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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

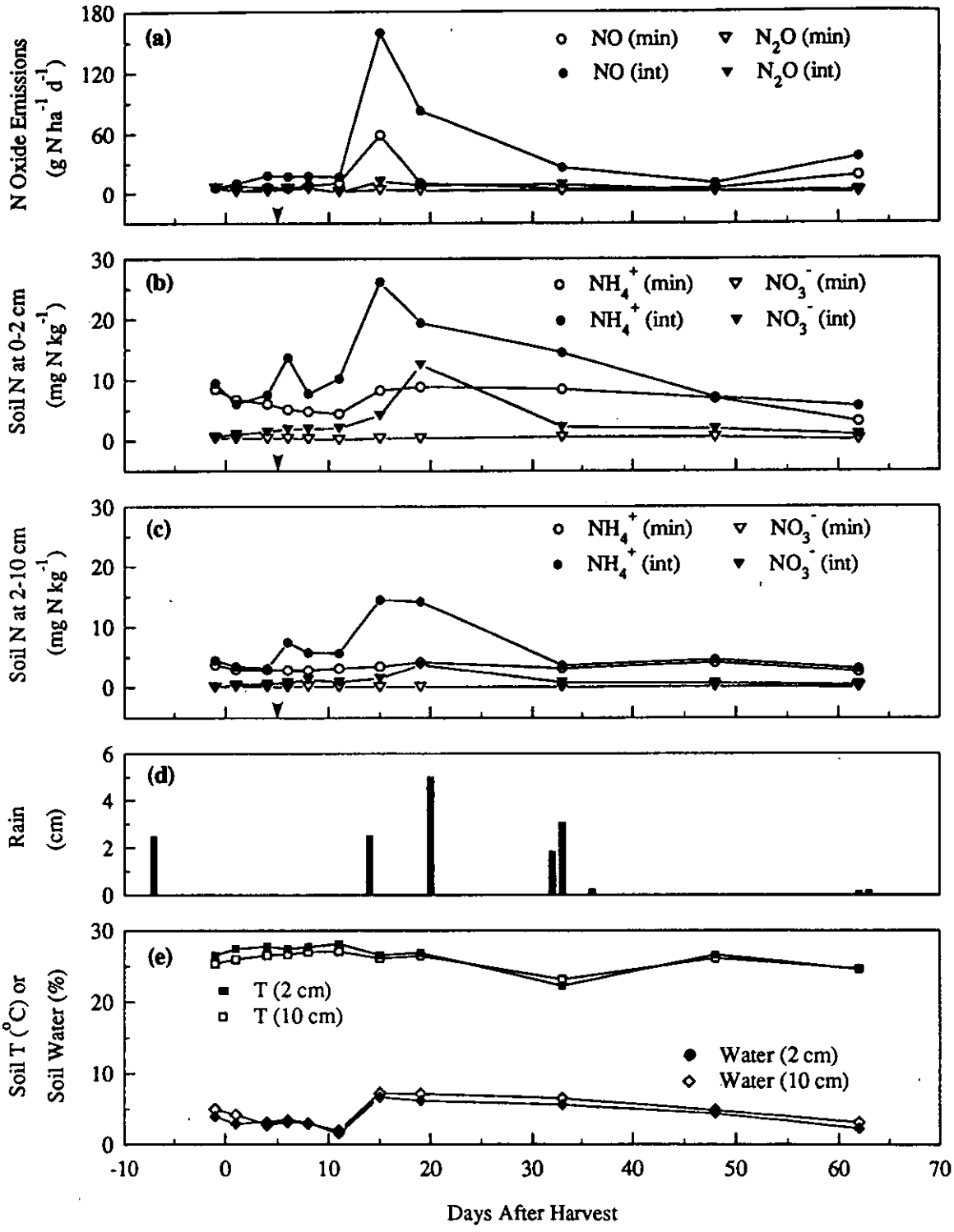

Fig. 1. Early summer data from a Bermuda grass pasture subject to minimum (min) or intensive (int) cultural management. (*a*) NO and N_2O emission rates. (*b*) Soil NH_4^+ and NO_3^- concentrations at 0- to 2-cm depth. (*c*) Soil NH_4^+ and NO_3^- concentrations at 2- to 10-cm depth. (*d*) Precipitation. (*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.

$(NH_4)_2SO_4$ 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_2O and especially NO were strongly stimulated by application of 52 kg N ha^{-1} as $(NH_4)_2SO_4$

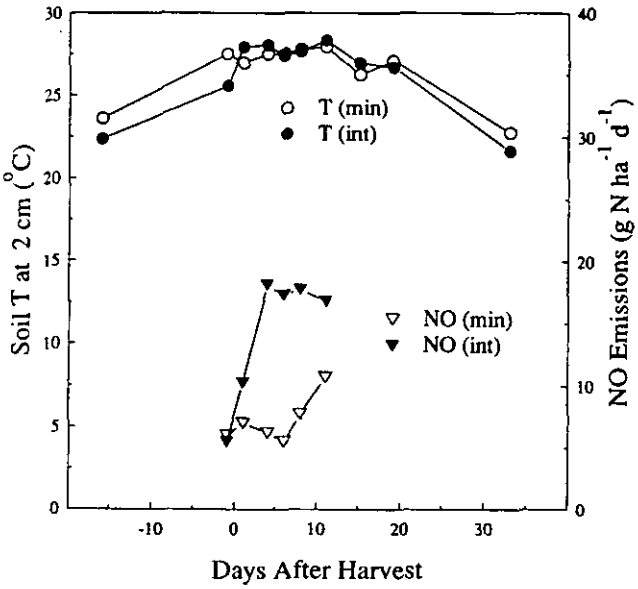

Fig. 2. NO emission rate and soil temperature at 2-cm depth during the period prior to and immediately following harvest of a Bermuda grass pasture subject to minimum (min) or intensive (int) cultural management. Data points represent the means of measurements from four replicate plots.

(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

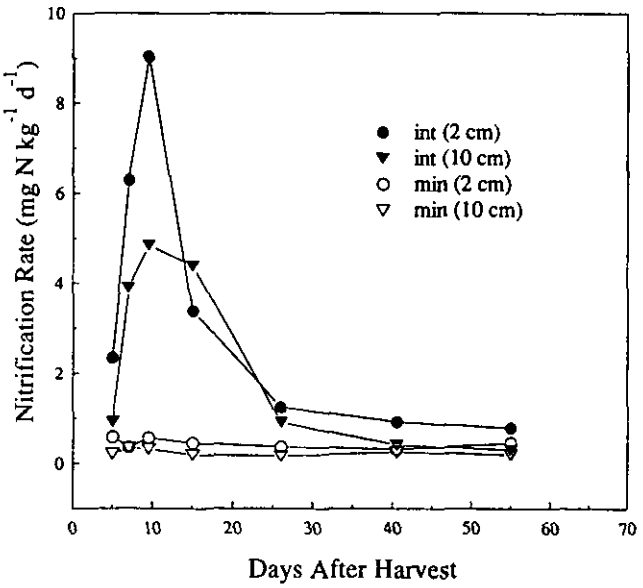

Fig. 3. Nitrification rates measured in soil samples taken from 0- to 2- and 2- to 10-cm depths and then buried in polyethylene bags at 2- and 10-cm depths, respectively, in a Bermuda grass pasture subject to minimum (min) or intensive (int) cultural management. Data points represent the mean change 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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REFERENCES

Anderson, I. C., and J. S. Levine, Relative rates of nitric oxide and nitrous oxide production by nitrifiers, denitrifiers and nitrate respirers, *Appl. Environ. Microbiol.*, *51*, 938–945, 1986.

Anderson, I. C., and J. S. Levine, Simultaneous field measurements of biogenic emissions of nitric oxide and nitrous oxide, *J. Geophys. Res.*, *92*, 965–976, 1987.

Anthony, W. H., and G. L. Hutchinson, Soil cover measurement of N_2O flux: Linear vs. nonlinear equations (abstract), in *Agronomy Abstracts*, p. 243, American Society of Agronomy, Madison, Wisc., 1990.

Bleakley, B. H., and J. M. Tiedje, Nitrous oxide production by organisms other than nitrifiers or denitrifiers, *Appl. Environ. Microbiol.*, *44*, 1342–1348, 1982.

Davidson, E. A., Sources of nitric oxide and nitrous oxide following wetting of dry soil, *Soil Sci. Soc. Am. J.*, *56*, 95–102, 1992.

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

Folorunso, O. A., and D. E. Rolston, Spatial variability of field-measured denitrification gas fluxes, *Soil Sci. Soc. Am. J.*, *48*, 1214–1219, 1984.

Hutchinson, G. L., and E. A. Davidson, Processes for production and consumption of gaseous nitrogen oxides in soil, in *Agricultural Ecosystem Effects on Trace Gases and Global Climate Change*, edited by L. A. Harper et al., Soil Science Society of America, Madison, Wisc., in press, 1992.

Hutchinson, G. L., and G. P. Livingston, Use of chamber systems to measure trace gas fluxes, in *Agricultural Ecosystem Effects on Trace Gases and Global Climate Change*, edited by L. A. Harper et al., Soil Science Society of America, Madison, Wisc., in press, 1992.

Hutchinson, G. L., and A. R. Mosier, Improved soil cover method for field measurement of nitrous oxide fluxes, *Soil Sci. Soc. Am. J.*, *45*, 311–316, 1981.

Hutchinson, G. L., and F. G. Viets, Jr., Nitrogen enrichment of surface water by absorption of ammonia volatilized from cattle feedlots, *Science*, *166*, 514–515, 1969.

Hutchinson, G. L., A. C. Tortoso, and W. D. Guenzi, Comparison of NO vs. N_2O production during aerobic and anaerobic soil incubations (abstract), in *Agronomy Abstracts*, p. 218, American Society of Agronomy, Madison, Wisc., 1988.

Hutchinson, G. L., W. D. Guenzi, and G. P. Livingston, Soil water controls on aerobic soil emission of gaseous nitrogen oxides, *Soil Biol. Biochem.*, in press, 1992.

Johansson, C., and L. Granat, Emission of nitric oxide from arable land, *Tellus*, *36B*, 26–37, 1984.

Kaplan, W. A., S. C. Wofsy, M. Keller, and J. M. Da Costa, Emission of NO and deposition of O_3 in a tropical forest system, *J. Geophys. Res.*, *93*, 1389–1395, 1988.

Klepper, L., Nitric oxide (NO) and nitrogen dioxide (NO_2) emissions from herbicide-treated soybean plants, *Atmos. Environ.*, *13*, 537–542, 1979.

Lipschultz, F., O. C. Zafiriou, S. C. Wofsy, M. B. McElroy, F. W. Valois, and S. W. Watson, Production of NO and N_2O by soil nitrifying bacteria, *Nature*, *294*, 641–643, 1981.

Logan, J. A., Nitrogen oxides in the troposphere: global and regional budgets, *J. Geophys. Res.*, *88*, 10,785–10,807, 1983.

Matson, P. A., and P. M. Vitousek, Ecosystem approach to a global nitrous oxide budget, *Bioscience*, *40*, 667–672, 1990.

McElroy, M. B., and S. C. Wofsy, Tropical forests: Interactions with the atmosphere, in *Tropical Rain Forests and the World Atmosphere, Selected Symp. 101*, edited by G. T. Prance, pp. 33–60, American Association for the Advancement of Science, Washington, D. C., 1986.

McRae, G. J., and A. G. Russell, Dry deposition of nitrogen-containing species, in *Deposition Both Wet and Dry*, chap. 9, edited by B. B. Hicks, Butterworth, Boston, Mass., 1984.

Mosier, A. R., and L. Mack, Gas chromatographic system for precise, rapid analysis of nitrous oxide, *Soil Sci. Soc. Am. J.*, *44*, 1121–1123, 1980.

Nelson, D. W., Gaseous losses of nitrogen other than through denitrification, in *Nitrogen in Agricultural Soils, Agron. Monogr. 22*, edited by F. J. Stevenson, pp. 327–363, American Society of Agronomy and Soil Science Society of America, Madison, Wisc., 1982.

Sahrawat, K. L., and D. R. Keeney, Nitrous oxide emission from soils, *Adv. Soil Sci.*, *4*, 103–148, 1986.

Shepherd, M. F., S. Barzetti, and D. R. Hastie, The production of atmospheric NO_x and N_2O from a fertilized agricultural soil, *Atmos. Environ.*, *25A*, 1961–1969, 1991.

Sinclair, T. R., and R. F. Van Houtte, Simulative analysis of ammonia exchange between the atmosphere and plant communities, *Agric. Environ.*, *7*, 237–242, 1982.

Slemr, F., and W. Seiler, Field measurements of NO and NO_2 emissions from fertilized and unfertilized soils, *J. Atmos. Chem.*, *2*, 1–24, 1984.

Sparrow, S. D., and D. T. Masiak, Errors in analyses for ammonium and nitrate caused by contamination from filter papers, *Soil Sci. Soc. Am. J.*, *51*, 107–110, 1987.

Tortoso, A. C., and G. L. Hutchinson, Contributions of autotrophic and heterotrophic nitrifiers to soil NO and N_2O emissions, *Appl. Environ. Microbiol.*, *56*, 1799–1805, 1990.

Tortoso, A. C., G. L. Hutchinson, and W. D. Guenzi, Nitric and nitrous oxide emissions during nitrification and denitrification in soil (abstract), in *Agronomy Abstracts*, p. 190–191, American Society of Agronomy, Madison, Wisc., 1986.

Williams, E. J., and F. C. Fehsenfeld, Measurement of soil nitrogen oxide emissions at three North American ecosystems, *J. Geophys. Res.*, *96*, 1033–1042, 1991.

Williams, E. J., D. D. Parrish, M. P. Buhr, F. C. Fehsenfeld, and R. Fall, Measurement of soil NO_x emissions in central Pennsylvania, *J. Geophys. Res.*, *93*, 9539–9546, 1988.

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