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AP42 Section:	9.2.1
Background Ch	4
Reference:	56
Title:	E. A. Davidson, et al., "Nitrous Oxide Controls and Inorganic Nitrogen Dynamics in Fertilized Tropical Agricultural Soils," *Soil Science Society of America Journal*, 60(4):1145-1152, 1996.

Sect 4 #56

Nitrous Oxide Emission Controls and Inorganic Nitrogen Dynamics in Fertilized Tropical Agricultural Soils

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ABSTRACT

Use of N fertilizers in tropical regions has recently surpassed use in temperate regions, but understanding of N_2O emissions from fertilized soils is based largely on experience from temperate regions. We studied N_2O emissions from a sugar cane (*Saccharum officinarum* L.) plantation on the Hawaiian island of Maui. Young cane fields that were routinely fertilized had >15 mg NH_4^+-N and NO_3^--N kg^{-1} soil, whereas mature cane fields not being fertilized had <2 mg NH_4^+-N and NO_3^--N kg^{-1} soil. Emissions of N_2O were also ≈ 10 times higher in the young cane fields than in the mature cane. The highest nitrification potentials and N_2O emissions occurred near buried irrigation lines and lowest values between plant rows. Added $^{15}NH_4^+$ was nitrified within 48 h in both young and mature cane fields. Hence, microbial populations exist in both young and mature cane fields that can rapidly produce NO_3^-, and production of N_2O is controlled primarily by when and where fertilizer N is applied. In contrast to many temperate agricultural soils where mineralization-immobilization-turnover processes contribute significantly to the supply of crop N, rates of gross N mineralization were low, indicating that the cane crop N came primarily from applied fertilizer. In the mature cane, soil inorganic-N remains low because of high plant and microbial demand, but in the young cane, fertilizer applications exceed the plant and microbial sinks, and N_2O emissions are large. Better fertilizer management in this early stage of the cane crop cycle might significantly reduce N_2O emissions.

Use of N fertilizer in developing nations, most of which are in tropical regions, has recently exceeded use in developed nations of temperate zones (Galloway et al., 1995; Vitousek and Matson, 1993). Because developing nations of the tropics have the most rapid population growth, the demand for and use of N fertilizers is likely to grow there, whereas N fertilizer use has leveled off in temperate regions (Duxbury et al., 1993). Use of N fertilizers in agriculture during the last four decades is one of several explanations for accumulation of atmospheric N_2O, which is a greenhouse gas and a reactant in destruction of stratospheric ozone (Houghton et al., 1992; Robertson, 1993). Our understanding of the magnitude of N_2O emissions (Eichner, 1990) and the factors that control N_2O production (Firestone and Davidson, 1989) in fertilized soils is based largely on studies conducted in temperate regions. It is unclear how applicable our experience in temperate regions will be for predicting the effects of increased use of N fertilizers on N_2O emissions from tropical agricultural soils.

Sugar cane is a good example of a tropical crop that is managed differently from most crops grown in temperate regions. On the island of Maui where this study is focused, the crop cycle is ≈22 mo. Although not part of a developing country, Hawaiian agriculture offers an opportunity to study processes that control N_2O emissions in tropical soils, thus providing a start for understanding N_2O emissions from a broad range of tropical soils and agricultural systems. The cane fields of Maui are intensively fertilized with N, P, and K during the first 12 mo of growth, followed by little or no N fertilizer applied during the last 10 mo. The cane produces tremendous biomass, creating a large plant sink for the applied nutrients and also producing C residues that may enhance microbial sinks of N in the soil. The objective of this study was to explore the factors that control N_2O emissions from intensively managed sugar cane fields of Maui.

MATERIALS AND METHODS

Study Site

Research was conducted on the fields of a large plantation operated by Hawaii Commercial and Sugar (HC&S) on the island of Maui. The plantation covers the low elevation isthmus between two mountains and extends across both wet and dry sides of the island. Mean annual precipitation is 1000 to 1250 mm on the windward side and 250 to 300 mm on the leeward side of the island. The plantation is divided into numerous fields, each of which is managed as an independent unit. Cane crops are rotated such that, at any point in time, a variety of different aged crops can be found on various fields throughout the plantation. Fields are typically cleared to bare soil and disked before planting. Drip irrigation lines are then buried in mounds of soil ≈ 10 cm tall and 50 cm wide. Cane is planted in rows, with two rows on either side of each buried irrigation line, so that all cane plants are within 30 to 70 cm of the irrigation line. Fertilizer is routinely added as urea dissolved in the irrigation water. Typical doses are 40 kg N ha^{-1} applied about once per month, although smaller (10 kg N ha^{-1}) and more frequent (weekly or biweekly) doses are also being applied on some fields. Irrigation is used on both sides of the island, although the dry side is obviously more dependent upon irrigation. common methods

Nitrification Potential

A survey of nitrification potentials in four young fertilized fields receiving routine fertilization and two old fields that were no longer being fertilized was conducted in December 1992. Both wet and dry sides of the island were sampled. Selected site properties are shown in Table 1. Soil samples were collected from the top 10 cm at 12 locations within each cane field: four from irrigation lines, four from the cane rows, and four from the areas between cane rows. The soil samples were mixed and stored in plastic bags at 4°C for no more than 4 d prior to analysis.

The method of Belser and Mays (1980) was used, except that chlorate was not added as an inhibitor of NO_2^- oxidation, because the inhibition is often incomplete (Hart et al., 1994). In brief, 20-g samples of field moist soil were added to flasks containing 100 mL of 1.5 m*M* $(NH_4)_2SO_4$ (the solution also

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Published in Soil Sci. Soc. Am. J. 60:1145–1152 (1996).

mg N / kg dry soil · h

Table 1. Summary of site characteristics and nitrification potential rates.

Field	Age of cane**	Side of island**	pH in H_2O	Classification	Soil texture	Nitrification potentials by field position**		
						Cane line	Inter-row	Irrigation line
	mo					mg N kg^{-1} dry soil h^{-1}		
101	3 (young)	wet	5.8	Oxic Haplustolls	clay	0.184 (0.018)†	0.193 (0.015)	0.261 (0.035)
105	14 (old)	wet	6.0	Oxic Haplustolls	clay	0.213 (0.009)	0.221 (0.047)	0.316 (0.042)
200	4 (young)	wet	4.2	Oxic Humitropepts	clay	0.062 (0.009)	0.074 (0.001)	0.154 (0.074)
914	14 (old)	dry	7.0	Aridic Haplustolls	sandy clay loam	0.156 (0.022)	0.393 (0.104)	1.226 (0.360)
819	2 (young)	dry	6.8	Aridic Haplustolls	clay	0.241 (0.021)	0.245 (0.007)	2.307 (0.311)
817	6 (young)	dry	7.4	Aridic Haplustolls	clay	0.344 (0.048)	0.267 (0.030)	1.511 (0.318)

** Class variables in an analysis of variance of nitrification potentials that were significant at $P = 0.01$. ns = not significant.
† Means (and standard errors) of four replicate samples.

contained phosphate buffers and was adjusted to pH 7 before adding the soil) and the soil slurries were shaken continuously for 24 h at 25°C. Aliquots of 10 mL were removed from each flask after 2, 8, 20, and 24 h of shaking and were centrifuged at 8000 × *g* for 15 min. The supernatant was decanted, frozen, and later analyzed for $NO_2^- + NO_3^-$ by cadmium reduction in an autoanalyzer. The rate of potential nitrification for each soil sample was calculated from a linear regression of the production of $NO_2^- + NO_3^-$ within each flask. Subsamples of soil were dried at 105°C, and all results are expressed on a dry-weight basis.

Nitrogen-15 Labeling

Two cane fields, one with a young cane crop (≈2 mo since planting; Field 100) and one with an old cane crop (21 mo since planting; Field 105), were chosen on the wet side of the island for an intensive study using a ^{15}N tracer in July 1993. Soils of both fields are of the Paia series (very-fine, kaolinitic, isohypothermic Oxic Haplustoll). The young cane field had received a routine application of 10 kg N ha^{-1} by the company 6 d before our labeling experiment. The young cane plants were generally <30 cm tall and were left in place. The old cane plants were >2 m tall, with many interpenetrating dead fronds forming a dense mat over the soil. A narrow strip (≈60 cm) of soil along the length of one irrigation line in the old cane field was cleared of dead and live fronds to expose the soil for adding the N label.

In the young and old cane fields used for the ^{15}N labeling, eight mini-plots, 50 by 100 cm, were established on the soil over the irrigation line in each field. The irrigation line was chosen because this is the area that typically has the highest N_2O fluxes (Matson et al., 1996). A single soil core (7.5 cm diameter by 10 cm deep) was removed from each plot to measure initial values of NH_4^+, NO_3^-, net mineralization, net nitrification, and water content. The flux of N_2O was measured using a chamber (see below). Four of the miniplots in each field were then sprayed with 5 L of a 12 m*M* $(NH_4)_2SO_4$ solution that was 11 atom % ^{15}N. This application is equivalent to 34 kg N ha^{-1}. The other four miniplots received 5 L of water. Clear plastic was stretched over a wire grate to form an arching enclosure placed over each miniplot to prevent rain from washing away the added ^{15}N. The enclosure was open at the bottom near the soil and at either end to permit circulation of air. A soil core was then removed from each miniplot at 5, 24, 48, and 96 h after adding the label. Soil from each core was mixed and subsampled for extraction in KCl within 2 h of sampling (20 g moist soil in 100 mL 2 *M* KCl). Net mineralization and net nitrification were calculated from the change in KCl-extractable inorganic N concentrations during a 7-d laboratory incubation of 20 g soil at ambient moisture and temperature (Hart et al., 1994). Subsamples were also dried at 105°C to determine moisture content.

Nitrous Oxide Flux Measurements

The flux chamber design, consisting of a polyvinyl chloride ring left in place and a chamber top fitted over the ring for flux measurements, has been described by Vitousek et al. (1989). The rings were placed in the soil 1 h before the pre-labeling flux measurement. Headspace gas was sampled by syringe at 0, 10, 20, and 30 min following placement of the chamber tops over the soil and analyzed the same day by gas chromatography using an electron capture detector. Most of the fluxes were calculated from linear regression of measured increases in N_2O concentration in headspace gas of the chambers. However, nonlinear increases were occasionally observed, and the nonlinear method described by Hutchinson and Livingston (1993) was used for these calculations.

A N_2O flux measurement was also made on each miniplot at each sampling time. At the end of the N_2O flux measurement, after the flux chamber had been in place for 30 min, a 60-cm^3 gas sample was removed from the headspace of the chamber and injected into an evacuated, 50-cm^3, crimp-seal serum bottle for later $^{15}N_2O$ analysis. The injection needle holes in the serum stoppers were covered with silicone sealant. Several standards of 0.513 μL L^{-1} N_2O in N_2 were similarly injected into evacuated serum bottles to check for leakage, which was found to be insignificant.

Nitrogen-15 Analyses

Serum bottles containing $^{15}N_2O$ in air were analyzed at the Univ. of California, Berkeley, using the method described by Brooks et al. (1993). In brief, N_2O was first trapped on a molecular sieve and then eluted into the inlet of a direct combustion mass spectrometer. The average ^{15}N enrichment of the N_2O source was calculated from the following equation:

$$\text{At\%15N of source} = \frac{\text{At\%15N}_2\text{O}[\text{N}_2\text{O}]_1 - 0.366[\text{N}_2\text{O}]_0}{[\text{N}_2\text{O}]_1 - [\text{N}_2\text{O}]_0} \times 100$$

where At%15N_2O within the flux chamber was measured at the end of the flux measurement, and $[N_2O]_0$ and $[N_2O]_1$ were the concentrations of N_2O within the flux chamber at the beginning and end of the flux measurement, respectively.

Soil extracts in KCl were prepared for ^{15}N analysis according to the diffusion procedure of Brooks et al. (1989) as described by Hart et al. (1994). Aliquots of 40 mL extract were measured gravimetrically, MgO was added to volatilize NH_4^+ as NH_3, and the NH_3 was trapped on an acidified filter disk. The filter disks were dried and analyzed by mass spectroscopy at the Univ. of California, Berkeley. After NH_4^+ was volatilized from each aliquot of KCl extract, Devarda's alloy was added to reduce NO_3^- to NH_4^+ and the N was volatilized and trapped as before. For extracts in which the mass of NO_3^-–N in the

40 mL aliquot was <100 μg, a spike of 100 μg of unlabeled KNO_3–N was added to provide sufficient mass for analysis by mass spectrometry. This step adds an additional possibility of analytical error, as the ^{15}N enrichments of the filter disks must be corrected for the amount of ^{14}N added in the spike. Small errors in these measurements could account for some NO_3^- extracts appearing to have somewhat higher ^{15}N enrichments than the reported enrichment of the salt used in the solution applied to the soil.

Dried soil samples were finely ground in a roller jar apparatus and were subsampled for analysis of total N and ^{15}N by direct combustion mass spectroscopy.

Statistical Analyses

For the nitrification potential survey, analysis of variance used the side of the island (wet vs. dry), the age of the cane crop (old vs. young), and microsite position (irrigation line, cane row, or inter-row) as class variables. For the ^{15}N study, a repeated measures design was used with the form of N (NH_4^+, NO_3^-, N_2O), fertilization (label added vs. control), and time as fixed effects and miniplot-within-form-of-N as a random effect. In these cases, time was treated as a class variable because NH_4^+ and NO_3^- concentrations and N_2O fluxes were expected to first increase and then decrease, and the statistical tests were designed only to determine if post-treatment measurements differed from pre-treatment measurements as well as controls. When a variable was expected to change unimodally with time, such as dilution of the ^{15}N enrichment of the NH_4^+ pool, time was treated as a covariate in an analysis of covariance, to test whether the slope of the change of the measured parameter with time was significantly different from zero. All analyses were performed on JMP-SAS software.

RESULTS AND DISCUSSION

Nitrification Potentials

The nitrification potential procedure provides excess NH_4^+ in a well mixed, well aerated slurry of a buffered solution at pH 7, so that the limiting factor to the production of NO_3^- should, in theory, be the population and activity of nitrifying bacteria present in the soil sample (Belser, 1979; Hart et al., 1994). As originally described by Belser and Mays (1980), phosphate buffers neutralize acid production from nitrification, so that the soil slurries remain at pH 7 during the incubation. We found, however, that the buffers are not effective at neutralizing alkaline or acidic soils. Although the buffered solution was adjusted to pH 7 before adding soil samples, we found that the pH of the soil slurries reflected the pH of the soils. Both pre- and post-incubation pH measurements of the soil slurries were between 7.7 and 8.2 for the soils from the dry side of the island and were between 5.9 and 6.6 for soils from the wet side of the island. The effect of varying acidity of the slurry conditions may be confounded with differences in nitrifier populations across soil samples. Hence, the assay provides an index of nitrifier populations at or near the pH of the soil.

In this study, differences among fields were related to the side of the island, which may result from differences in the acidity of the soils on the two sides of the island. Significantly higher nitrification potentials occurred in fields on the more alkaline dry side of the island compared with the more acidic wet side (Table 1). Circumneutral to somewhat alkaline conditions are known to be conducive to growth of nitrifying bacteria (Hutchinson and Davidson, 1993).

Consistent and significant differences in nitrifying potentials were found among microsite positions within cane fields. Nitrifying potentials of the soil samples taken from the irrigation lines of all of the fields were significantly higher than nitrifying potentials of samples from the cane lines or the inter-row areas (Table 1). Matson et al. (1996) have also found that emissions of N_2O in the irrigation line are often several times higher than are emissions from the cane line and the interrow areas. For example, our soil sampling for nitrification potentials in Field 817 coincided with N_2O flux measurements in December 1992, when N_2O emissions were 1.1, 0.8, and 0.2 ng N cm^{-2} h^{-1} in the irrigation line, cane line, and inter-row areas, respectively, before fertilization and were 22.8, 1.3, and 0.1 ng N cm^{-2} h^{-1} in the same areas 24 h after routine fertilization by the company.

These results indicate that some of the spatial heterogeneity of N_2O emissions within these sugar cane fields can be explained by variation in nitrification potentials and, presumably, associated differences in the distribution of populations of nitrifying bacteria. Repeated fertilizer application during a single cropping cycle apparently resulted in development of larger and/or more active populations of nitrifying bacteria nearest the source of incoming fertilizer from the irrigation lines. A well-established population of nitrifying bacteria in the soil near the irrigation line could then rapidly produce NO_3^- following each fertilization. Emissions of N_2O could result either directly from nitrification or from denitrification of the NO_3^-.

No significant differences in nitrification potentials were observed between young and old cane fields (Table 1). Apparently, the nitrifier populations remain viable in the old cane fields several months after N fertilization ceases. Nitrification began immediately when soil from the old cane fields was placed in the $(NH_4)_2SO_4$ slurry solution.

Nitrogen-15 Labeling Experiment: Dynamics of Soil Ammonium and Nitrate

Increased extractable $^{14+15}NH_4^+$ was detected in the soils sampled 5 h after adding the label in both young and old cane fields (Fig. 1). An increase in $^{14+15}NO_3^-$ could not be detected in the young cane field, because the background $^{14}NO_3^-$ concentration was already high in the young cane soil due to previous fertilization and the concentration was dropping (Fig. 1b). Net NO_3^- production was apparent in the old cane soil 48 h after the label was added (Fig. 1a).

The nitrification slurry assay was repeated for soils collected each day after the labeling, but no differences in nitrification potential among days was observed in any of the miniplots (data not shown). Because the old cane soil already had an active nitrifier population prior to adding the N label (Table 1), and because there was no increase in nitrification potential immediately follow-

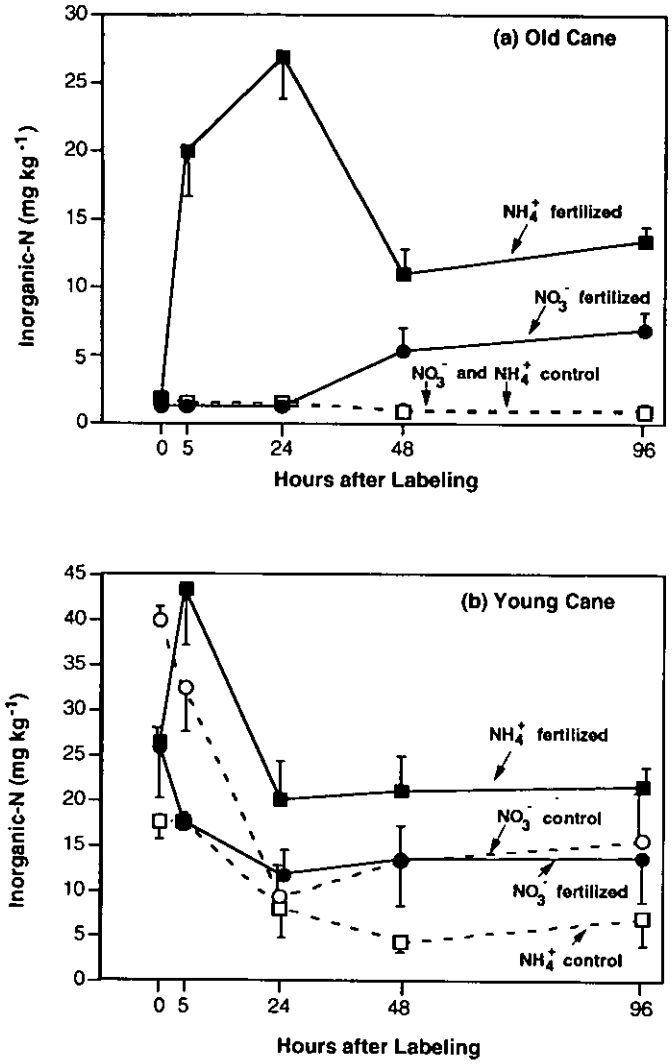

Fig. 1. Concentrations of KCl-extractable NH_4^+ and NO_3^- in the top 10 cm of a soil core removed from each miniplot. Means (points) and standard errors (bars) of four replicates miniplots for each treatment (control and fertilized with NH_4^+) in each field (young and old cane) are shown. For the unlabeled control soils of the old cane field, the concentrations of NH_4^+ and NO_3^- appear identical when plotted at this scale, so only one line is shown that applies to either species. Repeated measures design indicates that the effects of fertilizer, time, and their interaction are significant ($P = 0.01$) for both NH_4^+ and NO_3^- in the old cane field. In the young cane field, the fertilizer effect is significant ($P = 0.01$) for NH_4^+ only, time is significant ($P = 0.01$) for both NH_4^+ and NO_3^-, and the interaction is not significant ($P = 0.05$).

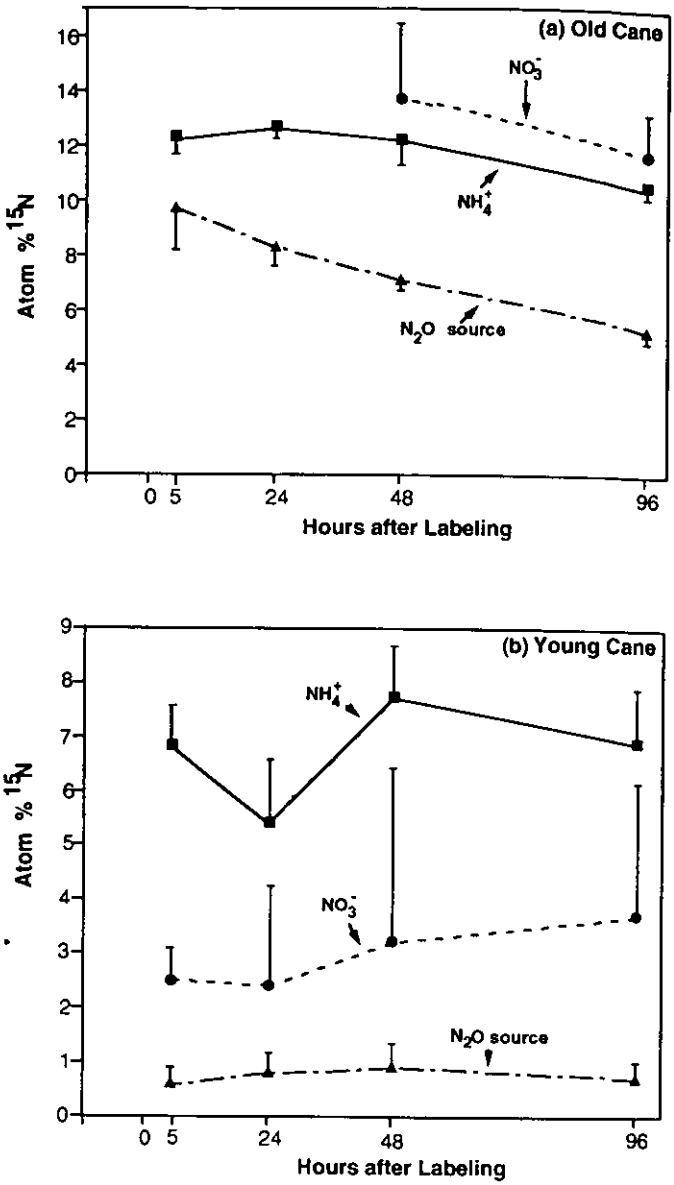

Fig. 2. ^{15}N enrichment measured in the NH_4^+ and NO_3^- pools of soil extracts of the top 10 cm of soil from each miniplot and the calculated average enrichment for the source of N_2O that accumulated within chambers used for flux measurements. Each miniplot received ^{15}N as NH_4^+. Means (points) and standard errors (bars) of four replicates miniplots for each field (young and old cane) are shown. Repeated measures design indicates that the enrichments of the NH_4^+ and NO_3^- pools were not statistically significantly different in the old cane field ($P = 0.05$), but they were different in the young cane field ($P = 0.01$). The large error bars reflect large spatial heterogeneity among replicates, but the repeated measures design for analysis of variance compares the enrichments of the NH_4^+ and NO_3^- pools within each replicate and these differences were consistent across time and across replicates. The enrichment of the N_2O source was significantly different from the inorganic N pools in both fields ($P = 0.01$). Analysis of covariance indicates significant decrease of the enrichment of the NH_4^+ pool ($P = 0.05$) and the N_2O source ($P = 0.01$) in the old cane field, but no other changes with time were significant.

ing N addition, nitrifier population growth does not appear to be the reason for the observed 24- to 48-h lag between the fertilizer application and the appearance of net NO_3^- production in the old cane soil (Fig. 1a). Perhaps nitrification was limited by the rate of diffusion of added N from the surface where it was applied to the microsites where the nitrifiers of this old cane field soil remain viable.

Although we were able to measure small quantities of ^{15}N in the NO_3^- pool of the old cane soil on all days, the NO_3^- pool was initially very small, so that small errors in either the measured $^{15}NO_3^-$ or $^{14}NO_3^-$ would cause unacceptably large errors in estimates of ratios of ^{15}N to ^{14}N. Once sufficient NO_3^- was produced in the old cane soil after 48 h, however, the ^{15}N enrichment of the NO_3^- pool could be reliably measured and the enrichments of the NH_4^+ and NO_3^- pools were not significantly different (Fig. 2a). Hence, the NO_3^- pool of the old cane soil came almost entirely from the labeled

NH_4^+ pool. In contrast, the young cane field already had high concentrations of NO_3^- prior to N labeling, and the NO_3^- pool consistently had lower enrichments than the NH_4^+ pool across replicate plots of the young cane field (Fig. 2b).

The enrichments of the NH_4^+ pools in the young cane field did not change significantly during the 96-h study period, which indicates that gross N mineralization rates were too low to detect by ^{15}N pool dilution. In the old cane field, NH_4^+ enrichment declined very slightly and at marginal statistical significance ($P = 0.05$ in analysis of covariance; Fig. 2), indicating modest rates of gross N mineralization. High spatial variability both within and among miniplots precludes reliable estimation of gross rates of mineralization from pool dilution using data from soil cores collected on successive days. By using means of $^{14}NH_4^+$ and $^{15}NH_4^+$ pool sizes across replicate plots of the old cane field for Days 0 and 3, much of the spatial and temporal noise in the data are smoothed, and estimates of gross mineralization can be made with pool dilution equations (Davidson et al., 1991). The mean gross mineralization rate for the old cane soils was 1 mg N kg^{-1} soil d^{-1} and the mean gross NH_4^+ consumption rate was 3 mg N kg^{-1} soil d^{-1}.

This gross mineralization rate of 1 mg N kg^{-1} soil d^{-1} is low relative to published values for forests (Davidson et al., 1992; Hart et al., 1994; Tietema and Wessel, 1992) and grasslands (Barraclough and Smith, 1987; Davidson et al., 1990). Had gross mineralization rates been higher, ^{15}N enrichment of the NH_4^+ pools would have declined more rapidly as mineralization of unlabeled native organic N diluted the enrichment of the inorganic N pools (Davidson et al., 1991). This result suggests that N availability in these fields is dependent on very recent N fertilization and that very little mineral N is derived from mineralization of soil organic matter. Furthermore, the gross N mineralization rates are matched or exceeded by gross rates of NH_4^+ consumption, so that only a small fraction of the mineralized N is probably available to the crop.

Further support for this conclusion comes from the laboratory assays for net mineralization and net nitrification of samples taken from each field prior to adding the N label. During this 7-d aerobic incubation, net mineralization was −0.4 mg N kg^{-1} soil [standard error (SE) of eight replicates was 0.1] in the old cane soil and −1.6 mg N kg^{-1} soil (SE 2.7) in the young cane soil, indicating that neither soil produced a net increase in mineral N and may have immobilized a small amount of inorganic N. Nitrate concentrations were below detection limits for the old cane soil, both before and after the incubation, rendering a net nitrification rate of zero. In contrast, net nitrification in the young cane soil was 18.3 μg N g^{-1} soil (SE 2.7). Inorganic N was converted from NH_4^+ to NO_3^- in the young cane soil, but no net increase in total inorganic N was observed.

The combination of zero or negative net mineralization rates in the laboratory and little or no dilution of the $^{15}NH_4^+$ pool in the field indicates that the cane crop must rely nearly entirely on fertilizer N for nutrition. This result differs from many temperate agricultural systems where so-called *mineralization–immobilization–turnover* often supplies significant N nutrition for the crop (Barraclough et al., 1985; Bristow et al., 1987; Duxbury et al., 1991). One implication of this finding is that if N_2O emissions from these cane fields are limited by N availability, then emissions would be controlled almost entirely by recent fertilizer applications.

Nitrogen-15 Labeling Experiment: Nitrous Oxide

Emissions of N_2O increased significantly relative to controls after adding label to the old cane field (Fig. 3a), which is consistent with the presence of a nitrifier population capable of quickly producing N_2O directly and producing NO_3^-, which can subsequently be reduced to N_2O via denitrification. Emissions also increased somewhat in the control miniplots of the old cane field relative to the rates observed before adding water, probably because of the wetting effect (Davidson, 1992a).

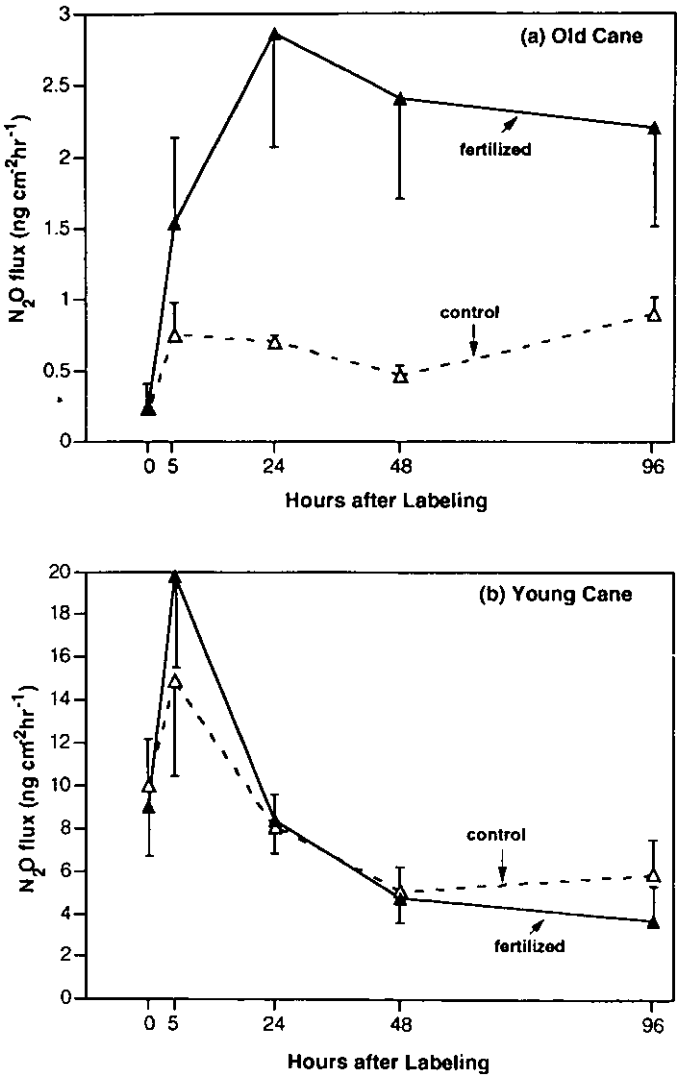

Fig. 3. Emissions of N_2O measured using flux chambers in each miniplot. Means (points) and standard errors (bars) of four replicate miniplots for each treatment (control and fertilized with NH_4^+) in each field (young and old cane) are shown. Repeated measures design indicated that emissions increased significantly in both fields following addition of label or water (i.e., time was significant at $P = 0.01$) and that the fertilized effect and the fertilization–time interaction effect were significant in the old cane field ($P = 0.01$) but were not significant in the young cane field ($P = 0.05$).

Emissions of N_2O were an order of magnitude higher in both labeled and unlabeled miniplots in the young cane field compared with the old cane field (Fig. 3b). These high background N_2O fluxes were probably the result of previous fertilization by the company in the young cane field. The difference in N_2O fluxes between labeled and control plots was not statistically significant in the young cane field, indicating that adding N to the already high ambient concentrations of NH_4^+ and NO_3^- did not further enhance N_2O emissions. There was a modest increase in N_2O emissions 5 h after adding label or water to the young cane soil.

The highest N_2O emissions were coincident with the highest NH_4^+ concentrations in labeled miniplots in both fields. This result could mean that nitrification was a direct source of N_2O, but it does not rule out simultaneous reduction of NO_3^- to N_2O by denitrifiers. Matson et al. (1996) used C_2H_2 to inhibit nitrification in laboratory assays of these same soils and found that denitrification contributed from 22 to 100% of the total N_2O flux. Very high rates of N_2O production, similar to those observed in the young cane field, are usually associated with denitrification (Aulakh et al., 1984; Casella et al., 1986; Davidson, 1992b; Davidson et al., 1993; Klemedtsson et al., 1988; Mummey et al., 1994; Parsons et al., 1993).

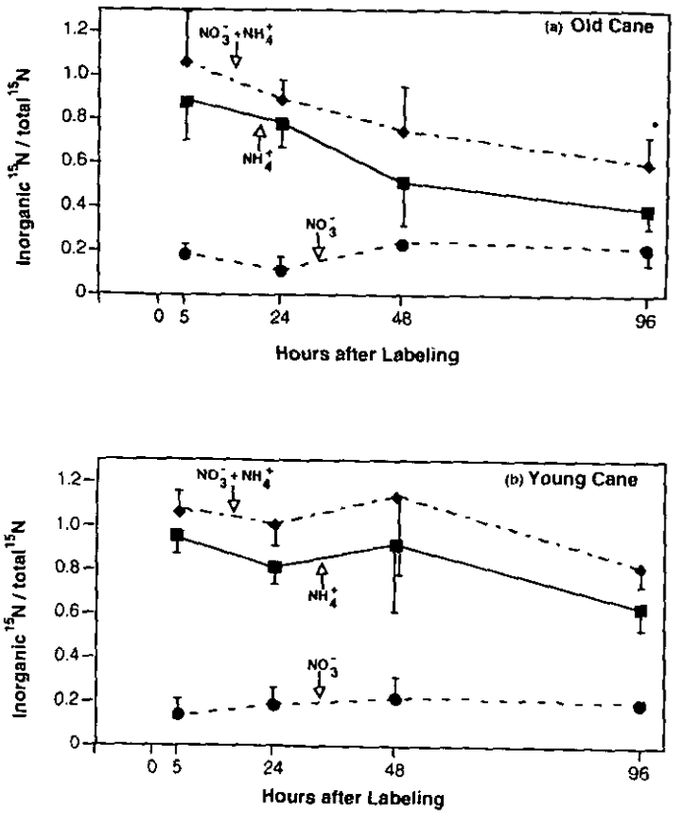

Fig. 4. The fraction of total ^{15}N recovered in 10-cm soil cores of soil found as extractable NH_4^+ or NO_3^-. Means (points) and standard errors (bars) of four replicate miniplots for each field (young and old cane) are shown. Analysis of covariance indicates that the fraction as inorganic N was never significantly below 1.0 in the young cane field ($P = 0.05$) but declined significantly with time in the old cane field ($P = 0.01$).

It is likely that a combination of N_2O sources contributed significantly to the observed emissions.

In both fields, the calculated atom% ^{15}N of the N_2O source was significantly lower than the enrichment of the measured NH_4^+ and NO_3^- pools (Fig. 2). A likely explanation for this apparent discrepancy is that some of the N_2O was being produced at microsites within the soil where the unlabeled inorganic N from previous fertilizer applications was not well mixed with the added label. For example, the interiors of soil aggregates at all depths and the soil below 10-cm depth could have had NH_4^+ and NO_3^- pools with lower enrichments than the mean enrichment measured in the soil cores we sampled, mixed, and analyzed for inorganic ^{15}N. The discrepancy between ^{15}N content of the N_2O source and of the NH_4^+ and NO_3^- pools is greatest in the young cane field (Fig. 2b), where inorganic N concentrations were high prior to the addition of the ^{15}N label (Fig. 1b). The ^{15}N content of the N_2O source was closer to the mean ^{15}N content of the NO_3^- pool than the NH_4^+ pool in the young cane field (Fig. 2b), possibly indicating a more important role for denitrification, but the results are equivocal in this field setting. Comparing the enrichment of the N_2O with that of the NH_4^+ and NO_3^- pools could be a powerful alternative to the use of inhibitors to distinguish between nitrification and denitrification (Hutchinson and Davidson, 1993), but the isotopic approach may be limited to laboratory incubations of well-mixed soils or to soils where added fertilizer is mixed into the soil at the time of tillage.

The average ^{15}N enrichment of the N_2O source did not change significantly with time in the young cane field, but it declined significantly in analysis of covariance of the old cane field data. This decrease in enrichment of the N_2O source is larger than the modest decrease in enrichment of the NH_4^+ pool in the old cane soil. The pulse of N_2O emissions within the first 24 h after addition of the label reflects the ^{15}N enrichment of the label, but the ^{15}N content of the N_2O declines as the pulse tapers and as the modest background emissions again become a larger fraction of the total N_2O emissions.

Nitrogen-15 Labeling Experiment: Total Nitrogen

Recovery of total ^{15}N applied to the soil was highly variable from day to day, ranging from 90 to 128% recovery in the old cane field and 44 to 104% in the young cane field. There was no trend relating total recovery with time. Variable total recovery probably results from spatial variability within each miniplot. The single soil core (necessitated by expense of analyses) apparently did not adequately represent the average ^{15}N content of the soil of its miniplot.

However, the recovery of ^{15}N as NH_4^+ or as NO_3^- relative to the total ^{15}N recovery within each soil core shows a consistent pattern with time. In the old cane field, $\approx 100\%$ of the ^{15}N recovered was as NH_4^+ or NO_3^- at 5 h after adding the label (Fig. 4a). The proportion as inorganic N declined steadily to $\approx 60\%$ at 96 h after adding the label, and this decline was statistically signifi-

cant. While some of the added $^{15}NH_4^+$ was being nitrified to $^{15}NO_3^-$, ≈40% of the label was apparently being incorporated into organic N in the old cane soil. In contrast, recovery of $^{15}NH_4^+$ + $^{15}NO_3^-$ in the young cane soil was never significantly lower than recovery of total ^{15}N (Fig. 4b). The young cane soil apparently did not remove N from the inorganic pools to form organic N. This interpretation assumes that label recovered as total N but not as inorganic N has been immobilized into an organic fraction. The only other possible fate would be adsorption of inorganic N that is no longer extractable in 2 *M* KCl, but it is unlikely that adsorption processes would differ between nearby old and young cane fields on the same soil series. Higher C availability in the old cane soil is a plausible explanation for immobilization of added ^{15}N label into an organic fraction.

Mature sugar cane fields have a dense mat of dead cane fronds covering the soil that are probably decomposing and adding available C to the soil. In addition to much larger above-ground living and dead biomass, the old cane fields have much larger root biomass than do young cane fields. Root exudates and root turnover may provide further available C in the soil. We noticed that soil extracts from the old cane field were colored, presumably with organic acids, whereas the young cane soil extracts were clear. It appears reasonable, then, that microbial immobilization fueled by readily available soil C could be a significant sink for added N in the old cane field, whereas it would be less important in the young cane soil. This interpretation is consistent with very low concentrations of inorganic N measured in the old cane soil prior to adding the label (Fig. 1a). The cane plants may also be important sinks for N, but of the ^{15}N recovered in the soil, 40% was no longer in inorganic form, indicating that the soil microorganisms within the irrigation line had immobilized 40% of the added ^{15}N into organic form within 4 d. Lower N availability and stronger plant and microbial sinks for N in old cane fields than in young cane fields probably also account for the lower background N_2O emissions measured in old cane fields.

Significance of Nitrous Oxide Emissions

The high emissions of N_2O from the young cane fields that accompany high NH_4^+ and NO_3^- concentrations do not constitute economically significant losses from the grower's point of view. Matson et al. (1996) showed that <1% of the fertilizer N is lost as N_2O in the Maui cane plantations. This economically insignificant N loss, however, is of sufficient magnitude to be significant to society vis-a-vis its effect on accumulation of heat trapping gases in the atmosphere (Duxbury et al., 1993). Management provides tools to further reduce the fraction of fertilizer N lost as N_2O (Mosier, 1994). Matson et al. (1996) showed that the subsurface fertilizer application used on Maui results in a smaller fraction of fertilizer N lost as N_2O and NO than occurs with surface applications on other cane plantations in Hawaii. Indeed, the fractions reported by Matson et al. (1996) for the Maui fields are generally less than the average of all fertilizer types reported for agricultural soils (Mosier, 1994), although they are higher than the average reported for urea applications in temperate zones (Eichner, 1990). In any case, inorganic N concentrations in the young cane field of this study were high, indicating that fertilizer N application rates exceeded crop demand and that N_2O emissions might be reduced by altering fertilizer application rates and timing.

CONCLUSIONS

Old sugar cane fields that are no longer being fertilized have viable populations of nitrifying bacteria that are capable of producing NO_3^- and N_2O when N fertilizer is added. However, concentrations of NH_4^+ and NO_3^- are low once fertilizer addition ceases, due to plant uptake and microbial immobilization of added N. About 40% of the fertilizer N within the soil surrounding the buried irrigation line was converted to organic N within 4 d of application, presumably due to microbial immobilization. These processes generally keep inorganic N concentrations and N_2O emissions low in old cane fields.

Availability of N in these sugar cane fields is strongly dependent on recent N fertilization. Unlike the mineralization-immobilization-turnover processes that have been shown to provide available N in many temperate agricultural soils, there was little contribution of available N from gross mineralization of soil organic N in the intensively managed sugar cane fields of Maui. Hence, emissions of N_2O from these fields, and perhaps from other similarly fertilized tropical agroecosystems, are likely to be determined by fertilizer management.

Inorganic N concentrations in the young cane field were high, indicating excessive fertilizer N application relative to plant and microbial demand. The high emissions of N_2O from the young cane fields do not constitute economically significant losses for the grower, but they are of sufficient magnitude to be significant to society because of their effect on accumulation of heat trapping gases in the atmosphere. It may be possible to reduce these N_2O emissions by altering the timing and application rates of N fertilizer.

ACKNOWLEDGMENTS

We thank Paul Lefebvre, Wendy Kingerlee, Tina Billow, and John Zachariessen for their hard work in the field and in the laboratory. We thank Doug Turner and Peter Vitousek for performing the analyses of inorganic N in soil extracts. We thank the Hawaii Commercial and Sugar Company for their cooperation and helpfulness. We also thank the director and staff of NifTAL for their their generous help and for making their laboratory facilities available to us. This research was supported by grant NAG 2-808 from the NASA Ames Research Center to E. Davidson and a NASA Terrestrial Ecosystems Program grant to P. Matson.

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