14\,g\,N} = 847.6\ \frac{g\,N_2O}{ha}$$

$$EF = \frac{847.6 - 270.9\ g\,N_2O/ha}{100\ kg\,N/ha} = \boxed{5.767\ g\,N_2O/kg\,N}$$

$$EF_{day} = \frac{5.767\ g\,N_2O/kg\,N}{30\ day} = \boxed{0.1922\ g\,N_2O/kg\,N\,day}$$

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6. Emission for NO_2, Tables 3 + 4

Repeat calculations as in step 4 except with $\frac{46\,g\,NO_2}{14\,g\,N}$ as conversion.

Bkg calculations for bare ground (Table 3)

$$b_1 = \frac{0.46\,mg\,N}{m^2} \times \frac{10^4\,m^2}{ha} \times \frac{g\,N}{10^3\,mg\,N} \times \frac{46\,g\,NO_2}{14\,g\,N} = 15.1$$

$$b_2 = \frac{0.09\,mg\,N}{m^2} \times \frac{10^4\,m^2}{ha} \times \frac{g\,N}{10^3\,mg\,N} \times \frac{46\,g\,NO_2}{14\,g\,N} = 2.96$$

$$\underline{Bkg_1} = \bar{x}_b = \frac{15.1 + 2.96\ g\,NO_2/ha}{2} = \boxed{9.03\ g\,NO_2/ha}$$

Bkg calc. for grass (Table 3)

$$\underline{Bkg_2} = \frac{-623\,mg\,N}{m^2} \times \frac{10^4\,m^2}{ha} \times \frac{g\,N}{10^3\,mg\,N} \times \frac{46\,g\,NO_2}{14\,g\,N} = \boxed{-204.7\ \frac{g\,NO_2}{ha}}$$

Bkg calc for bare ground (Table 4)

$$\underline{Bkg_3} = \frac{23.26\,mg\,N}{m^2} \times \frac{10^4\,m^2}{ha} \times \frac{g\,N}{10^3\,mg\,N} \times \frac{46\,g\,NO_2}{14\,g\,N} = \boxed{764.2\ \frac{g\,NO_2}{ha}}$$

<u>Example</u>: Bare $NaNO_3$ = 7.48 mg N/m² (Table 3) w/ Bkg 1
= 18 days

$$\Sigma\ flux = \frac{7.48\,mg\,N}{m^2} \times \frac{10^4\,m^2}{ha} \times \frac{g\,N}{10^3\,mg\,N} \times \frac{46\,g\,NO_2}{14\,g\,N} = \boxed{246\ \frac{g\,NO_2}{ha}}$$

$$EF = \frac{246\,g\,NO_2/ha - 9.03\,g\,NO_2/ha}{100\,kg\,N} = \boxed{2.37\ g\,NO_2/kg\,N}$$

$$EF_{day} = \frac{2.37\,g\,NO_2/kg\,N}{18\,day} = \boxed{0.131\ g\,NO_2/kg\,N\,day}$$

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PROJECT NO. ______ DRAWN Meller APPR. ______ DATE 9-21-92

Table 11-2 NO_2 Emissions

Plot	Fertilizer	Σ flux g NO_2/ha	EF	# days	EF/day	Source
bare	$NaNO_3$	246	2.37	18	0.131	Table 3
bare	NH_4NO_3	2108	20.99	18	1.166	
bare	NH_4Cl	3898	38.89	18	2.161	
grass	NH_4Cl	203	4.08 (m, n)	18	0.226	
bare	$NaNO_3$	1220	4.56	30	0.152	Table 4
bare	NH_4NO_3*	2530	17.65	30	0.588	
bare	NH_4Cl	2740	19.76	30	0.659	
bare	Urea	7955	71.90	30	2.397	

* = average of two results (74.54 + 79.43)/2 = 76.98

m = grass

n = plot acted as a sink at a rate of -205 g NO_2/ha

$$\therefore \quad \frac{203 - (-205)\ g\ NO_2/ha}{100\ kg\ N/ha} = 4.08\ g\ NO_2/kg\ N$$ total emission

Reasoning: = not all grass plots act as sinks in nature.

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Factors Influencing the Loss of Fertilizer Nitrogen Into the Atmosphere as N_2O

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In 1979–1981, experiments were carried out at four field stations near Mainz, Germany, to determine the loss of fertilizer nitrogen into the atmosphere as N_2O. Evolution rates from the soil into the atmosphere were measured by using the closed chamber technique. An automatic sampling and analyzing device was developed which allowed frequent determinations of N_2O evolution rates (one every 1.5 hours). The N_2O production rates were correlated to the surface soil temperature according to the Arrhenius equation and showed a diurnal rhythm with amplitudes reaching, sometimes, 1 order of magnitude. It seems that most of the N_2O emitted into the atmosphere is produced in the uppermost soil layer. N_2O evolution was stimulated by rain and increased with increasing soil moisture content. Application of fertilizer caused a dramatic increase of N_2O evolution rates with values up to 1000 μg N_2O–N $m^{-2}h^{-1}$. The magnitude of the fertilizer-induced N_2O evolution rates was dependent on the type, the application form, and the amount of fertilizer used. The total loss of fertilizer nitrogen as N_2O was in the range of 0.001 to 0.94%. Based on these figures, as well as on data from the literature, the total source strength of mineral fertilizers for atmospheric N_2O is calculated to 0.02 to 8 Tg N_2O–N yr^{-1}.

INTRODUCTION

The possible impact of the increased usage of mineral nitrogen fertilizers on the stratospheric ozone layer and on the climate has attracted a great deal of scientific and public attention. It has been proposed that fertilizer-derived N_2O may result in an increase of tropospheric N_2O, which in turn may be an important factor in the destruction of the stratospheric ozone layer [*Crutzen*, 1970, 1981; *McElroy et al.*, 1976; *Liu et al.*, 1977] and in the construction of a 'greenhouse effect' [*Wang et al.*, 1976; *Donner and Ramanathan*, 1980]. An increase of the tropospheric N_2O mixing ratio by approximately 0.2% per year was recently reported by *Weiss* [1981], who attributed this increase to the anthropogenic N_2O production by combustion of fossil fuel and application of mineral fertilizer. As a result of the increased usage of fossil fuel and mineral nitrogen fertilizers, a further increase of the N_2O mixing ratio in the atmosphere is predicted. The quantity of this increase can only be obtained if we know the N_2O production that is caused by the application of mineral fertilizer. This parameter is still subject to great debate. Data published so far indicate that N_2O production rates from mineral fertilizer vary between 6–100 Tg N_2O–N yr^{-1} [*McElroy et al.*, 1977; *Hahn and Junge*, 1977] and 0.004–12 Tg N_2O–N yr^{-1} [*Conrad and Seiler*, 1980]. This paper presents new data on the N_2O loss rate caused by application of mineral fertilizer, and they confirm the lower number.

N_2O flux from soil into the atmosphere has traditionally been ascribed to denitrification processes [*Garcia*, 1975; *Delwiche and Bryan*, 1976]. Hence, earlier N_2O loss rates caused by fertilizer application were calculated from denitrification rates and the relative amounts of N_2O to the other denitrification products [*Hahn and Junge*, 1977]. It is known, however, that N_2O is only an intermediate in the denitrification process [*John and Hollocher*, 1977] so that only part of the N_2O is released into the atmosphere. The rest is reduced in the soil to N_2 as the end product. The ratio of N_2O/N_2 as products of denitrification depends on soil environmental conditions, e.g., pH, redox potential, concentrations of oxidizable carbon, oxygen, nitrate, etc. [*Focht*, 1974; *Blackmer and Bremner*, 1978; *Firestone et al.*, 1979, 1980; *Terry and Tate*, 1980; *Letey et al.*, 1980*a*, *b*, 1981; *Betlach and Tiedje*, 1981]. Under anaerobic conditions, N_2O may even act as the main electron acceptor for denitrification so that these soils may even represent a sink for atmospheric N_2O [*Blackmer and Bremner*, 1976]. Recently, it has been shown that N_2O is also formed during nitrate dissimilation by nondenitrifying microorganisms [*Smith*, 1982; *Smith and Zimmerman*, 1981] and during nitrification by *Nitrosomonas* [*Yoshida and Alexander*, 1970; *Ritchie and Nicholas*, 1972; *Blackmer et al.*, 1980; *Goreau et al.*, 1980; *Lipschultz et al.* 1981]. The latter process was found to be especially important for N_2O evolution from well-aerated soils [*Bremner and Blackmer*, 1978, 1979, 1980, 1981] and for the loss of fertilizer nitrogen into the atmosphere as N_2O [*Conrad and Seiler*, 1980; *Breitenbeck et al.*, 1980; *Seiler and Conrad*, 1981*a*, *b*]. At the moment, it is impossible to evaluate the relative contribution of these processes to the total N_2O evolution from soils into the atmosphere. Therefore, it is also impossible to deduce reliable N_2O loss rates of fertilizer nitrogen from the measurement of denitrification or nitrification rates.

In order to obtain reliable figures for the fertilizer-induced N_2O emission into the atmosphere, the N_2O evolution rates must be measured directly under field conditions. In the last few years, field studies have been undertaken by a number of investigators [*McKenney et al.*, 1980*a*; *Ryden and Lund*, 1980; *Ryden*, 1981; *Breitenbeck et al.*, 1980; *Bremner et al.*, 1981*a*, *b*; *Cochran et al.*, 1981; *Mosier and Hutchinson*, 1981; *Mosier et al.*, 1981, 1982; *Conrad and Seiler*, 1980; *Seiler and Conrad*, 1981*a*]. N_2O evolution rates were generally obtained by placing sampling devices randomly on farmland treated with mineral fertilizers. Data obtained by this procedure show a high variation of the N_2O evolution rates, which are explained by the spatial variability resulting from inhomogeneous soil conditions caused by normal farming practice, e.g., plowing, sowing, fertilizing, irrigating, etc.

These problems are largely solved by restricting the treatments to those places where the sampling devices are installed. The data obtained at these places are then compared with those obtained at untreated controls [*Conrad and Seiler*, 1980; *Seiler and Conrad*, 1981*a*]. This approach is certainly less close to the normal farming management of a field but has the advantage

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TABLE 1. Characteristics of Field Stations and Soils

						Corn Fractions, %wt			
Field Station	Vegetation	Soil Type	ph, 0.1 N KCl	$CaCO_3$ % wt	Organic C, % wt	Clay, <2 μm	Silt, 2–20 μm	Fine Sand, 20–200 μm	Coarse Sand, 200–2000 μm
LPS, Mainz	Beet field, plants removed	Loess, brown soil	7.1	7.5	0.5	15	26	51	8
Finthen, Mainz	Meadow, grass	Loess pararendzina	7.4	2.0	0.8	20	21	56	3
MPI 1, Mainz	Lawn, grass, clover	Loess, unspecified	7.3	7.6	2.0	20	20	48	12
MPI 2	Lawn, grass	Loess, unspecified	7.3	4.1	2.6	15	15	51	19

that the measured N_2O evolution rates can be directly correlated to the type of treatment. It further allows one to make sure that the spatial variability in N_2O evolution between the experimental soil plots is insignificant for the interpretation of the results. In addition, this approach allows the application of an automatic device to the continuous measurement of N_2O evolution rates. This device provides more data during the observation period and gives better information on the temporal variation of N_2O evolution rates and allows the detection of diurnal variations and the correlation to soil temperature and soil moisture. This experimental approach has been used for determining the loss rates of fertilizer nitrogen into the atmosphere as N_2O; these are reported in this paper.

EXPERIMENTAL

The measurements were carried out in 1979–1981 at different field stations near Mainz, Germany. The main characteristics of the field stations as well as the principal physical and chemical properties of the soils are summarized in Table 1. The areas at the Landespflanzenschutzamt (LPS) were used intensively for agricultural purposes and managed in rotation by farming sugar beet, white beet, barley, and white beet. During the observation period, the field was planted with white beet. The young plants had been removed before the installation of the sampling devices, so that the soil was actually barren. Measurements of N_2O evolution rates at natural, agriculturally unused areas were carried out on a meadow (Finthen), which was kept under natural conditions except for cutting the grass twice a year. Additional measurements were carried out on areas close to the MPI (Max Planck Institute) that were covered by a grass lawn or by clover *(Trifolium hybridum)*. The experimental site MPI 1 remained in its original state; at MPI 2, the grass cover was removed during the observation period by cutting all green parts short above the soil surface.

Each field station consisted of several soil plots with an area of approximately 800 cm^2. Each plot was enclosed by a rectangular stainless steel frame pressed into the soil to a depth of approximately 10 cm. The physical structure of the soil inside the frame was not influenced by this procedure. First measurements were started at least 1 month after installation of the frames. The soil surface temperature was recorded by using temperature probes (iron-constatan) inserted into the soil (approximately 3 to 5 mm depth) of the soil plot. The bulk soil moisture content (g H_2O per 100 g moist soil) of the upper 10-cm layer of the soil profile was determined gravimetrically from soil samples taken at the surrounding area that had been treated in the same way as the experimental soil plots. Data on rainfall were provided by the meteorological station of the Landespflanzenschutzamt (LPS). These data are assumed to be representative for all field stations located within a distance less than 4 km from the LPS station.

The procedure for discontinuous determinations of the N_2O evolution rates has already been described in detail by *Conrad and Seiler* [1980] and *Seiler and Conrad* [1981*a*]. Using this technique, the soil plot was covered with a glass box ($V = 8$ l) which fit tightly into the stainless steel frame that had been pressed into the soil. The glass box was not shaded from sunlight during the experiment. The change of soil surface

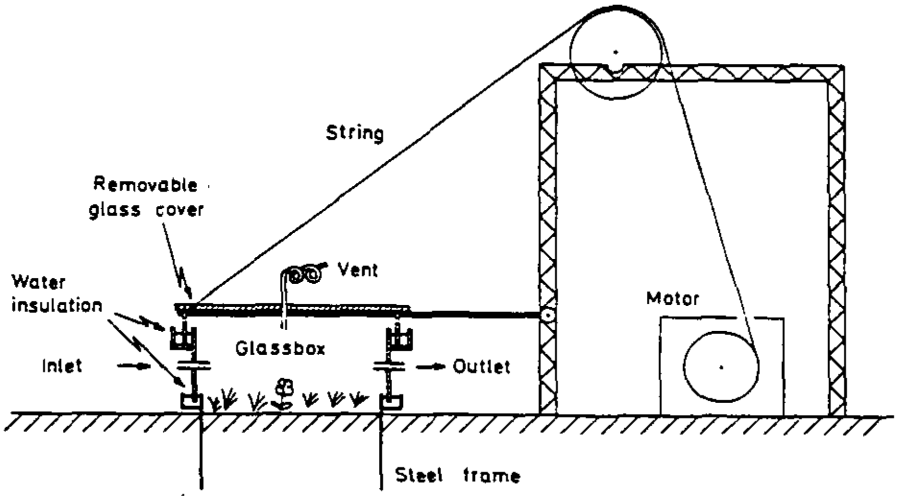

Fig. 1. Setup of the automatic system opening and closing the individual glass boxes for N_2O flux measurements.

temperature inside the glass box was identical to that outside. Shading the box generally caused a significant decrease of the inside soil surface temperature relative to the outside soil surface temperature, particularly during sunny days, and thus may result in untypical soil temperature records. The glass box contained a vent consisting of a glass coil (length = 20 cm, inner diameter = 3 mm) to ensure equilibration of the air pressure inside and outside the box. Gas samples (10 ml) from inside the box were taken by means of syringes at time intervals of 10 min. After the observation period of 1 hour, the cover was removed, exposing the soil plot to natural conditions. Generally, one flux rate per plot and day was measured in the morning (9 to 11 A.M.). Occasionally, an additional measurement was carried out in the afternoon (1 to 3 P.M.; LPS, spring 1980).

A better data base was obtained after an automatic device, illustrated in Figure 1 and 2, became available. In this system, up to three soil plots were equipped with glass boxes ($V = 8$ l) which could be sealed on top with removable glass covers (Figure 1). The glass boxes were closed alternatively for a period of approximately 1 hour, which is necessary for the determination of one N_2O evolution rate. For the rest of the time the glass boxes remained open to expose the soil surface to normal environmental conditions. The time sequence and the length of the observation period was given by an automatic timer which switched the removable glass covers, the valves, the gas chromatograph, etc. Figure 2 illustrates the flow scheme of the air when the N_2O evolution rates were determined at two soil plots. At the beginning of the measurement period, box 1 is closed and box 2 is open. During this time, the air is taken from box 1 by means of a metal bellows pump at a constant flow rate of 0.2 l min^{-1} and is recycled into the glass box. The airstream is passed through a refrigerator (−70°C) to remove the water vapor and subsequently is passed through the sampling loop ($V = 7$ ml) of the gas chromatograph. A gas sample is injected into the gas chromatrograph (GC) once every 9 min. After measurement of seven consecutive samples, corresponding to a time interval of 63 min, the GC is calibrated twice by opening S3 and S4, supplying the GC with a calibration standard. Subsequently, the selenoid valve S1 is closed, and S2 is opened. During this operation mode, the airstream passes through the open box 2 so that the sampling loop is supplied with ambient air. Then, box 1 is opened, and box 2 closed. A new sampling and analyzing cycle starts with the first sample being injected 9 min after the box has been closed. The whole system was tested regularly for possible leakages by comparing the data obtained via the automatic sampling system to those obtained from samples taken simultaneously by syringes.

The air samples were analyzed in a Perkin Elmer F22 gas chromatograph equipped with a ^{63}Ni electron capture detector and a stainless steel separation column (length, 4 m; diameter, 3.175 mm) filled with Porapac N. The time for one analysis was 6 min. Interferences by CO_2 were avoided by passing the air sample through Natron asbestos, which reacts quantitatively with CO_2 but does not change the N_2O content of the sample.

The N_2O evolution rate is calculated by using the slope of the temporal N_2O increase within the closed box. With N_2O measurements of 0.5 to 1% precision at the 300 ppbv level, an increase of the N_2O mixing ratio inside the glass box of 1.5 to 3 ppbv N_2O, corresponding to N_2O evolution rates of 0.2 to 0.4 μg N_2O-N m^{-2} h^{-1}, could be determined. The automatic system allowed the determination of one N_2O evolution rate every 1.5 hours. Using two soil plots, a semicontinuous measurement of N_2O evolution rates with a resolution time of 3 hours for each plot is possible.

Field experiments at the stations were carried out by defined treatments of the soil plots. One plot was treated as control. The other plots were used for the experiments studying the dependence of the N_2O flux rates on different types and amounts of fertilizers, on different forms of application, and on the vegetation cover. The spatial variability in N_2O evolution rates between the different soil plots was determined during the 1 to 2 weeks prior to the experiments. The spatial variability was insignificant compared to the effect of fertilization, so that we could conduct the experiments without replicates. Loss rates of applied N fertilizer as N_2O were determined by subtracting the N_2O evolution rates determined for the control plot from those determined for the fertilized plots, both integrated over the observation period. The observation period ended after the N_2O evolution rates observed at the fertilized plots had reached the value observed at the control plot.

Based on a fertilizer application rate of 100 kg N ha^{-1}, and assuming a total observation period of 1 month, the lowest detectable N_2O loss rate is 0.001 to 0.002% of the applied nitrogen.

RESULTS AND DISCUSSION

Field Measurements of N_2O Evolution Rates

Results of measurements carried out in 1979–1981 at the different field stations near Mainz are shown in Figures 3–7. The figures show the temporal change of the N_2O evolution rates obtained at the individual soil plots during the observation period and include the data on soil surface temperature, soil moisture content, and rainfall.

Prior to each experiment, the N_2O evolution of the individual, untreated soil plots of the experimental station had been determined for 2 to 3 weeks. The evolution rates of the unfertilized individual plots showed similar absolute values and similar trends with time. In none of the experiments did the values differ by more than a factor of 4. This observation contradicts results published by *Matthias et al.* [1980], who found high spatial variabilities of the N_2O evolution rates with values differing by more than a factor of 100. So far, we have no explanation for the different observations. However, it is possible that the low spatial variability observed at our field stations is due to particularly homogeneous soil conditions.

After application of fertilizer (100 kg ha^{-1}), a dramatic increase of the N_2O evolution rates, with maximum values approximately 1 to 2 days after fertilization (Figures 4–7), was observed. An exception was the experiment carried out at station LPS in April/May 1980 (Figure 3). In this case the maximum was delayed by 5 days, most probably because of the specific soil conditions during the experiment, with relatively low soil temperature and soil moisture content.

The elevated N_2O evolution rates persisted over a period of several days and finally reached the background rates of the unfertilized control again. The N_2O evolution rates often showed a second maximum with lower absolute values, when the soil moisture was increased by heavy rainfall (Figures 4 and 5). Further rainfall did not cause any significant change of the N_2O evolution rate (e.g., Figure 4). Apparently, at that time, the fertilizer was already depleted in the upper soil layers, where most of the N_2O emitted into the atmosphere is produced [*Seiler and Conrad*, 1981*a*]. In deeper soil layers the fertilizer-induced N_2O production may still have continued or may even have been enhanced by the additional nitrogen washed down from the surface. The N_2O produced in those deeper layers, however, may not reach the atmosphere because of N_2O consumption reactions in the upper soil layers. This conclusion is

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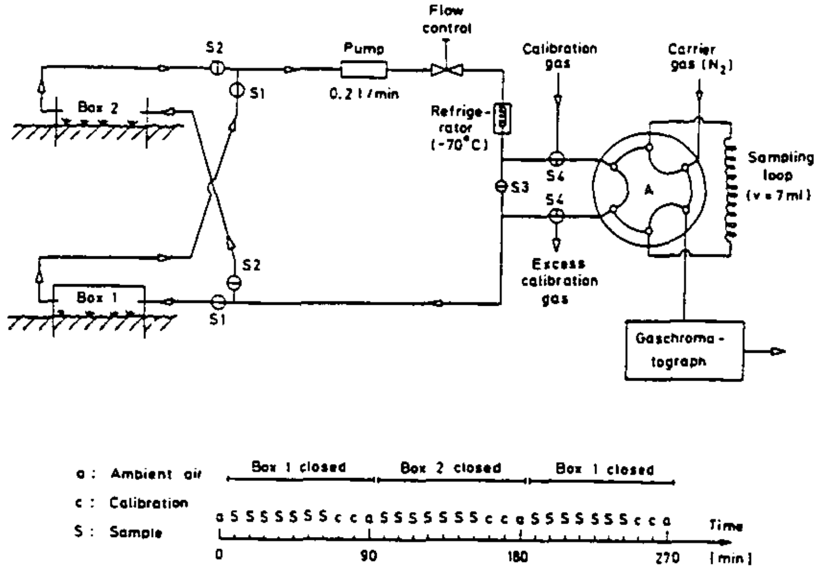

Fig. 2. Flow scheme of the automatic sampling and analysis system. Valve A is a six-port gas-sampling valve; valves S1 to S4 are selenoid valves.

in agreement with long-term measurements by *Seiler and Conrad* [1981*a*], which showed the highest N_2O mixing ratios in deeper layers of fertilized soil after the N_2O evolution rates at the surface had already returned to background rates.

Influence of Soil Temperature on N_2O Evolution

The N_2O evolution rates were dependent on the soil temperatures. Figure 3 shows N_2O evolution rates observed in spring, when soil temperatures varied considerably because of the rapidly changing weather situation. Although only two measurements were carried out per day, one clearly recognizes a strong positive correlation between the soil temperature and the N_2O evolution rates. Sometimes, the afternoon values exceeded the morning values by a factor of 10 when the soil temperature increased from 9 to 20°C.

The data obtained by the automatic technique demonstrated the existence of a diurnal rhythm of the N_2O evolution (Figures 5–7), which coincided with the diurnal variation of the soil surface temperature. The maximum rates were generally observed at 3 to 4 P.M. and the minimum rates in the early morning at approximately 6 A.M. There was no time lag between the maximum and minimum rates of N_2O evolution, and the maximum and minimum soil temperatures measured in 3 to 5 mm depth, indicating that most of the emitted N_2O was produced in the uppermost soil layers. Otherwise, N_2O evolution rates should be behind the measured soil temperatures, since the temperature maxima and minima occur progressively later with increasing soil depth. Our observations are in agreement with those reported by *Denmead* [1979] and *Denmead et al.* [1979], who found similar diurnal variations on a fertilized grass sward. Our results are not in agreement, however, with most of the observations recently reported by *Blackmer et al.* [1982]. These authors observed diurnal changes in N_2O evolution that were not in phase with the soil temperature measured in 2 cm depth but were 2 to 12 hours behind. They concluded that most of the emitted N_2O was produced in soil layers significantly lower than 2 cm depth and proposed that the diurnal N_2O emission patterns should be attributed to diurnal changes in the solubility of N_2O in soil water caused by the changing soil temperature profile. We have to assume that the differences in observations reported by *Blackmer et al.* [1982] from those reported by us or by *Denmead et al.* [1979] are due to differences in soil conditions.

Diurnal variations of N_2O evolution rates were observed on unfertilized as well as fertilized soil plots. However, the ampli-

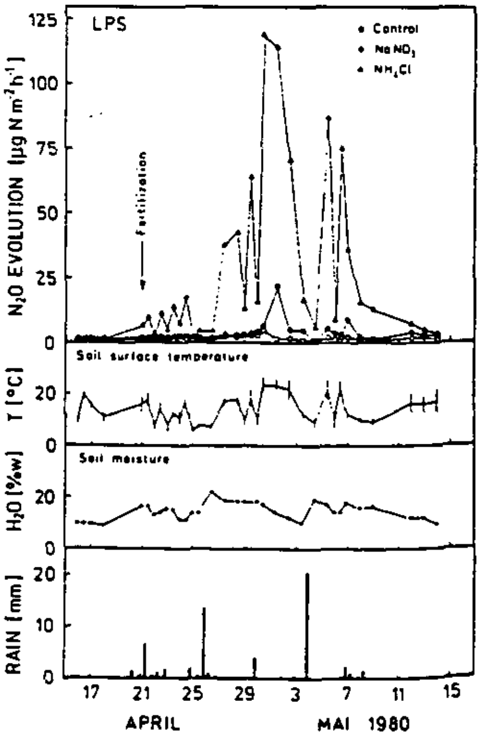

Fig. 3. N_2O evolution rates observed on fertilized and unfertilized (control) soil plots at the field station LPS. The fertilizers were applied as aqueous solution at a rate of 100 kg N ha⁻¹. The amount of water applied was added to the amount of rainfall observed on this day.

tudes were generally higher on fertilized than on unfertilized soil plots. Our measurements indicate that the amplitude of the diurnal variation was also influenced by the presence of a vegetation cover. The amplitudes were relatively small on the field plot with dense grass vegetation, but increased considerably after the grass had been cut (Figures 5 and 6). Since the removal of grass had no significant influence on the amplitude of soil temperature measured in 3 to 5 mm depth, we assume that most of the N_2O emitted into the atmosphere must have originated from the uppermost soil layer, where the solar radiation may have created a higher amplitude of temperature change after the vegetation cover had been removed. Other explanations could be the altered exchange rate of N_2O at the soil air interface, the altered soil water status affecting N_2O production, as well as temperature-induced changes in solubility of N_2O or direct influences of vegetation's metabolism on N_2O production.

The activation energy E_a of the N_2O evolution process is calculated by using the logarithmic form of a modified Arrhenius equation in which the reaction rate k is replaced by the N_2O evolution rate v, assuming a zero-order process:

$$\ln v = -\frac{E_a}{R}\frac{1}{T} + \text{const.}$$

The analysis of the data obtained during the semicontinuous measurements of the N_2O evolution rates (Figures 5–7) in fact demonstrated the linear correlation between ln v and $1/T$ for most of the days (Table 2). In Figure 8 an example of the N_2O evolution rates and soil temperatures observed on September 4, 1981, on a soil plot fertilized with NH_4Cl shows an activation energy for N_2O evolution of $E_a = 76$ kJ mol^{-1}. The linear correlation between ln v and $1/T$ has been found for each of the soil plots independently of the fertilization or the type of fertilizer. This result indicates that the diurnal patterns of N_2O evolution were mainly due to the temperature-induced changes in N_2O production rather than to the temperature-induced changes in solubility of N_2O in soil water as proposed by *Blackmer et al.* [1982]. In the latter case the N_2O evolution rates should be directly proportional to soil temperature and should not follow the Arrhenius correlation.

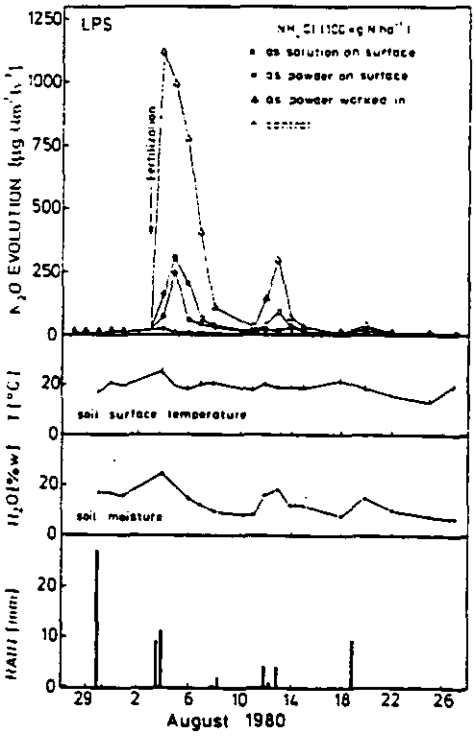

Fig. 4. Influence of form of application of fertilizer (NH_4Cl: 100 kg N ha^{-1}) on N_2O evolution rates. The experiments were carried out at field station LPS.

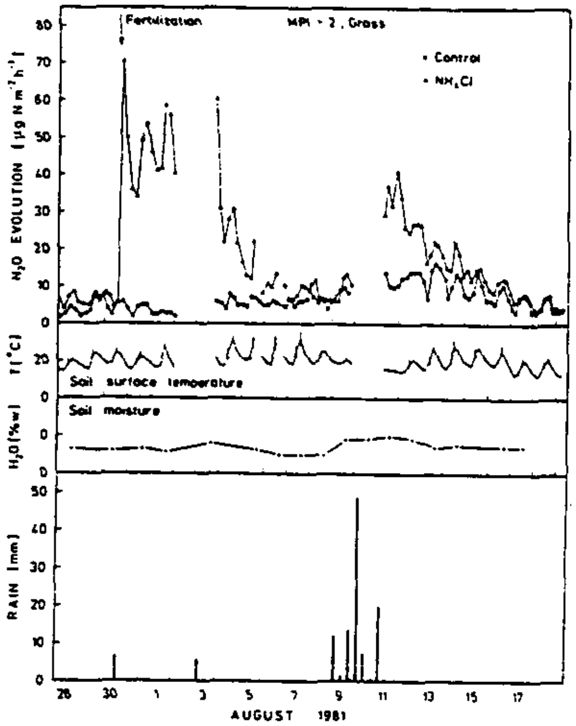

Fig. 5. N_2O evolution rates observed at field station MPI 2 using the automatic sampling and analysis system. The soil plots were covered with grass. NH_4Cl was applied as solution at a rate of 100 kg N ha^{-1}.

Table 2 summarizes the mean values of the activation energies determined for the individual days with significant correlation. Although different types of fertilizer had been used, the mean values of the activation energies (61 to 76 kJ mol^{-1}) agree reasonably well and are similar to the values (76–83 kJ mol^{-1}) calculated from Q_{10} values reported by *Denmead et al.* [1979]. The individual activation energies, however, show high variations, indicated by the large standard deviations summarized in the last column of Table 2. In fact, the activation energies sometimes changed from day to day, covering a range between 20 and 150 kJ mol^{-1}. It is interesting that this range is similar to the range of activation energies (28 to 166 kJ mol^{-1}) reported for microbial denitrification and nitrification [*Focht and Verstraete*, 1977; *McKenney et al.*, 1980*b*]. Focht and Verstraete reviewed reports showing that the activation energy of nitrification and denitrification are dependent on soil environmental factors such as pH, oxygen concentration, and nitrogenous substrate concentrations. Hence, it is possible that the high variability of the activation energies for N_2O evolution observed by us may be due to temporal changes of soil conditions at the microsites where microbial N_2O production occurs.

It is also possible, however, that the microbial N_2O pro-

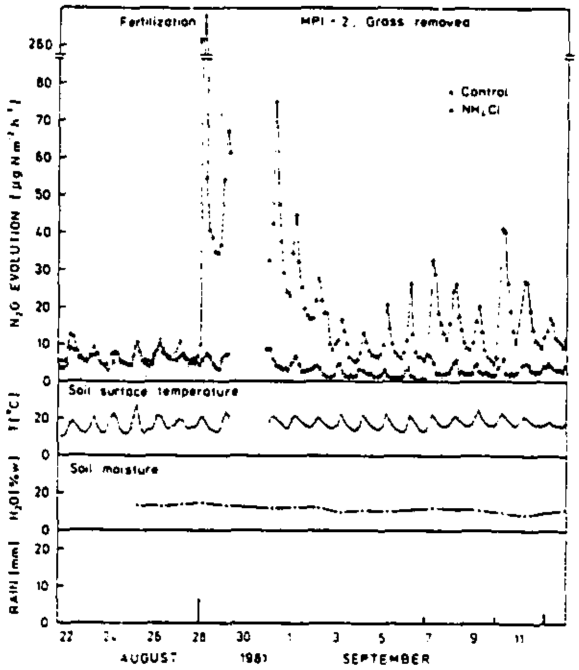

Fig. 6. N_2O evolution rates observed at field station MPI 2 using the automatic sampling and analysis system. After finishing the experiments shown in Figure 5, the grass was removed by cutting the stalks just above the soil surface and keeping it short subsequently. Then, the experiments shown in Figure 5 were repeated.

duction activities in the individual soil layers change with time, resulting in a change of their relative contribution to the overall N_2O evolution into the atmosphere. Since the amplitude of the diurnal changes in soil temperature decreases with increasing soil depth, the correlation of the N_2O evolution rates with soil temperatures measured in increasing soil depths would result in increasing activation energies. If we assume a constant activation energy for the microbial N_2O production processes in all soil layers, the observed variations in the activation energies for N_2O evolution would reflect the variations in the relative contribution of different soil layers to the N_2O evolution. This conclusion is only valid, however, when the changes of microbial activity occurred in the upper few centimeters of the soil profile, since otherwise N_2O evolution rates would not have been in phase with the soil temperature.

The strong dependency of the N_2O evolution rates on soil temperature clearly demonstrates that reliable N_2O loss rates caused by mineral fertilizer application can only be determined by repeated measurements per day. Estimates of N_2O evolution rates based on single measurements per day may differ by more than 1 order of magnitude from the actual value.

Influence of Soil Moisture on N_2O Evolution

N_2O evolution was influenced by rainfall. This influence can be recognized from Figures 4, 5, 6, and 7, showing coincidences of rain with elevated N_2O evolution rates. This is particularly true for the fertilized soils, where the increased soil moisture content stimulated the N_2O production at times when the rates had already decreased toward background values. The extent of stimulation decreased successively from rainfall to rainfall (Figure 4), approaching the conditions observed on unfertilized soil plots.

The influence of rain is very pronounced after relatively long periods of dryness. Under these conditions, even small amounts of rain (September 7 and 10, 1981, Figure 6) that did not cause any significant increase of the average soil moisture content of the upper 10 cm of the soil profile resulted in a stimulation of N_2O production. This observation again indicates that the processes inducing the evolution of N_2O into the atmosphere must be located in the uppermost soil layers [*Seiler and Conrad*, 1981*a*].

Figure 9 illustrates the influence of the soil moisture content on the N_2O evolution rates at an unfertilized soil plot. In this figure, the average daily N_2O evolution rates are plotted against the soil moisture contents determined within the upper 10 cm of the soil profile. Each data point is normalized to a constant average daily soil temperature of 20°C by using the Arrhenius correlation. The data were obtained from the measurements at the control plot of the field station MPI 2 (compare Figures 5–7) before and after removal of the grass cover. The soil moisture contents ranged between 8 and 22% (g H_2O per 100 g moist soil). Within this range the N_2O evolution rates increased dramatically with increasing soil moisture. At a soil moisture content of 20% the N_2O evolution rates were 3 to 10 times higher than at a soil moisture content of 10%.

Similar correlations of N_2O evolution rates with soil moisture contents were observed at other unfertilized control plots. At present the data base is too small to calculate a quantitative relation between the N_2O evolution rates and the soil moisture contents. However, our results support the observations of a positive correlation between N_2O evolution, rainfall, and soil moisture [*Denmead et al.*, 1979; *Ryden and Lund*, 1980; *Mosier and Hutchinson*, 1981; *Mosier et al.*, 1981; *Terry et al.*, 1981].

The effect of rainfall and increased soil moisture on N_2O evolution may be due to several causes: The moistening of soil may increase the activity of soil microorganisms [*Wilson and Griffin*, 1975]; it may also increase their population density [*Lund and Goksoyr*, 1980]. These events may be especially important after long periods of dryness. The increased soil

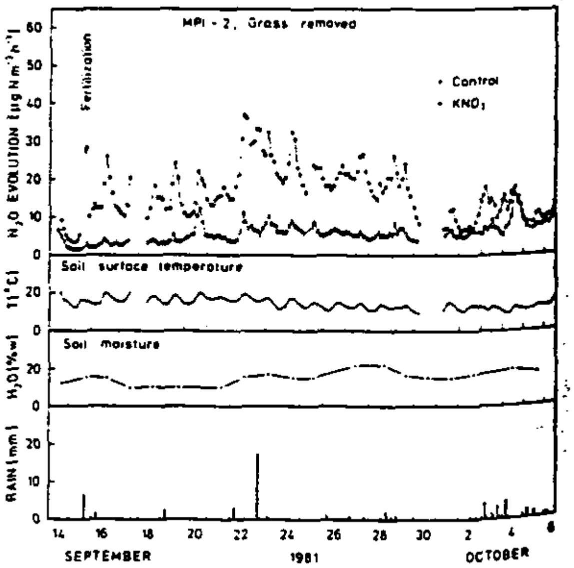

Fig. 7. N_2O evolution rates observed at field station MPI 2 using the automatic sampling and analysis system. After finishing the experiments shown in Figure 6, KNO_3 was applied as solution at a rate of 100 kg N ha^{-1}.

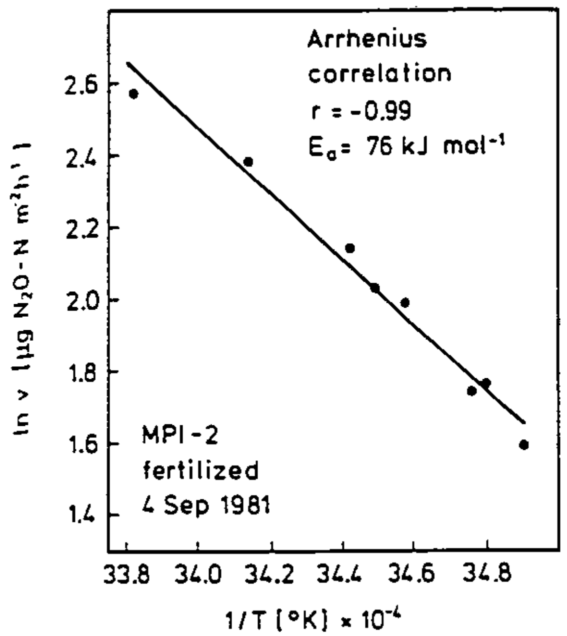

Fig. 8. Arrhenius correlation of the N_2O evolution rates (v) and the soil surface temperature (T). The data are taken from Figure 6.

moisture content may also stimulate the availability of dissolved nutrients by their transport to other soil sites. The availability of oxidizable organic matter, and of nitrate, is important for denitrification: the availability of ammonium is important for nitrification. The mobilization of nutrients by soil water may also cause an increased respiration rate of the heterotrophic microbial flora, that, in turn, may result in a reduction of the oxygen concentration in soil. Furthermore, the increased soil moisture content hinders the diffusion of oxygen into the soil, so that soil microsites with a small supply of oxygen may develop. Under these conditions, N_2O production by denitrification as well as by nitrification is stimulated (for discussion, see *Seiler and Conrad* [1981*b*]).

Influence of Fertilizer Type on N_2O Evolution

During our field experiments, we always observed that the N_2O evolution rates were strongly dependent on the type of nitrogen fertilizer. Application of nitrate usually caused significantly lower N_2O evolution rates than application of ammonium, although the temporal variations were similar (Figures 3, 6, and 7). This observation is in agreement with earlier observations [*Conrad and Seiler*, 1980; *Breitenbeck et al.*, 1980] and shows that nitrification of ammonium is an important process for N_2O production under field conditions. This conclusion is consistent with the results of laboratory experiments by *Bremner and Blackmer* [1978, 1979, 1980, 1981].

Only in one of our experiments the nitrate-induced N_2O loss rates were comparable to the ammonium-induced N_2O loss rates (Table 3). This experiment was carried out at the field station Finthen on a loess soil that had a small air-filled porosity (Table 1) and was covered by a dense grass layer. Hence, there is the possibility that this particular soil might have contained a relatively high number of anaerobic microsites caused by poor soil aeration, favoring the denitrificative N_2O production from nitrate.

The influence of the anion of the ammonium fertilizer on N_2O evolution was tested in an experiment carried out at field station MPI 2. One soil plot was treated with ammonium chloride and another with ammonium sulfate. The experiment was then repeated, but the first plot was treated with ammonium sulfate and the second with ammonium chloride. The N_2O evolution rates observed at the fertilized soil plots were almost identical, showing that ammonium-induced N_2O evolution rates were not affected by the counter anion. This experiment again showed that there was no significant difference in the pattern of N_2O evolution between the two soil plots that could be attributed to spatially nonhomogeneous soil conditions in our experiment.

Influence of Application Form and Amount of Fertilizer on N_2O Evolution

The N_2O evolution rates were strongly dependent on the forms of application of the fertilizer. This dependency is shown in Figure 4, which illustrates the results obtained by experiments using ammonium chloride as fertilizer. The ammonium salt was applied (1) as aqueous solution poured onto the soil surface, (2) as powder distributed onto the soil surface that had been moistened before fertilization, and (3) as powder worked into the upper 10 cm of the soil that had been moistened before. Case (1) represents the form of application used by us for the rest of the experiments. In each case we observed a temporal variation of N_2O evolution rates with maximum values 2 days after application. However, the absolute values were significantly different, with both the highest N_2O evolution rates (3) and the lowest values for form of application (2). Most interestingly, a second maximum had been observed approximately 10 days after fertilization, during a rainy period of several days, and consequently increased soil moisture contents. Surprisingly, however, the second maximum was only observed for application forms (1) and (3), but not for (2), when the fertilizer had been distributed as powder onto the soil surface. In this case a significant portion of the applied ammonium fertilizer was perhaps lost as a result of NH_3 volatilization.

TABLE 2. Correlation of N_2O Evolution Rates With Soil Temperature by the Arrhenius Equation

Soil Conditions MPI 2, 1981	Total Days With Semicontinuous Records	Days With Significant Correlation, $P < 0.05$	Mean Value of E_a, kJ mol^{-1}	Standard Deviation, kJ mol^{-1}
Unfertilized (July–October)	63	37 (59%)*	76	35
Fertilized with NH_4Cl (July–October)	38	28 (74%)	61	36
Fertilized with KNO_3 (September–October)	37	23 (62%)	70	27

*Percentage of total days.

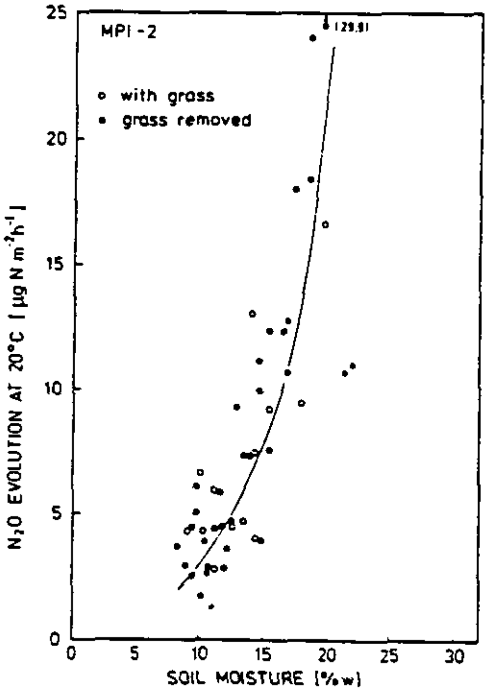

Fig. 9. Influence of the soil moisture content on the N_2O evolution rates. The data points represent average daily N_2O evolution rates observed at the unfertilized control plot of field station MPI 2 (Figures 5–7). The values have been normalized to a constant average soil surface temperature of 20°C by using the Arrhenius correlation.

The N_2O evolution rates were also influenced by the amount of fertilizer applied. Application of increasing amounts of NH_4Cl resulted in increasing N_2O evolution rates, but the change in N_2O evolution rates with time was similar for all fertilizer application rates. A positive correlation between amount of fertilizer applied and N_2O evolution rates has also been reported by *McKenney et al.* [1978; 1980*a*] for NH_4NO_3 and by *Cochran et al.* [1981] for anhydrous ammonia.

Most probably, the influence of amount and form of application of fertilizer is based on local concentrations of mineral nitrogen at soil microsites. Laboratory experiments did show an influence of the concentration of ammonium on the nitrificative N_2O production [*Bremner and Blackmer*, 1980, 1981]. Similar results were reported for the denitrificative N_2O production from nitrate [*Blackmer and Bremner*, 1978; *Firestone et al.*, 1979, 1980; *Terry and Tate*, 1980; *Letey et al.*, 1980*a*]. Therefore, one should assume that N_2O evolution rates would be correlated to the concentration of ammonium, nitrite, or nitrate in the soil. To date, however, field measurements have not revealed any significant correlation between N_2O evolution rates and simultaneously measured nitrate, nitrite, or ammonium concentrations (*Mosier and Hutchinson* [1981]; O. Heinemeyer, personal communication, 1982). We suggest that the effect of fertilizer nitrogen on N_2O evolution is exerted at small soil microsites in the uppermost soil layer; these sites are not analyzed appropriately for their actual concentration of mineral nitrogen when bulk samples of the upper centimeters of the soil profile are taken for the analysis.

Loss Rates of Fertilizer Nitrogen as N_2O

The previous chapters showed that N_2O evolution rates increase after mineral fertilizers have been applied, so there is no doubt that application of mineral fertilizers represents a source of atmospheric N_2O. The source strength and thus the impact of mineral fertilizers on the global N_2O budget can only be calculated if the loss rates of fertilizer nitrogen as N_2O relative to the total amount of applied fertilizer is known. These loss rates are obtained by subtracting the total amount P_0 of N_2O–N emitted from the unfertilized soil plot from that amount P_1 which has been obtained simultaneously from the fertilized soil plot and dividing this figure by the total amount M of the applied fertilizer nitrogen, i.e.,

$$L = \frac{P_1 - P_0}{M}$$

Values for P_1 and P_0 are obtained by integrating the N_2O evolution rates observed during a period of 20 to 30 days after fertilization. The total observation period, which is necessary to cover all N_2O evolution events caused by the fertilization, is dependent on the type of soil and the meteorological conditions. Care was taken that the elevated N_2O emission rates of the fertilized soil plot had returned to the background rates of the unfertilized control plot. Our observations did not provide a reasonable argument for a long-term influence of fertilization on N_2O evolution from soils. In none of our experiments did we observe increasing background rates as a result of repeated application of mineral fertilizer. Therefore, we may assume that

TABLE 3. Influence of Type of Fertilizer on the Total Loss of Fertilizer Nitrogen as N_2O

Field Experiment	Loss Rates, % of N applied Fertilizer Applied as Solution, 100 kg N ha^{-1}	
	$NaNO_3$	NH_4Cl
Finthen, Sep./Oct. 1979	0.073	0.053
LPS, Apr., May 1980	0.018	0.153
LPS, Aug. 1980		0.216
MPI 1, grass, Sep./Oct. 1979	0.007	0.025
MPI 1, grass, Aug. 1981	0.071	0.376
MPI 1, clover, Aug. 1981	0.001	0.065
MPI 2, Aug.–Oct. 1981	0.017*	0.070 (0.078)†

*KNO_3 instead of $NaNO_3$.
†Value in brackets: $(NH_4)_2SO_4$ instead of NH_4Cl.

our field measurements carried out over time periods up to 33 days covered the total loss of fertilizer nitrogen as N_2O from the soil.

Table 3 summarizes the N_2O loss rates obtained at the different field stations for nitrate and ammonium fertilizer applied as aqueous solution. The N_2O loss rates ranged between 0.001 and 0.073% for nitrate and between 0.009 and 0.376% for ammonium fertilizers. Higher loss rates (0.94%) were only observed when ammonium fertilizer had been applied as powder and worked into the soil (Figure 5). In contrast, the loss rates were only 0.15% when the ammonium had been distributed as powder onto the soil surface. The loss rates were not significantly influenced by different amounts (50, 100, and 200 kg N ha^{-1}) of ammonium fertilizer being applied (Figure 6). The values given in this paper agree very well with those reported by *Denmead et al.* [1979], *Breitenbeck et al.* [1980], *Conrad and Seiler* [1980], *Mosier and Hutchinson* [1981], *Mosier et al.* [1981, 1982], *McKenney et al.* [1980*a*], and *Ryden* [1981], who found values ranging between 0.001 and 1.67%. Higher loss rates were only reported for some individual cases, e.g., after fertilization with anhydrous ammonia [*Bremner et al.*, 1981*a*], for manure-treated fields [*Rolston et al.*, 1978], and for heavily irrigated and fertilized land [*Ryden and Lund*, 1980]; these rates however, do not contribute significantly to the overall N_2O release. Therefore, we assume an N_2O loss rate from fertilizer nitrogen of 0.01 to 2.0% to be representative of global conditions.

Additional N_2O may be formed from the fraction of mineral fertilizer leached from the field into the groundwater or into surface freshwater ecosystems, where the fertilizer nitrogen could again induce an N_2O emission into the atmosphere. Lysimeter experiments using ^{15}N as a tracer indicate that the loss of fertilizer nitrogen by leaching ranges between 0.4 and 3.4% [*Vömel and Ewert*, 1981]. It has been shown that groundwater and freshwater may be substantially supersaturated with N_2O [*Kaplan et al.*, 1978; *Lemon and Lemon*, 1981]. However, it remains uncertain which fraction of the observed dissolved N_2O is due to seepage fertilizer or due to N_2O production during the natural cycle of nitrogen in freshwater ecosystems [*Knowles et al.*, 1981; *Vincent et al.*, 1981]. If we assume that the N_2O loss rate of the leached fertilizer nitrogen corresponds to the values observed at fertilized fields, the total loss rate of fertilizer N as N_2O would be as low as 0.01 to 4.0%.

Using this figure and the annual fertilizer production rate of 55 Tg N y^{-1} (value for 1980, UN Statistical Yearbook), the total source strength of fertilizer-derived N_2O amounts to 0.005 to 2.2 Tg N_2O–N yr^{-1}. This range is considerably lower than that of 6 to 100 Tg N_2O–N yr^{-1}, obtained from earlier estimates [*McElroy et al.*, 1977; *Hahn and Junge*, 1977], and is also below a recent estimate of 2.3 to 3.0 Tg N_2O–N y^{-1} [*Weiss*, 1981], which is based on theoretical calculations and the observation of an increase of the tropospheric N_2O mixing ratio.

Following the general assumption of a steady increase of the mineral fertilizer production up to a value of 200 Tg N in the year 2000, we have to assume a global production of fertilizer-derived N_2O of 0.02 to 8 Tg N_2O–N in the year 2000. This would contribute up to approximately 110% of the global natural N_2O budget, which is approximately 7 to 20 Tg N_2O–N yr^{-1} [*Crutzen*, 1983], and therefore, may have some impact on stratospheric ozone and on the climate. However, we have to emphasize that the figures of the fertilizer-induced N_2O emission are still uncertain, particularly because the experiments have been limited to developed and industrialized countries located in the higher latitudes. However, there is a trend toward an increasing fraction of the annually produced mineral fertilizer being used in the developing countries, generally located in warmer climatic zones and where N_2O loss rates have not been determined so far.

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APPENDIX F

REFERENCE 6, ASSOCIATED HAND CALCULATIONS, AND SUPPORTING DOCUMENTATION

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Nitrous Oxide Emissions from Fertilized and Unfertilized Soils in a Subtropical Region (Andalusia, Spain)

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Abstract. Field measurements of N_2O emission rates were carried out from August until October 1982 in a subtropical region in Europe, i.e. in Andalusia, Spain. The measurements were performed by using an automatic sampling and analysis technique allowing the semi-continuous determination of N_2O emission rates. The N_2O emission rates were positively correlated to the soil surface temperature and exhibited a diurnal rhythm with maximum rates in the afternoon and minimum rates in the early morning with average values of 1 μg N_2O–N/m²/h for the grass lawn and 15 μg N_2O–N/m²/h for cultivated land. Application of urea and ammonium nitrate resulted in elevated N_2O emission rates when compared to the unfertilized control. The loss of fertilizer–nitrogen as N_2O was 0.18% for urea and 0.04% for NH_4NO_3 which compares very well with data obtained in a temperate climate (Germany). The total source strength of fertilizer-derived N_2O is estimated to be 0.01–2.2 Tg N_2O–N per year. The N_2O flux from unfertilized natural soils may be as high as 4.5 Tg N_2O–N, indicating that the N_2O emission from soils contributes significantly to the global N_2O budget.

Key words: N_2O emission, nitrogen fertilizer, soil, subtropics, atmospheric budget.

1. Introduction

Nitrous oxide is an intermediate product of the denitrification and nitrification in soil (Bremner and Blackmer, 1978; Bremner and Blackmer, 1981; Schmidt, 1982; Firestone, 1982). The N_2O in soil atmosphere was found to be produced and consumed simultaneously in the uppermost soil layer, resulting in a net flux of N_2O from soil into the atmosphere (Seiler and Conrad, 1981). The flux rates are dependent on the chemical composition of the soil, soil moisture, oxygen content in soil air, and soil temperature and thus show high spatial and temporal variations (Breitenbeck *et al.*, 1980; Blackmer *et al.*, 1982; Bremner *et al.*, 1980; Matthias *et al.*, 1980; McKenney *et al.*, 1978; Mosier *et al.*, 1981; Seiler and Conrad, 1981).

Application of mineral nitrogen fertilizer results in an enhancement of the N_2O production rates in soil and, thus, an increase of the total N_2O flux from soil into the atmosphere. The loss of fertilizer–nitrogen as N_2O ranges between 0.01 and 2.0% of the applied mineral nitrogen fertilizer (Breitenbeck *et al.*, 1980; McKenney *et al.*, 1978; Mosier and Hutchinson, 1981; Conrad and Seiler, 1980) and are dependent on the type of applied mineral fertilizer, application form, etc. (Conrad *et al.*, 1983).

Most of the measurements of N_2O emission rates from fertilized and unfertilized soils were carried out in countries with temperate climates. Data on N_2O flux rates from soils into the atmosphere in tropical and subtropical climates are lacking.

Since the nitrogen cycles in tropical and subtropical ecosystems are qualitatively and quantitatively different from those in temperate ecosystems (Clark and Rosswall, 1981), the N_2O emission rates may be different from those observed in temperate climates. Furthermore, because of the increasing application rates of mineral nitrogen fertilizers in developing countries (FAO, 1982), information on the N_2O emission in tropical and subtropical regions is of increasing importance for estimating the effect of fertilization on the global N_2O budget and, thus, on the chemistry and radiative budget of the atmosphere (Crutzen, 1970; Lacis *et al.*, 1981). This paper reports on results from field measurements carried out on cultivated land and a grass lawn in a subtropical region of Europe, i.e. in Andalusia, Spain.

2. Experimental

Measurements on cultivated land were carried out from August until October 1982 on a cultivated field of the farm station of BASF Española near Utrera (37°N, 5.6°W) approximately 30 km south of Sevilla, Spain. The soil of the field was reddish-brown and consisted of a loamy sand with a pH value of 7.4 and a size fraction of 7% for particles with $\emptyset < 2\,\mu m$, 4% for particles with $\emptyset$ between 2–20 μm and 89% for particles with $\emptyset$ between 20–2 000 μm. Soybeans were cultivated on the field during spring and summer 1981 and were ploughed under in September of the same year. Since then, until the measurements in August 1982, the field remained unplanted and did not receive any mineral nitrogen fertilizer.

The measurements on the grass-covered area were performed on the lawn of the station consisting almost exclusively of Bermuda grass (*Cynodon dactylon*). This grass lawn was fertilized in spring with ammonium nitrate fertilizer (75 kg N/ha) and irrigated using a lawn-sprinkler once every two or three days at a rate of a few millimeters per day. The regular irrigation was interrupted during the period of our experiments. During this time, the grass lawn received irregular watering on 18, 20, 23 and 25 August (see Figure 2).

Nitrous oxide measurements were performed on three plots on the cultivated land and on two plots on the grass lawn. Each plot had a surface area of approximately 800 cm^2. One plot in each experimental area remained unfertilized and was used as a control. The remaining two plots on the cultivated land were fertilized with urea and ammonium nitrate, respectively, both analytical grade (Merck, Darmstadt). The plot on the grass lawn received a commercial ammonium nitrate fertilizer (Hakaphos Naranja, BASF) including 15% P_2O_5 and 30% K_2O. The application rate was 100 kg N/ha for all cases. The fertilizers were applied as aqueous solutions. The amount of water added to the plots by this procedure was equivalent to a precipitation of 7 mm. To enable comparison of the N_2O emission rates obtained from the individual experimental plots, the unfertilized plots received the same amount of water without fertilizer. Water equivalent to a precipitation of 7 mm was applied for the artificial irrigations of the individual experimental plots.

The N_2O emission rates were determined by using the closed-box technique applying the automatic sampling and analysis technique. The applied boxes as well as the sampling technique have already been described by Conrad *et al.* (1983). This technique allowed the simultaneous determination of N_2O emission rates on several soil plots and provided six individual data points per plot and day on the cultivated field with a total of three plots, and eight individual data points per plot and day on the grass lawn with a total of two plots. The lower detection limit of the N_2O emission rates was 0.2 μg N_2O–N/m^2/h. The precision was 0.5% at 10 μg N_2O–N/m^2/h.

The total loss L of applied mineral fertilizer–nitrogen as N_2O was calculated by

$$L = \frac{\int_0^t (E_t - E_0)\,\mathrm{d}t}{M}$$

where E_t = Emission rates of N_2O–N measured on the fertilized plots.
E_0 = Emission rates of N_2O–N measured on the control plot.
M = Amount of applied mineral fertilizer–nitrogen.
t = Length of observation period.

Using this system, loss rates of $\geq 0.02\%$ can be determined.

The soil surface temperature was recorded at 3 to 5 cm depths using thermocouples (Iron/Constantan). The soil moisture content (g water/100 g moist soil) was determined gravimetrically in the soil samples taken from the top 5 cm soil layer of a nearby soil plot treated in the same way as the experimental plots.

3. Results

The temporal variations of the N_2O emission rates from cultivated land are illustrated in Figures 1a and 1b together with the temporal variation of the soil surface temperature and soil moisture. The soil surface temperature showed pronounced diurnal variations with maximum temperatures of 35–48°C in the afternoon and minimum temperatures of 18–24°C in the early morning. The soil moisture was extremely low during the whole observation period and generally ranged below the 2% indicative for the semi-arid climate of Andalusia during this particular season. Higher soil moisture was only observed during those periods with artificial irrigation (e.g. on 9, 16, 20, 24 September and 1 October) and rain showers on 25 September. During these days, the soil moisture of the upper 5 cm of the soil layer reached values of about 15% which, however, dropped very rapidly within 1 to 2 days to the former value of < 2%.

The N_2O emission rates measured on the unfertilized field plot showed long-term variations with a time-scale of several days superimposed by diurnal variations with maximum values in the afternoon. The N_2O emission rates varied between 4 and 35 μg N_2O–N/m^2/h with an average value of 15 μg N_2O–N/m^2/h. This figure is considerably higher than the

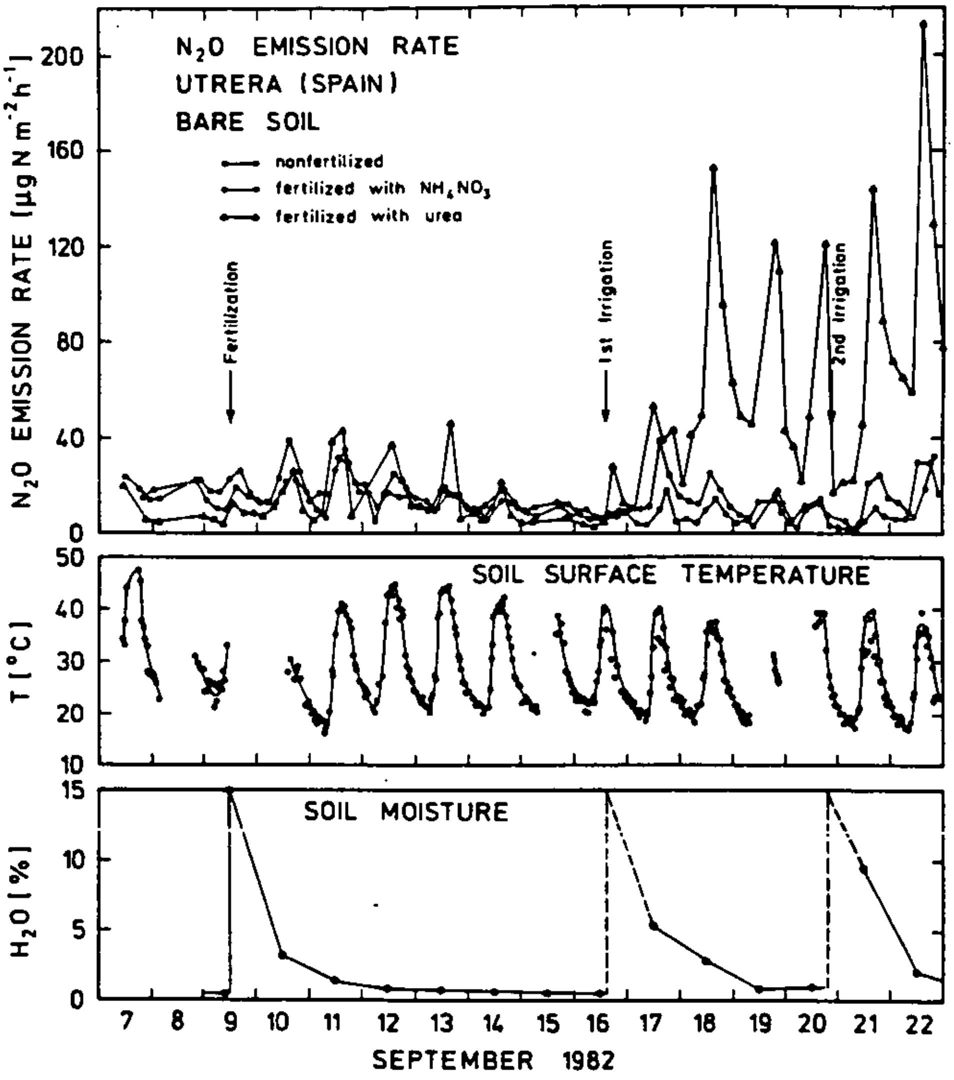

Fig. 1a. N$_2$O emission rates after fertilization with urea or ammonium nitrate. Nitrous oxide emission rates were measured between 7 September and 8 October on an unplanted field. Measurements were carried out on unfertilized soils and soils fertilized with urea or ammonium nitrate. The lower part shows the temporal variation of soil temperature at 3 to 5 mm depth and the soil moisture of the upper 5 cm.

N$_2$O emission rates observed on unfertilized field plots during our experiments in Germany where the individual figures varied between 1 and 15 μg N$_2$O–N/m^2/h with an overall average of about 4 μg N$_2$O–N/m^2/h. The latter values were calculated from data summarized in Figure 5–7 of the recently published paper by Conrad *et al.* (1983). The difference of the N$_2$O emission rates observed in Andalusia and Germany may be due to the influence of the soil temperature on the N$_2$O emission rate with higher soil tempera-

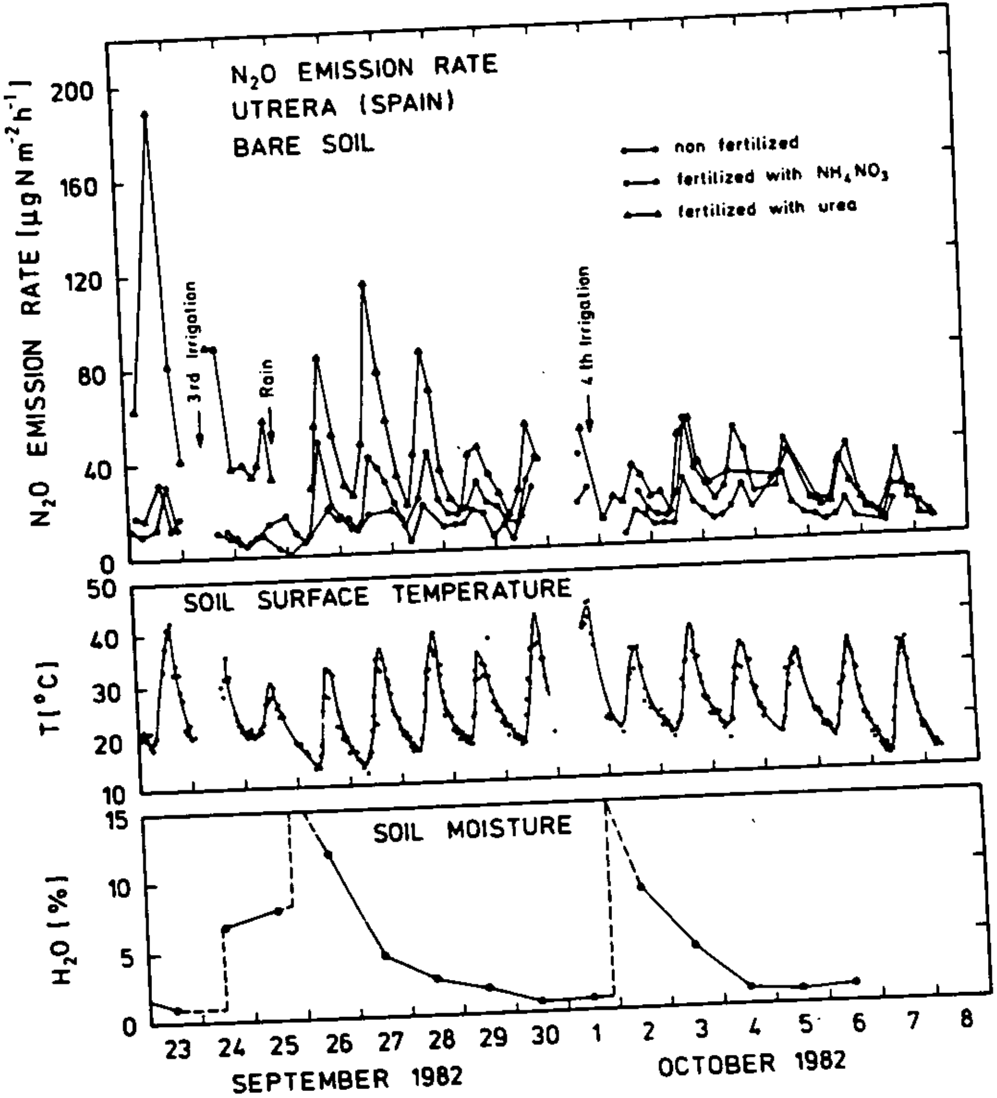

Fig. 1b. Continuation of Figure 1a.

tures and, consequently, higher N_2O emission rates in Andalusia. It is also possible that the higher N_2O emission rates found in Andalusia are due to the plant residues of soybeans which had been ploughed under one year before the measurements and which may still provide substrate for nitrification and/or denitrification.

It seems that the N_2O emission rates measured on the unfertilized plots are influenced by irrigation and, thus, by the soil-moisture content. This effect is very pronounced for the period between 9 and 15 September when the N_2O emission rates increased from 20 μg N_2O–N/m^2/h shortly before the irrigation to maximum values of 35 μg N_2O–N/m^2/h on 11 September. The influence of irrigation on the N_2O emission decreased with an increasing number of irrigations. A similar relationship has been observed by Conrad *et al.* (1983) on unfertilized noncultivated land where the N_2O emission rates increased from about 5 μg N_2O–N/m^2/h before heavy rain showers to 20 μg N_2O–N/m^2/h a few days later.

Nitrous oxide emission rates measured on fertilized plots also showed strong diurnal variations with maximum values in the afternoon and minimum values in the early morning. Very often, the maximum values exceeded the morning values by more than a factor of 3–5. The daily amplitudes as well as the daily average of the N_2O emission rates were found to be dependent on the magnitude and the variation of the soil surface temperature. Significant positive correlations between N_2O emission and soil-surface temperature were found on 48–57% of the total observation period (see Table I). The N_2O emission rates were also positively correlated with the soil moisture, with relatively low values at soil moistures lower than 5%.

Most surprisingly, the N_2O emission rates measured on the fertilized plots did not respond to the application of mineral fertilizers within the first week after fertilization. During this period, the N_2O emission rates were comparable to those obtained on the unfertilized plot. A substantial increase of the N_2O emission rates was observed on the experimental plot fertilized with urea after the first irrigation, which was seven days after fertilization. Maximum N_2O emission rates occurred on 22 September after the second irrigation. After the fourth irrigation, the N_2O emission rates approached the values observed at the unfertilized plot.

The temporal pattern of the fertilizer-induced N_2O emission is in contrast to the findings by different groups in temperate climates and higher soil moistures (for summary see Conrad *et al.*, 1983) which always show a very fast response of the N_2O emission rates on the application of nitrogen fertilization. Generally, the fertilizer-induced N_2O emission rates reached their maximum values one to five days later and approached the background values 10 to 12 days after fertilization.

The total loss of mineral fertilizer–nitrogen as N_2O is calculated to be 0.18% for urea and 0.04% for ammonium nitrate.

Table I. Activation energy of N_2O emission from unfertilized and fertilized soil of a bare field *in Utrera, Spain (9 September–7 October, 1982)*

Soil conditions (100 kg N ha^{-1})	Days with significant correlation ($P < 0.05$)	Activation Energy (kJ mole^{-1})	
		Range	Mean value
without fertilizer	6 (28%)	21–50	36.3 ± 10.7
NH_4NO_3	12 (57%)	26–64	47.2 ± 11.3
Urea	10 (48%)	40–75	55.0 ± 12.6

The N_2O emission rates obtained from measurements on the grass lawn are summarized in Figure 2 together with the soil surface temperature. The data obtained on the unfertilized plots show a large scatter of the individual emission rates and also very low N_2O flux rates with values of < 2.0 μg N_2O–N/m²/h. Despite the high scatter of the data, it seems that the daytime N_2O emission rates were higher than the nocturnal ones. The most

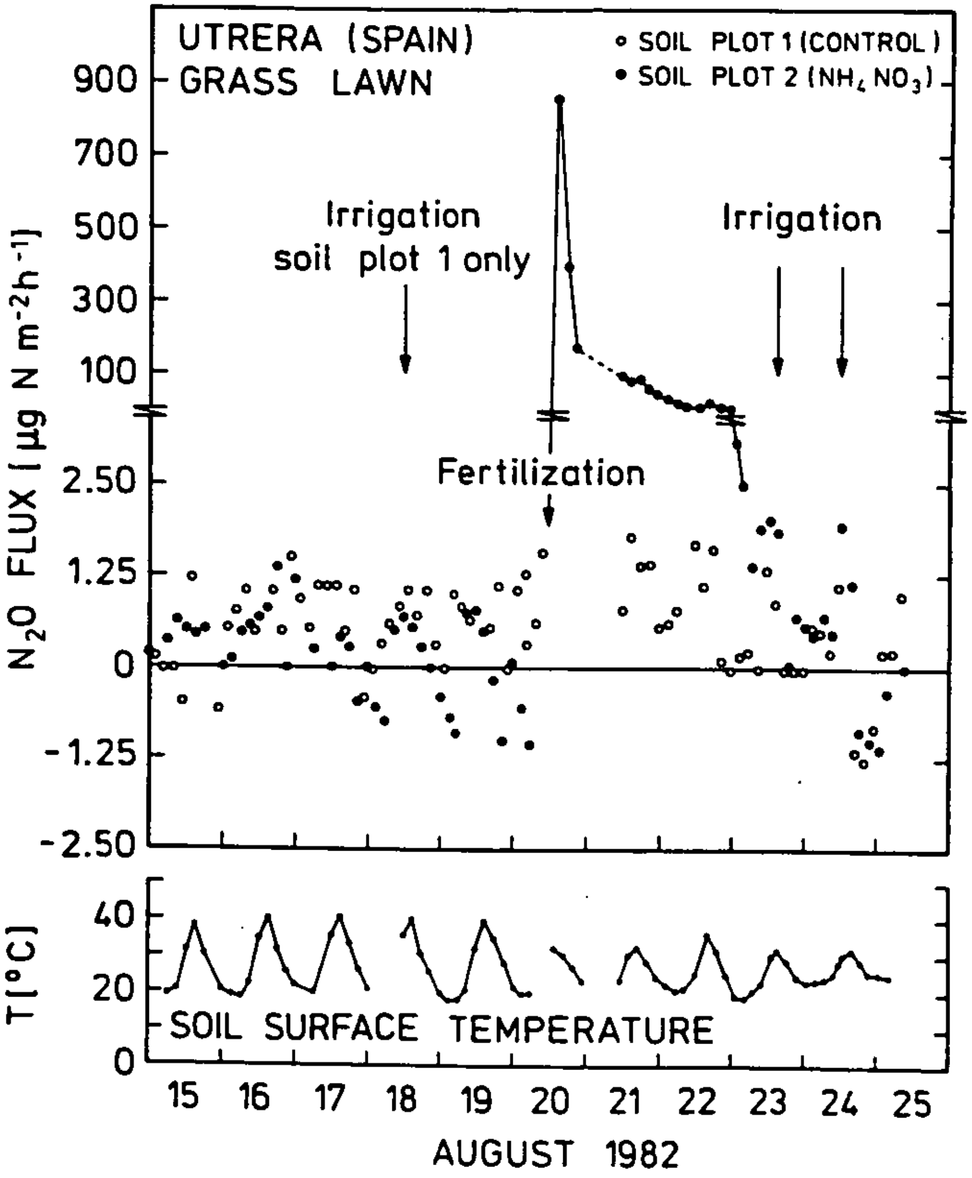

Fig. 2. N_2O emission rates measured on a Bermuda grass lawn. Plot 1 remained unfertilized; plot 2 was fertilized with ammonium nitrate (75 kg N/ha).

interesting result is the observation of negative fluxes at the soil-air interface indicating that the soil of the grass lawn acted both as a source and sink of atmospheric N_2O.

In contrast to the observations on the cultivated field plots, the fertilization of the grass lawn with NH_4NO_3 resulted in a rapid increase of the N_2O emission rates. Maximum rates of 850 μg N_2O–N/m^2/h were reached about 6 h after fertilization. The background values of 1 μg N_2O–N/m^2/h were approached 2 days after fertilization. Repeated irrigation of the grass lawn after fertilization with amounts of H_2O equivalent to 7 mm rainfall did not result in any significant enhancement of the N_2O emission rates. Despite these differences, the total loss of mineral fertilizer–nitrogen as N_2O (0.075%) agrees reasonably well with the corresponding figure (0.040%) obtained from the plot on the cultivated land.

4. Discussion

N_2O emission rates measured on fertilized and unfertilized soils are positively correlated with the soil surface temperatures indicating that the N_2O production processes must be located within the upper centimeters of the soil layers. Nitrous oxide production in deeper layers would cause a considerable time delay between the N_2O emission rates at the soil-air interface and the soil surface which, however, have never been observed. Similar findings were already reported for soils in Germany (Conrad *et al.*, 1983) and in Australia (Denmead *et al.*, 1979). The only contradictory data were published by Blackmer *et al.* (1982) who found a phase lag of 2 to 12 h between the maximum N_2O emission rates and the maximum soil temperature measured in a depth of 2 cm. They, therefore, concluded that the N_2O production must have occurred in layers considerably lower than 2 cm.

Using the data obtained on individual days with positive correlations between the N_2O emission and soil temperature and applying the Arrhenius equation, the activation energies are calculated to be 36–55 kJ/mole which are significantly lower than the values of 60–76 kJ/mole obtained from measurements in Germany (Conrad *et al.*, 1983). This difference may be explained by the possibility that the N_2O production in hot soils of arid climates may occur at slightly lower depths than in soils of midlatitudes.

In general, the soils both fertilized and unfertilized acted as a source of atmospheric N_2O. Exceptions were measurements on a grass lawn where small N_2O uptake rates were observed during nighttime. N_2O uptake was also observed by Ryden (1981) on soils covered with perennial ryegrass (*Lolium perenne*) which gives a similar lawn structure as the Bermuda grass (*Cynodon dactylon*) used for our experiments. Small N_2O sink activities have also been observed by Bremner *et al.* (1980) in spring on soils in Iowa (U.S.A.) which, however, are of minor importance for the global N_2O cycle.

Average N_2O emission rates on unfertilized soils varied between 1 μg N_2O–N/m^2/h on the grass lawn and 15 μg N_2O–N/m^2/h on the cultivated land. The latter figure is higher than the values of about 4 μg N_2O–N/m^2/h observed on unfertilized soils at midlatitudes in Germany (Conrad *et al.*, 1983). This difference may be explained either by the higher soil temperatures in arid climates and/or by the incorporation of plant residues of soybeans into the soil carried out one year before our measurements in Andalusia. Assuming the figures of 15 μg N_2O–N/m^2/h to be representative for subtropical and tropical regions with a total surface area of 25×10^6 km^2 (Lieth, 1975), the total N_2O emission from unfertilized soils of this climatic region may account for 3 Tg N_2O–N/yr. Correspondingly, the N_2O emission from soils of temperate climates (area 45×10^6 km^2) applying an average N_2O emission rate of 4 μg N_2O–N/m^2/h is calculated to be 1.5 Tg/yr so that the total N_2O flux from unfertilized soils may be as high as 4.5 Tg N_2O–N/yr.

Fertilization resulted in an increase of the N_2O emission rates reaching maximum values of 850 μg N_2O–N/m^2/h on the grass lawn fertilized with NH_4NO_3 and values up to 200 μg N_2O–N/m^2/h on the cultivated land fertilized with urea. In the case of regularly sprinkled humid soil of the grass lawn, the maximum N_2O emission rates were observed 6 h after fertilization. Two days later, the N_2O emission rates reached background values indicating that nitrification and/or denitrification of mineral fertilizer nitrogen had approached completion. This might be due to either the nitrogen uptake by the grass vegetation or by microorganisms associated with rhizosphere or by the leaching of nitrogen out of the root zone. The influence of vegetation and rhizosphere on denitrification and, thus, on the N_2O production, has recently been discussed by Firestone (1982) and Knowles (1982). Tiedje (1982) has pointed out that denitrification rates in the rhizosphere are only high as long as high nitrate concentrations are present. As soon as nitrate concentrations are low, the denitrification rates are much lower on vegetated than on unplanted soils. This finding is consistent with our observations of lower N_2O emission rates at the grass lawn relative to those at the cultivated land under unfertilized conditions.

In the case of cultivated land, the maximum N_2O emission rated did not occur until 13 days after fertilization with urea. This time lag may be caused by the low soil moistures which were generally lower than 5% and thus low denitrification and nitrification activities. Another explanation may be the gradual degradation of the applied urea by urea to NH_3 (Mulvaney and Bremner, 1981) that is necessary to initiate nitrification. A similar delay of fertilizer induced N_2O emission after treatment with urea was observed by Mosier *et al.* (1981) and Duxbury *et al.* (1982).

The loss of mineral fertilizer–nitrogen as N_2O obtained from the measurements in Andalusia varied between 0.04 and 0.075% for application of ammonium nitrate and 0.18% for application of urea. The higher loss rates by application of urea may be due to the hydrolysis of urea into NH_3 that increases the alcalinity and cation binding capacity of the soil (Boomsma and Pritchett, 1979) and thus stimulates nitrification and N_2O production (Bremner and Blackmer, 1981). Although the climatic conditions in Andalusia and Germany are quite different, the loss of mineral fertilizer-nitrogen as N_2O measured in both regions agree reasonably well with values of 0.04–0.18% for Andalusia and 0.01–0.38% for Germany (Conrad *et al.*, 1983). Based on these observations, it might be possible that the total loss of mineral fertilizer-nitrogen, as N_2O does not strongly depend on the climatic conditions. This would mean that the values of 0.01–2% as proposed by Conrad *et al.* (1983) for different types of mineral fertilizers, different application rates, and different forms of application may be representative for global conditions. In this case, the total source strength of fertilizer-derived N_2O would be in the range of 0.015–2.2 Tg N_2O–N/yr for present conditions.

Summing up, we receive a total N_2O emission of 4.5–7.7 Tg N_2O–N/yr from unfertilized and fertilized soils. Because of the limited data basis, the given figure is rather preliminary, but indicates that the soils may provide 50% of the N_2O source rate presently estimated to be 8–15 Tg N_2O–N/yr (Schmeltekopf *et al.*, 1977; Johnston *et al.*, 1979).

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MIDWEST RESEARCH INSTITUTE
PROJECT DEVELOPMENT SKETCH

TITLE Reference 12. R. Slemr et. al. J. Atmos Chem (1)

(2pgs)

PROJECT NO. 6500-3513 fert DRAWN Mmes J APPR. ______ DATE 9-17-92

1. Fertilizers: barren 0
   grass 75 kg N/ha NH_4NO_3 previously
   all tests at $\boxed{100\ kg/N\ ha}$ - Urea, NH_4NO_3
2. Pollutant: N_2O

3. Emissions (from abstract

Field	Range	Location
Barren, unfertilized	4-35 μg N/m²hr $\bar{x}$ = 15 μg N/m²hr	p. 161 last para
Barren, urea	total = 0.18% @ N_2O	p. 164 last para
Barren, NH_4NO_3	total = 0.04% @ N_2O	"
Grass, unfert.	$\bar{x}$ = 1 μg N/m²hr (from abstract)	
Gras, NH_4NO_3	total = 0.075% as N_2O	p. 167 last para

Convert % N_2O to g N_2O/ha

(a) $\text{emissions} = \frac{1\%\ N_2O/ha}{100\%} \times 100\,kg\ \cancel{N}/ha \times \frac{1000\,g\ \cancel{N}}{1\ \cancel{kg\ N}} \times \frac{44\,g\ N_2O}{\cancel{14\,g\ N}} = 3143\ \frac{g}{ha}$

(b) $EF = \frac{\text{emissions}}{\text{rate}}$ (c) $EF_{day} = \frac{EF}{\#\ days}$

$\boxed{\text{Barren urea}}$

$$\text{Emissions} = \frac{0.18\%}{100\%} \times 100\ kg\ N/ha \times \frac{1000\,g\ N}{kg\ N} \times \frac{44\,g\ N_2O}{14\,g\ N} = 566\ g\ N_2O/ha$$

$$EF = \frac{566\,g\ N_2O/ha}{100\ kg\ N/ha} = 5.66\ g\ N_2O/kg\ N$$

$$EF_{day} = \frac{5.66\ g\ N_2O/kg\ N}{30\ day} = 0.189\ g\ N_2O/kg\ N\ day$$

MRI-18

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PROJECT NO. 6500-3513 DRAWN Mewey APPR. DATE 9-17-92

Barren NH_4NO_3

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$$\text{Emissions} = \frac{0.04\%}{100\%} \times 100\ \text{kg N/ha} \times \frac{1000\ \text{g N}}{\text{kg N}} \times \frac{44\ \text{g}\ N_2O}{14\ \text{g N}} = 126\ \text{g}\ \frac{N_2O}{\text{ha}}$$

$$EF = \frac{126\ \text{g}\ N_2O/\text{ha}}{100\ \text{kg N/ha}} = 1.26\ \text{g}\ N_2O/\text{kg N}$$

$$EF_{day} = \frac{1.26\ \text{g}\ N_2O/\text{kg N}}{30\ \text{days}} = 0.042\ \text{g}\ N_2O/\text{kg N day}$$

Grass NH_4NO_3

$$\text{Emissions} = \frac{0.075\%}{100\%} \times \frac{100\ \text{kg N}}{\text{ha}} \times \frac{1000\ \text{g N}}{\text{kg N}} \times \frac{44\ \text{g}\ N_2O}{14\ \text{g N}} = 236\ \text{g}\ \frac{N_2O}{\text{ha}}$$

$$EF = \frac{236\ \text{g}\ N_2O/\text{ha}}{100\ \text{kg N/ha}} = 2.36\ \text{g}\ \frac{N_2O}{\text{kg N}}$$

$$EF_{day} = \frac{2.36\ \text{g}\ N_2O/\text{kg N}}{10\ \text{day}} = 0.236\ \text{g}\ N_2O/\text{kg N day}$$

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Factors Influencing the Loss of Fertilizer Nitrogen Into the Atmosphere as N_2O

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In 1979–1981, experiments were carried out at four field stations near Mainz, Germany, to determine the loss of fertilizer nitrogen into the atmosphere as N_2O. Evolution rates from the soil into the atmosphere were measured by using the closed chamber technique. An automatic sampling and analyzing device was developed which allowed frequent determinations of N_2O evolution rates (one every 1.5 hours). The N_2O production rates were correlated to the surface soil temperature according to the Arrhenius equation and showed a diurnal rhythm with amplitudes reaching, sometimes, 1 order of magnitude. It seems that most of the N_2O emitted into the atmosphere is produced in the uppermost soil layer. N_2O evolution was stimulated by rain and increased with increasing soil moisture content. Application of fertilizer caused a dramatic increase of N_2O evolution rates with values up to 1000 μg N_2O–N $m^{-2}h^{-1}$. The magnitude of the fertilizer-induced N_2O evolution rates was dependent on the type, the application form, and the amount of fertilizer used. The total loss of fertilizer nitrogen as N_2O was in the range of 0.001 to 0.94%. Based on these figures, as well as on data from the literature, the total source strength of mineral fertilizers for atmospheric N_2O is calculated to 0.02 to 8 Tg N_2O–N yr^{-1}.

Introduction

The possible impact of the increased usage of mineral nitrogen fertilizers on the stratospheric ozone layer and on the climate has attracted a great deal of scientific and public attention. It has been proposed that fertilizer-derived N_2O may result in an increase of tropospheric N_2O, which in turn may be an important factor in the destruction of the stratospheric ozone layer [*Crutzen*, 1970, 1981; *McElroy et al.*, 1976; *Liu et al.*, 1977] and in the construction of a 'greenhouse effect' [*Wang et al.*, 1976; *Donner and Ramanathan*, 1980]. An increase of the tropospheric N_2O mixing ratio by approximately 0.2% per year was recently reported by *Weiss* [1981], who attributed this increase to the anthropogenic N_2O production by combustion of fossil fuel and application of mineral fertilizer. As a result of the increased usage of fossil fuel and mineral nitrogen fertilizers, a further increase of the N_2O mixing ratio in the atmosphere is predicted. The quantity of this increase can only be obtained if we know the N_2O production that is caused by the application of mineral fertilizer. This parameter is still subject to great debate. Data published so far indicate that N_2O production rates from mineral fertilizer vary between 6–100 Tg N_2O–N yr^{-1} [*McElroy et al.*, 1977; *Hahn and Junge*, 1977] and 0.004–1.2 Tg N_2O–N yr^{-1} [*Conrad and Seiler*, 1980]. This paper presents new data on the N_2O loss rate caused by application of mineral fertilizer, and they confirm the lower number.

N_2O flux from soil into the atmosphere has traditionally been ascribed to denitrification processes [*Garcia*, 1975; *Delwiche and Bryan*, 1976]. Hence, earlier N_2O loss rates caused by fertilizer application were calculated from denitrification rates and the relative amounts of N_2O to the other denitrification products [*Hahn and Junge*, 1977]. It is known, however, that N_2O is only an intermediate in the denitrification process [*John and Hollocher*, 1977] so that only part of the N_2O is released into the atmosphere. The rest is reduced in the soil to N_2 as the end product. The ratio of N_2O/N_2 as products of denitrification depends on soil environmental conditions, e.g., pH, redox potential, concentrations of oxidizable carbon, oxygen, nitrate, etc. [*Focht*, 1974; *Blackmer and Bremner*, 1978; *Firestone et al.*, 1979, 1980; *Terry and Tate*, 1980; *Letey et al.*, 1980*a*, *b*, 1981; *Betlach and Tiedje*, 1981]. Under anaerobic conditions, N_2O may even act as the main electron acceptor for denitrification so that these soils may even represent a sink for atmospheric N_2O [*Blackmer and Bremner*, 1976]. Recently, it has been shown that N_2O is also formed during nitrate dissimilation by nondenitrifying microorganisms [*Smith*, 1982; *Smith and Zimmerman*, 1981] and during nitrification by *Nitrosomonas* [*Yoshida and Alexander*, 1970; *Ritchie and Nicholas*, 1972; *Blackmer et al.*, 1980; *Goreau et al.*, 1980; *Lipschultz et al.* 1981]. The latter process was found to be especially important for N_2O evolution from well-aerated soils [*Bremner and Blackmer*, 1978, 1979, 1980, 1981] and for the loss of fertilizer nitrogen into the atmosphere as N_2O [*Conrad and Seiler*, 1980; *Breitenbeck et al.*, 1980; *Seiler and Conrad*, 1981*a*, *b*]. At the moment, it is impossible to evaluate the relative contribution of these processes to the total N_2O evolution from soils into the atmosphere. Therefore, it is also impossible to deduce reliable N_2O loss rates of fertilizer nitrogen from the measurement of denitrification or nitrification rates.

In order to obtain reliable figures for the fertilizer-induced N_2O emission into the atmosphere, the N_2O evolution rates must be measured directly under field conditions. In the last few years, field studies have been undertaken by a number of investigators [*McKenney et al.*, 1980*a*; *Ryden and Lund*, 1980; *Ryden*, 1981; *Breitenbeck et al.*, 1980; *Bremner et al.*, 1981*a*, *b*; *Cochran et al.*, 1981; *Mosier and Hutchinson*, 1981; *Mosier et al.*, 1981, 1982; *Conrad and Seiler*, 1980; *Seiler and Conrad*, 1981*a*]. N_2O evolution rates were generally obtained by placing sampling devices randomly on farmland treated with mineral fertilizers. Data obtained by this procedure show a high variation of the N_2O evolution rates, which are explained by the spatial variability resulting from inhomogeneous soil conditions caused by normal farming practice, e.g., plowing, sowing, fertilizing, irrigating, etc.

These problems are largely solved by restricting the treatments to those places where the sampling devices are installed. The data obtained at these places are then compared with those obtained at untreated controls [*Conrad and Seiler*, 1980; *Seiler and Conrad*, 1981*a*]. This approach is certainly less close to the normal farming management of a field but has the advantage

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TABLE 1. Characteristics of Field Stations and Soils

						Corn Fractions, %wt			
Field Station	Vegetation	Soil Type	ph, 0.1 N KCl	$CaCO_3$, % wt	Organic C, % wt	Clay, <2 μm	Silt, 2–20 μm	Fine Sand, 20–200 μm	Coarse Sand, 200–2000 μm
LPS, Mainz	Beet field, plants removed	Loess, brown soil	7.1	7.5	0.5	15	26	51	8
Finthen, Mainz	Meadow, grass	Loess pararendzina	7.4	2.0	0.8	20	21	56	3
MPI 1, Mainz	Lawn, grass, clover	Loess, unspecified	7.3	7.6	2.0	20	20	48	12
MPI 2	Lawn, grass	Loess, unspecified	7.3	4.1	2.6	15	15	51	19

that the measured N_2O evolution rates can be directly correlated to the type of treatment. It further allows one to make sure that the spatial variability in N_2O evolution between the experimental soil plots is insignificant for the interpretation of the results. In addition, this approach allows the application of an automatic device to the continuous measurement of N_2O evolution rates. This device provides more data during the observation period and gives better information on the temporal variation of N_2O evolution rates and allows the detection of diurnal variations and the correlation to soil temperature and soil moisture. This experimental approach has been used for determining the loss rates of fertilizer nitrogen into the atmosphere as N_2O; these are reported in this paper.

EXPERIMENTAL

The measurements were carried out in 1979–1981 at different field stations near Mainz, Germany. The main characteristics of the field stations as well as the principal physical and chemical properties of the soils are summarized in Table 1. The areas at the Landespflanzenschutzamt (LPS) were used intensively for agricultural purposes and managed in rotation by farming sugar beet, white beet, barley, and white beet. During the observation period, the field was planted with white beet. The young plants had been removed before the installation of the sampling devices, so that the soil was actually barren. Measurements of N_2O evolution rates at natural, agriculturally unused areas were carried out on a meadow (Finthen), which was kept under natural conditions except for cutting the grass twice a year. Additional measurements were carried out on areas close to the MPI (Max Planck Institute) that were covered by a grass lawn or by clover *(Trifolium hybridum)*. The experimental site MPI 1 remained in its original state; at MPI 2, the grass cover was removed during the observation period by cutting all green parts short above the soil surface.

Each field station consisted of several soil plots with an area of approximately 800 cm^2. Each plot was enclosed by a rectangular stainless steel frame pressed into the soil to a depth of approximately 10 cm. The physical structure of the soil inside the frame was not influenced by this procedure. First measurements were started at least 1 month after installation of the frames. The soil surface temperature was recorded by using temperature probes (iron-constatan) inserted into the soil (approximately 3 to 5 mm depth) of the soil plot. The bulk soil moisture content (g H_2O per 100 g moist soil) of the upper 10-cm layer of the soil profile was determined gravimetrically from soil samples taken at the surrounding area that had been treated in the same way as the experimental soil plots. Data on rainfall were provided by the meteorological station of the Landespflanzenschutzamt (LPS). These data are assumed to be representative for all field stations located within a distance less than 4 km from the LPS station.

The procedure for discontinuous determinations of the N_2O evolution rates has already been described in detail by *Conrad and Seiler* [1980] and *Seiler and Conrad* [1981*a*]. Using this technique, the soil plot was covered with a glass box ($V = 8$ l) which fit tightly into the stainless steel frame that had been pressed into the soil. The glass box was not shaded from sunlight during the experiment. The change of soil surface

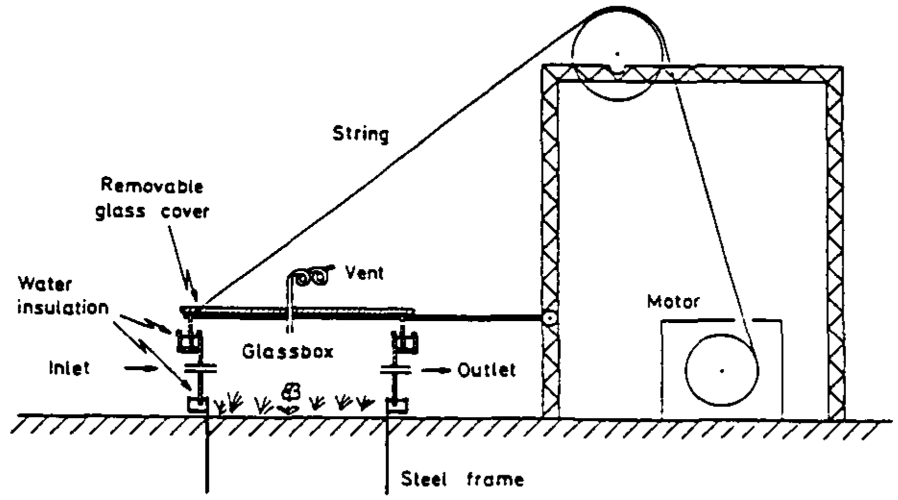

Fig. 1. Setup of the automatic system opening and closing the individual glass boxes for N_2O flux measurements.

temperature inside the glass box was identical to that outside. Shading the box generally caused a significant decrease of the inside soil surface temperature relative to the outside soil surface temperature, particularly during sunny days, and thus may result in untypical soil temperature records. The glass box contained a vent consisting of a glass coil (length = 20 cm, inner diameter = 3 mm) to ensure equilibration of the air pressure inside and outside the box. Gas samples (10 ml) from inside the box were taken by means of syringes at time intervals of 10 min. After the observation period of 1 hour, the cover was removed, exposing the soil plot to natural conditions. Generally, one flux rate per plot and day was measured in the morning (9 to 11 A.M.). Occasionally, an additional measurement was carried out in the afternoon (1 to 3 P.M.: LPS, spring 1980).

A better data base was obtained after an automatic device, illustrated in Figure 1 and 2, became available. In this system, up to three soil plots were equipped with glass boxes ($V = 8$ l) which could be sealed on top with removable glass covers (Figure 1). The glass boxes were closed alternatively for a period of approximately 1 hour, which is necessary for the determination of one N_2O evolution rate. For the rest of the time the glass boxes remained open to expose the soil surface to normal environmental conditions. The time sequence and the length of the observation period was given by an automatic timer which switched the removable glass covers, the valves, the gas chromatograph, etc. Figure 2 illustrates the flow scheme of the air when the N_2O evolution rates were determined at two soil plots. At the beginning of the measurement period, box 1 is closed and box 2 is open. During this time, the air is taken from box 1 by means of a metal bellows pump at a constant flow rate of 0.2 l min^{-1} and is recycled into the glass box. The airstream is passed through a refrigerator (−70°C) to remove the water vapor and subsequently is passed through the sampling loop ($V = 7$ ml) of the gas chromatograph. A gas sample is injected into the gas chromatrograph (GC) once every 9 min. After measurement of seven consecutive samples, corresponding to a time interval of 63 min, the GC is calibrated twice by opening S3 and S4, supplying the GC with a calibration standard. Subsequently, the selenoid valve S1 is closed, and S2 is opened. During this operation mode, the airstream passes through the open box 2 so that the sampling loop is supplied with ambient air. Then, box 1 is opened, and box 2 closed. A new sampling and analyzing cycle starts with the first sample being injected 9 min after the box has been closed. The whole system was tested regularly for possible leakages by comparing the data obtained via the automatic sampling system to those obtained from samples taken simultaneously by syringes.

The air samples were analyzed in a Perkin Elmer F22 gas chromatograph equipped with a ^{63}Ni electron capture detector and a stainless steel separation column (length, 4 m; diameter, 3.175 mm) filled with Porapac N. The time for one analysis was 6 min. Interferences by CO_2 were avoided by passing the air sample through Natron asbestos, which reacts quantitatively with CO_2 but does not change the N_2O content of the sample.

The N_2O evolution rate is calculated by using the slope of the temporal N_2O increase within the closed box. With N_2O measurements of 0.5 to 1% precision at the 300 ppbv level, an increase of the N_2O mixing ratio inside the glass box of 1.5 to 3 ppbv N_2O, corresponding to N_2O evolution rates of 0.2 to 0.4 μg N_2O-N m^{-2} h^{-1}, could be determined. The automatic system allowed the determination of one N_2O evolution rate every 1.5 hours. Using two soil plots, a semicontinuous measurement of N_2O evolution rates with a resolution time of 3 hours for each plot is possible.

Field experiments at the stations were carried out by defined treatments of the soil plots. One plot was treated as control. The other plots were used for the experiments studying the dependence of the N_2O flux rates on different types and amounts of fertilizers, on different forms of application, and on the vegetation cover. The spatial variability in N_2O evolution rates between the different soil plots was determined during the 1 to 2 weeks prior to the experiments. The spatial variability was insignificant compared to the effect of fertilization, so that we could conduct the experiments without replicates. Loss rates of applied N fertilizer as N_2O were determined by subtracting the N_2O evolution rates determined for the control plot from those determined for the fertilized plots, both integrated over the observation period. The observation period ended after the N_2O evolution rates observed at the fertilized plots had reached the value observed at the control plot.

Based on a fertilizer application rate of 100 kg N ha^{-1}, and assuming a total observation period of 1 month, the lowest detectable N_2O loss rate is 0.001 to 0.002% of the applied nitrogen.

RESULTS AND DISCUSSION

Field Measurements of N_2O Evolution Rates

Results of measurements carried out in 1979–1981 at the different field stations near Mainz are shown in Figures 3–7. The figures show the temporal change of the N_2O evolution rates obtained at the individual soil plots during the observation period and include the data on soil surface temperature, soil moisture content, and rainfall.

Prior to each experiment, the N_2O evolution of the individual, untreated soil plots of the experimental station had been determined for 2 to 3 weeks. The evolution rates of the unfertilized individual plots showed similar absolute values and similar trends with time. In none of the experiments did the values differ by more than a factor of 4. This observation contradicts results published by *Matthias et al.* [1980], who found high spatial variabilities of the N_2O evolution rates with values differing by more than a factor of 100. So far, we have no explanation for the different observations. However, it is possible that the low spatial variability observed at our field stations is due to particularly homogeneous soil conditions.

After application of fertilizer (100 kg ha^{-1}), a dramatic increase of the N_2O evolution rates, with maximum values approximately 1 to 2 days after fertilization (Figures 4–7), was observed. An exception was the experiment carried out at station LPS in April/May 1980 (Figure 3). In this case the maximum was delayed by 5 days, most probably because of the specific soil conditions during the experiment, with relatively low soil temperature and soil moisture content.

The elevated N_2O evolution rates persisted over a period of several days and finally reached the background rates of the unfertilized control again. The N_2O evolution rates often showed a second maximum with lower absolute values, when the soil moisture was increased by heavy rainfall (Figures 4 and 5). Further rainfall did not cause any significant change of the N_2O evolution rate (e.g., Figure 4). Apparently, at that time, the fertilizer was already depleted in the upper soil layers, where most of the N_2O emitted into the atmosphere is produced [*Seiler and Conrad*, 1981*a*]. In deeper soil layers the fertilizer-induced N_2O production may still have continued or may even have been enhanced by the additional nitrogen washed down from the surface. The N_2O produced in those deeper layers, however, may not reach the atmosphere because of N_2O consumption reactions in the upper soil layers. This conclusion is

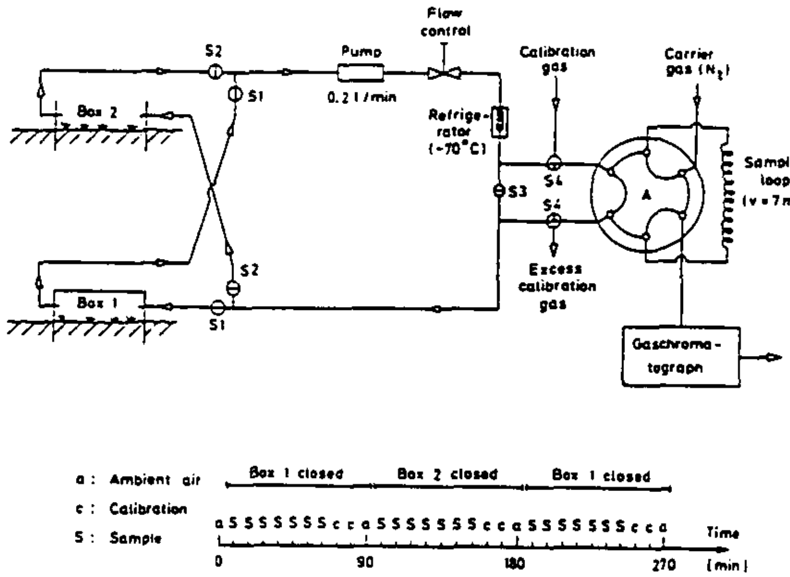

Fig. 2. Flow scheme of the automatic sampling and analysis system. Valve A is a six-port gas-sampling valve: valves S1 to S4 are selenoid valves.

in agreement with long-term measurements by *Seiler and Conrad* [1981*a*], which showed the highest N_2O mixing ratios in deeper layers of fertilized soil after the N_2O evolution rates at the surface had already returned to background rates.

Influence of Soil Temperature on N_2O Evolution

The N_2O evolution rates were dependent on the soil temperatures. Figure 3 shows N_2O evolution rates observed in spring, when soil temperatures varied considerably because of the rapidly changing weather situation. Although only two measurements were carried out per day, one clearly recognizes a strong positive correlation between the soil temperature and the N_2O evolution rates. Sometimes, the afternoon values exceeded the morning values by a factor of 10 when the soil temperature increased from 9 to 20°C.

The data obtained by the automatic technique demonstrated the existence of a diurnal rhythm of the N_2O evolution (Figures 5–7), which coincided with the diurnal variation of the soil surface temperature. The maximum rates were generally observed at 3 to 4 P.M. and the minimum rates in the early morning at approximately 6 A.M. There was no time lag between the maximum and minimum rates of N_2O evolution, and the maximum and minimum soil temperatures measured in 3 to 5 mm depth, indicating that most of the emitted N_2O was produced in the uppermost soil layers. Otherwise, N_2O evolution rates should be behind the measured soil temperatures, since the temperature maxima and minima occur progressively later with increasing soil depth. Our observations are in agreement with those reported by *Denmead* [1979] and *Denmead et al.* [1979], who found similar diurnal variations on a fertilized grass sward. Our results are not in agreement, however, with most of the observations recently reported by *Blackmer et al.* [1982]. These authors observed diurnal changes in N_2O evolution that were not in phase with the soil temperature measured in 2 cm depth but were 2 to 12 hours behind. They concluded that most of the emitted N_2O was produced in soil layers significantly lower than 2 cm depth and proposed that the diurnal N_2O emission patterns should be attributed to diurnal changes in the solubility of N_2O in soil water caused by the changing soil temperature profile. We have to assume that the differences in observations reported by *Blackmer et al.* [1982] from those reported by us or by *Denmead et al.* [1979] are due to differences in soil conditions.

Diurnal variations of N_2O evolution rates were observed on unfertilized as well as fertilized soil plots. However, the ampli-

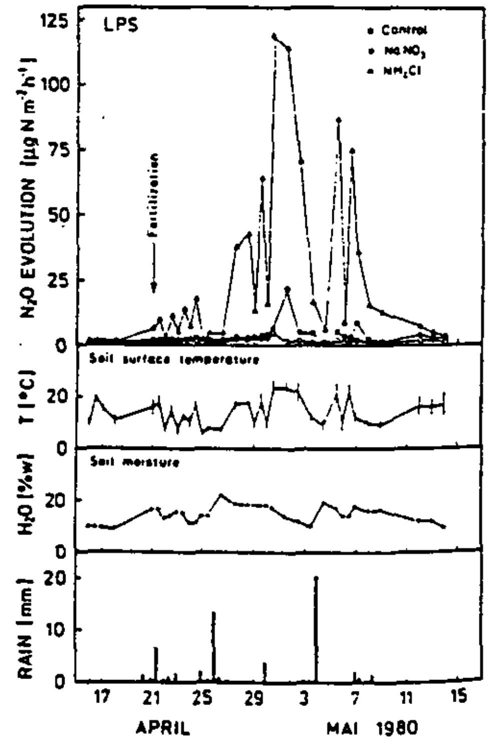

Fig. 3. N_2O evolution rates observed on fertilized and unfertilized (control) soil plots at the field station LPS. The fertilizers were applied as aqueous solution at a rate of 100 kg N ha^{-1}. The amount of water applied was added to the amount of rainfall observed on this day.

tudes were generally higher on fertilized than on unfertilized soil plots. Our measurements indicate that the amplitude of the diurnal variation was also influenced by the presence of a vegetation cover. The amplitudes were relatively small on the field plot with dense grass vegetation, but increased considerably after the grass had been cut (Figures 5 and 6). Since the removal of grass had no significant influence on the amplitude of soil temperature measured in 3 to 5 mm depth, we assume that most of the N_2O emitted into the atmosphere must have originated from the uppermost soil layer, where the solar radiation may have created a higher amplitude of temperature change after the vegetation cover had been removed. Other explanations could be the altered exchange rate of N_2O at the soil air interface, the altered soil water status affecting N_2O production, as well as temperature-induced changes in solubility of N_2O or direct influences of vegetation's metabolism on N_2O production.

The activation energy E_a of the N_2O evolution process is calculated by using the logarithmic form of a modified Arrhenius equation in which the reaction rate k is replaced by the N_2O evolution rate v, assuming a zero-order process:

$$\ln v = -\frac{E_a}{R}\frac{1}{T} + \text{const.}$$

The analysis of the data obtained during the semicontinuous measurements of the N_2O evolution rates (Figures 5–7) in fact demonstrated the linear correlation between ln v and $1/T$ for most of the days (Table 2). In Figure 8 an example of the N_2O evolution rates and soil temperatures observed on September 4, 1981, on a soil plot fertilized with NH_4Cl shows an activation energy for N_2O evolution of $E_a = 76$ kJ mol^{-1}. The linear correlation between ln v and $1/T$ has been found for each of the soil plots independently of the fertilization or the type of fertilizer. This result indicates that the diurnal patterns of N_2O evolution were mainly due to the temperature-induced changes in N_2O production rather than to the temperature-induced changes in solubility of N_2O in soil water as proposed by *Blackmer et al.* [1982]. In the latter case the N_2O evolution rates should be directly proportional to soil temperature and should not follow the Arrhenius correlation.

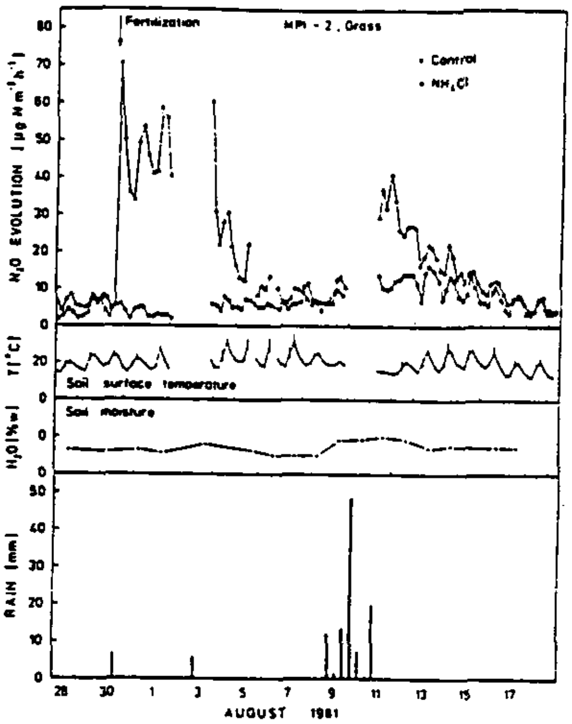

Fig. 5. N_2O evolution rates observed at field station MPI 2 using the automatic sampling and analysis system. The soil plots were covered with grass. NH_4Cl was applied as solution at a rate of 100 kg N ha^{-1}.

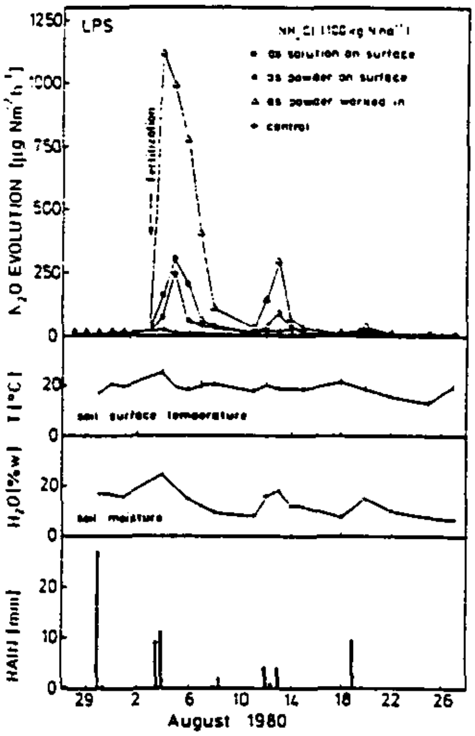

Fig. 4. Influence of form of application of fertilizer (NH_4Cl: 100 kg N ha^{-1}) on N_2O evolution rates. The experiments were carried out at field station LPS.

Table 2 summarizes the mean values of the activation energies determined for the individual days with significant correlation. Although different types of fertilizer had been used, the mean values of the activation energies (61 to 76 kJ mol^{-1}) agree reasonably well and are similar to the values (76–83 kJ mol^{-1}) calculated from Q_{10} values reported by *Denmead et al.* [1979]. The individual activation energies, however, show high variations, indicated by the large standard deviations summarized in the last column of Table 2. In fact, the activation energies sometimes changed from day to day, covering a range between 20 and 150 kJ mol^{-1}. It is interesting that this range is similar to the range of activation energies (28 to 166 kJ mol^{-1}) reported for microbial denitrification and nitrification [*Focht and Verstraete*, 1977; *McKenney et al.*, 1980*b*]. Focht and Verstraete reviewed reports showing that the activation energy of nitrification and denitrification are dependent on soil environmental factors such as pH, oxygen concentration, and nitrogenous substrate concentrations. Hence, it is possible that the high variability of the activation energies for N_2O evolution observed by us may be due to temporal changes of soil conditions at the microsites where microbial N_2O production occurs.

It is also possible, however, that the microbial N_2O pro-

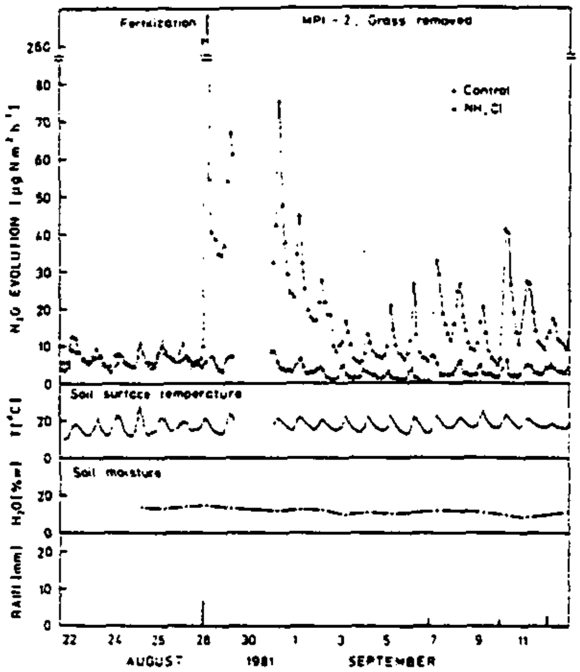

Fig. 6. N_2O evolution rates observed at field station MPI 2 using the automatic sampling and analysis system. After finishing the experiments shown in Figure 5, the grass was removed by cutting the stalks just above the soil surface and keeping it short subsequently. Then, the experiments shown in Figure 5 were repeated.

duction activities in the individual soil layers change with time, resulting in a change of their relative contribution to the overall N_2O evolution into the atmosphere. Since the amplitude of the diurnal changes in soil temperature decreases with increasing soil depth, the correlation of the N_2O evolution rates with soil temperatures measured in increasing soil depths would result in increasing activation energies. If we assume a constant activation energy for the microbial N_2O production processes in all soil layers, the observed variations in the activation energies for N_2O evolution would reflect the variations in the relative contribution of different soil layers to the N_2O evolution. This conclusion is only valid, however, when the changes of microbial activity occurred in the upper few centimeters of the soil profile, since otherwise N_2O evolution rates would not have been in phase with the soil temperature.

The strong dependency of the N_2O evolution rates on soil temperature clearly demonstrates that reliable N_2O loss rates caused by mineral fertilizer application can only be determined by repeated measurements per day. Estimates of N_2O evolution rates based on single measurements per day may differ by more than 1 order of magnitude from the actual value.

Influence of Soil Moisture on N_2O Evolution

N_2O evolution was influenced by rainfall. This influence can be recognized from Figures 4, 5, 6, and 7, showing coincidences of rain with elevated N_2O evolution rates. This is particularly true for the fertilized soils, where the increased soil moisture content stimulated the N_2O production at times when the rates had already decreased toward background values. The extent of stimulation decreased successively from rainfall to rainfall (Figure 4), approaching the conditions observed on unfertilized soil plots.

The influence of rain is very pronounced after relatively long periods of dryness. Under these conditions, even small amounts of rain (September 7 and 10, 1981, Figure 6) that did not cause any significant increase of the average soil moisture content of the upper 10 cm of the soil profile resulted in a stimulation of N_2O production. This observation again indicates that the processes inducing the evolution of N_2O into the atmosphere must be located in the uppermost soil layers [*Seiler and Conrad*, 1981*a*].

Figure 9 illustrates the influence of the soil moisture content on the N_2O evolution rates at an unfertilized soil plot. In this figure, the average daily N_2O evolution rates are plotted against the soil moisture contents determined within the upper 10 cm of the soil profile. Each data point is normalized to a constant average daily soil temperature of 20°C by using the Arrhenius correlation. The data were obtained from the measurements at the control plot of the field station MPI 2 (compare Figures 5–7) before and after removal of the grass cover. The soil moisture contents ranged between 8 and 22% (g H_2O per 100 g moist soil). Within this range the N_2O evolution rates increased dramatically with increasing soil moisture. At a soil moisture content of 20% the N_2O evolution rates were 3 to 10 times higher than at a soil moisture content of 10%.

Similar correlations of N_2O evolution rates with soil moisture contents were observed at other unfertilized control plots. At present the data base is too small to calculate a quantitative relation between the N_2O evolution rates and the soil moisture contents. However, our results support the observations of a positive correlation between N_2O evolution, rainfall, and soil moisture [*Denmead et al.*, 1979; *Ryden and Lund*, 1980; *Mosier and Hutchinson*, 1981; *Mosier et al.*, 1981; *Terry et al.*, 1981].

The effect of rainfall and increased soil moisture on N_2O evolution may be due to several causes: The moistening of soil may increase the activity of soil microorganisms [*Wilson and Griffin*, 1975]; it may also increase their population density [*Lund and Goksoyr*, 1980]. These events may be especially important after long periods of dryness. The increased soil

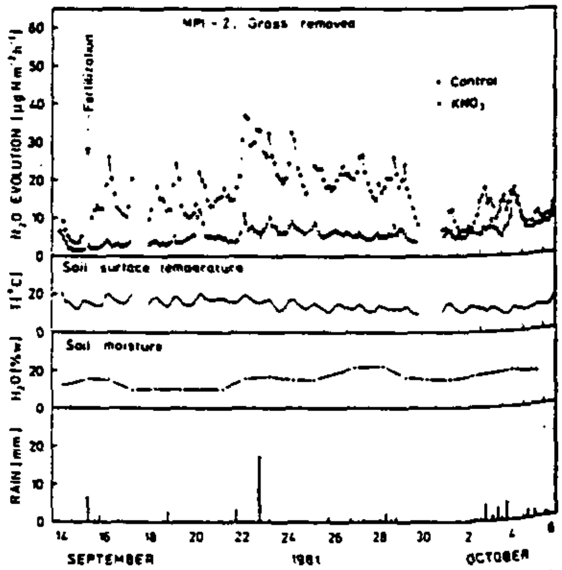

Fig. 7. N_2O evolution rates observed at field station MPI 2 using the automatic sampling and analysis system. After finishing the experiments shown in Figure 6, KNO_3 was applied as solution at a rate of 100 kg N ha⁻¹.

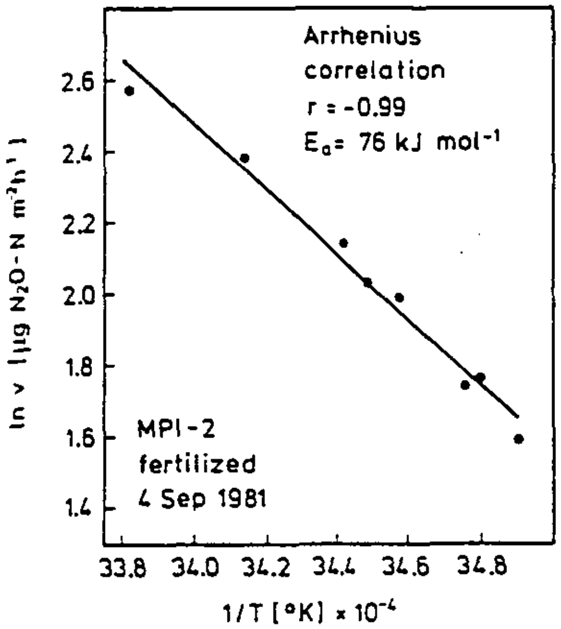

Fig. 8. Arrhenius correlation of the N_2O evolution rates (v) and the soil surface temperature (T). The data are taken from Figure 6.

moisture content may also stimulate the availability of dissolved nutrients by their transport to other soil sites. The availability of oxidizable organic matter, and of nitrate, is important for denitrification; the availability of ammonium is important for nitrification. The mobilization of nutrients by soil water may also cause an increased respiration rate of the heterotrophic microbial flora, that, in turn, may result in a reduction of the oxygen concentration in soil. Furthermore, the increased soil moisture content hinders the diffusion of oxygen into the soil, so that soil microsites with a small supply of oxygen may develop. Under these conditions, N_2O production by denitrification as well as by nitrification is stimulated (for discussion, see *Seiler and Conrad* [1981*b*]).

Influence of Fertilizer Type on N_2O Evolution

During our field experiments, we always observed that the N_2O evolution rates were strongly dependent on the type of nitrogen fertilizer. Application of nitrate usually caused significantly lower N_2O evolution rates than application of ammonium, although the temporal variations were similar (Figures 3, 6, and 7). This observation is in agreement with earlier observations [*Conrad and Seiler*, 1980; *Breitenbeck et al.*, 1980] and shows that nitrification of ammonium is an important process for N_2O production under field conditions. This conclusion is consistent with the results of laboratory experiments by *Bremner and Blackmer* [1978, 1979, 1980, 1981].

Only in one of our experiments the nitrate-induced N_2O loss rates were comparable to the ammonium-induced N_2O loss rates (Table 3). This experiment was carried out at the field station Finthen on a loess soil that had a small air-filled porosity (Table 1) and was covered by a dense grass layer. Hence, there is the possibility that this particular soil might have contained a relatively high number of anaerobic microsites caused by poor soil aeration, favoring the denitrificative N_2O production from nitrate.

The influence of the anion of the ammonium fertilizer on N_2O evolution was tested in an experiment carried out at field station MPI 2. One soil plot was treated with ammonium chloride and another with ammonium sulfate. The experiment was then repeated, but the first plot was treated with ammonium sulfate and the second with ammonium chloride. The N_2O evolution rates observed at the fertilized soil plots were almost identical, showing that ammonium-induced N_2O evolution rates were not affected by the counter anion. This experiment again showed that there was no significant difference in the pattern of N_2O evolution between the two soil plots that could be attributed to spatially nonhomogeneous soil conditions in our experiment.

Influence of Application Form and Amount of Fertilizer on N_2O Evolution

The N_2O evolution rates were strongly dependent on the forms of application of the fertilizer. This dependency is shown in Figure 4, which illustrates the results obtained by experiments using ammonium chloride as fertilizer. The ammonium salt was applied (1) as aqueous solution poured onto the soil surface, (2) as powder distributed onto the soil surface that had been moistened before fertilization, and (3) as powder worked into the upper 10 cm of the soil that had been moistened before. Case (1) represents the form of application used by us for the rest of the experiments. In each case we observed a temporal variation of N_2O evolution rates with maximum values 2 days after application. However, the absolute values were significantly different, with both the highest N_2O evolution rates (3) and the lowest values for form of application (2). Most interestingly, a second maximum had been observed approximately 10 days after fertilization, during a rainy period of several days, and consequently increased soil moisture contents. Surprisingly, however, the second maximum was only observed for application forms (1) and (3), but not for (2), when the fertilizer had been distributed as powder onto the soil surface. In this case a significant portion of the applied ammonium fertilizer was perhaps lost as a result of NH_3 volatilization.

TABLE 2. Correlation of N_2O Evolution Rates With Soil Temperature by the Arrhenius Equation

Soil Conditions MPI 2, 1981	Total Days With Semicontinuous Records	Days With Significant Correlation, $P < 0.05$	Mean Value of E_a, kJ mol^{-1}	Standard Deviation, kJ mol^{-1}
Unfertilized (July–October)	63	37 (59%)*	76	35
Fertilized with NH_4Cl (July–October)	38	28 (74%)	61	36
Fertilized with KNO_3 (September–October)	37	23 (62%)	70	27

*Percentage of total days.

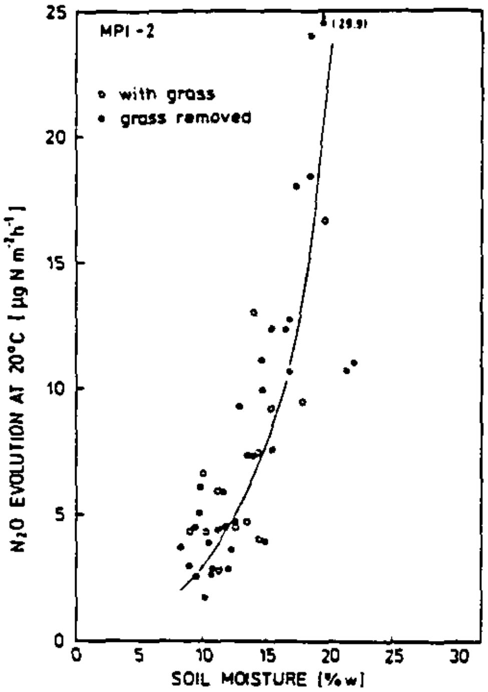

Fig. 9. Influence of the soil moisture content on the N_2O evolution rates. The data points represent average daily N_2O evolution rates observed at the unfertilized control plot of field station MPI 2 (Figures 5–7). The values have been normalized to a constant average soil surface temperature of 20°C by using the Arrhenius correlation.

The N_2O evolution rates were also influenced by the amount of fertilizer applied. Application of increasing amounts of NH_4Cl resulted in increasing N_2O evolution rates, but the change in N_2O evolution rates with time was similar for all fertilizer application rates. A positive correlation between amount of fertilizer applied and N_2O evolution rates has also been reported by *McKenney et al.* [1978; 1980*a*] for NH_4NO_3 and by *Cochran et al.* [1981] for anhydrous ammonia.

Most probably, the influence of amount and form of application of fertilizer is based on local concentrations of mineral nitrogen at soil microsites. Laboratory experiments did show an influence of the concentration of ammonium on the nitrificative N_2O production [*Bremner and Blackmer*, 1980, 1981]. Similar results were reported for the denitrificative N_2O production from nitrate [*Blackmer and Bremner*, 1978; *Firestone et al.*, 1979, 1980; *Terry and Tate*, 1980; *Letey et al.*, 1980*a*]. Therefore, one should assume that N_2O evolution rates would be correlated to the concentration of ammonium, nitrite, or nitrate in the soil. To date, however, field measurements have not revealed any significant correlation between N_2O evolution rates and simultaneously measured nitrate, nitrite, or ammonium concentrations (*Mosier and Hutchinson* [1981]; O. Heinemeyer, personal communication, 1982). We suggest that the effect of fertilizer nitrogen on N_2O evolution is exerted at small soil microsites in the uppermost soil layer; these sites are not analyzed appropriately for their actual concentration of mineral nitrogen when bulk samples of the upper centimeters of the soil profile are taken for the analysis.

Loss Rates of Fertilizer Nitrogen as N_2O

The previous chapters showed that N_2O evolution rates increase after mineral fertilizers have been applied, so there is no doubt that application of mineral fertilizers represents a source of atmospheric N_2O. The source strength and thus the impact of mineral fertilizers on the global N_2O budget can only be calculated if the loss rates of fertilizer nitrogen as N_2O relative to the total amount of applied fertilizer is known. These loss rates are obtained by subtracting the total amount P_0 of N_2O–N emitted from the unfertilized soil plot from that amount P_1 which has been obtained simultaneously from the fertilized soil plot and dividing this figure by the total amount M of the applied fertilizer nitrogen, i.e.,

$$L = \frac{P_1 - P_0}{M}$$

Values for P_1 and P_0 are obtained by integrating the N_2O evolution rates observed during a period of 20 to 30 days after fertilization. The total observation period, which is necessary to cover all N_2O evolution events caused by the fertilization, is dependent on the type of soil and the meteorological conditions. Care was taken that the elevated N_2O emission rates of the fertilized soil plot had returned to the background rates of the unfertilized control plot. Our observations did not provide a reasonable argument for a long-term influence of fertilization on N_2O evolution from soils. In none of our experiments did we observe increasing background rates as a result of repeated application of mineral fertilizer. Therefore, we may assume that

TABLE 3. Influence of Type of Fertilizer on the Total Loss of Fertilizer Nitrogen as N_2O

Field Experiment	Loss Rates, % of N applied Fertilizer Applied as Solution, 100 kg N ha^{-1}	
	$NaNO_3$	NH_4Cl
Finthen, Sep./Oct. 1979	0.073	0.053
LPS, Apr./May 1980	0.018	0.153
LPS, Aug. 1980		0.216
MPI 1, grass, Sep./Oct. 1979	0.007	0.025
MPI 1, grass, Aug. 1981	0.071	0.376
MPI 1, clover, Aug. 1981	0.001	0.065
MPI 2, Aug.–Oct. 1981	0.017*	0.070 (0.078)†

*KNO_3 instead of $NaNO_3$.
†Value in brackets: $(NH_4)_2SO_4$ instead of NH_4Cl.

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our field measurements carried out over time periods up to 33 days covered the total loss of fertilizer nitrogen as N_2O from the soil.

Table 3 summarizes the N_2O loss rates obtained at the different field stations for nitrate and ammonium fertilizer applied as aqueous solution. The N_2O loss rates ranged between 0.001 and 0.073% for nitrate and between 0.009 and 0.376% for ammonium fertilizers. Higher loss rates (0.94%) were only observed when ammonium fertilizer had been applied as powder and worked into the soil (Figure 5). In contrast, the loss rates were only 0.15% when the ammonium had been distributed as powder onto the soil surface. The loss rates were not significantly influenced by different amounts (50, 100, and 200 kg N ha^{-1}) of ammonium fertilizer being applied (Figure 6). The values given in this paper agree very well with those reported by *Denmead et al.* [1979], *Breitenbeck et al.* [1980], *Conrad and Seiler* [1980], *Mosier and Hutchinson* [1981], *Mosier et al.* [1981, 1982], *McKenney et al.* [1980*a*], and *Ryden* [1981], who found values ranging between 0.001 and 1.67%. Higher loss rates were only reported for some individual cases, e.g., after fertilization with anhydrous ammonia [*Bremner et al.*, 1981*a*], for manure-treated fields [*Rolston et al.*, 1978], and for heavily irrigated and fertilized land [*Ryden and Lund*, 1980]; these rates however, do not contribute significantly to the overall N_2O release. Therefore, we assume an N_2O loss rate from fertilizer nitrogen of 0.01 to 2.0% to be representative of global conditions.

Additional N_2O may be formed from the fraction of mineral fertilizer leached from the field into the groundwater or into surface freshwater ecosystems, where the fertilizer nitrogen could again induce an N_2O emission into the atmosphere. Lysimeter experiments using ^{15}N as a tracer indicate that the loss of fertilizer nitrogen by leaching ranges between 0.4 and 3.4% [*Vömel and Ewert*, 1981]. It has been shown that groundwater and freshwater may be substantially supersaturated with N_2O [*Kaplan et al.*, 1978; *Lemon and Lemon*, 1981]. However, it remains uncertain which fraction of the observed dissolved N_2O is due to seepage fertilizer or due to N_2O production during the natural cycle of nitrogen in freshwater ecosystems [*Knowles et al.*, 1981; *Vincent et al.*, 1981]. If we assume that the N_2O loss rate of the leached fertilizer nitrogen corresponds to the values observed at fertilized fields, the total loss rate of fertilizer N as N_2O would be as low as 0.01 to 4.0%.

Using this figure and the annual fertilizer production rate of 55 Tg N y^{-1} (value for 1980, UN Statistical Yearbook), the total source strength of fertilizer-derived N_2O amounts to 0.005 to 2.2 Tg N_2O–N yr^{-1}. This range is considerably lower than that of 6 to 100 Tg N_2O–N yr^{-1}, obtained from earlier estimates [*McElroy et al.*, 1977; *Hahn and Junge*, 1977], and is also below a recent estimate of 2.3 to 3.0 Tg N_2O–N y^{-1} [*Weiss*, 1981], which is based on theoretical calculations and the observation of an increase of the tropospheric N_2O mixing ratio.

Following the general assumption of a steady increase of the mineral fertilizer production up to a value of 200 Tg N in the year 2000, we have to assume a global production of fertilizer-derived N_2O of 0.02 to 8 Tg N_2O–N in the year 2000. This would contribute up to approximately 110% of the global natural N_2O budget, which is approximately 7 to 20 Tg N_2O–N yr^{-1} [*Crutzen*, 1983], and therefore, may have some impact on stratospheric ozone and on the climate. However, we have to emphasize that the figures of the fertilizer-induced N_2O emission are still uncertain, particularly because the experiments have been limited to developed and industrialized countries located in the higher latitudes. However, there is a trend toward an increasing fraction of the annually produced mineral fertilizer being used in the developing countries, generally located in warmer climatic zones and where N_2O loss rates have not been determined so far.

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APPENDIX G

REFERENCES 7 AND 8, ASSOCIATED HAND CALCULATIONS, AND SUPPORTING DOCUMENTATION

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TECHNICAL REPORTS

Atmospheric Dispersion of Ammonia During Application of Anhydrous Ammonia Fertilizer[1]

O. T. DENMEAD, J. R. FRENEY, AND J. R. SIMPSON[2]

ABSTRACT

There is a need to develop techniques for the prediction of the aerial spread of hazardous chemicals released in agricultural operations. The dispersion of ammonia (NH_3) gas during soil injection of anhydrous NH_3 is one such example. In previous work we established that after injection NH_3 escaped from the soil to the atmosphere at a rate that decreased exponentially with time; in our study the whole process took about 2 h. In this paper we combine the dynamics of the emission process with existing micrometeorological theory for atmospheric dispersion from line sources, to predict NH_3 concentrations in the air at the downwind edge of the field. The predictions are compared with concentrations measured during an injection operation.

Although the total NH_3 emission during the operation was only 1.2 kg/ha, NH_3 concentrations up to 213 $\mu g/m^3$ were recorded at the downwind edge in the early stages of injection. Wind speed and atmospheric stability had large influences on NH_3 dispersion. In light winds and stable conditions NH_3 concentrations >100 $\mu g/m^3$ were recorded when the applicator was >200 m upwind, and some NH_3 enrichment still occurred when it was 600 m upwind.

The model underestimates NH_3 concentrations when the treated width is <30 m, but predicts them very well at greater distances in both stable and unstable conditions. The model is used to predict NH_3 concentrations downwind of the applicator for a range of wind speeds and emission strengths.

The approach should prove useful not only for estimating NH_3 pollution hazards but also for predicting dispersion in related agricultural operations where a time-dependent decay and/or a line-source analogy are appropriate.

Additional Index Words: **atmospheric diffusion, atmospheric pollution, aerial spread, nitrogen loss.**

Denmead, O. T., J. R. Freney, and J. R. Simpson. 1982. Atmospheric dispersion of ammonia during application of anhydrous ammonia fertilizer. J. Environ. Qual. 11:568–572.

There is often a need to predict the aerial spread of hazardous chemicals released during applications of pesticides, herbicides, or fertilizers. In many cases the material is applied in rows or bands by continuous-applicator traverses. One such operation is the injection

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into the soil of anhydrous ammonia (NH_3) fertilizer, which results in the liberation of NH_3 gas to the atmosphere. Besides constituting a direct health hazard, NH_3 is involved in the formation of aerosols affecting health, visibility, corrosion, and precipitation processes and may contribute to N enrichment of water bodies (Hutchinson and Viets, 1969). In this paper, we report on the atmospheric dispersion of NH_3 gas during the injection of anhydrous NH_3 when the operation was proceeding at various distances up to 600 m away from the measuring point, and present a model for predicting NH_3 concentrations in the air at the downwind edge of the field. The model combines the dynamics of the emission process with existing micrometeorological theory for diffusion from line sources.

In usual practice, anhydrous NH_3 is injected in bands in the soil at a depth of 10–15 cm. The liquid boils and some NH_3 gas escapes to the atmosphere through the injection slits and soil cracks. This emission continues at a decreasing rate for some time after the initial injection (Denmead et al., 1977).

The emission pattern can thus be expected to have characteristics of both a moving, ground-level point-source, and a continuous, ground-level line-source, the former model accounting for crosswind dispersion associated with the initial NH_3 release and the latter for the downwind diffusion from the continuous line sources. The line-source releases will have an increasing influence on the concentrations at the downwind edge as the treated area grows; we have therefore chosen to examine the dispersion of NH_3 in terms of the simpler line-source solutions, bearing in mind that the analysis is likely to be less appropriate for the early stages of the injection operation.

METHODS

Experimental

The experimental layout, procedures, and methods of measurement during the first stages of the study have been described previously (Denmead et al., 1977). Briefly, anhydrous NH_3 was injected at a rate of 130 kg/ha into a bare, moist, clay soil (pH 8.2, total N 0.07%), 12 bands at a time (0.5 m apart), during each pass of an applicator that traversed the field across the wind, gradually working upwind. The mean injection depth was 0.12 m. Wind speeds, air temperatures, and NH_3 concentrations were measured at heights of 0.31, 0.74, 1.24, and 2.24 m at a point on the downwind edge of the field, midway along the track of the applicator. Wind directions were also recorded.

Sampling periods during the first stages of injection extended from the time the applicator passed directly upwind of the measuring point until just before it returned from the end of the field, 500 m away. The average time for one such traverse was 17 min. During the later stages of the experiment, the sampling periods were lengthened to embrace two, and then four, traverses.

Theoretical

The equation describing steady-state atmospheric diffusion in two dimensions is

$$\bar{u}(z)\frac{\partial \bar{c}}{\partial x} = \frac{\partial}{\partial z}\left[K(z)\frac{\partial \bar{c}}{\partial z}\right], \qquad [1]$$

where $\bar{u}$ is the mean horizontal wind speed at height, z; $\bar{c}$ the mean atmospheric NH_3 concentration in excess of the background level, a function of both height and distance from the source, x; and K the eddy diffusivity for vertical transfer (Sutton, 1953). Calder (1949) and Sutton (1953) have considered the diffusion from a single, crosswind line-source of infinite extent, emitting continuously at a steady rate. Both have based their analyses on power-law profiles for the variation of wind speed and eddy diffusivity with height, viz.,

$$\bar{u}(z) = u_1(z/z_1)^m \quad \text{and} \qquad [2]$$

$$K(z) = K_1(z/z_1)^n, \qquad [3]$$

where u_1 and K_1 are the values of $\bar{u}$ and K at a reference height, z_1. For convenience, z_1 may be set at unit height above the ground; in our case, at 1 cm. The empirical constants m and n are related to the aerodynamic roughness of the surface and the thermal stability of the atmosphere (Calder, 1949).

Throughout the paper we frequently refer to atmospheric stability, which we have specified by the Richardson number, Ri:

$$\mathrm{Ri} = g/T(\partial\overline{T}/\partial z + \gamma)/(\partial\bar{u}/\partial z)^2,$$

where g is the acceleration due to gravity, $\overline{T}$ is the mean absolute temperature, and γ the adiabatic lapse rate. Sutton (1953) gives a description of the theoretical basis of the Richardson number, but in short, it provides a means for specifying the relative effects of buoyancy and wind shear on vertical diffusion. A negative Ri denotes an unstable atmosphere, which usually occurs in daytime when the mechanical turbulence of the wind is augmented by buoyancy forces. A positive Ri, denoting a stable atmosphere, is characteristic of the nighttime, when the temperature inversion suppresses mechanical turbulence. Conditions are usually defined as near-neutral when $|\mathrm{Ri}| <$ about 0.03.

As will be shown later, Eq. [2] can provide a very good description of the wind profile near the ground. Furthermore, if the experimental area is large and uniform, the wind profile will be well-established and the shearing stress will be constant with height (Calder, 1949), which lead to the simplification that $n = 1\text{-}m$, $0 < m < 1$; hence,

$$K = K_1(z/z_1)^{1-m}. \qquad [4]$$

Calder's and Sutton's solution for the concentration distribution from a single line-source of strength, Q, along $x = z = 0$ has the form

$$\bar{c}(x,z) = \frac{Q}{u_1\Gamma(s)}\left[\frac{u_1}{(2m+1)^2K_1x}\right]^s \exp\left[-\frac{u_1z^{2m+1}}{(2m+1)^2K_1x}\right], \qquad [5]$$

where $s = (m+1)/(2m+1)$ and Γ denotes the gamma function.

Analytical

In order to apply Eq. [5] to the experimental data, it was first necessary to estimate the parameters m, u_1, and K_1. The first of these was estimated from twenty wind profiles measured at the site in periods of strong winds and near-neutral conditions by comparing wind speeds at the higher levels with those at 0.31 m. From Eq. [2],

$$m = \log(\bar{u}_z/\bar{u}_{0.31})/\log(z/0.31).$$

The mean of all such determinations of m was 0.225, with a standard deviation of 0.016. The reference wind speed, u_1, was calculated for each sampling period directly from Eq. [2] using this value of m and the $\bar{u}$ at 0.31 and 2.24 m. The excellent fit of Eq. [2] to all the wind-speed data collected at the site, which included periods of light winds and strong inversions, is shown in Fig. 1.

To calculate K_1 a low-level drag coefficient, C_z, was estimated from the 20 near-neutral wind profiles following the procedure of Deacon and Swinbank (1958). This coefficient was then used in conjunction with the wind speed at 0.31 m to calculate K_1 for each sampling period from the relationship

$$K_1 = C_{0.31}\, z_1\, \bar{u}_{0.31}^2/m\, u_1.$$

For this site, $C_{0.31}$ had an average value of 0.0127.

As noted in the introduction, NH_3 emission continues at a decreasing rate for some time after injection (Denmead et al., 1977). An analysis of the early stages of the experiment indicated that emission continued for about 2 h. The total emission was equivalent to 1.2 kg

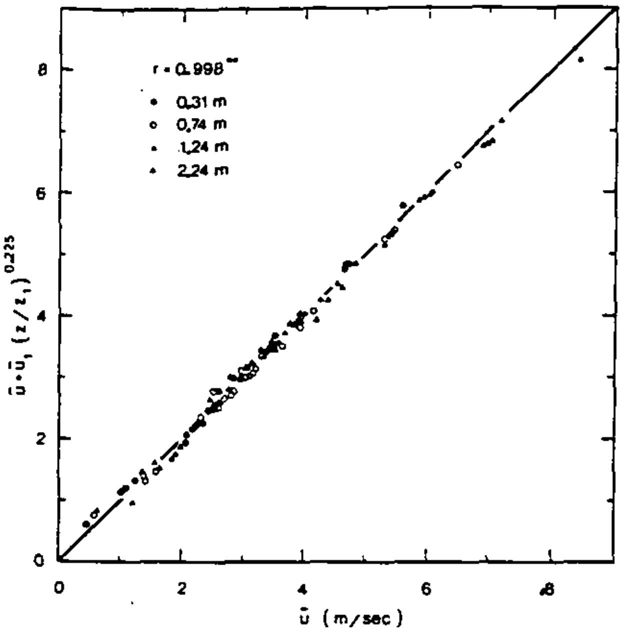

Fig. 1—Fit of power-law profile, Eq. [2], to wind-speed data.

NH_3/ha and the instantaneous emission rate, q, was described by the equation

$$q(t) = q_o \exp(-\lambda t), \quad [6]$$

where t is time (s), q_o is the initial rate (= 37.0 μg NH_3 m^{-1} s^{-1}), and λ is a rate constant (= 6.3×10^{-4} s^{-1}). The time constant of the decay was 26 min. Particular values of q_o and λ depend on how strongly NH_3 is absorbed by the soil and the nature of the escape path from the site of injection to the soil surface. They can thus be expected to vary from soil to soil and with the method of injection.

Since one traverse of the applicator required 17 min, the average concentrations measured at the downwind edge of the field during each sampling period were influenced by emissions from several upwind sources located at different distances from the edge and emitting at various rates, depending on their times of injection. To analyze the data, we therefore added the separate solutions given by Eq. [5] for each injected band with Q set equal to the appropriate average rate for that band during the sampling period. From Eq. [6],

$$Q = q_o\{\exp[-\lambda(t_1 - t_*)] - \exp[-\lambda(t_2 - t_*)]\}/\lambda(t_2 - t_1), \quad t_* \leq t_1 \leq t_2,$$

where t_* is the time (from the start of the operation) at which the band was injected, t_1 is the start of the sampling period, and t_2 is the end of the sampling period. In effect, we approximated the experimental situation by a series of steady line-sources at different distances upwind.

In applying Eq. [5], it was necessary to account for wind directions other than those normal to the edge of the field, since deviations from normality increased the effective upwind distance of the sources. This adjustment was made for each sampling period by dividing the nominal upwind distance of each source by the cosine of the deviation in wind direction.

RESULTS

Meteorological parameters and NH_3 concentrations during the experiment are listed in Table 1. Most of the observations were made in slightly unstable atmospheric conditions, but the last three sampling periods were in stable conditions.

The data in Table 1 illustrate the main features of the dispersion process. Concentrations were highest close to the ground, where they increased rapidly during the first three traverses. As more of the field was treated and the emitting sources became more remote, NH_3 diffused to greater heights in the atmosphere and concentration gradients lessened; concentrations at lower levels fell while those at higher levels increased. These features are evident in the NH_3 concentrations measured while the treated width was extended to 120 m. During this period, winds were steady at 3–4 m/s.

The effect of wind speed on the concentrations at the downwind edge is evident in sampling periods 14, 15, and 16. In period 15 the wind speed dropped to about one-half that in period 14 and this resulted in a doubling of NH_3 concentrations. In period 16 wind speed had dropped to about one-third that in period 14, and the concentrations were almost four times as high, despite the fact that by then most of the effective sources were twice as remote from the measuring point. However, an additional influence during this period was the develop-

Table 1—Meteorological data and atmospheric NH_3 concentrations during injection of anhydrous NH_3.

Sampling period†	Width injected	Wind direction‡	ū at 2.24 m	u_*	K_1	Ri at 1.67 m	Mean NH_3 concentration§			
							0.31 m	0.74 m	1.24 m	2.24 m
	m	degrees	m/s	m/s	m²/s		μg/m³			
1	0–6	6	3.80	1.15	0.0032	−0.038	169	37	7	0
2	6–12	12	3.48	1.03	0.0027	−0.034	195	101	66	8
3	12–18	24	3.16	0.95	0.0026	−0.044	213	157	94	17
4	18–24	43	3.49	1.05	0.0029	−0.056	119	104	62	13
8	30–36	30	3.88	1.15	0.0031	−0.047	59	47	24	21
9	36–42	20	3.39	1.01	0.0027	−0.054	63	54	33	22
10	42–48	40	3.96	1.19	0.0032	−0.038	49	43	31	17
11	48–60	31	3.97	1.19	0.0032	−0.044	45	40	26	28
12	60–72	25	3.82	1.14	0.0030	−0.039	50	38	21	22
13	72–96	47	3.95	1.17	0.0031	−0.019	39	26	25	14
14	96–120	41	3.94	1.15	0.0030	−0.003	28	29	24	17
15	120–144	48	1.90	0.56	0.0010	0.094	41	33	35	36
16	210–234	26	1.19	0.35	0.0004	1.814	104	114	100	60
17	600–600¶	30	0.70	0.21	0.0001	2.538	10	14	12	8

† Some data for sampling periods 1, 2, 3, 4 are cited in Denmead et al. (1977). The numbering here is consistent with that paper, but concentrations there are for NH_3-N. Injection was stopped during sampling periods 5, 6, and 7. Some data for these periods are given in Denmead et al. (1977).
‡ Deviation from a direction normal to edge of field.
§ The background concentration (during the experiment) of 3 μg/m³ has been subtracted from these values.
¶ Injection ceased at 600 m ½ h before sampling commenced. The sampling period was 1 h.

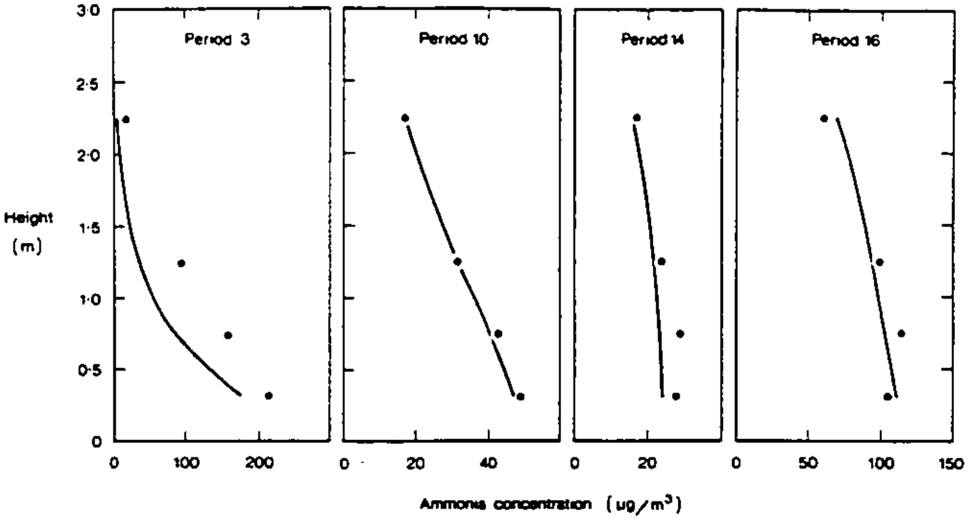

Fig. 2—Observed and calculated profiles of atmospheric NH_3 concentrations. Symbols for measurements; lines for calculations.

ment of a strong inversion and the consequent suppression of vertical diffusion (compare Ri and K_1 values for periods 16 and 14).

The extent to which these observed features are reproduced by the model is shown in Fig. 2–4. In Fig. 2 the calculated NH_3 concentrations at the downwind edge are compared with those measured during sampling periods 3, 10, 14, and 16.

As expected, agreement between prediction and observation was not good for short treated widths where the line-source analogy is less appropriate. This is evident in the comparison for period 3 when 18 m had been treated. In fact, the model underestimated the concentrations at all heights when the treated width was <30 m. For greater widths, however, agreement improved markedly, as the comparisons for periods 10, 14, and 16 show. The effects of source remoteness, wind speed, and atmospheric stability on the concentrations downwind were predicted very well. The same good agreement for treated widths >30 m can be seen in Fig. 3 and 4, which compare predictions and observations of NH_3 concentrations for all the sampling periods.

DISCUSSION

The comparisons presented here show that the dispersion of NH_3 following anhydrous NH_3 injection can be predicted satisfactorily by existing diffusion theory at distances of 30 m or more from the source. The theory should then be useful for estimating the extent of NH_3 pollution in other field situations.

Efficiencies of particular applications of anhydrous NH_3, and the dynamics of emission, can be expected to vary with soil conditions and the method and amount of application. In this experiment the total emission of NH_3 was 1.2 kg/ha. Other published estimates of NH_3 loss during the injection operation range from <1

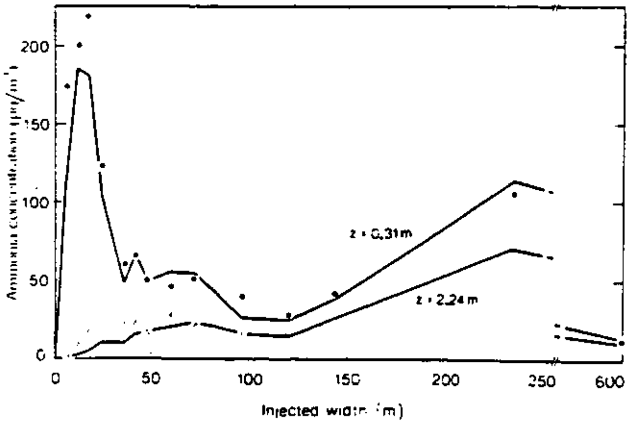

Fig. 3—Variation of NH_3 concentrations at two heights at downwind edge of field with distance from applicator. Symbols for measurements; lines for calculations.

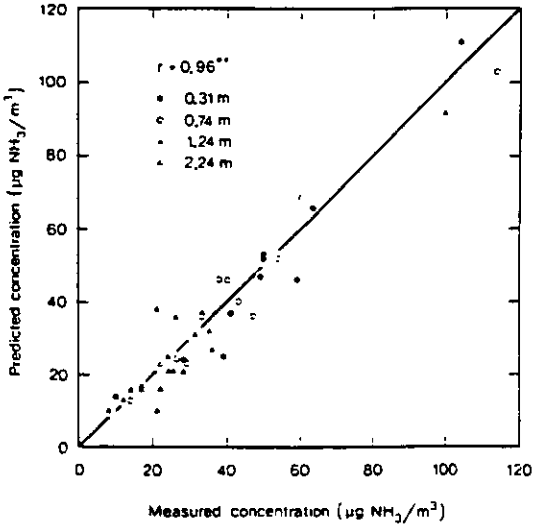

Fig. 4—Comparison of observed and predicted NH_3 concentrations for injected widths > 30 m.

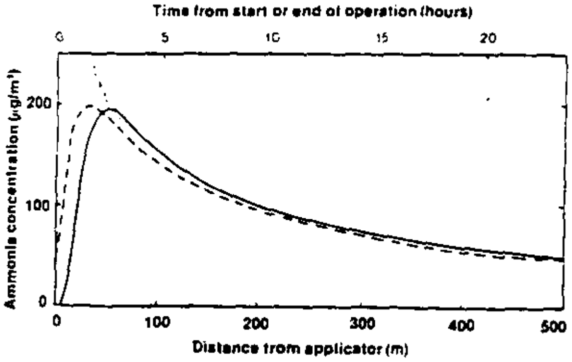

Fig. 5—Predicted NH_3 concentrations at downwind edge of field at height of 1.5 m. Solid line for applicator working away from edge; dashed line for applicator working towards it. See text for parameters used.

kg/ha (Baker et al., 1959) to as much as 45 kg/ha (Blue and Eno, 1954).

Equation [5] indicates that the concentrations at particular heights and distances downwind are directly proportional to the strength of the emitting source and inversely proportional to the wind speed. Assuming the same dynamics for NH_3 emission as we measured (as embodied in Eq. [6] and our value for λ), the same traverse time, and the same roughness characteristics and atmospheric stability (implying the same value for m and the same ratio between u_1 and K_1), it is a simple matter to calculate NH_3 concentrations for other source strengths and other wind speeds. Figure 5, for instance, shows expected concentrations on the downwind edge at a height of 1.5 m for a wind speed at 2 m of 4 m/s, a source strength of 5 kg NH_3/ha, a value of 0.225 for m, and the same ratio between u_1 and K_1 as in sampling period 1. (A height of 1.5 m was selected as a reasonable head height.) Two curves are shown in Fig. 5: one for injection starting at the downwind edge with the applicator traversing crosswind and gradually working upwind, the other for injection starting at the upwind edge with the applicator again traversing crosswind and gradually working downwind. The concentrations close to the downwind edge in the latter case are higher because of the greater extent of the upwind sources.

In both cases the concentrations can be scaled directly for different source strengths or wind speeds. For instance, an emission of 10 kg/ha would result in twice the concentrations shown in Fig. 5 at the same wind speed, or eight times, if the wind speed at 2 m was only 1 m/s. To take an extreme case: if the emission was as high as the 45 kg/ha reported by Blue and Eno (1954), the dynamics were the same as used here, and the wind speed at 2 m was 1 m/s, concentrations at the downwind edge would exceed 7,000 $\mu g/m^3$ in the early stages of injection and would still be $> 1{,}000$ $\mu g/m^3$ when the applicator was 500 m upwind.

Air quality standards for NH_3 are listed by Stern (1968) and discussed by the National Research Council (NRC, 1979). Of these, the most stringent is the USSR permissible standard, which is a concentration of 200 $\mu g/m^3$ persisting for 20 min. Conservative as the standard may be, it is evident from Fig. 5 that it would be breached during the injection operation in light to moderate winds if the NH_3 emission rate was 5 kg/ha or more. Other factors, such as temperature inversions that suppress vertical diffusion, as in sampling period 16, or reduced lateral dimensions of the treated field, which would make for a quicker injection operation and a more rapid concentration increase, could lead to concentrations in excess of the standard for even lower emission rates.

As discussed by the NRC (1979), there is a wide range in standards for different environments and between countries, so that the above examples can be no more than illustrative of potential health hazards. The underlying dispersion theory, however, should prove useful in related problems in agriculture where a time-dependent decay and/or a line-source analogy are appropriate; for instance, in estimating the atmospheric concentrations of pesticides or herbicides released from row applications.

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DIVISION S-8—FERTILIZER TECHNOLOGY AND USE

A Direct Field Measurement of Ammonia Emission After Injection of Anhydrous Ammonia[1]

O. T. DENMEAD, J. R. SIMPSON, AND J. R. FRENEY[2]

ABSTRACT

Studies of the efficiency of applications of anhydrous ammonia fertilizer require a measurement of ammonia retention or loss at the time of application. Because of sampling problems, conventional measurements based on soil analysis are difficult to make in the field. A new method is described, based on calculating the aerial transport of ammonia across the downwind edge of the treated field from measurements of wind speed, wind direction, and atmospheric ammonia concentration. Ammonia losses as small as 1 kg N/ha can be easily detected. Maximum errors are reckoned at no more than 20%. In a field experiment in which anhydrous ammonia was applied at 107 kg N/ha, aerial sampling gave a loss of 1 kg N/ha. Soil sampling detected no loss because of a large sampling error (SE 15 kg N/ha).

Additional Index Words: nitrogen loss, fertilizer efficiency, atmospheric pollution.

LOSSES OF AMMONIA to the atmosphere during application of anhydrous ammonia are of concern not only from the economic viewpoint, but also because of their possible involvement in eutrophication of nearby water bodies (3) and in atmospheric chemistry (6). While there have been numerous laboratory and greenhouse studies on the retention of anhydrous ammonia by soils (5), there have been few field measurements of ammonia losses during anhydrous ammonia application. So far as we know, there has been only one previous attempt at direct field determination (1). Usually, retention, and by inference, loss, are measured by total nitrogen analysis of the soil. The method is tedious and subject to large errors because of sampling problems.

This paper describes an aerial sampling technique and its use for the direct determination of ammonia loss to the atmosphere during injection of anhydrous ammonia in the field. The method is based on measuring the aerial transport of emitted ammonia across the downwind edge of the treated area. In a field experiment, the loss calculated by this method was compared with the loss calculated by a conventional soil sampling technique. The experiment also provided information on the kinetics of ammonia emission.

METHODS

Micrometeorological

Ammonia escaping from the soil after injection is spread vertically by turbulent diffusion and convected horizontally by the wind. Consequently, the concentration of ammonia in the air downwind of the treated area is increased. For a steady wind direction, the net flux of ammonia convected from the treated area can be calculated, in the manner described below, from measurements of ammonia concentrations and wind speeds at the downwind edge of the field. Since reabsorption of the emitted ammonia is likely to be negligibly small, this flux of ammonia from the field can be equated with the loss from the soil surface.

The basis of the aerial flux calculation can be understood by considering a perpendicular plane normal to the wind at the downwind edge of the field. The rate of transport of ammonia across a unit area of the plane at height z, due to emission from the soil, will be the product $u(z)c(z)$, where u is horizontal wind speed and c is the ammonia concentration in excess of the background level. The mean rate of transport over a period of time will be $\overline{uc}$.

The instantaneous wind speeds and concentrations, u and c, can be represented as sums of means, $\bar{u}$ and $\bar{c}$, averaged over the same time period, and deviations from the means, u' and c', so that

$$\overline{uc} = \bar{u}\,\bar{c} + \overline{u'c'}. \quad [1]$$

The first term on the right hand side of Eq. [1] represents the transport due to advection; the second, that due to horizontal diffusion. In micrometeorological treatments of this kind, it is usual to neglect the diffusion term because of its relative smallness (e.g., 7). Then $\bar{Q}$, the total mean flux of ammonia across a face of unit width in the plane, will be given by

$$\bar{Q} = \int_0^Z \bar{u}(z)\bar{c}(z)\,dz, \quad [2]$$

where Z is the height of the air layer affected by the emission. Note that $\bar{Q}$ is also the net rate of emission per unit width of soil surface upwind of the edge.

Experimental

The experimental site was in a field of 160 ha near Narrabri, New South Wales. The soil is a heavy clay, of pH 8.2, low in organic matter (0.07% N) and at the time of injection it was very moist so that the disturbed soil did not fall back readily to cover the injection slit. These factors could be conducive to large losses of ammonia (5).

The injector bar, pulled by a tractor, held six tool shanks at 1-m spaces. Each shank carried a delta-wing foot which lifted the soil and allowed ammonia to be injected horizontally under it. The injection tube bifurcated at the shank, resulting in the placement of two bands of ammonia per delta-wing and an effective band spacing of 0.5 m. The mean injection depth was 12.4 cm. Ammonia was metered on at the rate of 107 kg N/ha.

The layout of the experiment is shown in Fig. 1. Cup-anemometers (Casella) and ammonia traps (2) were mounted on masts at heights of 0.31, 0.74, 1.24, and 2.24 m above the ground at the downwind edge of the field, midway along the track of the injection rig. Wind direction was also recorded by a wind vane. The rig was drawn up and down the field in traverses parallel to the downwind edge, working progressively away from the masts. The first injection band was 0.5 m upwind.

During each traverse, $\bar{u}$ and $\bar{c}$ were measured from the instant the rig passed the masts to the moment it returned to the same point, i.e., over the period for the rig to travel to the end of the field (500 m away) and back. The average time for such a traverse was 17 min. After four traverses, the rig was stopped, but the measurements were continued in 17-min sampling periods for the equivalent of three more traverse times.

To measure ammonia concentration, $\bar{c}$, air was drawn at approx-

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[1] Contribution from CSIRO, Australia. Received 22 Feb. 1977. Approved 18 April 1977.

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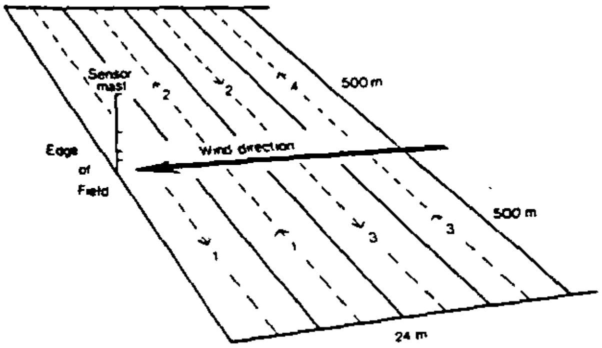

Fig. 1—Layout of experiment (not to scale). Dashed lines and arrows indicate direction of travel of injection rig. Numbers are traverse numbers.

imately 15 liters/min through acidified traps (2) via humidifiers containing 40 ml of 0.1*N* NaOH. At the end of the sampling period, the trapped ammonia was eluted with water and measured (2). [Experience has shown that humidifiers are necessary to reduce water loss (and consequent loss of efficiency) from the acid traps on warm, dry days.]

Previous tests showed that all the ammonia in an air sample was collected in one trap. The reproducibility of the measurements was examined by comparing ammonia concentrations measured with duplicate traps mounted at the same height. For 20 pairs of readings at an atmospheric ammonia concentration of 3.6 μg N/m^3, the mean difference between duplicates was 0.39 μg N/m^3, which indicates an uncertainty of approximately 10%.

Soil Sampling

The slits opened by the ammonia injection were marked on the soil surface and two steel plates, 30 by 40 cm, 5-cm apart, were driven into the ground, directly over and perpendicular to the direction of the slit. The isolated soil block was excavated and the center of the injection band was located using a pH indicator and a dusting of calcium sulphate (gypsum) on the soil surface. Four sampling rings of diameter 3.4, 7.3, 12.5, and 16.1 cm, were placed concentrically over the band center to give soil samples at known distances from it. Samples obtained in this way from 25 different positions across the field were dried, crushed, and analysed for total nitrogen by a micro-Kjeldahl method. Bulk density and soil water content were obtained on separate samples. The average volumetric soil moisture content was 0.34.

RESULTS

Micrometeorological

Table 1 lists the micrometeorological data for each sampling period, and Fig. 2 shows their general character. Notable features are the increased vertical dispersion of ammonia as the width of the treated area increased (compare, for instance, sampling periods 1 and 3 where *Z*, the height of the affected air layer, increased from approximately 1.6 to 2.5 m), and the fact that ammonia continued to be emitted for some time after injection was stopped (sampling periods 5 to 7).

To calculate the mean emission rates, $\overline{Q}$, plots of $\overline{u}\,\overline{c}$ vs. height, similar to those in Fig. 2, were drawn for each sampling period and the integrals in Eq. [2] determined by planimetry. This involved some extrapolation above and below the highest and lowest sampling positions, but the consequent errors are small because of the rapid decline in $\overline{c}$ at the higher levels and $\overline{u}$ at the lower. The integrated fluxes were then corrected for variations in wind direction by dividing each by the cosine of the deviation of the mean wind direction in that sampling period from 180°. The corrected emission rates are shown in Fig. 3.

Table 1—Micrometeorological data during the experiment.

Sampling period	Upwind distance treated	Mean wind direction†	Mean wind speed, Height, m: 0.31	0.74	1.24	2.24	Mean NH$_3$-N concentration‡, Height, m: 0.31	0.74	1.24	2.24
	m	degrees	m/sec				$\mu g/m^3$			
1	6	174	2.55	3.13	3.41	3.80	139	30	6	0
2	12	192	2.24	2.79	3.02	3.48	160	83	54	7
3	18	204	2.08	2.58	2.77	3.16	175	125	77	14
4	24	223	2.32	2.84	3.08	3.49	98	66	51	11
5	24	180	2.26	2.50	3.03	3.45	42	41	38	18
6	24	225	2.17	2.67	2.83	3.19	39	25	23	0
7	24	195	2.07	2.29	2.44	2.79	35	12	7	0

† A direction of 180° is normal to the edge of the field.
‡ The background concentration (during the experiment) of 3 $\mu g/m^3$ has been subtracted from these values.

That emission continued for a time period longer than each traverse of the injection rig is evidenced by the increase in emission rate as the treated area increased (compare, for instance, the rate for sampling periods 2, 3, and 4 with that for the first period), and the continued emission in sampling periods 5 to 7, after injection had ceased. Thus the ammonia fluxes calculated for sampling periods after the first contained residuals from previous traverses, and it was necessary to calculate the time dependence of the emission in order to arrive at the total ammonia loss.

The character of the data in Fig. 3 and consideration of the probable dynamics of ammonia evolution following injection suggest a rate of emission which depends on the concentration of ammonia in the soil air spaces, and which consequently decreases exponentially with time. Accordingly, we have adopted a relationship of the type

$$q(t) = q(o) \exp(-\lambda t) \qquad [3]$$

to describe the instantaneous emission rate from each injected band. In Eq. [3], q is the rate of emission per unit length of band, $q(o)$ being the initial rate, t is time, and λ is a rate constant. The mean emission rate $\overline{q}$ over the time τ of one complete traverse of the injection rig is then given by

$$\overline{q} = (1/\tau)\int_0^{\tau} q(t)\,dt = q(o)[1 - \exp(-\lambda\tau)]/\lambda\tau. \qquad [4]$$

If we designate the traverse number m and the sampling period n, so that $\overline{q}_{m,n}$ is the mean emission rate from each band injected in the mth traverse, in the nth sampling period, it follows that

$$\begin{aligned} \overline{q}_{1,1} &= q(o)[1 - \exp(-\lambda\tau)]/\lambda\tau, \qquad [5] \\ \overline{q}_{1,7} &= \overline{q}_{1,1} \exp(-6\lambda\tau) \\ \overline{q}_{2,2} &= \overline{q}_{1,1} \\ \overline{q}_{2,7} &= \overline{q}_{1,1} \exp(-5\lambda\tau) \\ \overline{q}_{m,n} &= \overline{q}_{1,1} \exp[(m - n)\lambda\tau], \; (m = 1, 4; n = 1, 7). \qquad [6] \end{aligned}$$

Recalling that twelve bands are injected in each traverse, the mean emission from all bands in the nth sampling period, $\overline{Q}_n$, is then obtained by summing the appropriate $\overline{q}_{m,n}$, so that

$$\overline{Q}_n = 12\overline{q}_{1,1} \sum_{m=1}^{n} \exp[(m - n)\lambda\tau], \qquad (n \leq 4); \qquad [7]$$

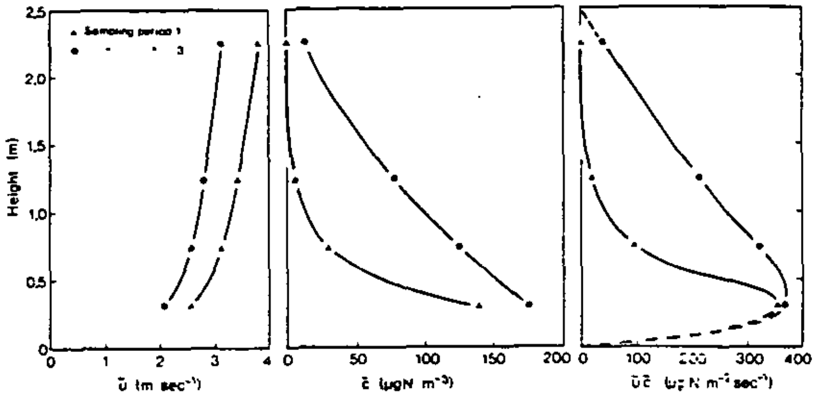

Fig. 2—Profiles of mean wind speed $\bar{u}$, mean atmospheric ammonia concentration $\bar{c}$, and horizontal flux density of ammonia $\overline{uc}$ in two periods.

and

$$\overline{Q}_n = 12\bar{q}_{1,1} \sum_{m=1}^{4} \exp[(m-n)\lambda\tau], \qquad (n \geq 5). \quad [7a]$$

Using Eq. [5], [6], and [7], we obtained those values of $q(o)$ and λ which gave the best least-squares fit to the data in Fig. 3. They were

$$\hat{q}(o) = 30.5\ \mu\text{g m}^{-1}\,\text{sec}^{-1},$$

and

$$\hat{\lambda} = 6.3 \times 10^{-4}\ \text{sec}^{-1}.$$

The curve in Fig. 3 is the emission calculated from these figures. The estimated time constant of the decay is 26 min. Ninety-nine percent of the ammonia emission from one band would occur in 122 min.

To complete the analysis, the total emission from each injected band, E, was obtained by integrating Eq. [3] with respect to time:

$$E = \int_0^{\infty} q(o)\exp(-\lambda t)\,dt = q(o)/\lambda. \qquad [8]$$

For the $\hat{q}(o)$ and $\hat{\lambda}$ above, the estimated total emission per band is 0.048 g/m, which represents a loss of 0.96 kg N/ha. Thus the estimated retention of nitrogen was 106 kg N/ha from an application of 107 kg N/ha.

Soil Sampling

The amount of ammonia retained per unit length of injection band was also determined from soil sampling and total N analysis. The ammonia remained in distinct bands even after 4 days. Of the applied nitrogen, 48% of the application remained within a ring of 7.3 cm diam; 86% remained within a 12.5-cm diam ring, and 100% within a 16.1-cm diam ring.

From soil analysis the recovery of ammonia was 106 kg N/ha (SE 15 kg N), which agrees extremely well with the result obtained by the aerial sampling technique, but because of the large SE, this good agreement can only be regarded as fortuitous.

DISCUSSION

For investigations of ammonia losses, and possibly other gaseous emissions, the aerial sampling technique described here has distinct advantages in terms of labor and accuracy over methods based on soil sampling. In this experiment, for instance, the aerial sampling and chemical analysis were completed in 2 hours, whereas the soil sampling alone required almost 2 days.

Some indication of the comparative sensitivities of the two methods can be obtained from sampling period 7 (Fig. 3), in which the mean rate of transport of ammonia across the edge of the field was 55 μg N m^{-1} sec^{-1} or approximately 0.02 kg N/ha over the whole period. The main errors in the aerial method are associated with the atmospheric ammonia concentrations and the graphical integration procedure. For the former, we estimate an uncertainty of approximately 10% (see Methods). The errors in the latter depend on how well the profiles of wind speed and ammonia concentration are defined; particularly, on how well they encompass the full height of the affected air layer. Allowing for an error of up to 10% in the procedure, the toal error is believed to lie between 10 and 20%. Thus in this example,

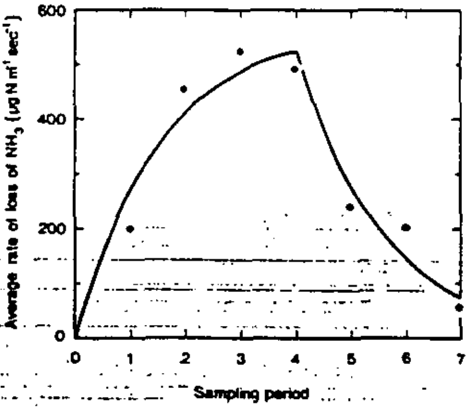

Fig. 3—Measured *(dots)* and calculated *(curve)* ammonia emission rates.

the uncertainty would be 0.004 kg N/ha. For the soil sampling, however, the uncertainty of ± 15 kg N/ha attached to the estimated loss, which is not inordinately large for the technique [c.f., 4, Table 1], indicates that such a sensitivity would be quite unattainable,

ACKNOWLEDGMENT

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Micronutrient Concentrations in Soil Solution After Ammonium Phosphate Applications[1]

J. J. MORTVEDT AND G. OSBORN[2]

ABSTRACT

Two fluid ammonium polyphosphates, 11-17-0 (11-37-0 oxide basis), a commercial 10-15-0 (10-34-0), and an equimolar mixture of mono- and diammonium phosphate (MAP-DAP), each with a solution pH of about 6.2, were well mixed with 1-kg lots of several soils to supply 2,000 ppm of P, which approximates the P concentration in soil near a fertilizer band at a P rate of 50 kg/ha. Each soil was then moistened to 0.2 or 0.3 atm and stored in plastic bags. After periods up to 28 days, soil samples were placed in a lucite cell and a portion of the soil solution was expressed by N_2 gas. These solutions were analyzed for Cu, Fe, Mn, Zn, organic C, and total and orthophosphate P.

Micronutrient concentrations in solutions of acid soils were temporarily increased by both ortho- and polyphosphates. Increases were related in part to the amount of soil organic matter solubilized by these fertilizers. Organic C in solutions of treated soils increased in the order: MAP-DAP, 10-15-0, and 11-17-0, which was related to the original percentage of the total P in polyphosphate form (0, 50, and 78, respectively). Micronutrient concentrations in solutions of acid soils were highest during the first week and decreased to those in untreated soil by 28 days. Soluble micronutrient concentrations in neutral and calcareous soils were not affected by phosphate applications even after 1 day. Thus, solubilization of soil micronutrients by polyphosphates does not appear to play an important role in micronutrient nutrition of crops, especially in calcareous soils.

Phosphorus concentrations in soil solution generally were higher in soils treated with ortho- than with polyphosphates. Decreasing polyphosphate concentrations in solutions of polyphosphate-treated soils with time indicated hydrolysis and precipitation of water-soluble polyphosphates; less than 25% of the soluble P was in polyphosphate form after 2 weeks, with higher polyphosphate concentrations found in 11-17-0 than in 10-15-0 treated soils during the first 2 weeks after application.

Additional Index Words: **polyphosphates, hydrolysis, sequestration, soil organic matter.**

AMMONIUM polyphosphate (APP) fertilizers have rapidly gained in popularity in the past 15 years. They usually contain about one-half of their P in the orthophosphate form, and the remainder as pyrophosphates or longer chain molecules. Recent advances in pipe reactor technology have resulted in increased polyphosphate contents. but triammonium pyrophosphate, $(NH_4)_3HP_2O_7$, still remains the major nonorthophosphate compound in both solid and fluid ammonium polyphosphates. Polyphosphate fertilizers are water soluble and generally are used in clear liquids or suspensions.

Polyphosphates generally are considered equal to monoammonium phosphate (MAP) for early growth response (Terman and Engelstad, 1966). Rates of polyphosphate hydrolysis to orthophosphates are quite rapid in most agricultural soils. Gilliam and Sample (1968) reported 50% hydrolysis of applied pyrophosphates within 28 days after soil application; highest hydrolysis rates were on acid soils. Hashimoto and Wakefield (1974) reported hydrolysis half-lives of 4 to 13 days in three soils incubated at 25°C. Terman (1975) concluded that APP fertilizers were usually equal to comparable orthophosphates as sources of N for crops and of P after hydrolysis.

Miner and Kamprath (1971) reported equal effectiveness of granular superphosphate and APP for supplying P to field corn (*Zea mays* L.) on an acid soil in North Carolina. Adriano and Murphy (1970) reported that MAP and APP were equally effective for irrigated field corn on noncalcareous soils in Kansas adequate in available Zn. However, row-applied MAP was more effective than APP if Zn was limiting; greater P uptake from APP antagonized Zn uptake of corn under these soil conditions and resulted in poorer growth. Subbarao and Ellis (1975) reported equal effectiveness of granular APP and diammonium phosphate (DAP) for corn on a neutral (pH 6.8) and calcareous (pH 8.2) soil in a growth chamber study.

Differential effectiveness of ortho- and polyphosphate fertilizers in some calcareous soils has been attributed by some workers to the effects of polyphosphates on micronutrient availability. Singh and Dartigues (1970) stated that

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[1] Contribution of the Soils and Fertilizer Research Branch, Div. of Agric. Dev., TVA, Muscle Shoals, AL 35660. Received 19 July, 1976, approved 15 June 1977.

[2] Soil chemist and analytical chemist, respectively.

MIDWEST RESEARCH INSTITUTE MRI-18

PROJECT DEVELOPMENT SKETCH

TITLE Reference No. 15, Denmead et al., J. Environ. Qual. 11(4) 1982

PROJECT NO. 6500-35 DRAWN ______ APPR. JSK DATE 9/14/92

Application Rate: 130 kg NH_3/ha from p. 569, Experimental

Total NH_3 Emissions: 1.2 kg NH_3/ha from p. 571, Discussion

$$\therefore\ 1.2\,\frac{\cancel{kg}\ \cancel{NH_3}}{\cancel{ha}} \times \frac{1\ \cancel{ha}}{130\ \cancel{kg\ NH_3}} \times \frac{17\ \cancel{kg\ NH_3}}{14\ kg\ N} \times 1000\,\frac{gm}{\cancel{kg}} = 11.2\,\frac{gm\ NH_3}{kg\ N}$$

For 2 hr emission duration: from p. 569, Analytical

$$11.2\,\frac{gm\ NH_3}{kg\ N} \times \frac{1}{2\ hr} = 5.60\,\frac{gm\ NH_3}{kg\ N \cdot hr}$$

ok mewy

$$130\,\frac{kg\ NH_3}{ha} \times \frac{14\ kg\ N}{17\ kg\ NH_3} = 107\,\frac{kg\ N}{ha}$$

Soil Biol. Biochem. Vol. 8. pp. 161 to 164. Pergamon Press 1976. Printed in Great Britain.

A CLOSED AMMONIA CYCLE WITHIN A PLANT CANOPY

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(*Accepted* 31 *October* 1975)

Summary—Ammonia losses to the atmosphere from a grass-clover pasture were measured by a combined chemical-micrometeorological technique. Losses from the pasture when grazed were quite considerable (~ 13 g N ha^{-1} h^{-1}) but when ungrazed they were comparatively small (2 g N ha^{-1} h^{-1}).

Measurements within the canopy of the ungrazed pasture at maturity indicated a large production of NH_3 near the ground surface and almost complete absorption of it by the plant cover. The amounts of NH_3 absorbed appeared to be too large for stomatal uptake alone.

This closed NH_3 cycle has important consequences for the field assessment of N_2 fixation and gaseous N losses.

INTRODUCTION

Nitrogen balance sheets have shown that considerable N is lost from agricultural soils each year (Allison, 1973). The relative importance of the different mechanisms of loss is poorly understood, but many researchers agree that volatilization of NH_3 is a potentially important pathway.

There is experimental evidence that NH_3 can be lost from N rich agricultural systems. Denmead *et al.* (1974), for instance, measured large losses of NH_3 to the atmosphere from a grazed alfalfa pasture, and Willis and Sturgis (1944), Martin and Chapman (1951) and Nõmmik (1973), among others, have shown that NH_3 losses occur from N fertilized soils.

Recently, we conducted an experiment in which the influence of grazing on NH_3 evolution was studied. Using techniques discussed in Denmead *et al.* (1974) we measured substantial losses of NH_3 from one half of a pasture, which was grazed, but detected only small losses from the other, ungrazed, half. The pasture contained a considerable proportion of subterranean clover and in such a N rich system, significant NH_3 losses might be anticipated, even in the ungrazed condition. This paper reports a further study on NH_3 exchange in the ungrazed pasture.

EXPERIMENTAL

Site

An area of 8 ha near Canberra, A.C.T., Australia, growing a mixture of Wimmera ryegrass (*Lolium rigidum* Gaud: 67% by dry weight) and sub clover (*Trifolium subterraneum* L.; 33%) was divided in half. One half was grazed with 90 sheep and the other half was left ungrazed.

At that time the ungrazed pasture was 70 cm high. The sub clover leaves formed a fairly dense layer between 10 and 20 cm from the ground, and most of the green leaves of the grass were between 30 and 50 cm above the ground surface (see Fig. 1).

A mulch of decomposing plant material, mostly clover leaves, existed at the soil surface. The underlying soil was derived from porphyry and the surface layers were slightly acidic (pH 6.0).

A micrometeorological mast was installed in each half to permit simultaneous measurements of NH_3 losses from each pasture. Here, we report mainly on measurements in the ungrazed half, but refer to measurements in the grazed half for comparison.

Measurements of temperature, net radiation, vapour pressure and NH_3 concentration were made within the ungrazed pasture at 5, 10, 20, 31 and 47 cm above the ground and also at three levels, 83, 119, and 171 cm, in the air layer above the pasture. They were used to calculate the vertical flux densities of NH_3 and water vapour at different heights within and above the pasture canopy.

Micrometeorological technique

The basic technique was one that has been used extensively in micrometeorology for measuring rates of gas and vapour exchange above natural surfaces, e.g. evaporation rates or rates of CO_2 exchange. The theory and methodology have been described in many works, e.g. Denmead and McIlroy (1971). Briefly, where there is an extensive, uniform source or sink of a gas at the ground surface and the atmosphere is turbulent, a gradient in the concentration of the gas develops in the air near the surface. The magnitude of the concentration gradient depends on both the strength of the source or sink and the extent of mixing in the atmosphere. This latter is determined by wind speed, wind shear and the temperature distribution. The relationship between the vertical flux density and the concentration gradient may be written as:

$$F = -K\,\partial c/\partial z \qquad (1)$$

where F is the flux density of the gas, K is the turbulent diffusivity in the air, c is gas concentration, and z is height.

Since K varies with atmospheric conditions, it must be measured, or inferred, in place. In our application we have inferred it from the energy balance. The net gain of radiant energy, the net radiation, is balanced

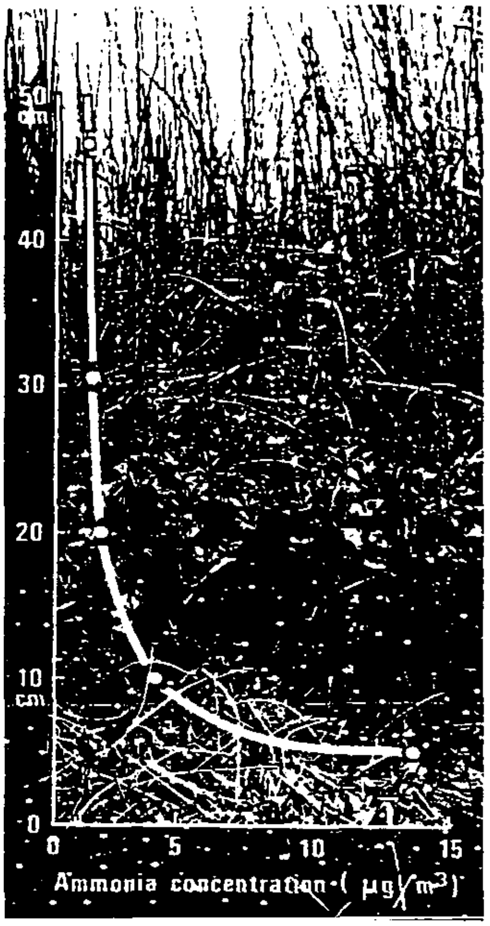

Fig. 1. Ammonia concentrations at various heights within a ryegrass sub clover pasture.

by a loss of energy as convective heat and latent heat and by a change in heat stored in the ground. Thus,

$$R = H + LE + G, \qquad (2)$$

where R is net radiation, H is the vertical flux density of convective heat, L is the latent heat of vaporization of water, E is the vertical flux density of water vapour, and G is the change in ground heat storage. Following equation (1),

$$H = -\rho c_p K\, \partial T/\partial z, \qquad (3)$$

where ρ is the density of air, c_p is the specific heat of air at constant pressure and T is temperature, and

$$LE = -\rho LK\, \partial q/\partial z, \qquad (4)$$

where q is specific humidity. Combining equations (2), (3), and (4), we have that

$$R - G = -\rho c_p K\left(\partial T/\partial z + \frac{L}{c_p}\partial q/\partial z\right)$$
$$= -\rho c_p K\, \partial T_e/\partial z. \qquad (5)$$

where $T_e\ (= T + Lq/c_p)$ is the equivalent temperature. Then, combination of equations (1) and (5) leads to

$$F = \frac{(R - G)}{\rho c_p}\frac{\partial c}{\partial T_e}. \qquad (6)$$

Equation (6) provides the practical means for calculating F, since all the variables on the right-hand side of the equation are physically measureable. In our application, R and G have been measured with standard instruments (net radiometers and soil heat flux plates), temperatures with radiation-shielded, aspirated, platinum-resistance thermometers, and humidities by wet- and dry-bulb thermometers. T_e was calculated for each of three heights above the pasture and five heights within the plant canopy, and the NH_3 concentration, c, was measured at the same heights by a technique described below. A plot of the corresponding values of T_e and c yielded $\partial c/\partial T_e$.

In this study, additional information was required on the distribution of evaporation sources in the canopy. For this purpose, the flux densities of water vapour were calculated by replacing the last term in equation (6) with measured values of $\partial q/\partial T_e$.

The analysis described above is a conventional one based on proportionality between flux and gradient. While it has been proved by numerous experiments to give a correct description of transfer processes in the air layers above natural surfaces, we note that certain theoretical difficulties can arise in its application within plant canopies, particularly where there are vertically distributed sources and sinks, as in the field situation described below. These difficulties have been discussed recently by Legg and Monteith (1975). In general, some distortion of the concentration gradients may be expected in the vicinity of the source or sink, but until an alternative formal description of transfer processes within the canopy is developed, it is not possible to estimate what effects these might have on the conventional flux-gradient analysis.

Determination of ammonia concentration

Atmospheric NH_3 concentrations were measured by drawing air through absorption traps at approximately 12 l. min^{-1} for 2 h. Connecting air lines from the mast to the NH_3 traps were interchanged daily to guard against contamination. Air was drawn through the lines for 10 min before starting the first collections of each day to remove any NH_3 that may have condensed overnight. The actual flow rates for each level were monitored with a flow meter. The traps were Plexiglass cylinders 24 × 2 (i.d.) cm filled with 3 mm glass beads between plugs of glass wool. Each trap contained 5 ml 2% phosphoric acid. At the end of the sampling period the traps were removed, the acid and collected NH_3 were eluted with water and the amount of NH_3 was determined with an Orion NH_3 specific ion electrode.

RESULTS AND DISCUSSION

At the time of the measurements described here, the average daytime losses of NH_3 from the grazed area were 13 g N ha^{-1} h^{-1} (in agreement with previous measurements, Denmead *et al.*, 1974) whereas from the ungrazed area, they were only 2 g N ha h^{-1}.

Table 1. Upwa
vapour from ar

Day	Local tim
21st Nov.	08.45 - 1(
1974	10.53 - 12
	13.05 - 1:
	15.10 - 1:
	17.17 - 1?
22nd Nov.	08.35 - 1
1974	10.36 - 1
	12.47 - 1.
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Table 1. Upward flux densities of ammonia and water vapour from an ungrazed ryegrass sub clover pasture.

Day	Local time	H_2O ($kg\ ha^{-1}\ h^{-1}$)	NH_3 ($g\ N\ ha^{-1}\ h^{-1}$)	
		At ground level (5-10 cm)	At ground level (5-10 cm)	Above canopy (>83 cm)
21st Nov. 1974	08.45 - 10.47	1730	36	1
	10.52 - 13.00	1670	32	1
	13.05 - 15.05	1510	19	4
	15.10 - 17.15	1760	18	2
	17.17 - 19.22	360	3	3
22nd Nov. 1974	08.35 - 10.36	1640	22	2
	10.38 - 12.43	1800	28	1
	12.47 - 14.47	1120	17	1
	14.52 - 16.52	720	9	0

Figure 1 shows the average NH_3 concentration profile between 10.38 and 14.47 h on 22 November 1974 superimposed on a photograph of the pasture. It is readily seen that the NH_3 concentration was greatest near the ground surface and decreased with height above the ground. For example, at 5 cm the average concentration was 13.5 μg N m^{-3}, whereas 1 m above the pasture the concentration was less than one tenth of this value. The profile suggests a large release of NH_3 at the soil surface and this is borne out by the flux calculations which are summarized in Table 1. It shows vertical flux densities of NH_3 in the layer from 5 cm to 10 cm and in the air layer, between 83 and 171 cm, above the pasture. The flux density between 5 and 10 cm represents the rate of production of NH_3 at the ground surface, while that between 83 and 171 cm is the net loss from the pasture to the atmosphere. The difference between them represents the net uptake of NH_3 by the vegetation.

Thus there appeared to be a very large production of NH_3 at the soil surface but almost all of this was sorbed by the vegetation. More detailed flux calculations (Fig. 2) showed that the sorption apparently occurred in the layer between 10 and 20 cm, which was that occupied by the clover leaves.

Other workers (Hutchinson *et al.*, 1972, Porter *et al.*, 1972) have shown that plants can absorb NH_3 from the air. Hutchinson *et al.* (1972) also found an apparent strong dependence of NH_3 uptake by plant leaves on stomatal opening. We have compared our rates of sorption with those to be expected if uptake occurred only by diffusion of NH_3 through the stomata. First, we calculated approximate stomatal diffusion resistances from the measurements of evaporation from the clover leaves and the temperature and humidity of the air around them, following procedures commonly employed in studies of gas exchange by leaves, e.g. Jarvis (1971). The average diffusive resistance of the clover leaves varied from 180 to 310 sec m^{-1}. Assuming that the NH_3 concentration inside the leaves was effectively zero, and that the ambient NH_3 concentration was the average of the air concentrations at 5, 10 and 20 cm, the rates of NH_3 uptake that could be expected from stomatal diffusion were between 1 and 3 g N ha^{-1} h^{-1} (on a ground area basis). These rates are only about one-tenth of those we calculated from the flux-gradient analysis (Table 1). Even allowing for possible errors in the latter it seems that mechanisms of uptake additional to stomatal diffusion were involved.

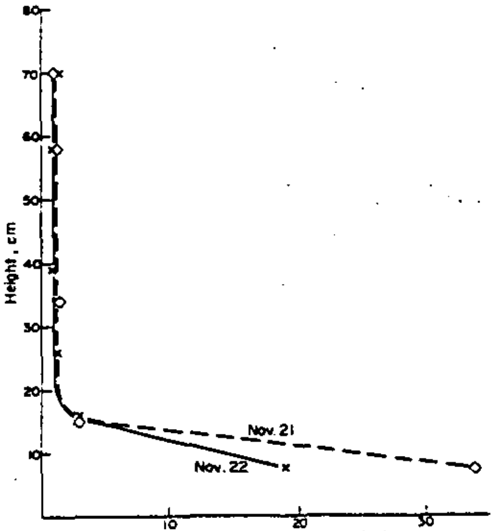

Fig. 2. The mean hourly flux of ammonia at different heights within the pasture on two consecutive days.

It is possible, for instance, that the NH_3 dissolves in water on the leaf surfaces. Dew was present in the bottom parts of the canopy each morning and drops of water were observed on some clover leaves as late as 14.30, and the average daytime relative humidity in the air around the leaves was 80%. Support for this mechanism of uptake is provided by the work of Fowler and Unsworth (1974) who found that the presence of dew greatly increased the ability of wheat leaves to absorb atmospheric SO_2. Ammonia when dissolved could take part in chemical reactions, e.g. with hydrogen ions in water, to form NH_4^+ ions which could be metabolized in the same way as foliar applications of urea (Wittwer and Teubner, 1959).

We found no indication that the absorbed NH_3 was subsequently released from the clover at night. Wind velocities then were small and thus diffusivities were low. Concentration gradients above the plant canopy were also very small (and sometimes reversed), and we conclude that night-time losses of NH_3 from the plant canopy to the atmosphere were negligible. It thus seems reasonable to assume that the NH_3 absorbed in the daytime was incorporated into the plant.

We are still exploring possible environmental influences on NH_3 production. So far, we have found no obvious relationship between NH_3 production and the temperature of the soil surface, or the temperature or humidity within the litter layer. The data in Table 1 suggest that the loss of NH_3 was greatest when the evaporation of water was greatest. The relationship between the two is described by the equation $y = 0.0214x - 5.5$ ($r = 0.74$) where y = the flux density of NH_3 and x = the flux density of water vapour between 5 and 10 cm. The intercept on the y axis is not significantly different from zero ($P < 0.05$). This suggests that even though NH_3 may be produced in the moist surface soil or litter continuously, NH_3 is not desorbed until evaporation of water commences.

It is obvious that the mechanisms of NH_3 production in the grazed and ungrazed pastures are very different because of the continual excretion of dung and urine on the grazed area. Moreover the removal of the dense clover cover in the grazed area produced a more open vegetation from which NH_3 could escape more easily to the atmosphere.

The results reported here suggest that NH_3 can be released beneath ungrazed pasture at high rates, but because of uptake by the vegetation above, the NH_3 is not lost to the atmosphere directly. The existence of this closed NH_3 cycle in pastures has important consequences for the field assessment of N_2 fixation by legumes and for conclusions about gaseous N losses that may be drawn from soil N balance sheets.

Acknowledgements—We are grateful for the competent technical assistance of Messrs F. J. Moore, J. Lazdovskis and J. W. B. Smith.

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APPENDIX H

REFERENCE 9, ASSOCIATED HAND CALCULATIONS, AND SUPPORTING DOCUMENTATION

VOL. 7, NO. 1 GEOPHYSICAL RESEARCH LETTERS JANUARY 1980

EFFECTS OF DIFFERENT NITROGEN FERTILIZERS ON EMISSION OF NITROUS OXIDE FROM SOIL

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Abstract. Field studies of emissions of nitrous oxide (N_2O) from a fallow soil treated with different forms and amounts of fertilizer N showed that N_2O emissions from plots treated with N in the form of ammonium sulfate or urea markedly exceeded those from plots treated with the same amount of N in the form of calcium nitrate. This supports evidence from laboratory research that most of the N_2O evolved from soils treated with ammonium and ammonium-producing fertilizers is generated by nitrifying microorganisms during oxidation of ammonium to nitrate and not, as previously assumed, through reduction of fertilizer-derived nitrate by denitrifying microorganisms. Emissions of N_2O from plots treated with fertilizer N as ammonium sulfate or urea increased with the amount of N applied. Emissions of N_2O in 25 days were increased 329-524% by application of 125 kg N ha^{-1} as ammonium sulfate or urea and increased 1024-1319% by the application of 250 kg N ha^{-1} in these forms, but these applications did not markedly increase N_2O emissions after 25 days, and the fertilizer-induced emissions of N_2O-N observed in 96 days from plots treated with ammonium sulfate or urea represented only 0.11-0.18% of the fertilizer N applied. Emissions of N_2O from plots treated with different amounts of N as calcium nitrate did not increase with the amount of N applied and were not appreciably greater than the emissions observed when no fertilizer N was added.

Introduction

There is concern that increased nitrogen (N) fertilization of soils to aid world food production may substantially increase emissions of nitrous oxide (N_2O) from soils and thereby pose a threat to the stratospheric ozone layer protecting the biosphere from biologically harmful ultraviolet radiation from the sun (see Council for Agricultural Science and Technology, 1976; Crutzen and Ehhalt, 1977; Liu et al., 1977; McElroy et al., 1977). Although it has been generally assumed that this threat is from N_2O produced by denitrification of fertilizer-derived nitrate in soils under anaerobic conditions, recent laboratory studies (Blackmer and Bremner, 1977; Bremner and Blackmer, 1978, 1979a,b) have provided evidence that N_2O is released to the atmosphere during nitrification of ammonium and ammonium-producing fertilizers in soils and that nitrifying microorganisms contribute significantly to emissions of N_2O from soils. Because most of the fertilizer N applied to soils is in the form of ammonium or ammonium-producing fertilizers, there is an urgent need for reliable information concerning the effects of these nitrifiable forms of fertilizer N on emissions of N_2O from soils.

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0094-8276/80/009L-1618$01.00

We report here the results of highly replicated field experiments showing that fertilizer-induced emissions of N_2O from plots treated with nitrifiable forms of fertilizer N (ammonium sulfate and urea) markedly exceed those from plots receiving an equivalent treatment of fertilizer N as calcium nitrate.

Experimental

The experiments reported were performed on a field at the Iowa State University Agronomy Research Center 10 km southwest of Ames. The soil in this field was representative of Harps soil used extensively for corn and soybean production in north-central Iowa. A composite sample of surface (0-15 cm) soil collected at 12 sites within the field had a pH of 8.2 and contained 32% sand, 32% clay, 4.9% organic carbon, 7.7% calcium carbonate, 15 μg ammonium N g^{-1} and 30 μg nitrate N g^{-1}.

To study the effects of different nitrogen fertilizers on emissions of N_2O, three forms of fertilizer N (ammonium sulfate, urea and calcium nitrate) were applied at two rates (125 to 250 kg N ha^{-1}) to 72 plots, and N_2O emissions from these plots were compared with those from 12 unfertilized plots. An area approximately 30 m by 30 m was rototilled to a depth of 20 cm and divided into 84 plots. After appropriate treatment, each plot was again rototilled to a depth of 20 cm. Treatments were applied by sprinkling the plots evenly with 1.5 liters of water or with 1.5 liters of water containing the appropriate form and amount of fertilizer N. Each of the seven treatments were replicated twice in each of six randomized complete blocks [each treatment was replicated 12 times to minimize error due to spatial variability in emission of N_2O from soils (Robbins et al., 1979)].

Rates of N_2O emission from the experimental plots were measured by a chamber technique (Matthias et al., 1979) involving placement of an insulated cylindrical metal chamber over the soil surface for 10 minutes and removal of air samples from the chamber at intervals for N_2O analysis by a gas chromatographic technique that permits use of the xenon in air as an internal standard (Blackmer and Bremner, 1978).

Soil temperature was measured at a depth of 7.5 cm below the soil surface by a mercury thermometer. Soil moisture content was determined by gravimetric determination of weight loss when soil samples collected 7.5 to 12.5 cm below the soil surface were dried at 105°C for 24 hours. It is expressed as a percentage of oven-dry soil. The field capacity of the soil in the experimental area was determined as described by Peters (1965). Exchangeable ammonium and nitrate in soil samples (0-15 cm) taken at various times after application of fertilizer N were determined as described by Bremner and Keeney (1966). ok

Table 1. Amounts of N_2O Evolved from Plots Treated with Different Forms and Amounts of Fertilizer Nitrogen

Nitrogen fertilizer added		Amount of N_2O-N evolved (g ha^{-1})				Fertilizer-induced emission of N_2O-N calculated as % of N added[d]			
Form[a]	Amount (kg N ha^{-1})	13 days[b]	25 days[b]	43 days[b]	96 days[b,c]	13 days	25 days	43 days	96 day
None	-	16	21	55	330 ✱	-	-	-	-
CN	125	23(144)	35(167)	77(140)	382(116)	0.01✓	0.01✓	0.02✓	0.04✓
CN	250	24(150)	34(162)	73(131)	358(109)	<0.01✓	0.01✓	0.01✓	0.01✓
U	125	83(519)	90(429)	136(247)	503(153)	0.05✓	0.06✓ J	0.07✓	0.14✓
U	250	215(1344)	236(1124)	288(524)	617(196)	0.08✓	0.09✓	0.09✓	0.12✓
AS	125	114(713)	131(624)	184(335)	557(169)	0.08✓	0.09✓	0.10✓	0.18✓
AS	250	267(1669)	298(1419)	355(645)	613(186)	0.10✓	0.11✓	0.12✓	0.11✓

[a] CN, calcium nitrate; U, urea; AS, ammonium sulfate.

[b] Figures in parentheses indicate amount of N_2O-N evolved calculated as percentage of amount evolved from unfertilized soil.

[c] Analysis of variance showed that emissions of N_2O from the plots treated with ammonium sulfate or urea were significantly higher ($P = 0.01$) than those from the plots treated with calcium nitrate and that emissions of N_2O from the plots treated with 250 kg N ha^{-1} as urea or ammonium sulfate were significantly higher ($P = 0.01$) than those from the plots treated with 125 kg N ha^{-1} as urea or ammonium sulfate.

[d] [(Amount of N_2O-N evolved from fertilized plot - amount evolved from unfertilized plot) ÷ amount of fertilizer N added] x 100.

Results and Discussion

Figure 1 and Table 1 show that treatment of plots with fertilizer N as ammonium sulfate or urea led to marked increases in emissions of N_2O, but that treatment of plots with fertilizer N as calcium nitrate did not lead to comparable increases in N_2O emissions. Table 1 also shows that, whereas an increase in the rate of application of ammonium sulfate or urea from 125 to 250 kg N ha^{-1} led to a marked increase in emission of N_2O, a corresponding increase in the amount of fertilizer N applied as calcium nitrate did not increase the amount of N_2O evolved.

Laboratory research (Bremner and Blackmer, 1978, 1979a) has shown that most of the N_2O evolved from soils fertilized with ammonium sulfate or urea is generated within 2 weeks and that N_2O emissions from such soils after about 3 weeks are not significantly greater than N_2O emissions from unfertilized soils. Figure 1 shows that a similar pattern of N_2O production was observed in our field study of emissions of N_2O from plots treated with ammonium sulfate or urea. Soil analyses indicated that most of the N added to these plots was nitrified (i.e. oxidized to nitrate) within 3 weeks (less than 5% of this N could be recovered as ammonium N after 21 days). These observations support our conclusion from laboratory research (Bremner and Blackmer, 1978, 1979a) that most of the N_2O evolved from soils fertilized with ammonium sulfate or urea is generated by nitrifying microorganisms during oxidation of ammonium to nitrate because Figure 1 shows that most of the N_2O evolved in 6 weeks from plots treated with ammonium sulfate or urea was produced within the first 3 weeks.

No data

In view of the general assumption that most of the N_2O evolved from soils treated with N fertilizers is produced through reduction of fertilizer-derived nitrate by denitrifying microorganisms under anaerobic conditions, attention should be drawn to our finding that application of fertilizer N as calcium nitrate did not lead to a marked increase in N_2O emissions from the plots studied (Figure 1 and Table 1) even though rainfall during the study period was considerably above average and the moisture content of the soil in the study area (see Figure 1) was frequently near, and at times above, field capacity (32%). This finding cannot be attributed to loss of nitrate by leaching because soil analyses showed that the nitrate-treated plots contained substantial amounts of nitrate throughout the study period. The fact that the nitrate-treated plots did not evolve substantial amounts of N_2O during this unusually wet period merits emphasis because it has been assumed that high soil moisture content promotes emission of N_2O through reduction of

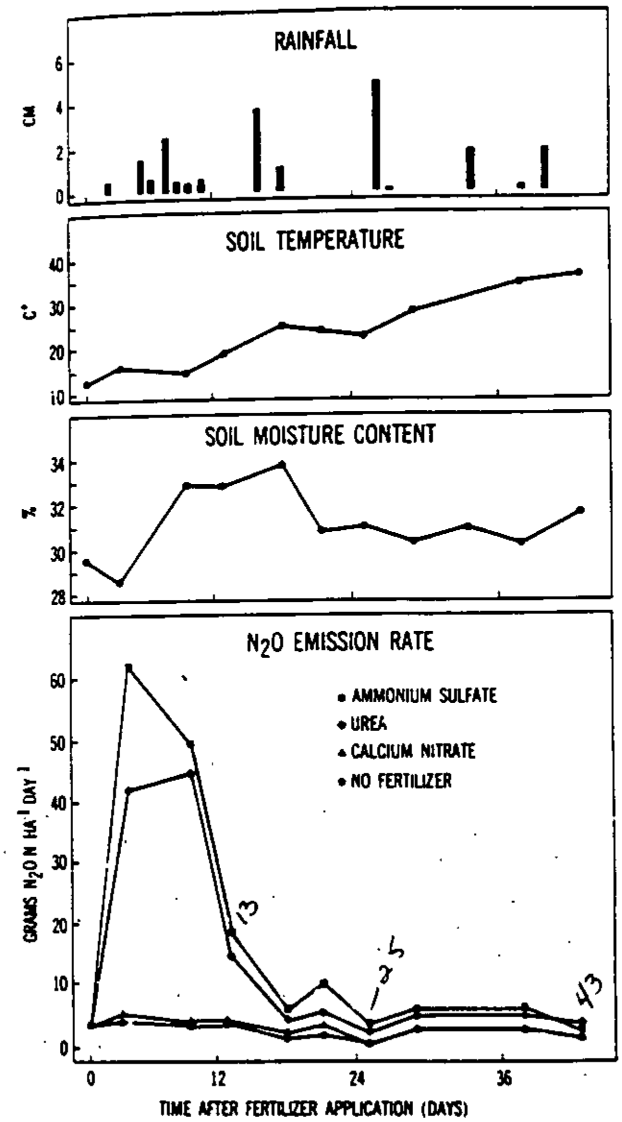

Fig. 1. Results of measurements of N_2O emission rates, soil temperature, soil moisture content, and rainfall during the period June 1 - July 14, 1979. Fertilizer N was applied on June 2 (250 kg/ha). Each N_2O emission rate reported represents the mean rate for 12 replicated plots.

nitrate to N_2O by denitrifying microorganisms.

Our finding that N_2O emissions from plots fertilized with calcium nitrate were much smaller than those from plots fertilized with ammonium sulfate or urea is in harmony with the results of laboratory studies of the effects of ammonium sulfate, urea, and potassium nitrate on N_2O emissions from soils at different moisture contents (Bremner and Blackmer, 1978, 1979a), and it clearly supports our conclusion that most of the N_2O evolved from soils treated with fertilizer N as ammonium sulfate or urea is produced by nitrifying microorganisms during oxidation of this N to nitrate and not, as previously assumed, by anaerobic denitrification of the nitrate produced by these microorganisms.

The work reported shows that, to obtain reliable data in studies of the effects of N fertilizers on N_2O emissions from soils, it is necessary to perform long-term studies because short-term studies can greatly overestimate these effects. This is illustrated by Table 1, which shows that, whereas the fertilizer-induced emissions of N_2O in 13 days from the plots treated with 250 kg N ha^{-1} as ammonium sulfate were 15.7 times greater than the emissions of N_2O from the unfertilized plots, the corresponding fertilizer-induced emissions in 96 days were only 0.86 times greater than the emissions from the unfertilized plots.

Hahn and Junge (1977) calculated that, when soils are treated with N fertilizers, the amount of fertilizer N converted to N_2O by soil microorganisms during the first one or two weeks after fertilization probably represents between 3 and 12% of the fertilizer N added. This seems a gross overestimate of the percentage of fertilizer N converted to N_2O in soils treated with ammonium sulfate, urea or calcium nitrate because Table 1 shows that the fertilizer-induced emissions of N_2O-N we observed in 13 weeks after application of these fertilizers represented only 0.01-0.18% of the fertilizer N added. It should be noted, however, that work in progress has shown that N_2O emissions from soils fertilized with anhydrous ammonia markedly exceed those from soils treated with ammonium sulfate, urea or calcium nitrate (Bremner and Blackmer, 1979b). The fertilizer-induced emissions of N_2O-N observed in the work reported in Table 1 are similar to those observed in recent laboratory studies (Bremner and Blackmer, 1978, 1979a) of the effects of ammonium sulfate, urea and potassium nitrate on N_2O emissions from Iowa soils and in a recent field study (McKenney et al., 1978) of the effects of different amounts of ammonium nitrate on N_2O emissions from two Canadian soils.

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accepted November 15, 1979)

MRI-18

MIDWEST RESEARCH INSTITUTE
PROJECT DEVELOPMENT SKETCH

TITLE Reference 18. 6 Breitenbeck et.al. Geophysical Res. Letters 7 (1), 1980.
(supporting articles attached) (2 pgs)

PROJECT NO. 6500-3513 fert. DRAWN Mulloy APPR. DATE 9-15-92

1. Fertilizers : Calcium nitrate } Spray
Urea
Ammonium sulfate
Blank

2. Rates : $\boxed{125\ kg\ N/ha}$ low conc
$\boxed{250\ kg\ N/ha}$ high conc

3. Data from Table 1, amounts from 13 days after application and from 96 days after application

Correct amounts for background and convert to $g\ N_2O/ha$

(a) Bkg Corr Amt = amount found − amt found in "none" field

ex. CN, 125, 13day = 23 g N/ha − 16 g N/ha = 7 g N/ha

(b) Corr. Amt = Bkg Corr Amt (g N/ha) $\times \frac{44\ g\ N_2O/ha}{14\cancel{29}\ g\ N/ha}$

ex. CN, 125 = 7 g N/ha $\times \frac{44\ g\ N_2O}{14\cancel{28}\ g\ N} = 22\ \frac{g\ N_2O}{ha}$

4. Emission factors (EF)

(c) $EF = \frac{\text{Corr Amt } (g\ N_2O/ha)}{\text{Rate } (kg\ N/ha)} = EF\ (g\ N_2O/kg\ N)$

(d) $EF_{day} = \frac{\text{corr Amt } (g\ N_2O/ha)}{\text{Rate } (kg\ N/ha)} \times \frac{1}{96\ day} =$ EF for total emissions (96 days) in $\frac{g\ N_2O}{kg\ N \cdot day}$

MIDWEST RESEARCH INSTITUTE
PROJECT DEVELOPMENT SKETCH

TITLE Ref 18 (pg 2 of 2)

PROJECT NO. 6500-3513 DRAWN MWillsey APPR. DATE 9-22-92

Example CaNO$_3$, rate = 125 kg N/ha, 96 days, Table 1, N_2O

$$Bkg = 330\ g\ N/ha \times \frac{44\ g\ N_2O}{14\ g\ N} = 1037\ g\ N_2O/ha$$

$$Emissions = (382 - 330\ g\ N/ha) \times \frac{44\ g\ N_2O}{14\ g\ N} = 163\ g\ N_2O/ha$$

$$EF = \frac{163\ g\ N_2O/ha}{125\ kg\ N/ha} = 1.307\ g\ N_2O/kg\ N$$

$$EF_{96} = \frac{163\ g\ N_2O/ha}{125\ kg\ N/ha \cdot 96\ day} = 0.0137\ g\ N_2O/kg\ N \cdot day$$

Table 18 - N_2O Emissions (Table 1, 96 days

Fertilizer	Rate	Corr Amt (Emissions g N_2O/ha)	EF (g N_2O/kg N)	EF_{day} (g N_2O/kg N day)
CaNO$_3$	125	163	1.307	0.0136
CaNO$_3$	250	88	0.352	0.0037
Urea	125	544	4.350	0.0453
Urea	250	902	3.608	0.0376
NH$_4$SO$_4$	125	713	5.707	0.0594
NH$_4$SO$_4$	250	889	3.558	0.0371

NOTE: 50-80% emissions occurred in 13 days.

Ref 1-5

(3)

A Simple Chamber Technique for Field Measurement of Emissions of Nitrous Oxide from Soils[1]

A. D. MATTHIAS, A. M. BLACKMER, AND J. M. BREMNER[2]

ABSTRACT

A simple technique for field measurement of the rate of emission of nitrous oxide (N_2O) from soil is described. It involves placement of an insulated cylindrical metal chamber over the soil surface for 20 min and removal of air samples from the chamber at 5-min intervals for N_2O analysis by a sensitive gas chromatographic technique that permits use of the xenon in air as an internal standard. The rate of N_2O emission is calculated from the rate of increase in the concentration of N_2O in the air within the chamber. This technique is sensitive and precise, and it has the important advantages that it does not significantly disturb the structure or environment of the soil under study and is not limited in use to sites where electricity or special equipment is available. The chamber described is inexpensive and easy to fabricate, transport, and use, and it is well suited for an extensive program of research on N_2O emissions from soils.

Additional Index Words: **soil disturbance, spatial variability, diurnal variability, gas chromatography, denitrification, nitrification, nitrogen fertilizers.**

Matthias, A. D., A. M. Blackmer, and J. M. Bremner. 1980. A simple chamber technique for field measurement of emission of nitrous oxide from soil. J. Environ. Qual. 9:251–256.

There is concern that increased nitrogen (N) fertilization of soils to aid food production will increase emissions of nitrous oxide (N_2O) from soils to the atmosphere and thereby pose a threat to the stratospheric ozone layer (CAST, 1976; Crutzen and Ehhalt, 1977; Liu et al., 1977; McElroy et al., 1977). To assess this threat, it is necessary to have reliable information concerning the effects of N fertilizers on N_2O emissions from soils. To obtain such information, it is essential to have a satisfactory method for field measurement of N_2O emissions from fertilized and unfertilized soils.

Several methods have been proposed for measurement of rates of N_2O emission from soils, including micrometeorological (e.g., Lemon, 1978), soil profile (e.g., Burford and Stefanson, 1973), and chamber (e.g., Burford and Hall, 1977; Rolston and Broadbent, 1977; Focht, 1978; McKenney et al., 1978; Ryden et al., 1978; Denmead, 1979) methods. Chamber methods have gained much greater acceptance than other techniques proposed, and most current research on N_2O emissions from field soils is being performed using chamber techniques. Recent work (Bremner and Blackmer, 1978a; S. G. Robbins, A. M. Blackmer, and J. M. Bremner. 1979. Spatial and diurnal variability in emission of nitrous oxide from soils, Agron. Abstr. p. 37) has shown, however, that use of chamber techniques is greatly complicated by spatial variability in N_2O emissions from soils and that emissions of N_2O from unfertilized soils often are <0.5 kg N_2O-N ha^{-1} $year^{-1}$. To overcome these problems, it is necessary to have a very sensitive chamber technique that is so simple and inexpensive that it is suitable for large-scale use and allows simultaneous measurement of N_2O emissions at numerous sites within the area of soil under study. The purpose of this article is to describe a chamber technique that meets these requirements and to report the results of studies to evaluate this technique.

MATERIALS AND METHODS

The chamber developed is illustrated diagrammatically in Fig. 1. It consists of an insulated, cylindrical, open-bottom chamber (diameter, 88 cm; height, 17 cm) fabricated from 16-gauge, galvanized sheet metal. The bottom of the chamber circumscribes an area of 6,080 cm^2. The chamber is insulated with white Styrofoam® (2 cm thick) and is fitted with a high density polyurethane foam collar (5 by 10 cm) covered with 6-mil polyethylene film. This collar is attached to the chamber by means of a tight-fitting metal band that encircles the collar and chamber. Its purpose is to insure a good seal between the chamber and the soil surface. When fitted with this collar, the effective height of the chamber is 17 cm.

A windbreak fabricated from 6-mil polyethylene film is used to minimize wind-induced movement of air into and out of the chamber. This windbreak extends from the top of the chamber to the soil surface about 80 cm outside the metal chamber. It is held to the soil surface by means of a 0.9-cm link chain placed along the perimeter of the windbreak.

The top of the chamber is fitted with an air sample port and a vent port. Both ports are 0.63-cm-O.D. stainless-steel tubes held in place by Swagelok® bulkhead unions. A short section of Tygon® tubing is attached to the air sample port for connection of air sample bottles to this port. The vent port is opened during removal of air samples from the chamber and is closed by a plastic cap in the intervals between removal of air samples.

Air samples are collected in 1-liter glass bottles fitted with glass stopcocks (1-mm-diam bore). Before being transported to the field, each bottle is evacuated, filled with purified N_2, and then reevacuated in the laboratory. A rotary-valve pump (Sargent-Welch Direct Torr Model 8810) is used to evacuate each sample bottle to a pressure of <0.1 mm Hg.

The procedure for using the chamber described involves placing the chamber on the soil surface, actuating a stopwatch timer, and deploying the windbreak. The chamber is kept on the soil surface for 20 min, and the air within the metal chamber is sampled at 5-min intervals by attaching an evacuated sample bottle to the sample port of the chamber and opening the stopcock on this bottle. The air samples removed from the chamber are analyzed for N_2O within 24 hours by a gas chromatographic procedure that utilizes the xenon in air as an

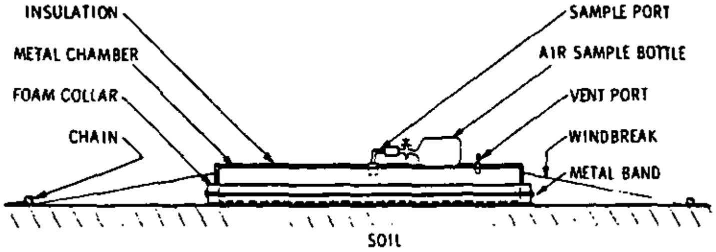

Fig. 1—Diagrammatic representation of chamber.

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internal standard (Blackmer and Bremner, 1977; A. M. Blackmer and J. M. Bremner. 1978. Determination of nitrous oxide in air. Agron. Abstr. p. 137).

The rate of N_2O emission is calculated from the equation

$$F = k(273/T)(V/A)(\Delta c/\Delta t)$$

where F is the rate of N_2O emission (kg N_2O-N ha^{-1} $year^{-1}$), k is a units conversion factor (0.066) for calculation of N_2O emission as kg N_2O-N ha^{-1} $year^{-1}$, T is the temperature of the air within the chamber (°K), V is the volume of the air within the chamber (cm^3), A is the area of the soil within the chamber (cm^2), and $\Delta c/\Delta t$ is the rate of change in the concentration of N_2O in the air within the chamber [ppb (vol/vol) N_2O min^{-1}].

Field testing of the chamber method described was performed in 1978 and 1979 at various sites within a 3-ha fallow field at the Iowa State University Agronomy Research Center 10 km southwest of Ames. The soil in the field selected had a wide range in properties representative of the Clarion-Nicollet-Webster soil association used extensively for agriculture in the north-central region of Iowa. It did not receive any fertilizer treatments during 1978 and 1979. Periodic cultivation maintained the field almost free of vegetation during the testing period.

Soil and air temperatures were determined to an accuracy of ±0.15°C by means of Markson Model 5750 digital thermometers fitted with vinyl-tip thermistor probes. The probes used were standardized with a mercury thermometer. The temperature of air within the chamber was measured at 10 cm above ground level by means of a thermistor probe extending through a sealable port in the chamber, and the temperature of air outside the chamber was measured at the same height by means of a radiation-shielded probe. The temperature of soil inside and outside the chamber was measured at a depth of 2 cm below the ground level.

RESULTS AND DISCUSSION

SORPTION OR EMISSION OF N_2O BY MATERIALS USED TO FABRICATE CHAMBER

To check that none of the materials used to construct the chamber described either sorbs or emits N_2O, we sealed the bases of several chambers with 6-mil polyethylene film, injected N_2O into these chambers (via the vent port) so that the concentration of N_2O in the air within the chambers was about 500 ppb (vol/vol), and removed air samples from each chamber after 1, 5, 15, 30, 45, and 60 min. Analysis of these samples for N_2O showed that no sorption or emission of N_2O occurred during this time.

EFFECT OF SOIL DISTURBANCE

All chamber techniques thus far proposed for measurement of N_2O emissions from soils involve insertion of the chamber into the soil under study, usually to a depth of 5 to 10 cm. The chamber technique described here is designed to avoid soil disturbance in this way because we have found that insertion of chambers into soil can lead to very marked increases in the rates of N_2O emission observed using chamber techniques. This is illustrated by Table 1, which shows the effect of soil disturbance on the rate of N_2O emission observed at 14 sites on a relatively wet (28% moisture) Webster soil. It can be seen that, on average, insertion of a metal cylinder into this soil to a depth of 5 cm led to a 250% increase in the rate of emission of N_2O. Smaller increases were observed when similar experiments were performed on soils having relatively low moisture contents. The increases observed as a result of soil disturbance cannot be attributed to diurnal variability in N_2O emissions (the measurements after disturbance were performed 1.5 hours after the measurements before disturbance) because simultaneous replicated measurements at undisturbed sites showed that N_2O emissions did not increase during the time that the measurements reported in Table 1 were performed.

Table 1—Effect of soil disturbance on rate of N_2O emission from soil at 14 sites.†

Site	Rate of N_2O emission Before soil disturbance	 After soil disturbance
	kg N_2O-N ha^{-1} $year^{-1}$	
1	6.0	64.7
2	5.6	7.1
3	32.1	71.5
4	6.5	33.1
5	17.1	35.4
6	0.6	7.6
7	7.5	45.2
8	1.1	8.4
9	0.3	4.1
10	3.5	14.8
11	8.1	13.1
12	5.5	11.0
13	5.0	16.3
14	2.9	26.3
Mean	7.3	25.6

† Measurements were performed at each site before and after disturbance of soil. Soil was disturbed by inserting a 16-gauge metal cylinder (diameter, 57 cm; height, 10 cm; open at both ends) about 5 cm into soil immediately before placement of chamber. Measurement before soil disturbance preceded measurement after soil disturbance by 1.5 hours.

It should be noted that, to prove unequivocally that insertion of a chamber into soil markedly affects the rate of emission of N_2O, we inserted a 57-cm-diam metal cylinder into soil to a depth of 5 cm and immediately covered this cylinder with our 88-cm-diam chamber. In other words, N_2O emission was measured from an area of soil ca 2.4 times greater than the area within the metal cylinder. If it is assumed that 50% of the emission induced by inserting a chamber into soil occurs in the inside of the chamber, it is evident from Table 1 that insertion of a 57-cm chamber into soil must markedly increase the rate of N_2O emission measured by such a chamber. The error in assessment of N_2O emissions caused by inserting chambers into soil should increase with decrease in the diameter of the chamber used because the proportion of soil under a chamber that is disturbed by insertion of the chamber obviously increases with decrease in the diameter of the chamber.

EFFECT OF WINDBREAK

The chamber described is fitted with a windbreak because we found that, although the foam collar effected a good seal between the chamber and the soil surface on calm days, it did not prevent movement of air into or out of the chamber on windy days. This became evident from plots of the concentration of N_2O in air within the chamber vs. the time the chamber was on the soil. These plots showed that, whereas the concentration of N_2O in air within the chamber increased linearly with time on calm days, it did not increase linearly with time on windy days. This is illustrated by Fig. 2, which shows

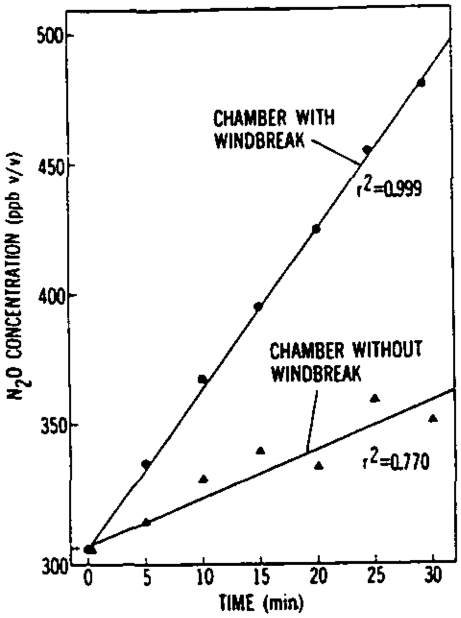

Fig. 2—Effect of windbreak on rate of N_2O emission observed by using chamber described.

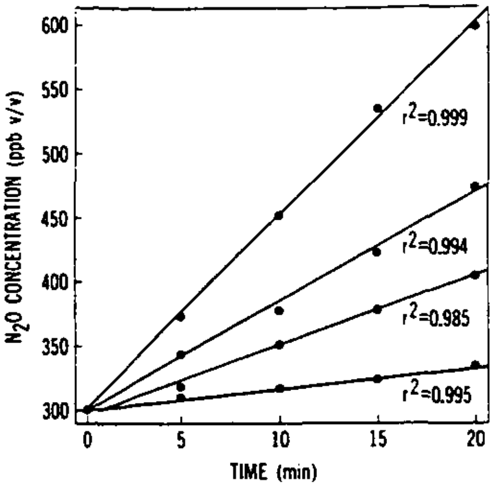

Fig. 3—Typical plots illustrating time dependency of N_2O concentration in air within chamber.

the effect of the windbreak on a windy day. It is noteworthy that tests showed that gusts of wind removed N_2O from chambers that had been inserted into soil to a depth of 5 or 10 cm, particularly when the soil under study had a low moisture content.

Studies under a variety of conditions showed that the concentration of N_2O in air under the windbreak did not increase linearly with time and that strong gusts of wind frequently caused a marked decrease in the concentration of N_2O in the air under the windbreak. The fact that we observed a linear increase with time in the concentration of N_2O in the air in the chamber even when such decreases occurred is evidence that the foam collar adopted effects a good seal between the chamber and the soil surface when the chamber is protected from the wind by the windbreak.

When applied to cropped fields, the chamber technique described has the advantage that it does not disturb plant roots. The windbreak easily fits over small plants, and the need for the windbreak is eliminated if the chamber is placed between rows of tall plants that act as a windbreak.

Several authors (Rolston and Broadbent, 1977; Focht, 1978; Matthias et al., 1978; Denmead, 1979) have noted that, when a chamber technique is used to measure the rate of emission of N_2O from soil, the true rate of emission will be underestimated if the concentration of N_2O in the air within the chamber becomes sufficiently high to significantly reduce the diffusive flow of N_2O from the soil. To minimize this problem, we use a tall chamber and place it over the soil surface for only a short time. Evidence that the problem is not serious using the chamber technique described is presented in Fig. 3, which shows typical examples of the linear relationships observed between the time the chamber is on the soil and the concentration of N_2O in the air within the chamber.

EFFECT OF CHAMBER ON TEMPERATURE OF SOIL AND AIR INSIDE CHAMBER

There is good evidence that the N_2O evolved from soils is produced by nitrifying microorganisms during oxidation of ammonium to nitrate and by denitrifying microorganisms during anaerobic reduction of nitrate (Alexander, 1977; Bremner and Blackmer, 1978a, 1978b, 1979). Because temperature has a very marked effect on the rates of microbial processes, it is obvious that any chamber technique used to measure N_2O emissions from soils should not significantly affect the temperature of the soil. Extensive tests showed that the chamber described meets this requirement. For example, a study was performed to determine the perturbation in soil temperature caused by placing a chamber over soil for 20 min at 2-hour intervals for 3 days (26 to 29 June 1978). The temperature perturbation observed in 37 tests during this time did not exceed 1.0°C and averaged 0.4°C (perturbation = temperature of soil at 2 cm below ground level inside chamber minus temperature of soil at same depth outside chamber). Concurrent measurements in this study of the perturbation in air temperature under the chamber described showed that it did not exceed 2.0°C in any 20-min period and averaged 0.6°C (perturbation = temperature of air at 10 cm above ground level inside chamber minus temperature of air at same height outside chamber). These perturbations in soil and air temperatures are insignificant compared with the 21°C variation in soil temperature and the 17°C variation in air temperature observed outside the chamber during the 3-day study.

The need to insulate the chamber described was demonstrated by studies illustrated by Fig. 4, which shows the effects of different chambers (diameter, 88 cm; height, 15 cm) on the temperature of air within these chambers when they were placed over soil for 20 min. It can be seen that the perturbation in the temperature of air within the insulated metal chamber was very small compared with the perturbations observed with the metal and Plexiglas® chambers.

Inasmuch as several chamber techniques proposed for

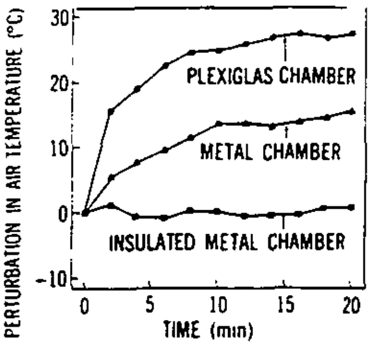

Fig. 4—Perturbation in temperature of air under different chambers placed over soil for 20 min. (Perturbation = temperature of air at 10 cm above ground level inside chamber minus temperature of air at same height outside chamber.)

measurement of N_2O emissions from soils require placement of the chamber over the soil surface for several hours, attention should be drawn to the fact that any type of chamber significantly affects the temperature of the soil and air within it if left in place for more than a short time. This is illustrated by Fig. 5 and 6, which show the perturbations in soil and air temperature observed when different chambers (diameter, 88 cm; height, 15 cm) were placed over soil and left in place for several days.

EFFECT OF AIR PRESSURE FLUCTUATIONS

Because studies by Kimball and Lemon (1971, 1972) and Kimball (1973) have suggested that air-pressure fluctuations caused by turbulent movement of air over the soil surface may affect gaseous mass flow within soil, we studied the possibility that the chamber described may mask these fluctuations and thereby affect the rate of emission of N_2O from soil. We found, however, that the rates of N_2O emission observed at various sites using the chamber described were not significantly affected by air-pressure fluctuations induced by withdrawing and reinjecting 300 ml of air at 20-sec intervals during the 20-min period the chamber was over the soil.

We also checked the possibility that the rate of N_2O emission from soil under the chamber described may be affected by withdrawal of air samples at 5-min intervals as specified. We found, however, that the concentration of N_2O in air under chambers allowed to stand over soil for 20 min without removal of air samples at 5-min intervals was not significantly different from that observed after 20 min when air samples were removed at 5, 10, and 15 min. Although these tests showed that the method used to remove air samples in the procedure described does not induce significant mass flow of N_2O from soil, we share the concern of Denmead (1979) that methods of measuring N_2O emissions that involve maintenance of a slight pressure deficit in chambers inserted into soil may induce significant mass flow of N_2O from soil.

EFFECT OF MIXING AIR WITHIN CHAMBER

Initially we used a small electric fan to mix the air within the chamber described because we suspected that failure to mix this air before sampling would lead to unsatisfactory results. The fan used was fitted so that it was near the center of the chamber and about 10 cm above the soil surface, and it was operated at about 500 rpm. However, repeated tests during the summer of 1978 revealed no significant difference between results obtained when this fan was operated and when it was not operated.

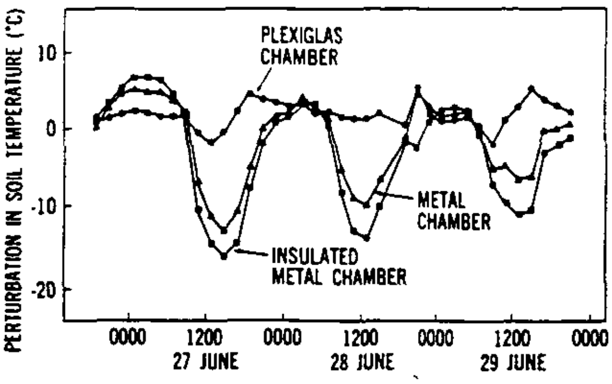

Fig. 5—Perturbation in temperature of soil under different chambers placed over soil for several days. (Perturbation = temperature of soil at 2 cm below ground level inside chamber minus temperature of soil at same depth outside chamber.)

EVALUATION OF TECHNIQUES USED FOR COLLECTION AND N_2O ANALYSIS OF AIR SAMPLES

No loss of vacuum could be detected when the evacuated bottles used to collect air samples were allowed to stand for 24 or 48 hours. Also, tests in which the evacuated bottles were filled with purified (N_2O-free) N_2 showed that no trace of N_2O could be detected when the contents of these bottles were analyzed after 24 or 48 hours.

The gas chromatographic procedure used for N_2O analysis has the important advantages that it permits use of the xenon in air as an internal standard and does not require frequent calibration to obtain satisfactory results. It allows analysis of >80 air samples for N_2O in a normal working day, and it enabled us to analyze

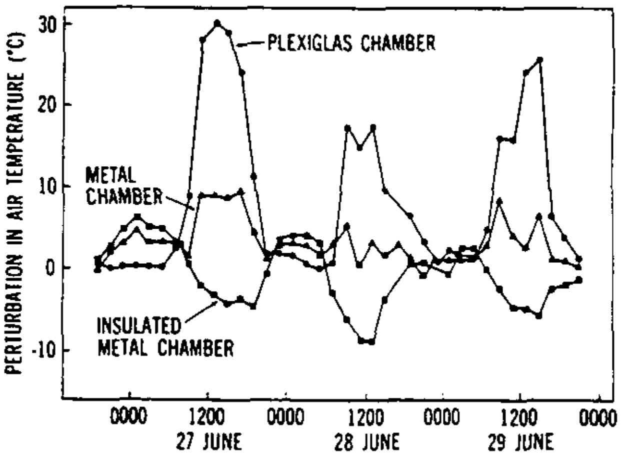

Fig. 6—Perturbation in temperature of air under different chambers placed over soil for several days. (Perturbation = temperature of air at 10 cm above ground level inside chamber minus temperature of air at same height outside chamber.)

Table 2—Results of triplicate measurements of N_2O emission rates at 10 sites.†

Site	Rate of N_2O emission				
	Measurement				
	1	2	3	Mean	SD
	kg N_2O-N ha^{-1} $year^{-1}$				
1	21.3	20.6	19.9	20.6	±1.2
2	150	147	134	144	±8.0
3	35.4	34.6	36.2	35.4	±0.8
4	16.2	13.0	15.7	15.0	±1.7
5	27.5	23.8	24.3	25.2	±2.0
6	15.5	17.5	17.7	16.9	±1.2
7	14.4	17.8	18.3	16.8	±2.1
8	42.8	31.2	37.2	37.1	±5.8
9	25.5	26.0	31.0	27.5	±3.0
10	119	135	121	125	±8.7
Mean	46.8	46.7	45.5		
SD	±47.7	±50.2	±44.0		

Analysis of variance

Source	Degrees of freedom	Sum of squares	Mean square	*F* value
Spatial variation among sites	9	60.155	6,689	319
Error	20	410	21	
Corrected total	29	60,565		

† Measurements were performed between 1000 and 1200 on 10 June 1979.

>24,000 air samples for N_2O during the past year. The standard deviation of the mean of the N_2O concentration values obtained by this procedure in 60 analyses of air from a cylinder of compressed air containing 305 ppb (vol/vol) N_2O was ± 1 ppb (vol/vol).

PRECISION OF TECHNIQUE

The precision of the technique described was studied by performing triplicate measurements of N_2O emission rates at a variety of sites during 1978 and 1979. These measurements were performed within 2 hours at each site to minimize error caused by diurnal variability in emissions. Typical data are reported in Table 2, which shows the results of triplicate measurements performed at 10 sites between 1000 and 1200 on 10 June 1979. The sites selected were within a small area (100 m^2) of seemingly uniform Webster soil. Table 2 shows that the results of triplicate measurements at each site were in good agreement. It also shows that the variability in measurements among sites was much greater than the variability in the measurements at each site. It is evident, therefore, that the accuracy of an assessment of N_2O emissions from a given area is much more dependent upon the number of sites studied within this area than on the accuracy of the measurement performed at any site.

SENSITIVITY OF TECHNIQUE

The technique described is more sensitive than chamber techniques previously proposed for measurement of N_2O emissions from soils, and it permits detection of N_2O emission rates as low as 0.1 kg N_2O-N ha^{-1} $year^{-1}$. It also permits studies of the ability of soils to act as sinks for atmospheric N_2O (i.e., to remove N_2O from air), and it enabled us to detect sink activity at several sites during a recent survey of the ability of unfertilized soils to act as sources or sinks of atmospheric N_2O. If the soil under study is evolving very small amounts of N_2O, the sensitivity of the technique described can be increased by increasing the time the chamber is placed over the soil surface. If the soil under study is evolving large amounts of N_2O, the time the chamber is placed over the soil surface can be reduced.

ADVANTAGES OF TECHNIQUE

To summarize, besides being simple and precise, the technique described has the following advantages: (i) it has high sensitivity and allows detection of very small emissions of N_2O from unfertilized soils; (ii) it does not involve significant disturbance of the soil structure or the soil environment; (iii) its use is not limited to sites where electricity or special equipment is available; and (iv) the chamber used is inexpensive and easy to fabricate, transport, and use, and it is well suited for an extensive program of research on N_2O emissions from fertilized and unfertilized soils.

The key advantage of the technique described is that it permits much more extensive monitoring of N_2O emissions than do other chamber methods proposed. For example, it allows two technicians to routinely monitor N_2O emissions at >100 sites in a normal working day.

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$$F = (0.066)\left(\frac{273}{\ }\right)\left(\frac{103360\ cm^3}{6080\ cm^2}\right)$$

Nutrients and Associated Ion Concentrations in Irrigation Return Flow from Flooded Rice Fields[1]

F. T. TURNER, K. W. BROWN, AND L. E. DEUEL[2]

ABSTRACT

A 3-year field study of nutrient and common ion concentrations in irrigation return flow (IRF) from flooded rice fields utilized replicated plots which received either recommended or excessive fertilizer rates with continuous flow or intermittent flood irrigation. All P and K and 40% of the $(NH_4)_2SO_4$ nitrogen (N) were applied preplant and incorporated. The remaining N was applied just prior to permanently flooding (40%) and at 2-mm panicle stage (20%). The irrigation and plot water were analyzed for NH_4^+-N, NO_3^--N, NO_2^--N, PO_4^{3-}-P, K^+, Ca^{2+}, Mg^{2+}, Na^+, Cl^-, and SO_4^{2-}. Highest nitrate-N concentrations occurred early in the season before the permanent flood period, but did not exceed drinking water standards. Nitrite-N concentrations in the IRF were low at all times. Maximum NH_4^+-N concentrations occurred following N fertilizer applications which were not incorporated into the soil and persisted in the floodwater for 5 to 7 days. These peak NH_4^+-N concentrations exceeded acceptable drinking water standards concentration by a factor of 10 or greater. Concentrations of PO_4^{3-}-P and K^+ in the floodwater were similar to those in the surface water used for irrigation. The concentration of the other common ions in the floodwater did not greatly exceed those in the irrigation water and all were within concentrations acceptable for drinking water. Method of fertilizer application had more influence on IRF nutrient concentrations than did fertilizer rates or irrigation management practices. Under the conditions of this study, it appears that only the ammonium concentrations may have a detrimental impact on the quality of IRF from flooded rice fields. This potential problem could be minimized by preventing IRF for a period of 1 week following surface applications of $(NH_4)_2SO_4$ fertilizer.

Additional Index Words: **water quality, pollution, runoff, rice culture.**

Turner, F. T., K. W. Brown, and L. E. Deuel. 1980. Nutrients and associated ion concentrations in irrigation return flow from flooded rice fields. J. Environ. Qual. 9:256-260.

Water draining from land has the potential for adding excessive amounts of sediment, pesticide, salts, or nutrients to the body of water into which it flows. Such water pollution problems have been discussed by Law and Skogerboe (8), Ryden et al. (11), and Viets (13). The problem considered in this investigation is restricted to nutrient concentrations in the irrigation return flow (IRF) from flooded rice fields. Literature on this subject is limited.

Gilmour et al. (6) found the average concentration of Ca^{2+}, Mg^{2+}, and Na^+ in runoff following winter (October through March) rains on a Crowley silt loam in Arkansas to be 19, 7, and 16 mg liters^{-1}, respectively, when the runoff was 40.1 cm; when the winter runoff was only 11.4 cm the average concentrations were 30, 9, and 26 mg liter^{-1}, respectively. The quantity of Ca^{2+}, Mg^{2+}, and Na^+ removed was 56, 26, and 57 kg ha^{-1}, respectively, for the greater runoff, and 24, 9, and 7 kg ha^{-1} in the lesser runoff. They concluded that removal of low-solubility salts by winter runoff is slow but continuous; whereas, the rate of removal of highly soluble salts is much greater and continues until the salt is dissolved. Surface runoff of salt appears to be more important than leaching as a means of salt removal from poorly drained rice soils because Brown et al. (2) reported that seepage through a Beaumont clay rice soil in Texas was a rather insignificant means of water and salt loss. However, Bilal et al. (1), working with a more permeable California rice soil, found significant inorganic nitrogen (N) loss in floodwater seepage through the soil profile and also in the IRF, from flooded rice culture. They measured inorganic N in the floodwater and soil solution of N-fertilized rice plots. Plots in which 112 kg $(NH_4)_2SO_4$-N ha^{-1} was incorporated into the dry soil just prior to flooding had NH_4^+-N floodwater concentrations of <2 mg liter^{-1} throughout most of the growing season. When the flooded soil was topdressed with 56 kg $(NH_4)_2SO_4$-N ha^{-1}, the NH_4^+-N floodwater concentration reached nearly 50 mg liter^{-1}, but decreased to below 2 mg liter^{-1} within 5 days after topdressing. Because of the high seepage (128 to 222 cm) and surface runoff (204 to 219 cm) during the 119 days that the soil was flooded, the inorganic N loss in runoff and seepage for the three water management systems used was 18.6, 36.4, and 30.2 kg N ha^{-1}, which represented 11, 22, and 18% of the applied N fertilizer, respectively. Nitrogen loss in seepage accounted for 45, 61, and 70%, respectively, of the total N loss in seepage and runoff. The amount of irrigation water that Bilal et al. (1) applied to compensate for evapotranspiration,

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(2)

Determination and Isotope-Ratio Analysis of Different Forms of Nitrogen in Soils: 3. Exchangeable Ammonium, Nitrate, and Nitrite by Extraction-Distillation Methods[1]

J. M. Bremner and D. R. Keeney[2]

ABSTRACT

Methods of determining exchangeable ammonium, nitrate, and nitrite in soils are described. They involve extraction of the soil sample with 2M KCl (10 ml/g of soil) and analysis of the extract by steam-distillation methods in which magnesium oxide is used for distillation of ammonium, ball-milled Devarda alloy for reduction of nitrate and nitrite to ammonium, and sulfamic acid for destruction of nitrite. The distillation methods are rapid, accurate, and precise, have high specificity, and are applicable to turbid, colored, and unfiltered soil extracts. They give quantitative recovery of ammonium, nitrate, and nitrite added to soil extracts and permit nitrogen isotope-ratio analysis of these forms of nitrogen in N^{15}-tracer studies of nitrogen transformations in soils.

THE METHODS CURRENTLY favored for determination of exchangeable ammonium, nitrate, and nitrite in soils involve extraction of these forms of nitrogen and analysis of the extract by colorimetric or distillation techniques. The defects of these methods have been discussed in a recent monograph (2), and it suffices here to say that most of them have serious limitations. For example, the extraction procedures commonly used for determination of nitrate or nitrite by colorimetric methods are not satisfactory for determination of exchangeable ammonium, which means that at least two extractions must be performed when analyses for exchangeable ammonium, nitrate, and nitrite are required. Also, some of the extraction procedures used lead to biological or nonbiological reactions resulting in an increase or decrease in the amount of the form of nitrogen under analysis or yield extracts which are unstable and cannot be safely stored before analysis. The main defects of the methods generally used for determination of inorganic forms of nitrogen in soil extracts are that they lack sensitivity, are subject to interference by organic or inorganic soil constituents, are inapplicable to turbid or colored extracts, or are tedious and time-consuming.

Development of a method for determination of exchangeable ammonium in soils is complicated by lack of generally accepted definitions of exchangeable ammonium and fixed ammonium. The Soil Science Society of America (9) has recommended definition of ammonium fixation as "the adsorption or absorption of ammonium ions by the mineral or organic fractions of the soil in a manner that they are relatively insoluble in water and relatively unexchangeable by the usual methods of cation exchange", but it has not proposed definitions of fixed or exchangeable ammonium. However, most workers have found it convenient to define fixed (nonexchangeable) ammonium as ammonium which is not extractable by 1*M* KCl at laboratory temperatures, and, since this definition has gained considerable acceptance, it seems logical to define exchangeable ammonium as ammonium which is extractable by 1*M* KCl at room temperature. In the methods of analysis described here, exchangeable ammonium in soils is arbitrarily defined as ammonium extractable by 2*M* KCl at room temperature, because it has been found that use of 2*M* KCl has practical advantages and that the amount of ammonium extracted from soils by 2*M* KCl is identical to the amount extracted by 1*M* KCl.

The objective in the work reported was to develop methods of determining exchangeable ammonium, nitrate, and nitrite in soils in which only one extraction of the soil sample is required for performance of these analyses and the extract can be stored for some time before analysis. Additional requirements were that the methods should be rapid, specific, and precise and should permit nitrogen isotope-ratio analysis of exchangeable ammonium, nitrate, and nitrite in N^{15}-tracer studies of nitrogen transformations in soils. The methods described have been found to meet these requirements. They involve extraction of the soil sample by shaking it with 2*M* KCl (10 ml/g of soil) for 1 hr and analysis of the extract by steam-distillation methods in which the form of nitrogen under analysis is converted to, and estimated as, ammonium, which is readily oxidized to nitrogen gas for mass-spectrometer assay of N^{15} (8). The distillation techniques employed have been described (4). They involve use of ignited magnesium oxide for distillation of ammonium, finely-divided Devarda alloy for reduction of nitrate and nitrite to ammonium, and sulfamic acid for destruction of nitrite ($NH_2SO_3H + HNO_2 = N_2 + H_2SO_4 + H_2O$). They are rapid, accurate, and precise, have high specificity, and are applicable to turbid, colored, and unfiltered soil extracts.

MATERIALS

Soils—The soils used (Table 1) were surface (0- to 15-cm) samples previously air-dried and crushed to pass a 2-mm

Table 1—Analyses of soils

Soil No.	Soil Type	pH	Organic carbon	Total nitrogen	Cation-exchange capacity
			%	%	meq/100 g
1	Nicollet l	6.9	1.53	0.168	20.5
2	Houston sic	7.9	2.33	0.195	41.8
3	Marshall sicl	4.8	2.12	0.209	26.8
4	Webster cl	6.6	3.19	0.244	40.2
5	Tama sil	6.0	3.04	0.272	23.8
6	Primghar sicl	7.0	3.41	0.313	33.2
7	Clyde sil	5.5	4.30	0.402	29.9
8	Glencoe sic	8.0	9.60	0.910	58.5

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sieve. In the analyses reported in Table 1, total nitrogen was determined by a semimicro-Kjeldahl procedure (1), organic carbon by the method of Mebius (7), pH by a glass electrode (soil/water ratio, 1:2.5), and cation-exchange capacity by the ammonium acetate procedure described by Jackson (6).

METHODS FOR DETERMINATION OF EXCHANGEABLE AMMONIUM, NITRATE, AND NITRITE

Apparatus

Steam-distillation apparatus—The apparatus used has been described (3). It is designed so that flasks fitted with standard-taper (19/38) ground-glass joints can be used as distillation chambers. Before use, the apparatus should be steamed out for about 10 min to remove traces of ammonia, and the rate of steam generation should be adjusted so that about 7.5 ml of distillate are collected/min.

Distillation flasks—The flasks used are 100-ml Kjeldahl flasks fitted with a side-arm, standard-taper ground-glass joints, and glass hooks, the neck of the side-arm being fitted with a standard-taper polyethylene stopper (4). The flask dimensions should be such that, when the flasks are connected to the distillation apparatus, the distance between the tip of the steam inlet tube and the bottom of the flask is approximately 4 mm.

Reagents

Potassium chloride solution, approximately 2*M*—Dissolve 1,500 g of reagent-grade KCl in 8 liters of water and dilute the solution to 10 liters.

Magnesium oxide—Heat heavy magnesium oxide (U.S.P.) in an electric muffle furnace at 600 to 700C for 2 hr. Cool the product in a desiccator containing KOH pellets and store it in a tightly stoppered bottle.

Boric acid-indicator solution—Prepare as previously described (3).

Devarda alloy—Ball-mill reagent-grade alloy until the product will pass a 100-mesh screen and at least 75% of it will pass a 300-mesh screen (4).

Sulfamic acid—Dissolve 2 g of purified sulfamic acid (4) in 100 ml of water. Store the solution in a refrigerator.

Sulfuric acid—0.005*N* standard.

Standard (ammonium + nitrate)-N solution—Dissolve 0.236 g of ammonium sulfate and 0.361 g of potassium nitrate in water, dilute the solution to 1,000 ml in a volumetric flask, and mix the solution thoroughly. If pure, dry reagents are used, this solution contains 50 μg of ammonium-N and 50 μg of nitrate-N/ml. Store the solution in a refrigerator.

Standard (ammonium + nitrate + nitrite)-N solution—Dissolve 0.236 g of ammonium sulfate, 0.123 g of sodium nitrite, and 0.361 g of potassium nitrate in water, dilute the solution to 1,000 ml in a volumetric flask, and mix the solution thoroughly. If pure, dry reagents are used, this solution contains 50μg of ammonium-N, 50μg of nitrate-N, and 25 μg of nitrite-N/ml. Store the solution in a refrigerator.

Procedure

PREPARATION OF SOIL EXTRACT

Place 10 g of soil in a 250-ml, wide-mouth bottle and add 100 ml of 2*M* KCl. Stopper the bottle and shake it on a mechanical shaker for 1 hr. Then allow the soil-KCl suspension to settle until the supernatant liquid is clear (usually about 30 min) and perform the analyses described on aliquots of this liquid. If the KCl extract cannot be analyzed soon after its preparation (within 24 hr), filter the soil-KCl suspension (Whatman no. 42 filter paper) and store the filtrate in a refrigerator until analyses can be performed.

ANALYSIS OF EXTRACT WHEN NITRITE IS PRESENT

Ammonium-N—Add 5 ml of boric acid-indicator solution to a 50-ml Erlenmeyer flask marked to indicate a volume of 30 ml and place the flask under the condenser of the steam-distillation apparatus so that the end of the condenser is about 4 cm above the surface of the boric acid. Pipette an aliquot (usually 20 ml) of the soil extract into a distillation flask and add 0.2 g of MgO through a dry powder funnel with a stem reaching into the bulb of the flask. Attach the flask to the distillation apparatus by spiral steel springs with loop ends and commence distillation by closing the stopcock on the steam-bypass tube of the distillation apparatus. When the distillate reaches the 30-ml mark on the receiver flask, stop the distillation by opening the stopcock on the steam-bypass tube, rinse the end of the condenser, and determine ammonium-N in the distillate by titration with 0.005*N* H_2SO_4 from a 5-ml microburette graduated at 0.01-ml intervals (1 ml of 0.005*N* H_2SO_4 = 70 μg of NH_4-N). The color change at the end-point is from green to a permanent, faint pink.

(Nitrate + nitrite)-N—After removal of ammonium-N from the sample as described in the previous section, remove the stopper from the side-arm of the flask, add 0.2 g of Devarda alloy through a dry powder funnel with a stem reaching into the flask about 1 cm below the base of the ground joint on the side-arm, and immediately replace the stopper in the neck of the side-arm. Then determine the ammonia-N liberated by steam distillation as described in the previous section.

(Ammonium + nitrate + nitrite)-N—Follow the procedure described for determination of ammonium-N, but add 0.2 g of Devarda alloy to the distillation flask immediately after addition of MgO and before connection of the flask to the distillation apparatus.

(Ammonium + nitrate)-N—Follow the procedure described for determination of (ammonium + nitrate + nitrite)-N, but before addition of MgO and Devarda alloy, treat the sample in the distillation flask with 1 ml of sulfamic acid solution and swirl the flask for a few seconds to destroy nitrite before connecting it to the distillation apparatus.

Nitrate-N—Follow the procedure described for determination of (nitrate + nitrite)-N, but perform the analysis on a sample that has been treated with sulfamic acid to destroy nitrite as in the procedure for determination of (ammonium + nitrate)-N.

ANALYSIS OF EXTRACT WHEN NITRITE IS ABSENT

Ammonium-N—Follow the procedure described for determination of ammonium-N in the presence of nitrite.

Nitrate-N—Follow the procedure described for determination of (nitrate + nitrite)-N in the presence of nitrite.

(Ammonium + nitrate)-N—Follow the procedure described for determination of (ammonium + nitrate + nitrite)-N in the presence of nitrite.

CONTROL AND CHECK ANALYSES

Controls should be performed in each series of analyses to allow for ammonium-N derived from the reagents used, and the steam-distillation procedures should be checked at intervals by analyzing 5-ml aliquots of the standard (ammonium + nitrate) -N and (ammonium + nitrate + nitrite)-N solutions. Both solutions are stable for several months if stored in a refrigerator.

DISTILLATION FOR N^{15} ANALYSIS

If the ammonium liberated by distillation in the various methods of analysis described is to be analyzed for N^{15}, modify the distillation technique as described by Bremner and Edwards (3).

RESULTS AND DISCUSSION

Unless otherwise specified, all analytical data reported represent the means of results of replicate analyses which were in close agreement.

Table 2—Ammonium-N extracted by shaking incubated soils with KCl solution (10 ml/g of soil) for 1 hr

Soil no.	Molarity of KCl solution					
	0.125	0.25	0.50	1.0*	2.0	4.0†
	Ammonium-N extracted, ppm of soil					
1	21	23	24	26 (27)	27	27 (27)
2	68	76	80	81 (82)	82	82 (82)
3	85	94	95	96 (98)	98	98 (98)
4	39	43	46	49 (52)	52	52 (52)
8	230	237	242	246 (252)	252	252 (252)

* Figures in parentheses are values obtained using 20 ml of 1.0M KCl/g of soil.

† Figures in parentheses are values obtained using 5 ml of 4.0M KCl/g of soil.

Table 3—Ammonium-N extracted by shaking incubated soils with different volumes of 2*M* KCl for 1 hr

Soil no.	Milliliters of 2M KCl/g of soil			
	2	5	10	20
	Ammonium-N extracted, ppm of soil			
1	24	26	27	27
2	79	82	82	82
3	94	95	98	98
4	44	49	52	52
8	236	244	252	252

Table 4—Ammonium-N extracted by shaking incubated soils with 2M KCl (10 ml/g of soil) for different times.

Soil no.	Shaking time, min					
	15	30	45	60	120	480
	Ammonium-N extracted, ppm of soil					
1	26	27	27	27	27	27
2	81	82	82	82	82	82
3	96	97	97	98	98	98
4	50	51	52	52	51	52
8	237	249	251	252	253	252

Extraction Procedure

Development—Since preliminary work using soils 2, 5, 6, and 7 showed that nitrate and nitrite added to these soils were readily extracted by a short (5- to 10-min) period of shaking with water or dilute KCl solution, the problem of developing an extraction procedure for determination of exchangeable ammonium, nitrate, and nitrite was basically that of finding a satisfactory KCl treatment for extraction of exchangeable ammonium. The extraction procedure recommended developed from studies using different volumes and concentrations of KCl solution and different shaking times. These studies showed that, when an equilibrium extraction technique is used, the amount of ammonium extracted from soils by KCl solution at room temperature is essentially maximal if 2*M* KCl is used and the soil sample is shaken with this reagent for 1 hr using 10 ml of 2*M* KCl/g of soil. This is illustrated by the data in Tables 2, 3, and 4, which show the effects of varying the concentration of the KCl solution used for extraction, the volume of 2*M* KCl/g of soil, and the time of shaking with 2*M* KCl on the amount of ammonium extracted by KCl solution from various soils. To ensure accurate evaluation of these effects, the soils studied were incubated under waterlogged conditions at 30C for 4 weeks and air-dried before use so that they would contain an appreciable amount of exchangeable ammonium. It can be seen that the amount of ammonium extracted by the 2*M* KCl technique recommended (10 ml of 2*M* KCl/g of soil) was identical to the amount extracted by 1*M* KCl using 20 ml/g of soil or by 4*M* KCl using 5 ml/g of soil (Table 2), and that it was not increased if either the volume of 2*M* KCl or the time of shaking recommended was increased (Tables 3 and 4). In other words, these studies showed that the amount of ammonium extracted by shaking soil with KCl solution at room temperature for 1 hr is the same whether 1*M*, 2*M*, or 4*M* KCl is used, provided that the amount of KCl solution employed contains the equivalent of 20 meq of K/g of soil; and that it is not increased if the meq of K/g of soil exceeds this value or if the time of shaking is increased. The 2*M* KCl extraction procedure was adopted because use of 2*M* KCl instead of 1*M* KCl reduces the size of the aliquot of extract required for satisfactory analysis by the steam distillation methods described, and analyses of several soils showed that the results obtained using 2*M* KCl for extraction had slightly higher precision than those obtained using 3*M* KCl or 4*M* KCl.

Table 5—Analyses of filtered and unfiltered soil extracts by steam-distillation methods described

Soil no.	Extract*	Method†				
		1	2	3	4	5
		μg of N/20 ml of extract				
1	F	9	4	13	4	13
	U	9	4	13	4	13
2	F	8	4	12	4	12
	U	8	4	12	4	12
3	F	26	18	44	18	44
	U	26	18	44	18	44
	F‡	26	217	243	418	443
	U‡	26	218	244	417	444
4	F	8	4	12	4	12
	U	8	4	12	4	12
	F‡	8	204	212	405	412
	U‡	8	205	211	404	412
5	F	70	6	76	6	77
	U	70	6	76	6	76
8	F	16	6	22	6	22
	U	17	6	22	6	22

* Extracts were prepared by shaking soil samples with 2M KCl (10 ml/g of soil) for 1 hr. F, filtered extract; U, unfiltered extract. Analyses were performed on 20-ml aliquots of extracts.

† 1, ammonium-N; 2, nitrate-N; 3, (ammonium + nitrate)-N; 4, (nitrate + nitrite)-N; 5, (ammonium + nitrate + nitrite)-N.

‡ Aliquot of extract (20 ml) was treated with 5 ml of solution containing 200μg of nitrate-N (as KNO_3) and 200 μg of nitrite-N (as $NaNO_2$) immediately before analysis.

Filtration—Soil extracts prepared by the procedure recommended need not be filtered for analysis by the steam-distillation methods described (Table 5). Moreover, the aliquot of unfiltered extract taken for analysis need not be free of suspended soil material because the distillation methods of analysis described are not affected by this material. However, pipettes with wide tips should be used to sample supernatant liquids that are not clear, because pipettes with fine tips are liable to become clogged by suspended material. Filtration is recommended if the extract must be stored for some time before analysis because filtered extracts can be stored safely for several weeks if kept in a refrigerator (Table 7).

Recovery tests—Table 6 shows results of studies to determine the recoveries by the methods described of ammonium,

Table 6—Recoveries of ammonium-N, nitrate-N, and nitrite-N by methods described

Soil No.	Recovery of N added to soil, %*						Recovery of N added to soil extracts, %		
	NH_4-N		NO_3-N		NO_2-N		NH_4-N	NO_3-N	NO_2-N
	A	B	A	B	A	B			
1	99.5	91.0	100.6	100.6	99.8	94.9	100.1	99.6	100.0
2	100.5	84.5	99.6	99.6	99.8	99.1	100.0	99.9	99.8
3	99.5	95.4	100.5	100.5	99.6	95.5	100.2	99.8	100.2
4	99.8	79.8	99.6	100.4	99.7	96.6	99.8	100.1	100.1
5	99.6	97.4	99.1	99.4	100.6	98.4	100.1	99.6	100.2
6	99.8	96.6	100.0	99.8	99.5	98.5	99.8	99.9	99.9
7	100.0	92.7	100.1	99.6	99.5	93.0	100.0	99.9	99.8
8	99.8	87.2	99.9	99.6	99.9	97.4	100.0	99.9	99.8
Avg.	99.8	90.6	99.9	100.0	99.8	96.7	100.0	99.8	100.0

* A, standard (ammonium + nitrate + nitrite)-N solution was added to soil immediately after addition of KCl solution; B, standard (ammonium + nitrate + nitrite)-N solution was added to soil immediately before addition of KCl solution.

nitrate, and nitrite added to various soils. Recoveries were determined by analyzing extracts obtained by shaking 10 g of soil with 100 ml of 2*M* KCl and 10 ml of standard (ammonium + nitrate + nitrite)-N solution for 1 hr, the latter solution being added immediately before or after the addition of 2*M* KCl, and by subtracting the ammonium-N, nitrate-N, and nitrite-N values obtained in analyses of extracts obtained by shaking 10 g of soil with 100 ml of 2*M* KCl and 10 ml of water for 1 hr. It can be seen that the methods described gave quantitative recoveries of ammonium-N, nitrate-N, and nitrite-N added to soils after addition of KCl, and that, when these forms of nitrogen were added before addition of KCl, their recoveries averaged 90.6, 100.0, and 96.7%, respectively. Failure to achieve quantitative recovery of ammonium added before addition of KCl is readily explicable on the grounds that the soils used had the capacity to fix ammonium. Work in progress indicates that the failure to obtain completely quantitative recovery of nitrite-N added before addition of KCl is due to chemical decomposition of nitrite by soil constituents.

Table 6 also shows data obtained in studies to determine the recoveries by the steam-distillation procedures described of ammonium, nitrate, and nitrite added to 2*M* KCl extracts of soils. The extracts used were prepared by shaking 10 g samples of soils with 100 ml of 2*M* KCl for 1 hr and filtering the resulting suspensions, and the recoveries reported were calculated from analyses of 20-ml aliquots of these extracts before and after addition of 5 ml of standard (ammonium + nitrate + nitrite)-N solution. Exchangeable ammonium-N, nitrate-N, and (nitrate + nitrite)-N were determined by the procedures recommended for determination of these forms of nitrogen in the presence of nitrite, and nitrite-N was calculated by difference. It can be seen that the distillation procedures described gave quantitative recoveries of ammonium-N, nitrate-N, and nitrite-N added to KCl extracts of all soils studied. Similar studies showed that these distillation procedures also gave quantitative recoveries of ammonium-N, nitrate-N, and nitrite-N added to water, NaCl, and K_2SO_4 extracts. The standard (ammonium + nitrate + nitrite)-N solution used in the recovery tests reported contained 200 μg/ml of ammonium-N [as $(NH_4)_2SO_4$], nitrate-N (as KNO_3), and nitrite-N (as $NaNO_2$).

Changes during extraction—To be satisfactory, a method used to prepare soil extracts for determination of exchangeable ammonium, nitrate, or nitrite should neither cause nor permit biological or nonbiological reactions which lead to an increase or decrease in the amounts of these forms of nitrogen. The recovery tests reported in Table 6 indicate that the extraction procedure recommended meets this requirement, and other tests performed support this conclusion. We found, for example, that the results of soil analyses by the methods described are not affected if the 2*M* KCl used for extraction is treated with toluene to inhibit microbial transformations of inorganic forms of nitrogen during extraction. We also tested the possibility that use of a neutral extractant such as 2*M* KCl might lead to chemical decomposition of nitrite during extraction of acidic soils or to volatilization of ammonium during extraction of calcareous soils, but were unable to detect such reactions in recovery studies using soil 3 (pH 4.8) and samples of soils 1, 2, and 8 treated with $CaCO_3$ (10% by weight). Nevertheless, we recommend that the extraction procedure recommended be checked by recovery tests if it is to be applied to highly acidic or calcareous soils and quantitative analyses for nitrite and exchangeable ammonium are desired. The literature on determination of nitrite in soils shows that the instability of nitrite in acidic media has not been fully appreciated and that several workers have used acidic reagents for extraction of nitrite (2).

The possibility that analyses of soils for inorganic forms of nitrogen may be vitiated by enzymatic reactions during preparation of extracts for these analyses deserves attention because it is now well established that soils contain a variety of enzymes capable of transforming nitrogenous compounds. Dashevskiy (5) obtained some evidence that the determination of exchangeable ammonium in soils may be complicated by enzymatic hydrolysis of amides during preparation of extracts for this determination. We have been unable to confirm his findings using unamended soils, but have been able to detect enzymatic activity during extraction of soils treated with urea. We found, for example, that the values obtained in analyses of soils 5 and 6 for exchangeable ammonium-N by the extraction-distillation procedure described increased significantly (4 to 8 ppm) when these soils were treated with urea (200 ppm of N) immediately before analysis.

Storage of extracts—Studies using field-moist and air-dried soils showed that the stability of extracts obtained by the procedure recommended is markedly increased if the extracts are filtered before storage, but that unfiltered extracts can be stored safely for up to 24 hr at 25 C and for up to 48 hr at 5C. Filtered extracts can be stored for at least 45 days at 25C

Table 7—Effect of storing filtered and unfiltered soil extracts on the values obtained in their analysis for ammonium, nitrate, and nitrite*

Storage		Filtered extract			Unfiltered extract		
Temperature	Time	NH_4-N	NO_3-N	NO_2-N	NH_4-N	NO_3-N	NO_2-N
°C	days	μg of N/20 ml of extract					
25	0	108	103	50	108	103	50
	1	107	104	51	108	102	51
	2	108	103	50	107	103	41
	4	109	102	50	111	104	36
	7	107	91	41	113	94	29
	14	108	80	32	130	84	24
	21	108	70	26	161	73	19
5	0	107	104	51	107	103	51
	1	108	103	50	107	103	51
	2	108	103	51	108	103	51
	4	109	104	50	110	104	50
	7	108	102	50	113	102	42
	14	107	104	51	129	87	37
	21	108	103	50	140	69	32
	120	107	103	51	—	—	—

* Extracts were prepared by shaking 60 g samples of soil 4 with 600 ml of 2M KCl solution containing 3 mg of ammonium-N [as $(NH_4)_2SO_4$), 3 mg of nitrate-N (as KNO_3), and 1.5 mg of nitrite-N (as $NaNO_2$) for 1 hr.

and for up to 4 months if kept in a refrigerator at 5C. Table 7 shows data obtained in a study of the effect of storing 2*M* KCl extracts of Webster soil.

Steam-Distillation Procedures

Specificity and interference tests—Tests using 69 organic nitrogen compounds, including amino acids, purine and pyrimidine derivatives, and alkali-labile substances such as amides and hexosamines, showed that the steam-distillation methods of analysis described had high specificity and that only two compounds, namely glucosamine and galactosamine, yielded detectable amounts of ammonium under the conditions of these methods (4). If a soil extract contained a significant amount of glucosamine or galactosamine, interference by these hexosamines in analyses for ammonium, nitrate, and nitrite could be eliminated by use of the methods for ammonium-N, (ammonium + nitrate)-N, and (ammonium + nitrate + nitrite)-N, and reduction of the time of distillation in the method for ammonium-N to 2 min (4). However, hexosamines are so labile in alkaline media that their presence in an extract analyzed for ammonium by steam distillation with MgO can readily be detected by studying the effects of varying the amount of MgO and the time of distillation (4), and such studies showed that hexosamines are either completely absent from KCl extracts of soils or are present in such low concentration that they do not release measurable amounts of ammonium under the conditions of the MgO distillation method recommended for ammonium analysis. The finding that KCl extracts of soils do not contain organic nitrogen compounds which yield ammonium in alkaline media as rapidly as hexosamines is illustrated by Table 8 which shows the amounts of ammonium liberated by steam distillation of 2*M* KCl extracts of soils with various alkaline reagents. It can be seen that the amount of ammonium liberated by steam distillation with MgO was not affected if the amount of MgO used was increased from 0.1 to 1.0 g or if the time of distillation was increased from 2 to 6 min; and that the amount liberated by distillation with a mildly alkaline potassium phosphate buffer (pH 8.0) or with CaO was identical to the amount released by MgO distillation. The data in Table 8 also show that the results obtained by the MgO-Devarda alloy distillation method of determining (ammonium + nitrate + nitrite)-N were not affected if the period of distillation was increased to 6 min. Other studies showed that the results obtained with soil extracts by the methods for determination of nitrate-N, (ammonium + nitrate)-N, and (nitrate + nitrite)-N were similarly unaffected if the time of distillation was increased to 6 min. The results using NaOH for distillation merely confirm previous evidence that soil extracts contain organic nitrogen compounds which decompose with formation of ammonium when distilled with strong alkali.

Table 8—Ammonium-N liberated by steam distillation of soil extracts with various reagents

Reagent	Time of distillation, min†	Extract*		
		Soil 3	Soil 4	Soil 8
		Ammonium-N liberated, μg/20 ml of extract		
MgO (0.1 g)	2	26	8	16
	R	26	8	16
	6	26	8	16
MgO (0.2 g)	2	26	8	16
	R	26	8	16
	6	26	8	16
MgO (1.0g)	2	26	8	16
	R	26	8	16
	6	26	8	16
MgO (0.2g) + Devarda alloy (0.2g)	2	44	12	22
	R	44	12	22
	6	44	12	22
Potassium phosphate buffer, 1M, pH 8.0 (10 ml)	2	26	8	16
	R	26	8	16
	6	26	8	16
CaO (0.2g)	2	26	8	16
	R	26	8	16
	6	26	8	16
NaOH (0.2g)	2	32	12	20
	R	34	14	26
	6	35	15	28
NaOH (1.0g)	2	36	18	38
	R	44	24	50
	6	46	26	52

* Extracts were prepared by shaking soil samples with 2M KCl (10 ml/g of soil) for 1 hr. Analyses were performed on 20-ml aliquots of filtered extracts.
† *R*, time used in methods described (ca. 3.3 min); rate of distillation, ca. 7.5 ml/min.

Studies of the effects of various cations and anions on the steam-distillation methods of analysis described have already been reported (4), and it suffices here to state that extensive tests indicate that these methods are not subject to interference by inorganic or organic substances present in soil extracts. This conclusion is supported by the findings that these methods give quantitative recovery of ammonium, nitrate, and nitrite added to soil extracts (Table 6) and that the results obtained with soil extracts by these methods are not affected if the sample of extract analyzed contains suspended soil material (Table 5). Work reported in the next paper in this series has shown that these steam-distillation methods of analysis have such high specificity and are so unaffected by soil constituents that it is possible to apply them directly to most types of soils (i.e., eliminate the extraction step in the procedures described). It should be noted, however, that the reduction of nitrate and nitrite by

Table 9—Precision of methods

Amount of soil analyzed, g*	Method†	µg N/g of soil‡		
		Range	Average	Standard deviation
10.0	1	11–12	12	1.0
	2	53–55	54	1.4
	3	65–67	66	1.5
	4	53–55	54	1.4
	5	64–67	66	1.5
5.0	1	11–12	12	1.1
	2	54–55	54	1.4
	3	65–67	66	1.1
	4	53–54	54	1.3
	5	65–67	66	1.5
2.0	1	11–12	12	1.2
	2	53–55	54	1.5
	3	64–67	66	1.6
	4	53–54	54	1.3
	5	65–66	66	1.2

* Extracts were prepared by shaking soil samples with 2N KCl (10 ml/g of soil) for 1 hr. Analyses were performed on 20-ml aliquots of filtered extracts.

† 1, exchangeable ammonium-N; 2, nitrate-N; 3, (exchangeable ammonium + nitrate)-N; 4, (nitrate + nitrite)-N; 5, (exchangeable ammonium + nitrate + nitrate)-N.

‡ Results of 6 analyses of soil 6 by each method.

Devarda alloy and MgO is affected by the presence of an appreciable concentration of dissolved phosphate or silicate (4), and that the methods of analysis involving use of Devarda alloy cannot therefore be applied to soil extracts obtained by treating soils with phosphate or silicate solutions.

Accuracy and precision—The steam-distillation procedures described give quantitative results when applied to 20-ml aliquots of solutions containing up to 100 µg/ml of ammonium-N, nitrate-N, and nitrite-N (4), and give quantitative recovery of ammonium-N, nitrate-N, and nitrite-N added to soil extracts (Table 6).

The high precision of the extraction-distillation methods of analysis is illustrated by Table 9, which shows results obtained by these methods in replicate analyses of air-dried Primghar soil (< 2 mm). The data in Table 9 also show that the results by these methods using 2 or 5 g of soil were identical to, and as precise as, those obtained using 10 g of soil. Tests using soils 1, 3, 4, and 6 showed that the results obtained by the extraction-distillation methods with field-moist, < 2 mm samples of these soils were as precise as those obtained with air-dried samples.

Apparatus and reagents—Description of the steam-distillation methods has been simplified by specification that distillation flasks fitted with a side-arm be used. This side-arm is not required when the method of analysis does not involve addition of Devarda alloy after removal of ammonium by steam distillation with MgO.

The MgO used for distillation of ammonium is ignited to remove carbonate and stored in an air-tight container to protect it from atmospheric CO_2 because use of MgO containing carbonate can lead to liberation of CO_2 which interferes with determination of ammonium by titration methods.

The Devarda alloy used for reduction of nitrate and nitrite must be ball-milled to obtain a very finely divided product because the reactivity of this alloy increases with decrease in its particle size, and finely divided alloy must be used to obtain quantitative reduction of nitrate and nitrite within the period of distillation recommended (4).

Calibrated glass spoons (9) can be employed for addition of MgO and Devarda alloy because it is not necessary to use accurately weighed amounts of these reagents.

Reagent-grade sulfamic acid sometimes contains an appreciable quantity of ammonium, and it usually requires purification for use in the methods described. Sulfamic acid is hydrolyzed in aqueous solution with formation of ammonium bisulfate ($NH_2SO_3H + H_2O = NH_4HSO_4$), but this reaction is very slow at 5C, and only trace amounts of ammonium have been detected in sulfamic acid solutions prepared as recommended and subsequently stored in a refrigerator for 6 months.

Additional information concerning the apparatus and reagents used can be found in previous papers (3, 4).

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Distribution of Zn, Mn, and Cu Among Soil Fractions. L. M. Shuman, University of Georgia College of Agriculture Experiment Stations, Georgia Station.

Successive extractions were made to solvate Zn, Mn, and Cu in the exchangeable, organic matter, and Fe oxide fractions of eight southeastern soils. Exchangeable ions were extracted with 1 M $MgCl_2$, organic matter forms were released using H_2O_2 followed by extraction with 1 M $MgCl_2$, and elements associated with Fe oxides were solvated with acid ammonium oxalate. The residue was separated into sand, silt and clay size particles and these, along with whole soil samples were totally dissolved and analyzed for Zn, Mn and Cu. The proposed fractionation scheme was satisfactory for most soils, but is considered to be preliminary. The data for the sums of fractions agreed well with the whole soil data. The fine-textured soils had a large proportion of their Zn and Cu in the clay fraction but the coarse-textured soils had a higher percent in the exchangeable and organic matter fractions. Fertilizer Mn was found mainly in the exchangeable and organic matter fractions. Percent Cu was highest in the organic matter and clay fractions when averaging the data for the eight soils studied.

Kinetics of Potassium Exchange in a Paleudult from the Coastal Plain of Virginia. D. L. Sparks*, L. W. Zelazny, and D. C. Martens, Virginia Polytechnic Institute and State Univ.

The kinetics of K exchange were investigated on four horizons of the Dothan soil (Plinthic Paleudult). Time studies were performed on Ca and Al-saturated samples using 1, 5, 10, 25, 50, 75, and 100 μg/ml K solutions equilibrated for 0, 1, 2, 24, 96, and 192 hours. The rate of K exchange was relatively slow with equilibrium being reached in 2 hours with K concentrations of 25 μg/ml or less and in 24 hours with the 100 μg/ml solution. This slow K exchange may be diffusion-controlled which could be ascribed to the presence of vermiculitic minerals. Adsorption rate coefficients (ka) conformed to Bronsted's activity rate theory and decreased with increasing ionic strength. Small differences in ka values occurred between horizons which suggests that similar exchange reactions were taking place. Potassium sorption studies conformed to Freundlich plots. Sorption of K increased with both K concentration and horizon depths and was greater for Ca than for Al-saturated systems.

A New Procedure for the Control of Ionic Concentrations of Heavy Metals and pH in Aqueous Systems. M. A. Turner, R. B. Corey* and D. R. Keeney, University of Wisconsin.

A method has been developed to establish and maintain ionic heavy metal activities and pH in solutions or suspensions for use in adsorption or complexation studies. A chelating cation-exchange resin is employed to buffer changes in pH and maintain a constant activity of heavy-metal ions in solution. The ratio of heavy metals to Ca on the resin establishes the solution activity of the heavy-metal ions at a given solution Ca concentration and pH. If necessary, additional pH buffering can be obtained with added Ca-saturated, weak acid cation-exchange resin. Depending on the requirements of the experiment, the resin can be mixed with the solution or suspension or one of the components can be enclosed in a dialysis bag. This resin system was successfully employed in determining heavy-metal sorption on an iron oxide and a muck. It has also been used to determine degree of complexation of heavy metals. The method offers a convenient system for studying the interaction of soils and soil components with heavy metals at levels consistent with normal soil-solution concentrations.

DIVISION S-3 -- SOIL MICROBIOLOGY AND BIOCHEMISTRY

Includes Joint Meetings With: Div. S-1 -- Soil Physics
Div. S-2 -- Soil Chemistry
Div. S-4 -- Soil Fertility and Plant Nutrition

Nodulation Effectiveness and pH Resistance of Rhizobium meliloti Strains Isolated from Oregon Soils. L. Barber*, W. M. Murphy, and C. Hagedorn, Oregon State University.

Soil samples were collected from alfalfa-growing areas in Oregon and analyzed for total exchangeable hydrogen, pH, and other chemical parameters. The number of infective Rhizobium meliloti cells in each soil was estimated using the plant infection assay. The nodulation effectiveness of each isolated R. meliloti strain was ranked using alfalfa growth response in tube culture and was compared to non-inoculated and nitrogen-amended controls. Most of the soils had less than 100 infective R. meliloti cells per gram of soil. In studies of the growth of isolates on agar media, few strains were resistant to streptomycin or tetracycline, about half of the strains grew in the presence of novobiocin or kanamycin, and most of the strains were resistant to chloramphenicol (10, 0.5, 10, 100, and 30 μg/ml respectively). The significant differences between strains in growth in mannitol broth at low pH were not usually related to the acidity of the soil from which the strain had been isolated.

Determination of Nitrous Oxide in Air. A. M. Blackmer*, and J. M. Bremner, Department of Agronomy, Iowa State University.

A procedure for determination of nitrous oxide (N_2O) in air is described that allows use of the xenon (Xe) in air as an internal standard. It involves quantitative removal of N_2O and Xe from the air sample by Porapak Q cooled to -135°C and subsequent determination of these gases by a gas chromatographic technique in which N_2O and Xe are separated by a column of Porapak Q at 65°C and determined by a Tracor ultrasonic detector. The procedure is rapid and precise, and it permits quantitative measurement of small variations in the atmospheric concentration of N_2O. Analyses by this procedure are not affected by air pollutants or by gases evolved from soils, and the ultrasonic detector used has the advantages that it is very durable and does not require frequent recalibration. Measurement of the ratio of N_2O to Xe in air samples greatly simplifies research to identify and assess natural sources and sinks of atmospheric N_2O.

Effect of Mycorrhizal Fungal Species, N, P, Fumigation, and Location on Soybean Yields. D. E. Carling, V. D. Luedders*, and M. F. Brown, Univ. of Missouri and USDA-SEA-FR.

Plots were fumigated with Vapam and fertilized with 200 kg P/ha at two locations. Subplots (treatments) were inoculated with Gigaspora margarita, Glomus mosseae, G. caledonius, G. fasciculatus, and G. microcarpus; plots with and without

APPENDIX I

REFERENCE 10, ASSOCIATED HAND CALCULATIONS, AND SUPPORTING DOCUMENTATION

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NITROUS OXIDE EVOLUTION RATES FROM FERTILIZED SOIL: EFFECTS OF APPLIED NITROGEN

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McKENNEY, D. J., SHUTTLEWORTH, K. F. AND FINDLAY, W. I. 1980. Nitrous oxide evolution rates from fertilized soil: Effects of applied nitrogen. Can. J. Soil. Sci. **60**: 429–438.

Nitrous oxide emission from agricultural soil has been measured in two relatively long-term studies over two different soil types, Brookston clay and Fox sandy loam, located at Woodslee and Harrow Ontario, respectively. The clay plots treated with various amounts (0–366 kg N · ha^{-1}) of ammonium nitrate, potassium nitrate, or urea were routinely monitored for periods up to 1 yr. Extreme variability in rates within the range 10^9–10^{13} molecules · cm^{-2} · s^{-1} was observed (1×10^9 molecules · cm^{-2} · s^{-1} = $4.02 = 10^{-4}$ kg N · ha^{-1} · day^{-1} = 1.68 μg N · m^{-2} · h^{-1}). Over sandy loam, rates which were lower and more uniform (10^8–10^{11} molecules · cm^{-2} · s^{-1}) showed a strong correlation with amount of NH_4NO_3 applied. About 0.25% of applied fertilizer was released as N_2O within 80 days following treatment.

Total

On a mesuré l'émission d'azote nitreux dans le cadre de deux études de longue haleine portant sur deux types de sols agricoles, soit l'argile Brookston et le loam sableux Fox, situés à Woodslee et Harrow (Ontario) respectivement. Les parcelles d'argile diversement fumées (0–336 kg de N/ha) au nitrate d'ammonium, au nitrate de potassium ou à l'urée ont été régulièrement étudiées pendant certaines périodes allant jusqu'à 1 an. On observe une extrême variabilité des taux d'émission dans l'écart de 10^9–10^{13} molécules/s/cm. Sur loam sableux, les taux d'émission, plus faibles et plus uniformes (10^8–10^{11} molécules/s/cm) révèlent une forte corrélation avec les apports de NH_4NO_3. Environ 0.25% de l'engrais appliqué se dégage sous forme de N_2O dans les 80 jours suivant le traitement.

We have recently published reports (McKenney and Findlay 1978; McKenney et al. 1978) of our study showing a strong correlation between nitrous oxide (N_2O) production and extent of nitrogen fertilizer application on Fox sandy loam. In this paper an extension of the investigation involving two relatively long-term studies is presented.

Some incentives for interest in this problem are: Nitrous oxide is a product of denitrification and other processes in soils. These constitute a major source of atmospheric N_2O (Hahn and Junge 1977) which in turn is considered to be the dominant source of stratospheric nitric oxide, NO (Crutzen 1971). Since subsequent chemical reaction of NO and NO_2 can catalytically destroy O_3 in the stratosphere there is concern over anthropogenic activities that might alter global N_2O levels. In particular, the effect on atmospheric N_2O levels resulting from the rapidly increasing agricultural use of industrially produced N-fertilizer has been the subject of a number of reports (Crutzen 1974; McElroy 1976; McElroy et al. 1976; Crutzen and Ehhalt 1977; Liu et al. 1976, 1977; Sze and Rice 1976). Estimates of the extent of O_3 depletion, however, show considerable disagreement, largely because major gaps exist in our understanding of the nitrogen cycle. Without precise quantitative knowledge of global sources and sinks of

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atmospheric N_2O, no confidence can be placed in any predictions. Essential information includes knowledge of the fraction of applied N-fertilizer that is returned to the atmosphere as N_2O in a relatively short period of time, and whether there is a long-term effect on N_2O evolution rates from agricultural soils or associated lakes and river systems which are major receptacles for large quantities of nitrogenous wastes. This work is addressed primarily to the former (short-term) problem.

In addition, more efficient use of nitrogen fertilizer depends on an adequate knowledge of potential losses of soil nitrogen. Dentrification and other processes of nitrogen removal have not been fully evaluated, partly because of difficulties in measuring flux of N_2O and N_2 under natural field conditions.

MATERIALS AND METHODS

Sites

HARROW. The sample sites were located on Fox sandy loam, a well-drained soil described by Richards et al. (1949) and currently classified as a Gray Brown Luvisol. The plots were planted to corn (*Zea mays* L.) and treated with different rates of NH_4NO_3 in the range 0–336 kg N·ha^{-1}. The fertilizer was broadcast (17 May 1978 and 10 May 1979) and incorporated into the soil. Planting took place on 19 May 1978 and 10 May 1979. The sample chambers were placed mid-row. These plots were part of a longer-term study where the treatments had been repeated on the same plots annually since 1970. Consequently the rate information must include consideration of any residual effects from previous years.

WOODSLEE. In this case the sites were located on Brookston clay (Orthic Humic Gleysol) with poor natural drainage (Richards et al. 1949). A 10-m^2 plot was cultivated and divided into five 2-m^2 sites. Four of these sites were treated with different rates of fertilizer: KNO_3 and urea each at 168 and 336 kg N·ha^{-1}, respectively. KNO_3 was applied on 19 Oct. 1977 and urea was applied on 11 Apr. 1978. One site was left untreated as a control plot. Four chambers were installed in each for replicate measurements. During the period 14 May–13 June 1979, sites of the same soil type treated with NH_4NO_3 at rates of 0, 112, 224, 336 kg N·ha^{-1} and planted to corn were studied. In this case, fertilization and planting was done on 16 May 1979.

Field Chambers

The chambers or canopies were open-ended aluminum cylinders, ~15 cm diam by ~25 cm length. The cylinders had a sharpened cutting edge on the bottom and were carefully driven about 5–10 cm into the soil by even pressure applied to a heavy metal plate placed on top of the cylinder. Care was taken to minimize disturbing the soil. The cylinders were left in place throughout the entire study, open to the atmosphere except during the actual sampling period. Immediately prior to sampling, a plexiglass lid, fitted with a compression-sealing neoprene 0-ring, was applied. Air samples were drawn into the evacuated tubes through a hypodermic needle inserted through a septum port in the cover. The needle was left in the chamber cover throughout the sampling period in order to minimize pressure fluctuations between the inside and the outside of the chamber. Losses of N_2O due to diffusion through the needle were calculated to be insignificant. A paddle-wheel fitted through the lid was gently rotated several times before each sampling. Air and soil temperatures could be measured inside and outside the chamber.

Sampling

Gas samples were collected as described previously (Findlay and McKenney 1979) using small (~20 cm^3) evacuated Pyrex tubes fitted with rubber septums.

For the long-term studies it was considered advantageous to monitor as many as 12 chambers over three different plots (four replicates) within a reasonably convenient time interval. In most cases, therefore, it was necessary to sample only three times per chamber at 30-min intervals

Analytical

Analyses for N_2O were carried out in the laboratory using a Perkin-Elmer 3920 B gas chromatograph equipped with a ^{63}Ni electron capture detector and a Porapak Q stainless steel column, 3 m × 0.3 cm (10 ft × 1/8 inch). Operating temperatures of the detector, interface between column and detector (ECD), and column were 350, 150 and 50°C, respectively (Rasmussen et al. 1976). The carrier gas (95% argon, 5

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methane) flow rate was 30 $cm^3 \cdot min^{-1}$. The standing current was 3.0 × 10^{-9}A. Precise injection to the G.C. was accomplished through a hypodermic needle into an evacuated 1-cm^3 loop of a gas sampling valve. Precision of 1% or better was possible using peak height measurements.

Soil moisture was determined gravimetrically.

Calibration

The G.C. was routinely calibrated (usually daily) against 20–100 ppm mixtures of N_2O in air (Liquid Carbonic Analyzed Calibration mixtures). Calibrations were made using aliquots chosen to span the range of N_2O levels normally measured, ~10 ppb to >10^4 ppb. We have found no evidence of instability of the primary reference standards over durations of more than 1 yr.

Holding times, Denmead?

Calibration drift resulting from variations in laboratory temperature (Pierotti et al. 1978) was taken into account. Possible error caused by variations of moisture level (relative humidity) in samples (Goldan et al. 1978) was investigated using standards containing known added amounts of water vapor. The ECD sensitivity for N_2O was apparently unaffected by the relatively small quantities of water vapor in field samples.

Ambient N_2O levels were measured routinely and were similar to those reported by others (Pierotti et al. 1978; Goldan et al. 1978; Pierotti and Rasmussen 1977). For the period July 1977–July 1979, ambient levels averaged 335.7 ± 15.8 ppb (±δ). This value is higher than the value we reported earlier (303 ± 10 ppb, Findlay and McKenney 1979) when a different calibration standard was used.

Several papers (Pierotti et al. 1978; Goldan et al. 1978; Pierotti and Rasmussen 1977) have stressed the need for interlaboratory comparisons of calibration standards where absolute accuracy is to be estimated. Whereas this is required for determining absolute tropospheric concentrations of N_2O and possibly for identifying long-term trends, it should perhaps be emphasized that rate measurements reported here require only relative concentration measurements. Thus rates can, in principle at least, be measured quite accurately. Although good precision can be obtained in practice, it is extremely difficult to determine the level of accuracy because of experimental and environmental factors (Denmead 1979; Mathias et al. 1979). The scatter observed in yield-time plots (5 or more points) corresponded to a resolution of ~8 × 10^8 molecules · $cm^{-2} \cdot s^{-1}$; i.e. about ±5% uncertainty for rates greater than 15 × 10^9 molecules $cm^{-2} \cdot s^{-1}$ (Findlay and McKenney 1979).

Reproducibility of measurements on a field sample taken from a Pyrex sample tube was better than 1% and the reproducibility of successive measurements of ambient air drawn in from inside or outside the laboratory over a period ~2 h was typically 0.7%. Reproducibility of successive measurements of standard mixtures was similar or better.

Calculation of Rates

Rates of N_2O emission from soils in the field were calculated from the slopes (least squares) of linear N_2O yield versus time plots. As reported previously (McKenney et al. 1978; Findlay and McKenney 1979), ordinarily samples would be taken at 15-min intervals over a period of 60–75 min. The linear plots obtained indicated no obvious effect of increasing concentration of N_2O in the chamber on the measured rate of N_2O evolution. Obviously the N_2O concentration will increase within the closed chamber to a limit. It is therefore expected that yield-time curves should be non-linear. Initially, however, even for relatively high rates of production, approximate linearity was observed. No great advantage was obtained by using curvilinear analysis to calculate initial rates (Findlay and McKenney 1979).

RESULTS AND DISCUSSION

Harrow Site (Fox Sandy Loam)

Nitrous oxide emission rates were measured in the range ~10^8 to 6 × 10^{10} molecules N_2O $cm^{-2} \cdot s^{-1}$, which were comparable to rates measured on the same site during the summer of 1977 (McKenney et al. 1978). Table 1 shows the calculated rates measured for the periods 9 June–16 Nov. 1978 and 9–16 May 1979. It should be noted that over much of the early time period (9 June–20 July 1978), despite considerable variability, there was clearly a strong correlation between N_2O flux and rate of nitrogen fertilizer (NH_4NO_3) treatment. The data can be represented by a simple regression equation (Table 2) during the month or two following fertilization.

These observations confirm our earlier 1977 study (McKenney et al. 1978) where a similar correlation was obtained for this type of soil. In that case, $\log_{10}$ [Flux (molecules

Table 1. Mean N_2O emission rates ± σ (three replicates) measured over Fox sandy loam, Harrow, for the period June 9–16 Nov. 1978 and 9–16 May 1979

	$\bar{v}$ Molecules $N_2O \times 10^9 \cdot cm^{-2} \cdot s^{-1}$			
	NH_4NO_3 treatment (kg N · ha^{-1})			
Date	0	112	224	336
06-09-78	1.43±1.13	3.04±1.94	14.3±2.84	24.8±11.5
06-12-78	1.84±1.01	3.67±1.76	23.5±19.2	41.4±25.4
06-15-78	1.82±1.42	5.39±1.82	31.4±29.3	41.8±24.2
07-06-78	3.26±1.89	2.73±1.23	18.6±20.4	23.4±18.4
07-13-78	1.03±0.20	1.42±0.84	1.43±0.33	4.35±4.10
07-20-78	0.53±0.09	0.70±0.54	3.16±3.12	4.08±0.80
07-27-78	0.28±0.27	0.65±0.71	2.66±1.80	2.30±0.58
08-03-78	1.03±1.20	0.30±0.28	7.92±6.02	2.80±1.12
08-17-78	0.64±0.56	0.85±0.52	2.35±2.90	3.86±3.20
08-24-78	0.41±0.70	6.52±10.6	1.63±2.01	0.82±0.98
09-07-78	0.81±0.36	0.85±0.79	1.22±0.63	2.21±1.65
09-19-78	1.65±0.24	1.52±0.42	2.61±2.18	5.69±4.19
09-28-78	0.52±0.60	0.58±0.49	1.69±0.59	4.17±1.02
10-04-78	1.19±0.56	3.55±4.27	2.08±1.43	3.14±1.16
10-19-78	1.05±0.59	0.01±0.01	0.83±0.76	3.86±4.77
10-30-78	0.53±0.49	1.26±1.08	1.15±0.10	3.21±4.19
11-16-78	1.32±1.01	0.37±0.41	1.63±1.49	4.70±5.03
05-09-79	0.16±0.14	0.41±0.12	0.53±0.33	0.71±0.30
05-11-79	0.27±0.10	0.47±0.31	0.37±0.16	0.65±0.18
05-16-79	0.24±0.10	0.32±0.25	0.53±0.22	1.00±0.53

$N_2O\ cm^{-2} s^{-1})] = 0.00232\ [NH_4NO_3$ (kg N · ha^{-1}] + 9.39 over the period 20–24 June 1977. It appears, therefore, that loss of fertilizer nitrogen as N_2O occurs soon after application and may persist for several months before emission rates are reduced to "background." Weather conditions will have an influence. For example, increased moisture levels will increase rates of N_2O evolution (Hahn and Junge 1977; Freney et al. 1978; Hutchinson and Mosier 1979).

Figure 1 shows a rate versus time graph for the plot treated with 336 kg N · ha^{-1}. The data plotted are those measured in the chamber which showed the largest emission rates, along with the data from the control site for comparison.

Graphical integration of the curve obtained for the most heavily fertilized site over the first 80 days indicates a total loss of ≈0.846 kg N · ha^{-1}. This amounts to only 0.25% of the applied NH_4NO_3. Losses measured on the other sites were smaller. It should be emphasized, however, that the soil here is coarse-textured and was considered to be well-aerated with a moisture level well below field capacity (13%, McKenney et al. 1978) over most of the period (Table 2). The variability observed (Table 1) may be the result of changing oxygen levels at microscopic sites in the soil (Hutchinson and Mosier 1979; Smith et al. 1978) where denitrification processes are assumed to occur (Russell 1973; Alexander 1977). There is laboratory evidence, however, to show that significant production of N_2O can be obtained by autotrophic nitrification (Bremner and Blackmer 1978). Our earlier field measurements (McKenney et al. 1978) and those reported here from over well aerated sandy loam lend some support to the suggestion (Hutchinson and Mosier 1979

Table 2. Regression analysis $Y = a + bX$, where $Y = \text{Log}_{10}$ [N_2O flux (molecules $cm^{-2} \cdot s^{-1}$)] and $X = NH_4NO_3$, kg $N \cdot ha^{-1}$, applied N fertilizer. Field 52. Fox sandy loam, Research Station, Harrow

Date†	*a*	*b*	*r*‡	*F*	Soil moisture (%)
06-09-78	9.00	.00432	0.87	31.90**	11.4
06-12-78	9.17	.00421	0.87	32.44**	8.2
06-15-78	9.14	.00464	0.84	24.11**	8.5
07-06-78	9.34	.00281	0.75	13.13**	8.1
07-13-78	8.96	.00137	0.61	6.00*	5.4
07-20-78	8.61	.00293	0.78	15.76**	-
07-27-78	8.42	.00283	0.55	4.40	2.2
08-03-78	8.95	.00181	0.48	3.08	3.6
08-17-78	8.86	.00144	0.46	2.73	5.6
08-24-78	9.38	.0005	−0.14	<1	3.0
09-10-78	8.90	.0009	0.46	2.63	2.8
09-19-78	9.09	.00119	0.34	1.35	11.9
09-28-78	8.66	.00253	0.78	15.63**	8.1
10-04-78	9.05	.00153	0.48	3.04	10.6
10-19-78	8.20	.00167	0.25	<1	11.8
10-30-78	8.87	.00100	0.38	1.70	10.1
11-16-78	9.08	.00090	0.27	<1	-
05-09-79	9.18	.00238	0.60	6.75*	-
05-11-79	9.50	.00090	0.53	3.98	-
05-16-79	9.35	.00191	0.69	9.21*	-

*, ** = Significant at a probability of 0.05 and 0.01, respectively.

†Sample collection dates, fertilized with 0, 112, 224 and 336 kg $N \cdot ha^{-1}$ on 17 May 1978 and 10 May 1979.

‡*r* = correlation coefficient; *F* = ratio, regression mean square/residual mean square.

that nitrification processes can contribute substantial amounts of N_2O to the atmosphere.

Woodslee Site (Brookston Clay)

Nitrous oxide emission rates measured over Brookston clay generally tended to be one or two orders of magnitude greater than those over sandy loam. Fluxes ranging from 7 × 10^8 to 1.5 × 10^{13} molecules $N_2O \cdot cm^{-2} \cdot s^{-1}$ were measured over the period 3 Oct. 1977–Nov. 1978 on the control, KNO_3 and urea sites, and for the period 14 May–13 June 1979 on the NH_4NO_3 site. Rate data are shown in Fig. 2 and 3 and Table 3. It is evident that the degree of variability is much more pronounced over this type of soil than over sandy loam. Variations in rate from day to day and site to site were often as much as two or more orders of magnitude over clay. On sandy loam, variability of about one order of magnitude was the maximum observed. Figure 2 shows rates measured on the KNO_3 site for the period 3 Oct. 1977–20 Dec. 1978, and illustrates the typical variability observed from chamber to chamber within one 2-m^2 area sampled only minutes apart. Figure 2 and 3, and Table 3 clearly show that there is no apparent correlation between N_2O emission and KNO_3 application rate. N_2O flux is more pronounced during the fall and spring periods where high moisture levels limit aeration.

The urea plots (not shown) also showed similar variability from site to site and from day to day. Again no obvious correlation was seen between N_2O flux and fertilizer treatment.

Results obtained from the plots treated with NH_4NO_3 are shown in Table 3. The extreme variability observed can also be seen in Table 4 which shows a regression analysis for data obtained over the NH_4NO_3

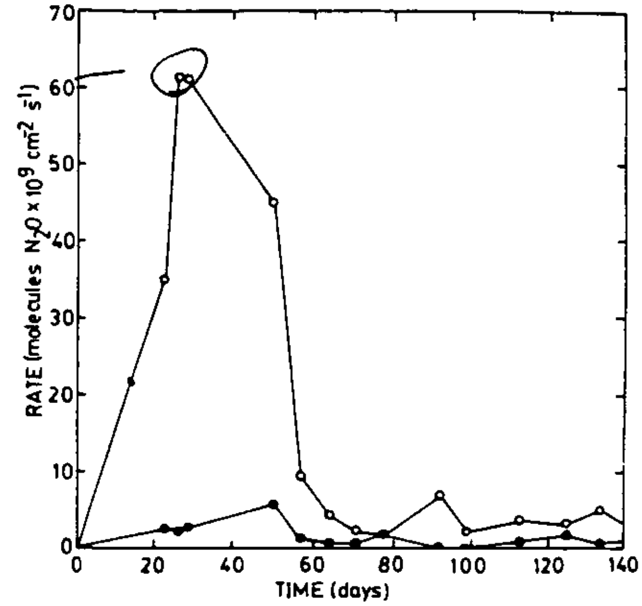

Fig. 1. N_2O emission rates for 140 days following NH_4NO_3 fertilization 17 May 1978 on Fox sandy loam. Harrow. Results shown are from the chamber giving highest rates over the site treated with 336 kg N · ha^{-1} (○). Control site data (●) are shown for comparison.

sites. Comparison of Tables 2 and 4 shows the marked contrast between results obtained from Fox sandy loam and from Brookston clay where the same fertilizer was used. The precise reason for the difference is not clear. The soils are different with respect to texture, organic matter and drainage. In addition the sandy soil had been fertilized since 1970 at the rates indicated so that the control plots were undoubtedly lower in N than their clay counterparts. In any case there was no apparent correlation of N_2O rate with the substantial amounts of fertilizer nitrogen added to the clay soil.

CONCLUSIONS

The data presented here are not sufficient to distinguish between the possible mechanisms of N_2O production. The results do not disagree with the well-known hypothesis

Table 3. Mean N_2O emission rates ± σ (3 replicates) measured over Brookston clay, Woodslee for the period 14 May–13 June 1979

	Molecules $N_2O \times 10^9$ · cm^{-2} · s^{-1}			
	NH_4NO_3 treatment (kg N · ha^{-1})			
Date	0	112	224	336
05-14-79	15.5±5.20	2.65±1.16	34.5±39.6	8.74±10.6
05-17-79	17.0±13.0	5.35±1.18	13.4±16.9	19.5±9.16
05-22-79	14.7±189	20.3±14.4	16.8±15.8	43.4±41.8
06-04-79	580±690	1190±1060	641±460	2180±1370
06-13-79	16.1±12.8	5.63±5.70	43.0±56.3	32.2±42.0

5/16 fert

Bkg

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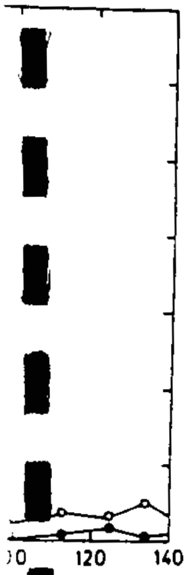

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kston clay, Woodslee for the period 14

224	336
34.5±39.6	8.74±10.6
±16.9	19.5±9.16
±15.8	43.4±41.8
±460	2180±1370
43.0±56.3	32.2±42.0

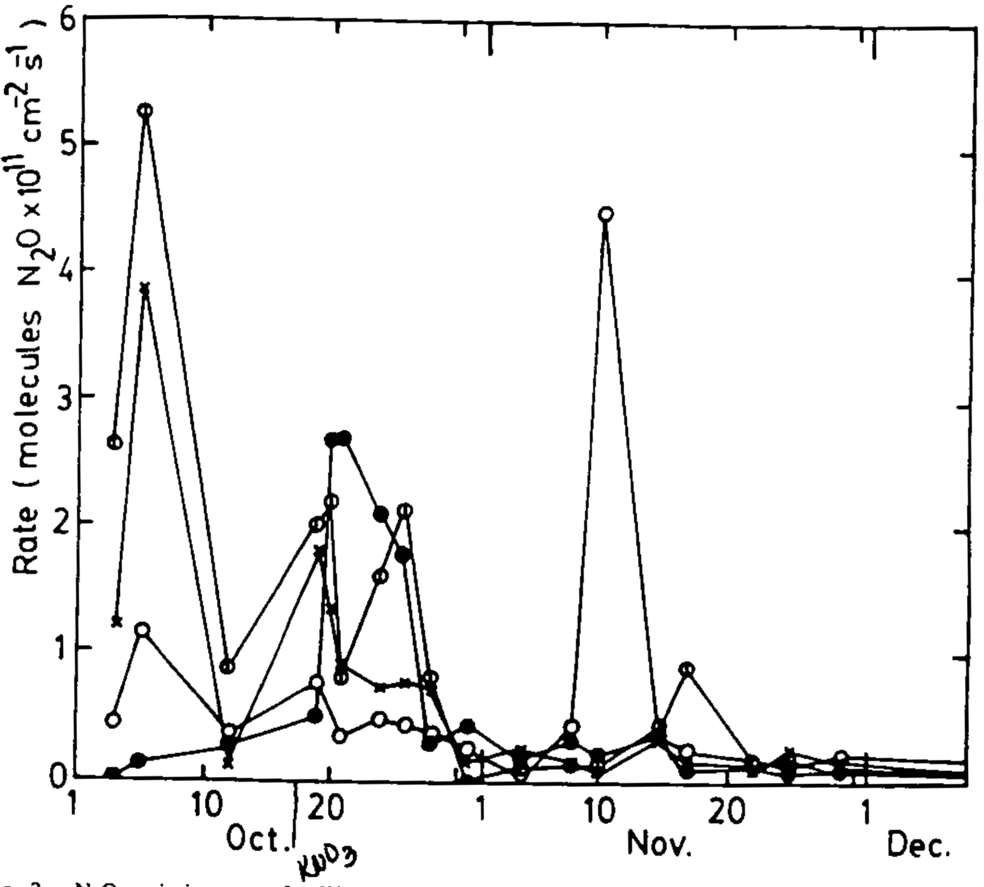


Fig. 2. N_2O emission rates for Woodslee Brookston clay, October–December 1977 illustrating typical variability for this soil. Results shown were obtained from the four chambers situated on the site treated with KNO_3 at 336 kg N · ha^{-1}.

Table 4. Regression analysis $Y = a + bX$, where $Y = \text{Log}_{10}$ [N_2O flux (molecules · cm^{-2} · s^{-1})] and $X = NH_4NO_3$, kg N · ha^{-1}, applied N-fertilizer, Brookston clay, Woodslee

Date†	a	b	Correlation coefficient r	F-value F
05-14-79	9.86	−0.00167	−0.17	<1
05-17-79	9.86	0.00069	0.22	<1
05-22-79	10.57	−0.00092	−0.24	<1
06-04-79	11.37	0.00227	0.43	2.32
06-13-79	9.69	−0.00113	−0.09	<0.09

†Sample collection dates, fertilized with 0, 112, 224 and 336 kg N · ha^{-1} on 16 May 1979.

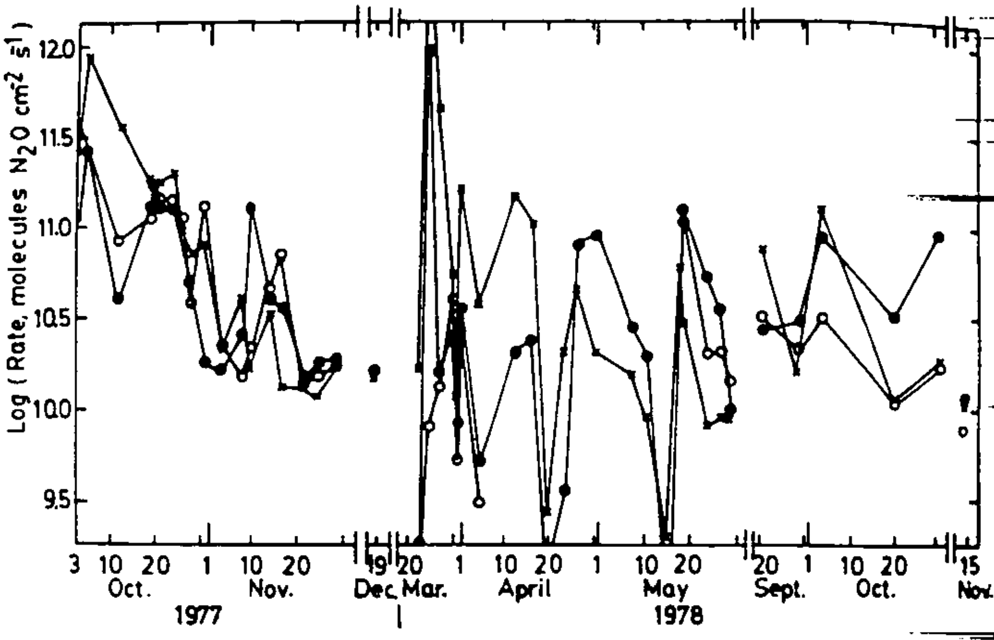
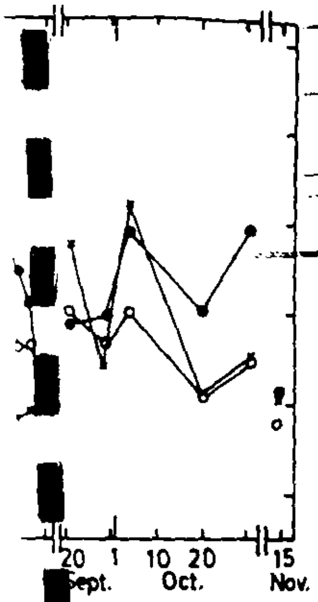


Fig. 3. Log average N_2O emission rates over Brookston clay, Woodslee, for the period 3 Oct. 1977–15 Nov. 1978. KNO_3 treatment: •, 336; ○, 168; ×, 0 kg N · ha^{-1}.

that denitrification may occur in anaerobic microsites in a generally aerobic soil mass (Russell 1973; Alexander 1977). If so, these data show that N_2O evolution from such microsites must be quite intense and persistent over a relatively long period of time. The data also suggest that the number of such microsites is much greater in clay soil where aeration may be more restricted. According to Smith et al. (1978), denitrification rates in some soils are apparently not increased by either NO_3^- or NO_2^- additions. It is possible that the N_2O produced, especially in the well-aerated sandy loam, may be from nitrification processes as indicated earlier (Hutchinson and Mosier 1979).

The relatively large variability in rates of N_2O evolution, particularly from clay soil, illustrates the difficulty involved in assessing net global production rates required for calculation of effects on the ozone layer. Rates integrated over relatively long durations and under many soil situations are required if long-term effects of applied fertilizer on N_2O evolution are to be observed. Our results for sandy loam show that it is possible to obtain reasonable estimates of fertilizer-derived nitrogen returned to the atmosphere as N_2O for periods of several months following application, information which is required to assess the impact on stratospheric ozone levels. Our data which show relatively small losses of fertilizer nitrogen as N_2O during the few months following fertilization agree with those reported by Hutchinson and Mosier (1979). The control site on sandy loam had not been fertilized with nitrogen since 1969, a period of 9 yr. Consequently, soil nitrogen levels on this site were considerably below those required for adequate plant growth, yet N_2O emission rates remained measureable at $\sim 10^9$ molecules · cm^{-2} · s^{-1}. Within about 80 days following fertilization, "background" rates of N_2O evolution were obtained on all sites. It would appear,



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therefore, that short-term (decade or less) effects on tropospheric N_2O levels from applied fertilizer may be less serious than that suggested by McElroy et al. (1977).

The apparent lack of correlation between N_2O flux and fertilizer treatment on Brookston clay in natural field conditions also suggests that short-term effects on N_2O emission are unlikely to be very large.

Our data can be used to roughly estimate total N_2O production from land surfaces. Using a rate of 3×10^{10} molecules $\cdot$ $cm^{-2} \cdot s^{-1}$, which may be considered typical for Brookston clay, and multiplication by the reported (CAST 1976) estimates of harvested and non-harvested land areas, we obtain 13×10^9 kg $N \cdot yr^{-1}$ in reasonable agreement with the estimate, 20×10^9 kg $N \cdot yr^{-1}$ made by Hutchinson and Mosier (1979), but considerably less than the global estimate of 120×10^9 kg $N \cdot yr^{-1}$ (McElroy et al. 1977). The implication of this lower value in view of the known burden of atmospheric N_2O has been discussed by Hutchinson and Mosier (1979). We concur with their conclusion that either the atmospheric lifetime is considerably greater than 10 yr as estimated by Junge (1974), thus implying smaller global emissions, and/or that the oceans, fresh water media or some unknown source constitute a substantial net source of N_2O.

ACKNOWLEDGMENTS

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MIDWEST RESEARCH INSTITUTE

PROJECT DEVELOPMENT SKETCH

MRI-18

TITLE 2.7 Reference 19 [illegible] – 1980

PROJECT NO. 6500-35 **DRAWN** **APPR.** JSK **DATE** 9/20/92

From Abstract & Tables 1 & 2 } Applic. Rates = 112, 224, and 336 kg N/ha; Emission Rate = 0.25% of [illegible] fertilizer in 50 days

* For 112 kg N/ha – Urea, NH_4NO_3, or KNO_3

$$112\ \frac{\text{kg N fert}}{\cancel{\text{ha}}} \times \frac{0.25\ \text{kg N}}{100\ \text{kg N fert}} \times \frac{44\ \text{kg}\ N_2O}{14\ \text{kg N}} \times \frac{10^3\ \text{gm}}{\cancel{\text{kg}}} \times \frac{1\ \cancel{\text{ha}}}{112\ \text{kg N fert}} = 7.86\ \frac{\text{gm}\ N_2O}{\text{kg N}}$$

$$7.86\ \frac{\text{gm}\ N_2O}{\text{kg N fert}} \times \frac{1}{50\ \text{days}} = 0.0982\ \frac{\text{gm}\ N_2O}{\text{kg N}\cdot\text{day}}$$

* For 224 kg N fertilizer/day – Urea, NH_4NO_3, or KNO_3

$$224\ \frac{\text{kg N fert}}{\text{ha}} \times \frac{0.25\ \text{kg N}}{100\ \text{kg N fert}} \times \frac{44\ \text{kg}\ N_2O}{14\ \text{kg N}} \times \frac{10^3\ \text{gm}}{\text{kg}} \times \frac{1\ \text{ha}}{224\ \text{kg N fert}} = \boxed{7.86\ \frac{\text{gm}\ N_2O}{\text{kg N}}}$$

$$7.86\ \frac{\text{gm}\ N_2O}{\text{kg N fert}} \times \frac{1}{50\ \text{days}} = 0.0982\ \frac{\text{gm}\ N_2O}{\text{kg N}\cdot\text{day}}$$

* For 336 – same proportion as above

$$7.86\ \frac{\text{gm}\ N_2O}{\text{kg N fert}} = 0.0982\ \frac{\text{gm}\ N_2O}{\text{kg N}\cdot\text{day}}$$

SOIL SURVEY
OF DURHAM COUNTY

●

BY

L. R. WEBBER and F. F. MORWICK
ONTARIO AGRICULTURAL COLLEGE
AND
N. R. RICHARDS
EXPERIMENTAL FARMS SERVICE

●

GUELPH, ONTARIO
DECEMBER 1946

●

REPORT No. 9 OF THE ONTARIO SOIL SURVEY

Mapping Map Rein according to [illegible]

EXPERIMENTAL FARMS SERVICE, DOMINION DEPARTMENT OF
AGRICULTURE AND THE ONTARIO AGRICULTURAL COLLEGE

FIG. 1—Outline map of Ontario showing the location of Durham County and other areas for which soil maps have been published. (1-6 map only; 7-9 map and report.)

PART I

GENERAL DESCRIPTION OF AREA

Location and Area

Durham County is located in central Ontario on the north shore of Lak Ontario. Adjoining counties include, Victoria on the north, Peterborough an Northumberland on the east and Ontario on the west. The town of Po Hope situated in the southeast corner is 53 miles from Toronto, 242 mil from Ottawa and 286 miles from Montreal.

The area of the county is approximately 402,560 acres (1941 Census (Canada), with about 371,000 acres of assessed land. The difference in acreaş is accounted for by road allowances, bodies of water and areas of marsh.

County Seat and Principal Towns

Some time after the original land surveys were made, Durham and Nortl umberland were united for the purposes of municipal government. The tv counties are served by one county council which meets in Cobourg in Nortl umberland County. The office of the agricultural representative for Durha is located in Bowmanville.

The location and population of the principal towns and villages are show in Figure 2.

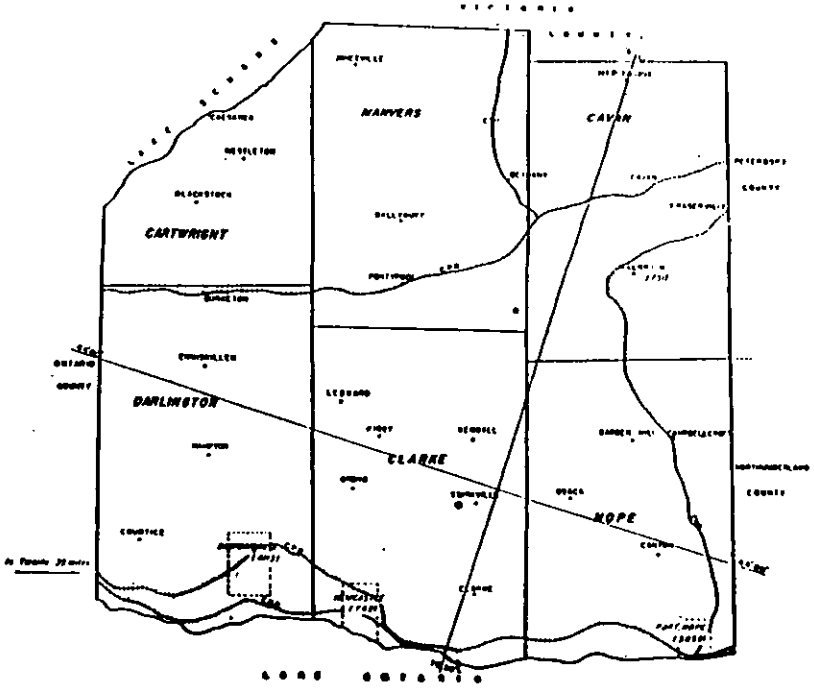

FIG. 2—Outline map of Durham County showing the location of towns, villages and railways.

PART II

FACTORS AFFECTING THE FORMATION OF DURHAM COUNTY SOILS

The soil occupies a layer on the surface of the earth varying in depth from less than an inch to several feet. Soil is a natural body and the medium in which plants grow. It is a mixture of minerals, water, air and organic matter which occur in varying proportions. These four constituents exist in a soil in a finely divided and intimately mixed condition. The factors which are largely responsible for the occurrence, composition and mixture of the constituents, *include the geological materials as a source of soil-forming materials.* In addition the differences among soils and their ability to support the growth of many plants are attributed to landscape relief, climatic conditions and the natural vegetation. *The length of time a soil has been in the process of formation will account for certain differences as well as the use or misuse of land by man.*

THE GEOLOGICAL MATERIALS FROM WHICH DURHAM COUNTY SOILS ARE FORMED

The first step in the development of soil is the formation of parent material largely from the disintegration and weathering of rocks. Parent material may be shallow or deep. It may consist of coarse rock fragments alone or mixed with finer materials; it may consist of single grain minerals high in silica as in coarse sands; or it may consist of very fine clays and silts. The parent material may be relatively uniform in chemical composition or may be particularly varied. *Some materials are weathered more easily to form soils than are other materials.*

The parent materials of Durham County soils may be grouped into three *main classes according to the influence of their chemical composition on soil* development: (a) Calcareous materials rich in lime as are found in limestone, etc.; (b) Siliceous materials originating from granite, etc.; (c) Argillaceous or clayey *materials derived from shales, etc. The physiographic divisions of* surface materials in the county are based largely on land form and characteristics of the parent materials.

South-central Ontario was within the area covered by the glacier in the Pleistocene period. The late Wisconsin drift resulted from the glacial action on the Trenton and Black River limestone series and some Precambrian material. In the south-west corner of the county appreciable amounts of Utica shale were deposited. The drift is relatively deep over the bedrock of limestone. Exposures of bedrock occur in the bed of the Ganaraska River near Port Hope and in some stream beds near Bowmanville.

The continental glacier advanced from a north-easterly direction. As the great sheet of ice retreated by melting, the margins assumed lobate forms. The juncture of two lobes extended east and west across the middle of the county. The sandy and gravelly materials were deposited by the water flowing through the outlet formed by the two lobes. Local bodies of water were formed by obstructing masses of ice. The recession of the ice mantle continued in the two-lobe formation and laid down the till in various formations or hemmed in meltwater that deposited lacustrine materials. Streams flo into these glacial lakes formed deltas of stratified sand and gravel.

The physiographic divisions of Durham County may be outlined as foll

1. Drumlinized limestone till plains.
2. Smooth limestone till plains.
3. Plains of fine-textured water-laid sediments.
4. Smooth sandy plains.
5. Sandy and gravelly ridges.

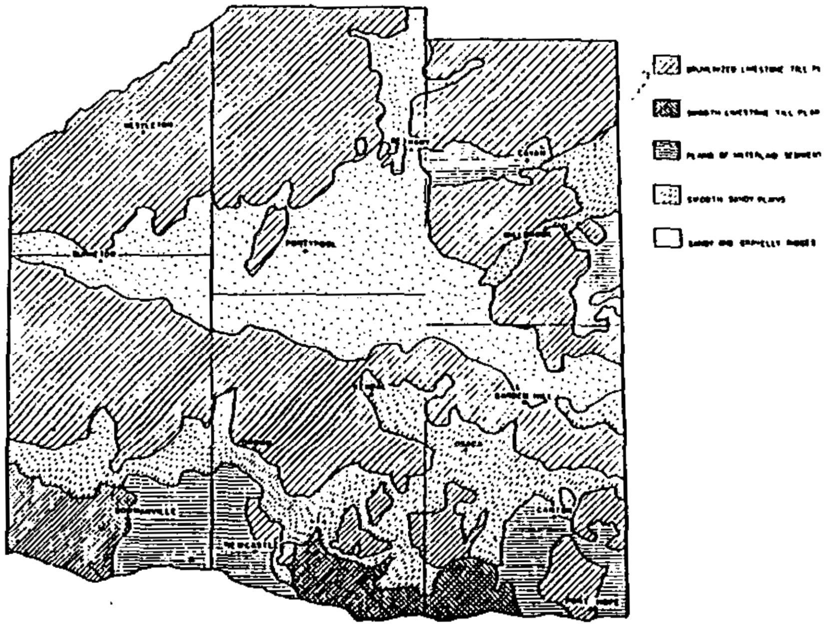

FIG. 3—Outline map of Durham County showing the Physiographic Division

1. Drumlinized Limestone Till Plains

The drumlinized plains occupy the largest area of any physiogra division in Durham County. The areas immediately north and south of central belt of gravel and sand ridges are well drumlinized. Drumlins are formed oval hills, a mile or less in length, a third or quarter mile in width ranging up to a hundred or more feet in height. Their longest axis is rou parallel to a north-east and south-west line. These distinctive oval hills formed during the time of glaciation.

The materials within a drumlin are commonly referred to as till or bou clay. The till is composed of limestone from the Trenton and Black R series with varying amounts of Precambrian rocks. Boulders and sto *some of which are a foot in diameter and of limestone or granite origin,* associated with a loamy matrix and numerous small rounded stones. The pressure created by the ice has compacted these stones and finer materials to such an extent that soil water moves freely but a droughty condition is not common.

Some variation in the composition and condition of the till is found throughout the area. Gravelly deposits are often located at one end of the drumlins. In other places there are fewer large boulders and stones and the till is more compact and slightly heavier. The occurrence of Precambrian materials on the surface is also variable. The depth of the till over the bedrock is generally quite deep.

2. Smooth Limestone Till Plains

The smooth undulating limestone till *plains are found in the extreme* southern part of the county. In general this physiographic division is located south of the old gravelly beaches marking the borders of glacial Lake Iroquois. *In this* position the limestone materials have undergone some reworking by the action of water at the time Lake Iroquois was in existence.

The composition of the till is dominated by the limestone content despite the occurrence of some of the dark greyish Utica shale. The till contains fewer large stones and boulders than is characteristic of the drumlinized plains. The matrix is generally heavier as it consists of more silt and clay from the weathering of the shale and small depositions of water-laid materials. The occurrence of Precambrian rocks is not as noticeable as in the limestone till soils to the north. The depth of the till is shallower over most of the area but bedrock is rarely exposed. Frequently the till is underlain by *heavy compact* lacustrine deposits as found in exposures along the lake shore.

3. Plains of Fine Textured Water-Laid Sediments

Water-laid sediments or lacustrine deposits are characterized by fine textured materials *like* silts and clays and typically stone free except for some gritty material. In many lacustrine deposits alternate layers of dark and light silts and clays *are common. These varves are destroyed by the* weathering processes but are found intact in the unweathered parent material.

The parent materials in the lacustrine deposits are relatively high in lime and are often referred to as ground limestone flour. These materials were carried in by water moving slowly and having much silt and clay in suspension or *finely dispersed.* In most areas especially in the southern parts, the texture of the surface soil is lighter than the parent material.

4. Smooth Sandy Plains

The smooth sandy plains include well-sorted deltaic and outwash deposits as well as low gravelly beaches. The deltaic plains occupy a considerable area around Osaca where the sandy materials were carried into bodies of water and allowed *to settle out. The relief* is typically nearly level but subsequent water erosion has dissected the area by numerous gullies and channels. The shoreline of glacial Lake Iroquois is prominently defined in some areas by gravel beaches.

The lime content of the material of the sandy plains is relatively high despite the siliceous nature of the sand particles. The texture of the parent material is rather coarse, grading in *size from small cobbles and* gravel stone to coarse and fine sands and a small percentage of silt and clay. The dept of the sandy materials is variable; in some places the material is quite deep an uniform while elsewhere compact till or lacustrine deposits are within a fe feet of the surface.

5. Sandy and Gravelly Ridges

The sandy *and gravelly ridges* are occasionally referred to as fluvio glacial or interlobate deposits of unassorted gravel, sand and till. This grou occupies a broad area in the central region with an area northward nea *Bethany.* In many cases these ridges represent the height of land with th streams flowing north or south depending on which side of the ridge the *originate.*

This physiographic division is characterized by light soil materials hig in lime. The texture *of the materials is quite variable* ranging from limeston and igneous boulders to fine sands and silts. The inclusion of small till deposit is recognized. The area is marked by a strongly rolling to hilly *topograph* and numerous glacial pot holes which have no other drainage than dow through the soil materials. The materials are relatively deep and lack uni*formity in the size of particles throughout* their depth.

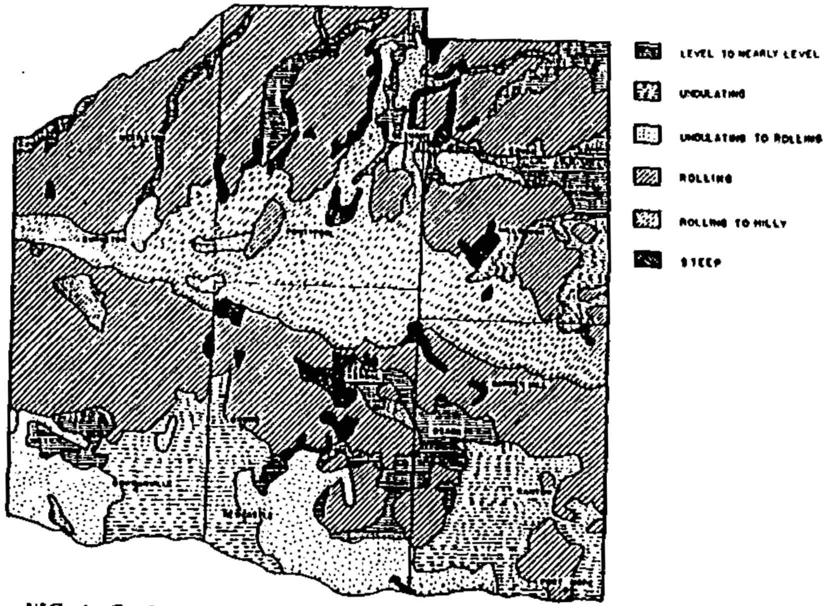

FIG. 4—Outline map of Durham County showing the topographic regions.

Relief

The elevation of the land in Durham County is given on the topographica sheets published by the Department of National Defence. There are thre natural separations for describing the altitudes. From Lake Ontario northward to the fluvio-glacial deposits, the elevation ranges from 245 feet to approximately 1,000 feet *above sea-level*. The *fluvio-glacial* area represents the height of land in the county. Elevations in this section reach 1,200 feet. From here the land slopes toward Lake Scugog whose elevation is 820 feet above sea-level.

One of the more important factors related to soil formation and soil management is the topography or relief of the land. The degree of slope influences drainage, run-off of surface water and erosion while in actual farming the slope often restricts the use of certain farm machinery. In Table 2 the topography classes are expressed as slope groups.

TABLE 2

SLOPE GROUPS IN RELATION TO TOPOGRAPHY

Slope Group	Per Cent Slope	Topographic Term
A	0—3%	level to nearly level
B	3—8%	undulating
C	8—15%	rolling
D	15—25%	hilly
E	25—35%	very hilly
F	35% and over	steep

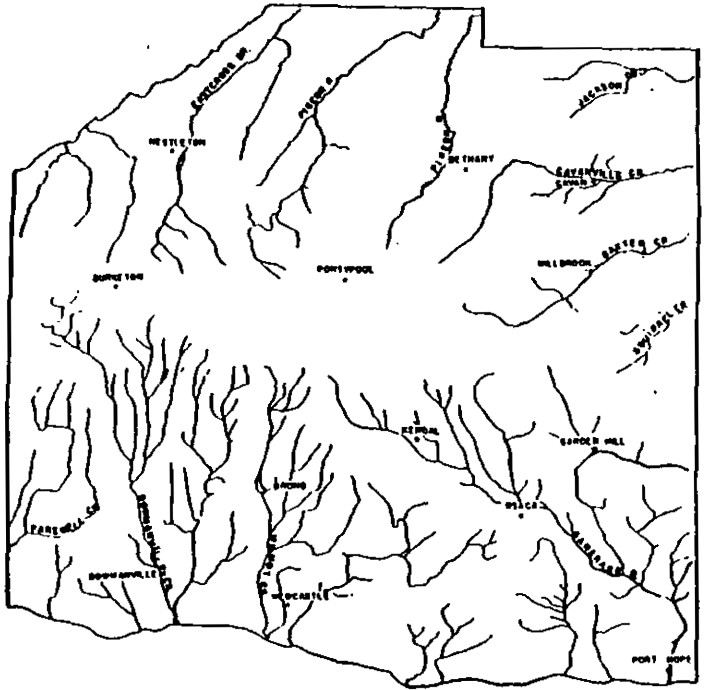

FIG. 5—Outline map of Durham County showing the natural stream courses.

Rolling and very hilly topography is found in the broad central are light textured soils. The slopes are frequent and comparatively short. S depressions are characteristic of the relief. The areas where drumlins o are considered to be strongly undulating to rolling. In some areas particu where the Otonabee type is mapped the topography may be hilly. The sl of the drumlins are long and gentle occurring less frequently than in the hi soils.

With the height of land across the middle of the county, the drain system is *naturally divided into two parts*. The northerly flowing stre (Figure 5), drain into the Trent system. Eastcross Creek and two bran of the Pigeon River are slow sluggish streams with wide courses of m muck and swamp. The channels change very little and *stream erosion* is a serious problem. The four creeks flowing eastward are less sluggish smaller areas of adjoining wetland. Those streams emptying into Lake Ont differ in several respects from the northern system. With *a greater dro* an outlet the southern creeks and rivers flow relatively fast. The usual adja flooded land is missing; the stream courses are deeper and erosion is sev The friable till and lacustrine materials are rapidly cut into, leaving deep gu with barren slopes. Several large ravines appear at the outlets of the sm streams.

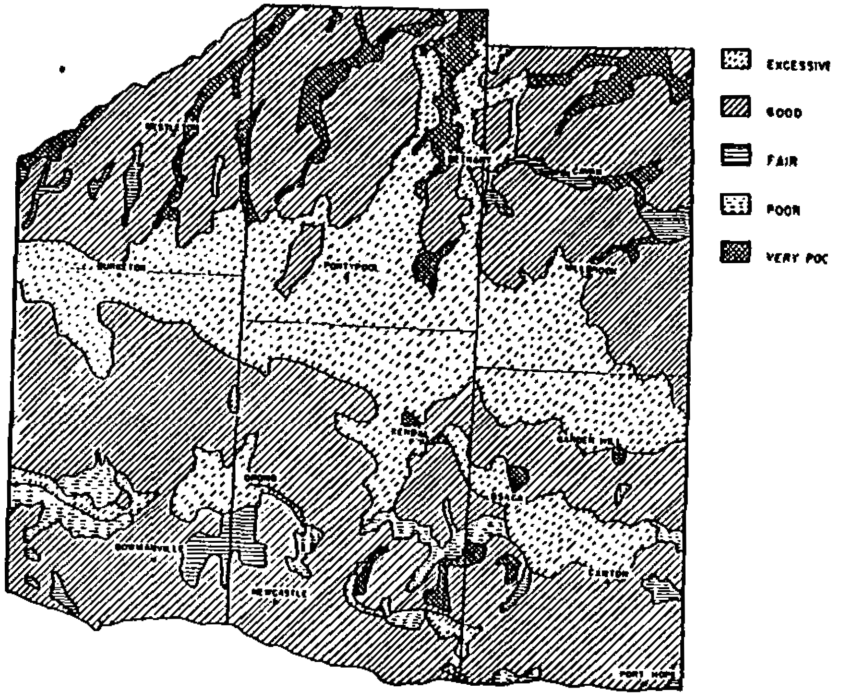

FIG. 6—Outline map of Durham County showing the natural drainage conditions of the soils.

Natural Vegetation

In Southern Ontario most of the original forest cover has been *removed*, leaving only occasional woodlots that can be used in reconstructing a picture of the original vegetation. The occurrence of pine stumps in stump fences give evidence of the occurrence of large pines in the former forest on the sandy soils.

Halliday* includes Durham County in the Huron-Ontario section of the Great Lakes-St. Lawrence Forest Region. The prevailing association is composed of broad-leaved trees, particularly sugar maple and beech. Basswood, white elm, birch, white ash and several oaks occur in the association as well as a scattered distribution of hemlock, white pine, hickory, ironwood, butternut *and black cherry*.

The common forest association in Durham County comprises the sugar maple and beech. These broad-leaved, hardwood trees are generally associated with the *till* soils of the drumlinized and smooth limestone plains. (Figure 3.) This variety of soils is characterized by good drainage, medium texture and adequate amounts of lime. Local differences in drainage, particularly *poorly drained* soils, can be spotted by the presence of white cedar, species of elm, tamarack, alders and willows. The broad-leaved association includes ironwood, basswood, white spruce and white pine. There is a great *variety of shrubs, including* choke cherries and species of hawthorn. The concentration of buckthorn in the vicinity of Nestleton is quite noticeable.

The soils on the sandy and gravelly ridges are droughty and the topography is hilly and steep. The principal tree growth on these soils is composed of red and white pine, red oak, hickory and white birch. Cut-over and burned-over areas have a large proportion of pines and poplars. Many cleared and cultivated areas have been planted with pine.

The heavy and intermediate textured soils, largely of water-laid sediments are cleared of their forest cover. There are indications that hardwoods and some pine once grew on these soils.

The following quotation from the Townships of Darlington and Clarke by John Squair is included at this time, since it gives a broad picture of forest conditions and of the lumbering business during the last century:

"On the best clay loam soils it was essentially a beech and maple forest . . . with *some admixture of other deciduous* woods and some white pine and hemlock. On the lighter sandy soils there was often a fine growth of hardwood with a larger mixture, however, of pine and hemlock than on the heavy land. . . . On both higher and lower land there was *some oak but that valuable* kind of wood was found in greater abundance on the ridges to the north.

"As early as 1830 anxiety was expressed over the rapid disappearance of woodlots. Pine was in particular demand for the steamboats plying between Toronto and Quebec. From 1811 to 1842, 1,002 masts and 900 immense sticks of squared oak and pine were supplied to the English shipyards. From *1850 on, Newcastle was the chief G.T.R.* wood depot on the Montreal-Toronto run; beech and maple were the chief types of wood. Perhaps 1880 might be taken as the date of the end of the cordwood trade at Newcastle."

Climate

The *climate* of Southern Ontario is usually stated to be of the modific humid continental type*. The variations in climate are generally attribute to the presence of frequent storm paths across the area and the modifyin effect of *the Great Lakes. Physiographic features* tend to effect climatic var ations through the modification of wind and changing temperatures.

The climate of Durham County is relatively cool and humid. The locatio with respect to Lake Ontario tends to make the *climate somewhat* warme than areas lying in Eastern Ontario or immediately north. The mean annu temperature is 42° to 44° F. The average annual precipitation ranges from 26. to 33 inches with about half the amount falling in the growing season. Th frost free period ranges from 120 to 140 days with a growing season of 18 to 195 days.

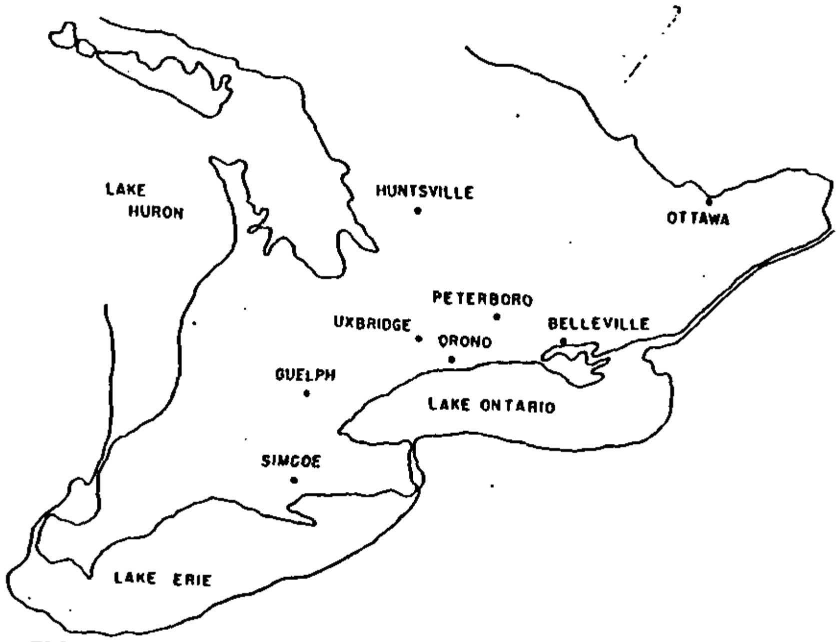

FIG. 7—Outline map of Southern Ontario showing the location of several representative meterological stations.

The only meteorological station within the county is a station at Orono providing 15 years of records. Figure 7 shows the location of several othe stations whose records are included here. The data from the other station will give a general picture of the climate of the region. The Simcoe station i included, since it lies in an extensive and older tobacco growing region.

The mean annual temperature at Orono over a *period of 15 years* ha averaged 43.7° which is not greatly different from the 43.4° at Peterboroug and only slightly lower than an average of 44.1° for Belleville. The mea

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* A Forest Classification for Canada by W. E. D. Halliday.

* The Climate of Southern Ontario by Putnam, D. F. and *Chapman, L. J. Scientifi Agriculture*. Volume 18, No. 8, April 1938.

annual at Uxbridge, northwest of Orono in Ontario County and located on slightly higher land, was a little lower. The 2° higher mean for Toronto may be due in a large part to the station's proximity to Lake Ontario. The differences as compared with the more distant stations are attributed to geographical locations north or south of Orono. See Table 3.

An average winter temperature for December, January and February is about 21° as compared with a mean of 14° at Ottawa or 21° at Guelph. January and February are the coldest months with February having a slightly lower average over the 15 years. The spring mean temperature of 40° at Orono is about the same as at Guelph and Ottawa. The mean temperature at Simcoe for the same period is 43°. A summer average of around 66° is common to much of Southern Ontario except in the more southerly counties where slightly higher averages are recorded. The mean fall temperatures at Guelph and Orono are around 47° while at Simcoe the average is slightly higher at 50°.

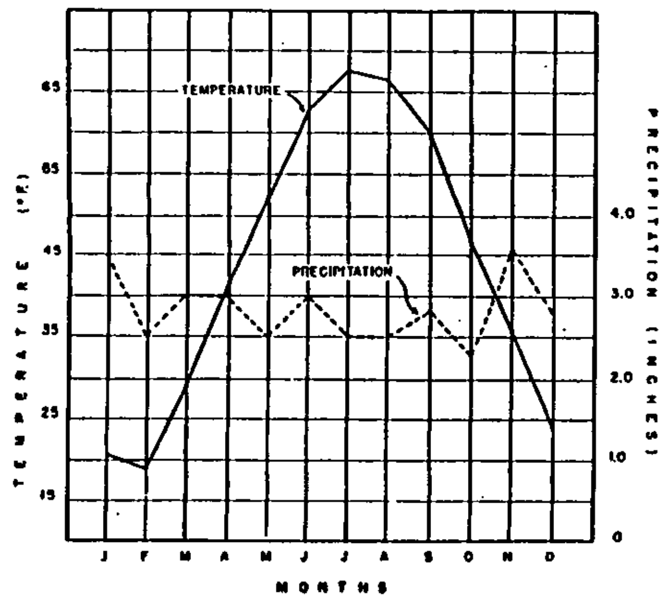

FIG. 8—Chart showing the mean monthly temperature and precipitation at Orono, Ont. (15-year period).

Most of Durham County lies within two climatic regions — Simcoe-Kawartha Lakes and the South Slopes as defined by Putnam and Chapman. The growing season in the Simcoe-Kawartha region ranges from 188 to 195 days which is about five days shorter than the South Slopes. In calculating the length of the growing season, a mean of 42° F. was chosen as the beginning of the season. For each species and variety of plant there is a temperature

TABLE 3

MEAN MONTHLY TEMPERATURE FOR SEVERAL SELECTED POINTS

Temperature in Degrees Fahrenheit

	PERIOD OF RECORD	JAN.	FEB.	MAR.	APR.	MAY	JUNE	JULY	AUG.	SEPT.	OCT.	NOV.	DEC.	YEAR
MMEDIATE STATIONS														
Orono	15	20.8	19.0	28.7	40.8	52.2	62.8	68.0	66.5	59.2	46.4	35.8	24.0	43.7
Belleville	47	18.6	18.8	28.2	42.0	54.2	64.9	70.1	67.8	60.2	47.1	35.1	21.8	44.1
Peterboro	61	17.3	16.3	27.7	42.4	54.5	63.8	69.0	66.6	59.7	47.6	34.1	21.5	43.4
Uxbridge	29	18.0	16.2	26.2	40.5	52.9	63.2	68.0	65.0	58.4	46.4	33.8	22.2	42.6
DISTANT STATIONS														
Ottawa	52	11.8	12.7	24.7	41.4	54.9	64.6	68.9	66.3	58.5	46.2	32.4	17.3	41.6
Huntsville	30	13.0	12.0	22.0	38.0	52.0	61.0	65.0	63.0	56.0	44.0	31.0	18.0	40.0
Guelph	55	20.0	19.0	28.0	42.0	53.0	63.0	68.0	66.0	59.0	47.0	36.0	24.0	44.0
Simcoe	22	23.8	23.5	31.2	43.2	54.6	64.6	69.3	67.3	61.6	49.8	38.4	27.5	46.2

TABLE 4

MEAN MONTHLY PRECIPITATION IN INCHES FOR SEVERAL SELECTED POINTS

	PERIOD OF RECORD	JAN.	FEB.	MAR.	APR.	MAY	JUNE	JULY	AUG.	SEPT.	OCT.	NOV.	DEC.	YEAR
MMEDIATE STATIONS														
Orono	15	3.58	2.56	3.01	2.99	2.51	3.02	2.47	2.47	2.83	2.29	3.65	2.84	34.22
Belleville	47	3.26	2.46	2.63	2.17	2.37	2.66	2.52	2.63	2.78	2.28	2.85	2.54	31.17
Peterboro	61	2.19	1.98	2.43	1.74	2.18	2.24	2.32	2.05	2.68	2.19	2.45	2.21	26.66
Uxbridge	29	2.64	1.95	1.98	2.37	2.67	2.25	3.51	2.99	2.45	2.57	2.44	2.12	29.94
DISTANT STATIONS														
Ottawa	52	2.98	2.40	2.65	2.32	2.74	3.39	3.67	3.00	2.94	2.68	2.63	2.84	34.24
Huntsville	30	3.09	2.45	2.78	2.09	2.85	3.69	2.96	2.70	3.84	3.44	3.29	3.28	36.46
Guelph	55	2.35	1.79	1.88	2.30	2.80	2.89	3.24	2.87	2.67	2.39	2.48	1.99	29.65
Simcoe	22	3.51	2.64	2.93	3.20	2.51	2.81	2.92	2.59	3.00	2.68	3.31	3.05	35.15

below which growth is not possible. With such cool-season crops as oats, rye, wheat and barley the minimum is 32° to 41° F. and the optimum 77° to 87° F.* From the many species and varieties of hay and pasture plants, a selection or combination can usually be made that provides ample forage for various lengths of growing seasons. Winter killing of alfalfa is often associated with lack of sufficient moisture during the preceding summer and fall by which the vigor of the plants has been reduced to such an extent that they are unable to endure low temperatures. Apples, sour cherries and American plums under some conditions usually stand temperatures as low as -30° F. without severe injury. *Heavy losses of fruit trees have occurred at warmer* temperatures than -30° F. under various combinations of humidity, ground moisture conditions and sharp freezing. Peaches and apricots are likely to be injured at -15° F.* In Durham County, the fruit growing area is largely concentrated along the Lake Ontario shore where the extreme low was -30° F. The lowest temperature recorded in the South Slopes is -39° F. and -42° F. in the Simcoe-Kawartha region.

The mean annual rainfall at Orono has averaged slightly over 34 inches for a 15-year period. This figure is somewhat higher than recorded at the stations at Belleville, Peterborough or Uxbridge. The rainfall for the growing period, approximately May to September, has averaged 13 inches. At Ottawa where the total is nearly identical, the rainfall for the growing season has averaged slightly under 16 inches. For the same period at Simcoe the figure is almost 14 inches. Snowfall varies from 50 to slightly over 100 inches for the whole county with a 15-year average at Orono of 59 inches and nearly 70 inches at Peterborough for 61 years. See Table 4.

In general, the climate of Durham is characterized by moderately cold winters and warm summers. The temperature ranges do not limit the growing of most common farm crops like cereal grains, roots, ensilage corn and many hay and pasture plants. Farmers located in the fruit belt on the lake shore *specialize in apple growing, while near Osaca flue-cured tobacco has developed* in recent years into a successful venture. The distribution of rainfall is favourable to farming; the frequency of droughts does not reach a critical point in regularity nor in severity.

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* Climate and Man—U.S.D.A. Yearbook. 1941.

PART III

THE CLASSIFICATION AND DESCRIPTION OF DURHAM COUNTY SOILS

Soil is a complex body formed by the interaction of many forces. It h developed through the operation of climatic agencies on various kinds parent materials and modified by such factors as vegetation, relief, draina *and use*. To attempt a classification of soils, the interaction of all forces mu be capable of being appraised. The effect of a single force is frequently diffic to evaluate but the sum total of several forces is expressed in the soil profile.

If a hole *is dug in a well drained soil*, one can see a series of horizont layers of soil of varying thickness. (Figure 9.) These layers are called horizo and differ from one another in such properties as colour, texture, structu thickness and clarity of demarcation. The succession of layers from th surface down to and including the parent material is called the soil profile.

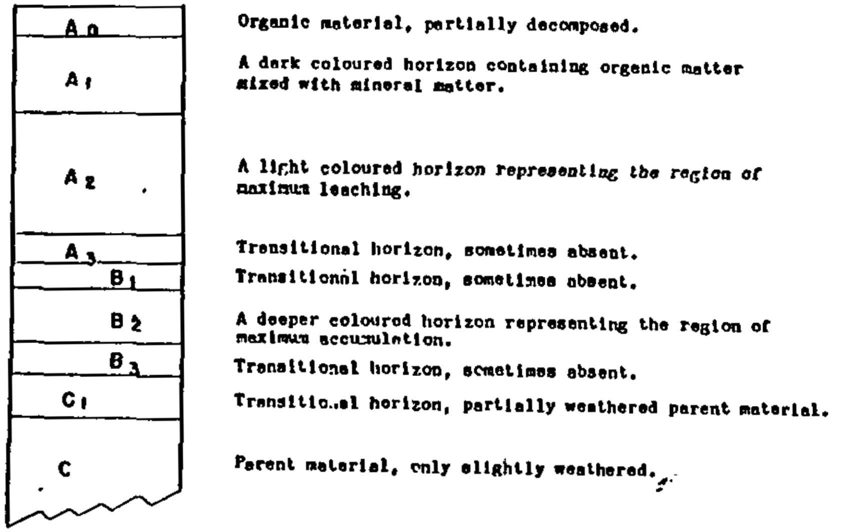


FIG. 9—A diagrammatic vertical cross-section of a well-drained natural soil, showing the naming of horizons.

The Soil Profile

For convenience, the soil layers or horizons are grouped under thr *headings*—A, B, and C. The A horizon includes the various layers in the upp part of the profile where soil forming processes are most active. Under foreste conditions the A_0 exists in the form of organic materials—leaves and decayin wood; the A_1 is the layer in which the *mineral particles are* covered with coating of humus which gives the soil a dark colour; the A_2 horizon has litt or no organic coating and presents a leached appearance and the A_2 in this region usually has a still lighter and more greyish appearance. In general the A horizons include that part of the profile from which some materials have moved downward by leaching.

The B horizons are identified by deeper colours, heavier texture and blocky or angular structure. Some of the materials which have leached out of the A horizon have accumulated in the B horizon, particularly the iron and alumina compounds and some of the fine clay. The B_2 horizon is the area of maximum accumulation and the B_1 and B_3 are transitional horizons. (See Figure 9.)

The C horizon consists of parent material from which the soil is developed. The upper part of the C may be slightly influenced by soil-forming processes but usually the finer differentiations are not attempted.

Profile Variations

The diagrammatic profile, Figure 9, represents the normal type of development associated with forest vegetation and good drainage. The indicated horizons do not always occur in sufficient clarity of demarcation that they can be identified and adequately described. Variations can be attributed to differences in geological parent materials, drainage conditions, relief, texture, erosion, vegetation, climate and land use. Various combinations of these factors account for the identifiable differences in profiles. The presence of a deeply weathered profile on the droughty sands having a thin A, and little or no B horizon largely represent the effects of parent materials, drainage and texture. On poorly drained soils, the A_1 becomes relatively deep and high in organic matter while the B, if present, is usually an area of rusty blotches. Under cultivation the ploughed layer of a soil includes all or part of the A_1 and where the profile is very shallow may include all the A and B as well as the Upper C. While the interaction of the soil forming processes tend to produce a great number of individual conditions that can be recognized in soil classification, there is an overall type of soil development particular to the region of Ontario which includes Durham County.

Regional Soil Profile

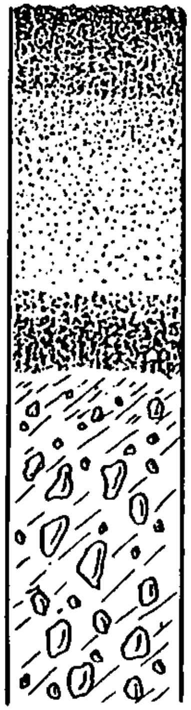
Durham County soils have developed under a forest vegetation dominated by broad-leaved trees principally maple and beech and in a relatively cool, humid climate. These Grey-Brown Podsolic soils have several characteristic features that differentiate this zone from others. The A_1 layer is usually a greyish brown colour with organic matter mixed and incorporated into the mineral fraction. The A_2 is a light greyish or yellowish brown loamy layer, while the B is of brownish heavier materials with a characteristic structural development.

The following description of a Bondhead fine sandy loam profile is typica of the development on a well-drained site.

Location: Lot 13, Conc. VIII—Manvers Township.

Site: South easterly exposure on a large drumlin; slope 13 per cent.

Vegetation: Sugar maple, beech, ironwood; heavily forested; little or n grass but a forest mat of leaves.



—A_0 and A_{00} horizons (0-1 inch). A covering o recent leaves mixed with and grading int a shallow layer of leaves partially decom posed; pH 5.8.

—A_1 horizon (6 inches), dark grey brown fin sandy loam; porous crumb structure pH 6.3.

—A_2 horizon (13 inches), light grey brown sand loam; approaching a single grain structure pH 6.2.

—A_3 horizon (1-2 inches), yellowish grey sand loam; weak platy structure; bleache appearance; pH 6.8.

—B_1 horizon (1 inch). A shallow layer, slightl mottled and transitional to B_2; pH 6.8.

—B_2 horizon (2 inches), brownish loam; smal angular, nutlike structure of soft aggre gates; pH 6.8.

—C_1 horizon (3 inches), greyish calcareous till indication of some weathering; stony sand loam; pH 7.2.

—C_2 horizon a grey stony, highly calcareous till sandy loam texture; pH 8.0.

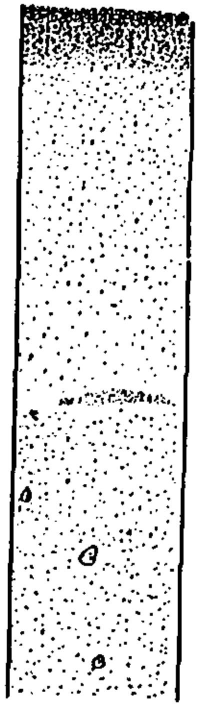
Because of the coarse nature of the materials of the light textured soil in the central part of the county, a dry azonal podsolic type of profile com monly occurs. The coarse nature of the materials and their light textur limit the profile development. The A_1 is normally a thin layer relatively lov in organic matter; the A_2 occurs generally as a structureless sand and deepe than the A_2 of the other local soils; the B, where present, occurs as a wea accumulation of a colloidal material eluviated from the A horizons.

The following description of a Pontypool sand illustrates the degree and type of development.

Location: Lot 2, Conc. IV—Cavan Township.

Site: Northerly exposure on interlobate materials; slope 12 per cent.

Vegetation: Sugar maple, beech, white birch, some white pine and basswood; thick growth of poverty grass, bracken and poison ivy.



—A_0 and A_{00} horizons (0-1 inch). A shallow layer of leaves and twigs in various stages of decomposition.

—A_1 horizon (3 inches), coarse sand mixed with decaying leaves, etc., no aggregation of sand particles; lower part of layer somewhat greyish in colour; pH 6.6.

—A_2 horizon (22 inches), *light yellow brown* structureless sand; pH 6.4.

—B horizon (0-1 inch), weak development; largely a concentration of faintly mottled materials; pH 6.4; a colour horizon more strongly developed than a textural horizon.

—C horizon grey poorly sorted calcareous sand; a few small rounded stones; pH 7.4.

Soil Series, Types and Phases

The term soil series is used to designate a group of soils whose profiles are alike in general character and appearance and developed from similar parent materials. The effect of climate and vegetation may alter profiles even though parent materials resemble one another. While any given area may be labelled as one soil series, deviations and variations do occur but the dominant profile, the one occurring *most frequently, is taken as representative of the area.* The soil series is usually given a geographical name from a town, village, township, etc., where the soil was first identified. Thus, the Newcastle series was first mapped in the Newcastle area and all soils mapped as Newcastle *should have similar profiles.*

While the profiles of a soil series are alike in their general characteristics, they frequently differ in texture. This textural difference constitutes the basis for *subdivision into soil types.* The name Newcastle clay loam as applied to a soil would infer that the soil was of the Newcastle series and a clay loa surface layer.

Variations other than surface texture frequently occur in a soil seri and are termed phases. Variations from the normal in topography, erosio shallowness, stoniness, etc., are accounted for by phases. A Bondhead loa bouldery phase would indicate that the soil is considered to be a member the Bondhead series with a loam surface soil but *abnormally stony ar* bouldery.

KEY TO THE CLASSIFICATION OF THE SOILS IN DURHAM COUNTY

A. SOILS FORMED FROM LIMESTONE TILL

I. Good drainage	
(a) Drumlin-like topography	
(i) Normal profile	
1. Bondhead loam	35,700 ac
2. Bondhead fine sandy loam	74,900 ac
3. *Bondhead fine sandy loam, bouldery phase*	1,700 ac
(ii) Shallow profile	
1. Otonabee loam	22,800 ac
2. Otonabee loam, steep phase	13,500 ac
(b) Morainic slopes with an outwash covering	
1. Dundonald sandy loam	30,100 ac
(c) Undulating till plain	
1. Darlington loam	15,400 ac
2. Darlington sandy loam	2,700 ac
II. Imperfect drainage	
1. Guerin loam	1,600 ac
2. Guerin sandy loam	1,100 ac
3. Guerin sandy loam, bouldery phase	3,600 ac
III. Poor drainage	
1. Lyons loam	5,400 ac

B. SOILS FORMED FROM FLUVIO-GLACIAL MATERIALS

(Eskers, Kames and Interlobate Moraines)

I. Good to excessive drainage	
1. Pontypool sandy loam	8,900 ac
2. Pontypool sand	38,000 ac
3. Pontypool gravelly sand	10,200 ac

C. SOILS FORMED FROM DELTAIC OR OUTWASH MATERIALS

I. Good to excessive drainage	
1. Brighton sandy loam	9,500 ac
2. Brighton sand	11,100 ac
3. Brighton gravelly sand	6,600 ac
4. Brighton sandy loam, bouldery phase	600 ac
II. *Imperfect drainage*	
1. Tecumseth sandy loam	4,000 ac
III. Poor drainage	
1. Granby sandy loam	6,700 ac
2. Granby sandy loam, bouldery phase	1,300 ac

D. SOILS FORMED FROM LACUSTRINE MATERIALS

I. Good drainage	
(i) Normal profile	
1. Newcastle loam	17,300 acres
2. Newcastle clay loam	6,000 acres
(ii) *Shallow profile*	
1. Schomberg clay loam	5,300 acres
2. Schomberg silt loam	2,000 acres
3. Percy loam	4,000 acres
II. Imperfect drainage	
1. Smithfield clay loam	1,800 acres

E. MISCELLANEOUS SOILS

Bridgman sand	4,000 acres
Bottom land	19,100 acres
Muck	22,100 acres
Marsh	2,200 acres

DESCRIPTION OF DURHAM COUNTY SOILS

A. SOILS FORMED FROM LIMESTONE TILL

Soils formed from limestone till correspond to the soils likely to be found in the two physiographic regions, drumlinized limestone till plains and smooth limestone till plains. The *well drained series included in this* group are Bondhead, Otonabee, Dundonald and Darlington. The imperfectly drained member is the Guerin series and the poorly drained associate is the Lyons loam.

The parent materials of these soil series are a mixture of Trenton and Black River limestones with smaller yet recognizable amounts of Precambrian rocks. In the south-western corner of the county these materials contain relatively small amounts of the greyish black Utica shale. The till is a compact unassorted mixture but dominated in chemical properties by the limestone. Partical sizes range from a *small percentage of fine clay to greater* percentages of pebbles, large stones and boulders. The degree of compaction permits the soil water to move freely through the normal well drained profile.

Bondhead Loam (35,700 acres)

" Fine Sandy Loam (74,900 acres)

" Fine Sandy Loam—Bouldery Phase (1,700 acres)

The Bondhead series display those characteristics that are common to the Grey Brown Podsolic soils. The topographic position is *favorable for the* maximum amount of profile development resulting from the influence of soil forming factors in Durham County.

I-24

The following is a profile description of a cultivated soil:

A_c—4-6 inches of a grey-brown loam or fine sa loam; friable crumby structure; stones; weakly alkaline; pH 7.2.

A_2—8-12 inches of a greyish brown sandy loan loam; *tending to weak platy structi* pH 6.8.

A_3—2 inches brownish grey *sandy loam or lo* slightly cemented and compact pH 7.0.

B —2-4 inches of a brownish loam; weak blo structure; pH 7.2.

C —A grey calcareous till dominated by limest materials and containing some fragme from Precambrian rocks; frequent sto and boulders; pH 8.0.

The *topography of the Bondhead* series is characterized by drumlins elongated hump-backed hills. Long and gentle slopes form a part of e drumlin but on the sides and near the top, steeper slopes are common. T topography is considered rolling with slopes generally ranging from 5-25 The drainage is good.

The natural vegetation includes sugar maple, *beech, basswood, some* and ash. The areas of lighter soils support appreciable amounts of white pi

Bondhead loam occurs in relatively large tracts near Millbrook and scattered locations south of the *height of land.*

Bondhead fine sandy loam is the major type in the northern parts of Ca wright and Manvers Townships, while other areas of the type are distribut throughout the county. The loam and fine sandy loam are among the bet agricultural soils of the county.

Bondhead fine sandy loam (bouldery phase). The areas mapped as a bo dery phase are recognized by the numerous boulders and stones on the surf soil. The stoniness is a limiting factor in the agricultural development of t type. *Generally, this* soil is left in pasture.

Agriculture

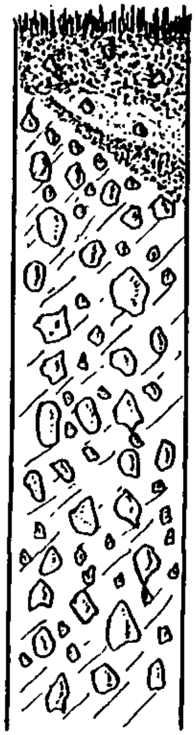
The Bondhead types (except *the* bouldery phase) are good soils for gene farming which includes grain growing, hay and pasture, and the raising livestock.

The greater part of the series is used for this purpose but some dairying, apple growing and canning crops are featured in the southern townships. Over most of the area an increased acreage of alfalfa would assist in maintaining the fertility and provide excellent hay or pasture. Where commercial fertilizers are used, phosphorus and potassium are particularly recommended. The steeper slopes of the drumlins should be left in hay, pasture or bush as long as possible. Methods that retard soil erosion must be considered and used on the Bondhead types.

Otonabee Loam (22,800 acres)
" Loam—Steep Phase (13,500 acres)

The Otonabee loam is mapped entirely in Cavan Township, while the steep phase is found in small areas through the county.

The following is a profile description of a cultivated soil:



A_c—4-6 inches dark grey brown loam; crumb structure; moderately stony; free carbonates; pH 7.8.

A_x—0-4 inches greyish brown loam; more open and incoherent than A_c; pH 7.8.

B —0-3 inches brownish loam or clay loam; nut-like structure; pH 8.0

C —A grey limestone till containing some fragments of Precambrian rocks; compact; frequent stones and boulders; pH 8.2.

The Otonabee series has been separated from the Bondhead on the basis of a shallower profile that has developed from similar parent materials. The greyish parent material is frequently turned up when plowed.

The Otonabee series is included with the Grey-Brown Podsolic soils, the characteristics being less well defined than in the Bondhead series. It may be better correlated with the Brown Forest soils.

The topography of the Otonabee loam is recognized by numerous well-formed drumlins. In some instances the topography approaches the hilly condition where steep slopes are more common. The drainage, internal a external, is good but considerable runoff of the rainfall occurs. In the narr troughs between the drumlins, imperfectly drained areas too small to delineated at the inch to the mile scale of mapping, are included.

The hardwoods, sugar maple and beech are the common trees. Whi pine, elm and ash occur less prominently.

Otonabee loam (*steep phase*) is mapped throughout the county. Due the excessive runoff on these slopes, the profiles are even shallower than t normal. The type includes any very steep till soil that should be left in p manent pasture or bush. Generally, the slopes are above 30 per cent.

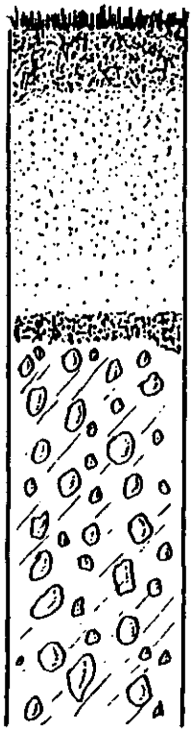
Agriculture

The agriculture differs very little from the general type of farming on t Bondhead types. Cereal grains, hay, clover, ensilage corn and pasture rep sent the important land uses. Livestock raising and some dairy farming pr vide a large portion of the sources of farm income. The high lime soil is w adapted to growing alfalfa and clovers. Suitable fertilizers generally contain high percentage of phosphorus and potassium. There are some general s conserving practices that could be applied to the Otonabee loam; pasturi or using the steep slopes as hay fields, cultivating and plowing "around t hill" rather than up and down the slope and using a longer rotation with mo grass or legumes.

Dundonald Sandy Loam (30,100 acres)

Dundonald sandy loam is the only member of the series mapped in Du ham County. The greater areas of the type are found adjacent to the Pont pool series. In Darlington and Clarke Townships the Dundonald is locat on the southern slopes while smaller areas are found on the northern slope For the most part the profile is developed on stonefree outwash sandy materia carried from the interlobate moraine that traverses the central part of t county. This sandy overburden was deposited on the high lime till pare material similar to that of the Otonabee and Bondhead series. Thus, t Dundonald series may be said to consist of the sandy materials of the Ponty pool series washed over the stony parent material of the high lime till soils.

The following is a profile description of a non-eroded cultivated soil.



A_c—4-6 inches grey-brown sandy loam; approaching a single grain structure; generally low organic matter content; stonefree; pH 6.8.

A_2—10-15 inches of light brownish sand; single grain structure; open and porous; pH 6.4.

B —2-3 inches brownish loam; soft friable structure; pH 6.8.

C —Grey calcareous till with frequent stones and boulders in some areas; very compact till; pH 7.8.

The Dundonald profile is generally developed in the sandy materials that are underlain by limestone till. The B horizon occurs at the juncture of the sandy outwash deposit and the till.

Drumlin formation is less distinct but 10-25% slopes are common. The topography is strongly rolling. The drainage is good with the lighter materials occasionally permitting an excessive rate of percolation.

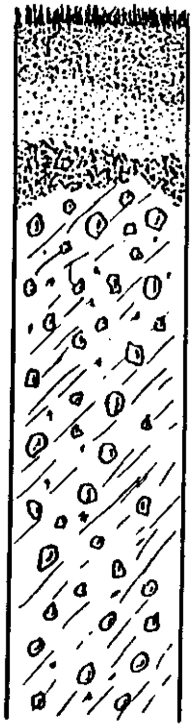
Coniferous and hardwood trees are about equally distributed over the type. A shallow eroded profile and proximity to the till are often associated with the presence of hardwoods.

Agriculture is general in nature with some orchards and canning crops in the southern townships. Special practices are used in some localities to increase the organic matter content of the surface soil by ploughing down green manuring crops. Erosion is common where the soils are cultivated up and down the slopes and when the surface is left unprotected for long periods of time.

Darlington Loam (15,400 acres)
" Sandy Loam (2,700 acres)

Most of the Darlington series is found in the south-western part of Darlington Township. In Cartwright and Cavan Townships small areas of similar soils are mapped in association with the Bondhead series. The parent material, although high in lime, contains a fair proportion of grey-black Utica shale thus differentiating it from that of the Bondhead and Otonabee soils. The profile is slightly less well-developed than the zonal type of the region.

The following profile description is fairly typical of the development of the loam type in Darlington Township:



A_c—4-6 inches moderately dark grey-brown loam; crumb structure; relatively stonefree with occasional boulders; pH 7.6.

A_2—4-8 inches of light brown loam; mottling may occur immediately above the B horizon; pH 7.3.

B —1-4 inches light brownish loam or clay loam; small blocky structure; fairly compact. The B layer reflects the series immaturity by the insistent and spotty development; pH 7.8.

C —A greyish calcareous till; dominantly limestone in origin but containing some grey-black Utica shale; moderately compact and impervious; pH 8.0.

The topography is moderately undulating with slopes ranging from 3 to 8%. Generally, the drainage is good but locations with a gentle relief are handicapped by inadequate facilities for removing excess surface water.

Elm, sugar maple and beech are the common trees found on the loam type, while white pine is noticeable on the lighter textured soils.

Darlington loam is the more important type of the series. The undulating topography and associated areas of smoother deposits are typical of a reworked ground moraine. Some of the larger lacustrine deposits have been mapped as Newcastle but numerous smaller areas have been included in this type.

Darlington sandy loam occurs mainly near Courtice and north of Bowmanville. The lighter surface soil and deeper profile permit better drainage conditions than exist in the loam type.

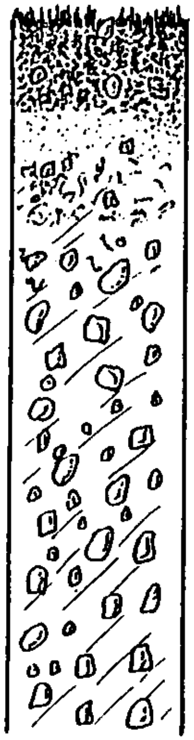
Agriculture

The loam type represents an excellent soil for general agriculture and is well located for transportation and marketing of farm products. Soil erosion is less severe than on some other soil types; the generally accepted practices of good management reduce erosion to a minimum. The compact parent material handicaps optimum root development of apple trees. Some areas within the sandy loam type are devoted to special farming, particularly truck crops.

Guerin Loam (1,600 acres)
" Sandy Loam (1,100 acres)
" Sandy Loam—Bouldery Phase (3,600 acres)

Members of the Guerin series are principally located in the three southern townships with isolated areas throughout the county. Formed on high lime materials, the series represents the imperfectly drained associate of the limestone till soils.

The profile horizons are less distinct than in the well drained soils, due in large part to the imperfect drainage.



A_c—5-7 inches of dark loam or sandy loam; somewhat above average in organic matter; relatively stony; pH 7.4.

A_2—5-10 inches greyish brown mottled loam; pH 7.4.

B —Relatively indistinct and not always present; pH 7.8.

C —Greyish calcareous stony till; moderately compact; pH 8.0.

The Guerin series frequently occupies small depressions in the limestone till plains. The topography is nearly level to undulating.

The smooth relief, depressional location, compact parent material and the difficulty of obtaining adequate outlets are the chief causes of the imperfect drainage conditions.

White cedars, hemlock, tamarack and some white birch are the principal trees found growing in this soil series.

Guerin loam as mapped near Hampton is the imperfectly drained associat of the Bondhead loam. These areas are under regular cultivation and represen some of the better soil conditions found in the series.

Guerin sandy loam is principally located near Frazerville and Cavan. Som areas are under farm crops but much is in permanent pasture.

Guerin sandy loam (bouldery phase). This type is frequently found adjacen to poorly drained outwash or deltaic soils in the Lake Iroquois plain. Mos of the finer soil materials were washed away by wave action at the time o Lake Iroquois leaving the surface heavily coated with stones and boulders.

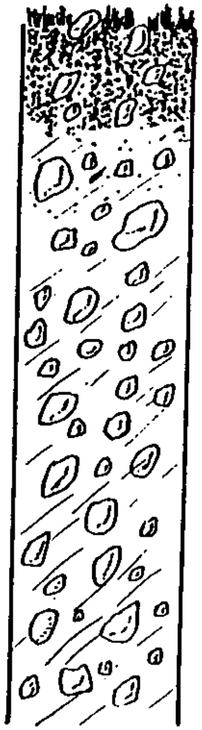
Agriculture

Under present farming conditions, the Guerin series is used mainly a a semi-permanent pasture to provide grass during the dry summer months Where local drainage conditions are better, particularly near Hampton, th Guerin loam with favourable weather at seeding time, does support som spring grains. Buckwheat is well adapted to the type.

Lyons Loam (5,400 acres)

Lyons loam is the poorly drained associate of the limestone till soils. Th type represents poorer drainage conditions than the imperfectly draine Guerin.

The profile horizons are poorly defined except the A_1;



A_c—6-8 inches dark stony loam; high in organi matter and alkaline; pH 7.8.

A_2—6-12 inches mottled grey stony loam that grades into the parent material; pH 7.8.

C —Greyish calcareous stony till; pH 8.0.

Most of the Lyons occurs in depressions where the relief is very poor. On some hillsides larger seepage areas are mapped as Lyons.

The natural drainage is poor because of the depressed location or being a seepage spot.

White cedar is the principal tree growth.

Agriculture

The stony and bouldery surface and poor drainage restrict the use of Lyons loam as a type for general farming. The cost of installing an artificial drainage system and the removal of stones, boulders and tree growth are almost prohibitive when the soil is to be used for general farm crops. The present land use is largely pasturage which is generally the best use.

B. SOILS FORMED FROM FLUVIO-GLACIAL MATERIALS

(Eskers, Kames and Interlobate Moraines)

The fluvio-glacial materials occupy a position roughly corresponding to the location of a great ice crevice that formed following a split in the main ice lobe, during the time of the melting-back of the glacier. Through this crevice a great volume of meltwater found an outlet and deposited the materials from which the present soils were formed. The materials are predominantly poorly sorted sand, gravel and boulders; isolated till deposits occur but are of a minor concern. The nature, mode of deposition and coarseness of these materials together with the hilly relief provide difficult circumstances for general farming conditions.

Pontypool Sandy Loam (8,900 acres)
" Sand (38,000 acres)
" Gravelly Sand (16,200 acres)

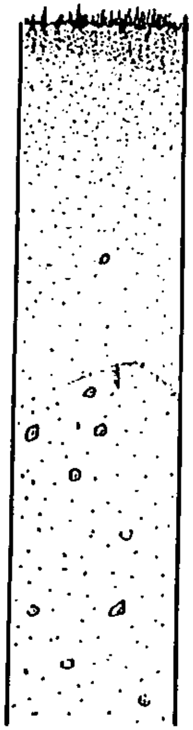
The series occupy a large tract of land extending east and west across the middle of the county. A narrower tract is mapped from Bethany to the northern boundary. As a series they are fairly well centralized and do not occur in small isolated areas as do other soil types.

The well-drained till soils support a tree growth of hardwoods. Maple and beech usual dominate.

This profile of the Bondhead
ne sandy loam is typical of
he regional well-drained soils.
The pick marks indicate the
ompact nature of the parent
material.

Many of the hilly areas of the Pontypool series have suffered extensively from the ravages of wind erosion. When severely wind-eroded areas occur in mappable size, they are called Bridgman sand.

The profile is almost featureless but examinations of non-eroded sites indicate extensive weathering.



A_c—2-3 inches light grey brown sand or sandy loam; coarse single grain structure; low in organic matter; slightly acid to slightly alkaline; frequently stony; pH 6.8.

A_2—10-30 inches yellowish sand; in the sandy loam profile an incipient B horizon generally exists but it is usually absent in the sand. When present it displays more of the characteristics of a colour B layer than a textural horizon; pH 6.4.

C—Grey coarse calcareous sand; poorly sorted; numerous cobbles and gravelly stones; pH 7.4.

The topography is hilly with frequent steep slopes and small depressional areas, a "knob and basin" relief. Generally, the sandy loam type is strongly rolling with slopes that are longer and less abrupt. The topography varies from small areas of undulating deposits to areas that are very hilly with a common slope range from 8 to 35 per cent. In view of the coarse nature of surface and parent materials, low organic matter content of the topsoil and the hilly terrain, the drainage is rapid and excessive.

The vegetative growth normally varies with the soil type in the Pontypool series. The sand is most favourable to growing white pine with smaller proportions of red, jack and Scotch pine and hardwoods. The natural grasses on abandoned farms are usually Redtop and Canada Blue. The gravelly type is broadly associated with sugar maple, red oak, beech, hickory and white pine; Canada Blue grass is common on this type.

Pontypool sandy loam. A rather small percentage of the series is mapped as a sandy loam. Such areas are usually local conditions where a type of general farming is fairly successful.

Pontypool sand. More than one-half of the series is mapped as a sand with the variations to be expected for such rough topography. The type represents a poor soil for agricultural purposes. Erosion is severe; the natural fertility is low.

Pontypool gravelly sand. The gravelly sand differs from the other types by having large deposits of gravel in the parent material. In many areas the *gravel appears in the surface soil. Near Pontypool, farming is more successful* on the gravelly sand than on the sand.

Agriculture

Undoubtedly, a large portion of the series is not adapted to general farming and some areas now under cultivation should be retired from agriculture. There are other land uses for which the series is suitable; large permanent and improved pastures, reforestation, game preserves and recreational areas. Pontypool sandy loam offers the best in the series for farming but even then, conservation farming and heavy applications of manure and fertilizers and plowed in green crops are necessary to maintain adequate fertility levels. The coarse nature of the sandy materials, low organic matter content and generally lower natural fertility along with a strong topography and erosion are the *principal factors limiting the agricultural possibilities of the Pontypool series.*

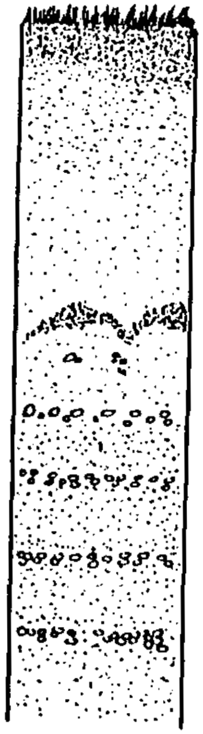
C. SOILS FORMED FROM DELTAIC OR OUTWASH MATERIALS

The parent material of this group of soils was carried by streams of water from melting ice and dropped as the streams slowed up or emptied into large bodies of still water or spread out over level land. The topography is normally smooth and undulating but is frequently cut up by recent gullying. In Durham County the outwash materials are well sorted coarse sands and gravels mainly of limestone origin.

Brighton Sandy Loam (9,500 acres)
" Sand (11,100 acres)
" Gravelly Sand (6,600 acres)
" Sandy Loam—Bouldery Phase (600 acres)

The series occurs largely within the area once covered by Lake Iroquois; *other deposits are mapped in isolated areas over the county.*

The profile development bears out the relative youthfulness of soils within the Iroquois basin.



A_c—3-4 inches of sand or sandy loam; low in organic matter; stonefree; pH 6.6.

A —15-20 inches of a coarse yellowish sand; single grain structure; pH 6.4.

B —2-4 inches of brownish loam; structure poorly developed; in the sand type the colour layer is much better developed than the *textural horizon*; pH 6.6.

C —A grey calcareous stratified sand and gravel; pH 7.6.

While the *Brighton series* were undoubtedly deposited in nearly level relief, stream gullying and erosion have effected noticeable changes in the topography. Except for isolated areas and near stream courses most of the slopes range from 3 to 8 per cent. The *drainage conditions* are good; the coarse materials promote rapid and in some cases excessive removal of soil water.

The dominant vegetation is white *pine, especially in* the Osaca district, while near Orono the alkaline gravel supports pines, hardwoods and some cedar.

Brighton sandy loam. The sandy loam type is more suitable for general farming than the remainder of the *series*. *The slightly heavier* texture and better fertility are the principal differences.

Brighton sand. The sand is located mostly in the Ganaraska Valley. The coarse sand is low in fertility, excessively drained, *subject* to severe erosion and poorly adapted to general agriculture. A small acreage is producing tobacco.

Brighton gravelly sand. The type exhibits a very shallow profile over the calcareous stratified gravel. Most of the type indicates the location and extent of the beaches of Lake Iroquois. The deposits are usually low rounded ridges of gravel or appear as broad fans as found near Orono.

Brighton sandy loam (*bouldery phase*), is mapped to indicate extremely stony, light-textured soils that are well drained. The total acreage of the bouldery phase is small and occurs for the most part northwest of Newcastle.

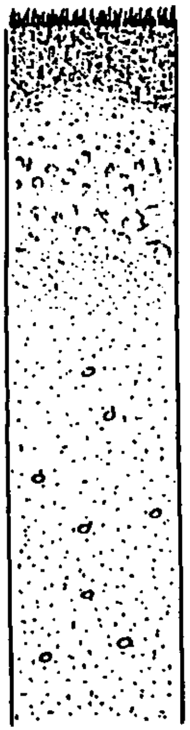
Agriculture

Excepting the sandy loam, very little of the series is adapted to general agriculture. Heavy applications of manure and fertilizers are necessary to produce farm crops satisfactorily. The organic matter content of the surface soil must be increased to prevent excessive drainage and leaching of plant nutrients. Tobacco appears to thrive on the sand, providing the profile is of a fair depth and not eroded. Isolated orchards are in good condition but the success is largely one of excellent management. The gravelly sand supports fair stands of grass, particularly Canada Blue, in seasons with favourable distribution of rainfall.

Tecumseth Sandy Loam (4,000 acres)

Tecumseth sandy loam is the imperfectly drained outwash soil frequently occurring in association with the well drained Brighton series. The greater part of the type is mapped east of Cavan and in Hope Township while other isolated areas were separated out.

The profile development is fairly typical for soil materials with a moderately high water-table.



A_c—5-7 inches of dark sandy loam; fairly high in organic matter; weak crumb structure; pH 7.4.

A —5-10 inches of mottled yellowish sand; intensity of mottlings increase with increase of depth; pH 7.0.
(B rarely identifiable except under local conditions of improved drainage.)

C —Greyish calcareous sand which may be underlain at varying depths by gravel; pH 7.6.

The Tecumseth sandy loam is located in areas with very smooth or level

The natural drainage is imperfect. Where the type occurs in relatively broad tracts and suitable outlets can be established, artificial draining may be profitable. Small areas are frequently surrounded by morainic soils through which it is difficult to secure outlets. Occasionally the sandy materials are underlain by heavy clay and silt materials which increases the problem of artificial drainage.

Tamarack and white cedar trees are commonly found on the Tecumseth sandy loam. A variety of grasses adapted to soils with a high water-table are common on pastured areas.

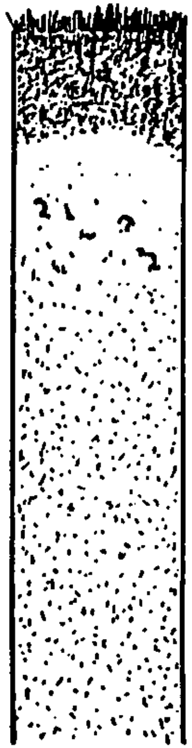
Agriculture

A fair acreage with better than average drainage conditions is under regular cultivation and supports some spring grains, particularly buckwheat. The general adaptability of the type depends a great deal on the type of weather at seeding. Permanent unimproved pastures are fairly general.

Granby Sandy Loam (6,700 acres)
" Sandy Loam—Bouldery Phase (1,300 acres)

The poorly drained associate of the sandy outwash soils is mapped as Granby sandy loam. The larger and more important locations of the series occur north of Courtice and south of Starkville and Osaca.

The following description is fairly representative of the type of development:



A_c—6-8 inches of very dark sandy loam; high in organic matter; soft and porous; pH 7.6.

A_2—6-10 inches light grey coarse sand; pH 7.2.

G —8-12 inches greyish brown and yellowish brown sand with rusty mottling; pH 7.4.

C —Greyish calcareous sand underlain in some instances by gravel or heavy till; occasional strata of silt and clay; substratum of clay at 3 feet or lower in included areas; pH 7.6.

Granby sandy loam is found in areas with level and depressional topography. The natural drainage is poor but the cost involved in improving it by artificial means usually is not warranted.

The series supports a type of vegetation adapted to an abundant supply of water. White cedars, *tamarack and alders are the common trees and shrubs.*

Granby sandy loam is typically stonefree and is commonly used for permanent pasture.

Granby sandy loam (bouldery phase), is mapped on some areas near Newcastle and Courtice. *Very little of the area is cleared of stones but is left as* permanent pasture land.

Agriculture

A *relatively small percentage of the series is used for general farm crops* other than pasture grasses. The Granby soils are late in the spring but are sometimes used for short season crops such as buckwheat. Perhaps the more profitable land use is to seed the areas with suitable grasses to provide forage when upland pasturage is suffering from drought.

D. SOILS FORMED FROM LACUSTRINE MATERIALS

During the recession of the ice lobes, bodies of water were hemmed in by the ice masses or by deposits of glacial drift. These glacial lakes were fed by streams of melt-water from the ice. The streams carried fine-textured soil-forming materials that slowly settled out in the still water, the finer materials remaining in suspension longer than the coarser particles. This sediment occurs as alternate layers of coarser and finer textured layers, which are commonly referred to as varves.

The main characteristics of the lacustrine soil-forming materials in Durham County are the intermediate or heavy texture and the freedom from stones. The topography varies from level to undulating. The depth of the lacustrine materials shows some variation being shallow in the Schomberg and relatively deep in the Newcastle series.

The well-drained series are Newcastle, Schomberg and Percy. The principal difference between the first two is the shallower profile frequently underlain by heavy morainic deposits of the Schomberg. The Newcastle series has probably developed on materials not so high in lime. The Percy is a well-drained loam soil on undulating to rolling topography and underlain at varying depths by Morainic materials. The Smithfield is the imperfectly drained associate of the well-drained soils.

Newcastle Loam (17,300 acres)
" Clay Loam (6,000 acres)

The Newcastle series is mapped within the area covered by glacial Lake Iroquois. This plain extended over a portion of the three southern townships. The beaches of the lake are marked by Brighton gravelly sand and are about 450 feet above sea-level and 200 feet above Lake Ontario.

The following is a profile description of a cultivated soil:

A_c—4-7 inches of a moderately dark grey brown loam or clay loam; crumb structure; friable under optimum conditions; stonefree; pH 7.2.

A_2—8-15 inches of greyish brown loam; nut structure; pH 6.6.

A_3—1-2 inches drab grey loam; slightly compacted; pH 6.8.

B —4-10 inches of brownish sticky clay; when dry breaks into nutlike structure; pH 7.0.

C —Greyish calcareous stonefree lacustrine silts and clays; very compact and frequently varved; pH 8.0.

The areas of Newcastle loam and clay loam are considered to be undulating in topography marked by gentle slopes of about 5%. In some instances steeper slopes are found that are the result of recent stream erosion; bluffs are common along the lake shore providing excellent locations for examining the varves.

There are some areas where the drainage is only fair; water accumulates between the swells of land after heavy rains and in the spring. Generally the drainage is fair to good.

The woodlots are scarce but those remaining are composed of sugar maple and beech; elm is frequently found in the areas with only fair drainage.

Newcastle loam is generally considered the better orchard soil because of the adequate drainage, fewer low areas and more friable consistency allowing deeper root penetration. The natural fertility is above average excepting the supply of available phosphorus. The loam type is well suited for the growing of canning and general farm crops.

Newcastle clay loam. The heavier type in the series is a productive soil for general farm crops. This soil generally has the highest natural fertility of any type in the county but like all the others, requires phosphatic supplements. The areas of fair drainage are more common in the clay loam type.

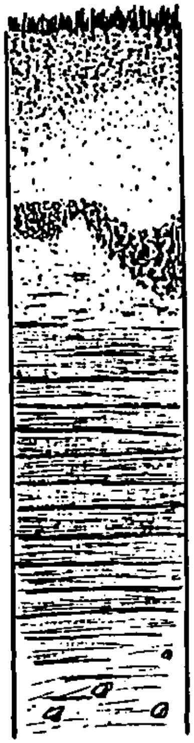
Agriculture

The orchards are pretty well confined to the Newcastle loam since it is generally better drained in the upper soil layers. The loam type is underlain by silts and clays very similar to the parent material of the clay loam type. The Newcastle series is well adapted to general farming and dairying, and produces excellent crops of cereal grains, legumes, ensilage corn and other intertilled crops. The lower swells or small depressions could be improved by artificial drainage. The clay loam type is more susceptible to erosion on the slopes, which requires some consideration as to applicable control measures to prevent the removal of the topsoil by washing.

Schomberg Clay Loam (5,300 acres)
" Silt Loam (2,900 acres)

The Schomberg soils are located almost entirely north of the height of land and out of the Iroquois plain. Several small areas east of Canton are included.

The profile is relatively shallow, frequently eroded and exhibits slightly better developed characteristics than the Newcastle series.



A_c—4-6 inches moderately dark grey-brown silt loam or clay loam (a greyish surface indicates severe sheet erosion); crumb structure; nearly stonefree; free carbonates; pH 7.8.

A_2—6-10 inches greyish silt loam; sharp demarcation; platy structure; pH 7.2.

B — 3-6 inches brownish sticky clay; blocky nutlike structure; pH 7.6.

C —Dull grey or greyish silts and clays; lacustrine origin; highly calcareous; usually varved; till occurs where the lacustrine veneer is shallow; pH 8.0.

The dominant slopes measure about 8%, while near Bethany in the silt loam some 2-3% slopes occur.

The internal drainage is good; the rapid runoff of excessive surface water

sheet erosion.

Hardwoods, including maple, beech, ash and some elm are common trees associated with the series.

Schomberg clay loam is developed in this area on a lacustrine veneer underlain by till. The profile is formed in the water-laid sediments with the stony materials occurring at variable depths. Where the sheet erosion has been severe some stones may appear on the surface soil.

Schomberg silt loam. This type is mapped in the vicinity of Bethany. The topography is somewhat smoother than in the clay loam type. The lacustrine deposit is generally deeper with the till occurring less frequently.

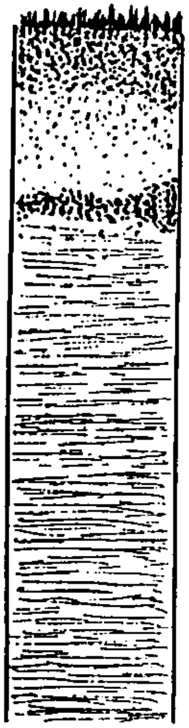
Agriculture

The undulating slopes of a lacustrine soil are very susceptible to sheet erosion unless control measures are employed. Such soils respond to long rotations with a minimum of cultivated crops. The Schomberg series is a high lime soil well suited to clovers and alfalfa. Commercial fertilizers should contain relatively high percentages of phosphorus and potassium. The use of improved pastures on slopes now showing the effects of erosion is strongly recommended. Areas likely to erode badly should be dealt with according to soil conservation plans.

Percy Loam (4,000 acres)

The only member of the series is the Percy loam that was mapped near Norrish and Campbellcroft. The Percy series is the light textured associate of the heavier lacustrine soils, Newcastle or Schomberg. Fine sands and loams over heavier materials is the general condition as mapped in Durham County.

A normal non-eroded profile shows a moderately good development.



A_c—4-6 inches grey-brown loam or fine sandy loam; crumb structure; generally stonefree; pH 7.2.

A_2—6-8 inches greyish fine sandy loam; weak platy structure; pH 6.6.

B —1-4 inches brownish loam; weak nut structure; pH 6.8.

C —Greyish calcareous fine sands, silts and clays; may be underlain at varying depths by till; pH 7.4.

The topography is generally strongly undulating with relatively short slopes lacking uniformity in any general direction but making the type fairly susceptible to sheet erosion.

The natural drainage conditions are good.

Sugar maple, beech and the occasional elm are the main trees associated with the type.

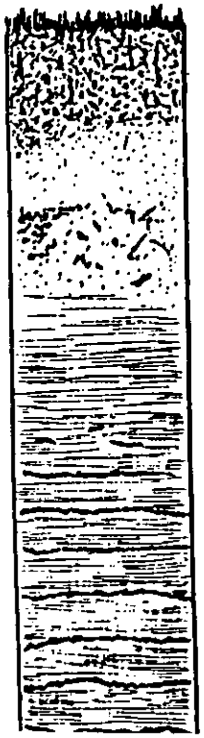
Agriculture

The Percy series was first mapped in Northumberland County where it was considered an excellent soil for general farming. The Percy loam near Norrish in Durham County has been subjected to considerable sheet erosion which has removed much of the topsoil. The other areas included as Percy are more adapted to general farming. Where climatic conditions are favourable the type is well suited to the growing of fruit and canning crops.

Smithfield Clay Loam (18,000 acres)

The Smithfield clay loam represents the imperfectly drained associate of the heavier lacustrine soils. The areas mapped as Smithfield occupy small depressions lacking adequate drainage facilities. Formed from high lime parent material, free carbonates commonly occur in the surface soil.

The profile horizons are often difficult to identify but may be generalized as indicated in the following descriptions:



A_c—5-7 inches of dark greyish brown clay loam; stonefree and alkaline; crumb structure; pH 7.8.

A_2—6-10 inches greyish silty loam, marked by a rusty brown mottling; tending toward massive structure; pH 7.6.

B —Generally occurs as a stronger accumulation of mottling in the lower part of the A_2 and immediately above the parent material; structure coarse blocky to massive; pH 7.8.

C —Greyish, calcareous clay; moderately compact and impervious; varves may be found in the deeper deposits; pH 8.0.

The topography ranges from level to gently undulating.

The natural drainage is inadequate for growing most farm crops, especially fall wheat and clovers.

Elm is the chief tree growth associated with the series.

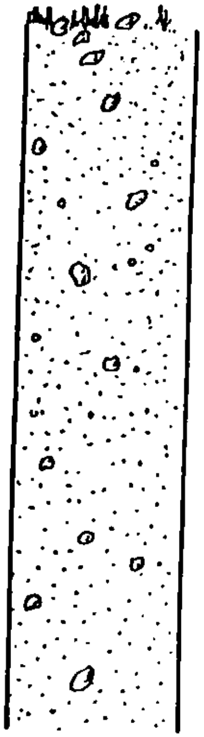
Agriculture

Where the drainage has been artificially improved, the type is fairly well adapted to general farming. The higher organic matter content in the surface soil holds considerable moisture as well as improving the workability of the heavy surface layer. Artificial drainage by tile or open ditches should be a worthwhile practice to improve the productivity and usefulness of the type.

E. SOILS DEVELOPED FROM ERODED SANDS

Bridgman Sand (4,000 acres)

Bridgman sand may be found in areas of the Pontypool or Brighton series where the dark surface soil has been entirely removed by wind and water erosion. It is not unusual to find the sand drifting. Bridgman sand includes the eroded areas and the places where the eroded materials are accumulating.



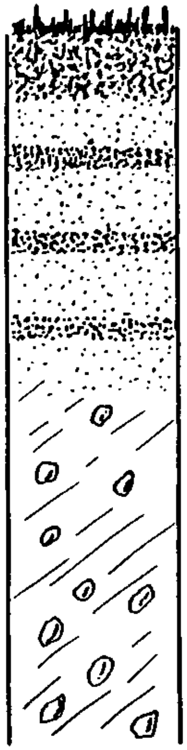
Loose, incoherent, coarse sand with gravel stones and some boulders, very droughty, and contains little or no organic matter.

Bridgman sand is a non-agricultural soil. In its present condition the sand is drifting and accumulates on cropland, pastureland or woodland and even barricades some road allowances. The area mapped as Bridgman sand and many other small "blow-outs" too small to indicate on the map should be reforested and fenced from livestock.

F. SOILS DEVELOPED ON FLOOD LANDS ALONG STREAM COURSES

Bottom Land (19,100 acres)

Bottom land should be considered as a complex soil condition adjoining stream courses. These areas are subject to flooding and surface-depositions of materials carried by the streams. Under these conditions a variety of soil materials is to be expected.



Frequently some form of layering appears that marks the yearly depositions. In other places the surface is well covered with gravel, stones and boulders. The underlying material at greater depths is usually a compact heavy till.

Areas of Bottom land often provide good areas for permanent pasture with water close at hand. The pastures are seldom of the improved type and are often looked upon as waste land. There is little agricultural development of the type beyond the use of the areas for grazing.

G. SOILS DEVELOPED ON ORGANIC MATERIALS

Muck (22,100 acres)

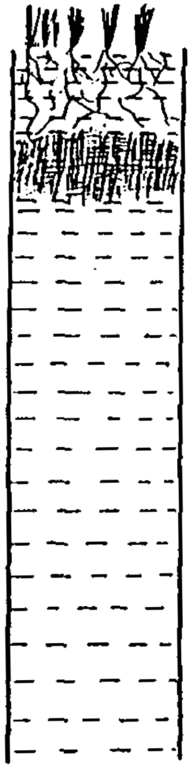
Muck soils generally occur in depressions or along the slow streams flowing in a northerly direction.

A blackish layer ranging in depth from one foot to several feet composed of organic material fairly well decomposed. Frequently underlain by clay, till or greyish marl. The water table is high.

At the present time muck soils are not used in Durham County for general crops. Some areas provide a little pasture but nearly all is left in a wooded condition. Tamarack and white cedar are the common trees along with numerous grasses and sedges adapted to soils with a high water table.

Marsh (2,200 acres)

Approximately two thousand acres of marsh were mapped largely in the southwestern end of Lake Scugog.



The areas of Marsh are continually under water. Cattails and other water plants grow under these conditions with some of their roots anchored in a floating mass of raw organic material that accumulates with the dying down of the vegetation.

The agricultural possibilities of this water-logged soil amount to very little. The chief agricultural function would be the supplying of water to livestock and the storing of water to supply the underground systems for wells or springs. Marsh could be developed into a reserve for water fowl and animals.

PART IV

AGRICULTURE AND LAND USE

EARLY SETTLEMENT AND AGRICULTURAL DEVELOPMENT

The *settlement* and agricultural development of Durham County pi ceeded from the lake-shore townships towards the interior. Settlers arriv by *boat, the only means of travel* for many years in the young communiti Their exports were moved by lake boats and barges until roads and railwa *were established.*

Shortly before 1800 land grants were made to families in Clarke ai Darlington *townships to be followed* by grants under Lieutenant-Govern Simcoe's plan. The war of 1812-1814 retarded settlement but a period of co siderable *expansion followed.* In this new country the cropping and s management methods of Europe were not always practical. The soil exhibit considerable *variation and the judgment* of settlers had a great influence what was to be grown. The general idea was to judge land by the quali and yields of wheat produced. The inadequate *preparation of the soil* f seeding and the lack of good rotations precipitated widespread beliefs that t soils were exhausted. Coincident with the *raising of cattle a marked* improv ment in soil fertility was noticed.

The early type of agriculture *may be gathered* from the following list exports from Port Darlington for the years 1844 and 1850.

TABLE 5

PORT DARLINGTON EXPORTS

	1844	1850
Lumber	254,000 bd. ft.	700,000 bd. ft.
Flour	6,027 bbls.	29,113 bbls.
Oatmeal	203 bbls.	910 bbls.
Whiskey	102 bbls.	188 bbls.
Pork	16 bbls.	80 bbls.
Potatoes	102 bus.	5,830 bus.
Wheat	2,300 bus.	27,880 bus.

Other exports included butter, potash, ashes, barley, etc.

Before grist mills were built the wheat was ground by hand using han *mills, wooden mortars* or flat stones. Some farmers took the wheat to mi as far away as Kingston. The first mill in Bowmanville was in operatio around 1824. From 1830 to *roughly 1875* the milling business was enormou At one time during this period there were 13 mills within 8 miles of Bowma ville having an aggregate *capacity of 700* barrels per day from wheat grow locally. In 1851 at the World's Exhibition in London, England, two Darling ton citizens received medals *for their produce,* one for flour from Durha County wheat and the other for native oatmeal.

In Hope township, settlement *commenced at an* Indian trading pos "Cochingomink," which was later called Toronto and still later Port Hop Here, Elias Smith was offered a tract of land by *the government* providing h built grist and saw mills. These mills were in operation by 1798 to serv settlers as far north as Lindsay. The Midland railway which terminated a

TABLE 9

SOIL RATING FOR GENERAL FARM CROPS

The crop adaptability rating for each soil type is indicated as follows:
G — Good; G-F — Good to Fair; F — Fair; F-P — Fair to Poor; P — Poor.

	Mixed Grains, Oats and Barley	Fall Wheat	Fall Rye	Peas and Beans	Buckwheat	Corn	Hay and Clovers	Pasture	Potatoes	Orchards
Good Cropland										
Newcastle loam	G	G	G	G	G-F	G	G	G	G-F	G
Newcastle clay loam	G	G	G	G	F	G	G	G	F-P	G-F
Percy loam	G-F	G-F	G-F	G-F	G-F	G-F	G-F	G-F	G-F	G
Schomberg silt loam	G	G	G	G	F	G-F	G-F	G-F	F	F
Schomberg clay loam	G	G	G	G	F	G	G	G	F-P	F
Darlington loam	G	G	G	G	F	G-F	G	G	F	G-F
Bondhead loam	G	G	G	G	F	G-F	G	G	F	F
Otonabee loam	G	G	G	G	F	G-F	G	G	F	F
Darlington sandy loam	G-F	G-F	G	G-F	G-F	F	G-F	G-F	G-F	G
Bondhead sandy loam	G-F	G-F	G-F	G-F	G-F	F	G-F	G-F	G-F	G-F
Good to Fair Cropland										
Smithfield clay loam	G-F	F	F-P	F	G-F	G-F	G-F	G-F	F-P	F
Brighton sandy loam	F	F	G-F	F-P	F	F	F	F	G-F	F
Tecumseth sandy loam	G-F	F	F	F	G-F	F	F	F	F	F-P
Dundonald sandy loam	G-F	G-F	G-F	F	F	F	G-F	F	G-F	F
Fair Cropland										
Guerin loam	F	F-P	F-P	F	F-P	F	G-F	G-F	P	F-P
Guerin sandy loam	F	F-P	F-P	F-P	G-F	F	F	F	P	F-P
Pontypool sandy loam	F	F-P	F	F-P	F-P	F-P	F	F	F	F
Granby sandy loam	F-P	P	P	F-P	F	F	F	F	P	P
Brighton sand	F-P	F-P	F	F-P	F-P	P	P	P	F-P	F
Brighton gravelly sand	F-P	F-P	F	F-P	F-P	P	P	P	P	P
Fair to Poor Cropland										
Otonabee loam, steep phase	F-P	P	P	P	P	P	F	F	P	P
Pontypool gravelly sand	F-P	P	F	P	P	P	P	P	P	P
Pontypool sand	F-P	P	F-P	P	P	P	P	P	P	P
Bottom Land	....	....	....	....	....	....	F	F-G	....	....
Bondhead loam, bouldery phase	....	....	....	....	....	....	....	F	....	....
Guerin loam, bouldery phase	....	....	....	....	....	....	....	F	....	....
Lyons loam	....	....	....	....	....	....	....	F	....	....
Granby sandy loam, bouldery phase	....	....	....	....	....	....	....	F	....	....
Brighton sand, bouldery phase	....	....	....	....	....	....	....	P	....	....
Muck	....	....	....	....	....	....	....	P	....	....
Bridgman sand	....	....	....	....	....	....	....	....	....	....

PART V

ANALYTICAL DATA

The chemical and physical analyses of 75 samples of surface soil in Durham County during the survey are shown in Table 10. The cl analyses indicate the levels of some of the plant nutrients in the so physical analyses record the relative amounts of sand, silt and clay in t that were analysed.

Sampling

The samples were taken after the area had been mapped. The and distribution of samples taken from the county generally depen the extent and importance of the soil types. In an attempt to avoid th of different cultural and management practices, the samples were tak pasture fields that appeared to have been pastured for several years recent applications of manure or fertilizer.

Reaction

The soils of Durham County are mostly in the neutral to mildly range. Only 3 samples out of 75 were below a pH of 6.0 and 10 sampl above a pH of 8.0.

Only local areas on the well-drained non-eroded sands are suf acid to indicate a need for liming. Samples from individual fields sh tested before applying lime extensively.

Phosphorus

The supply of phosphorus in Durham County soils is much high in most of the counties farther west. However, with the alkaline react high calcium content on many of the soils, the phosphorus is not as a to the plants as it would be if the soil were slightly acid.

In describing the method used in the determination of readily phosphorus Lohse and Ruhnke state that soils containing less than 60 of phosphorus per acre appear to indicate very marked phosphate def No figure however is proposed that would indicate an adequate sup some later work on Carleton County soils would indicate that 200 lbs be accepted as a tentative figure for soils near neutral or acid. For tl alkaline soils some additional phosphorus in the form of phosphatic fe usually gives good crop response, even though the soil contains a fair am

In plants, phosphorus is largely concentrated in the seeds; in phosphorus and calcium are important elements in the bones. A lo phorus content in the soil is reflected in a delayed maturity of the pla plant growth and root development.

Potassium

The figures for the replaceable potassium (K) indicate the supply element that is available to growing plants. The total amount in s generally much greater but becomes available slowly through vari reactions. The necessary amount of replaceable potassium for most farm crops is approximately 167 pounds of potassium (K) per acr somewhat larger amounts for crops like potatoes or tobacco.

TABLE 10

CHEMICAL AND PHYSICAL ANALYSES OF SAMPLES OF SURFACE SOILS FROM DURHAM COUNTY

Analyzed by A. L. Willis

Soil Type	Sample No.	Location			Per Cent Sand	Per Cent Silt	Per Cent Clay	Reaction (pH) Glass Electrode	Phosphorus Readily Soluble lbs. P/acre	Potassium Replaceable lbs. K/acre	Calcium Replaceable lbs. Ca/acre	Magnesium Water Soluble lbs. Mg/acre	Organic Matter % Carbon x 1.724
		Township	Con.	Lot	1.0—.05mm	.05—.002mm	Less than .002mm						
Bondhead loam	2	Darlington	9	34S	45.8	42.4	11.8	7.95	160	94	8,952	40	2.98
	3	Darlington	8	30C	38.2	51.6	10.2	7.58	170	90	8,640	40	5.43
	35	Cavan	5	5S	30.2	52.8	17.0	7.95	392	97	10,560	40	2.72
	36	Darlington	5	12C	64.6	31.0	4.4	6.27	88	127	2,568	40	2.60
	38	Darlington	6	22C	42.6	44.6	12.8	7.18	248	96	7,200	50	3.66
	39	Darlington	7	31S	42.6	47.2	10.2	7.70	176	71	6,696	45	3.45
	40	Darlington	5	30C	51.6	38.8	9.6	7.80	172	86	9,648	50	2.10
	57	Clarke	5	25N	50.4	41.0	8.6	7.60	196	120	6,120	56	3.48
Bondhead sandy loam	1	Cartwright	4	6C	42.8	49.8	7.4	7.22	132	95	4,872	48	3.24
	4	Cartwright	1	9N	75.2	38.4	4.4	6.52	122	88	2,712	45	2.60
	5	Cartwright	5	15S	50.4	38.2	11.4	7.09	196	130	10,536	40	4.38
	7	Manvers	11	6NW	56.8	29.0	14.2	8.09	232	121	13,440	40	2.84
	8	Manvers	9	4S	52.8	33.4	13.8	8.15	184	94	14,136	45	2.89
	9	Manvers	6	10C	46.0	45.8	8.2	8.10	108	80	12,600	45	4.09
	11	Cartwright	8	12W	81.6	15.6	2.8	6.88	62	130	2,784	45	2.36
	13	Hope	7	2	53.2	39.2	7.6	7.03	316	121	3,072	50	1.86
	23	Cavan	3	16S	77.2	17.0	5.8	6.33	128	47	2,064	40	1.48
	28	Cavan	12	2S	65.2	28.8	6.0	7.81	324	67	10,416	40	2.50
	29	Manvers	12	17S	42.0	47.2	10.8	7.92	220	73	9,600	40	4.07
	55	Clarke	2	12N	56.2	34.4	9.4	7.73	352	77	6,336	40	2.36
	59	Hope	4	34S	49.6	40.8	9.6	6.60	122	56	3,096	40	2.66
Brighton sand	49	Darlington	4	1S	80.1	14.4	5.5	7.49	172	86	3,072	50	1.91
	67	Hope	4	21N	90.3	6.8	2.9	5.83	70	35	1,056	40	1.57
Brighton sandy loam	52	Clarke	3	21C	91.6	5.1	3.3	5.90	54	42	696	40	1.10
	64	Hope	2	10C	74.8	18.4	6.8	7.11	158	62	2,448	40	1.76
	69	Hope	7	22N	70.2	25.0	4.8	6.53	20	56	4,752	40	8.07
	70	Clarke	7	6S	63.0	33.6	3.4	6.45	36	59	3,624	50	3.98
Darlington loam	0	Cartwright	7	14S	59.8	31.2	9.0	8.10	128	98	11,040	45	3.56
	10	Manvers	8	15N	42.8	50.2	7.0	7.32	176	209	11,928	50	6.58
	37	Darlington	6	15S	64.2	29.6	6.2	7.10	44	68	5,184	40	4.35
	41	Darlington	B.F.	24N	54.0	30.6	15.4	7.88	172	98	12,336	50	3.72
	45	Darlington	1	19C	49.6	35.8	14.6	7.73	108	55	10,986	50	7.05
Darlington sandy loam	43	Darlington	2	24C	56.6	32.4	11.0	8.09	188	79	13,128	50	5.21
Dundonald sandy loam	16	Hope	7	18S	77.4	20.2	2.4	6.43	122	124	1,536	45	1.48
	17	Hope	9	10N	39.6	49.0	11.4	7.45	296	133	5,280	40	2.72
	30	Manvers	4	21C	51.6	43.2	5.2	6.57	112	71	4,056	45	3.83
	60	Hope	4	30C	71.2	23.6	5.2	5.91	38	58	2,232	40	3.40
	71	Darlington	8	17C	40.8	48.2	11.0	7.78	116	71	7,584	25	4.40
	73	Clarke	7	35N	46.6	47.6	5.8	7.38	264	126	6,720	56	4.42
	74	Clarke	7	20N	43.4	41.0	15.6	7.93	308	332	9,888	40	3.30
Granby sandy loam	15	Hope	6	11N	35.4	56.2	8.4	8.00	236	98	18,288	45	9.22
	44	Darlington	4	23S	68.4	26.0	5.6	7.92	188	117	8,784	50	2.64
	56	Clarke	4	9C	46.2	40.8	13.0	7.05	400+	94	16,080	56+	5.86
Guerin sandy loam (bouldery phase)	54	Clarke	1	18C	56.2	31.2	12.6	7.74	80	150	7,032	45	4.45
	61	Hope	2	26C	66.0	25.6	7.8	6.48	104	49	2,280	40	1.86
Newcastle loam	47	Darlington	B.F.	4C	58.0	31.4	10.6	7.13	190	68	3,456	40	1.67
	51	Clarke	1	30C	39.8	39.8	20.4	6.08	292	159	4,104	56	3.52
	62	Hope	2	20C	40.4	45.2	14.4	6.33	196	161	4,584	50	4.71
	63	Hope	2	2C	48.2	39.0	12.8	7.19	192	105	5,304	50	3.40
	65	Hope	3	15C	41.8	44.2	14.0	6.68	96	94	6,816	50	3.65
Newcastle clay loam	46	Darlington	B.F.	13C	33.6	45.8	20.6	7.40	248	133	7,632	56	4.17
	48	Darlington	2	2C	38.2	42.6	21.2	6.44	184	132	4,512	56+	3.45
	50	Clarke	4	33C	39.2	46.0	14.8	7.25	252	71	6,960	45	4.38

TABLE 10

CHEMICAL AND PHYSICAL ANALYSES OF SAMPLES OF SURFACE SOILS FROM DURHAM COU

Analyzed by A. L. Willis

Soil Type	Sample No.	Location			Per Cent Sand	Per Cent Silt	Per Cent Clay	Reaction (pH) Glass Electrode	Phosphorus Readily Soluble lbs. P/acre	Potassium Replaceable lbs. K/acre	Calcium Replaceable lbs. Ca/acre
		Township	Con.	Lot	1.0—.05mm	.05—.002mm	Less than .002mm				
Bondhead loam	2	Darlington	9	34S	45.8	42.4	11.8	7.95	160	94	8.952
	3	Darlington	8	30C	38.2	51.6	10.2	7.58	170	90	8.640
	35	Cavan	5	5S	30.2	52.8	17.0	7.95	392	97	10.560
	36	Darlington	5	12C	64.6	31.0	4.4	6.27	88	127	2,568
	38	Darlington	6	22C	42.6	44.6	12.8	7.18	248	96	7.200
	39	Darlington	7	31S	42.6	47.2	10.2	7.70	176	71	6.696
	40	Darlington	5	30C	51.6	38.8	9.6	7.80	172	86	9.648
	57	Clarke	5	25N	50.4	41.0	8.6	7.60	196	120	6.120
Bondhead sandy loam	1	Cartwright	4	6C	42.8	49.8	7.4	7.22	132	95	4.872
	4	Cartwright	1	9N	75.2	38.4	4.4	6.52	122	88	2.712
	5	Cartwright	5	15S	50.4	38.2	11.4	7.99	196	130	10.536
	7	Manvers	11	6NW	56.8	29.0	14.2	8.09	232	121	13,440
	8	Manvers	9	4S	52.8	33.4	13.8	8.13	184	94	14.136
	9	Manvers	6	10C	46.0	45.8	8.2	8.10	108	80	12.600
	11	Cartwright	8	12W	81.6	15.6	2.8	6.88	62	130	2,784
	13	Hope	7	2	53.2	39.2	7.6	7.03	316	121	3,072
	23	Cavan	3	16S	77.2	17.0	5.8	6.33	128	47	2,064
	28	Cavan	12	2S	65.2	28.8	6.0	7.81	324	67	10.416
	29	Manvers	12	17S	42.0	47.2	10.8	7.92	220	73	9.600
	55	Clarke	2	12N	56.2	34.4	9.4	7.73	352	77	6.336
	59	Hope	4	34S	49.6	40.8	9.6	6.60	122	56	3,096
Brighton sand	49	Darlington	4	1S	80.1	14.4	5.5	7.49	172	86	3,072
	67	Hope	4	21N	90.3	6.8	2.9	5.83	70	35	1.056
Brighton sandy loam	52	Clarke	3	21C	91.6	5.1	3.3	5.90	34	42	696
	64	Hope	2	10C	74.8	18.4	6.8	7.11	158	62	2.448
	69	Hope	7	22N	70.2	25.0	4.8	6.53	20	56	4,732
	70	Clarke	7	6S	63.0	33.6	3.4	6.46	36	59	3,624
Darlington loam	6	Cartwright	7	14S	59.8	31.2	9.0	8.10	128	98	11.040
	10	Manvers	8	15N	42.8	50.2	7.0	7.32	176	209	11,928
	37	Darlington	6	15S	64.2	29.6	6.2	7.10	44	68	5.184
	41	Darlington	B.F.	24N	54.0	30.6	15.4	7.88	172	98	12,336
	45	Darlington	1	19C	49.6	35.8	14.6	7.73	108	55	10,986
Darlington sandy loam	43	Darlington	2	24C	56.6	32.4	11.0	8.09	188	79	13,128
Dundonald sandy loam	16	Hope	7	18S	77.4	20.2	2.4	6.43	122	124	1,536
	17	Hope	9	10N	39.6	49.0	11.4	7.45	296	133	5,280
	30	Manvers	4	21C	51.6	43.2	5.2	6.57	112	71	4.056
	60	Hope	4	30C	71.2	23.6	5.2	5.91	36	58	2,232
	71	Darlington	8	17C	40.8	48.2	11.0	7.78	110	71	7,584
	73	Clarke	7	35N	46.6	47.6	5.8	7.38	264	126	6,720
	74	Clarke	7	20N	43.4	41.0	15.6	7.93	308	332	9,888
Granby sandy loam	15	Hope	6	11N	35.4	56.2	8.4	8.00	236	98	18,288
	44	Darlington	4	23S	68.4	26.0	5.6	7.92	188	117	8,784
	56	Clarke	4	9C	46.2	40.8	13.0	7.95	400+	94	16,080
Guerin sandy loam (bouldery phase)	54	Clarke	1	18C	56.2	31.2	12.6	7.74	80	150	7.032
	61	Hope	2	26C	66.0	25.6	7.8	6.48	104	49	2,280
Newcastle loam	47	Darlington	B.F.	4C	58.0	31.4	10.6	7.13	190	68	3,436
	51	Clarke	1	30C	39.8	39.8	20.4	6.08	292	159	4,104
	62	Hope	2	20C	40.4	45.2	14.4	6.33	106	161	4,584
	63	Hope	2	2C	48.2	39.0	12.8	7.19	192	105	5,304
	65	Hope	3	15C	41.8	44.2	14.0	6.68	96	94	6,816
Newcastle clay loam	46	Darlington	B.F.	13C	33.6	45.8	20.6	7.40	248	133	7,032
	48	Darlington	2	2C	36.2	42.6	21.2	6.44	184	132	4.512
	50	Clarke	4	33C	39.2	46.0	14.8	7.25	252	71	6,060

Soil Type	Sample No.	Location			Per Cent Sand	Per Cent Silt	Per Cent Clay	Reaction (pH) Glass Electrode	Phosphorus Readily Soluble lbs. P/acre	Potassium Replaceable lbs. K/acre	Calcium Replaceable lbs. Ca/acre	Magnesium Water Soluble lbs. Mg/acre	Organic Matter % Carbon x 1.724
		Township	Con.	Lot	1.0—.03mm	.05—.002mm	Less than .002mm						
Otonabee loam	10	Cavan	4	10S	44.6	43.2	12.2	8.08	276	102	10,824	40	3.32
	21	Cavan	4	16N	33.2	42.0	24.8	7.96	332	161	13,968	40	3.71
	22	Cavan	7	12S	34.6	38.8	26.6	7.40	324	197	9,984	45	4.54
	25	Cavan	13	7S	40.0	38.8	13.2	7.90	240	170	13,536	40	3.00
	26	Cavan	11	15C	46.6	43.0	10.0	7.83	240	112	9,096	40	3.80
Perry loam	53	Clarke	1	25C	59.4	28.2	12.4	7.25	128	77	4,344	40	2.78
	58	Clarke	B.F.	7N	38.6	50.0	11.4	7.64	120	97	5,808	40	2.81
	75	Hope	8	14S	34.8	44.2	21.0	7.01	204	128	14,400	50	3.72
Pontypool sand	32	Manvers	3	21N	74.8	19.0	6.2	7.74	244	65	6,528	40	2.60
	33	Clarke	10	19N	86.7	9.2	4.1	7.37	170	50	2,400	40	1.21
	34	Manvers	2	16S	84.4	11.1	4.5	7.88	288	35	4,704	40	1.21
	72	Darlington	9	4C	79.6	16.1	4.3	7.46	142	35	3,120	40	1.64
Pontypool sandy loam	31	Manvers	4	18S	60.8	36.0	3.2	6.01	154	58	1,440	43	1.91
Schomberg clay loam	12	Hope	7	1S	35.0	44.6	20.4	7.98	252	135	12,744	45	3.91
	18	Cavan	1	20S	33.2	41.8	25.0	7.54	272	188	10,560	56	5.12
	20	Cavan	4	22S	27.6	45.0	27.4	7.84	340	221	16,560	56	6.31
	66	Hope	4	7S	46.4	40.4	13.2	8.04	172	114	15,648	56+	5.05
Schomberg silt loam	27	Cavan	9	4S	35.6	42.6	21.8	7.84	276	135	11,736	56	3.80
Tecumseth sandy loam	14	Hope	7	8C	51.4	41.8	6.8	5.96	66	265	2,362	40	3.69
	24	Cavan	9	22N	61.0	27.0	12.0	8.04	212	73	13,296	40	3.80
	42	Darlington	1	24N	55.8	33.0	11.2	8.01	172	62	11,928	50	5.40
	68	Hope	4	30N	69.6	24.4	6.0	7.02	32	56	7,080	33	6.41

Analytical Methods:

Mechanical Analysis—Bouyoucos Hydrometer Method.
Phosphorus—Lohse, H. W., and Ruhnke, G. N.—Soil Science 35:6, 1933.
Reaction—Glass Electrode.
Potassium—Volk, N. J., and Truog, E.—Jour. Amer. Soc. of Agron. 26, 537-46, 1934.
Calcium—The replaceable calcium was determined on the same extract that was used in the determination of potassium.
Magnesium—Spurway, C. H.—Mich. State College Technical Bulletin 132.
Organic Carbon—Allison, L. E.—Soil Science, Oct. 1935, p. 311.

SOIL SURVEY OF
PRINCE EDWARD COUN

BY

N. R. RICHARDS
EXPERIMENTAL FARMS SERVICE

AND

F. F. MORWICK
ONTARIO AGRICULTURAL COLLEGE

GUELPH, ONTARIO
NOVEMBER 1948

REPORT No. 10 OF THE ONTARIO SOIL SURVE

EXPERIMENTAL FARMS SERVICE, DOMINION DEPARTMENT
AGRICULTURE AND THE ONTARIO AGRICULTURAL COLL

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APPENDIX J

REFERENCE 11 AND ASSOCIATED HAND CALCULATIONS

Chapter 48

Aerodynamic measurement of ammonia volatilization from urea applied to bluegrass - fescue turf (1)

R.W. SHEARD and E.G. BEAUCHAMP

ABSTRACT

Ammonia (NH_3) volatilization from 100 kg N ha^{-1} applied as urea to a closely mowed Poa pratensis - Festuca rubra turf was measured using aerodynamic procedures. A volatilization loss of 13.1% occurred where no rain occurred for 8 days after application in contrast to [illegible].7% where rain occurred in 72 hr. Strong diurnal changes in the flux of NH_3 were observed, reaching maxima near midday and minimal values during the night. High values of NH_3 volatilization measured by closed chamber techniques which have been recorded in the literature may be considered erroneous because they do not consider all the direct and interactive effects of the total environment.

Additional key words Ammonia, Volatilization,Urea, Poa pratensis, Festuca rubra

INTRODUCTION

The economic advantage of urea as a solid nitrogen source for turf is often discounted due to the incipient volatilization loss of ammonia (NH_3) following surface application. Estimates of volatilization loss range from 10% (Torillo et al., 1983) to 68% (Fenn and Kissel, 1974). The range is partially due to the experimental procedure used in measuring the NH_3 flux; the use of enclosure techniques with atypical microenvironments provided higher estimates of NH_3 loss compared with aerodynamic field measurements which do not disturb the physical environment and provide lower estimates of NH_3 loss. The micrometeorological conditions are important because temperature, humidity, wind speed and solar radiation directly or interactively influence NH_3 volatilization.

Other factors affecting the volatilization of NH_3 from urea are soil pH, cation exchange capacity, rate of urea application, type of vegetation and occurance of thatch in turf which may have 18 to 25 times greater urease activity than the underlying soil (Torello and Wehner, 1983). Maximum volatilization, therefore, may be expected to occur from heavily thatched turf, excessively fertilized with urea in warm, humid weather without subsequent irrigation or rainfall.

The current study was conducted to obtain estimates of the magnitude of NH_3 loss from urea applied to mowed bluegrass-fescue turf using a aerodynamic diffusion method.

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(1) A contribution from the Department of Land Resources Science, O.A.C., University of Guelph, Ontario, N1G2W1 Canada.

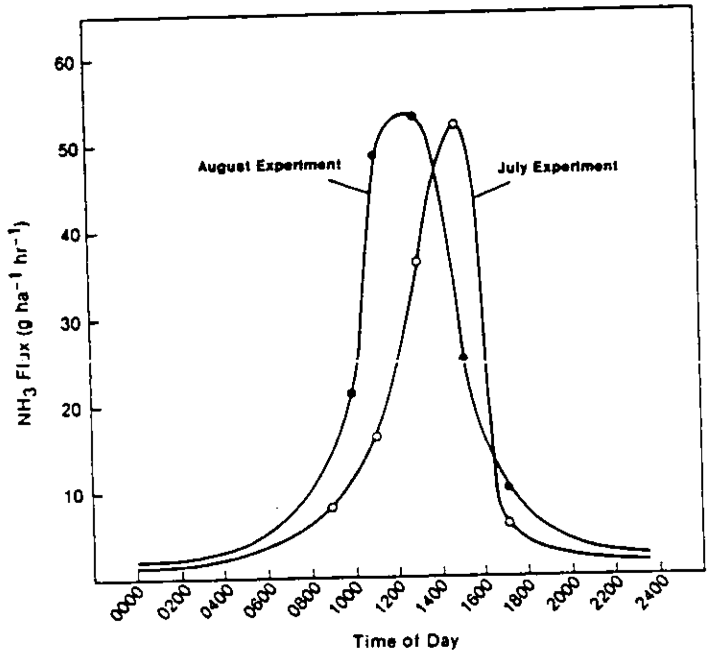

Fig. 1. Diurnal change in the background ammonia flux for the July and August experiments.

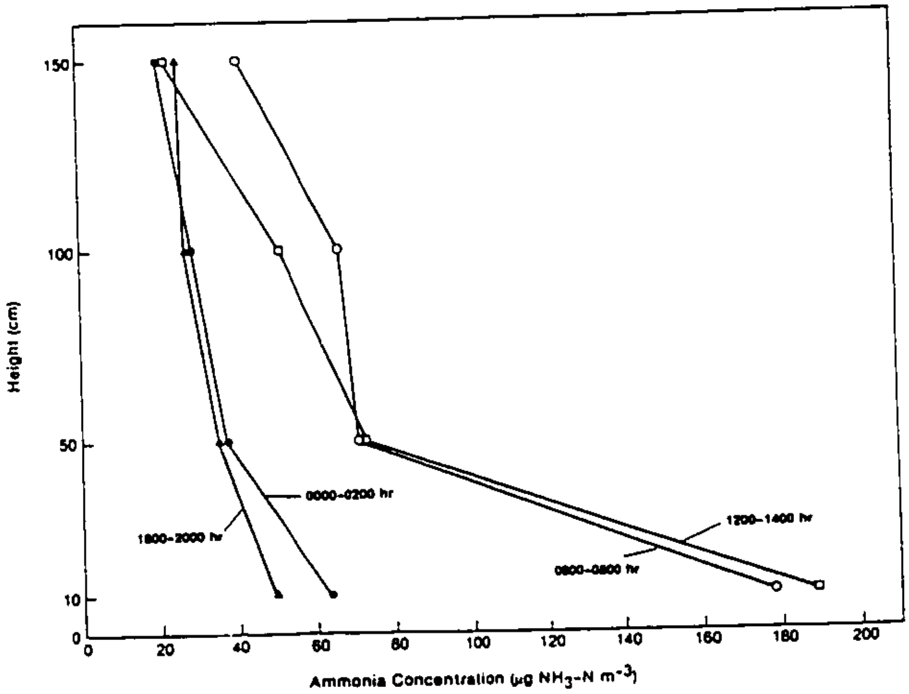

Fig. 2. The influence of time of day on the ammonia profile above turf grass.

MATERIALS AND METHODS

Ammonia flux from an application of urea to a Kentucky bluegrass (Poa pratensis L.) - creeping red fescue (Festuca rubra L.) sod, mowed at 7.5 cm, was measured by the aerodynamic procedure outlined by Beauchamp et al. (1978). Two experiments were conducted, one during the period July 11 to July 19, and the second during the period August 22 to 27.

The procedure consisted of placing a mast in the center of a circular area (0.405 ha) on to which urea had been broadcast at 100 kg N ha^{-1}. Ammonia gas collector flasks and sensitive anemometers were mounted on the mast to obtain measurements at heights of 10, 50, 100 and 150 cm above the soil surface. The gas collector flasks were 500 mL glass tubes (4.1 cm i.d., 64 cm long and tapered at one end) containing approximately 90 cm^3 of 3 mm diam glass beads and 75 mL 3% (v/v) H_3PO_4 solution. Air sampling was performed by continually drawing air through a 0.7 mm glass tube orifice and then through the gas collectors on the mast for 2-hr periods by an electromagnetic piston air pump. The air flow rate (10-20 L min^{-1}) was measured with a mass flow indicator (Model 8143, Matheson Gas Products) and a mass flow controller (Model 8163, range 0-50 SLPM, Matheson Gas Products). Multi-wire cable and plastic tubing connected the anemometers and gas collecting flasks on the mast to the pumps and air flow measurement devices in a mobile laboratory located adjacent to the experimental area. The NH_4^+-N concentration in the gas collector solution was determined colorimetrically by a Technicon AutoAnalyzer procedure having a sensitivity of 0.1 µg N mL^{-1}. The NH_3-N concentration in the air sampled at each height during a 2-hr period was calculated as:

$$\text{Atm } NH_3\text{-N concn } (\mu g\ m^{-3}) = \frac{NH_4\text{-N in } H_3PO_4 \text{ soln } (\mu g\ 2\ hr^{-1}) \times 1000\ L\ m^{-3}}{120\ min\ 2\ hr^{-1} \times \text{air flow } (L\ min^{-1})}$$

The vertical flux of NH_3 from the turf surface was assumed equal to the integrated product of wind speed x atmospheric NH_3 concentration by height to 150 cm, divided by the radius of the application area. Integration was accomplished by a planimeter estimate of the area enclosed by a graphical plot of height against the product of wind speed x atmospheric NH_3 concentration. The integral below 150 cm was multiplied by a constant factor of 1.38 to give the total integral according to the predicted model (Wilson et al., 1982, Beauchamp et al., 1978). Background measurements of NH_3 flux were made for several 2-hr periods prior to spreading the urea and were subtracted from measured flux values for the corresponding experimental period. Detail of the theory and practice of aerodynamic procedures may be found in Wilson et al. (1982) and Denmead (1983).

RESULTS

Previous studies have shown a strong diurnal shift in the NH_3 flux measured by the aerodynamic procedure (Beauchamp et al., 1978). A similar shift was considered likely to occur in background readings, therefore NH_3 fluxes were measured for several 2-hr periods prior to spreading the urea (Fig. 1). Estimates of the background flux for each 2-hr period during 24 hr were obtained from a plot of the data.

In general NH_3-N concentration profiles increased curvilinearly toward the soil surface (Fig. 2). The data for July 15 illustrate the typical profile changes which were measured during a 24-hr period, beginning with a relatively vertical profile at 0100 hr, increasing to high concentrations near the turf surface near midday, then returning to a vertical profile at 0700 hr.

In the July experiment the NH_3 flux exhibited the characteristic diurnal fluctuations, reaching a maximum value of 668 g ha^{-1} hr^{-1} at 1100 hr after an elapsed time of 118 hr following urea application (Fig. 3). Maximum fluxes of 459, 488, 226 and 419 g ha^{-1} hr^{-1} had been measured on previous days and subsequent maximum values averaged 260 g ha^{-1} hr^{-1}. During the August experiment a maximum value of 1067 g ha^{-1} hr^{-1} was attained at 1300 hr after an elapsed time of only 26 hr following urea application (Fig. 4). This high value occurred 8 hr after a 3.4 mm rain which would dissolve the urea but not move it into the dry soil surface. An 18.7 mm rainfall 6 hr after the maximum value greatly reduced further NH_3 flux. Minimal values over the five days, which occurred between 2200 and 0200 hr, averaged 32 g ha^{-1} hr^{-1}.

The accummulated total volatilization loss of NH_3-N in the July experiment for the 8-day period was 15.06 kg N ha^{-1}, representing 15.1% of the urea-N applied. In contrast the total volatilization loss of NH_3-N in the August experiment for a 5-day period was 6.68 kg N ha^{-1}, representing 6.7% of the applied urea-N.

DISCUSSION

Various experiments using a similar technique have suggested uptake of NH_3 by plants from the atmosphere (Denmead et al., 1976; Porter et al., 1972; Harper et al., 1983 b; Lemon and Van Houtte, 1980). In this study, however, the NH_3 concentration profiles suggested near equilibrium to net loss situations throughout the day (Fig. 2). Any indication of plant uptake in this experiment was probably masked by the continued relatively high flux densities of greater than 100 g NH_3-N ha^{-1} hr^{-1} after application of urea in contrast to values of 50 g NH_3-N ha^{-1} hr^{-1} for background conditions. Furthermore the closely mowed turf contrasted sharply to the tall grass canopies used by Denmead et al (1976), Lemon and Van Houtte (1980) and Harper et al. (1983 a).

Diurnal cycling has been demonstrated by others (Denmead et al., 1974; Beauchamp et al., 1978; Harper et al., 1983 b). Factors believed to result in the diurnal change in flux density are the direct and interactive effects of temperature (Fenn and Kissel, 1974), windspeed and turbulent transport (Denmead et al., 1982) dew formation and evaporation (Beauchamp et al., 1982) and urease activity in the thatch; activities which reach a maximum near midday under a natural environment. During the morning hours after sunrise evaporation of dew increases the NH_3-N concentration in solution, raising the partial pressure gradient and enhances the flux of NH_3 to the air. Later in the afternoon with decreasing air temperature and a concurrent decrease in water vapour pressure deficit the evaporation rate would decrease. Urease activity increases markedly with organic matter content (McGarity and Hoult, 1971; Torello and Wehner, 1983) and temperature (Bremner and Mulvaney, 1978). Wind speed and air turbulence increase with rising daily temperature increasing the transport of NH_3 from the air-soil-plant interface, thus more rapidly depleting the concentration

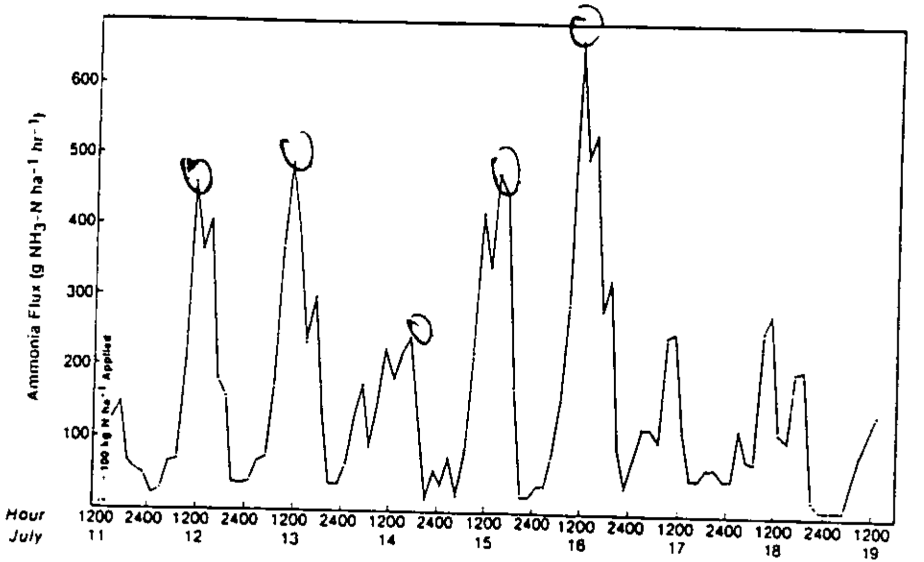

Fig. 3. The diurnal change in the net ammonia flux following an application of urea on July 11.

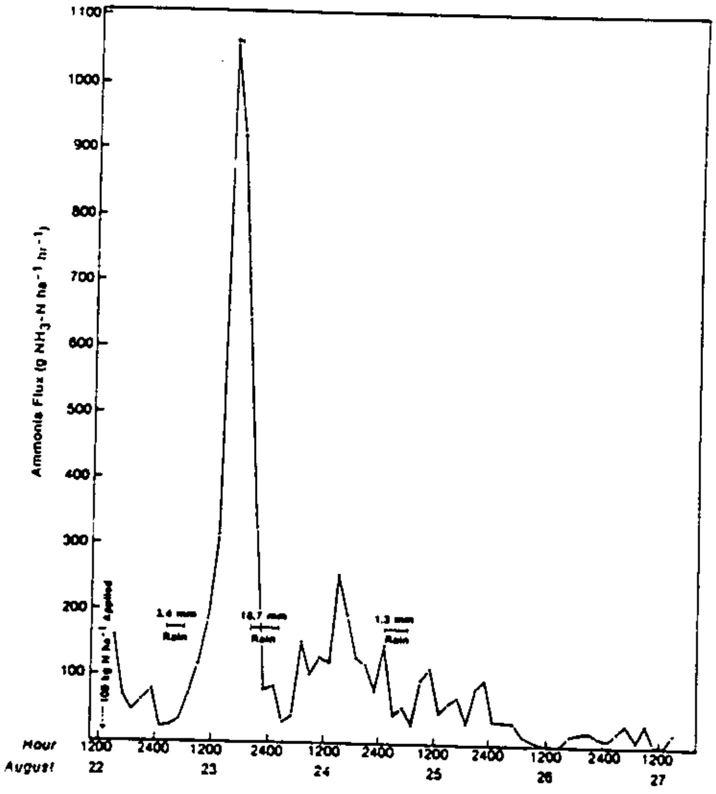

Fig. 4. The diurnal change in the net ammonia flux following an application of urea on August 22.

at the evaporative surface (Denmead et al., 1982). The diurnal cycle of NH_3-flux suggests measurements under constant laboratory conditions or single daily measurements in the field may grossly misrepresent NH_3 volatilization from urea.

Although no direct correlations between meteorological measurements and NH_3 flux were obtained it is interesting to note that during the July 11 to 19 experiment the minimum daily flux (July 14) occurred under conditions of 7.6 hr sunshine, an average 7 km hr^{-1} windspeed at 10 m and a maximum air temperature of 30.3 C. The maximum daily NH_3 flux (July 15) occurred under conditions of 14 hr sunshine, an average 12 km hr^{-1} windspeed and a maximum air temperature of 28.4 C. In contrast the maximum daily flux of the August experiment occurred on August 23 under 0.5 hr sunshine, an average 13 km hr^{-1} windspeed and a maximum air temperature of 24.8 C. These comparisons illustrate the complexity of the relationship of environmental conditions to NH_3 volatilization.

Measurements by the aerodynamic procedure of NH_3 volatilization from urea applied to grass in a tropical pasture range from 9 to 40% (Harper et al., 1983a). In this experiment the loss ranged from 6.7% where rainfall occurred within 72 hr to 15.1% where rainfall did not occur for eight days. Harper et al. (1983 b) also reported that the duration of high flux densities of NH_3 from urea-fertilized grass coincided with the number of rainless days after urea application. The use of urea in turf management, therefore, would be acceptable where irrigation is available or where rainfall may be predicted with a degree of reliability.

The loss of NH_3-N observed in this experiment is consistent with observed differences in turf quality, clipping weight and tissue nitrogen concentration where urea and ammonium nitrate have been compared on bluegrass (Sheard, R.W., Unpublished data). Where irrigation was not used urea was found to be inferior to ammonium nitrate, but never by more than 15%. Where irrigation was used they were equivalent.

ACKNOWLEDGEMENTS

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SUMMARY IN FRENCH

Mesure aérodynamique de la volatilisation ammoniacale à partir d'urée appliquée à un gazon composé de pâturin et de fétuque,

La volatilisation du gaz ammoniac (NH_3) aprés un apport de 100 Kg ha^{-1} azote sous forme d'urée à un gazon composé de *Poa pratensis* et de *Festuca rubra* a été mesuré par des procédés aérodynamiques. Une perte de 15.1% par volatilisation s'est produite, en absence de pluie, pendant 8 jours aprés l'apport tandis qu'elle se chiffrait à 6.7% dans les cas d'une pluie dans les premières 72 heures. De fortes variations journalières du flux de NH_3 furent observées, atteignant un maximum prés de midi et un minimum durant la nuit. Les valeurs élevées de volatilisation de NH_3 mesurées par de techniques de chambre close, telles que relatées dans la littérature peuvent être considérées comme erronées du fait qu'elles ne considèrent pas tous les effets directs ni les interactions avec tous les facteurs de l'environnement.

MIDWEST RESEARCH INSTITUTE
PROJECT DEVELOPMENT SKETCH

TITLE Reference 20 R.W. Sheard Chapter 48 ?

PROJECT NO. 6500-3513 fert. DRAWN Mcueoy APPR. DATE 9-16-92

1. Fertilizer: Urea - broadcast

Rate : $\boxed{\frac{100 \text{ kg N}}{\text{ha}}}$

2. Emissions in July, summary in text, p. 552, para. 3 $\boxed{\text{NO RAIN}}$

Convert to kg NH_3/ha

Total emissions = ~~15.1% x 100 kg N~~ 1506 kg N/ha x $\frac{17 \text{ kg } NH_3}{14 \text{ kg N}}$

$$= \frac{18.3 \text{ kg } NH_3}{\text{ha}} \quad \text{over} \quad 8 \text{ days}$$

3. Emission factor in July (EF)

$$EF = \frac{\text{emissions}}{\text{applied rate}} = \frac{18{,}300 \text{ g } NH_3/\text{ha}}{100 \text{ kg N}/\text{ha}} = \boxed{\frac{183 \text{ g } NH_3}{\text{kg N}}}$$

4. Emission in August, summary in text, p. 552, para. 3

Convert to g NH_3/ha

$$\text{Total Emissions} = \frac{6.68 \text{ kg N}}{\text{ha}} \times \frac{17 \text{ kg } NH_3}{14 \text{ kg N}} \times \frac{1000 \text{ g } NH_3}{1 \text{ kg } NH_3} = \frac{8{,}110 \text{ g } NH_3}{\cancel{\text{kg N}}\ \text{ha}}$$

5. Emission factor in August

$$\text{Total Emissions} = \frac{8{,}110 \text{ g } NH_3/\text{ha}}{100 \text{ kg N}/\text{ha}} = \frac{81.1 \text{ g } NH_3}{\text{kg N}}$$

APPENDIX K

REFERENCE 12, ASSOCIATED HAND CALCULATIONS, AND SUPPORTING DOCUMENTATION

Determination of Application Losses of Anhydrous Ammonia[1]

J. H. Baker, Michael Peech, and R. B. Musgrave[2]

SYNOPSIS. Application losses of anhydrous ammonia from soils at optimum moisture content were found to be negligibly small when ammonia was applied at practical rates, even at a depth of only 4 inches below the surface, as revealed by a method described in this paper.

IN THE direct application of anhydrous ammonia to soils, ammonia is injected into the soil as a mixture of gas and liquid. The proportion of gas to liquid depends upon the tank temperature. At 70° F., about one-fifth of the ammonia is vaporized at the time of injection into the soil. The remaining liquid ammonia also vaporizes rapidly, and unless the ensuing ammonia gas is completely absorbed by the soil, appreciable losses of ammonia may occur. An application of anhydrous ammonia at the rate of 100 pounds of nitrogen per acre for a 40-inch spacing between applicator blades corresponds to about 6 liters of ammonia gas per lineal foot of row.

Laboratory studies of the losses of anhydrous ammonia upon application have been reported by Jackson and Chang (3), Stanley and Smith (6), and McDowell and Smith (4), but little attempt has been made to measure directly the losses of ammonia upon application of the anhydrous compound under field conditions. Blue and Eno (1) calculated the loss of ammonia as the difference between the amount of ammonia applied and that extracted from the soil by sodium chloride solution. Such calculations assume that the rate of injection of ammonia is uniform within the row and that there is no fixation of ammonia into nonexchangeable form. Both of these assumptions may introduce serious errors depending upon the nature of the soil and the type of equipment employed in the application of the ammonia.

This paper describes a quantitative method for measuring directly the application losses of ammonia under field conditions. In this method the ammonia escaping from the soil is caught and absorbed in standard acid. Since this work was completed, Hansen et al. (2) have reported a similar method in their studies of the application losses of ammonia. A very simple and rapid qualitative method, involving the use of pH color indicator, is also described and has been found very useful in establishing the soil conditions under which the losses of anhydrous ammonia upon application may be expected to be high.

MATERIALS AND METHODS

Application of ammonia—The anhydrous ammonia was metered through a Weatherhead Type D Ammotrol and a flowrator to a single John Blue applicator blade. The meter was calibrated by passing the ammonia into a known volume of water (5 gallons) for a specified period of time and titrating an aliquot of the resulting aqua ammonia with standard acid. A rolling coulter was mounted just ahead of the applicator blade in the application of ammonia to the soil under sod. The speed of the tractor in going over the plot was accurately measured so that the amount of ammonia applied per lineal foot of row could be calculated.

Quantitative method—Immediately following the injection of anhydrous ammonia into the soil, a pan 9 inches long, 5 inches wide, and 2½ inches deep was inverted and pressed firmly into the soil directly over the ammonia band which could be readily located by the disturbed soil or the crevice left by the applicator blade. An additional amount of loose soil was packed around the edges of the pan. The pan was provided with inlet and outlet glass tubes which were inserted through rubber stoppers into holes made in the opposite sides of the pan. The pan was connected to an acid absorption tower which, in turn, was connected to a vacuum pump. The acid absorption tower, containing 250 ml. of $0.05N$ H_2SO_4, consisted of a 700 ml. cylinder equipped with a fritted glass gas scrubber. A tractor-driven electric generator was used as a power source for the operation of the vacuum pump. Air was pulled through the pan at the rate of 3 liters per minute and any ammonia escaping from the soil within the pan was thus swept into the acid absorption tower. As many as 20 pans were connected simultaneously to the vacuum pump by means of rubber tubing, thus permitting measurement of losses of ammonia from different sites chosen at random or selected to represent different depths and rates of application. After the desired period of aeration (usually six hours) the amount of ammonia absorbed by the acid in the absorption tower was determined by titrating the excess acid with standardized NaOH.

The rate of flow of air through the pan (3 liters per minute) was sufficiently high to renew the air within the pan once every 30 seconds without creating a negative pressure within the pan, as was indicated by a water manometer connected to the inlet tube. This rate of flow of air was found to be effective in sweeping out the ammonia gas escaping from the soil before any appreciable amount of the ammonia could be absorbed by the surface of the soil. Preliminary trials showed that about 90% of a measured volume of ammonia gas, introduced slowly into the pan through the inlet tube, could be recovered in the absorption tower. The volume of ammonia gas introduced into the pan in these trials represented about 10% of the amount of ammonia applied to the soil area enclosed by the pan with an application rate of 85 pounds N per acre on a 14-inch spacing.

Qualitative method—In this method a neutral indicator-gypsum suspension (prepared by triturating 1 gram of phenol red with 28 ml. of $0.1N$ NaOH, diluting to 1 liter with water, adding 300 grams of finely divided $CaSO_4 \cdot 2H_2O$ powder, and adjusting the color of the indicator to orange) was sprayed on the cross section of the ammonia band exposed by making a vertical cut across the band with a spade. In the more compacted soils, the entire face of the crevice made by the applicator blade, extending from the point of injection to the soil surface, was also sprayed with the indicator-gypsum suspension after carefully spading and removing the opposite face of the crevice. The indicator-gypsum suspension was sprayed with a conventional household insect sprayer. The spray was applied slowly in order to prevent downward flow of any excess of the indicator-gypsum suspension that may have accumulated on the soil. The distribution of ammonia within the band and any upward movement of ammonia through the

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[1] Contribution from the Department of Agronomy, New York State College of Agriculture, Cornell University, Ithaca, N. Y., as Agronomy Paper No. 453. This work was supported by research grants from Olin Mathieson Chemical Corporation and the Sun Oil Company.

[2] Graduate Research Assistant, Professor of Soil Science, and Professor of Field Crops, respectively.

Table 1—Loss of ammonia from various soils upon application of anhydrous ammonia.

Soil type	Condition of soil			Application of NH_3		Loss of ammonia*			
	Surface	pH	Moisture	Depth	Rate†	Pan 1	Pan 2	Pan 3	Pan 4
			%	inches	lb. N/A.	% of amount applied			
Mardin silt loam	plowed	7.0	24	4 8	202 191	Nil‡ Nil	Nil Nil	8§ Nil	Nil Nil
Mardin silt loam	plowed	5.1	24	4	260	Nil	Nil	Nil	0.3
Mardin silt loam	sod¶	6.6	19	4 8	85 65	Nil Nil	Nil Nil	Nil Nil	Nil Nil
Sassafras f.s.l.	plowed	5.9	18	4	243	Nil	Nil	0.6	Nil

* After 6 hours aeration for Mardin soils and 9 hours for Sassafras soil.
† On basis of 14-inch spacing. ‡ Nil represents a loss of less than 0.1%.
§ Insufficient amount of acid in tower; loss was estimated by back-titration of NH_4OH and consequently may be low. ¶ Alfalfa-grass sod.

crevice left by the applicator blade could be clearly established by the color change of the indicator as observed against the white gypsum background.

RESULTS AND DISCUSSION

Typical results showing losses of anhydrous ammonia applied to Sassafras fine sandy loam and Mardin silt loam at different rates and depths, as measured by the quantitative method, are presented in table 1. The application losses were found to be negligible even when ammonia was applied at fairly high rates to a depth of only 4 inches. The relatively large loss of ammonia (8% of that applied) observed at one of the sites on Mardin silt loam was found to be due to very shallow application of ammonia as the applicator blade was raised in going over a large stone.

In order to determine whether there was any application loss of ammonia during the short interval of time before the test pan was placed in position, one pan was mounted immediately behind the applicator blade so that it was about one inch above the soil when ammonia was applied at a depth of 4 inches. A long piece of rubber tubing connected the vacuum pump to the acid absorption tower which was mounted on the tractor. Air was pulled from the pan into the acid absorption tower at the rate of 3 liters per minute, and any ammonia escaping immediately behind the applicator blade was thus caught in the pan and swept into the absorption tower. The pertinent details of these tests and the results are given in table 2. The results show that the application losses of ammonia immediately behind the applicator blade are negligibly small.

Because of its simplicity and rapidity, the qualitative pH indicator-gypsum spray method can be used to study the distribution of applied ammonia in the soil as affected by the rate of application, soil moisture, soil reaction, and exchange capacity. Obviously, the method cannot be used to determine the magnitude of the application losses, but can be very useful in showing whether application losses occur at all by noting the color change of the indicator sprayed on the faces of the crevice left by the applicator blade.

The results of these tests would indicate that application losses of anhydrous ammonia from soils at optimum moisture content are negligibly small when ammonia is applied at all practical rates even to a depth of only 4 inches below the surface. The minimum depth of application should be determined by the radial distance of diffusion of ammonia as measured from the point of injection, and this, in turn, can be shown to be dependent upon the ammonia retention capacity, soil bulk density, and rate of application in accordance with the following equation:

$$r = 0.1\sqrt{\frac{SA}{CD}}$$

Table 2—Loss of ammonia immediately behind the applicator blade.

Soil type	Condition of soil			Application of NH_3		Ammonia loss†
	Surface	pH	Moisture content	Depth	Rate*	
			%	inches	lb. N/acre	%
Sassafras f.s.l.	plowed	5.9	18	4	257	0.0
Lima silt loam	plowed	7.2 7.2	16 16	4 4	224 261	0.0 0.0
Lima silt loam	alfalfa sod	6.9	13	5	261	0.0

* On basis of 14-inch spacing.
† Ammonia lost expressed as percent of the amount applied.
‡ This test covered a distance of 200 feet; the other tests covered a distance of [illegible]

where r is the theoretical minimum depth of application in inches; S is the spacing between rows in inches; A is the nominal rate of application in pounds N per acre; D is the bulk density of the soil in grams per cubic centimeter; and C is the ammonia retention capacity of the soil in milliequivalents per 100 grams of soil. The method for determining the ammonia retention capacity of the soil has been described by Sohn and Peech (5). The ammonia retention capacity is essentially equal to the exchangeable hydrogen content of the soil as determined by the $BaCl_2$-triethanolamine method. Field observations have shown that the radial distance of diffusion of ammonia in the band in loose soils is in fairly good agreement with that given by this equation. In compacted soils, however, the crevice made by the applicator blade is not sealed sufficiently to prevent some upward diffusion of ammonia through the crevice. Under such conditions, the cross section of the ammonia band does not approach circular symmetry, and the minimum depth of application must well exceed that given by the above equation in order to prevent the escape of ammonia.

SUMMARY

A qualitative and a quantitative method for measuring directly the application losses of anhydrous ammonia under field conditions are described. In the quantitative method, the ammonia escaping from the soil is caught and absorbed in standardized acid. In the qualitative method, the exposed cross and longitudinal sections of the ammonia band are sprayed with an indicator-gypsum suspension, and the movement of ammonia within the ammonia band and through the crevice left by the applicator blade is clearly shown by the color change of the indicator. The results of these tests would indicate that application losses of anhydrous ammonia from soils at optimum moisture content are negligibly small when ammonia is applied at practical rates even at a depth of only four inches below the surface.

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K-4

MIDWEST RESEARCH INSTITUTE
PROJECT DEVELOPMENT SKETCH

TITLE Reference 26. J.H. Baker, et. al. Agron. J. 51, pp361-362. 1959.
(3pgs)

PROJECT NO. 6500-3513 fert. DRAWN Meurs APPR. DATE 9-14-92

1. Fertilizer: Anhydrous Ammonia (l-NH_3)

Rate: variable in lb N / Acre

Convert $\frac{\text{lb N}}{\text{Acre}}$ to $\frac{\text{kg N}}{\text{ha}}$ by

(a) $$\text{Rate}\left(\frac{\text{kg N}}{\text{ha}}\right) = \frac{\text{lb N}}{\text{Acre}} \times \frac{2.471 \text{ acres}}{\text{ha}} \times \frac{0.451 \text{ kg}}{\text{lb}}$$

Example:
Table 1, Marcia silt loam, 4", plowed

$$\text{Rate} = \frac{202 \text{ lb N}}{\text{A}} \times \frac{2.471 \text{ acres}}{\text{ha}} \times \frac{0.454 \text{ kg}}{\text{lb}} = \boxed{\frac{227 \text{ kg N}}{\text{ha}}}$$

2. Emissions: flux air samples, 6 or 9 hr sample
Pollutant: Ammonia - immediate
Total Time: 6 or 9 hrs

Arithmetic average of 4 replicates

(b) $$\text{Avg emission } (\%) = \frac{\Sigma \text{ 4 reps } (\%)}{4}$$

where Nil = 0.1% for Table 1 data

Convert to concentration ($g\,NH_3/ha$)

(c) $$\text{Conc}_{\text{period}} = \frac{\text{Average emission } (\%)}{100\%} \times \text{Rate}\left(\frac{\text{kg N}}{\text{ha}}\right) \times \frac{17 \text{ kg } NH_3}{14 \text{ kg N}} \times \frac{1000 \text{ g } NH_3}{1 \text{ kg } NH_3}$$

Example: Table 1, Marcia Silt loam, 4" plowed
avg = 0.1% where 8% emission is deleted as explained in the text.

MIDWEST RESEARCH INSTITUTE
PROJECT DEVELOPMENT SKETCH

TITLE Ref 26 (pg 2 of 3)

PROJECT NO. 6500 3513 fed. DRAWN Mewey APPR. DATE 9-14-92

$$\text{Conc}_{\text{period}} = \frac{0.1\%}{100\%} \times \frac{227\ \text{kg N}}{\text{ha}} \times \frac{17\ \text{kg NH}_3}{14\ \text{kg N}} \times \frac{1000\ \text{g NH}_3}{\text{kg NH}_3} = \frac{276\ \text{g NH}_3}{\text{ha}}$$

$$\text{Conc} = 276\ \frac{\text{g NH}_3}{\text{ha}} \div 6\ \text{hr} = 45.9\ \text{g NH}_3/\text{ha}\cdot\text{hr}$$

Convert for sampling period

(A) $$\text{Conc} = \frac{\text{Conc}_{\text{period}}}{\text{timeperiod (hr)}}$$

3. (e) Emission factor of test (EF_{test}) = $\frac{\text{Conc (g NH}_3\text{/ha hr)}}{\text{Rate (kg N/ha}}$

$$\text{Example} = \frac{45.9\ \text{g NH}_3/\text{ha-hr}}{227\ \text{kg N/ha}} = \boxed{0.202\ \frac{\text{g NH}_3}{\text{kg N}\cdot\text{hr}}}$$

(f) Emission factor = Avg EF_{test} x 48 hr

4. Data from Tables 1 and 2, p. 362, all results.

5. Sampling Times for "Behind Blade" application.

$$\frac{6\ \text{L NH}_3}{\text{ft}} \times \frac{\text{min}}{3\ \text{L}} \times 200\ \text{ft} = 400\ \text{min} = 6.67\ \text{hr}$$

$$\frac{6\ \text{L NH}_3}{\text{ft}} \times \frac{\text{min}}{3\ \text{L}} \times 100\ \text{f} = 200\ \text{min} = 3.33\ \text{hr}$$

MIDWEST RESEARCH INSTITUTE
PROJECT DEVELOPMENT SKETCH

TITLE Ref. 26 (pg. 3 of 3)

PROJECT NO. 6500-35-13 fert. DRAWN Murray APPR. DATE 4-14-92

Table: Ref 26-1

Soil	Time Period Length (hr)	Orig Rate (lbN/A)	(a) Rate (kgN/ha)	(b) Avg Emission (%)	(c) Computed (gNH$_3$/ha)	(d) Conc (gNH$_3$/ha·hr)	(e) EF$_{test}$ (gNH$_3$/kg N·hr)
Mardin	6	202	227	0.10	276	45.9	0.202
		191	214	0.10	260	43.3	0.202
Mardin	6	260	292	0.15	~~438~~ 532	~~73.0~~ 88.6	~~0.250~~ 0.304
Mardin sod	6	85	95	0.10	115	19.2	0.202
		85	95	0.10	115	19.2	0.202
Sassafras	9	243	272	0.22	727	80.7	0.297
						$\bar{x}$(low) = 0.202 $\bar{x}$(hi) = 0.251 ± 0.06[illegible]	
Behind Blade							
Sassafras	3.33	257	288	0.001	3.50	1.05	0.0036
Lima	6.67	224	251	0.006	18.3	2.74	0.0109
	3.33	261	293	0.65	178	53.4	0.182
Lima sod	3.33	261	293	0.01	35.6	10.68	0.0364
			*				$\bar{x}$ = 0.058 ± SD = 0.084

Overall Emission Factors:

$$EF_{test} \times \text{Time Period} = g\ NH_3/kg\ N \text{ fertilizer applied}$$

For example: Mardin Silt Loam, 4" plowed shown above

$$0.202\ \frac{g\ NH_3}{kg\ N \cdot hr} \times 6\ hrs = 1.21\ \frac{g\ NH_3}{kg\ N\ fert}$$

factors affect plant response to these chemicals. The most desirable effects on vegetative growth, flowering, maturity, and fruit setting occur under the best conditions of temperature, sunlight and mineral nutrition. Top yields of treated crops will probably result only if adequate fertility, especially nitrogen levels, are maintained in the soil. This has been proved with pasture grasses, pineapple and sugarcane.[15]

For many of the flowering and vegetative responses described, repeated treatments may be necessary. For others, a single dosage early in the growth of the plant is sufficient.

Crops can be treated at various stages. As a given plant grows in size (leaf numbers increase), greater quantities are needed for a given result, and greater dosages can be given without injury:

For flowering in some annuals and biennials, several hundred micrograms per plant may be needed. Others respond to 100 or less. On the other hand, only a few micrograms are required to set tomato fruit, increase the weight of celery by 50 percent, and change the growth habits of dwarf peas and bush beans to the tall or poletypes.

Although the safety factor is large, overdoses of gibberellins may injure some crops. The growing tips of treated plants may die back or "top out". This has happened occasionally with lettuce and endive when very rapid seedstalk growth resulted. Use of the chemical on some greenhouse crops may cause excessive growth and result in weakened stems. This has been noticed especially during the winter when sunlight is scarce. In some cases, young leaves have shown marginal burning. With beans, excessive quantities (100 micrograms or more per plant) caused new growth to twist and curl temporarily.

Much laboratory, greenhouse, and field testing is needed before the full power of the gibberellins will be realized. By that time, the farmer will be able to buy ample quantities from commercial sources. Because of cost, present uses will probably be with high-value greenhouse, nursery, and garden crops as a fruit setting agent and in seed production.

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[15] Imperial Chemical Industries Limited (1955). Op. cit. See also Chardon, C. E. (1950). Gibberellin, a new plant growth promoting substance. Paper read before the Association of Sugar Technologists of Puerto Rico, San Juan, Puerto Rico, December 1, 1950.

A TECHNIQUE TO DETERMINE VOLATIZATION LOSSES IN THE APPLICATION OF FERTILIZERS WHICH CONTAIN FREE AMMONIA[1]

By C. M. HANSEN, M. M. MORTLAND and L. S. ROBERTSON

Departments of Agricultural Engineering and Soil Science

Farmers and agricultural research workers have been concerned about the losses of nitrogen when anhydrous ammonia is applied directly to the soil or compounded in a low vapor pressure solution.

A new technique to determine losses of ammonia has been developed which utilizes two 6-volt magnetic (neoprene diaphragm) fuel pumps.[2] The gas trapped in a chamber is forced through a boric acid solution. The ammonia in the boric acid solution can be titrated with standard acid to quantitatively determine nitrogen losses.

EQUIPMENT AND PROCEDURE

The dual pumps move air at the rate of 11½ cubic feet per minute (c.f.m.). They will operate successfully for 24 hours on a fully charged 6-volt battery drawing about 1½ amperes. The design of the applicator foot for direct application of anhydrous ammonia influences the retention of ammonia, as do depth of application and soil physical characteristics.

A hood built around the applicator foot traps any ammonia which escapes from the soil (Fig. 1). Rubber flaps or curtains at the rear end of the applicator foot hood allow soil to flow from the hood without any loss of ammonia to the atmosphere. A known rate of anhydrous ammonia is applied for a given distance.

The hose supplying ammonia to the applicator foot is unclamped at the beginning of the test run and clamped off at the conclusion;

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[1] Acknowledgment is made to Nitrogen division, Allied Chemical and Dye Corporation, New York, N. Y., for financial assistance in this project.

[2] Model 500, Auto Pulse Manufacturing Co., Ludington, Michigan.

ARTICLE 39-48

the result is a definite rate of application per acre. The pumps (Fig. 2) are started at the beginning of the test run and continued until no further ammonia is picked up by the boric acid solution. Periodic sampling and titration determines the quantity of ammonia picked up by the solution.

At the same time, a second applicator foot is fed an equal amount of anhydrous ammonia. At a predetermined spot in the test run, a shroud (in the form of an inverted V) having an opening of 2¾ inches by 24 inches is placed over the slit in the soil made by the second applicator foot. The pumps on the second unit (Fig. 3) are started and continued until no further ammonia is picked up by the solution.

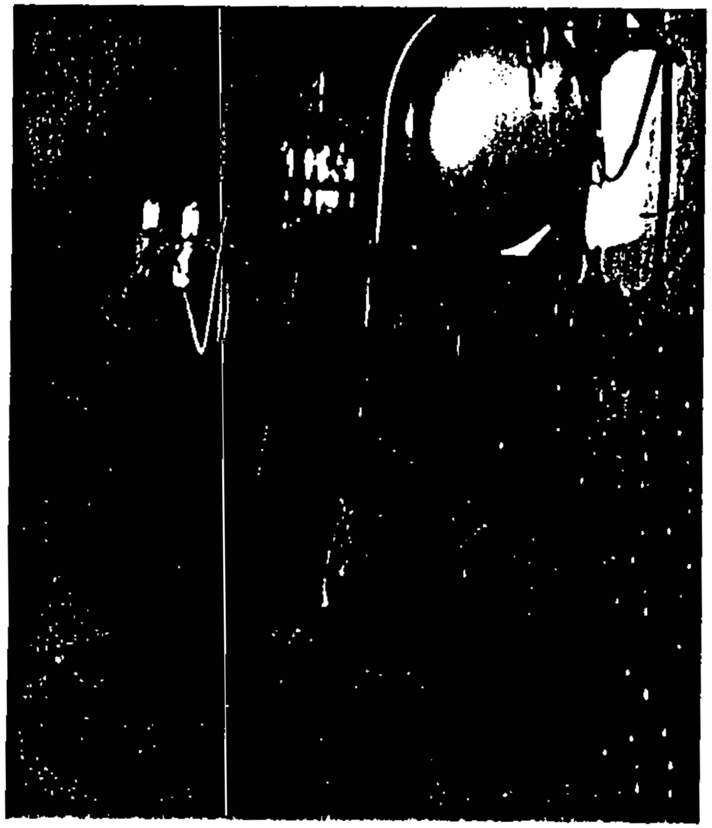

Fig. 1. The hood around the applicator foot traps the gas which is pumped through a boric acid solution.

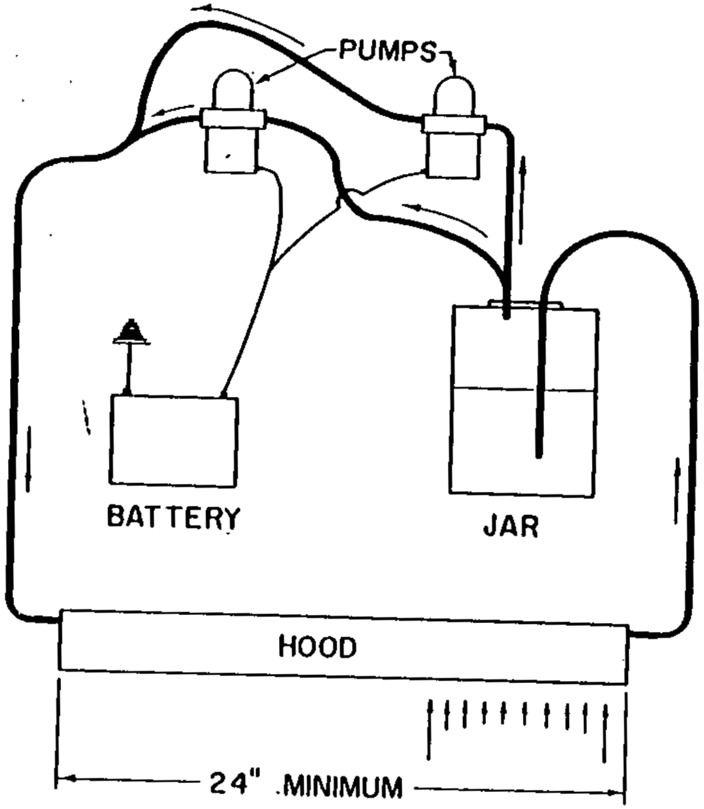

Fig. 2. Schematic drawing of system.

RESULTS

Fig. 4 presents the data obtained using the above equipment. These curves show ammonia losses from a low pressure solution applied on the soil surface and again at a depth of 2 inches. Using this equipment, we found that the large differences in ammonia losses are due to placement.

When the material was applied to the soil surface, the rate of loss was greatest immediately after application and decreased at a slower rate as time passed. The loss-rate curve was almost logarithmic in nature. Losses were still observed after 6 hours. Loss of ammonia

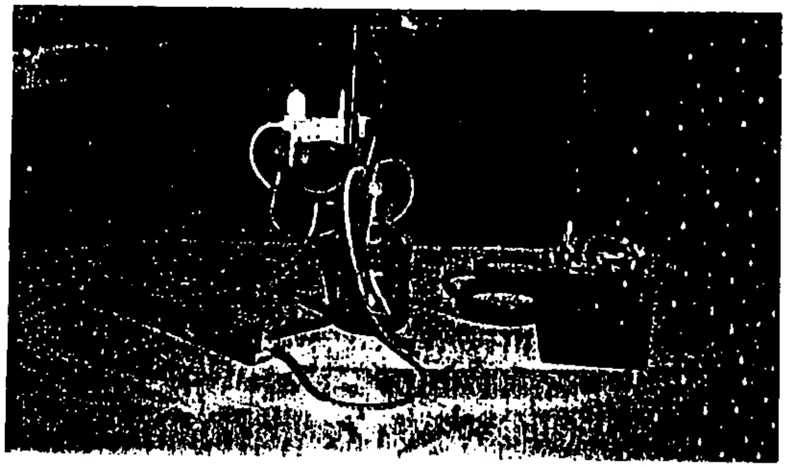

Fig. 3. To recover any lost ammonia, the inverted "V" trough is placed over the slit made by the applicator foot or the applied solution.

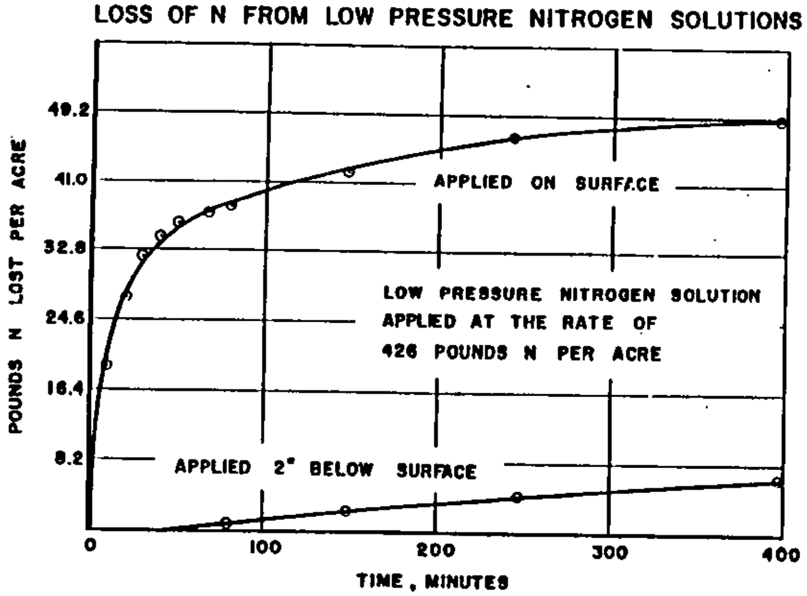

Fig. 4. Curves of data obtained during test run.

from the surface application amounted to 27 percent of the total volatile ammonia in the solution. Ammonia loss from placement at 2 inches was about 4 percent after 6 hours.

SUMMARY

The data indicates that this equipment is well suited to the study of ammonia losses in the field. The data show heavy ammonia losses from surface application of nitrogen solutions containing free ammonia. Results suggest that application depths should be greater than 2 inches.

APPENDIX L

REFERENCE 13 AND ASSOCIATED HAND CALCULATIONS

The Influence of Plant Residues on Denitrification Rates in Conventional and Zero Tilled Soils[1]

M.S. AULAKH, D.A. RENNIE, AND E.A. PAUL[2]

ABSTRACT

A field study was conducted with treatments consisting of a factorial combination of N (0 or 100 kg N ha^{-1} as $(NH_4)_2SO_4$, straw (0 or 3000 kg ha^{-1}), and two tillage treatments. Ground straw was mixed with the plow layer of soil in the conventional till (CT) plots and chopped straw was spread over the surface of the zero till (ZT) plots. Wheat (*Triticum aestivum* L.) was grown as the test crop. Gaseous losses of N were measured using the acetylene inhibition-soil core technique and compared with loss estimates obtained from the imbalance in the N budget of ^{15}N-treated microplots located within the larger yield plots. When adequate inorganic N was present, the incorporation of straw in CT soil or the application of straw on the surface of ZT soil approximately doubled the accumulative gaseous N losses. The straw apparently increased the supply of energy material available to denitrifying organisms, and also increased surface soil moisture content (particularly during the month of June). This further stimulated denitrification in ZT soil. Unaccounted ^{15}N on the fertilizer N balance studies agreed closely with cumulative N losses using the acetylene inhibition technique.

Additional Index Words: **wheat grain yield, protein content, N uptake, soil moisture, mineral N.**

Aulakh, M.S., D.A. Rennie, and E.A. Paul. 1984. The influence of plant residues on denitrification rates in conventional and zero tilled soils. Soil Sci. Soc. Am. J. 48:790–794.

RECENT field studies using the acetylene inhibition technique have demonstrated that the moisture content of surface soil is a singlular environmental variable affecting gaseous losses of N; even rather small increases in volumetric soil moisture can be accompanied by very large increases in the rate of denitrification (3, 4). It was also found that gaseous N losses were 2 to 3 times higher from zero till (ZT) than conventional till (CT) soils (4). However, multiple regression analyses showed that such factors as moisture, temperature, inorganic $NO_3^- - N$ and $NH_4^+ - N$ accounted for only 37 to 66% of the variations in rate of denitrification. Soil bulk density also was shown to be of importance but no quantitative assessment of its significance was possible (1, 5).

Crop residue placement is a significant environmental difference between CT and ZT soils. In CT, crop residues are frequently worked uniformly into the surface soil, while in ZT they are left scattered on the surface or as standing stubble. There is reason to believe that the difference in crop residue placement may influence denitrification rates. For instance, the addition of a readily decomposable carbon material such as manure greatly enhanced denitrification (relatively high in N) in both laboratory and field studies (9, 15). Other studies have shown that the addition of wheat straw to undisturbed soil cores (7) or field plots (8) reduced N losses by denitrification due to increased immobilization of inorganic N. Aulakh et al. (1, 2, 4) have shown that rates of denitrification are only slightly or not at all influenced by rather wide variations in nitrate-N concentrations in the soil, and accordingly, immobilization may not be a significant factor influencing denitrification rates unless it is relatively complete.

The acetylene inhibition technique (17) developed as a means of assessing gaseous N losses has been used successfully in recent laboratory and field studies (1, 2, 3, 4, 14, 16). This method has been validated by ^{15}N measurements in anaerobic soil systems (12) and by ^{13}N measurements in a soil-water slurry (16) under laboratory conditions. In a recent study (2) we carried out its validation under field conditions by comparing the cumulative gaseous N losses with the amount of unaccounted fertilizer N in ^{15}N balance studies; the two techniques agreed very closely, although the losses were relatively low (1–2 kg N ha^{-1}). The present field study further confirms the close agreement between these two techniques when losses were as high as 25 kg N ha^{-1}. This paper also documents the influence of decomposing crop residues on denitrification rates in the presence and absence of applied N under field conditions.

MATERIALS AND METHODS

The experiment was established in the spring of 1981 on an Elstow clay loam, a Dark Brown Chernozemic soil (Typic Haploborolls). Some of the important soil characteristics and agronomic history of the CT and ZT fields (which have been under these tillage treatments since 1978) were reported earlier (1,4).

The treatments consisted of a factorial combination of two levels each of N [0 or 100 kg N ha^{-1} as $(NH_4)_2SO_4$] and wheat straw (0 or 3000 kg ha^{-1}) replicated twice in individual 2 × 2 m macroplots in both the CT and ZT fields. Hard red spring wheat (*Triticum aestivum* L. var. Neepawa) was used as the test crop. After seeding the wheat in the ZT plots water with the required amount of fertilizer N was sprayed uniformly on the soil surface using a back-pack sprayer. To minimize NH_3 volatilization, some additional water was added to move the fertilizer N a few centimeters into the plow layer. The required amount of chopped wheat straw (3–5 cm long) was uniformly spread over the surface and the macroplots were covered with steel netting (chicken wire) to minimize straw losses by wind erosion. The netting was removed after four weeks when the crop was well established. To obtain uniform mixing and make the applied straw more effective, it was finely ground and mixed with the plow layer of CT plots before seeding wheat. Then fertilizer was applied as in ZT plots using the same amount of water in all the plots.

Four microplots were established in both CT and ZT fields by inserting an open aluminum cylinder (20 cm i.d. by [illegible] cm long) in each N-fertilized macroplot, taking special care to prevent soil compaction. Each microplot treatment was prepared in a manner similar to the macroplot which su

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[2] Commonwealth Scholar; Professor, Dep. of Soil Science, Univ. of Saskatchewan, Saskatoon, Canada; and Professor and Chair, Dep. of Plant and Soil Biology, Univ. of California, Berkeley, CA 94720.

Table 1—The effect of various N and straw treatments on the wheat grain yield, protein and plant N uptake under conventional- and zero-till systems.

Treatment	Grain yield, kg ha^{-1}	Grain protein, %	Total N uptake kg ha^{-1}
	Conventional-till		
Control	1681c§	12.6b	73.4c
Straw†	811a	10.7a	37.0a
N_{100}‡	1972d	15.9de	105.4e
	(1954)¶	(16.5)	(117.2)
N_{100} + straw	1947d	16.6e	105.4e
	(1910)	(18.1)	(116.7)
	Zero-till		
Control	1468b	12.0b	62.1b
Straw	1697c	11.1a	66.6b
N_{100}	2009d	15.1cd	96.4d
	(2098)	(16.2)	(108.4)
N_{100} + straw	2400e	14.9c	119.1f
	(2555)	(13.3)	(116.3)

† Straw = 3000 kg ha^{-1}.

‡ N_{100} = 100 kg ha^{-1}.

§ Values in the same column are significantly different at $P \leq 0.05$ (using Duncan's multiple range test) when not followed by the same letter.

¶ Figures in parenthesis represent values obtained from ^{15}N-microplots.

rounded it except that ^{15}N-labelled $(NH_4)_2SO_4$ (5.4% excess) was used as the source of fertilizer N. 92 days

Gaseous N losses were measured during the growing season (5 June–4 Sept. 1981) by removing three pairs of undisturbed soil cores from each treatment every week. The reader is referred to our earlier publication (1) for procedures used to measure: gaseous N losses with the acetylene inhibition technique, soil moisture, and inorganic soil N (NO_3^- + NO_2^-, NH_4^+). The cores were incubated 24 h in 1100 cm^3 glass jars with airtight covers fitted with serum stoppers. Incubation under shaded conditions in soil outside the laboratory closely approximated the temperature within the canopy of grain crops in the field. Oxygen contents in the jars, monitored at various times with a gas chromatograph, remained above 19% during most of the incubations, but dropped as low as 15% on straw-amended samples with high soil moisture. Rainfall data were recorded at a meteorological station on the site.

At the end of the growing season, 1 m^2 area from each macroplot and all plants within each cylinder were harvested, dried at 60 ± 1°C, separated into grain and straw and weighed. The cylinders including the soil were removed, and representative soil samples were taken from the 45 to 60-cm depth. In the laboratory, the cylinders were cut open and the soil was sectioned into 0- to 15-, 15- to 30-, and 30- to 45 cm depths, each of which was weighed and air-dried. Roots plus crowns were collected, washed, dried, and weighed. Soil subsamples, ground to pass a 10-mesh (2-mm) sieve were extracted with 2*M* KCl for mineral-N analysis. Additional 100-mesh samples were digested for total Kjeldahl N analysis. The nonexchangeable NH_4^+ (commonly known as fixed NH_4^+) in the 0 to 15- and 15- to 30-cm soil samples was determined (10). Wheat grain, straw, and root + crown fractions were ground to pass a 100-mesh sieve, and assayed for total N. Kjeldahl digestion and distillation methods described by Rennie and Paul (13) were followed. Soil organic N was calculated by subtracting mineral N from total Kjeldahl N. Grain protein was estimated as 5.7 × percentage of N and expressed on a 13.5% moisture basis.

RESULTS AND DISCUSSION

Grain Yield, Protein Content, and Plant N Uptake

In the CT field, wheat grain yield was increased by 17% by the addition of fertilizer N, mixing 3000 kg wheat straw into the plow layer resulted in a 50% yield reduction, probably due to immobilization of mineral N (Table 1). When the N and straw were both applied, there was sufficient N for both immobilization and plant growth, and the grain yields were equal to those obtained with N alone.

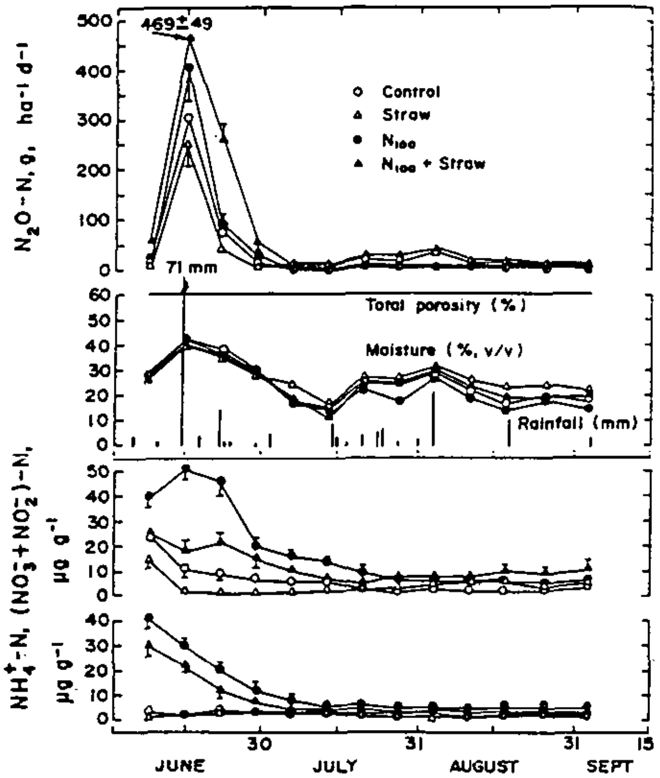

Fig. 1—Gaseous N losses (N_2O–N), soil moisture, rainfall, (NO_3^- + NO_2^-)–N and NH_4^+–N of conventional-tilled Elstow clay loam seeded to wheat with various straw and N treatments. Φ indicates standard deviation within three replicates.

Grain yield from the ZT control was lower than from the CT control plot, but increased significantly with applied N. In contrast to the CT field, grain yield was increased 16% by the addition of straw, probably because surface placement of the straw provided a thick continuous layer of mulch that conserved a greater amount of rain water without immobilizing all available mineral N. The highest yield (63% above the control) was obtained from the ZT plots where N was applied in conjunction with the straw mulch surface. Nitrogen uptake by wheat (grain plus straw), followed the same pattern as grain yield.

The addition of straw without N lowered wheat grain protein content by 20% in both tillage systems. This can be attributed to immobilization of N in the CT plots and simple N dilution frequently associated with large yield increases due to more favorable moisture conditions in the ZT plots. The relatively high protein levels achieved with the N_{100} and N_{100} plus straw treatments for both cropping systems suggest that available N was more than adequate in these treatments.

Although the ZT control had a higher soil moisture regime than the CT control (Fig. 1 and 2), its grain yield, protein content, and N uptake were all lower. The high grain yield and N uptake obtained with the application of 100 kg N ha^{-1} in conjunction with a straw mulch emphasizes the need to ensure optimum fertility in ZT studies; otherwise, the greater moisture conserving characteristics of the surface straw mulch may not be reflected in greater production (6, 11). The yields obtained from ^{15}N-microplots were, in general, comparable to those from corresponding macroplots (Table 1), thus confirming that realistic field conditions were achieved in the microplots.

Recovery of Fertilizer N

As has already been suggested from the total N uptake data given in Table 1, plant uptake of fertilizer N was not significantly influenced by the incorporation of crop residues on the CT plots (Fig. 3); about 40% of the added fertilizer N was taken up by the crop. The greater fertilizer N uptake by the crop on the straw mulched ZT plots is a reflection of the more favorable growing conditions, especially the higher moisture level.

The amount of fertilizer N immobilized (organic N) or present in the inorganic form (extractable mineral N plus fixed NH_4^+) in the 0- to 60-cm profile varied rather widely between treatments (Fig. 3). A greater amount of fertilizer N was immobilized in the CT soil when straw was incorporated. This difference was partially offset by a lower content of inorganic N and the recovery of fertilizer N from these two CT treatments was quite similar. In contrast, while the amounts of fertilizer N immobilized in the no-straw treatments on CT and ZT soils were very similar, much less fertilizer N was immobilized on the ZT-straw treatment than on the CT-straw treatment. This could be attributed to higher plant uptake and denitrification which competed with immobilization for fertilizer N. In addition, washing the fertilizer N a few centimeters into the soil (see Materials and Methods) may have separated the fertilizer N from surface-placed straw enough to partially inhibit its immobilization. Only a very small portion (0.5–2%) of the fertilizer N was recovered as fixed ammonium.

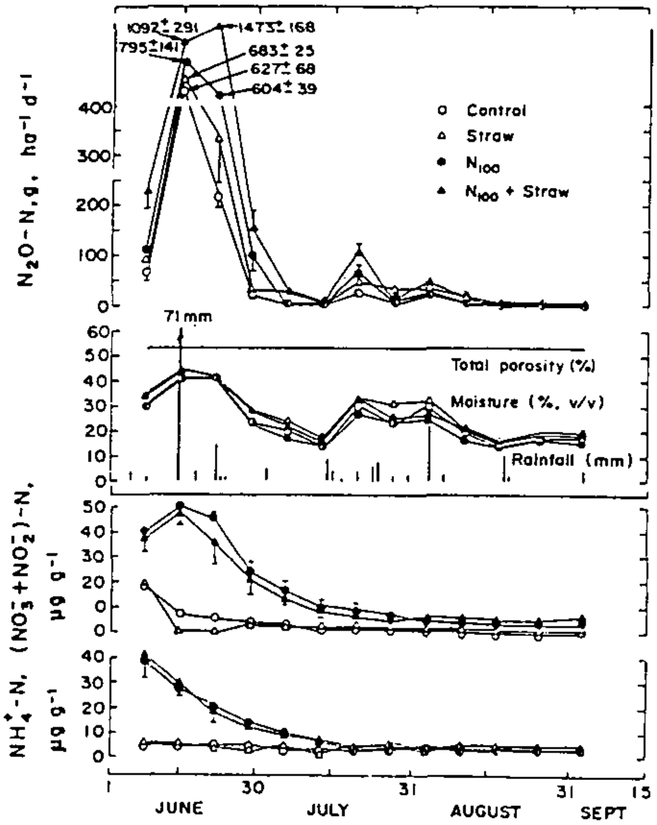

Fig. 2—Gaseous N losses (N_2O-N), soil moisture, rainfall, $(NO_3^- + NO_2^-)-N$ and NH_4^+-N of zero-tilled Elstow clay loam seeded to wheat with various straw and N treatments. Φ indicates standard deviation within three replicates.

Most of the fertilizer N recovered from the soil was found in the 0- to 30-cm depth (data not presented). However, management did influence the amount of fertilizer N found below the 30-cm depth; 1.5 and 1% of the applied fertilizer N was recovered in the 30- to 60-cm depth on the no straw and straw-CT treatment. In contrast, 6.6 and 3.6% were recovered in the no straw and straw-ZT treatments. Only trace amounts of the fertilizer N were found below 45 cm. It was therefore assumed that most of the unaccounted N was lost through denitrification. It is unlikely that significant amounts of the fertilizer were lost by the volatilization in light of the application procedure used. The ^{15}N data (Fig. 3) show that denitrification was stimulated by the addition of straw, whether fully incorporated or left on the surface. On ZT soil, surface placement of the crop residue resulted in a twofold increase in unaccounted N compared to the no-straw treatment.

Gaseous Losses of N

Gaseous losses of N measured by the acetylene inhibition technique (N_2O-N g ha^{-1} day^{-1}) followed similar patterns under both CT and ZT tillage systems (Fig. 1 and 2). The relatively high rates of N_2O evolution that prevailed during June were related to heavy mid-June rainfall. During this period the unfertilized ZT-straw treatment lost N at a higher rate than the

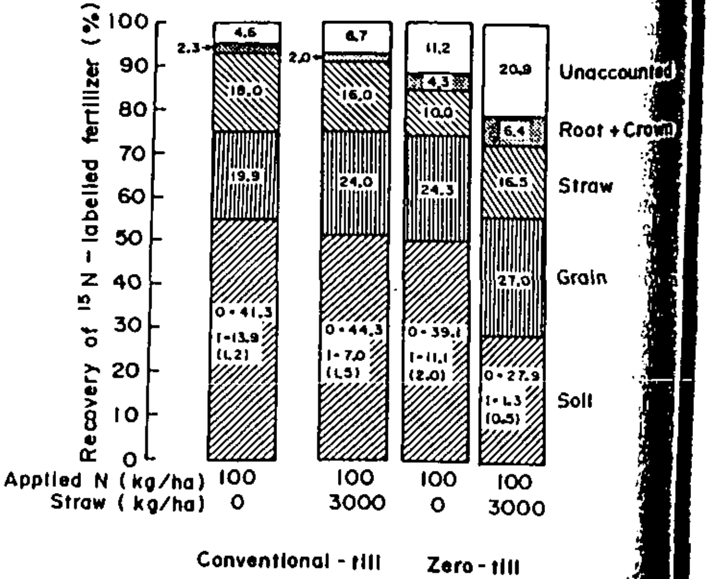

Fig. 3—Balance sheet of ^{15}N-labelled fertilizer nitrogen. O = organic N, I = inorganic N including amount of fixed NH_4^+ (given in parentheses).

ZT control, but the relationship between these two treatments on CT soil was reversed. This is the only indication in these data that the addition of straw caused a decrease in denitrification rates compared to the controls.

The inorganic N data given in Fig. 1 show that incorporation of 3000 kg ground wheat straw immobilized mineral N rapidly and reduced gaseous N losses early in the growing season. However, at later stages of plant growth when levels of mineral N were very low in both untreated and straw treated plots (Fig. 1), a higher rate of N_2O emission was recorded from the straw treatment possibly due to a 2 to 4% higher soil moisture. The higher soil moisture may have resulted from lower water use by the poor crop on this treatment. Therefore, the cumulative losses of N were similar for both the untreated and straw-treated plots (Table 2). In a one-week incubation study, Craswell (7) noted rapid immobilization of labelled NO_3^- and reduced denitrification losses when added straw was added to small soil cores. Our results confirm this observation, but also indicate that in the field the reduced denitrification losses are later offset by higher gaseous N losses as water accumulates due to poor plant growth. The much higher rates of N_2O evolution from ZT than CT soil during the month of June produced a twofold difference in the total amount of N lost from the no-straw treatments and a threefold difference for the straw treatments (Table 2). The more favorable moisture conditions prevailing on the ZT-straw treatments is probably a major contributing factor to the higher N_2O evolution rates and results in rather high accumulative N losses. Higher NO_3^-—N levels in the soil on both N_{100} treatments also encouraged higher rates of denitrification.

The data for cumulative gaseous N losses measured with acetylene inhibition techniques were in close agreement with N unaccounted for in the ^{15}N balance studies (Table 2). The ^{15}N technique measures only the fate of fertilizer N. The C_2H_2 inhibition method should reflect denitrification of both the fertilizer and the soil N. Denitrification activity was at a maximum in June shortly after fertilizer N was added and it is probably safe to assume that the majority of the N_2O measured using the acetylene inhibition technique was derived from this source. Thus it has confirmed our earlier study (2) that these two different approaches of assessing gaseous N losses give quite similar results under field conditions.

Table 2—Cumulative gaseous N losses (kg N ha^{-1}) measured with acetylene inhibition technique (AIT) and ^{15}N-balance approach.

	Conventional-till		Zero-till	
Treatment	AIT	^{15}N	AIT	^{15}N
Control	3.20 ± 0.42a§	–	7.25 ± 0.48b	–
Straw†	3.41 ± 0.44a	–	9.85 ± 0.23c	–
N_{100}‡	4.28 ± 0.51a	4.62 ± 1.08a	11.88 ± 0.43d	11.20 ± 3.78d
N_{100} + straw	7.25 ± 0.43b	6.65 ± 1.41b	22.51 ± 2.24e	20.87 ± 4.32e

† Straw = 3000 kg ha^{-1}.

‡ N_{100} = 100 kg N ha^{-1}.

§ Values are significantly different at $P \leq 0.05$ (using Duncan's multiple range test) when not followed by the same letter.

CONCLUSIONS

This study, using the acetylene inhibition technique to assess denitrification rates, has shown that the addition of wheat straw residues, either as a mulch on the surface or fully incorporated, resulted in a doubling of the accumulative gaseous N losses over the growing season. It is significant that fertilizer N balance studies provided an estimate of unaccountable ^{15}N which coincided very closely with that obtained using the acetylene reduction technique.

The ^{15}N balance approach permitted the measurement of the distribution of fertilizer N in the plant and soil at the end of the growing season. Under the conditions prevailing during this field study, immobilization of the added ^{15}N was significantly higher under conventional till than zero till. It can therefore be concluded that under conventional till where the straw facilitated the fertilizer N immobilization, it also increased the supply of energy material available to the denitrifying organisms and thus denitrification rates for the growing season increased sharply. Denitrification would appear to have been increased under zero till primarily because of the more favorable moisture conditions. Thus this study has clearly shown that the use of both the ^{15}N balance study and the acetylene reduction technique has materially added to our understanding of factors influencing denitrification under field conditions, and the influence of management on these rates.

Absolute validation of either the acetylene inhibition methods or the ^{15}N technique is difficult under field conditions. The acetylene method requires addition of an external gas and enclosure in some type of chamber. Sampling to ensure that all denitrification events are recorded could involve an even more intense program than that carried out in this study. The ^{15}N technique involves problems with uniform distribution of tracer, possible alterations of the size or distribution of the potentially denitrifiable N pool, and the uncertainties associated with possible leaching or volatilization. These losses were minimized in this study as the major denitrification events occurred in June before there was opportunity for substantial alteration of the soil N pool by mineralization.

The fact that the two methods gave very similar results in a number of different treatments is encouraging but must be considered somewhat coincidental. However, it is of interest that the decrease measured in ^{15}N immobilization coincided with a doubling of gaseous N losses as measured by both the ^{15}N balance and the summation of C_2H_2 inhibition studies conducted weekly. The acetylene inhibition method makes it possible to relate the dynamics of N loss to short-term environmental changes such as rainfall events, soil type management such as ZT or straw incorporation and crop development. The ^{15}N technique involves a balance sheet approach that does not distinguish the source of loss but provides an integrated measurement of the fate of added N.

ACKNOWLEDGMENTS

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Aerobic and Anaerobic Microbial Populations in No-till and Plowed Soils[1]

D. M. LINN AND J. W. DORAN[2]

ABSTRACT

Surface soils from long-term tillage comparison experiments at six U.S. locations were characterized for aerobic and anaerobic microbial populations and denitrification potential using an in situ acetylene blockage technique. Measurements of soil water content, bulk density, and relative differences in pH, NO_3^--N, water-soluble C, and total C and N contents between tillage treatments were also determined at the time of sampling. Numbers of aerobic and anaerobic microorganisms in surface (0–75 mm) no-till soils averaged 1.35 to 1.41 and 1.27 to 1.31 times greater, respectively, than in surface-plowed soils. Bulk density, volumetric water content, water-filled pore space, and water-soluble C and organic C and N values were similarly greater for surface no-till soils compared to conventionally tilled soils. Deeper in the soil (75–300 mm), however, aerobic microbial populations were significantly greater in conventionally tilled soils. In contrast, below 150 mm, the numbers of anaerobic microorganisms differed little between tillage treatments. In no-till soils, however, these organisms were found to comprise a greater proportion of the total bacterial population than in conventionally tilled soils. Measurements of the denitrification potential from soils at three locations generally followed the observed differences in anaerobic microbial populations. Denitrifying activity, after irrigation with 15 mm of water, was substantially greater in surface 0- to 75-mm no-till soils than in conventionally tilled soils at all locations. At the 75- to 150-mm soil depth, however, the denitrification potential in conventionally tilled soils was the same or higher than that of no-till soils. In surface no-till soils, increased numbers of anaerobic microorganisms and a substantially greater denitrification potential, following irrigation, indicate the presence of less-aerobic conditions in comparison to conventionally tilled soils. This condition appears to result from greater soil bulk densities and/or water contents of no-till soils, which act to increase water-filled porosity and the potential for water to act as a barrier to the diffusion of oxygen through the soil profile.

Additional Index Words: **Soil aeration, denitrification, conservation tillage, microbial ecology.**

Linn, D. M., and J. W. Doran. 1984. Aerobic and anaerobic microbial populations in no-till and plowed soils. Soil Sci. Soc. Am. J. 48:794–799.

THE NUMBERS, types, and activities of soil microorganisms are important to the productivity of soil through their regulatory effect on soil carbon (C) and nitrogen (N) levels. Several early studies comparing the microbial populations of reduced-tillage and plowed soils demonstrated that greater numbers of aerobic microorganisms were often associated with the surface 0 to 150 mm of reduced-tillage soils (Dawson et al., 1948; Gamble et al., 1952; Schaller and Evans, 1954). More recently, Barber and Standell (1977) and Doran (1980b) found that microbial numbers, dehydrogenase activities, and respiration rates in surface no-till soils were significantly greater than those in plowed soils. However, at a soil depth below 50 to 75 mm, these indexes of microbial activity were often

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Work Sheet ☒

Page 1 of 1

POLLUTANT: N_2O

FERTILIZER: AMMONIUM SULFATE (AS)

APPLICATION METHOD -- AQUEOUS SOLUTION; BACK-PACK SPRAYER

APPLICATION RATE -- 100 kg N/ha

SAMPLING PERIOD: 92 days

1. CORRECTION FOR BACKGROUND: TOTAL CUMULATIVE LOSS - TOTAL LOSS IN CONTROL

TREATMENT	BKG. CORRECTED LOSS (kg N/ha) CT	ZT
AS	1.08	4.63
AS+STRAW	4.05	15.26

2. N_2O EMISSIONS: $\text{BKG. CORRECTED LOSS} * \dfrac{44\text{ g } N_2O/\text{ha}}{14\text{ g N/ha}}$

TREATMENT	EMISSIONS OF N_2O (kg N_2O/ha) CT	ZT
AS	3.39	14.55
AS + STRAW	12.73	47.96

3. N_2O EMISSION FACTORS: $EF = \dfrac{N_2O\text{ EMISSIONS}}{\text{APPLICATION RATE}}$

APPLICATION RATE = 100 kg N/ha

EF UNITS: g N_2O/kg N applied

TREATMENT	N_2O EMISSION FACTOR (g N_2O/kg N) CT	ZT
AS	33.9	146
AS + STRAW	127	480

EXAMPLE: $E.F. = \dfrac{3.39\ \frac{\text{kg } N_2O}{\text{ha}} * 10^3\ \frac{\text{g}}{\text{kg}}}{100\ \frac{\text{kg N}}{\text{ha}}} = 33.9$ g N_2O emitted/[illegible] kg N applied

APPENDIX M

REFERENCE 14 AND ASSOCIATED HAND CALCULATIONS

(14)

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N_2O AND CH_4 FLUXES IN SOIL INFLUENCED BY FERTILIZATION AND TRACTOR TRAFFIC

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Summary—The effects of fertilization and tractor traffic on N_2O emission and CH_4 uptake in agricultural soil were studied in a field trial with different fertilization and soil compaction. The soil was a well-drained sandy loam and the crop rotation was rich in ley and legumes. The fertilization treatments were: NPK fertilizer (140 kg NH_4NO_3-N ha^{-1}); cattle slurry (CS) (189 kg total N ha^{-1}), CS (81 kg total N ha^{-1}), and an unfertilized treatment. The soil was experimentally compacted by two passes with a tractor, wheel by wheel, shortly before fertilization. Gas fluxes at the soil surface were measured by the soil cover method. Soil air at a depth of 7–12 cm was sampled through stationary soil air samplers. Concentrations of N_2O in soil air were more than seven times higher in compacted, NPK-fertilized soil than in any other treatments. Maximum concentrations (1900 μl N_2O l^{-1}) were observed shortly after periods with heavy rain. The accumulated N_2O emissions from the NPK-fertilized treatment (4 June–8 July) corresponded to 5.3% of added NH_4NO_3-N in compacted soil, and 3.9% in uncompacted soil. Fertilization with cattle slurry equivalent to 81 kg total N ha^{-1} gave an N_2O emission corresponding to 3.1% of added NH_4-N in uncompacted soil, and 2.7% in compacted soil. Increasing levels of cattle slurry resulted in a reduction in N_2O emission per kg NH_4-N added. The accumulated CH_4 uptake (4 June–8 July) in the soil was 9.7 mg CH_4 m^{-2} in unfertilized and uncompacted soil. It was reduced by 52% by soil compaction, 50% on average by fertilization and 78% by soil compaction and fertilization combined. Fertilization with NH_4NO_3 or cattle slurry resulted in similar effects.

INTRODUCTION

Soil is an important source of atmospheric N_2O, and a sink for CH_4 (Mosier *et al.*, 1991). The emission of N_2O may be perceived as a leakage of intermediate products in nitrification and denitrification. These reactions are influenced by oxygen supply, water content, temperature, soil pH, organic matter, the presence of plants (Byrnes, 1990) and the concentrations of NH_4-N and NO_3-N in the soil (Jones and Morita, 1983). A well-drained soil acts as a sink for atmospheric CH_4 due to methane oxidation, by either ammonia oxidizers or methanotrophs (Bedard and Knowles, 1989). In arable land agricultural practices such as fertilization and tractor traffic as well as climate and soil type are likely to influence these gas fluxes. Numerous studies reviewed by Eichner (1990) show great variability in N_2O fluxes from agricultural soils. Less work has been done on CH_4 flux. Mosier *et al.* (1991) report a CH_4 uptake of 2.6, 1.8 and 1.3 g C ha^{-1} d^{-1} in native grassland, fallow and wheat sites, respectively.

In some areas soil compaction is a serious problem. Very little work has been reported on the effect of soil compaction on N_2O emission in a humid climate and no work on the effect on CH_4 uptake. In western Norway large areas are easily compacted, partly because of humid climate and partly because of fine textured soils and high content of organic material in the soils. The aim of this investigation was to study the influence of soil compaction through tractor traffic and fertilization with NH_4NO_3 or cattle slurry on CH_4 and N_2O fluxes in an easily compacted soil in a humid climate.

MATERIALS AND METHODS

Gas fluxes and soil air composition were measured during the seventh year of a field experiment with different fertilization and soil compaction treatments (growth season 1991). The field experiment was located in Surnadal, Norway 25 m a.s.l., 63°00′00″ N, 8°88′44″ E. Precipitation in April, May and June was 457 mm, which is 179% of the normal precipitation. The average temperature for April, May and June was 7.7°C (normal 8.4°C). Soil temperature and precipitation during the period of measurement are given in Fig. 1.

The experiment had a split-plot factorial design with two replicates, soil compaction on main plots and fertilization on small plots (2.8 × 8 m, sample area 1.5 × 6.5 m). For each flux measurement, two soil cover chambers were placed at random within each field plot (minimum spacing 1 m). Soil air was sampled using two stationary soil air samplers (equilibrium chambers) in each plot. Thus, for each

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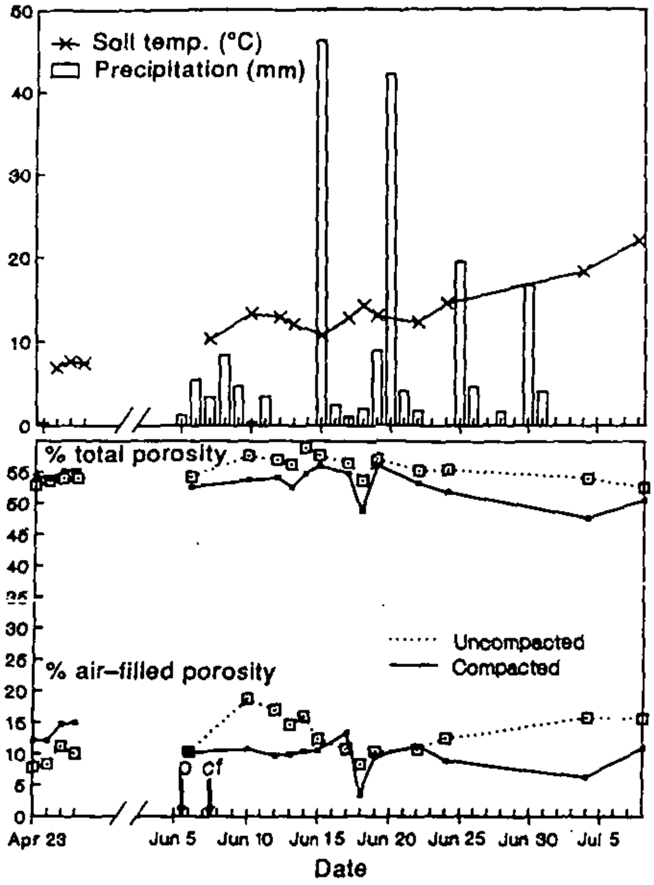

Fig. 1. Soil temperature (°C) at 15 cm depth, precipitation (mm), total porosity and air-filled porosity as a percentage of soil volume.

treatment, there were four parallel flux and soil air measurements taken on each day of measurement.

The fertilization treatments were: NPK fertilizer (18% N, 3% P, 15% K) with 140 kg NH_4NO_3-N ha^{-1}, cattle slurry (CS) equivalent to 189 kg total N (116 kg NH_4-N) ha^{-1}, CS equivalent to 81 kg total N (50 kg NH_4-N) ha^{-1}, and an unfertilized treatment. CS was diluted with water up to 200% of the original volume and spread by can with a small spreading plate. NPK fertilizer was spread by hand. Fertilizers were raked into the top 5 cm of the soil immediately after application. This loosened the soil in the upper surface. Samples of cattle slurry were frozen for later analyses following the method described by Horwitz (1980).

The diluted slurry contained 64 g dry matter l^{-1}, 2.8 g Kjeldahl-N l^{-1}, 1.7 g NH_4-N l^{-1}, 25 mg NO_3-N l^{-1}, 1.5 g water soluble organic C l^{-1} and had a pH of 7.6.

In 1991, soil compaction treatment comprised two passes of a 4 tonne tractor, wheel by wheel, shortly before fertilization, at a soil moisture tension equal to pF *ca* 2. The rear wheels were double-settings with a total tyre width of 140 cm (inflation pressure of 57 kPa). In front there were low pressure tyres with a total width of 100 cm.

Similar fertilizer and compaction treatments have been carried out every year from 1985 with the exception of 1990, when no extra compaction or fertilization was applied.

Tillage treatments (ploughing, two harrowings, rolling) and sowing were carried out across the experimental plots with tractors similar to those used for compaction. Thus, the uncompacted soil was to some extent affected by tractor traffic.

The experimental field has a slope of <2% and is placed on a naturally-drained sandy loam developed on fluvial deposits. The soil profile has a contrasting character in the subsoil layer (beneath 30–100 cm), with *ca* 50% by volume containing stones bigger than 4 cm, while the remainder is rich in gravel and coarse sand (Table 1).

The top soil contained 2.2% organic C, 0.17% organic N and had a pH (H_2O) of 6.1. Average bulk densities (7–11 cm depth) were 1.21 g cm^{-3} in uncompacted soil and 1.30 g m^{-3} in compacted soil.

The experiment was started in 1985. The crop rotation was adapted to ecological farming with milk production and had a high frequency of ley and legumes.

The 1991 crop was green fodder with rape (*Brassica napus*), barley (*Hordeum vulgare*), peas

Table 1. Soil texture. Percent by weight of the fraction <2 mm, *except for gravel* which is given as a percentage of the total weight. Determined following Elonen (1971)*

	Soil layer		
	0–20 cm	20–25 cm	*Subsoil*
Gravel (0.2–4 cm)	1–3	1–3	70–90
Coarse *sand (2.0–0.6 mm)*	1–2	1–2	34–68
Medium sand (0.6–0.2 mm)	5–7	7–15	22–37
Fine sand (0.2–0.0 mm)	38–44	33–42	5–27
Coarse silt (0.06–0.02 mm)	27–29	27	1–6
Medium silt (0.02–0.006 mm)	13–17	13	0–5
Fine silt (0.006–0.002 mm)	4–6	6–7	0–1
Clay (<0.002 mm)	4–6	4	1–4

*Three samples behind the determination of soil texture 0–20 cm and 20–25 cm, eleven samples behind the determination of subsoil.

(*Pisum arvense*), vetch (*Vicia sativa*) and Westerwolth rye-grass (*Lolium multiflorum* Lam. var. *Westerwoldicum auct.*). Crops from 1985 to 1990 were: greenfodder, barley, 3 yr ley and oats. The oats straw was left on the soil surface during the winter and was removed shortly before ploughing in spring 1991.

The soil porosity and water content were determined in undisturbed soil samples taken by means of 100 cm^3 cylinders. At each sampling date, three samples were taken in both compacted and uncompacted areas (7–11 cm depth). Particle density used to calculate material and pore volume was determined following the method of De Boodt *et al.* (1967).

Gas measurements

Gas fluxes were measured shortly after snowmelt (23, 24 and 26 April), before and after ploughing (4 and 7 June) and after compaction and fertilization treatments (10, 12, 13, 14, 15, 17, 18, 19, 22, 24 June; 4 and 6 July).

Gas fluxes at the soil surface were measured by soil cover chambers (thin-walled tin cans, 22.5 cm i.d., 23 cm high) with a reflecting outer surface similar to that described by Bakken *et al.* (1987). This ensured minimal heating by direct sunlight. In order to prevent bulk flow of air into the soil while pushing the soil cover chambers into the ground (1 cm), three holes (12 mm dia) on the top were kept open. After placement of the chambers, these holes were closed with butyl rubber stoppers (type 20-B3P, Chromacol Ltd, London). Gas samples were taken through these stoppers with a two-way blood collection needle. The needle was pierced through the rubber stoppers and connected to 12 ml evacuated glass vials (N 20-10 Macherey–Nagel, Düren) as outlined by Magnusson (1989). Before sampling, the vials were closed with the same type of stoppers, covered with a layer of silicone and evacuated to $<10^{-3}$ atm.

Equilibrium chambers for soil air sampling at depths of 7–12 cm were installed shortly after rolling the field. The equilibrium chambers were constructed of pointed cylinders of stainless steel, with 19.5 cm length, 9 mm o.d. and 4 mm i.d., and eleven 1 mm holes. The holes were countersunk in order to avoid clogging by the soil. Gas samples (6 ml) were taken through viton rubber septa at the top of the equilibrium chambers in the same way as for flux measurements (N 20-5/4 Machercy–Nagel, Düren).

Within 14 days after sampling, the gas samples were analysed on a gas chromatograph (Fractovap 4200, Carlo Erba, Italy) equipped with three detectors. The storage of gas samples in the same vials and rubber stoppers was tested by Sitaula *et al.* (1992). After 30 days storage they found a recovery of 97% N_2O, 100% CH_4 and 94% CO_2.

Moderate concentrations ($<40\ \mu l\ l^{-1}$) of N_2O were measured on an ECD (electron capture detector, type ECD40), and higher concentrations on a TCD (thermal conductivity detector). CH_4 was measured by FID (flame ionizing detector), and CO_2 by TCD. The column was a 25 m × 0.53 mm Poraplot Q (Chrompac, Middelburg, The Netherlands), connected directly to a 6-port injection valve (type C6W, VALCO Instrument Co. Inc., Houston, U.S.A.) with a 0.2 ml sampling loop. The carrier gas (He) flow was 7 ml min^{-1}. The temperatures of the oven, TCD and ECD were 35, 70 and 350°C, respectively. The outline of the gas chromatograph system is described by Sitaula *et al.* (1992).

N_2O and CH_4 concentrations in the soil cover chambers at the start of each closure period were estimated by the arithmatical mean of air samples taken 20 cm above the ground simultaneously with samples of flux and soil air. These measurements of atmospheric background displayed some variability ($SD = 0.09\ \mu l\ l^{-1}$ for CH_4 and $0.1\ \mu l\ l^{-1}$ for N_2O, $n = 19$). This variability was a combination of real variation in gas concentrations and analytical errors. The latter was important for ambient concentrations of N_2O due to base line instability. Standards with higher N_2O-concentrations gave reasonable stable signals (coefficient of variation = 5% for ECD determination of a 6.43 $\mu l\ l^{-1}$ standard and only 2–3% for TCD determinations of standards $>40\ \mu l\ l^{-1}$).

Gas samples were taken 3 h after placement of the soil cover chambers, except for two measurements which were extended to 5 h. In these cases (15 and 17 June) samples were taken after both 3 and 5 h. Flux was estimated by the increased concentration ← during the first 3 h. A comparison of 0–3 and 3–5 h flux measurements in 15 and 17 June gave an average estimated flux of 12.6 mg N_2O-N $m^{-2}\ d^{-1}$ in the 0–3 h estimate and 13.2 mg N_2O-N $m^{-2}\ d^{-1}$ in the 3–5 h estimate. Thus, there was no evidence of a retardation of the fluxes towards the end of the 5 h incubation.

The area under the flux curves (straight lines between data points, Figs 2 and 3) were used to estimate the accumulated N_2O emission and CH_4 uptake during the period of measurements (4 June–8 July).

Statistical analyses and calculations

The main effects and interactions of soil compaction, fertilization and date were tested with analyses of variance (ANOVA) and the Newman–Keul's test. The interaction replicate–compaction was used as an error term to test the effect of compaction. Studentized residuals were used to test the normality of the distributions with residual plots and procedure Univariate (SAS Institute, 1988). The concentration of CH_4 in the soil air was normally distributed and the CH_4 flux and the CO_2 concentrations were so close to normal distribution that they were treated statistically as if that was the case. Fluxes and soil atmospheric concentrations of N_2O were log-normally distributed and the data were log-transformed with natural logarithms before the statistical analyses were run. In the case of N_2O fluxes, some of the data were negative and a constant number (10) was added to all numbers before log-transformation and analyses of variance.

The means and standard errors of the mean (SEM) of log-normally distributed N_2O data were calculated using Finney's method, described by Parkin *et al.* (1988). They compared the method of moments, maximum likelihood and Finney's method to estimate mean, variance and coefficient of variation of log-normally distributed data. It was found that Finney's method had least bias when the coefficient of variation of the underlying log-normal frequency distribution exceeded 100%, which is the case for our N_2O data.

CH_4 uptake rates were calculated in accordance with first-order kinetics. This is in agreement with the observations by Sitaula and Bakken (unpubl.), who found that CH_4 concentrations in a soil cover chamber closely followed an exponential function during the first 8 h of incubation.

Since estimates of accumulated N_2O emission and CH_4 uptake are linear functions of the flux data, the standard error could be calculated accordingly, based on the estimate variance for each sampling day (after Cochran and Cox, 1957, p. 71).

In order to compare the fertilization effects on N_2O emission rates with those reported by Eichner (1990), the average value for daily fertilizer-derived N_2O emissions in g N_2O-N kg^{-1} mineral N added has been calculated (Table 2). This is calculated as the average daily N_2O emission in fertilized treatments minus average daily N_2O emission in the unfertilized treatment, divided by the amount of mineral N in the fertilizer.

In order to investigate treatment effects on N_2O diffusion, the ratio between measured flux and the measured concentration gradient (C_S–C_A, C_S = N_2O-concentration at soil depths of 7–12 cm, C_A = N_2O-concentration 20 cm above soil surface) was calculated for each treatment. The ratio was log-normally distributed and treatment means and SEM were calculated according to Finney's method (Parkin *et al.*, 1988). Log-transformed data were used in analyses of variance and the Newman–Keul's test. To avoid negative flux values, the calculations were based on observations from 15 June to 8 July.

RESULTS

N_2O emission and soil air concentration

Fertilization resulted in increased N_2O emission and concentration in soil air ($P < 0.01$). There was no significant difference between cattle slurry and NPK fertilization in uncompacted soils (Fig. 2, Table 2). In compacted soils the average soil air concentrations of N_2O were seven times higher in NPK-fertilized plots than in plots fertilized with 189 kg N ha^{-1} in cattle slurry. Very high N_2O concentrations in soil air were found in compacted, NPK-fertilized soil after heavy rain (Fig. 2). Moreover, high N_2O fluxes were observed from NPK-fertilized treatments, but in compacted soil the N_2O flux was lower than might have been expected considering the extremely high N_2O concentrations in the soil air (Fig. 2, Table 2). The amounts of cattle slurry added had little effect on N_2O flux and soil atmospheric concentration (Fig. 2, Table 2).

Emissions of <2.5 mg N_2O-N m^{-2} d^{-1} were found in the measurements taken in April. These data are not presented in the tables or figures.

The accumulated N_2O emission from the NPK-fertilized treatment for the period from June 4 to July 8 (Table 2) corresponded to 5.3% of added NH_4NO_3-N in compacted soil, and 3.9% in uncompacted soil. Fertilization with cattle slurry equivalent to 81 kg total N ha^{-1} gave an N_2O emission that corresponded to 3.1% of added NH_4-N in uncompacted soil, and 2.7% in compacted soil. Increasing levels of cattle slurry resulted in a reduction in N_2O emission per kg NH_4-N added. Fertilization with cattle slurry equivalent to 189 kg total N ha^{-1}, gave an N_2O emission of 1.9% of added NH_4-N in uncompacted soil, and 1.4% in compacted soil. The N_2O emissions from unfertilized treatments are subtracted from the total emissions in these estimates.

An increase in N_2O flux was first observed about 7 days after fertilization and was found to be most marked for compacted soils fertilized with NPK fertilizer (Fig. 2). Plots treated with cattle slurry gave lower N_2O fluxes and later increases than NH_4NO_3-fertilized plots. This was particularly obvious for compacted soils fertilized with a high level of cattle slurry, in which maximum N_2O emissions were observed at the end of the examination period.

The N_2O concentrations in soil air varied throughout the growing season (Fig. 2) with a temporal pattern depending on the fertilizer type ($P < 0.01$). The N_2O concentration in soil air started to increase 7 days after fertilization, in both NPK and cattle slurry fertilization. In unfertilized soil there was no marked increase in N_2O concentration in soil air throughout the investigation period. As for the N_2O flux, the seasonal variation in the soil air concentration was significantly affected by soil compaction ($P < 0.01$), fertilization ($P < 0.01$) and the interaction between soil compaction and fertilization

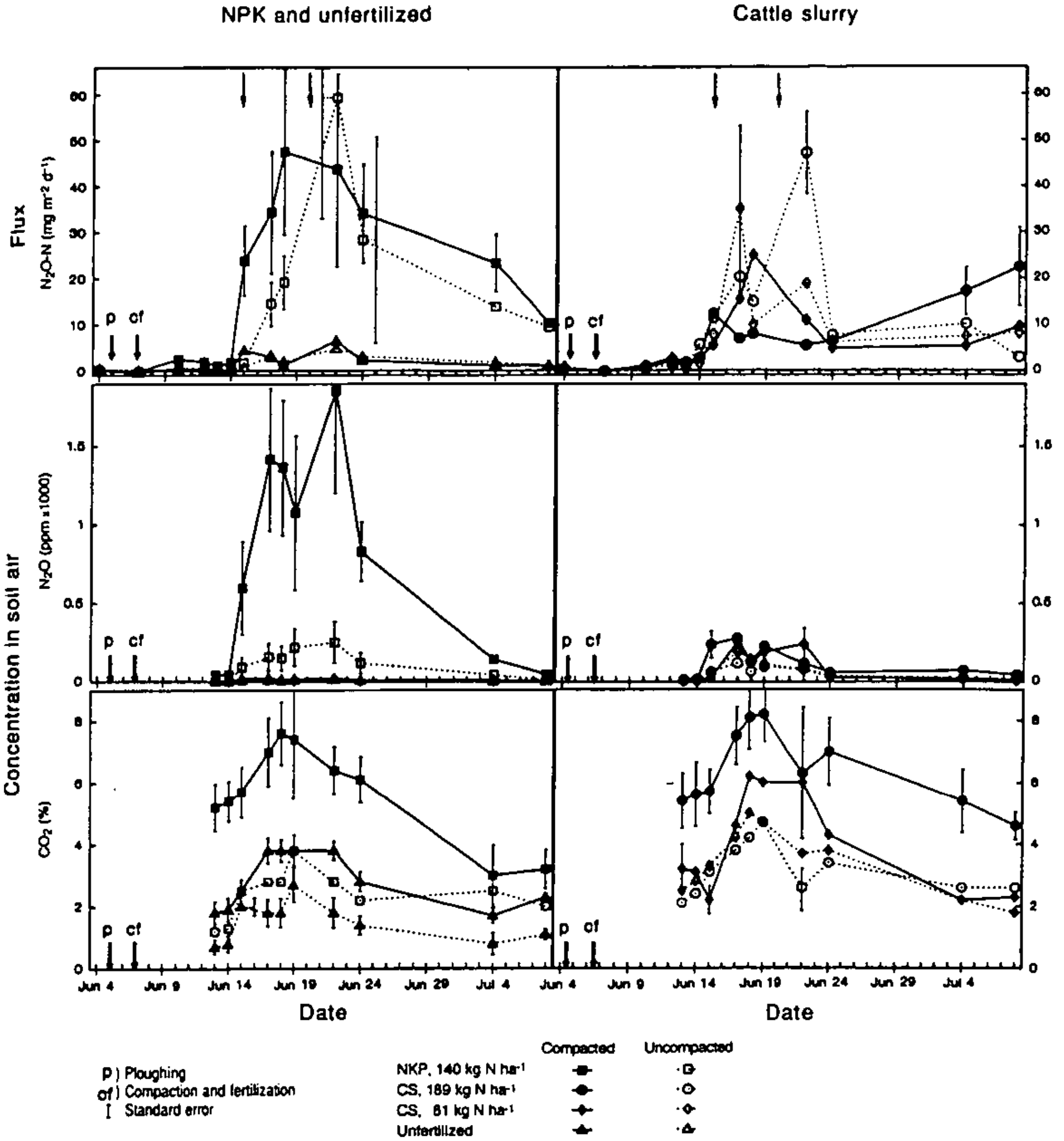

Fig. 2. N_2O and CO_2 concentrations in soil air (7–12 cm deep) and N_2O fluxes with different soil compaction, cattle slurry (CS) and NPK fertilization. Vertical lines are means ± SEM ($n = 4$). Arrows at the top indicate heavy rainfall (>40 mm d^{-1}).

($P < 0.01$). This is illustrated by the large peak in N_2O concentration in soil air in the compacted, NPK-fertilized treatment (Fig. 2). These effects were tested with ANOVA as interactions between time, fertilization and soil compaction.

There was a good correlation between N_2O concentration in the soil air and N_2O flux ($r = 0.67$, $P < 0.01$). The closest correlation was found in NPK-fertilized, uncompacted soil, where 50% of the variation in N_2O flux could be explained by the variation in N_2O concentration in soil air (Table 3). In compacted soil fertilized with 189 kg N in cattle slurry, the flux and soil air concentrations were not significantly correlated. The N_2O emission was either weakly correlated or not correlated with concentrations of CO_2 in soil air, but N_2O concentrations in soil air were more strongly correlated with CO_2 concentrations (Table 3). The air-filled porosity was negatively correlated with both N_2O parameters in the uncompacted soil, in contrast to compacted soil where no significant correlation was found.

Periods with heavy rain, resulting in lowered air-filled porosity, increased CO_2 and N_2O concentrations and N_2O fluxes. Peak values for N_2O fluxes were observed about 2 days after heavy rainfall (Figs 1 and 2).

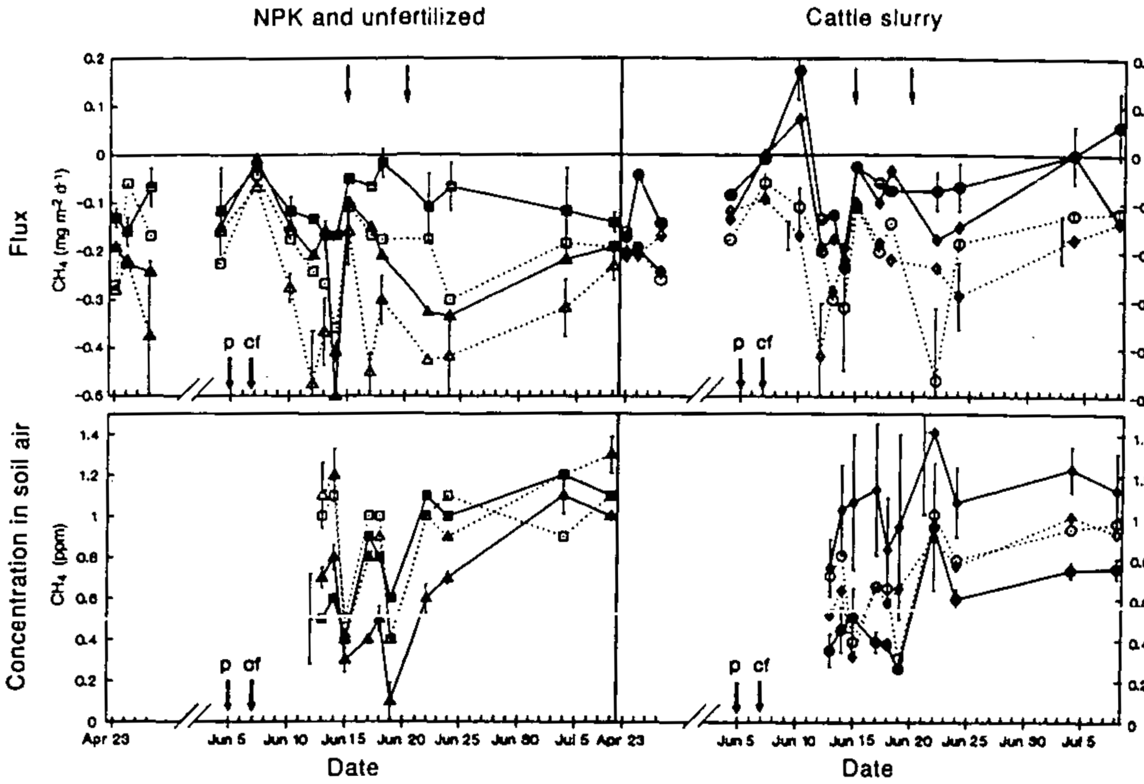

Fig. 3. CH_4 fluxes and concentrations in soil air (7–12 cm deep) with different soil compaction, cattle slurry (CS) and NPK fertilization. Same symbols as in Fig. 2.

Theoretically, an incubation period lasting as long as 3 h could cause retarded N_2O emissions as a result of a reduction in the concentration gradient from soil to chamber air. In >90% of the cases the N_2O concentration at 7–12 cm in soil air was more than eight times higher than that measured in the soil cover chambers after a 3 h closure (Table 4). Under such circumstances the N_2O concentration gradient was not reduced by more than 12–13% during the 3 h. Hence, the flux is unlikely to be more seriously affected.

CH_4 uptake and concentration in soil air

The accumulated CH_4 uptake by soil, for the period 4 June–8 July, ranged from 1 to 10 mg CH_4 m^{-2} (Table 2). Both fertilization ($P < 0.01$) and soil compaction ($P = 0.06$) reduced CH_4 uptake. Estimates of total CH_4 uptake based on straight lines between measured fluxes (Fig. 3) are presented in Table 2. The CH_4 uptake was reduced by 52% by soil compaction, 50% by fertilization and 78% by the combination of soil compaction and fertilization.

Table 2. CH_4 and N_2O-flux in the period 4 June–8 July, based on measured flux during the first 3 h of incubation; average values for each treatment ± SE and ratio between N_2O emission and concentration gradient from soil to atmosphere

Treatment	Accumulated flux		Fertilizer derived flux g N_2O-N d^{-1} kg^{-1} min-N†	Ratio*‡
	CH4 (mg m^{-2})*	N_2O (mg N m^{-2})		
Uncompacted				
NPK, 140 kg N ha^{-1}§	6.2 ± 0.6^{a}	532 ± 162^{a}	1.1	38 ± 13^{a}
CS, 189 kg N ha^{-1}	5.6 ± 0.4^{a}	358 ± 36^{a}	0.8	48 ± 9^{a}
CS, 81 kg N ha^{-1}	6.4 ± 0.6^{a}	252 ± 37^{a}	1.2	38 ± 10^{a}
Unfertilized	9.7 ± 0.6^{b}	62 ± 12^{b}		57 ± 15^{a}
Compacted				
NPK, 140 kg N ha^{-1}	3.0 ± 0.4^{a}	736 ± 112^{a}	1.6	12 ± 4^{b}
CS, 189 kg N ha^{-1}	1.1 ± 0.6^{a}	268 ± 44^{b}	0.6	19 ± 7^{ab}
CS, 81 kg N ha^{-1}	2.4 ± 0.7^{a}	217 ± 41^{b}	1.0	49 ± 23^{a}
Unfertilized	6.8 ± 0.5^{b}	57 ± 10^{c}		21 ± 5^{a}

*Within each column, figures which are not significantly different, share the same letter (Newman-Keul's test, $\alpha = 0.05$).

†Average daily fertilizer derived N_2O emission in g N_2O-N kg^{-1} mineral N added.

‡Ratio = 100 emission (mg N_2O-N m^{-2} d^{-1})/concentration gradient (μl l^{-1} N_2O), average values for each treatment ± SEM.

§NPK = NPK fertilizer; CS = cattle slurry.

Table 3. Correlation between N_2O emission, N_2O and CO_2 concentration in soil air and air-filled porosity (Pearson correlation coefficients)†

	N_2O-emission‡			Soil-N_2O	
Treatments	Soil-N_2O	Soil-CO_2	Air-filled porosity	Soil-CO_2	Air-filled porosity
Uncompacted					
NPK, 140 kg N ha^{-1}§	0.71^{***}	0.46^{**}	-0.48^{**}	0.78^{***}	-0.65^{***}
CS, 189 kg N ha^{-1}	0.59^{***}	0.15^{ns}	-0.45^{**}	0.59^{***}	-0.77^{***}
CS, 81 kg N ha^{-1}	0.54^{***}	0.33^{ns}	-0.49^{**}	0.72^{***}	-0.77^{***}
Unfertilized	0.44^{**}	0.24^{ns}	-0.32^{ns}	0.76^{***}	-0.57^{***}
Compacted					
NPK, 140 kg N ha^{-1}	0.64^{***}	0.48^{**}	-0.22^{ns}	0.41^{*}	0
CS, 189 kg N ha^{-1}	0.23^{ns}	-0.55^{**}	-0.14^{ns}	0.21^{ns}	0
CS, 81 kg N ha^{-1}	0.58^{***}	0	-0.14^{ns}	0.54^{***}	0
Unfertilized	0.60^{***}	0.56^{***}	0.22^{ns}	0.63^{***}	0

*Significant at 5% level; **significant at 1% level; ***significant at 0.1% level.

†*Numbers of observations behind each correlation coefficient are 33–36.*

‡N_2O-emission = ln N_2O emission; soil-N_2O = ln N_2O concentration 7–12 cm in soil air; Soil-CO_2 ± CO_2 concentration 7–12 cm in soil air; air-filled porosity = % air of soil volume 7–11 cm in soil.

§NPK = NPK fertilizer; CS = cattle slurry.

^{ns}Non-significant.

Table 4. Measured concentrations of N_2O in chambers after 3 h, expressed as a percentage of the concentrations measured in soil air. Frequency distribution of all measurements in the period 4 June–July

Chamber concentration in % of soil air concentration	Relative frequency
0.01	0.33
0.5–2.5	0.41
2.4–12.5	0.18
12.5–62.5	0.06
62.5–125	0.02

There was no significant difference between fertilization with NH_4NO_3 or that with cattle slurry. Neither did the amount of cattle slurry added affect the CH_4 uptake significantly. There was no interaction between fertilizers and soil compaction with respect to CH_4 uptake.

Both CH_4 uptake and CH_4 concentration in soil air varied throughout the growing season ($P < 0.01$), but there was no significant correlation between these two parameters.

In three of the fertilizer treatments (NPK, CS 189 and unfertilized), CH_4 concentrations and fluxes were lower in compacted than in uncompacted soil. In the CS 81 treatment, compacted soil had lower fluxes and much higher concentrations than those in uncompacted soil (Fig. 3).

Favourable conditions for N_2O production are unfavourable for CH_4 oxidation and a negative correlation between these two processes was expected. No clear correlation between CH_4 uptake or CH_4 concentration in soil air and N_2O emission or concentration in soil air was found, however (Table 5). The CH_4 concentration in soil air was negatively correlated with CO_2 concentration in soil air (Table 5), but there was no correlation between CO_2 concentration in soil air and CH_4 uptake in the soil.

DISCUSSION

N_2O emission and soil air concentration

Our estimated N_2O emissions (corresponding to 1–5% of added mineral N, Fig. 2, Table 2) are large compared with results reported in the review by Eichner (1990) where N_2O emissions corresponding to 0.01–1.7%, or 4.4–174.5 mg daily N_2O-N kg^{-1} added NH_4NO_3-N are reported. The large N_2O emissions found in our study can probably be explained by the extremely high precipitation together

Table 5. Correlation between uptake and soil air concentration of CH_4, N_2O emission and N_2O and CO_2 concentration in soil air (Pearson correlation coefficients)†

	CH_4-uptake‡		Soil-CH_4		
Treatments	N_2O-flux	Soil-N_2O	N_2O-flux	Soil-N_2O	Soil-CO_2
Uncompacted					
NPK, 140 kg N ha^{-1}§	0	0.37^{*}	0.06^{ns}	0.41^{*}	-0.73^{***}
CS, 189 kg N ha^{-1}	-0.37^{*}	0	0.29^{ns}	-0.20^{ns}	-0.47^{**}
CS, 81 kg N ha^{-1}	0	0.11^{ns}	0	-0.25^{ns}	-0.53^{***}
Unfertilized	0	0	0	-0.51^{**}	-0.76^{***}
Compacted					
NPK, 140 kg N ha^{-1}	0.35^{*}	0.44^{**}	0.17^{ns}	0.31^{ns}	-0.49^{**}
CS, 189 kg N ha^{-1}	0.13^{ns}	0.39^{*}	0.44^{**}	0	-0.47^{**}
CS, 81 kg N ha^{-1}	0.26^{ns}	0.12^{ns}	-0.26^{ns}	0	0.29^{ns}
Unfertilized	-0.17^{ns}	0.22^{ns}	-0.21^{ns}	-0.38^{*}	-0.53^{***}

*Significant at 5% level; **significant at 1% level; ***significant at 0.1% level.

†Numbers of observations behind each correlation coefficient are 33–36.

‡CH_4-flux = CH_4 uptake; Soil-CH_4 = CH_4 concentration 7–12 cm in soil air.

§NPK = NPK fertilizer; CS = cattle slurry.

^{ns}Non-significant.

with soil conditions that preclude efficient draining of the topsoil. As a result of abrupt textural change between the top layer and the gravelly subsoil, there is poor capillary contact to deeper soil layers and the soil moisture tension has to reach a relatively low level (pF 1.5–2) before draining to the gravel layer can begin. Thus the water will not drain out during long periods of rain and the water content in the soil will remain high. From 15 to 22 June there was 107 mm rain and the soil was already wet in advance of this rain [water-filled pore space (WFPS) in compacted soil was 81 and 73% in uncompacted soil]. Throughout this rainy period the water-filled pore space increased further and air-filled porosity in the soil decreased (Fig. 1). Even in uncompacted soil, air-filled porosity decreased to $<10\%$.

Because of the high water content in the soil and the weak structure in this sandy loam, the soil structure is easily deteriorated by soil compaction. Thus the tractor traffic on the compacted soils has probably caused greater damage on the soil structure and more anaerobic conditions than similar compaction would do in most areas with similar agricultural practises. We observed that soil compaction resulted in reduced air-filled porosity (Fig. 1) and increased CO_2 concentration in soil air (Fig. 2). In addition, Hansen (unpubl. data) demonstrated a decreased number of earthworms as a result of the compaction. The low air-filled porosity and high CO_2 concentrations in compacted soil indicate retarded diffusion through the upper soil layer. The CO_2 concentrations were particularly high in the treatments fertilized with 140 kg NH_4NO_3-N or 189 kg N in cattle slurry (Fig. 2). The same treatments had a very low N_2O emission: N_2O gradient ratio (Table 2).

As reviewed by Davidson (1991), denitrification becomes increasingly important as a source of N_2O when WFPS exceeds 60%. In our experiment the mean WFPS (10 June–8 July) was 82% in compacted soils. Fertilization with NO_3-N in compacted soil would therefore easily cause N_2O release by denitrification. The high peaks in N_2O concentration in soil air that were found when soil compaction and NH_4NO_3 fertilization were combined (Fig. 2) are probably due to high denitrification rates. N_2O emission caused by nitrification has probably played a minor role in our investigation because of the high moisture content in the soil. According to Davidson (1991), 30–70% WFPS is an optimal range for nitrification; in our study WFPS varied between 68 and 93%.

Considering the high WFPS values in our soil, a significant fraction of the N lost through denitrification will probably end up as N_2 (Davidson, 1991). Thus, measured N_2O-emissions (Table 2) probably constitute only a portion of nitrogen loss caused by denitrification. In a previous study in the same experimental field Hansen and Bakken (unpubl. data) estimated that nitrogen loss by denitrification during the first 2 weeks after fertilization with 126 kg NH_4NO_3-N ha^{-1} was increased by about 50 kg N ha^{-1} as a result of compaction. Nitrogen losses caused by denitrification are also reported elsewhere and the potential losses are large. von Rheinbaben (1990) refers to denitrification estimates by the ^{15}N balance and acetylene inhibition methods ranging from 0 to 77% of total fertilizer N. With the help of the acetylene method, Colbourn *et al.* (1984) found a denitrification potential of 320–390 g N ha^{-1} d^{-1} kg^{-1} applied NO_3-N in field and laboratory experiments.

In compacted soil fertilized with cattle slurry the denitrification rate is likely to increase throughout the growth period. This is indicated by increasing N_2O emissions towards the end of the examination period in these treatments (Fig. 2). Organic material and NO_3-N from nitrification of NH_4-N in the cattle slurry are available, and at the same time the air content in the compacted soil is very low. In uncompacted soil, the risk of denitrification towards the autumn is much less. The plants grow better, more NO_3 is taken up by the crop and more oxygen is available.

Source of error in the N_2O emission estimates

The use of an average value for atmospheric N_2O concentration as a starting concentration for each cylinder (time zero) creates some uncertainty in flux estimates. The variability of atmospheric background was quite large; the SD being 0.1 μl l^{-1}. An error of 0.1 μl l^{-1} in estimated N_2O accumulation during a 3 h incubation period is equivalent to a flux error of 0.2 mg N_2O-N m^{-2} d^{-1}. This is equivalent to 7 mg N_2O-N m^{-2} for the whole 35-day period of our measurements, which probably represents the maximum error due to the uncertainty in the initial concentrations. This uncertainty is equivalent to 12–13% of the total estimated emission in unfertilized treatments and $<4\%$ in the fertilized ones.

As most measurements in the present investigation were carried out around noon, diurnal variation and temperature increase could theoretically cause erroneously high N_2O emissions (Denmead *et al.*, 1979; Ryden *et al.*, 1978). The total N_2O flux values are probably not seriously affected. This is because of the reflecting surface of the soil cover chambers (Bakken *et al.*, 1987), and because most of the measured N_2O release took place in periods with cloudy weather (Blackmer *et al.*, 1982).

CH_4 uptake and concentration in soil air

Our estimates of CH_4 uptake in agricultural soil are in the same order of magnitude as the estimates of Mosier *et al.* (1991). The decrease in CH_4 uptake caused by fertilization is probably an effect of nitrogen (Fig. 2, Table 2). This is in agreement with the findings of Mosier *et al.* (1991), Steudler *et al.* (1989) and has been attributed to concentration of NH_3: NH_4^+ in the soil (Bedard and Knowles, 1989). NH_3

and CH_4 apparently compete for the same active site on the monooxygenases, the enzymes catalyzing the first oxidation step of CH_4 and NH_4^+ in methanotrophs and nitrifiers (Bedard and Knowles, 1989). Jones and Morita (1983) found that a concentration level of NH_4-N or NO_3-N of $10\,\mu l\,l^{-1}$ increased the CH_4 oxidation by ammonia oxidizers (*Nitrosomonas europea, Nitrosococcus oceanus*). Increasing concentrations of NH_4-N above this level (50 and $100\,\mu l\,l^{-1}$) decreased CH_4 oxidation, but CH_4 oxidation was not influenced by a similar increase in NO_3-N concentration.

In our study the mineral N concentrations in the soil were not determined during the growing season 1991, but earlier observations of NH_4-N concentrations in the same field experiment showed a range of NH_4-N concentration in the soil from 2 to $15\,\mu g\,g^{-1}$ dry wt (three measurements yearly in 5 previous years, unpubl.). Fertilization seemed to increase the amount of NH_4-N in the soil only slightly (average increase $= 0.5\,\mu g\,g^{-1}$ dry wt, max registered increase $= 6.4\,\mu g\,g^{-1}$ dry wt). We neither know the reactions of nitrifiers in this range, nor how methanotrophs would respond to increasing NH_4-N concentrations, but the slight differences in concentrations of NH_4-N suggest that the inhibiting effect of fertilization on CH_4 uptake cannot only be due to the NH_4-N concentration in the soil. On the other hand a bulk measurement of NH_4-N in the soil might be very different from the NH_3 actually available in the active site of the monooxygenases in nitrifiers and methanotrophs. Measured nitrification would be a much better measurement of ammonia available for nitrifiers and methanotrophs. Mosier *et al.* (1991) suggested that it is the N turnover rate (mineralization and nitrification) rather than the mineral N content that influences the CH_4 oxidation.

The reduction in CH_4 uptake caused by soil compaction (Fig. 2, Table 2) is probably attributable to retarded diffusion. This explanation is supported by the fact that soil compaction reduced the soil air concentration as well as the flux. The only exception to this pattern was CS 81 kg N ha^{-1}.

The lack of correlation between CH_4 uptake and N_2O emission (Table 5) is in contrast to the results of Mosier *et al.* (1991), who found that N_2O emissions from the soils were inversely related to CH_4 uptake. We had a very high moisture content and consequently low air-filled porosity during the whole period of measurement. Our results would probably have been different if we had measured flux over a large range of soil moisture contents.

To summarize, soil compaction and fertilization had an effect on both N_2O and CH_4 flux. The accumulated N_2O emission from the NPK-fertilized treatment corresponded to 5.3% of added NH_4NO_3-N in compacted soil, and 3.9% in uncompacted soil. Fertilization with cattle slurry equivalent to 81 kg total N ha^{-1} gave an N_2O emission corresponding to 3.1% of added NH_4-N in uncompacted soil, and 2.7% in compacted soil. Fertilization with cattle slurry equivalent to 189 kg total N ha^{-1}, gave a N_2O emission of 1.9% of added NH_4-N in uncompacted soil, and 1.4% in compacted soil. Increasing levels of cattle slurry resulted in a reduction in N_2O emission per kg NH_4-N added. The CH_4 uptake in the soil, ranging from 1 to 10 mg CH_4 m^{-2}, was reduced by 52% by soil compaction, 50% on average by fertilization and 78% by a combination of soil compaction and fertilization. Fertilization with NH_4NO_3 or cattle slurry had a similar effect on CH_4 uptake.

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Project Title Reference 14 HANSEN, MAEHLUM, BAKKEN Meeting Notes ☐
Work Sheet ☒
Signature Verified by ______ (signature/date)
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POLLUTANT: N_2O

FERTILIZER: (1.) AMMONIUM NITRATE (AN)
Application Method -- Hand Broadcast
Application Rate -- 140 kg N/ha

(2.) CATTLE SLURRY (CS)
Application Method -- Watering Can
Application Rate -- 189 kg N/ha
81 kg N/ha

Sampling Period: 27 days

1. Correction for Background: Total Cumulative flux − Total Cumulative flux
flux in mg N/m²

	AN			CS (189)			CS (81.)		
Soil Type	flux	BKG	NET	flux	BKG	NET	flux	BKG	NET
UnCompacted	532	62	470	358	62	296	252	62	190
Compacted	736	57	679	268	57	211	217	57	160

2. Conversion of Accumulated Flux to kg/ha   1 ha = 10^4 m²; 1 kg = 10^6 mg

	AN		CS (189)		CS (81)	
Soil Type	mg/m²	kg/ha	mg/m²	kg/ha	mg/m²	kg/ha
UnCompacted	470	4.7	296	3.0	190	1.9
Compacted	679	6.8	211	2.1	160	1.6

3. N_2O Emissions: Accumulated Loss * $\frac{44\ g\ N_2O/ha}{14\ g\ N/ha}$

	kg N_2O/ha		
Soil Type	AN	CS (189)	CS (81)
Uncompacted	14.8	9.4	6.0
Compacted	21.4	6.6	5.0

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4. N_2O EMISSION FACTORS: $E.F. = \dfrac{N_2O \text{ Emissions } (g\ N_2O/ha)}{\text{Application Rate } (kg\ N/ha)}$

APPLICATION RATES

$1\ kg = 10^3\ g$

AN = 140 kg N/ha

CS(189) = 189 kg N/ha

CS(81) = 81 kg N/ha

Example: AN - UNCOMPACTED SOIL

$$E.F. = \frac{14.8\ kg\ N_2O/ha \times \frac{10^3\ g}{kg}}{140\ kg\ N/ha\ \text{applied}} = \frac{14800\ g\ N_2O/ha}{140.\ kg\ N/ha} = \frac{106\ g\ N_2O\ \text{emitted}}{kg\ N\ \text{applied}}$$

	g N_2O emitted per kg N applied		
SOIL TYPE	AN	CS(189)	CS(81)
UNCOMPACTED	106	50	~~73.9~~ 74
COMPACTED	153	35	62

APPENDIX N

REFERENCE 39 AND ASSOCIATED HAND CALCULATIONS

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NO Versus N_2O Emissions From an NH_4^+-Amended Bermuda Grass Pasture

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We used an enclosure technique to monitor soil NO and N_2O emissions during early summer regrowth of Bermuda grass (*Cynodon dactylon*) on sandy loam in a humid, subtropical region of southern Texas. The evolution of both gases was substantially higher from plots harvested at the beginning of the experiment and fertilized 5 days later with 52 kg N ha^{-1} as $(NH_4)_2SO_4$ than from plots not harvested or fertilized. Emission of NO, but not N_2O, was stimulated by clipping and removing the grass, probably because eliminating the shading provided by the dense grass canopy changed these plots from cooler to warmer than unharvested plots, thereby stimulating the activity of soil microorganisms responsible for NO production. Neither gas flux was significantly affected by application of N until the next rainfall dissolved and moved the surface-applied fertilizer into the soil. Immediately thereafter, emissions of NO and N_2O increased dramatically to peaks of 160 and 12 g N ha^{-1} d^{-1}, respectively, and then declined at rates that closely paralleled the nitrification rate of added NH_4^+, indicating that the gases resulted from the activity of nitrifying microorganisms, rather than denitrifiers. Nitric oxide emissions during the 9-week measurement period averaged 7.2 times greater than N_2O emissions and accounted for 3.2% of the added N. The data indicate that humid, subtropical grasslands, which not only have large geographical extent but also have been subject to intense anthropogenic disturbance, contribute significantly to the global atmospheric NO_x budget.

INTRODUCTION

Numerous articles in both the popular and technical press reflect increasing public and scientific concern regarding not only the prospect for global climate change, but also additional potential health and environmental effects of changing atmospheric trace gas concentrations. Gaseous N oxides, N_2O and NO_x ($NO + NO_2$), are directly or indirectly involved in "greenhouse warming," as well as the production and consumption of atmospheric oxidants (e.g., ozone and hydroxyl radical) and the photochemical formation of nitric acid, which is the fastest growing component of acidic deposition [*Logan*, 1983]. Because microbial processes in soil is one of the principal sources of atmospheric N oxides, it becomes important to determine the magnitude of this source and, if appropriate, to develop control technologies, such as alternative soil management practices or improved fertilizer formulations and application techniques.

During the last decade, numerous measurements of soil N_2O emissions have enhanced understanding of the factors controlling this process and of the importance of soil emissions compared to other sources of this gas [*McElroy and Wofsy*, 1986; *Sahrawat and Keeney*, 1986; *Eichner*, 1990; *Matson and Vitousek*, 1990]. This paper focuses instead on NO_x exchange between soil/plant systems and the atmosphere, for which relatively few measurements have been made, and compares the magnitude of soil NO_x exchange with that of N_2O. In addition to its important impacts on the chemistry of the atmosphere, it has been suggested that soil NO evolution comprises a significant fraction of the unaccounted N losses typically observed in soil N balance sheets, and that the emission, transport, and subsequent redeposition of NO_x results in substantial redistribution of N both within and among natural and agricultural ecosystems (E. J. Williams et al., NO_x and N_2O emissions from soils, submitted to *Global Biogeochemical Cycles*, 1992; hereinafter referred to as submitted manuscript, 1992).

Short-term soil emission of NO_x (usually greater than 90% NO) has recently been measured from several different ecosystem types under a variety of soil and climatic conditions around the world (E. J. Williams et al., submitted manuscript, 1992, Table 1). Conspicuously absent from the literature, however, are comprehensive longer-term studies that yield tenable estimates of total annual NO evolution from any particular site. Further extrapolating existing data to assess the overall contribution of soil NO emissions to the global atmospheric NO_x budget is also confounded by the apparent existence of multiple biotic and abiotic sources of the gas. For example, elevated NO emission rates are sometimes associated with very wet or waterlogged soils and are stimulated by addition of NO_3^-, indicating that the source of NO is denitrification [*Johansson and Granat*, 1984; *Kaplan et al.*, 1988]. In drier situations, however, NO emissions apparently arise primarily from chemoautotrophic nitrification [*Anderson and Levine*, 1987; *Tortoso and Hutchinson*, 1990], which is subject to an entirely different set of controllers. Because NO and N_2O are produced by the same microbial processes, there may exist a relationship between their evolution rates from soil that would permit using the extensive data base of N_2O emission measurements to forecast NO emissions at similar sites, but the paucity of simultaneous field measurements of the two gas emission rates precludes describing any such relationship.

To overcome some of these limitations of the existing data base of soil N oxide emission measurements, we measured NO and N_2O emissions from a Bermuda grass (*Cynodon dactylon*) pasture in a humid, subtropical region of southern

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Texas. This typical subtropical grassland site was chosen because of its similarity to tropical grasslands that are believed to be one of the more important biogenic sources of atmospheric N oxides, and because subtropical ecosystems not only have large geographical extent but also have typically been subject to intense anthropogenic disturbance. Specific objectives of the research were to determine the effect on the pasture's NO and N_2O emission rates of (1) selected environmental parameters, (2) various cultural practices such as harvest and fertilization, and (3) changes in soil inorganic N pool sizes and transformation rates.

METHODS AND MATERIALS

Two management schemes were imposed on 10 m × 30 m rectangular plots in an established 30-ha Bermuda grass pasture on well-drained, very uniform Kenney sandy loam (a member of the loamy, siliceous, thermic, *Grossarenic paleudalfs*). Selected soil and climatic parameters are listed in Table 1. The two treatments, namely, minimum cultural management (spring harvest followed by a single annual maintenance application of N and P fertilizers) and intensive cultural management (harvest and fertilization repeated on a 9-week cycle throughout the growing season), were replicated four times in a completely randomized block design. The source of fertilizer N was $(NH_4)_2SO_4$; the amount applied on each fertilization date (which always followed harvest by 5 days) was that recommended for maximum protein production based on soil tests performed by the Texas A&M University Soil Testing Laboratory at College Station, Texas.

The data reported here were taken during the second of four 9-week harvest/fertilization cycles during the 1989 growing season and immediately followed the early spring cycle during which plots under both management schemes were treated identically. Measurements commenced May 24, the day before harvest, and continued through July 26. Plots under intensive cultural management received 52 kg N ha^{-1} on May 30. The scheduled frequency of NO and N_2O flux measurements was highest immediately following harvest and fertilization because these management inputs were expected to cause highest soil N transformation rates and therefore highest N oxide emission rates. Precipitation was measured and recorded daily at a meteorological station located about 100 m outside the field plots.

TABLE 1. Selected Soil and Climatic Data for the Experimental Site

Parameter	Value
Soil (0–15 cm)	
*p*H (1:1 water)	6.1
Cation exchange capacity, cmol kg^{-1}	4.8
Bulk density, g cm^{-3}	1.6
Infiltration rate, cm h^{-1}	20
Organic matter, g kg^{-1}	17
Sand g kg^{-1}	770
Silt, g kg^{-1}	130
Clay (predominantly kaolinite), g kg^{-1}	90
Water retention, g kg^{-1}	
0-kPa suction	250
30-kPa suction	70
Climate	
Mean annual rainfall, cm	102
Mean annual air temperature, °C	
Maximum	26.7
Minimum	13.0
Growing season, days	304

The N_2O fluxes for this period are a subset of a full year's measurements reported elsewhere (G. L. Hutchinson et al., Microbial, environmental, and management controls on nitrous oxide emission from a Bermuda grass pasture, submitted to *Soil Science of America Journal*, 1992; hereinafter referred to as submitted manuscript, 1992) and are repeated here to facilitate comparing them with NO fluxes from the pasture, which were measured during only one 9-week cycle. To begin each measurement of N_2O flux, a vented, cylindrical soil cover (30 cm diameter × 30 cm high) was mounted atop a permanently installed ring (30 cm diameter × 7.5 cm high) driven 5 cm into the soil, and the two were sealed together by overlapping the seam between them with an external large rubber band. The enclosures (about 25-L total volume) were constructed from rigid polyvinyl chloride pipe using design criteria suggested by *Hutchinson and Mosier* [1981], then insulated with polyurethane foam and covered with reflective aluminized polyester film to minimize internal heating by solar radiation. The enclosures caused no significant perturbation of air or soil temperatures over relatively short deployment periods [*Hutchinson and Livingston*, 1992].

Accumulation of N_2O beneath each enclosure after 10 and 20 min was determined by drawing 30-mL air samples through the covers' sampling ports using 60-mL polypropylene syringes fitted with nylon stopcocks. The sampling rate was slow enough to avoid imposing significant negative pressure on the covered soil. The N_2O concentration at the time of each cover's installation was assumed the same as that of an ambient air sample collected at the field site. All samples were collected between 1100 and 1200 LT and transported to the laboratory in an insulated container for analysis within 12 hours by gas chromatography using electron capture detection [*Mosier and Mack*, 1980]. The nonlinear equation proposed by *Hutchinson and Mosier* [1981] was adopted to calculate the flux when the data met criteria established by *Anthony and Hutchinson* [1990].

Nitric oxide flux from the soil areas defined by the permanent rings described earlier was measured using a soil cover similar to that described above, but modified to recirculate air from beneath the enclosure through a Scintrex LMA-3 Luminox Monitor. (Trade names and company names are included as a matter of convenience to the reader, and such inclusion does not constitute any preferential endorsement by the U.S. Department of Agriculture of products named over similar products available on the market.) Because the instrument is sensitive only to NO_2, the 1.4 L min^{-1} sample air stream passed first through a CrO_3 converter to oxidize NO to NO_2, then through the analyzer, and finally through a scrubber to remove remaining NO, NO_2, and water vapor before returning to the enclosure. Concentration data were recorded once per minute.

Because NO emitted by soil is rapidly oxidized by ambient ozone to NO_2, which is strongly sorbed by both soil and plant surfaces, no readings were taken during the first 2 min after cover installation to allow time for ambient ozone and NO_2 captured beneath the enclosure to be destroyed or sorbed. Periodic checks confirmed that the concentrations of both gases declined to near zero within this period, which we also interpreted as evidence that net soil emission of NO_2

was negligible. After correcting for the dilution caused by returning NO_x-free air, the flux of NO was computed from its rate of accumulation (estimated by linear regression) between 2 and 6 min following installation of the cover on each permanent ring. Consistently strong correlations between the observed concentrations and time (R^2 was greater than 0.96 in all but four of 88 cases) was interpreted as compelling evidence that mixing within the enclosure was adequate. The additional complexity associated with air recirculation was required to avoid introducing ambient NO, NO_2, or ozone during the sampling period without creating the need to carry cylinders of compressed zero air into the field. All NO flux measurements were completed between 1400 and 1600 LT.

Each day that gas fluxes were determined, we recorded the outputs of soil water/temperature sensors (model MC-310A, Soiltest, Inc., Evanston, Illinois) buried at 2- and 10-cm depths in each plot, collected duplicate soil samples from 0- to 2- and 2- to 10-cm depths in each plot, and subsampled duplicate polyethylene bags of soil that had been buried at 2- and 10-cm depths in each plot on the day of fertilization. Soil in the buried bags was a subsample of the 0- to 2- and 2- to 10-cm samples taken the day prior to fertilization and was amended with sufficient N to simulate each plot's fertilization rate; the bags buried at both depths received identical amendments. On days 19, 33, and 48 following harvest, the remaining soil in each buried bag was replaced with a fresh sample to ensure that the N transformation data they yielded were measured at inorganic N concentrations similar to those in bulk soil outside the bags. All soil samples were immediately frozen until they could be extracted for analysis.

To determine soil NH_4^+, NO_2^-, and NO_3^- pool sizes and transformation rates, inorganic soil N was extracted from the frozen soil samples by shaking with 1 *M* KCl (1:5 soil to solution ratio) on a wrist action shaker for 1 hour. The suspensions were filtered through glass fiber filters [*Sparrow and Masiak*, 1987] and analyzed using modified Technicon Industrial Method 786-86T for NH_4^+ analysis and modified Technicon Industrial Method 818-87T for NO_2^- and NO_3^- analyses on a Technicon TRAACS 800 continuous flow analytical system (Technicon Industrial Systems, Bran + Luebbe Analyzing Technologies, Elmsford, New York).

RESULTS AND DISCUSSION

Rates of NO and N_2O evolution from the field plots under both minimum and intensive cultural management are presented in Figure 1*a* along with soil NH_4^+ and NO_3^- concentrations (Figures 1*b* and 1*c*) and soil temperatures and water contents (Figure 1*e*) at both sampling depths. Soil temperature data are included only to show that there were no significant long-term temperature trends that might account for observed changes in the soil's inorganic N concentrations or N oxide emission rates. Rainfall during the experimental period is presented in Figure 1*d*. The NO_2^- concentrations of both bulk soil samples and buried bag subsamples never exceeded 0.05 mg N kg^{-1} and are not presented.

Effect of Harvest

Soil emission of NO, but not N_2O, was apparently stimulated by clipping and removing the grass from plots under intensive cultural management (Figure 1*a*). The near doubling in NO evolution rate from the day preceding to day following harvest was statistically significant ($P < 0.05$) and was reinforced by an additional 77% increase over the next 3 days (Figure 2). Nitric oxide emissions then remained nearly constant at about 17 g N ha^{-1} d^{-1} (2–3 times the emission rate of unharvested plots) until at least the eleventh day after harvest. Before the next scheduled set of measurements on day 15, rainfall washed the $(NH_4)_2SO_4$ (surface-applied on day 5) into the soil, causing the effect of harvest to be obscured by the much larger response to fertilization.

It is possible that the enhancement of NO evolution by harvest resulted from microbial transformation of N contained in exudates from the cut grass stems or in detritus that fell to the soil surface during harvest. Indirect support for this hypothesis was provided by *Bleakley and Tiedje* [1982], who found that N_2O was evolved from bruised or lacerated excised plant tops after several hours aerobic incubation in sealed bottles under light; the amount of NO evolved was not determined. Apparently, the damaged tissue stimulated growth of N_2O-producing microorganisms commonly isolated from plants (e.g., *Serratia* sp.). *Bleakley and Tiedje* [1982] also presented evidence that *Serratia* sp. produce N_2O, but not NO, from labeled NO_3^- + NO_2^-, but because the data were obtained in anaerobic culture, they do not rule out the possibility of aerobic NO production by these organisms. Nevertheless, it is unlikely that this potential source of NO would persist more than a day or two in the hot, dry weather that prevailed following harvest.

A second potential explanation for elevated NO emissions during this period is that harvest eliminated foliar NO uptake and metabolism by the grass canopy; however, reported NO deposition velocities are too low to account for the large difference in measured net emission rates of harvested versus unharvested plots [*McRae and Russell*, 1984]. Also unlikely is an explanation based on work by *Klepper* [1979], who proposed that the NO_x evolved from herbicide-treated soybean (*Glycine max*) leaves resulted from reaction of accumulated NO_2^- with other unidentified plant metabolites. We know of no reason to suspect that clipping the grass stimulated NO_2^- accumulation in either the dead or live plant material that remained on the plots.

We believe that the enhancement of NO emissions by harvest was more likely related to the increase in soil temperature that accompanied eliminating the shading provided by the dense grass canopy on intensively managed plots. Figure 2 shows that after harvest, these plots changed from cooler to warmer than unharvested plots, which would be expected to stimulate the activity of soil microorganisms responsible for NO production, probably chemoautotrophic nitrifying bacteria [*Hutchinson et al.*, 1992]. Other authors [*Slemr and Seiler*, 1984; *Williams et al.*, 1988] have reported that NO emission from aerobic soil is extremely sensitive to changes in temperature. Although the temperature difference between plots under the two treatments disappeared with the onset of a lengthy period of cloudy weather on day 5 following harvest, elevated NO emissions from the plots under intensive cultural management continued, probably because nitrifier activity continued unabated, as evidenced by the continually increasing NO_3^- concentrations shown in Figure 1*b*. The most probable source of substrate NH_4^+ during the early postharvest period was mineralization of organic N in response to the abrupt rise in soil temperature, but after day 5, slow diffusive movement of surface-applied

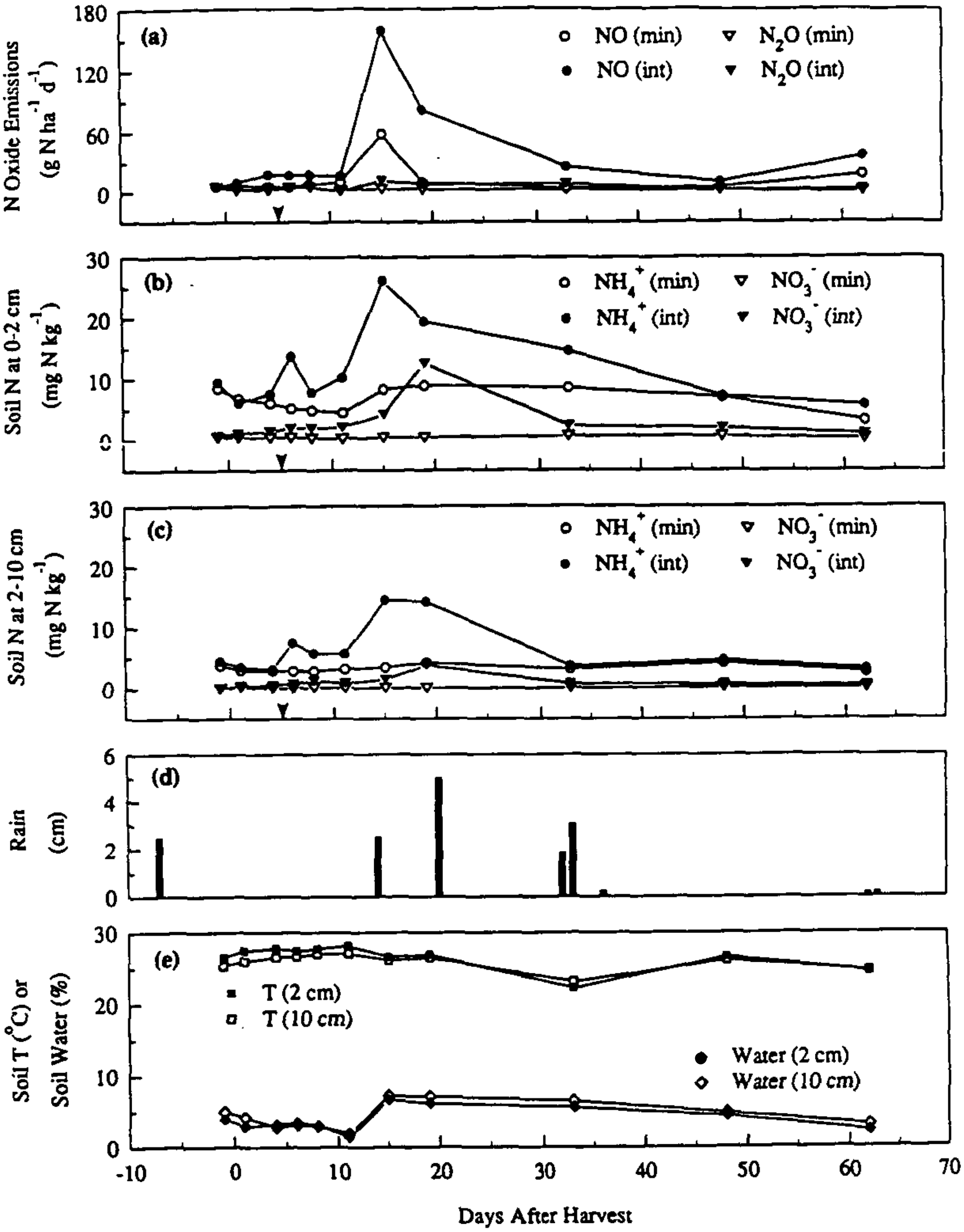

Fig. 1. Early summer data from a Bermuda grass pasture subject to minimum (min) or intensive (*int*) cultural management. (*a*) NO and N$_2$O emission rates. (*b*) Soil NH$_4^+$ and NO$_3^-$ concentrations at 0- to 2-cm depth. (*c*) Soil NH$_4^+$ and NO$_3^-$ concentrations at 2- to 10-cm depth. (*d*) Precipitation. (*e*) Soil temperature and water content at 2- and 10-cm depths. Data points represent (*a*) the means of measurements from four replicate plots ($n = 4$), (*b*) and (*c*) the means of duplicate samples from each of the four replicate plots ($n = 8$), and (*e*) the means over the four replicates of both treatments ($n = 8$). The date of N fertilizer application is indicated by a pointer on the abscissa.

(NH$_4$)$_2$SO$_4$ into the soil probably contributed and may have dominated. As a result, only the data measured on days 1 and 4 in Figures 1 and 2 should be interpreted as reflecting the unconfounded effect of harvest.

Effect of Fertilization

Soil emission of N$_2$O and especially NO were strongly stimulated by application of 52 kg N ha^{-1} as (NH$_4$)$_2$SO$_4$

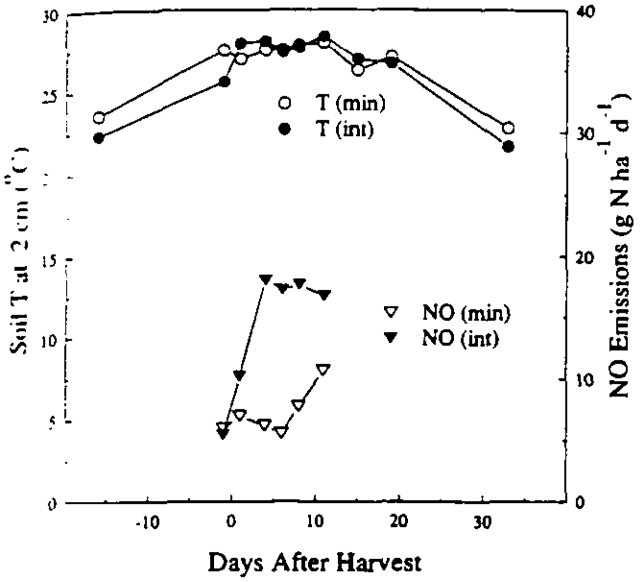

Fig. 2. NO emission rate and soil temperature at 2-cm depth during the period prior to and immediately following harvest of a Bermuda grass pasture subject to minimum (min) or intensive (int) cultural management. Data points represent the means of measurements from four replicate plots.

(Figure 1*a*). Although the fertilizer was applied on day 5 following harvest, its effect on N oxide evolution was small until the first rainfall (Figure 1*d*) dissolved and moved the surface-applied fertilizer into the soil. Presence of the $(NH_4)_2SO_4$ is also not fully reflected in the data in Figures 1*b* or 1*c* until after rainfall, because most of the fertilizer granules were apparently included in the surface litter that was purposely brushed aside prior to soil sampling.

Soil N dynamics. The rain on day 14 moved a substantial fraction of the fertilizer into the 2- to 10-cm soil layer ($P <$ 0.05), where the NH_4^+ concentration increased from 5.7 to 15 mg N kg^{-1}, compared to an increase from 10 to 26 mg N kg^{-1} in the surface layer ($P < 0.005$). Ammonium concentrations then decreased to prefertilization levels over a 1- to 2-week period in the lower soil layer and a 3- to 4-week period in the surface layer. Rapid accumulation of NO_3^- in both soil layers during the early part of this period confirms that microbially mediated nitrification was at least partially responsible for the observed reduction in NH_4^+ concentration. The sharp reduction in NO_3^- concentration at both sampling depths between days 19 and 33 was probably due both to root uptake and to leaching during the large precipitation event on day 20. Soil NO_3^- concentration in plots under minimum cultural management remained consistently very low at both sampling depths. On day 15 the difference in total inorganic N (NH_4^+ + NO_2^- + NO_3^-) contents of the top 10 cm of plots under minimum versus intensive cultural management accounted for only about one-half of the applied fertilizer, suggesting that a significant fraction may have been lost by NH_3 volatilization during the 9 days that fertilizer granules laid on the soil surface exposed to the hot, dry conditions that prevailed during this period [*Nelson*, 1982].

Note that the NH_4^+ concentration of the surface layer of unfertilized plots also increased significantly ($P < 0.005$) following the rain on day 14 (from 4.5 to 8.3 mg N kg^{-1}). Possible explanations for this observation include (1) movement by rainwater of applied $(NH_4)_2SO_4$ from fertilized to unfertilized plots, either by surface flow or lateral subsurface flow, both of which seem extremely unlikely in soil with such a high infiltration rate (Table 1), (2) deposition on the surface litter of a portion of the gaseous NH_3 that was probably volatilized from adjacent intensively managed plots over the previous 9 days, and (3) the burst of mineralization/nitrification activity that typically occurs immediately after wetting very dry soil [*Davidson*, 1992; *Hutchinson et al.*, 1992]. The second alternative was proposed to be a significant pathway for N redistribution by *Sinclair and Van Houtte* [1982] and was measured (albeit on a larger scale) by *Hutchinson and Viets* [1969]. However, the total inorganic N content of unfertilized soil in the bags buried at 2-cm depth in these plots increased over the first 10 days by an amount nearly double the aforementioned rise in NH_4^+ concentration of bulk soil. Because the buried bags were isolated from atmospheric NH_3, we concluded that mineralization, followed by nitrification, was responsible for the increases in their total inorganic N contents, and was probably also responsible for the rain-induced increase in NH_4^+ concentration of plots under minimum cultural management measured on day 15.

The nitrification rate of fertilizer NH_4^+ is shown in Figure 3. These data were computed from changes in the NO_2^- + NO_3^- concentrations of soil in the buried bags and represent mean rates of nitrification from one sampling date to the next, so they were plotted midway between the two dates. Because $(NH_4)_2SO_4$ was thoroughly mixed with soil placed in the bags buried in intensively managed plots on the day of fertilization, its nitrification was not subject to the same 9-day delay as fertilizer applied to the surface of the same plots. Nitrification rates at 2- and 10-cm depths rose for

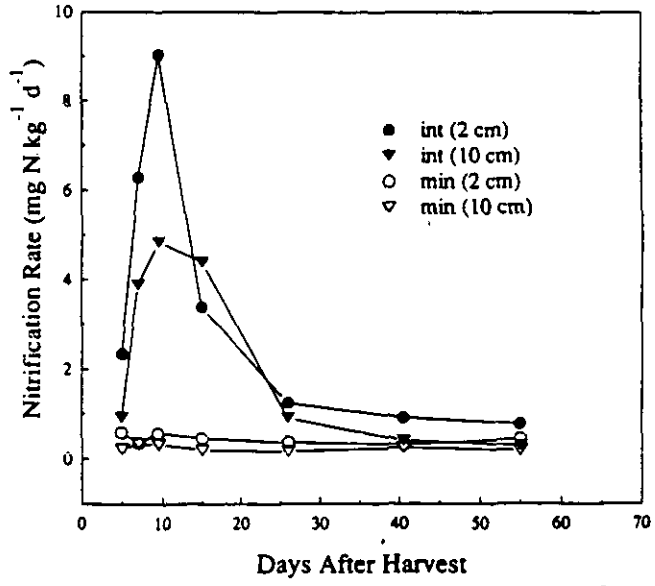

Fig. 3. Nitrification rates measured in soil samples taken from 0- to 2- and 2- to 10-cm depths and then buried in polyethylene bags at 2- and 10-cm depths, respectively, in a Bermuda grass pasture subject to minimum (min) or intensive (int) cultural management. Data points represent the mean change in soil NO_2^- + NO_3^- concentration in duplicate bags buried at each depth in each of the four replicate plots and are plotted at the midpoint of the period over which the change was determined ($n = 8$).

about 5 days to peaks of 9.0 and 4.8 mg N kg^{-1} d^{-1}, respectively, following which they decreased rapidly at first, then more slowly as the process neared completion after 3–4 weeks. Continual increases in the total inorganic N concentrations of the buried bags reflect the soil's nontrivial capacity for N mineralization; mean mineralization rates computed from the data for bags buried 2 cm beneath the surface of plots under minimum and intensive cultural management were 0.5 and 0.9 mg N kg^{-1} d^{-1}, respectively, and for bags buried at the 10-cm depth, 0.3 and 0.6 mg N kg^{-1} d^{-1}, respectively.

Soil N oxide emissions. The response of soil NO emissions to fertilization followed by rainfall was both large and rapid (Figure 1). After only 1 day, the emission rate from plots under intensive cultural management had increased to 160 g N ha^{-1} d^{-1}, nearly an order of magnitude greater than the rate measured prior to rainfall. Thereafter, NO evolution declined slowly over a 3- to 4-week period to the levels observed before harvest and fertilization. The unexpectedly large increase in NO emission from plots under minimum cultural management on day 15 had much shorter duration. Peak emissions of 58 g N ha^{-1} d^{-1} had decreased by day 19 to the level measured prior to the precipitation event that triggered enhanced NO evolution. It is likely not fortuitous that the increase in soil NH_4^+ concentration induced by the same event (described earlier) was also much smaller than the coincident increase in intensively managed plots.

The statistically significant ($P < 0.05$) increase in NO evolution from intensively managed plots to 36 g N ha^{-1} d^{-1} on the final sampling day of the experimental period probably resulted from the same phenomenon responsible for enhanced emissions from unfertilized plots on day 15, i.e., a burst of mineralization/nitrification activity induced by the 0.08-cm rain shower that fell on very dry soil just prior to sampling. Although the shower was small and did not cause a measurable increase in soil NH_4^+ or NO_3^- concentration, even smaller precipitation amounts have been shown to have this consequence. For example, *Williams and Fehsenfeld* [1991] measured an immediate 10-fold increase in the NO emission rate of very dry native shortgrass prairie in Colorado following precipitation less than 0.03 cm. Emission of NO from plots under minimum cultural management also responded to the small rain shower that occurred prior to sampling on day 62, but with the smaller magnitude expected of a soil-plant system under greater N stress.

Emission of N_2O from intensively managed plots followed a pattern similar to that of NO, but on a much smaller scale. For example, the peak emission rate on day 15 following harvest was only 12 g N ha^{-1} d^{-1}, compared to 160 g N ha^{-1} d^{-1} for NO. The evolution of N_2O from plots under minimum cultural management was frequently not significantly different from zero ($P < 0.05$). G. L. Hutchinson et al. (submitted manuscript, 1992) gave a detailed description of the N_2O emission rates of plots under both treatments.

Temporal variation in the N oxide emission rates shown in Figure 1*a* was strikingly similar to that of the nitrification rates plotted in Figure 3, after allowing for the offset in time between nitrification of the fertilizer in buried bags versus that applied to the surface of the same plots. Comparison of Figure 1*a* with Figure 1*b* suggests an equally strong relationship between the soil's N oxide emission rates and its NH_4^+ concentration at 0–2 cm, probably because of the dependence of the emission rates on nitrifier activity [*Hutchinson et al.*, 1992], which is in turn a function primarily of soil NH_4^+ levels. Based on measurements at several sites in Pennsylvania, *Williams et al.* [1988] reported that the correlation of NO emissions with soil NO_3^- concentration was much stronger than its correlation with soil NH_4^+ concentration, but the opposite was true at this site ($R^2 = 0.69$ for NH_4^+ at 0–2 cm, and 0.34 for NO_3^- at the same depth). One possible reason for these opposing observations is that denitrification was the source of at least part of the NO measured by *Williams et al.* [1988], while oxygen diffusion rates in the well-drained sandy loam studied here were probably never restricted enough to support denitrification activity. An alternative explanation that does not require assumption of a denitrification source is that in comparisons across widely divergent ecosystem types, N oxide emissions may be related to NO_3^- concentration simply because this ion generally accumulates where N availability exceeds C availability to soil microorganisms, a condition that also favors a leaky N cycle [*Hutchinson and Davidson*, 1992].

Spatial variability in the NO emission rates reported in Figure 1*a* was substantially smaller than for N_2O. For example, the coefficient of variation (CV) for NO emissions from plots under intensive cultural management averaged 40%, and for N_2O, 117%. High CVs for soil N_2O evolution have been reported by many other authors [e.g., *Folorunso and Rolston*, 1984], particularly when the source of N_2O is denitrification. Because the source of both the NO and N_2O at our site was probably nitrification, an oxidative process that typically exhibits smaller spatial variability, we suspect that the threefold difference in CVs reflects the greater importance of sampling and analytical errors for N_2O, which had a much lower ratio of mean flux to minimum detectable flux than was the case for NO.

The ratio of NO to N_2O emission rates over the 11 sampling days averaged 6.7 ± 2.9 (standard error (SE)) for plots under minimum cultural management and 7.7 ± 2.1 (SE) for plots under intensive cultural management. These values are similar to ratios observed in other studies where nitrification was the predominant source of both gases [*Slemr and Seiler*, 1984; *Davidson*, 1992] but somewhat larger than ratios observed where denitrification was a significant source. For example, *Kaplan et al.* [1988] reported that soil NO evolution was only about 3 times greater than N_2O evolution from a tropical rain forest where denitrification undoubtedly contributed to N oxide production, and *Anderson and Levine* [1987] found that annual NO and N_2O emissions from a Virginia corn (*Zea mays*) field differed by less than a factor of 2. The latter authors also reported that N_2O evolution exhibited much greater variability and was generally detectable only when soil water content approached or exceeded field capacity, indicating that the principal source of N_2O was denitrification. Water content of the well-drained sandy loam at our site (Figure 1*e*) never exceeded that at 30 kPa soil water suction (Table 1), thus supporting our contention that both gases resulted from the activity of nitrifying microorganisms, which have been shown in several laboratory incubation studies to exhibit larger NO:N_2O production ratios than denitrifiers [*Lipschultz et al.*, 1981; *Anderson and Levine*, 1986; *Hutchinson et al.*, 1988].

TABLE 2. Total and Fertilizer-Derived NO and N_2O Emissions During the 9-Week Experimental Period

Management	Parameter and Units	NO	N_2O
Intensive	Total emissions, kg N ha^{-1}	2.37 (0.32)	0.35 (0.03)
Minimum	Total emissions, kg N ha^{-1}	— 0.69 (0.21)	0.15 (0.03)
Intensive	Fertilizer-derived emissions, kg N ha^{-1}	—	—
		1.68 (0.39)	0.20 (0.03)
Intensive	Fertilizer-derived emissions (% of applied)	3.22 (0.74)	0.39 (0.06)

Values in parentheses are the SE of each mean.

SUMMARY AND PERSPECTIVE

Soil emission of NO, but not N_2O, was slightly enhanced by clipping and removing the grass from plots under intensive cultural management, probably because eliminating the shading provided by the dense grass canopy changed these plots from cooler to warmer than unharvested plots, thereby stimulating the activity of soil microorganisms responsible for NO production. The evolution of both gases, but especially NO, was strongly enhanced by application of 52 kg N ha^{-1} as $(NH_4)_2SO_4$. Because N oxide emission rates paralleled the nitrification rate of applied NH_4^+, and because soil water content never exceeded field capacity, we believe that both gases resulted from the activity of nitrifying microorganisms, rather than denitrifiers. This conclusion is consistent with data recently reported by *Tortoso and Hutchinson* [1990] and was confirmed by *Hutchinson et al.* [1992] during laboratory incubation of soil from the field plots described here. They reported that high NO emission rates induced by soil amendment with NH_4NO_3 were virtually eliminated by nitrapyrin [2-chloro-6-(trichloromethyl)-pyridine], a potent, specific inhibitor of chemoautotrophic nitrification. There was no evidence that denitrification contributed to the NO or N_2O emissions measured in their study, even when the soil was incubated at high water content (10 kPa soil water suction).

Emission of NO from the well-drained sandy loam at our research site exceeded that of N_2O by a large factor, suggesting that recent efforts to characterize gaseous N losses from various ecosystem types may be incomplete, and in some cases substantially inaccurate, unless NO emission measurements were included. However, the NO:N_2O emissions ratio we measured (mean over all plots 7.2 ± 1.7 SE) exhibited considerable variability as a function of N supply and is apparently strongly dependent on whether nitrification or denitrification represents the principal source of the gases. All this uncertainty precludes (except in unusually well-defined situations) combining measured NO:N_2O emission ratios with the existing extensive data base of N_2O emission measurements to forecast NO evolution at similar sites.

The area beneath each emissions curve in Figure 1*a* was integrated to provide estimates of total NO and N_2O evolution during the 9-week experimental period (Table 2). Data in the table indicate that 0.69 and 2.37 kg N ha^{-1} were lost as NO from plots under minimum and intensive cultural management, respectively. The difference amounted to 3.2% of the 52 kg N ha^{-1} applied as $(NH_4)_2SO_4$, nearly an order of magnitude greater than the fraction of applied fertilizer lost as N_2O. Such large fractional conversion of fertilizer N to NO_x has previously been observed only by *Slemr and Seiler* [1984] for urea applied to bare loamy sand in Spain (5.4% conversion), by *Shepherd et al.* [1991] for NH_4NO_3 applied to bare fine sandy loam in Canada (11% conversion), and by *Tortoso et al.* [1986] for $(NH_4)_2SO_4$ added to sandy loam in an aerobic laboratory soil incubation study (10% conversion).

G. L. Hutchinson et al. (submitted manuscript, 1992) reported that total N_2O evolution during this 9-week experimental period represented 26% and 29% of annual N_2O emissions from the plots under minimum and intensive cultural management, respectively. If the same were true for NO, annual evolution of the gas from plots under the two management schemes would total about 3 and 8 kg N ha^{-1}, respectively. Emissions of this magnitude would place humid, subtropical grasslands among the largest biogenic NO sources, suggesting that they contribute significantly to the global atmospheric NO_x budget.

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MIDWEST RESEARCH INSTITUTE

Project/Acct. No. 4604-04 Date/Time 9/97

Project Title Fertilizer Application AP-42

REFERENCE 39 EMISSION FACTOR CALCULATIONS

Signature B. WATSON Verified by 9/26/97 (signature/date)

Phone Contact ☐

Meeting Notes ☐

Work Sheet ☒

Page 1 of 1

FERTILIZER: $(NH_4)_2SO_4$, SOLID

POLLUTANT: NO

APPLICATION: ASSUMED BROADCAST

RATE: 52 Kg N/ha

EMISSION FACTOR

$$1.68\ \frac{\text{Kg/N}}{\text{ha}} \times \frac{30\ \text{Kg NO}}{14\ \text{Kg N}} = \frac{3.60\ \text{Kg NO}}{\text{ha}}\ \text{emitted} \div 52\ \frac{\text{Kg N}}{\text{ha}} = 0.0692\ \frac{\text{Kg NO}}{\text{Kg N Applied}}$$

$$= 69.2\ \frac{\text{g NO}}{\text{Kg N applied}}$$

$$= 138.4\ \frac{\text{lb NO}}{\text{ton N applied}}$$

EMISSION GENERATION PERIOD = 9 WEEKS

POLLUTANT: N_2O

EMISSION FACTOR

$$0.20\ \frac{\text{KgN}}{\text{ha}} \times \frac{44\ \text{Kg}\ N_2O}{28\ \text{Kg N}} \div 52\ \frac{\text{KgN}}{\text{ha}} = 6.04 \times 10^{3}\ \frac{\text{Kg}\ N_2O}{\text{Kg N}} = 6.04\ \frac{\text{g}\ N_2O}{\text{Kg N}}$$

$$= 12.1\ \frac{\text{lb}\ N_2O}{\text{ton N applied}}$$

APPENDIX O

REFERENCE 41 AND ASSOCIATED HAND CALCULATIONS

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Soil Emissions of Nitric Oxide and Nitrous Oxide from No-till Corn

Frank C. Thornton* and Ralph J. Valente

ABSTRACT

Fertilized agricultural soils can be a significant source of emissions of NO and N_2O into the atmosphere. This study was conducted to determine the influence of N rate on the emissions of these gases in a no-till corn (*Zea mays* L.) crop grown in western Tennessee. The influence of N rate was assessed for a 210-d period on replicated plots receiving 0, 140, and 252 kg N ha^{-1} (0N, 140N, and 252N) as ammonium nitrate (AN). Plots were located on a Routon silt loam (fine-silty, mixed, thermic Typic Ochraqualf) at the West Tennessee Agricultural Experiment Station in Jackson, TN. Gas fluxes were measured by static chamber boxes located on plots. The measurement technique was automated and replicate chamber estimates were made eight times daily for the entire study period. Fertilizer application significantly affected both NO and N_2O emission rates. The cumulative N_2O–N lost from the fertilizer treatments was from 10 to 20-fold that of NO. On an areal basis, the 140N treatment emitted 4.23 kg N_2O–N and 0.19 kg ha^{-1} of NO–N whereas the 252N treatment emitted 6.56 kg N_2O–N and 0.50 kg ha^{-1} NO–N. Soil parameters of water-filled pore space (WFPS), NO_3^- and NH_4^+, were correlated with N_2O emissions but only soil NO_3^- was correlated with NO flux. Our data, and more recent data in the literature, suggest that N_2O emissions from fertilized soil may be considerably higher than previously thought. Emissions of N_2O were 2.6 to 3.0% of the fertilizer amounts applied. These higher emissions may, in part, explain some of the reason for the shortfall in the global N_2O budget.

NITROGEN OXIDES (N_2O, NO, and NO_2) are important trace gases in terms of the atmospheric chemistry of both the stratosphere and troposphere. As a greenhouse gas, N_2O tends to warm the lower atmosphere and the earth's surface by its absorption and re-emission of radiation in the atmosphere (Bouwman, 1990). Nitric oxide (NO_x = NO + NO_2) is important in controlling troposphere ozone levels through its reaction with volatile organic compounds in the atmosphere. Tropospheric ozone is a pollutant that negatively impacts forest and crop growth, as well as human health. Despite efforts to control NO_x emissions, tropospheric ozone concentrations have continued to increase during the past decade (National Research Council, 1992).

Prior to industrialization, the main source of these emissions into the atmosphere was biological activity related to the soil processes of nitrification and denitrification. A number of key factors such as soil moisture, C content, and soil aeration affect emission processes (Aulakh, 1992). The magnitude of these emissions however, is also dependent on soil levels of NH_4^+ and NO_3^-, and with the advent of modern agriculture and the increased use of mineral fertilizers there has been an increase in soil emissions of these gases. **Agriculture is presently estimated to contribute from 65 to 80% of the total anthropogenic N_2O, or up to 2 Tg N_2O–N yearly** (International Panel on Climate Change, 1990; Iserman, 1994). Cropland is also thought to be a major emitter of NO. Davidson's (1991) analysis, albeit made from a limited data base, suggests that 30% of the 20 Tg of the total NO budget is attributable to soil emissions from agricultural activity.

Although only a few studies have been performed to determine the influence of N fertilizer application on the simultaneous emissions of N_2O and NO, they consistently demonstrate that fertilization increases emissions of nitrogen oxides (see Williams et al., 1992). The estimates of global emissions span a wide range and indicate that the NO/N_2O ratios of emissions vary widely among studies. For example, Galbally et al. (1987) reported that <0.002% of applied urea was lost as NO, whereas Hutchinson and Brams (1992) reported that 3.2% of AN applied to a bermudagrass (*Cynodon dactylon* [L.] Pers.) pasture was lost as NO after 9 wk. Typically, soil efflux of NO and N_2O does not result in substantial N losses compared with the amount of fertilizer applied, but these emissions are important in atmospheric chemical reactions in both the troposphere and stratosphere (see Williams et al., 1992). Shepherd et al. (1991) observed very large losses where 11% of fertilizer N was lost as NO and 5% was lost as N_2O over 5 mo. The wide divergence in the estimates of NO and N_2O emitted from soils is a result of both the large temporal and spatial variability associated with the ecological processes that control the emissions of these gases as well as differences associated with the measurements and the measurement methodologies used. Environmental factors such as precipitation events can also significantly change efflux patterns by changing soil redox potential or affecting soil gas diffusivity and microbial activity (e.g., nitrification and denitrification) and subsequent N gas production and efflux (Valente and Thornton, 1993). Coefficients of variation associated with emissions estimates for these gases are typically between 100 and 300% (Williams et al., 1992; Valente and Thornton, 1993; Valente et al., 1995). To some extent, this variation is due to the fact that discrete point estimates of gaseous emissions have been used to calculate flux. It is only recently that quasi-continuous measurements for extended periods of time have been made to [redacted] a[redacted] V[redacted]93). Many of the point estimates of soil trace gas efflux are not adequate to assess seasonal or annual losses of NO and N_2O because continuous measurements are needed (Aulakh, 1992).

To address the need for daily flux measurements to estimate NO and N_2O emissions from fertilized soils, we continuously measured NO and N_2O emissions over a 210-d period from no-till corn fertilized at three N rates. In addition to gaseous emissions, we monitored

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Abbreviations: AN, ammonium nitrate; WFPS, water-filled pore space; ICP, inductively coupled plasma emissions spectroscopy.

soil chemical and physical properties in an attempt to understand mechanisms that controlled these effluxes.

MATERIAL AND METHODS

Site

Emissions estimates were made at the West Tennessee Agricultural Experiment Station in Jackson, TN (35°37′ N, 88°50′ W) from 27 Apr. through 30 Nov. 1993. The soil is a Routon silt loam derived from loess deposits 2 to 5 m thick, overlaying Coastal Plain sediments. Table 1 lists selected properties of the soil. The field used for this experiment has been in no-till corn for the past 4 yr. The long-term climatic data (30-yr average) for the site indicate that mean annual rainfall is 1320 mm, with a mean annual temperature of 17°C, and approximately 193 frost-free days during the growing season (Springer and Elder, 1980).

A randomized complete block design with three N rates and three replications was used to assess N gas efflux. The three fertility treatmentswere 0N, 140N, and 252N applied as AN on 26 Apr. 1993. Corn (Pioneer 3925) was planted 21 Apr. 1993 in 76 cm rows at 39 000 seeds ha^{-1}. The N rates were those recommended dryland corn for this soil, 140 kg N ha^{-1}, and the 252 kg N ha^{-1} rate was the upper-end N rate for corn grown on this soil under irrigation (irrigation was not used in our experiment). Four measurement plots were randomly established within each treatment × block combination for a total of 36 measurement locations. At the start of the experiment on 27 Apr. 1993, two of the four sampling locations within each treatment in Block 1 were used to make measurements of NO and N_2O. The following week the two locations that were not chosen in Week 1 were used to make measurements. The following week the same procedure was used for the second experimental block to locate sample locations. This procedure was repeated, starting in Week 5 for the third replicate block, after which the same selection sequence was repeated among blocks until the end of the experiment (30 Nov. 1993). Thus, each chamber replicate within a measurement plot for a treatment was sampled every 3 h for approximately 1 wk ($n = 56$) and each block was sampled five time (two consecutive weeks at a time) throughout the experiment.

To minimize soil disturbance associated with the relocation of the measurement chambers throughout the experiment, the six frames used to make measurements (see below) were placed in the ground 1 wk before the measurements were made. This enabled quick placement of chambers onto frames with minimal soil disturbance.

Yield estimates were obtained by harvesting two 4.65-m sections of row in the middle of each plot. Plots were harvested by hand and grain yields are expressed on a 10% moisture basis.

Table 1. Soil characteristics of the 0- to 15-cm layer of a Routon silt loam prior to the start of the experiment.

Texture, %	
Sand	24
Silt	52
Clay	24
Bulk density, Mg m^{-3}	1.61 (0.14)†
pH	5.75 (0.23)
NH_4^+, mg kg^{-1}	4.3 (0.4)
NO_3^-, mg kg^{-1}	16.7 (2.4)
P, mg kg^{-1}	113 (17)
Ca, mg kg^{-1}	1061 (211)
Mg, mg kg^{-1}	42 (7)
K, mg kg^{-1}	114 (26)

† Mean with standard deviation in parentheses.

Gas Measurements

Measurements of NO and N_2O emissions were made with a static-chamber technique as previously described by Valente and Thornton (1993). Briefly, aluminum chambers (L by W by H = 76.2 by 45.7 by 20.3 cm) opened and closed pneumatically over an aluminum frame driven into the ground to a depth of 20 cm. Multiport sequencing of chamber air samples allowed withdrawal of air samples from different chambers at 3-min intervals. In contrast to the method described by Valente and Thornton (1993) the Teco Model 46 N_2O gas correlation instrument (Thermo Environmental Instruments, Franklin, MA) was placed upstream of the Teco Model 42 used to determine NO. The pump of the Teco Model 46 was bypassed and the Teco Model 42 pump was used to withdraw sample air from chambers. This was done to reduce the amount of sample withdrawn from chambers since the Model 42 withdrew only 0.7 L min^{-1} rather than the 1 L min^{-1} for the Teco Model 46. At 3-min intervals, NO and N_2O measurements were performed and the emission rate and deposition rate calculated from the change in gas concentrations during the measurement period. The calculation of NO efflux rate was identical to that described by Valente and Thornton (1993) in which a first-order differential equation of the form

$$\frac{d[NO]}{dt} = k_1 - k_2[NO]$$

was used to calculate a gross emissions rate; where k_1 is a constant emission rate term, k_2 is a loss term due to deposition within the chamber, and [NO] is NO concentration. Emission estimates for N_2O were calculated using a linear model. The lower limit of sensitivity for NO–N emissions was 0.002 ng N m^{-2} s^{-1} and the lower limit for N_2O was 0.02 ng N m^{-2} s^{-1}. At the end of the measurement period, all six chambers were opened and remained open for 2 h until the next measurement cycle began. This sequence, of automated chamber closure and the attendant sampling of NO and N_2O concentrations with time within chambers, was repeated every 3 h, 24 h a day, throughout the experiment. A Campbell Scientific Model CR7 data logger (Campbell Scientific, Logan, UT) was used to control the opening and closing of chambers and collect and store data gathered during each measurement cycle.

Weekly calibration checks were made for both N_2O and NO analyzers. Certified gases (Scott Specialty Gases, Plumsteadville, PA) of NO (19.24 µL L^{-1}) and N_2O (80.6 µL L^{-1}) were used to make multipoint calibrations. Coefficients of determination for standard curves for both gases was consistently 0.995 or greater throughout the study. Several times during the study, line loss tests were performed by introducing standard gases directly into the sample lines of chambers. Gas loss throughout the 40-m sample lines averaged approximately 5% and was considered negligible for the calculations of emissions rates. These finding are consistent with a previous test of the system (Thornton and Valente, 1992, unpublished data).

Ancillary Measurements

Soil temperature at 5- and 15-cm depths was continuously monitored by means of a thermocouple during the study. Gravimetric water content determinations, based on oven-dry soil (105°C), for the 0- to 15-cm depth were made weekly. A soil moisture retention curve was determined using triplicate undisturbed soil cores for 0.03, 0.06 and 0.1 MPa tensions; tensions of 0.3, 0.5, and 1.5 MPa were determined on disturbed samples. The weekly determinations of gravimetric soil moisture were used to determine WFPS from the relationship where:

$$\mathrm{WFPS} = \frac{\mathrm{Grav.H_2O} \times \mathrm{Bulk\ Density}}{\mathrm{Total\ Porosity}}$$

$$\text{where porosity} = 1 - \left(\frac{\mathrm{Bulk\ Density}}{2.65}\right)$$

Rainfall was recorded using a tipping bucket rain gauge (Climatronics. Bohemia. NY). Soil samples were also collected weekly from the top 15-cm layer for chemical analysis of NO_3^- and NH_4^+. Soils were extracted with 2 *M* KCl and NO_3^- and NH_4^+ determined by titration. Cation determinations were made using Mehlich 3 procedures (Mehlich. 1984) followed by ICP determinations.

Statistical Analysis

Gas flux data were analyzed using the general linear models procedure in the Statistical Analysis Systems for personal computers (SAS Institute, 1993). Differences among treatment means were evaluated using a Bonferroni *t*-test. Mean emission rates for NO and N_2O were calculated for each treatment from the entire 210-d experimental period. Correlation coefficients between soil parameters and trace gas efflux were estimated for the combined N treatments and the daily average efflux values for NO and N_2O for the days on which the soil parameters were measured. A 0.05 probability level was used to determine significant differences.

RESULTS AND DISCUSSION

Fertilizer application significantly affected emissions of both N_2O and NO (Table 2, Fig. 1-3). Emissions of N_2O were more episodic in nature than NO, which was emitted at a somewhat uniform rate during the course of the study. The loss of fertilizer N during the study period was significantly influenced by N application rate for both N_2O ($F = 73.5$, $P = 0.0001$) and NO ($F = 184.1$, $P = 0.0001$) The efflux of N_2O was 4.23 kg of N from the 140N treatment and 6.56 kg N in the 252N treatment (Table 2). Average emissions rates with no N application (control plots) were 10.4 and 3.5 ng N m^2 s^{-1} for N_2O and NO, respectively, resulting in a loss of 1.98 kg N_2O-N and 0.63 kg NO-N during the 210-d study. Emission rates of NO from the fertilized treatments were considerably lower than we measured in past studies on fertilized row crops. On a similar silt loam soil in middle Tennessee that had received 100 kg N ha^{-1}, we previously reported a midsummer rate of 24 ng NO-N m^2 s^{-1} (Valente and Thornton, 1993). In a separate study on a red clay soil in Alabama, a cotton (*Gossypium hirsutum* L.) crop receiving 112 kg N ha^{-1} had an average emission rate of 17 ng NO-N m^2 s^{-1} (Valente et al., 1995) or an emission rate that was approximately five times higher than the present study. Williams et al. (1988) reported an even higher mean NO emission rate of 94 ng N m^2 s^{-1} for corn in Pennsylvania. Our results are more similar to those reported by Anderson and Levine (1987), who reported an average soil NO efflux rate of approximately 6.5 ng NO-N m^2 s^{-1} for plots receiving 163 kg N ha^{-1}. However, in as much as variation in emission rates across a single site is typically threefold (Davidson, 1991), it is not unreasonable to expect that variation among sites would have a variation that is 10-fold due to differences in soil texture and attendant water-holding capacity (i.e., WFPS), timing and uptake of soil N, and cultural practices such as fertilizer type and placement that may affect emissions.

Table 2. Mean soil efflux rates and total losses of N as N_2O and NO related to N fertilization rate for a 210-d period.

Treatment	Emission rate	N loss	N loss
kg N ha^{-1}	ng N m^{-2} s^{-1}	kg N ha^{-1}	% of applied N
		N_2O	
0	10.4 (34.9)†	1.98 (–)‡	–
140	28.1 (91.8)	6.21 (4.23)	3.02
252	38.4 (112.7)	8.54 (6.56)	2.60
		NO	
0	3.5 (4.6)	0.63 (–)	–
140	4.5 (5.3)	0.81 (0.19)	0.13
252	6.4 (6.5)	1.13 (0.50)	0.20

† Mean rate and standard deviation, $n = 2705$.

‡ Total N loss was calculated. N loss attributable to fertilizer application indicated in parentheses.

Except for a few instances of significant denitrification

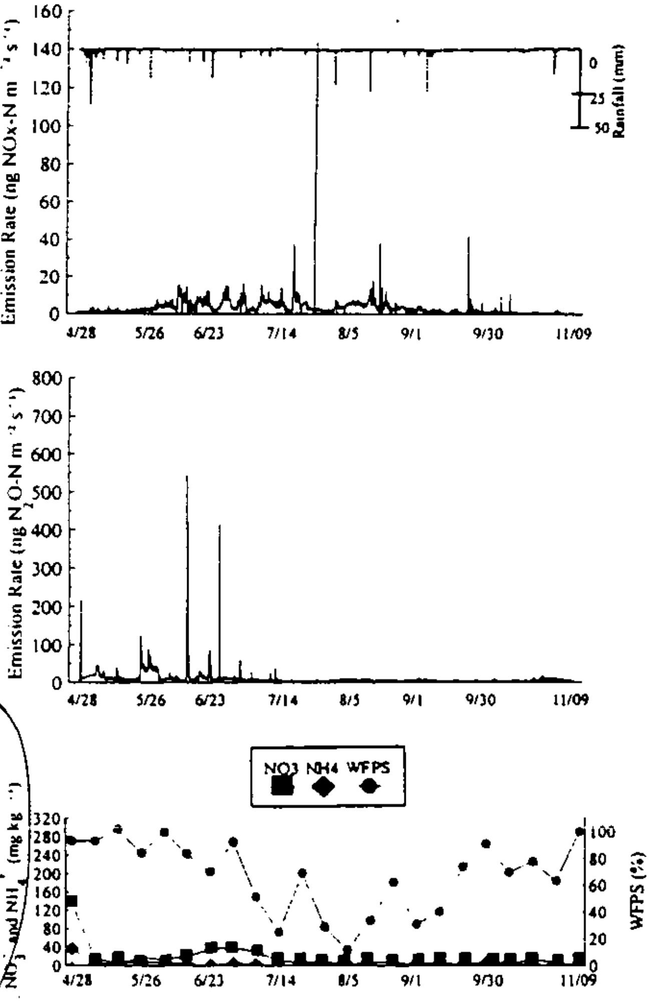

Fig. 1. Data for a 210-d period for no-till corn receiving 0 N kg ha^{-1}: (a) NO emission rate and rainfall, (b) N_2O emission rate, and (c) soil NO_3^-, NH_4^+, and water-filled pore space (WFPS) for the 0- to 15-cm depth.

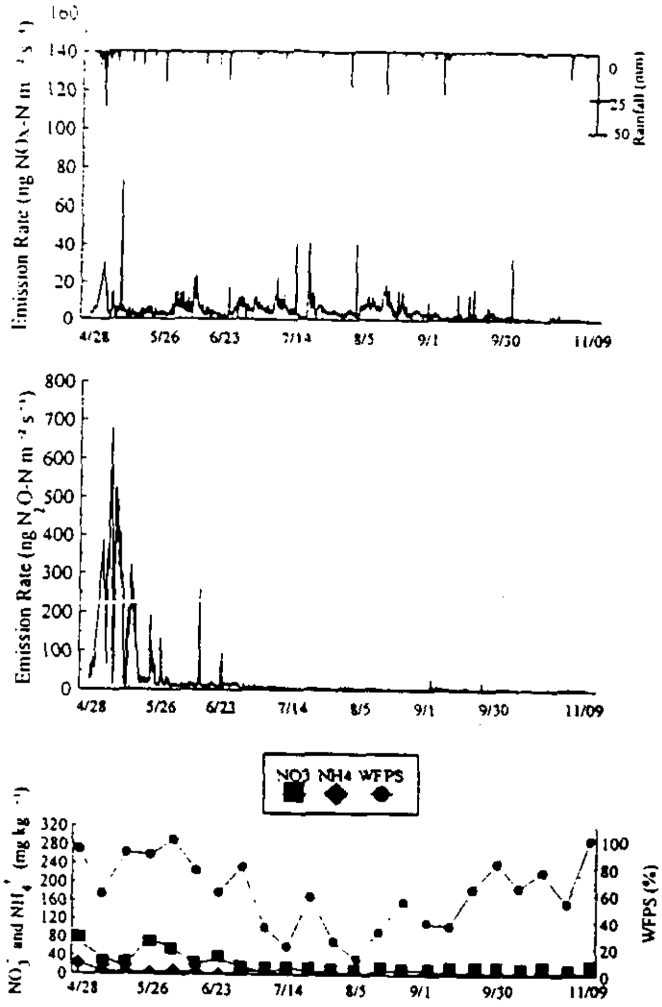

Fig. 2. Data for a 210-d period for no-till corn receiving 140 N kg ha^{-1}: (a) NO emission rate and rainfall, (b) N_2O emission rate, and (c) soil NO_3^-, NH_4^+, and water-filled pore space (WFPS) for the 0- to 15-cm depth.

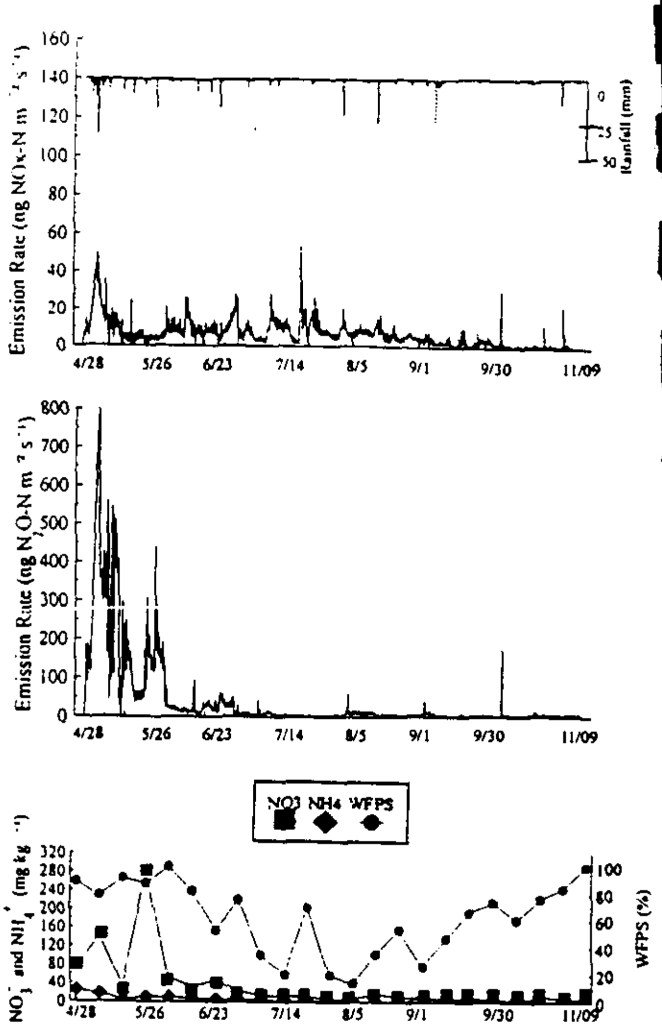

Fig. 3. Data for a 210-d period for no-till corn receiving 252 N kg ha^{-1}: (a) NO emission rate and rainfall, (b) N_2O emission rate, and (c) soil NO_3^-, NH_4^+, and water-filled pore space (WFPS) for the 0-15 cm depth.

activity later in the season, most of the N_2O emission occurred during the first month of the study. The typical, usually immediate, increase in N_2O emissions following N application (Breitenbeck et al., 1980; Duxbury et al., 1982) was evident in this study (Fig. 1-3). The N loss of N_2O from nonfertilized soil was considerably higher than that cited by Eichner (1990), who reported an average emission of 0.8 kg N ha^{-1} yr^{-1} for nonfertilized soils. The amount of fertilizer-derived N_2O emissions in the present study is approximately sevenfold the average loss of 0.44 kg N ha^{-1} reported for AN in the review by Eichner (1990). The substantially higher values in our study, compared with the average given by Eichner (1990), may be related to a number of factors including soil type, rainfall, timing of fertilizer application, and management practices, which can strongly influence emissions on a site-specific basis. These differences may also result from using average daily emission rates that are calculated from discrete point samples that are oftentimes only made once a week. Annual estimates require methods that use both long-term and highly time-resolved determinations of flux (Loftfield et al., 1992) and this study attempts to address this need by having replicated measurements every several hours over 7 mo.

Soil emissions of NO and N_2O were not affected by harvesting. We found no increase in emissions after the 9 September harvest. We had speculated that increased C supply due to harvest residue would promote denitrification; however, soil moisture was very low and apparently little denitrification occurred. Hutchinson and Brams (1992) reported a stimulation in soil NO emission, but not N_2O, after harvesting bermudagrass and speculated that increased soil temperature increased soil efflux of NO.

More recent studies of N_2O and NO emissions from soils, not available at the time of Eichner's (1990) review, show higher emissions than she reported. Hutchinson and Brams (1992) reported that NO emissions during a 9-wk study resulted in a 2.37 kg N ha^{-1} loss while N_2O accounted for 0.35 kg N ha^{-1}. Recent studies by Bronson et al. (1992) on conventially tilled corn over a 2-yr period measured N_2O losses of 3.2 and 1.6 kg N, similar to this study. Studies in Canada (Shepherd et al., 1991) and in Sweden (Hansen et al., 1993) measured losses

Table 3. Correlation coefficients for NO and N_2O soil emissions rates with soil N and moisture at Jackson, TN.

	NO emission rate	N_2O emission rate
Water-filled pore space	0.14 (NS)†	0.32 (0.0001)
NO_3^-	0.25 (0.03)	0.39 (0.0009)
NH_4^+	0.11 (NS)	0.30 (0.10)

† Parenthetical values are the probability levels associated with the correlation; NS indicates statistical nonsignificance.

up to 5.3% of the applied AN as N_2O. In the Canadian studies, 11% of the fertilizer N applied was lost as NO and efflux rates as high as 74 ng NO-N m^2 s^{-1} were reported (Shepherd et al., 1991). Although we measured NO efflux rates as high as 143 ng NO-N m^2 s^{-1} in our study, >95 % of all NO measurements, or 7584 separate measurements, indicated the NO emission rate was below 14 ng N m^2 s^{-1} Recent studies indicate greater loss rates of N via N_2O efflux from soil, but our study, to the best of our knowledge, has some of the highest N_2O emissions rates reported. Values calculated from the work of Eichner indicate an average emission rate of 34 ng N_2O-N m^2 s^{-1}, but Clayton et al. (1994) reported values as high as 1766 ng N m^2 s^{-1}. Emission values for N_2O as high as 994 ng N m^2 s^{-1} were measured in our study for the 252N treatment.

Table 3 shows the correlation coefficients of NO and N_2O efflux with soil WFPS, soil NO_3^- and NH_4^+. These parameters have been reported to strongly influence trace gas emissions from soil (Davidson, 1991). During the first 55 d of the study (through 30 June), WFPS averaged 85% among the three treatments, the same time frame in which most of the N_2O was emitted from the soil. The high values for WFPS are reflected in the above-average rainfall for this period; precipitation was 20% above normal, or 50 mm in excess of the 30-yr average (National Oceanic and Atmospheric Administration, 1993). Denitrification becomes increasingly important as WFPS exceed 60% (Davidson, 1991) and our data support this observation. With decreasing rainfall in July, WFPS was typically <60% (the lowest value recorded was 14% on 5 August; see Fig. 1-3) and denitrification became less important as a factor in N loss. Precipitation for June through August was 50% below normal, or 192 mm below the 30-yr average (National Oceanic and Atmospheric Administration, 1993). This moisture deficit severely limited grain filling and yields for all treatments; yields for the 0N, 140N, and 252N treatments were 2.62, 6.22, and 6.56 Mg ha^{-1}, respectively.

Soil NO_3^- and NH_4^+ concentrations were correlated with N_2O emissions but only soil NO_3^- was significantly linked to NO emissions (Table 3). The literature reports of correlations between soil parameters such as NO_3^-, NH_4^+, and WFPS and emissions of NO and N_2O are conflicting (Williams et al., 1992). Our results are similar to those of other researchers (Aulakh et al., 1992; Bronson and Mosier, 1993) who have reported weak or no relationship between gaseous efflux and soil chemical and physical properties. Slemr and Seiler (1991) contend that although ample data exist showing that NO and N_2O emission rates are dependent on soil chemical and physical properties, it is usually just one variable that dominantly influences the emission rate. These researchers further maintained that this masking of variables at a particular point in time, location, or study is, in part, responsible for the oftentimes conflicting reports in the literature concerning the importance of a particular variable in influencing trace gas emissions. Several researchers have speculated that C availability, and factors controlling C supply to microbial populations, may be more important in regulating denitrification than has customarily been thought, and most studies dealing with trace gas emissions have not dealt with this important aspect of trace gas efflux (Groffman and Tiedje, 1991; Wheatley and Williams, 1989).

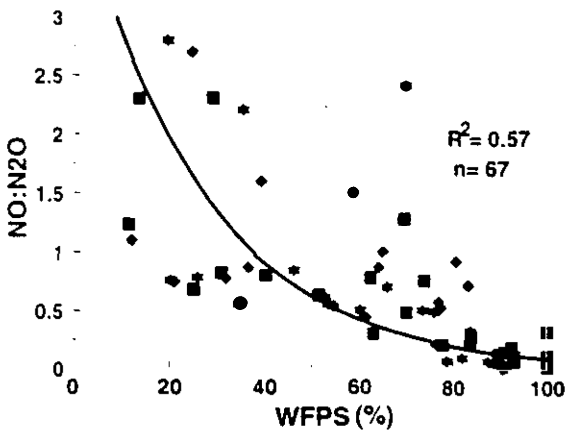

Fig. 4. Relationship between NO/N_2O emission rate ratio and soil water-filled pore space (WFPS) during the study period.

Although individual soil properties were poorly correlated with N gas emissions, WFPS did a reasonable job (R^2 = 0.57) of predicting the NO/N_2O ratio (Fig. 4). These data support recent work (Davidson, 1993; Riley and Vitousek, 1994) indicating that this ratio is low when the soil is wet, typically in the spring, as in our study, and N_2O emissions from denitrification dominate. Conversely, ratios increase as the soil becomes drier and nitrification and NO efflux become more important.

SUMMARY

This experiment demonstrated that loss of fertilizer N as N_2O was far greater than loss as NO; N loss via N_2O was 10 to 20-fold more than that of NO for the study. Nitrous oxide fluxes were positively correlated to WFPS, NO_3^-, and NH_4^+ but only soil NO_3^- values were correlated to NO flux. The ratio of NO/N_2O emissions was reasonably well correlated (R^2 = 0.57) with WFPS and supports the conceptual hole-in-the-pipe model of Firestone and Davidson (1989). In their model the sum of NO + N_2O emissions is related to the N applied, whereas the relative proportion of NO vs. N_2O is linked with WFPS. This experiment suggests that the magnitude of fertilizer-derived emissions estimated by Eichner (1990) from AN may be low. This contention is also supported by recent studies (Hansen et al., 1993; Shepherd et al., 1991) that also indicate much higher emissions rates and subsequent N from applied AN. Using an average emission rate of 40 mg N_2O-N from each kilogram of applied N, Eichner

(1990) estimated that 64.4 Gg N_2O-N was associated with the application of 16.2 Tg AN worldwide for the year 1988. Using the mean efflux value of the two fertilizer rates in our experiment to extrapolate, we would estimate that approximately 455 Gg N_2O-N would be released from AN-fertilized soil annually. Admittedly, extrapolation of emissions data from one location for 1 yr on a fine-textured soil like the one used in this study is fraught with problems; however, this higher estimate in N_2O release may be of importance in light of the fact that global N_2O budgets cannot account for some 7 to 8 Tg of emissions. It is also probable that the techniques used in this experiment and those of Loftfield et al. (1992) better characterize temporal emissions patterns, which can affect budget estimates for a given biome. However, there are still a number of key areas yet to be adequately addressed in attempting to resolve emission estimates on a global basis. Several of those requirements are mentioned in the recent modeling effort of Yienger and Levy (1995), who point to the need to (i) better characterize agricultural emissions from Europe and northern China and (ii) better estimate emissions from tropical grasslands.

The present work also demonstrates an improved sampling technique to allow for quasi-continuous sampling of both N_2O and NO gas efflux from ecosystems. We are currently modifying this system to accommodate greater replicate sampling to improve our estimates of soil efflux for future study sites.

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Determination of Microbial Biomass and Nitrogen Mineralization following Rewetting of Dried Soil

A. J. Franzluebbers,* R. L. Haney, F. M. Hons, and D. A. Zuberer

ABSTRACT

Routine soil testing procedures that are rapid and precise are needed to evaluate agricultural surface soils for their potential to mineralize C and N. Our objectives were to determine the optimum preincubation time after rewetting of dried soil for estimating soil microbial biomass (SMB) and to identify a quick, reliable biochemical predictor of soil N mineralization potential. Biochemical determinations of SMB were screened on a Weswood silty clay loam (fine, mixed, thermic Fluventic Ustochrept) having five levels of soil organic C (SOC) as a result of long-term management. Determinations used (i) field-moist soil and (ii) soil that was air dried, rewetted, and preincubated for 0.2, 1, 3, 6, 10, and 15 d. Biochemical determinations included arginine ammonification, substrate-induced respiration (SIR), cumulative C and net N mineralization, and SMBC using the chloroform fumigation-incubation (CFI) method. Preincubation periods of 1 and 15 d prior to fumigation gave estimates of SMBC using CFI most similar to those determined on field-moist soil. Arginine ammonification and SIR determinations on dried soil were highly variable, making longer preincubation periods necessary. Carbon mineralization during all preincubation periods was highly correlated to (i) SMBC using CFI determined on field-moist and dried soil with all preincubation periods and (ii) net N mineralization during 21 d for the Weswood soil, as well as for seven additional soil series each having five to eight levels of SOC. The CO_2-C evolved during the first day after rewetting of dried soil is recommended for rapid estimation of SMBC and potential N mineralization because of its simplicity and precision.

THE IMPORTANCE of soil microorganisms to soil fertility is recognized, but rapid, accurate soil testing procedures that reflect potential C and N mineralization have not been routinely adopted (Keeney, 1982). A valid index of soil N availability that is simple, rapid, and reproducible may preclude the use of a biological method despite its importance, because of the long time period required to estimate the relatively small amount of mineralized N due to microbial activity. Incubations lasting 1 to 2 wk for determination of mineral N accumulation are considered too time-consuming for adoption by routine soil testing programs.

The N-supplying potential of agricultural soils has been related to SMB and its activity (Carter and Rennie, 1982; Doran, 1987; Franzluebbers et al., 1994a). Measurement of SMB is sensitive to changes in the active fraction of SOM (Powlson et al., 1987; Anderson and Domsch, 1989) and therefore, should provide insight into the potential of soils to mineralize N. The most commonly used method for estimating SMB is CFI, although field-moist soil and a 10-d incubation are needed (Jenkinson and Ladd, 1981; Nannipieri et al., 1990; Parkinson and Coleman, 1991), which limit its adoption by soil testing programs. Several rapid methods for estimating SMB and its activity (i.e., C and N mineralization) have been developed during the past few decades including SIR (Anderson and Domsch, 1978) and AA (Alef and Kleiner, 1986), which require only 1 to 6 h of incubation, but as described, also require use of field-moist soil.

Soil testing protocol normally requires that dried soil be used because samples collected by producers and soil testing services are shipped to the soil testing facility, which may take several days, thereby altering the biochemical status if kept moist. We hypothesized that dried, rewetted, and preincubated soil could be used to obtain an estimate of SMB. The optimum preincubation period for estimating SMB and mineralizable N, therefore, needs to be established.

Our objectives were to: (i) evaluate the feasibility of using dried and preincubated soil for measurement of AA, SIR, cumulative C and net N mineralization, and SMBC using CFI and (ii) determine the optimum time of preincubation for these biochemical estimates.

MATERIALS AND METHODS

Five soil samples with SMBC levels ranging from 279 to 1260 mg kg^{-1} soil (Table 1) were collected shortly after planting wheat (*Triticum aestivum* L.) in November 1991 from a long-term field experiment established on a Weswood silty clay loam in 1982 (Table 2). Fifteen soil cores (19 mm diam.) per 4 by 12.2 m plot were collected and composited from three replications of the treatments listed in Table 1. Field-moist

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Abbreviations: AA, arginine ammonification; BSR, basal soil respiration; CFI, chloroform fumigation-incubation; SIR, substrate-induced respiration; SMB, soil microbial biomass; SMBC, soil microbial biomass carbon; SOC, soil organic carbon; SOM, soil organic matter.

MIDWEST RESEARCH INSTITUTE

Project/Acct. No. 4604-04 Date/Time 9/97

Project Title Fertilizer Application AP-42 Reference 41 Emission Factor Calculations

Signature B. Watson Verified by 9/26/97 (signature/date)

Phone Contact ☐

Meeting Notes ☐

Work Sheet ☒

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FERTILIZER: AN (NH_4NO_3)

POLLUTANT: NO, N_2O

APPLICATION: ASSUMED SOLID BROADCAST - SEE COMPARISON TO REF. 1

RATE: 140 Kg N/ha, 252 Kg N/ha

EMISSION FACTORS - NO

140: $0.19 \frac{\text{Kg NO}}{\text{ha}} \times 1000 \frac{\text{g}}{\text{Kg}} \times \frac{\text{ha}}{\text{140 KgN applied}} = 1.36 \frac{\text{g NO}}{\text{KgN applied}} = 2.72 \frac{\text{lb NO}}{\text{ton N applied}}$

252: $0.50 \frac{\text{Kg NO}}{\text{ha}} \times 1000 \frac{\text{g}}{\text{Kg}} \times \frac{\text{ha}}{\text{252 KgN applied}} = 1.98 \frac{\text{g NO}}{\text{kgN applied}} = 3.96 \frac{\text{lb NO}}{\text{ton N applied}}$

EMISSION FACTORS - N_2O

140: $4.23 \frac{\text{Kg } N_2O}{\text{ha}} \times 1000 \frac{\text{g}}{\text{Kg}} \times \frac{\text{ha}}{\text{140 KgN}} = 30.2 \frac{\text{g } N_2O}{\text{Kg N}} = 60.4 \frac{\text{lb } N_2O}{\text{ton N}}$

252: $6.56 \frac{\text{Kg } N_2O}{\text{ha}} \times 1000 \frac{\text{g}}{\text{Kg}} \times \frac{\text{ha}}{\text{252 KgN}} = 26.0 \frac{\text{g } N_2O}{\text{Kg N}} = 52.1 \frac{\text{lb } N_2O}{\text{ton N}}$

APPENDIX P

REFERENCE 43 AND ASSOCIATED HAND CALCULATIONS

ORIGINAL PAPER

G. Benckiser · R. Eilts · A. Linn · H.-J. Lorch
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N_2O emissions from different cropping systems and from aerated, nitrifying and denitrifying tanks of a municipal waste water treatment plant

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Abstract Nitrous oxide emissions, nitrate, water-soluble carbon and biological O_2 demand (BOD_5) were quantified in different cropping systems fertilized with varying amounts of nitrogen (clayey loam, October 1991 to May 1992), in an aerated tank (March 1993 to March 1994), and in the nitrification-denitrification unit (March to July 1994) of a municipal waste water treatment plant. In addition, the N_2O present in the soil body at different depths was determined (February to July 1994). N_2O was emitted by all cropping systems (mean releases 0.13–0.35 mg N_2O m^{-2} h^{-1}), and all the units of the domestic waste water treatment plant (aerated tank 0–6.2 mg N_2O m^{-2} h^{-1}, nitrification tank 0–204.3 mg N_2O m^{-2} h^{-1}, denitrifying unit 0–2.2 mg N_2O m^{-2} h^{-1}). During the N_2O-sampling periods estimated amounts of 0.9, 1.5, 2.4 and 1.4 kg N_2O-N ha^{-1}, respectively, were released by the cropping systems. The aerated, nitrifying and denitrifying tanks of the municipal waste water treatment plant released mean amounts of 9.1, 71.6 and 1.8 g N_2O-N m^{-2}, respectively, during the sampling periods.

The N_2O emission were significantly positively correlated with nitrate concentrations in the field plots which received no N fertilizer and with the nitrogen content of the aerated sludge tank that received almost exclusively N in the form of NH_4^+. Available carbon, in contrast, was significantly negatively correlated with the N_2O emitted in the soil fertilized with 80 kg N ha^{-1} year. The significant negative correlation between the emitted N_2O and the carbon to nitrate ratio indicates that the lower the carbon to nitrate ratio the higher the amount of N_2O released. Increasing N_2O emissions seem to occur at electron donor-to-acceptor ratios (C_{H_2O} or BOD_5-to-nitrate ratios) below 50 in the cropping systems and below 1200–1400 in the waste water treatment plant. The trapped N_2O in the soil body down to a depth of 90 cm demonstrates that agricultural production systems seem to contain a considerable pool of N_2O which may be reduced to N_2 on its way to the atmosphere, which may be transported to other environments or which may be released at sometime in the future.

Key words N_2O release · Cropping systems · Waste water treatment · Activated sludge · Nitrification · Denitrification · Carbon availability · Available carbon-to-nitrate ratio

Introduction

In soils and waste water, even if well aerated, anaerobic energy-conserving processes can occur inside aggregates and sewage flocculates in the sequence NO_3^-, MnO_2 and Fe_2O_3 respiration followed by SO_4^{2-} and CO_2 reduction (Ottow and Glathe 1973). Much work has been done to clarify the effect of the variables, water-soluble carbon (C_{H_2O}), BOD_5, nitrate concentration (NO_3^-), moisture content, temperature and oxygen partial pressure on the onset of anaerobic nitrate respiration (Benckiser et al. 1987; Ottow 1992; Ottow and Benckiser 1994; Sümer et al. 1996). Despite these endeavors, the role of the above parameters on the denitrification process remains unclear because of the high spatial and temporal variability in soil and waste water systems diffusional constraints and the numerous feedbacks of the process itself in the different environments ((Benckiser 1994; Sümer et al. 1995). Products of anaerobic energy-conserving processes are, in addition to CO_2, N_2, Mn^{2+}, Fe^{2+} and H_2S, the greenhouse gases CH_4, NO and N_2O. Nitrous oxides are well-documented gaseous products of the lithotrophic ammonia-oxidizers (Blackmer et al. 1980; Tortoso and Hutchinson 1990; Hooper et al. 1990; Martikainen and de Boer 1993; Sümer et al. 1996) and the heterotrophic denitrifiers (Abou-Seada and Ottow

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Dedicated to Professor J.C.G. Ottow
on the occasion of his 60th birthday

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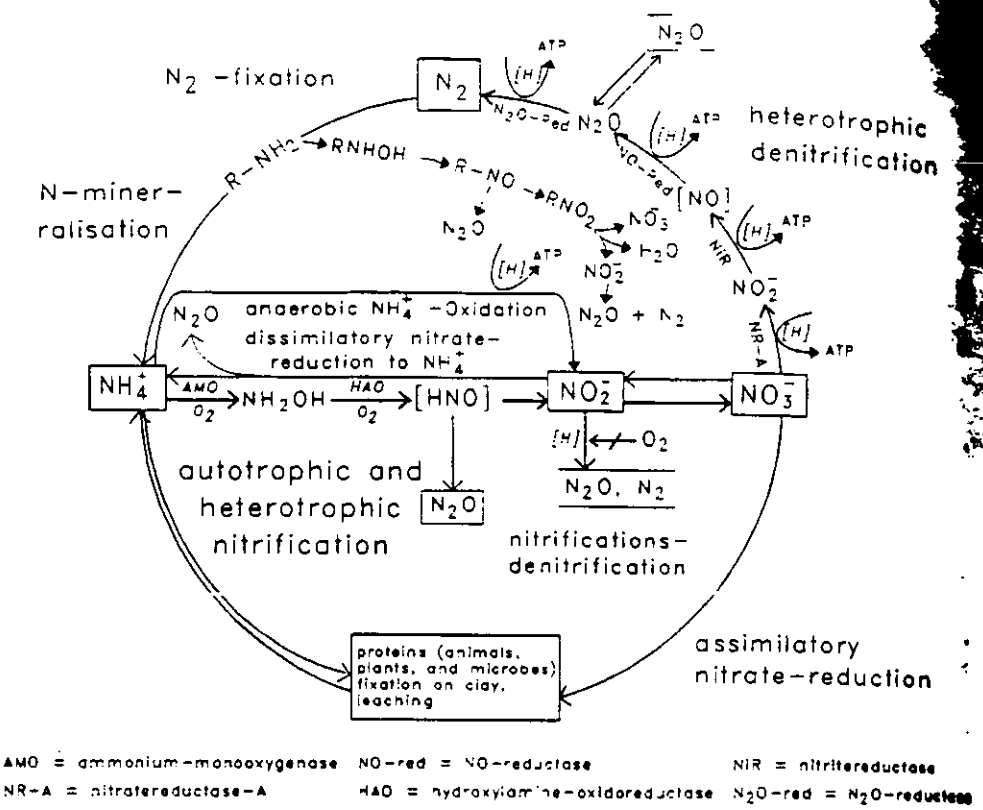

Fig. 1 Microbial N_2O-forming processes known so far

1985; Myrold and Tiedje 1985; Benckiser and Simarmata 1994). The main and so far known N_2O-forming processes are summarized in Fig. 1. "Nitrification-denitrification" and heterotrophic denitrification appear to be the dominant processes. Essential prerequisites for both energy-conserving processes are nitrate, nitrite and available carbon. In natural and agricultural used soils, nitrification and denitrification contribute to the N-availability of plants; and in waste water, which might be considered a model for soil solutions rich in organics and N, both processes are increasingly being used to avoid eutrophication by N-species in the "receiving" water. As side effects of soil and waste water management, increasing N_2O emissions are being reported (Simarmata et al. 1993; Lorch 1993; Wicht and Beier 1995). N_2O, which has a mean resistance time of 132 years in the troposphere combined with a considerable ozone-destroying capacity in the stratosphere, has a 260 times greater greenhouse effect potential than CO_2 (Papen and Seiler 1994). Consequently, this trace gas should not be underestimated as a potential hazard on a long-term scale. Unfortunately, local and global estimates of the quantity of N_2O from various terrestrial ecosystems, oceans, waste water treatment systems and combustion are scarce, if not totally lacking (Ottow and Benckiser 1994).

This paper compares the N_2O emissions from various cropping systems and municipal waste water treatment plant units (activated sludge, nitrification, denitrification tanks) in order to ascertain to what extent the N_2O releases depend on nitrate (end product of nitrification) and carbon availability (prerequisite of heterotrophic denitrification). Another objective of this paper was to estimate the amounts of N_2O still stored in the soil body in order to obtain information on the fate of N_2O during diffusion from its place of production to the atmosphere.

Materials and methods

Experimental design and field management

Cropping systems

The experiments to quantify N_2O emissions from different cropping systems were carried out at the Experimental Station of the Institute for Agronomy and Plant Breeding, Justus-Liebig University, Gießen, Germany. The topsoil (0–35 cm) was a clayey loam (clay 31%, silt 60% and sand 5%) with a pH (H_2O) of 6.2. Total organic C was 1.41% and total organic N 0.15%. The soil was classified as an allochtone brown earth derived from river sediments. The average precipitation of the experimental site is ca. 640 mm $year^{-1}$ and the mean temperature 8.9°C. The experimental design was a Latin Square (8×10 m, four replicates each), which was established in 1982 to obtain information about the biological N-supply of different cropping systems. The different cropping systems at this site have three rotation units in common, winter wheat, winter rye and barley, and one different one: A=*Vicia faba*, B=*fallow land*, H=*Avena sativa*, K=*Trifolium campestre* and M=*Zea mays*. Further treatments were achieved by different fertilizer applications (1–4). Treatments A-M1 received no fertilizer. Treatments A-M2–4 received 37 kg P and 100 kg K ha^{-1} $year^{-1}$ and different rates of N as follows: Treatments A-M2 received no nitrogen, treatments A-M3 80 kg N ha^{-1} $year^{-1}$ and the treatments A-M4 120 kg N ha^{-1} $year^{-1}$ as ammonium nitrate split into three applications (40, 20, 20 or 60, 30, 30). During the growth of *Vicia faba* or *Zea mays* no nitrogen or 180 kg N ha^{-1} $year^{-1}$

pied, respectively. The *Trifolium campestre* rotation was cut during the growing season followed by mulching each time.

Before starting with the N_2O-flux measurements in October 1991, the experimental site was ploughed (25 cm deep), levelled by rotary harrow and sown with winter rye (20 September 1991). Phosphorus and potassium were applied on 10 March and the first nitrogen was applied on 20 March 1992. Herbicides (Starane, 0.8 l ha^{-1}, and Pointer3, 25 g ha^{-1}, Dow Elanco, Germany) were spread on 7 April and the second N split application took place on 21 April. The fungicide Corbel (0.75 l ha^{-1}, BASF, Germany) and the growth regulator Terpal C (2.0 l ha^{-1}, BASF, Germany) were applied together with the third N split on 5 May. The N_2O surface flux measurements were carried out more frequently over the winter months (1 October 1991 to 2 May 1992). During the period 1 December 1991 to 1 March 1992 the soil temperature was below 5 °C. Consequently, the N_2O surface flux measurements were carried out mostly during October, November, March, April and May at temperatures between 5° and 15 °C. The soil humidity varied between 20% and 25% (w/w) during this period.

Waste water treatment plant

The in situ N_2O measurements in an aerated fluid-bed reactor, and a nitrification-denitrification tank, were carried out at the municipal waste water treatment plant of Gießen, Germany (Fig. 2). In this plant the waste water from about 150000 inhabitants is purified daily. One-third of the waste water, with a mean BOD_5 of 170 (10–510) mg l^{-1}, COD of 196 (32–756) mg l^{-1}, NH_4^+-N of 33 (5.7–52) mg l^{-1} and NO_3^--N of 2.5 (0.3–13.8) mg l^{-1} (Sümer et al. 1996), passes through a screen, a grit chamber (1170 m^3) and a sedimentation tank (2080 m^3, 45 min, to remove the coarse particles), a trickling filter filled with coarse and porous lava stones for biofilm development during irrigation with waste water (3900 m^3, 50 min) and a aeration tank (1700 m^3, 120 min, for BOD_5 degradation and NO_3^--formation) before it is discharged to a secondary sedimentation tank (2980 m^3, 15 min), a polishing pond (11000 m^3, a type of lake in which the biologically treated waste water is ameliorated during longer periods of residence) and the "receiving" water. The other two-thirds or 52000 m^3 day^{-1} pass the screen, the grit chamber (1170 m^3) and the sedimentation tank (1760 m^3, 45 min), but then goes through an anaerobic tank (4000 m^3, 70 min) and nitrifying and denitrifying units (16000 m^3, 140 min) before the clarified waste water is discharged into the secondary sedimentation tank (13450 m^3, 18 min), the polishing pond (11000 m^3) and the "receiving" water (Fig 2, Linn et al. 1995).

Nitrous oxide flux measurements and N_2O quantification inside the soil body

The in situ N_2O fluxes to the atmosphere in the cropping systems were determined as described by Schwarz et al. (1994), but without flushing the soil with C_2H_2. Briefly, open chambers (50 cm×10 cm×15 cm, four in parallel) equipped with a sharpened steel base and a removeable lid were inserted about 5 cm deep into the soil between the plant rows. The plants under the boxes were removed. Before each N_2O-sampling period of 4 h day^{-1} the lid was made air tight and the open chambers continuously flushed with an air stream (20 l h^{-1}) using a vacuum pump (Vacubrand M2, Germany) and flow meters (Platon, Germany). After each N_2O measurement the lids were removed to avoid the development of a different microclimate under the cover boxes. The N_2O released into the air stream was collected on three 0.5-nm molecular sieve traps (19 cm in length, 2.5 cm in diameter; ca. 35-g 2-mm pellets; Merck, Germany).

The development of a method to quantify the N_2O retained by the soil body has been described in detail by Weiske et al. (1995). Briefly, soil samples from the cropping system K2 and M3 down to 90 cm depth were taken in the field (February–July 1994) with an auger (three parallel samples per treatment), and divided into subsamples (0–30 cm, 30–60 cm, 60–90 cm). To avoid major degassing of N_2O, portions of the parallel soil samples were transferred straight from the auger into 100-ml Erlenmeyer flasks (about 40–60 g fresh soil). The Erlenmeyer flasks were immediately closed and made air tight with a rubber septum seal (Venerett, France) and stored in a cooling box (ca. 4 °C) to keep the microbial activity at a low level during the transfer to the laboratory (ca. 15 min). On reaching the laboratory the flasks were heated in a water bath to 80 °C over a period of 80 min. Using this procedure, N_2O formation during incubation was completely suppressed (pasteurization) and a total release of the N_2O trapped in the soil body was achieved (Weiske et al. 1995).

The in situ N_2O emissions from the aerated fluid-bed reactor and the nitrification-denitrification tank of the waste water purification plant in Gießen were quantified with floating self-constructed open PVC covers (dimensions 60×40×20 cm, six in parallel) as recently described by Körner et al. (1993) and slightly modified by Sümer et al. (1995). For sampling dates see Sümer et al. (1995) and Linn et al. (1995). The atmosphere of the covers was transported continuously

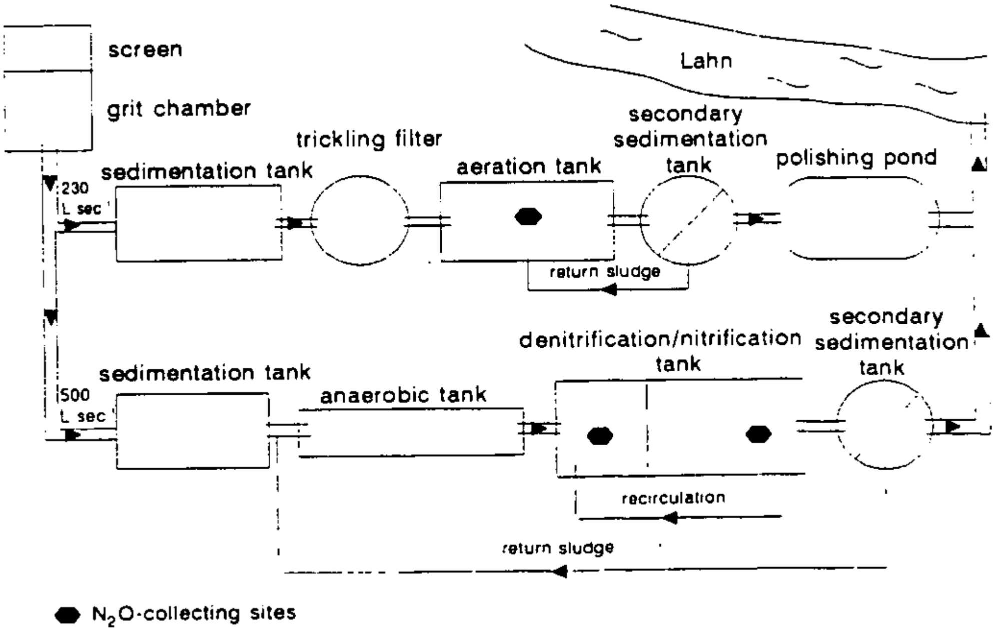

Fig. 2 Schematic diagram of the waste water treatment plant at Gießen, Germany, and the N_2O-measuring sites

by a membrane pump (air stream of 90 l h^{-1}) over silica gel and sodium hydroxide traps (to remove the H_2O and CO_2, respectively) into colums of 0.5-nm molecular sieve filled with 2-mm pellets (Merck, Germany, to absorb the N_2O quantitatively). To obtain a homogeneous air stream, two uniformly perforated PVC plates (with holes, each 0.8 cm in diameter) were fixed perpendicularly to the air stream inside the chambers. At each sampling the chambers were flushed for 2 h. To compensate the frequently changing air fluxes by the waste water aeration device, the total air stream of 90 l h^{-1} was subdivided into a 20-l-h^{-1} stream (for N_2O collection) and a 70-l-h^{-1} bypass (to avoid uncontrolled lifting up of the chambers). Both air streams were controlled by flow meters (Platon, Germany).

The N_2O released from the different cropping systems as well as from the different units of the waste water treatment plant, absorbed on the molecular sieve, was desorbed in evacuated Erlenmeyer flasks ca. 1 l in volume containing 150 ml water (Benckiser et al. 1995). Gas portions of the atmosphere of the Erlenmeyer flasks either used to desorb N_2O from the molecular sieve or to release N_2O from the soil solution were analysed gas chromatographically. A gas chromatograph equipped with an electron capture detector (ECD; Sigma 300, Perkin Elmer, Germany; Porapak Q column 2 m, 120 mesh; N_2 carrier gas; detector 300°C; injector 150°C; column 50°C; flow 30 ml min^{-1}) was employed to quantify the N_2O. The amount of N_2O dissolved in the water was calculated according to Moraghan and Buresh (1977). The N_2O concentration in the surrounding air was determined in separate units and subtracted from the measurements. N_2O surface fluxes were calculated as milligrams N_2O per metre per hour.

Analytical procedure

Soil samples (ten samples per treatment) were collected with an auger (0–30 cm), combined, mixed and freed from roots and organic remains by passing through a 2-mm sieve and stored at 4°C. NO_3^- was extracted following the procedure of Scharpf and Wehrmann (1976). Twenty grams of fresh soil was shaken with 100 ml extracting solution (1 *N* NaCl to 0.1 *N* $CaCl_2$) for 1 h and filtered (595 1/2, Schleicher and Schüll, Germany). The filtrate was analysed for NO_3^- by ultraviolet absorption at 210 nm. Water-soluble carbon (C_{H_2O}) was determined following the procedure of Burford and Bremner (1975). Twenty grams of air-dried soil was shaken with 40 ml distilled water for 30 min at 130 U min^{-1}, which 10 ml of a 4 *M* Na_2SO_4 solution was added and by shaking poured through a filter (595 1/2, Schleicher and Schüll, Germany). From the filtrate an aliquot of 20 ml was transferred into 100-ml Erlenmeyer flasks and the water evaporated at 80°C. Then 5 ml 2 *N* $K_2Cr_2O_7$ and 9 ml concentrated H_2SO_4 were added and allowed to oxidize for 90 min at 120°C. After cooling down to room temperature, the samples were filled with distilled water to the 50-ml marker, centrifuged for 15 min (3000 U min^{-1}, Heraeus, Germany) and the reduced Cr^{3+} ions analysed photometrically at 578 nm (Hitachi, Germany).

Simultaneously to each N_2O measurement waste water samples were taken from a depth of 0–20 cm. NO_3^- was determined in 100-ml waste water samples by extraction with 100 ml of a 0.1 *N* NaCl and 0.01 *N* $CaCl_2$ solution for 1 h and analysis of the filtrate by ultraviolet absorption at 210 nm (Navone 1964). The biological oxygen demand after 5 days of incubation (BOD_5) was determined manometrically with a WTW BOD-analyser (Model 1002, Germany) or wi a Sapromat BOD analyser (type B 12, Voith, Germany) in samples t ken close to the N_2O-measuring sites. The unfiltered waste wat samples (150–250 ml) were incubated over 5 days at 20°C in a water bath and the O_2 demand l^{-1} was recorded directly.

Simple and multiple regressions for evaluating the soil and wast water parameters which might influence the microbial N_2O formatio were carried out with the SPSS for Windows Release 5.01.

Results

Figure 3 compares the nitrate contents at the N_2O-sampling sites with the N_2O surface fluxes. N_2O was emitted by all the cropping systems studied and the domestic waste water treatment plant units. The cropping systems released mean amounts of 0.08, 0.14, 0.22 and 0.13 mg N_2O m^{-2} h^{-1} (Fig. 3 A–D) and the aerated, nitrifying and denitrifying tanks released mean amounts of 1.0, 19.5 and 0.5 mg N_2O m^{-2} h^{-1} (Fig. 3 E–G), respectively. The highest N_2O fluxes in the cropping systems occurred in the plots fertilized with 120 kg N ha^{-1} $year^{-1}$ and with maize in the rotation (Fig. 3 C). In the waste water treatment plant the highest N_2O releases occurred in the nitrification tank (Fig. 3 F). As frequently observed with field data, the correlations between soil or waste water nitrate and N_2O emissions were relatively poor. A positive correlation significant at the 95% probability level was found for the field site which received no mineral nitrogen fertilization (Fig. 3 D) and in the aerated tank which receives nitrogen almost exclusively in organic form or as NH_4^+. The correlation coefficients for the cropping systems (Fig. 3 A–D), in particular, but also for the waste water treatment plant (Fig. 3 E–G) suggest that decreasing N-fertilization or N-inputs improves the positive relationship.

Figure 4 compares the water-soluble or available carbon contents at the N_2O-sampling sites with the N_2O surface fluxes. In contrast to nitrate (Fig. 3) the correlation coefficients were generally negative. The cropping system with *Vicia faba* in the rotation and fertilized with 80 kg N ha^{-1} $year^{-1}$ showed a significant negative correlation (Fig. 4 A). This significant correlation, supported by the others, obviously shows that with increasing amounts of available carbon the N_2O emissions are lowered.

The water-soluble carbon- or BOD_5-to-nitrate ratios at the N_2O-sampling sites are compared with the N_2O surface fluxes in Fig. 5. A significant negative correlation is shown by the cropping system fertilized with 120 kg N ha^{-1} $year^{-1}$ and *Vicia faba* in the rotation (Fig. 5 B) and by

Table 1 Amounts of nitrous oxide (mg N_2O kg^{-1} dry soil) released from soil samples taken during 1994 from different depths of two cropping systems planted to winter rye (K2 = no N-fertilization, M3 = 80 kg N ha^{-1})

Cropping system	Soil depth (cm)	Sampling dates during 1994						
		9.2	17.2	1.3	22.4	19.5	21.6	27.7
K2	0–30	0	0	8.8±0.13	3.6±0.05	7.8±0.08	6.6±0.07	4.2±0.05
	30–60	0	0	0	1.4±0.08	2.6±0.04	0	0
	60–90	0	0	0	0	0	0	4.3±0.08
M3	0–30	11.0±0.13	6.1±0.1	35.4±0.2	45.8±0.9	21.5±0.3	19.5±0.22	6.8±0.15
	30–60	0	6.1±0.17	11.2±0.14	2.8±0.02	9.9±0.13	9.1±0.16	3.1±0.02
	60–90	0	3.5±0.05	0	0	3.3±0.02	1.4±0.03	0

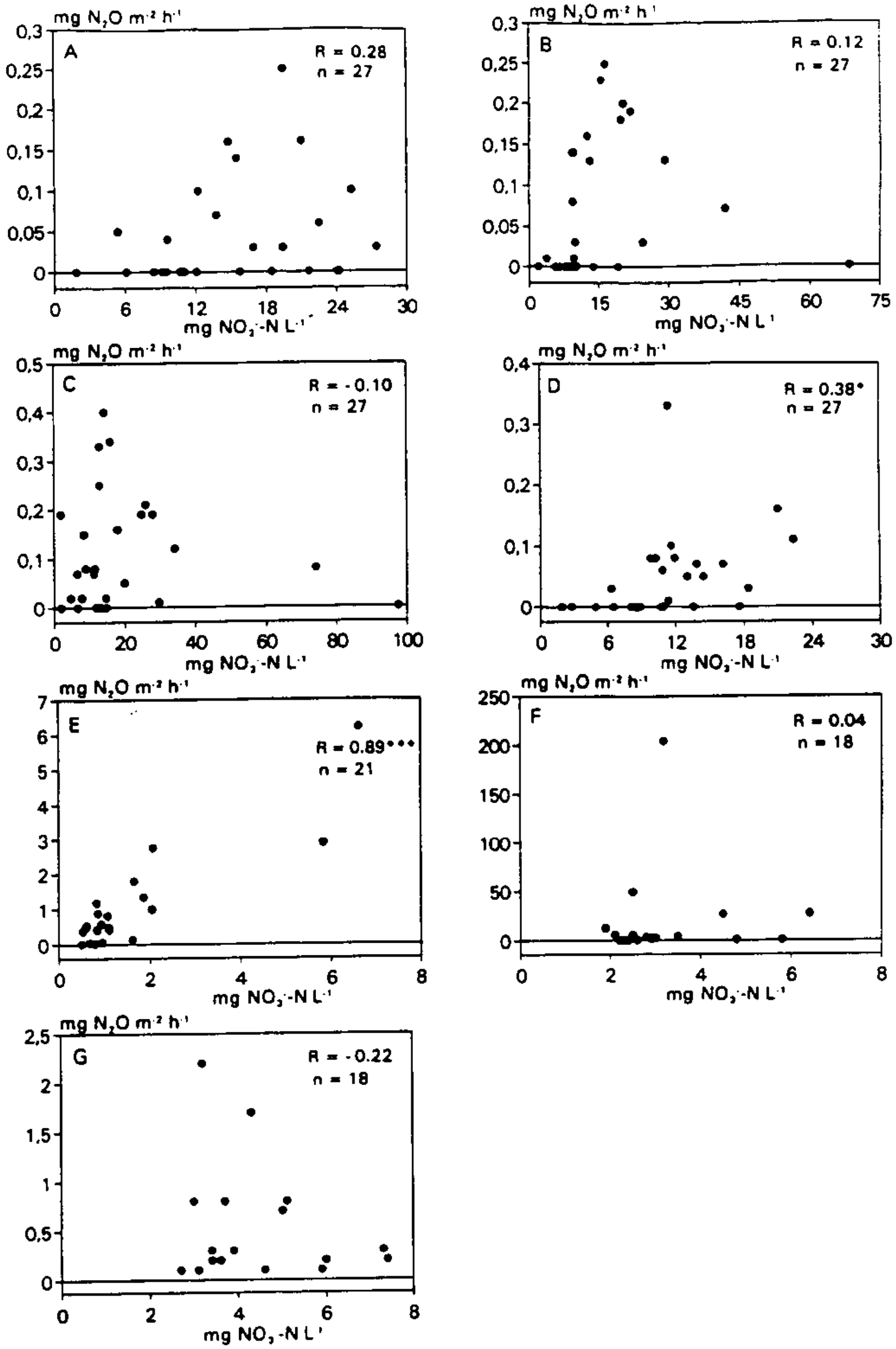

Fig. 5A–G Nitrous oxide surface fluxes from different cropping systems and the aerated, nitrifying and denitrifying tanks of the waste water treatment plant in Gießen, Germany, in comparison to the nitrate contents. **A** A3=*Vicia faba*, 80 kg N ha^{-1} kg; **B** A4 *Vicia faba*, 120 kg N ha^{-1}; **C** M4 *Zea mays*, 120 kg N ha^{-1}; **D** K2 *Trifolium campestre*, no nitrogen fertilization; **E** aerated tank; **F** nitrification tank; **G** denitrification tank

the aerated tank (Fig. 5E). From Fig. 5B, E as well as tentatively from the other investigated cropping and waste water systems, it can be concluded that the wider the carbon-to-nitrate ratio the lower the N$_2$O fluxes. This suggests that the cropping and waste water treatment systems can be potential N$_2$O sinks if organic carbon availability is high compared to nitrate. Water-soluble carbon-to-nitrate ratios above 60 in the cropping systems and BOD$_5$-to-nitrate ratios above 600–800 in the waste water treatment systems generally correspond to decreasing N$_2$O emissions.

Fig. 4A–G Nitrous oxide surface fluxes from different cropping systems and the aerated, nitrifying and denitrifying tanks of the waste water treatment plant in Gießen, Germany, in comparison to the water-soluble carbon contents or the biological oxygen demand (BOD_5). For legend see Fig. 3

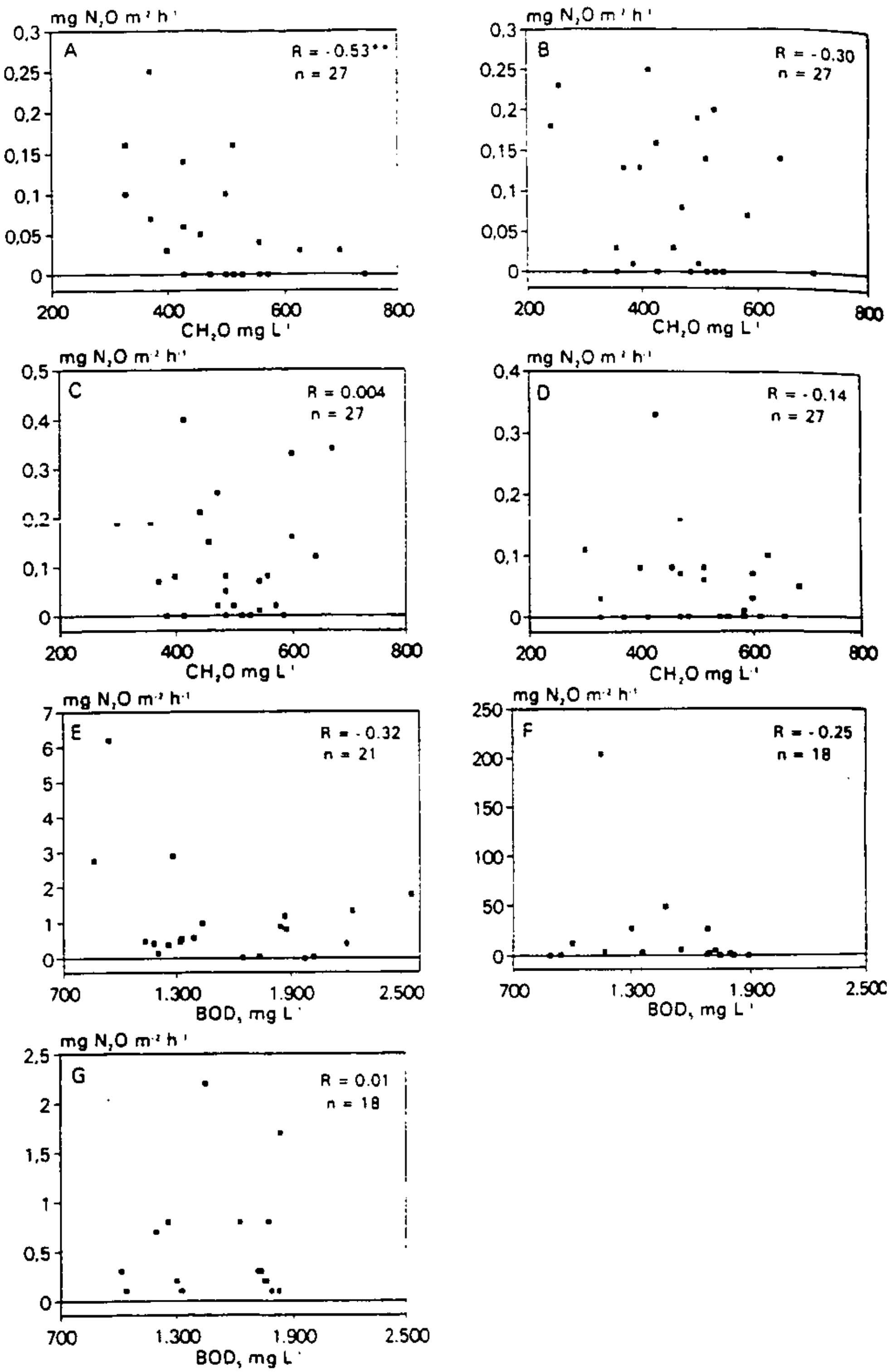

Table 1 shows the amounts of N_2O trapped during February to July 1994 in the soil bodies of the cropping systems M3 (80 kg N ha^{-1} $year^{-1}$) and K2 (no N-fertilization) down to a depth of 90 cm. Despite an unknown amount of N_2O which might be lost to the atmosphere during the transfer of the soil samples from the auger to the Erlenmeyer flasks, the following conclusions can be drawn from Table 1. First, both cropping systems cover significantly different amounts of N_2O in their soil bodies. The retained N_2O amounts of the variant M3 are about 40 times higher than those from the variant K2. Secondly, in both cropping systems the highest amounts of N_2O are in

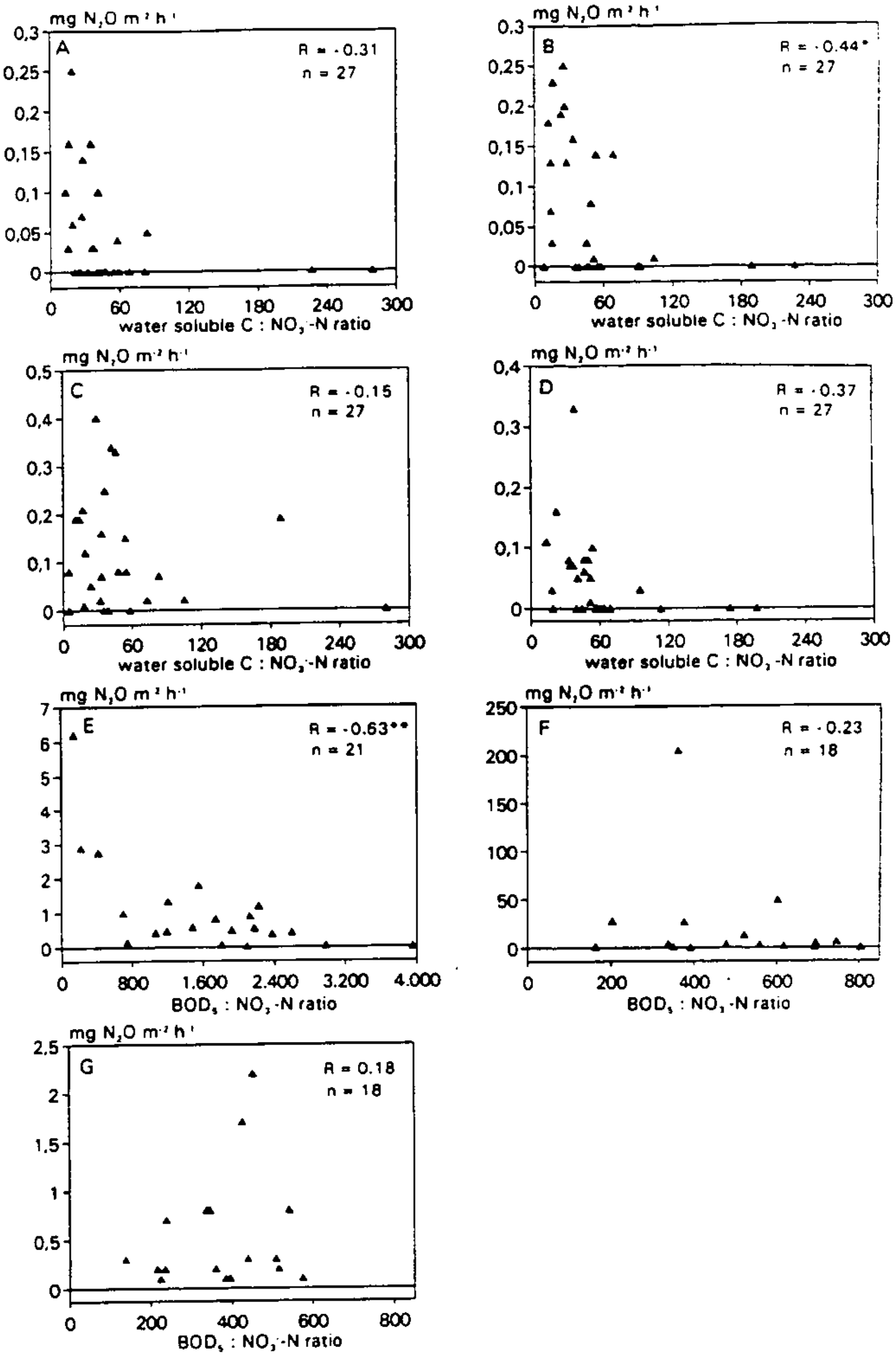

Fig. 5A–G Nitrous oxide surface fluxes from different cropping systems and the aerated, nitrifying and denitrifying tanks of the waste water treatment plant in Gießen, Germany, in comparison to the water-soluble carbon or biological oxygen demand (BOD_5)-to-nitrate ratio. For legend see Fig. 3

the 0- to 30-cm soil layer. Third, in the deeper soil layers (30–60 cm and 60–90 cm) the amounts of N_2O are still considerable. This N_2O formation seems to be restricted to distinct periods during the cropping season.

Discussion

The data presented show that the N_2O emissions from soils and waste waters seem to depend predominantly on the carbon-to-nitrate ratio. In some of the cropping and waste water systems studied it was even found that N_2O

release was highly affected by the availability of both carbon and nitrate. The various N_2O-forming processes (Fig. 1) can occur simultaneously in soil aggregates and sewage sludge flocculates, even if the soils and waste water are well aerated. Most of these N_2O-forming processes need available carbon as the electron donator and nitrate or nitrite as the electron acceptor. In the presence of oxygen, the availability of carbon and nitrate is generally improved. In reverse, oxygen diffuses more slowly than nitrate into the inner parts of the soil aggregates or sewage flocculates. Consequently, instead of O_2, nitrate and nitrite are preferentially used as e^--acceptors for energy conservation and N_2O may be formed. N_2O can now diffuse into the atmosphere of is dissimilated into N_2 by acting as the e^--acceptor. Depending on the nitrate-to-carbon ratio more or less N_2 will be released during denitrification. In this context, it is not surprising that the N_2O release from the well-aerated nitrification tank is about 40 times higher than from the un-aerated denitrification tank. Simple (Figs. 3–5E) as well as multiple correlations between the spatially and temporally highly variable in situ N_2O emissions and factors such as water-soluble carbon (C_{H_2O}), BOD_5, NO_3^-, NO_2^- concentrations and pO_2, temperature and pH showed that in the aerated tank N_2O increased with NO_3^- and NO_2^- concentration as well as with the pH, but remained nearly unaffected by changes in pO_2, temperature and C_{H_2O} or BOD_5 (Sümer et al. 1995, 1996). Nitrite and nitrate has been identified as one of the proximal controls in the denitrification of nitrifiers (Blackmer et al. 1980; Bock et al. 1988; Tortoso and Hutchinson 1990; Robertson and Kuenen 1991; Hooper et al. 1990; Mosier and Schimel 1993; Sümer et al. 1996) and in the heterotrophic denitrification process (Tiedje 1988; Benckiser 1994; Ottow and Benckiser 1994). In well-aerated topsoils and waste water treatment systems N_2O emission should be ascribed essentially to nitrification-denitrification rather than heterotrophic denitrification. At reduced oxygen pressue the ammonium and nitrite oxidizers of the genera *Nitrosomonas* and *Nitrobacter* are able to use organic compounds and/or NH_4^+ for supplying reduction equivalents. With nitrite and/or nitrate as electron acceptors in order to continue their energy conservation (Körner et al. 1993; Sümer et al. 1995; Bock et al. 1995).

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O \quad DG^0 = -360\,\mathrm{kJ\,mol^{-1}} \qquad (1)$$

This alternative strategy of nitrifiers of continuing ATP synthesis by using part of their own end products of aerobic metabolism at reduced oxygen supply may make a considerable to temporary contribution to the N_2O emissions from topsoils or waste water tanks. If more sophisticated biological waste water purification plants are installed world wide in the next 10–30 years, nitrate pollution and eutrophication of our waters will be reduced but as a side effect the global contribution of waste water purification plants to the atmospheric N_2O budget might be increased. At present the N_2O concentration in the atmosphere is increasing by 0.2–0.3% annually (Papen and Seiler 1994). An annual increase of 0.25% corresponds to an additional amount of 3.5 Tg N_2O-N year^{-1} on a global scale. The amounts of N_2O released from terrestrial ecosystems (agricultural soils, grassland and forests) on a global scale have been budget at ca. 5 Tg a^{-1} and from Germany in the range of 0.075 Tg year^{-1} (Davidson 1991; Dritter Bericht der Enquete-Kommision 1994). The aerated tank and the nitrification-denitrification units (Fig. 2) release about 0.001% N or 0.04% N, respectively, if N_2O-N is expressed as a percentage of the total amount of N received (Figs. 3–5E–G; Linn et al. 1995; Sümer et al. 1995, 1996). German waste water treatment plants receive N-inputs from 161×10^6 inhabitant-equivalents. Based on the above N_2O percentage and the inhabitant-equivalents and considering that all German waste water treatment plants are equipped with N-elimination units (Fig. 2), the N_2O emission will increase from about 7 Mg N_2O year^{-1} (roughly estimated from the data of the aerated tank; Sümer et al. 1995a) to about 350 Mg N_2O year^{-1} (roughly estimated from the data of the nitrification-denitrification tank; Linn et al. 1995). Compared to the estimates of total German anthropogenic N_2O emissions (206–276 Gg N_2O year^{-1}), these amounts of N_2O, should be considered insignificant. In view of the characteristics of N_2O that it is trapped in considerable amounts in the soil (Table 1; Weiske et al. 1995) and waste water (Linn et al. 1995) as well as being characterized by an atmospheric lifetime of about 100–200 years and a relatively high potential for IR adsorption, this trace gas should not be underestimated (Sümer et al. 1996). Our measurements of trapped N_2O are based on soil samples taken with an auger (Table 1). Compared with the amounts of dissolved N_2O, determined in soil solutions drawn up in a southeastern hardwood forest (USA) using high-flow porous cups (0.07–ca. 8 µg N_2O-N l^{-1}; Davidson and Swank 1990), the amounts of N_2O trapped in the soil body (76 mg N_2O-N l^{-1} in the K2 plots, which received no mineral N-fertilizer; 74.6 mg N_2O l^{-1} in the M3 plots, which received 80 kg ha^{-1} year^{-1}) are approximately 10^3–10^4 times higher. The quantities of N_2O trapped in the soil seem to depend on fertilization, seasonal constraints and soil depth. Subsoils have a potential for N_2O production which should be not neglected (Lehn-Reiser et al. 1991). In phreatic aerobic aquifers, nitrate enriched by diposal of human and animal wastes, the N_2O concentrations are up to 3 orders of magnitude higher than the concentrations expected as a result of equilibrium with the atmosphere (Ronen et al. 1988). This N_2O, which may be entrapped in soil aggregates (Kemper et al. 1985), dissolved in the soil water (Minami 1987) or sorbed on clay minerals and organic substances (Hazzard et al. 1985; Chalamet 1990) may dissimilated to N_2 and/or released somewhere at some future time into the atmosphere, potentially increasing the hazardous greenhouse effect.

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MIDWEST RESEARCH INSTITUTE

Project/Acct. No. 4604-04 Date/Time 9/97

Project Title Fertilizer Application AP-42 Reference 43 Emission Factor Calculations

Signature BRIAN SHRAGER Verified by ______ (signature/date)

Phone Contact ☐
Meeting Notes ☐
Work Sheet ☒

Page ___ of ___

FERTILIZER: AN → (NH_4NO_3)

POLLUTANT: N_2O

FOUR SAMPLING PERIODS, A, B, C, D

APPLICATION: ASSUMED DRY BROADCAST

APPLICATION RATES:

PERIOD		EMISSION RATES
A	80 Kg N/ha	0.9 Kg N_2O-N/ha
B	120 kg N/ha	1.5 Kg N2O-N/ha
C	120 Kg N/ha	2.4 Kg N2O-N/ha
D	0	

EMISSION FACTORS

A: $0.9 \frac{Kg\ N2O\text{-}N}{ha} \times \frac{44}{28} \frac{kg\ NO}{kg\text{-}N} \div 80 \frac{Kg\ N}{ha} \times 1000 \frac{g}{kg} = 17.7 \frac{g\ N_2O}{Kg\ N} = 35.4$ lb/ton

B: $1.5 \frac{Kg\ N_2O\text{-}N}{ha} \times \frac{44}{28} \frac{Kg\ NO}{Kg\ N} \div 120 \frac{Kg\ N}{ha} \times 1000 \frac{g}{Kg} = 19.6 \frac{g\ N_2O}{Kg\ N} = 39.2$ lb/ton

C: $2.4 \frac{Kg\ N_2O\text{-}N}{ha} \times \frac{44}{28} \frac{Kg\ NO}{Kg\ N} \div 120 \frac{Kg\ N}{ha} \times 1000 \frac{g}{Kg} = 31.4 \frac{g\ N2O}{Kg\ N} = 62.8$ lb/ton