

## Controls on annual emissions of nitric oxide from soils of the Colorado shortgrass steppe

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**Abstract.** Estimates of NO<sub>x</sub> (NO+NO<sub>2</sub>) emissions from temperate grasslands range from 0.003 to 101 ng NO-N m<sup>-2</sup> s<sup>-1</sup> (average 4.17 ng NO-N m<sup>-2</sup> s<sup>-1</sup>). As a result of this uncertainty, the potential contribution of soil NO<sub>x</sub> emissions to the global budget and to nitrogen loss for this ecosystem is unclear. The few existing measurements are short-term observations of growing-season fluxes. We measured soil NO<sub>x</sub> emissions from six sites within the shortgrass steppe at the Central Plains Experimental Range in Colorado from June 1994 through October 1995. The soils at these sites provided a range of texture (from a sandy loam to a clay loam) and soil moisture. Mean NO<sub>x</sub> emissions over the sampling period ranged from 2.6 to 5.7 ng NO-N m<sup>-2</sup> s<sup>-1</sup> from the four unfertilized sites. Temperature was the dominant control on seasonal variations in NO<sub>x</sub> fluxes. Seasonal fluxes were highest in the summers (5.4 to 10.5 ng NO-N m<sup>-2</sup> s<sup>-1</sup>) and lowest in the winter (0.2 to 1.5 ng NO-N m<sup>-2</sup> s<sup>-1</sup>). The winter NO<sub>x</sub> emissions contribute up to 25% to the mean annual flux. Water-filled pore space (WFPS) alone was a poor predictor of NO<sub>x</sub> emissions; however, peak NO<sub>x</sub> emissions were found near the field capacities for these soils (32-35% WFPS for coarse soils and 66% WFPS for fine-textured soils). Water additions produced large (22-51 ng NO-N m<sup>-2</sup> s<sup>-1</sup>) but short-lived (24 hour) pulses of NO<sub>x</sub> emissions that were independent of both the amount of water added and the number of antecedent dry days. Short-term increases in NO<sub>x</sub> flux stimulated by wetting are significant, and increase the summer estimate of NO<sub>x</sub> emissions 8 times estimates calculated from periodic sampling. Nitrogen applied in previous studies, 5 to 12 years earlier, increased the average annual NO<sub>x</sub> emissions approximately 1.5 times. Extrapolating our estimate to similar systems around the world, we estimate that grassland ecosystems, globally, emit 1.0 Tg N yr<sup>-1</sup> as NO<sub>x</sub>. A current estimate of NO<sub>x</sub> emissions from grassland soils is 0.6 Tg N yr<sup>-1</sup> [Davidson, 1991].

### 1. Introduction

Nitric oxide emissions from soils represent an important pathway for nitrogen loss from the soil system as well as a pathway for gaseous exchange of nitrogen between the soil and the atmosphere. Nitric oxide (which we will refer to as NO within the soil atmosphere) is produced during the microbial processes of nitrification and denitrification that occur naturally in the soils of many ecosystems. Once emitted from soil NO is quickly (within seconds) converted to NO<sub>2</sub> and persists in chemical equilibrium with NO and ozone; thus when discussing the biosphere-atmosphere exchange of these gases it is more convenient to refer to NO + NO<sub>2</sub> as NO<sub>x</sub> [Prather *et al.*, 1995].

NO<sub>x</sub> controls the oxidative capacity of the troposphere [Prather *et al.*, 1995]. At high concentrations (>30 parts per trillion by

volume (pptv)), NO<sub>x</sub> contributes to the net production of ozone and the HO<sub>2</sub> radical through the oxidation of carbon monoxide (CO) and methane (CH<sub>4</sub>). At low concentrations (10-20 pptv) NO<sub>x</sub> will destroy ozone and OH radicals during the oxidation of CO and CH<sub>4</sub> [Crutzen, 1979; Prather *et al.*, 1995]. Owing to the relatively short atmospheric lifetime of NO<sub>x</sub>, approximately 1 day [Prather *et al.*, 1995], the impact of soil NO<sub>x</sub> emissions on tropospheric chemistry tends to be highly localized [Williams *et al.*, 1992a].

Emissions from soils are a major source of NO<sub>x</sub> globally, contributing between 4 and 20 Tg of N yr<sup>-1</sup> to the atmosphere, accounting for up to 40% of the global NO<sub>x</sub> source (a range of 25-99 Tg N yr<sup>-1</sup>) [Davidson, 1991; Logan, 1983; Williams *et al.*, 1992a]. Williams *et al.* [1992a] estimated that grassland emissions comprise about 28% of the total soil NO<sub>x</sub> emissions estimated for natural land areas, but this value is based on a wide range of flux estimates (0.003 to 101 ng NO-N m<sup>-2</sup> s<sup>-1</sup>). Furthermore, measurements used to develop regional and global estimates of NO<sub>x</sub> from grasslands have been taken only during the summer or growing season and neglect winter measurements. Although Davidson *et al.* [1991] estimates that grassland emissions only contribute 3% to the global N source, they may have a large impact on the regional air chemistry in unpolluted rural regions [Williams *et al.*, 1992a].

NO is produced during nitrification, denitrification, and through the chemical decomposition of HNO<sub>2</sub> [Firestone and Davidson, 1989]. Factors such as temperature, soil water content, soil texture, wetting of dry soil, and fertilization practices have all been shown

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to be key controls over NO<sub>x</sub> emissions from soils [Anderson and Levine, 1987; Galbally, 1989; Rosswall et al., 1989; Williams et al., 1992b].

We examined the influence of biotic and abiotic factors on seasonal soil NO<sub>x</sub> emissions from the shortgrass steppe at the Central Plains Experimental Range (CPER) in Colorado. We focused our study on the quantification of NO<sub>x</sub> emissions throughout the year, including the winter, as well as following wetting of a dry soil, the interacting effects of texture, soil temperature, and soil water content, and the effect of N application history on NO<sub>x</sub> emissions. This experiment is part of a larger, long-term study examining the biogeochemistry of and trace gas emissions (N<sub>2</sub>O, CH<sub>4</sub>, and CO<sub>2</sub>) from soils at the CPER [Mosier et al., 1981, 1991, 1996; Mosier and Parton, 1985; Schimel and Parton, 1986; Parton et al., 1988, 1996].

## 2. Site Characteristics

This experiment was conducted at the Central Plains Experimental Range (CPER) (40°48'23"N, 104°45'15"W, and elevation 1650 m) about 60 km northeast of Fort Collins, Colorado. The precipitation averages approximately 322 mm a year, with 70% of the precipitation falling between April and September. The vegetation is characteristic of a shortgrass steppe, dominated by blue gramma (*Boutelous gracilis* Lag.), with fringed sagebrush (*Artemisia frigida* Wild.) and plains prickly pear (*Opuntia polyacantha* Haw.) as secondary dominants [Lauenroth and Milchunas, 1992]. Soil textures ranged from sandy loam (three sites, SL1, SL2, one fertilized SL2F) to a sandy clay loam (two sites, SCL, one fertilized SCLF) to a clay loam (CL) (Table 1). Nitrogen was applied to soils at two sites during previous experiments 5 to 12 years earlier. The SL2F site was fertilized with 2.2 g N m<sup>-2</sup> yr<sup>-1</sup> of ammonium nitrate from 1976 to 1989 [Mosier et al., 1996]. The SCLF is located on a 25 m<sup>2</sup> area that was fertilized once in 1982 with a solution containing 45 g m<sup>-2</sup> of urea-N [Mosier and Parton, 1985].

## 3. Methods

### 3.1. Field NO Measurements

Soil NO<sub>x</sub> measurements were made using a flow-through chamber method [Slemr and Seiler, 1984]. At each site, soil NO<sub>x</sub> measurements were taken by fitting a 6.28 L chamber (lined with Teflon to inhibit chemical transformation of NO) onto a PVC pipe anchor. A portable Scintrex LMA-3 chemiluminescent instrument and LNC converter (Scintrex Unisearch, models LMA-3 and LNC-3) were used to measure soil NO<sub>x</sub> in the field. The instrument was

calibrated monthly in the laboratory. A calibration curve was determined using at least four data points with a dilution of an NO gas standard (10.8 ppm).

Steady increases of NO<sub>x</sub> within the chamber were observed between 2 and 8 min after the chamber was placed on the anchor. Sampling times of 3 and 6 min within this steadily increasing range were chosen for calculation of the NO<sub>x</sub> concentration within the chamber. Fluxes were calculated using the following equation:

$$r = F(C_{\text{chamber}} - C_{\text{ambient}}) W_N 10^9 / (V_{\text{mole}} A (1 - e^{-Ft/V}))$$

where  $r$  is the rate of NO production (ng NO-N m<sup>-2</sup> s<sup>-1</sup>),  $F$  is the flow rate through the chamber (m<sup>3</sup> s<sup>-1</sup>),  $C_{\text{ambient}}$  is the ambient concentration of NO in the atmosphere at the location of the inlet port (in parts per billion by volume),  $C_{\text{chamber}}$  is the concentration of NO (in parts per billion by volume) measured from the chamber at a given time  $t$ ,  $W_N$  is the molecular weight of nitrogen (g mol<sup>-1</sup>),  $V_{\text{mole}}$  is the molar volume of NO (m<sup>3</sup> mol<sup>-1</sup>) at a given chamber temperature,  $A$  is the area of soil (in square meters) which the chamber covers,  $V$  is the chamber volume, and  $t$  is a finite time after chamber closure (seconds) [Martin, 1996].

Following the procedures used in previous experiments at these sites summarized by Mosier et al. [1996], six anchors (20.3 cm inside diameter and 8 cm deep) were installed at random locations at each site (except sandy clay loam fertilized (SCLF) where four previously established anchors were sampled) in mid-May 1994, at least 3 weeks prior to sampling to minimize the effect of disturbance [Mosier et al., 1991]. Fluxes were sampled weekly except in the winter when they were sampled biweekly. Fluxes were sampled at each sampling date from the six anchors and used as replicates in statistical analyses.

### 3.2. Ancillary Measurements

Air temperature (measured approximately 10 cm above the soil surface) and soil temperature (measured at a depth of 5 cm) were taken before and after every set of NO<sub>x</sub> flux measurements. Soil samples to 10 cm depth were collected for determination of gravimetric moisture content (GMC) on each sampling date. GMC was then used to calculate percent water-filled pore space (WFPS) when

$$\%WFPS = 100 \text{ GMC } D_B / P$$

where GMC is gravimetric moisture content (g H<sub>2</sub>O g dry soil<sup>-1</sup>),  $D_B$  is the bulk density (mg m<sup>-3</sup>), and  $P$  is porosity of the soil =  $1 - (D_B/2.65)$ , where 2.65 is the particle density for most soils in this region (mg m<sup>-3</sup>) [Linn and Doran, 1984].

**Table 1.** Site Characteristics

Site	Site Abbreviation	Texture	Sand, %	Silt, %	Clay, %	Bulk Density, g cm <sup>-3</sup>	Total N, %	Total C, %
Sandy loam-1	(SL1)	sandy loam	70	17	13	1.33	0.14	1.30
Sandy loam-2	(SL2)	sandy loam	74	13	13	1.41	0.12	1.07
Fertilized sandy loam-2	(SL2F)	sandy loam	74	11	15	1.34	0.14	1.18
Sandy clay loam	(SCL)	sandy clay loam	58	18	24	1.34	0.19	1.84
Fertilized Sandy Clay Loam	(SCLF)	sandy clay loam	58	18	24	1.34	0.22	2.22
Clay Loam	(CL)	clay loam	42	18	30	1.32	0.17	1.80

All soil characteristics were measured in the top 15 cm of the soil [modified from Mosier et al., 1996].

**Table 2.** Details of Field Wetting Experiments

Date	Site	Amount of Water Added, mm	Number of Replicate Anchors	NO Emissions Sampling Times (Hours Since Wetting)
<i>Experiment A (Wetting to Field Capacity)</i>				
June 7, 1994	SL2F	6.4	6	0, 0.5, 2, 4, 6, 8, 24, 48, 72
June 8, 1994	SL2	16.0	6	
June 13, 1994	CL	22.3	6	
June 14, 1994	SL1	22.3	6	
June 15, 1994	SCL	27.9	6	
<i>Experiment B ("Small" and "Large" Water Additions)</i>				
July 26, 1994	SL2F	4.0	3	0, 0.5, 2, 4, 6, 21, 26, 29, 48
		25.5	3	
		0	3	
July 27, 1994	SL2	4.0	3	
		25.5	3	
		0	3	
August 16, 1995	SCL	4.0	3	0, 0.5, 2, 4, 7, 24, 48
		25.5	3	
		0	3	
August 17, 1995	SL2	4.0	3	
		25.5	3	
		0	3	

### 3.3. Field-Wetting Experiments

Soil-wetting experiments were conducted in the field in June, July, and September 1994 and August 1995 to examine the effects of precipitation on soil NO<sub>x</sub> emission. In each experiment described below, different amounts of deionized water were sprinkled on the soil inside the PVC anchors at each of the sites using a watering can. NO<sub>x</sub> fluxes were recorded several times from 0.5 to 72 hrs, post-wetting (Table 2). Soil samples for GMC were collected from additional anchors at each site. Two additional anchors for each water treatment were installed at each site. Soil samples for GMC were collected during every set of flux measurements, except during experiment A when they were only collected at 0, 0.5, 8, 24, 48, and 72 hours after wetting. Details of the amount of water added, number of anchors, and sampling times for each experiment are given in Table 2.

**3.3.1. Experiment A: Wetting above field capacity, June 1994.** In order to examine the effect of precipitation on NO<sub>x</sub> emissions deionized water was added to each site. Field capacity was approximately 12% GMC for the sites with coarser soils (SL2F, SL2, and SL1) and 25% GMC for finer soils (CL and SCL) [Mosier *et al.*, 1991]. Calculated WFPS is 32% for SL2F and SL1, is 35% for SL2 and is 66% for CL and SCL.

**3.3.2. Experiment B: "Small" and "large" water additions, July 1994 and August 1995.** Two treatments of water were added to the SL2 site (both 1994 and 1995), the SL2F site (1994), and the SCL site (1995) to examine the effect of light (125 mL = 4.0 mm) and heavy (800 mL = 25.5 mm) rains. Water was added to three anchors per treatment (Table 2).

### 3.4. Data Analysis

We used regression analyses to examine the relationship between NO<sub>x</sub> emissions, soil temperature, WFPS, and soil texture [Systat, version 5.0]. All data were log-transformed prior to analysis to satisfy the assumptions of normality. Average seasonal NO<sub>x</sub> fluxes and associated standard errors were calculated by

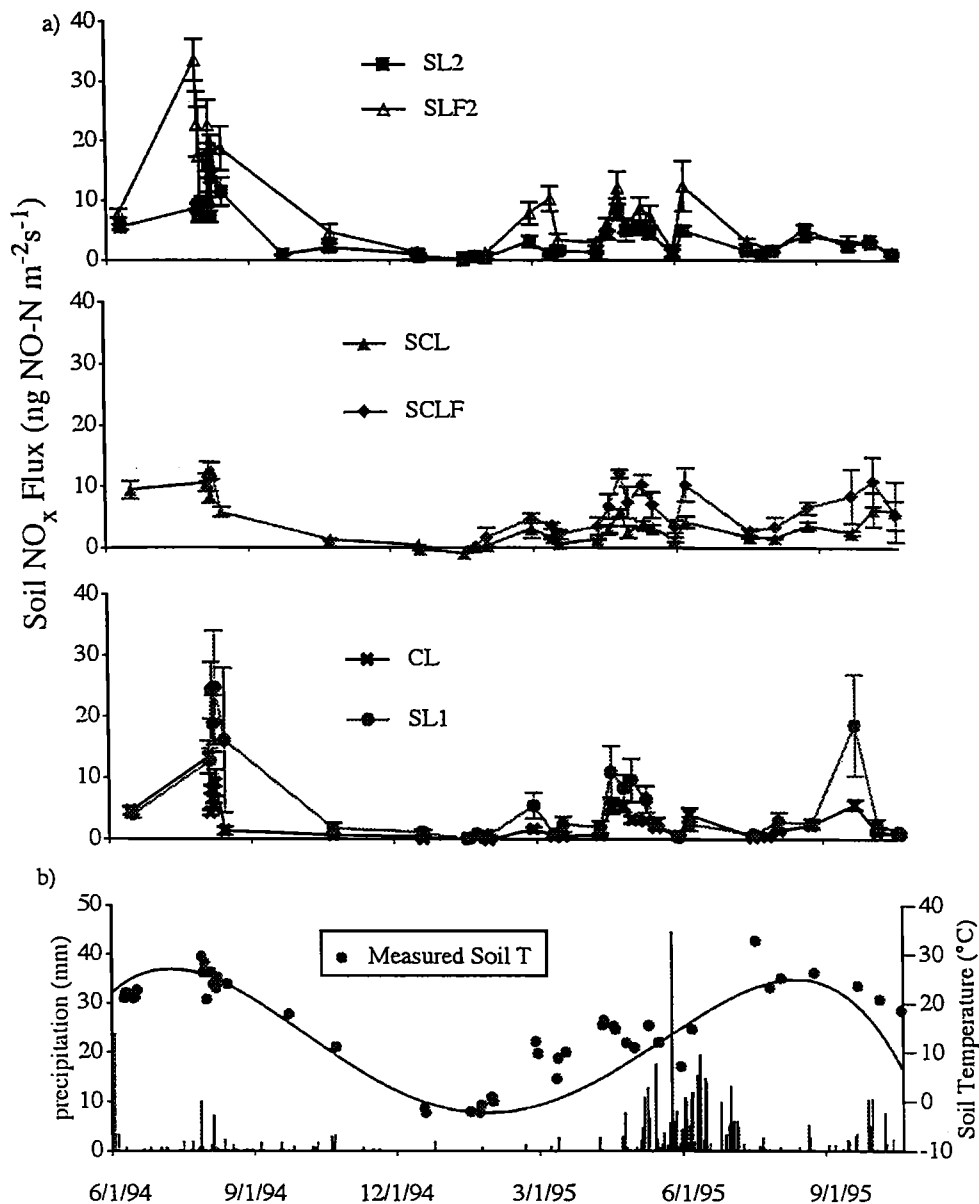
averaging NO<sub>x</sub> fluxes measured from each anchor at each sampling time during the season and then averaging the six anchors at each site. The summer, and consequently, the annual calculations include data from both 1994 and 1995 because there were relatively fewer measurements collected in 1995. Mean annual NO<sub>x</sub> fluxes and standard errors were calculated by averaging the seasonal NO<sub>x</sub> fluxes from each anchor and then averaging the six anchors at each site. For consistency with previous experimental design at this site, we used the Wilcoxon rank sum test with Tukey's multiple comparison of ranks [SAS/STAT, 1991] to test for the effects of texture and previous nitrogen application on NO<sub>x</sub> emissions. In the wetting experiments, NO<sub>x</sub> emissions were integrated over 24 hours post-wetting for each anchor. Owing to the small sample size, the Wilcoxon rank sum test [Systat, version 5.0] was used on these integrated fluxes to examine the effect of water addition. Regression analysis was used to examine the relationship between initial NO<sub>x</sub> flux and peak NO<sub>x</sub> flux after wetting. Initial and peak NO<sub>x</sub> fluxes were calculated as the mean of NO<sub>x</sub> flux measurements from three to six anchors, depending on the experiment.

## 4. Results

### 4.1. Mean Seasonal Emissions

Mean seasonal NO<sub>x</sub> emissions from the unfertilized sites (SL2, SL1, CL, and SCL) varied by an order of magnitude at the CPER, ranging from approximately 0.8 ng NO-N m<sup>-2</sup> s<sup>-1</sup> in the winter to 7.7 ng NO-N m<sup>-2</sup> s<sup>-1</sup> in the summer. The NO<sub>x</sub> emissions from the fertilized sites range from 2.0 ng NO-N m<sup>-2</sup> s<sup>-1</sup> in the winter to 14.5 ng NO-N m<sup>-2</sup> s<sup>-1</sup> in the summer (Figure 1, Table 3).

Fluxes of NO<sub>x</sub> were largest in the summer and were lowest in the winter at all sites, corresponding to seasonal changes in temperature (Table 3). Of the measurements made, soil temperature was found to be the most important control on seasonal NO<sub>x</sub> emissions from all sites ( $r^2 = 0.31$  and  $p < 0.05$ , Figure 2). The soil temperature at 5 cm measured at the time of the flux measurements varied between -7.5°C and 35.8°C. WFPS was a poor predictor of NO<sub>x</sub> flux ( $r^2 =$



**Figure 1.** a) Average seasonal soil NO<sub>x</sub> emissions (ng NO-N m<sup>-2</sup> s<sup>-1</sup>) from six sites at the Central Plains Experimental Range (CPER). Error bars are standard error  $n = 6$  for SL2F, SL2, SL1, and CL, and  $n = 4$  for SCL and SCLF. b) Precipitation (in millimeters, bars) and soil temperature (in degrees Celsius, line) measured at the CPER weather station and measured soil temperature (in degrees Celsius, dots) from the time of the flux measurements.

0.001) using a linear relationship; however, the inclusion of WFPS strengthened the relationship between NO<sub>x</sub> emissions and temperature. The relationship between NO<sub>x</sub> emissions and soil temperature was strongest in a range bracketing the field capacity of the soils in our study (35±10% WFPS for coarser soils and 70±10% WFPS for finer textured soils). The correlation between NO<sub>x</sub> flux and soil temperature improved to  $r^2 = 0.81$  ( $p < 0.05$ ) for the combined coarse- and fine-textured sites (Figure 3). When we aggregated the data by soil texture, the correlation between NO<sub>x</sub> flux and soil temperature was  $r^2 = 0.88$  ( $p < 0.05$ ) for coarser soils (Figure 4a), and  $r^2 = 0.76$  ( $p < 0.05$ ) for finer textured soils (Figure 4b).

#### 4.2. Effect of Water Addition

Large transient pulses of NO<sub>x</sub> were observed at all sites when water was added to anchors. The peak NO<sub>x</sub> flux occurred between 30 min and 4 hours after wetting (Figure 5). The magnitude of peak NO<sub>x</sub> emissions was independent of the amount of water added (Tables 4 and 5). Furthermore, the peak NO<sub>x</sub> emission values were not correlated to the initial NO<sub>x</sub> fluxes.

NO<sub>x</sub> emissions, averaged over 24 hours postwetting, from five sites wet above field capacity did not differ significantly from each other (Table 4). NO<sub>x</sub> emissions, averaged over 24 hours postwetting, increased significantly ( $p < 0.05$ ) from the integrated

**Table 3.** Mean and Median Soil NO Flux for Five Sites at the CPER Measured From June 1994 Through October 1995

Site (Abbreviation)	Season	Soil NO Flux Mean, ng NO-N m <sup>-2</sup> s <sup>-1</sup>	Median, ng NO-N m <sup>-2</sup> s <sup>-1</sup>
Sandy loam-1 (SL1)	Spring	4.6±1.5*	2.7 <sup>‡</sup>
	Summer	10.5±2.5*	9.2 <sup>‡</sup>
	Fall	6.0±2.5*	3.6 <sup>‡</sup>
	Winter	1.5±0.6*	10.9 <sup>‡</sup>
	Annual	5.7±1.9 <sup>†</sup>	4.1 <sup>‡</sup>
Sandy loam-2 (SL2)	Spring	3.2±0.7	3.0
	Summer	6.8±0.6	6.3
	Fall	1.9±0.2	1.9
	Winter	0.9±0.2	0.9
	Annual	3.2±0.3	3.6
Fertilized sandy loam-2 (SL2F)	Spring	7.0±1.2	7.1
	Summer	14.5±1.8	13.6
	Fall	3.1±0.5	2.9
	Winter	2.0±0.5	1.9
	Annual	6.6±0.9	6.5
Sandy Clay Loam (SCL)	Spring	2.7±0.4	2.4
	Summer	8.0±0.6	8.7
	Fall	3.0±1.4	2.0
	Winter	0.2±0.2	0.1
	Annual	3.5±0.6	3.4
Clay Loam (CL)	Spring	2.5±0.3	2.4
	Summer	5.4±0.5	5.7
	Fall	2.1±0.3	2.2
	Winter	0.4±0.1	0.4
	Annual	2.6±0.2	2.7

\*Average seasonal soil NO fluxes and associated standard error were calculated by averaging the measurements from each anchor over the season and then averaging the six anchors at each site ( $n=6$  for all sites, except SCL where  $n=4$ ).

<sup>†</sup>The average annual soil NO fluxes (ng NO-N m<sup>-2</sup> s<sup>-1</sup>) were calculated by using the seasonal NO flux for each anchor to calculate and average annual flux for each anchor and then averaging the six anchors at each site ( $n=6$  for all sites, except SCL where  $n=4$ ).

<sup>‡</sup>Seasonal median soil NO fluxes were calculated from all the anchors for all sampling times during the season at each site.

<sup>§</sup>The annual median soil NO fluxes were calculated from all the anchors for all the sampling times throughout the experiment at each site ( $n = 114$  for SL1;  $n = 104$  for SL2;  $n = 114$  for SL2F;  $n = 76$  for SCL;  $n = 76$  for SCLF; and  $n = 111$  for CL).

control for 4 mm and 25.5 mm of water added to both the SL2 and SL2F sites in July 1994 (Table 5). In August 1995, the NO<sub>x</sub> emissions, averaged over 24 hours post wetting, were significantly higher ( $p < 0.05$ ) for 4 mm of water added to the SL2 site and 25.5 mm of water added to the SCL site (Table 5).

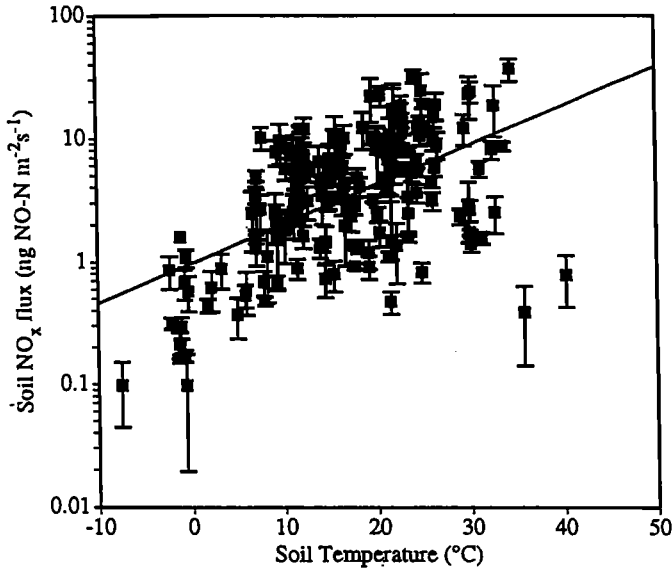
Soil NO<sub>x</sub> fluxes in the summer were 8 times greater following simulated summer rainfall. The increase was estimated by comparing the NO<sub>x</sub> flux measured 24 hours following the application of water with anchors that had not received any additional water. The largest increase was in the July 1994 experiment (NO<sub>x</sub> flux was 15 times larger when water was added), while the smallest increase (3.5 times) occurred in August 1995 (Table 5).

Inclusion of the influence of precipitation in the calculation of our summer resulted in enhancement of NO<sub>x</sub> flux of 12.6 ng NO-N m<sup>-2</sup> s<sup>-1</sup>. The increase in summer NO<sub>x</sub> flux stimulated by water

addition was calculated by multiplying the average summer NO<sub>x</sub> flux from the unfertilized sites (3.8 ng NO-N m<sup>-2</sup> s<sup>-1</sup>) by 8. This enhanced NO<sub>x</sub> flux was then multiplied by number of precipitation events (21 events) during the summer of 1994, and the average summer emissions were recalculated. The summer of 1994 had a typical number of precipitation events as well as an typical amount of rainfall (21 days and 134 mm, Table 6).

#### 4.3. Textural Influences

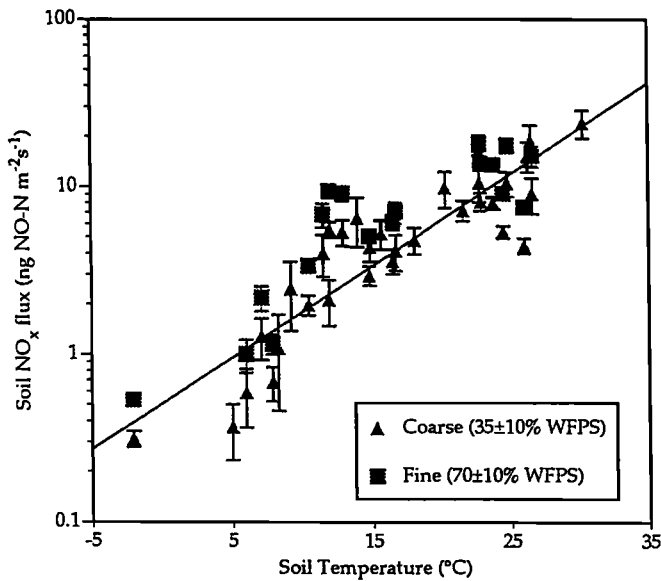
Data from all replicates on the four unfertilized sites (SL2, SL1, CL and SCL), measured from June 1994 to October 1995, were used to examine the effect of texture on NO<sub>x</sub> fluxes. Average soil NO<sub>x</sub> fluxes were greatest from SL1 and were lowest from CL ( $p < 0.05$ , Figure 6). Although NO<sub>x</sub> emissions appear to increase with increasing sand content, the sites did not differ significantly from one another.



**Figure 2.** Mean soil  $\text{NO}_x$  flux ( $\text{ng NO-N m}^{-2}\text{s}^{-1}$ ) versus soil temperature (in degrees Celsius) for all measurements ( $r^2 = 0.31$ , and  $p < 0.05$ ).

#### 4.4. Effects of Nitrogen Application From Previous Studies

Annual  $\text{NO}_x$  fluxes were 1.5 times greater from sites where nitrogen was applied in studies 5 to 12 years earlier (SL2F and SCLF) than from sites of like texture (SL2 and SCL) ( $p < 0.05$ , Figure 7). The increase was independent of soil texture; SL2 had a sand content of 74%, whereas SCL had a sand content of 58%. The effects of previous nitrogen application may have been complicated



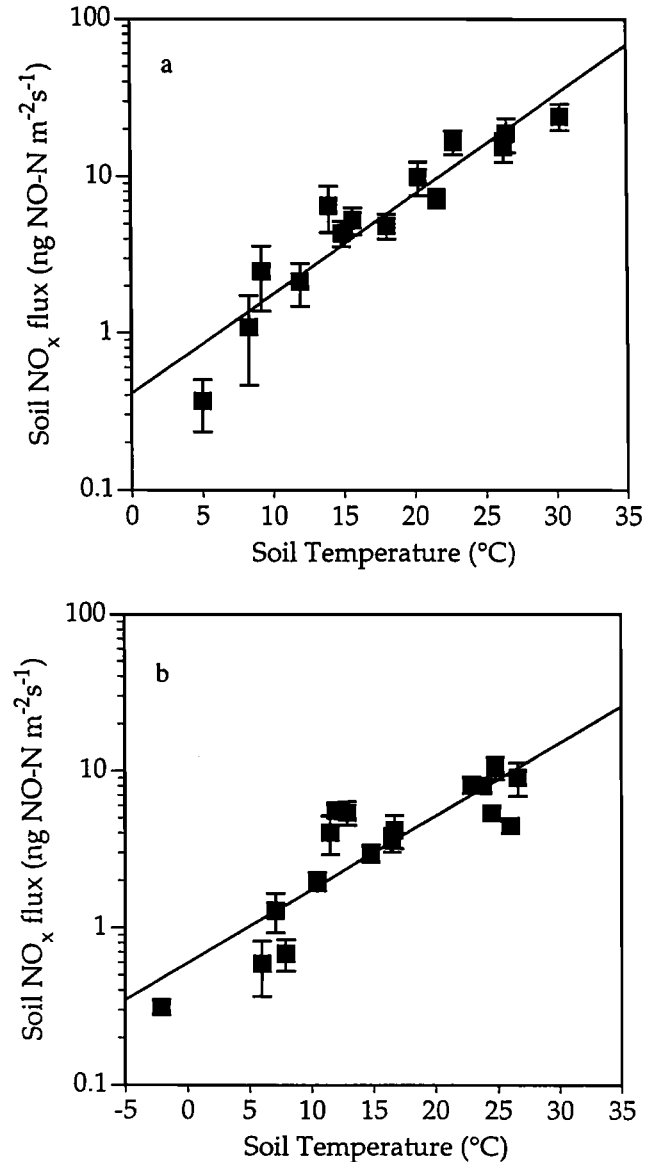
**Figure 3.** Soil  $\text{NO}_x$  flux ( $\text{ng NO-N m}^{-2}\text{s}^{-1}$ ) versus soil temperature (in degrees Celsius) for the coarse-textured sites ( $\geq 70\%$  sand and  $\leq 15\%$  clay) sites, SL2 and SL1, and the finer-textured ( $\leq 58\%$  sand and  $\geq 24\%$  clay) sites, CL and SCL. The error bars represent standard error  $n = 6$  for SL2, SL1, and CL, and  $n = 4$  for SCL. Value  $r^2 = 0.81$ ,  $p < 0.05$ , and  $y = \exp(-0.68 + 0.13(\text{soil } T))$ .

by differences in bulk density between the SL2 and SL2F sites. Aside from the nitrogen applications, all other management practices were identical on the paired sites.

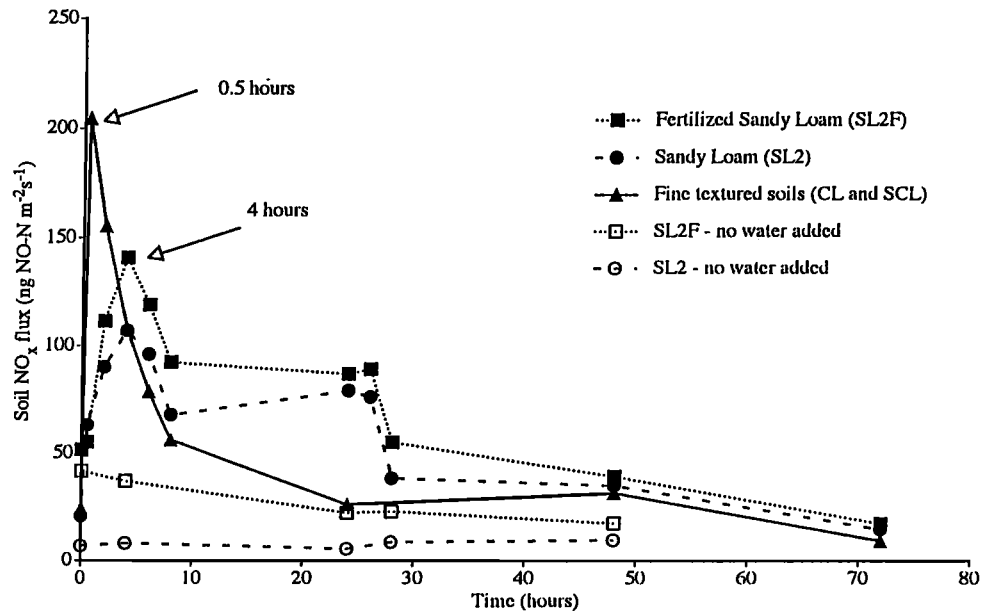
## 5. Discussion

### 5.1. Seasonal and Annual $\text{NO}$ Emissions

Soil  $\text{NO}_x$  emissions averaged over the year from the unfertilized sites at the CPER were  $3.8 \text{ ng NO-N m}^{-2}\text{s}^{-1}$  ( $2.7$  to  $4.1 \text{ ng NO-N m}^{-2}\text{s}^{-1}$ ) (Table 3). Our average included winter measurements, which although it was low,  $0.8 \text{ ng NO-N m}^{-2}\text{s}^{-1}$  ( $0.2$  to  $1.5 \text{ ng NO-N m}^{-2}\text{s}^{-1}$ )



**Figure 4.** Soil  $\text{NO}_x$  flux ( $\text{ng NO-N m}^{-2}\text{s}^{-1}$ ) versus soil temperature (in degrees Celsius) for the coarser-textured ( $\geq 70\%$  sand and  $\leq 15\%$  clay) sites, SL2 and SL1 (a). Value  $r^2 = 0.88$ ,  $p < 0.05$ , and  $y = \exp(-0.90 + 0.15(\text{soil } T))$ . Soil  $\text{NO}$  flux ( $\text{ng NO-N m}^{-2}\text{s}^{-1}$ ) versus soil temperature (in degrees Celsius) for the finer-textured ( $\leq 58\%$  sand,  $\geq 24\%$  clay) sites, CL and SCL (b). Fluxes were optimized over water-filled pore space levels of  $70 \pm 10\%$ . Value  $r^2 = 0.76$  and  $y = \exp(-0.52 + 0.11(\text{soil } T))$ . Error bars represent the standard error.



**Figure 5.** Examples of the short-term effect of water addition on soil  $\text{NO}_x$  emissions from sites differing in nitrogen content and texture.

$\text{s}^{-1}$ ), accounted for up to 25% of the  $\text{NO}_x$  emissions from soils at the CPER.

*Williams and Fehsenfeld [1991]* measured  $\text{NO}_x$  emissions from a similar site at the CPER during the growing season. Their average  $\text{NO}_x$  flux ( $10 \text{ ng NO-N m}^{-2} \text{ s}^{-1}$ ), although it was higher than we measured at the CPER ( $3.8 \text{ ng NO-N m}^{-2} \text{ s}^{-1}$ ), falls within the range of our summertime fluxes ( $5.4$  to  $10.5 \text{ ng NO-N m}^{-2} \text{ s}^{-1}$ ) (Table 3). The average soil  $\text{NO}_x$  emissions from the CPER,  $3.8 \text{ ng NO-N m}^{-2} \text{ s}^{-1}$ , are consistent with measurements made from other grasslands compiled by *Davidson [1991]*, ranging from  $1.7$  to  $10 \text{ ng NO-N m}^{-2} \text{ s}^{-1}$  with an average of  $4.2 \text{ ng NO-N m}^{-2} \text{ s}^{-1}$  based on four experiments.

## 5.2. Influences of Temperature

We found a positive exponential relationship between  $\text{NO}_x$  and soil temperature at our sites at the CPER ( $r^2 = 0.31$  and  $p < 0.05$ ). Similar exponential relationships between soil temperature and  $\text{NO}_x$  flux have been observed in other studies on grasslands, agricultural sites, and savannas in temperate regions [*Johansson and Granat, 1984; Slemr and Seiler, 1984; Anderson and Levine, 1987; Hutchinson and Brams, 1992; Skiba et al., 1992; Yamulki et al.,*

*1995*]. The relationship between temperature and  $\text{NO}_x$  emissions was strongest for water contents close to field capacity ( $35 \pm 10\%$  WFPS for coarser-textured soils,  $r^2 = 0.88$  and  $70 \pm 10\%$  for finer-textured soils,  $r^2 = 0.76$ , Figures 4a and 4b, respectively).  $Q_{10}$  values calculated for our  $\text{NO}_x$  emissions at the CPER were  $3.0$  for finer-textured soils and were  $4.6$  for coarser-textured soils. These are higher than those found by *Johansson and Granat [1984]* in savanna systems, where  $Q_{10}$  values ranged from  $2.7$  to  $3.6$ . However, our  $Q_{10}$  estimates are consistent with those found for  $\text{N}_2\text{O}$  production from the same soils during nitrification ( $1.5$  to  $5$ ) [*Mosier and Parton, 1985*]. Our higher  $Q_{10}$  estimates could be due to two factors: (1) We used seasonal data, which may include changes in nutrient availability, thereby adding the effects of seasonal changes in temperature, (2) We included  $\text{NO}_x$  emissions measured at soil water contents near field capacity thus limiting the interaction of soil water content and temperature.

## 5.3. Influences of Soil Water

At our sites, the WFPS measured at the time of the flux measurements ranged from  $7$  to  $48\%$  on sand-textured soils and  $13$  to  $79\%$  on finer-textured soils [*Martin, 1996*].  $\text{NO}_x$  emissions

**Table 4.** Initial, Peak, and Integrated  $\text{NO}$  Fluxes, Field-Wetting Experiment A June 1994

Site	Amount of Water Added, mm	Initial $\text{NO}$ Flux,* $\text{ng NO-N m}^{-2} \text{ s}^{-1}$	Peak $\text{NO}$ Flux,* $\text{ng NO-N m}^{-2} \text{ s}^{-1}$	Integrated $\text{NO}$ Flux,† $\text{mg N m}^{-2} \text{ d}^{-1}$
SL2F	6.4	7.8	37.6	2.4 a
SL2	15.9	5.5	31.6	2.0 a
SL1	22.3	4.1	46.4	2.6 a
CL	22.3	4.6	44.7	1.1 a
CLL	27.9	9.4	51.4	1.9 a

\*Initial and peak  $\text{NO}$  fluxes ( $\text{ng NO-N m}^{-2} \text{ s}^{-1}$ ) are means of measurements from six replicate anchors at each site.

† $\text{NO}$  fluxes ( $\text{mg NO-N m}^{-2} \text{ d}^{-1}$ ) averaged over 24 hours postwetting are means of measurements from six replicate anchors at each site.

**Table 5.** Initial, Peak, and Integrated NO Fluxes, Field-Wetting Experiment B

Site	No Water Added		4.0 mm H <sub>2</sub> O		25.5 mm H <sub>2</sub> O	
	Initial NO Flux*	Integrated NO Flux†	Peak NO Flux*	Integrated NO Flux†	Peak NO Flux*	Integrated NO Flux†
<i>July 1994</i>						
SL2	8.8	0.2 a	46.9	2.5 b	44.0	2.9 b
SL2F	32.2	0.9 a	54.8	3.2 b	52.6	3.3 b
<i>August 1995</i>						
SL2	4.0	0.2 a	31.1	1.2 a	31.7	1.3 b
SCL	4.4	0.2 a	38.4	0.7 ab	31.7	0.9 a

\*Initial and peak NO fluxes (ng NO-N m<sup>-2</sup> s<sup>-1</sup>) are means of six replicate measurements at each site.

†NO fluxes (mg NO-N m<sup>-2</sup> d<sup>-1</sup>) averaged over 24 hours postwetting are means of measurements from six replicate anchors at each site. Compared across rows values followed by a different letter differ significantly at the  $p < 0.05$  level (analysis of variance with Tukey mean comparison tests).

increased with increasing WFPS until field capacity (32-35% WFPS for the coarser-textured sites, SL2 and SL1, and 66% for the finer-textured sites, CL and SCL) and decreased thereafter. This relationship between NO<sub>x</sub> emissions and WFPS has been observed in other studies [Cardenas *et al.*, 1993; Davidson *et al.*, 1991, and 1993; Davidson, 1992; Yamulki *et al.*, 1995]. Two possible explanations for the decrease in soil NO<sub>x</sub> emissions at higher soil water contents are (1) that the microbial production of NO from nitrification decreases and (2) that diffusion is limited. Microbial production of NO from nitrification is decreasing at higher water contents. Nitrification dominates in soils with low soil water contents (< 60% WFPS and well aerated [Linn and Doran, 1984]). Nitrification inhibitors were not used in our study; therefore we cannot accurately assess this mechanism. The diffusion of NO through the soil is slowed at higher soil water contents, decreasing the rate of escape of NO to the surface, as well as increasing the probability of consumption of NO [Davidson, 1991]. NO diffuses 10<sup>5</sup> times slower through water than through the equivalent thickness of air [Galbally, 1989; Galbally and Johansson, 1989].

The relationship between NO<sub>x</sub> emissions and soil water content is complicated by the effect of small precipitation events. On average, small events (< 5 mm) dominate the precipitation regime at the CPER, accounting for 87% of the total number of precipitation events annually [Sala *et al.*, 1992]. In this study, water was added to the anchors to simulate rain, caused large but transient pulses of NO<sub>x</sub>. NO<sub>x</sub> emissions increased to between 22 and 55 ng NO-N m<sup>-2</sup> s<sup>-1</sup> from initial values ranging from almost 0.5 to 32 ng NO-N m<sup>-2</sup> s<sup>-1</sup>. Peak fluxes were not related to the number of days without rain prior to wetting. The average number of antecedent dry days before a wetting experiment was 4, with the shortest dry period lasting 1 day and the longest lasting 6 days. In contrast, Davidson [1992] found a relationship between antecedent dry days and peak flux when there was a prolonged dry season before the wetting [Davidson, 1992]. The summer at the CPER is drier than the winter, but even in the summer there are frequent small rain events (twice a week on average). Our data suggest that large short-term (24 hour) pulses caused by wetting events significantly increase summer NO<sub>x</sub> fluxes. These precipitation

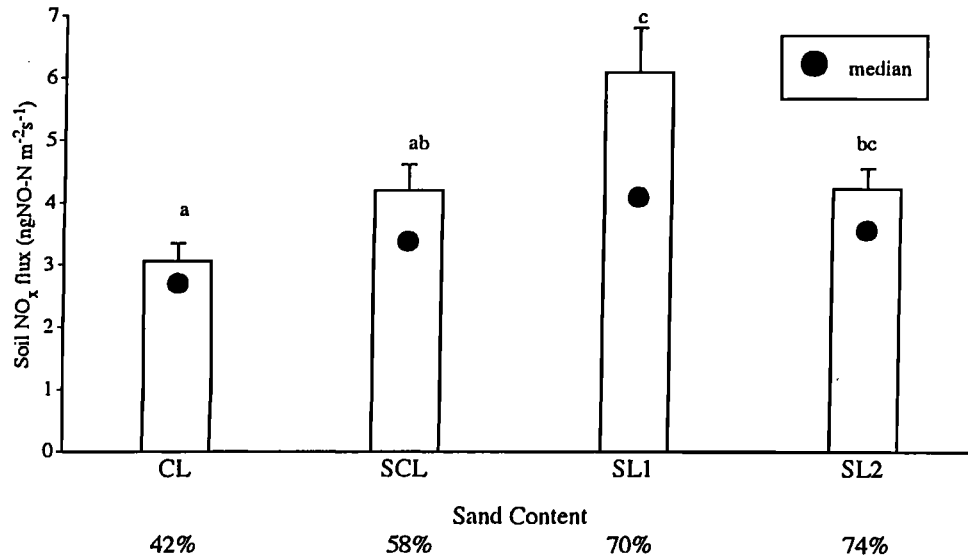
**Table 6.** Total Number of Precipitation Events and the Total Amount of Precipitation calculated for Each Month

	1994		1995	
	Total Precipitation Events	Total Precipitation, mm	Total Precipitation Event	Total Precipitation, mm
January	2	2.8	1	0.5
February	5	4.6	1	1
March	10	6.9	2	3.3
April	11	23.8	10	21.6
May	8	22.4	24	181.8
June	5	28.2	16	117.7
July	7	15.8	8	6.6
August	9	12.7	6	10.4
September	4	4.1	7	47.8
October	7	10.7	8	ND*
November	3	1	ND*	ND*
December	1	1.8	ND*	ND*

Calculated from unpublished Long Term Ecological Research data.

\*ND indicates no data available.





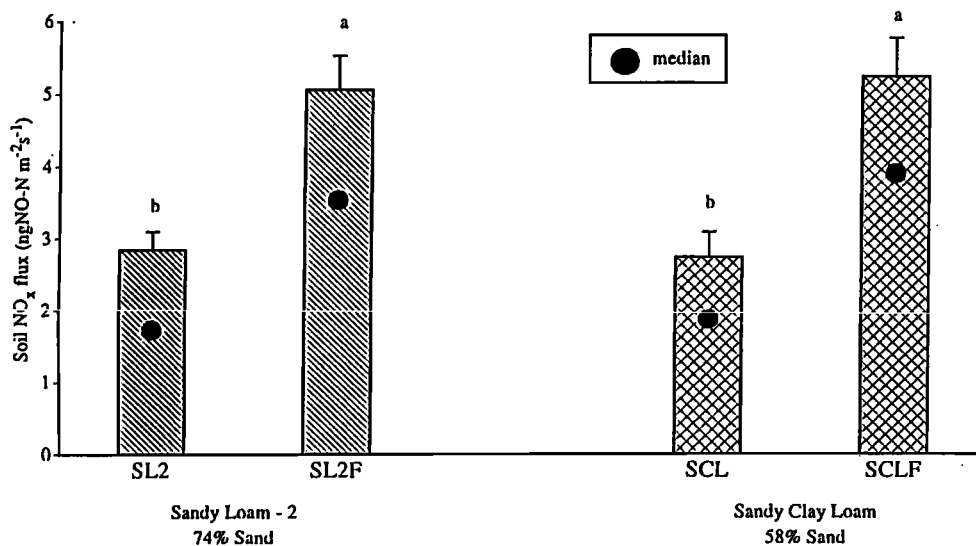
**Figure 6.** Mean and median soil NO<sub>x</sub> fluxes (ng NO-N m<sup>-2</sup> s<sup>-1</sup>) for all data collected from the unfertilized sites (SL2, SL1, CL, and SCL). Error bars are standard error ( $n = 188, 171, 186,$  and  $136,$  respectively). Means with a different letter differ significantly at the  $p < 0.05$  level.

event-driven pulses are often missed by periodic sampling and require quantification in order to obtain an accurate annual estimate of NO<sub>x</sub> emissions.

#### 5.4. Influences of Texture

In this study, NO<sub>x</sub> emissions were measured from four soil types ranging in texture from sandy loam soil (74% sand and 13% clay) to clay loam soil (42% sand and 30% clay). Although NO<sub>x</sub> emissions increase slightly with increasing sand content, only the

NO<sub>x</sub> emissions from the site with the lowest sand content, CL, were significantly different than those found on the sandy loam sites (SL2 and SL1), 2.7 ng NO-N m<sup>-2</sup> s<sup>-1</sup> compared to 3.6 and 4.1 ng NO-N m<sup>-2</sup> s<sup>-1</sup> (Table 3). Few studies report soil texture associated with NO<sub>x</sub> emissions. However, the trend of higher NO<sub>x</sub> emissions from coarser soils was also found by *Bakwin et al.* [1990] in their study in a tropical rainforest. NO<sub>x</sub> fluxes from sandy-textured soils were higher than those measured from a fine-textured soil by nearly a factor of 4. A similar trend was also observed on agricultural soils in Scotland [*Skiba et al.*, 1992]. In finer-textured soils, molecular



**Figure 7.** Average and median soil NO<sub>x</sub> fluxes (ng NO-N m<sup>-2</sup> s<sup>-1</sup>) for data collected on the SL2, SL2F, SCL and SCLF sites. Error bars represent standard errors ( $n = 104$  for SL2;  $n = 114$  for SL2F;  $n = 76$  for SCLF;  $n = 76$  for SCL). The error bars represent standard error. The data were taken from only the time both fertilized sites were measured (January 19, 1995 to October 11, 1995). Means with different letters differ significantly at the  $p < 0.05$  level.

diffusion dominates gas transport, whereas in coarser, sandier soils the importance of advective transport increases [Livingston and Hutchinson, 1995]. This has the potential to increase the soil-atmosphere exchange rate several fold over that due to molecular diffusion alone [Livingston and Hutchinson, 1995]. The mechanism maintaining high diffusivity through the soil is continuous air-filled porosity [Livingston and Hutchinson, 1995; Bakwin et al., 1990]. Therefore, coarser soils tend to be better ventilated, allowing  $\text{NO}_x$  to escape more freely [Bakwin et al., 1990; Skiba et al., 1992]. The escape efficiency of  $\text{NO}_x$  is more important than that of other trace gases, such as  $\text{N}_2\text{O}$  and  $\text{CO}_2$ , because of its high reactivity. A larger range of soil texture would provide more information about the relationship between soil texture and  $\text{NO}_x$  emissions at the CPER.

### 5.5. Influences of Nitrogen Application From Previous Studies

Increases in  $\text{NO}_x$  fluxes have been associated with the application of nitrate, nitrite, and urea ammonium. In contrast with these other studies which observed short-lived increases in  $\text{NO}_x$  fluxes (a few days, weeks, or months) after nitrogen application, we observed increases in  $\text{NO}_x$  fluxes 5 and 12 years following nitrogen application. Soil  $\text{NO}_x$  fluxes from the SCLF site were 1.9 times higher than from the SCL site ( $5.2 \text{ ng NO-N m}^{-2} \text{ s}^{-1}$  compared to  $2.7 \text{ ng NO-N m}^{-2} \text{ s}^{-1}$ ). Soil  $\text{NO}_x$  fluxes from the SL2F site were 1.5 times higher than from the SL2 site ( $4.3 \text{ ng NO-N m}^{-2} \text{ s}^{-1}$  compared to  $2.8 \text{ ng NO-N m}^{-2} \text{ s}^{-1}$ ).

The increases in  $\text{NO}_x$  fluxes mirror increases in  $\text{N}_2\text{O}$  fluxes measured by Mosier et al. [1996]. Measurements made from 1991 to 1995 show an increase in soil  $\text{N}_2\text{O}$  emissions,  $1.9$  to  $2.8 \mu\text{g N m}^{-2} \text{ h}^{-1}$  from SCL compared to SCLF and  $1.7$  to  $3.0 \mu\text{g N m}^{-2} \text{ h}^{-1}$  from SL2 compared to SL2F [Mosier et al., 1996]. These elevated  $\text{N}_2\text{O}$  fluxes from the SL2F site remain despite a large drop in ammonium concentration from  $10 \mu\text{g N g}^{-1}$  in 1991 to back to the level found on the SL2 site ( $1 \mu\text{g N g}^{-1}$ ) in 1994 [Mosier et al., 1996]. The persistence of elevated fluxes of both  $\text{NO}_x$  and  $\text{N}_2\text{O}$  indicate that bulk soil nitrogen measurements may not reflect the relative amounts of N turnover needed to sustain these fluxes.

### 5.6. Annual N Flux

The annual release of  $\text{NO}_x$  was  $1.3 \text{ kg N ha}^{-1}$  ( $0.8$  to  $1.8 \text{ kg N ha}^{-1}$ ) for the CPER calculated as a weighted mean of the coarse- and fine-textured soils. Following the calculations of Mosier et al. [1996], the annual release of  $\text{NO}_x$  from the spatial extent of the CPER was calculated using a mean weighted by soil texture (70% coarse-textured soils and 30% fine-textured soils) based on a spatial textural analysis by Yonker et al. [1988].

The gaseous  $\text{NO}_x$  flux is approximately 10 times that of  $\text{N}_2\text{O}$ ,  $0.14 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  [Mosier et al., 1996], and equivalent to 3 to 4% of the annual net nitrogen mineralization rate [Schimel et al., 1985; D. Valentine, personal communication, 1995]. The  $\text{NO}:\text{N}_2\text{O}$  of 10 indicates that nitrification is the dominant pathway of N gas production at the CPER. This is consistent with other controls on the microbial production of N gases. The soil moisture content at the CPER is generally at or below field capacity, the range most suitable for nitrification [Mosier et al., 1996]. The use of the acetelyne inhibition technique in a previous study on  $\text{N}_2\text{O}$  indicated that 60 to 80% of the  $\text{N}_2\text{O}$  production at the CPER was through nitrification [Parton et al., 1988].

Measurements of  $\text{NO}_2$  made using the eddy-correlation method from towers at 2 and 6 m heights at the CPER found approximately

the same concentrations of  $\text{NO}_x$  as measured from soil chambers [Williams et al., 1987; Williams and Fehsenfeld, 1991; and Stocker et al., 1993]. This suggests two things: (1) chambers which enclose the canopy include the effect of  $\text{NO}_x$  scrubbing by the canopy, and (2) the  $\text{NO}_x$  escaping the soil persists in the atmosphere to at least 6 m, well above the plant canopy of the CPER. The annual release of  $\text{NO}_x$  is a significant nitrogen loss from the ecosystem, representing 20% of the total annual nitrogen inputs, which are low,  $6.0 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  wet deposition [recorded by the National Atmospheric Deposition Program (NADP) site at the CPER in 1994 and 1995, NADP/National Trends Network (NTN), (NADP/NTN Coordination Office, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins.)

## 6. Conclusions

Seasonal  $\text{NO}_x$  emissions at the CPER ranged from barely detectable fluxes and  $1.5 \text{ ng NO-N m}^{-2} \text{ s}^{-1}$  in the winter to highs between  $5.4$  and  $10.5 \text{ ng NO-N m}^{-2} \text{ s}^{-1}$  in the summer. The  $\text{NO}$  flux is 10 times greater than the  $\text{N}_2\text{O}$  flux at the CPER, indicating that nitrification is the dominant pathway for the microbial production of N gases. Winter  $\text{NO}_x$  emissions added up to 25% to the annual  $\text{NO}_x$  flux from the CPER. Winter fluxes are often assumed to be zero so they are rarely collected or considered when calculating annual  $\text{NO}_x$  flux estimates from temperate regions. Water additions performed in concert with the long-term periodic sampling show that wetting of dry soil at the CPER can produce pulses of  $\text{NO}_x$  that are 8 times greater on average than the fluxes from unamended soils. The inclusion of the elevated  $\text{NO}_x$  fluxes translates into a 230% increase in the estimate of summer  $\text{NO}_x$  emissions at the CPER. Water addition experiments or an event-driven sampling scheme in conjunction with year-round periodic sampling is needed to obtain an accurate annual estimate of  $\text{NO}_x$  fluxes. Temperature was the strongest predictor of  $\text{NO}_x$  flux from the CPER. Although WFPS alone was a poor predictor of  $\text{NO}_x$  flux, the  $\text{NO}_x$  fluxes produced from soils with soil water contents near field capacity exhibit a stronger relationship with temperature.  $\text{NO}_x$  fluxes increase slightly with increasing sand content but are significantly lower only from the site with the lowest sand content (CL, 42% sand) compared to the sites with the greatest sand content (SL1, 70% sand and SL2, 74% sand). The relation between sand content and  $\text{NO}_x$  flux may be improved by the addition of sites that extend the range of soil textures.  $\text{NO}_x$  fluxes from sites on which N was applied in previous studies 5 and 12 years earlier were at least 1.5 times greater than the unamended sites despite the fact that the bulk soil nitrogen contents had returned to the levels of that on the control sites. Nitrogen application has a long lasting effect on gaseous N emissions from the CPER.

The annual soil  $\text{NO}_x$  emissions calculated as the annual flux estimate from the grassland ecosystems globally contribute  $1.0 \text{ Tg N}$  per year to the global  $\text{NO}$  flux, slightly higher than the average global flux estimate ( $0.6 \text{ Tg N yr}^{-1}$ ) calculated by Davidson [1991]. His estimate was based on only fluxes from four experiments. The value  $1.0 \text{ Tg N}$  per year represents 5% of the total global  $\text{NO}_x$  flux ( $20 \text{ Tg N yr}^{-1}$ ) [Davidson, 1991].

**Acknowledgments.** We thank Larry Tisue and Anita Kear for the hours of assistance and company in the field. This project was supported by the NASA-EOS Program for Research Support (NAGW-2662) and NSF support for database/modeling analysis (TRAGNET-NSF-DEB-9416813). We graciously thank our reviewers for helpful questions and extensive editorial comments.

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(Received May 14, 1997; revised October 8, 1997; accepted November 24, 1997.)