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Fluxes of nitrous oxide and methane from nitrogen-amended soils in a Colorado alpine ecosystem

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Abstract. In order to determine the effect of increased nitrogen inputs on fluxed of N_2O and CH_4 from alpine soils, we measured fluxes of these gases from fertilized and unfertilized soils in wet and dry alpine meadows. In the dry meadow, the addition of nitrogen resulted in a 22-fold increase in N_2O emissions, while in the wet meadow, we observed a 45-fold increase in N_2O emission rates. CH_4 uptake in the dry meadow was reduced 52% by fertilization; however, net CH_4 production occurred in all the wet meadow plots and emission rates were not significantly affected by fertilization. Net nitrification rates in the dry meadow were higher in fertilized plots than in non-fertilized plots throughout the growing season; net mineralization rates in fertilized dry meadow pots were higher than those in non-fertilized plots during the latter half of the growing season.

Introduction

The atmospheric trace gases N_2O and CH_4 may play significant roles in greenhouse warming and in atmospheric chemistry (Watson et al. 1992). Production of both gases occurs in soils during the oxidative and reductive processes of microbial metabolism. N_2O production in soils occurs during the processes of nitrification and denitrification. The availability of nitrogen plays a crucial role in determining the rate of these processes (Robertson 1989) and can represent a primary limitation on N_2O production (Firestone & Davidson 1989). Nitrogen availability also affects CH_4 fluxes by directly affecting the microbial communities and biochemical processes involved in CH_4 consumption (Mosier et al. 1991). As a result, anthropogenic disturbances such as increased nitrogen deposition can strongly influence the exchange of these gases between the atmosphere and biosphere (Melillo et al. 1989). However, the processes governing N_2O and CH_4 production and consumption are also sensitive to variations in carbon availability, oxygen concentrations and temperature and these factors can mediate N_2O and CH_4 flux responses to increased N deposition (Ciceron & Oremland 1988; Firestone & Davidson 1989).

Nitrogen fertilization results in reduced CH_4 consumption and increased N_2O production in the northeast hardwood forests of the United States and in temperate and tropical agricultural systems (Bowden et al. 1991; Keller et al. 1990; Mosier et al. 1991; Steudler et al. 1989). The impact of changes in nitrogen inputs on N_2O and CH_4 production and consumption have not been examined in alpine regions. Alpine systems are characterized by a wide range of vegetation communities differing in moisture, total soil nitrogen and net primary productivity. Because of this heterogeneity, the effect of increased nitrogen inputs on N_2O and CH_4 production and consumption is likely to vary both spatially and temporally.

In this study, we evaluated the influence of increased nitrogen inputs on N_2O and CH_4 fluxes in two plant communities that represent the endpoints of a gradient in moisture, substrate quality and productivity in an alpine environment. We focused our research on alpine regions of the Colorado Front Range where rates of wet and dry deposition have increased and are expected to increase as a result of extensive urbanization (Sievering et al. 1992).

Materials and methods

The study site was located at 3500 meters in the Niwot Ridge Biosphere Reserve, administered by the University of Colorado's Mountain Research Station. We chose two plant communities for our measurements: a wet meadow site dominated by *Carex scopulorum* and a dry meadow site dominated by *Kobresia myosuroides*. The sites were located within 50 meters of one another on a south facing slope. Ten 4 m^2 plots were established in each site. These plots were initiated and are maintained as a part of the National Science Foundation's Long Term Ecological Research (LTER) program. Five plots in each site were fertilized with 500 grams of slow release 40-0-0 Urea nitrogen in both the summers of 1990 and 1991. No fertilizer was applied to the plots in 1992, the year we made our flux measurements. Average annual inputs through the release of fertilizer nitrogen for 1990 and 1991 were 25 g m^{-2} $year^{-1}$ (see Bowman et al. 1993).

One week prior to the first sampling, we installed a single static flux chamber base in five control and five nitrogen-amended plots in each community. The chambers consisted of a 25 cm diameter polyvinylchloride (PVC) base 15 to 20 cm tall with a removable cover of white, molded acrylonitrile-butadiene-styrene (ABS) plastic. The lower edge of the chamber was inserted approximately 5 cm beneath the soil surface. Chamber rings remained in place for throughout the summer. We measured fluxes by sealing the chambers with an ABS cover fitted with a single injection port and a second port to equalize pressure during sampling (Matson et al. 1991).

Fluxes were measured three times in June and twice in July and August of 1992. Duplicate gas samples were taken in 25 ml plastic syringes fitted with adjustable stopcocks. Temperature variations in alpine environments are extreme (Greenland 1989). To ensure that all chambers experienced similar temperature regimes, chambers were sealed and sampled at approximately 0, 75 and 105 minutes, as close together in time as possible. Unfortunately the resulting sample period was longer than desirable. Changes in concentration were linearly regressed against time for flux calculations and then corrected for pressure and temperature. In some cases, CH_4 consumption rates declined over the sampling period as headspace concentrations dropped. In the cases where this occurred, we used first order rate kinetics to obtain a rate constant for CH_4 oxidation in each chamber and then estimated oxidation rates at 5 minutes into the sampling period. Despite the long sampling period, N_2O fluxes exhibited no signs of decreasing flux over time. The resulting values were averaged and tested for significance using a 2 way analysis of variance (site by treatment) with Tukey mean comparison tests (significance determined at the $p < 0.05$ level) in SYSTAT (Systat Inc., Evanston, Illinois).

Both CH_4 and N_2O were analyzed in the syringe air samples within 24 hours by gas chromatography at the National Center for Atmospheric Research in Boulder, Colorado. Following sampling, the barrel of the syringe was filled with deionized water to minimize loss of gas due to pressure changes during transport to Boulder for analysis. CH_4 was analyzed on a Shimadzu GC-8A (oven temperature 70 °C) with a 3 m column packed with Haysep D (80/100 mesh). N_2O was analyzed on an HP 5880A (oven temperature 50 °C) equipped with a 0.5 m pre-column and a 3 m main column packed with Porapak Q (80/100 mesh). Detection limits were ± 3 ppb for N_2O and ± 0.05 ppm for CH_4. We sampled standard canister in the field with the same protocol used for flux measurements and found that losses during sampling and transport were minimal (<2%).

On the last day of sampling in August of 1992, a soil sample (0–10 cm depth) in each chamber was collected and analyzed for extractable NO_3^- and NH_4^+ and total soil organic C and N.

In the dry meadow plots, we measured net N mineralization and nitrification rates between June 12 and July 24 and between July 24 and September 6 using PVC core incubations (10 cm depth) fitted with ion exchange resin bags on the bottom to catch leachate. Soil solution NH_4^+ and NO_3^- were measured by extracting with a 2 M KCl solution which was then analyzed on a flow-injection colorimetric analyser (Lachat Instruments, Mequon, WI, USA). Net nitrogen mineralization was calculated as $(NH_4^+ + NO_3^-)_{final}$ minus $(NH_4^+$

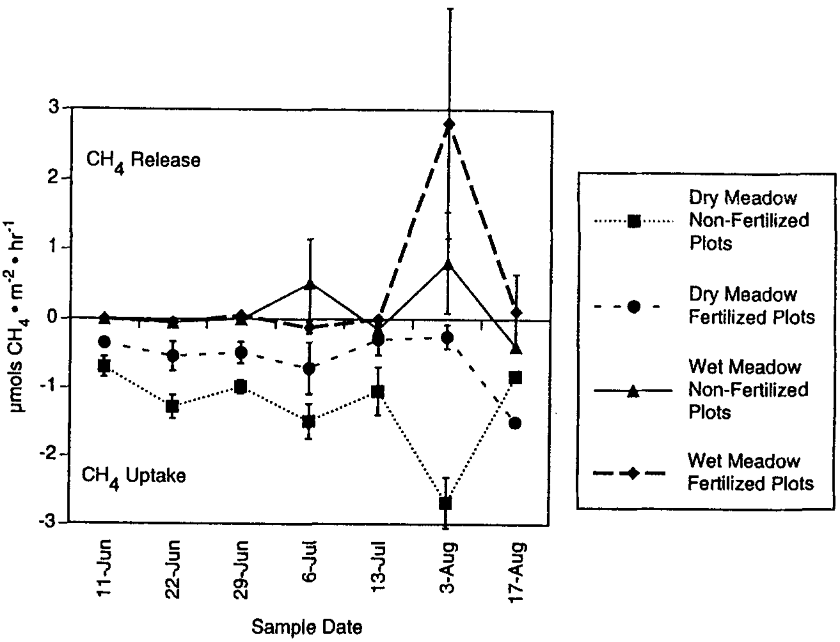

Fig. 1. Methane fluxes from fertilized and control plots in wet and dry meadow communities on Niwot Ridge, Colorado, USA, 1992. Error bars represent standard errors (on average n = 5).

+ $NO_3^-)_{initial}$ and net nitrification as $(NO_3^-)_{final}$ minus $(NO_3^-)_{initial}$. We used a C:N analyzer (Carol Erba Instruments, division of Fisions Instruments, Saddle Brook, New Jersey, USA) to determine total soil organic C and N values.

Results and discussion

Methane

Both control and fertilized plots in the dry meadow were a net sink for CH_4 throughout the growing season of 1992 (Fig. 1), but CH_4 uptake in the fertilized dry meadow plots was 48% of that in the control plots (Table 1). The magnitude of CH_4 oxidation in dry meadow soils on Niwot Ridge lies between rates found in Eastern deciduous forest soils (-0.72 ±mol m^{-2} hr^{-1}, Keller et al. 1983) and the shortgrass steppe of Colorado (-2.18 ±mol m^{-2} hr^{-1}, Mosier et al. 1991).

The reduction in rates of CH_4 uptake in fertilized dry meadow soils is consistent with a general pattern that has been observed in several fertilization studies. Fertilization decreased CH_4 uptake in temperate forest soils by 33%

Table 1. Range, means ± standard error of methane fluxes (μmols m^{-2} hr^{-1}), nitrous oxide fluxes (ng N cm^{-2} hr^{-1}) and soil characteristics of fertilized and non-fertilized plots in the dry and wet meadow communities. All soil nitrogen values were determined from a single sampling (10 cm depth) on August 17th, 1992 (μg NO_3^--N and NH_4^+-N · g dry $soil^{-1}$). Soil moisture values are growing season averages from 1982–1989 (Walker et al. 1994) and Water Filled Pore Space calculations were based on average bulk density values (wet meadow bulk density values (wet meadow bulk density from DA Walker, 1984 unpublished data). Mean values in columns followed by the same letter do not differ significantly at $P = 0.05$, using Tukey's mean comparison in a 2 way ANOVA (site by treatment).

	Methane		Nitrous Oxide						Soil	
	Range	Mean	Range	Mean	C:N ratio	% Organic N	Nitrate	Ammonium	Moisture	WFPS
Dry meadow Control plots	0–(−)1.87	−1.29 ± 0.14a	0–0.22	0.07 ± 0.21a	19.0 ± 0.8a	0.47 ± 0.07a	2 ± 0a	14 ± 3a	63.1 ± 1.0	52%
Dry meadow Fertilized plots	0–(−)1.48	−0.62 ± 0.14b	0.10–8.49	1.44 ± 0.21b	17.9 ± 0.7a	0.71 ± 0.12a	15 ± 3b	49 ± 17b		
Wet meadow Control plots	0–3.32	0.13 ± 0.24c	0–0.71	0.08 ± 0.39a	15.6 ± 0.6b	1.24 ± 0.29b	2 ± 1a	75 ± 29b	133.9 ± 2.6	90%
Wet meadow	0–5.41	0.44 ± 0.23c	0.37–10.75	3.43 ± 0.41c	15.9 ± 0b	1.11 ± 0.07b	12 ± 3b	86 ± 42b		

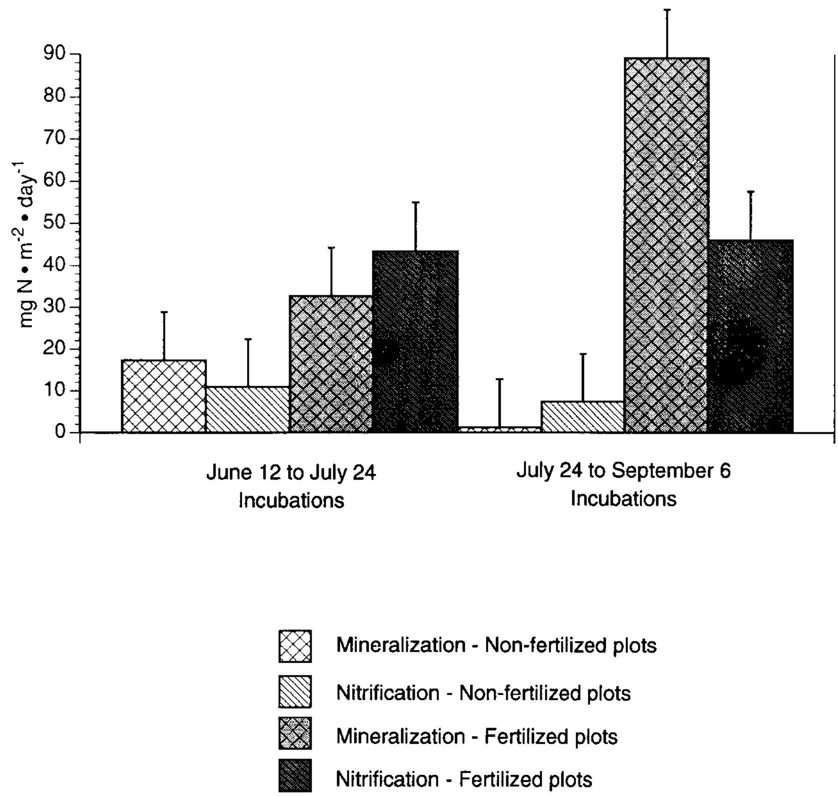

Fig. 2. Net nitrogen mineralization and nitrification measured in six-week, 10 cm deep soil core incubations in *n*-fertilized and control (non-fertilized) dry meadow plots on Niwot Ridge, Colorado, USA, 1992. Error bars represent standard errors ($n = 5$).

(Steudler et al. 1989) and by 41% in Colorado grassland soils (Mosier et al. 1991). The decrease in rates of CH_4 oxidation following nitrogen additions may be the result of increased soil ammonium concentrations and the suppression of methanotrophic bacteria populations (Mosier et al. 1991; Steudler et al. 1989).

Field measurements of net N mineralization and net nitrification in the dry meadow indicate enhanced N turnover in the fertilized plots (Fig. 2). Net mineralization rates in the dry meadow from mid-June to mid-July were not significantly higher in the fertilized plots than the control plots. However, during the latter half of the growing season (mid-July to early-September) mineralization rates were approximately 77 times higher in the fertilized plots than in the control plots (Fig. 2). Dry meadow net nitrification rates were also significantly enhanced by nitrogen fertilization (Fig. 2).

While we found a general correspondence between enhanced nitrification and suppression of CH_4 uptake, the relationship between NH_4^+ concentrations in the soil and CH_4 flux was not significant. Bulk soil NH_4^+ concentrations do not appear to be good predictors of instantaneous CH_4 oxidation rates.

Unlike the dry meadow which was a net sink of CH_4, the wet meadow was a net source of CH_4 through the growing season of 1992 (Fig. 1). Average CH_4 fluxes from fertilized wet meadow plots were higher than those from non-fertilized plots, but this difference was not significant (Table 1). CH_4 fluxes from wet meadow plots on Niwot Ridge are within the range of CH_4 production found by Sommerfeld et al. (1993) at a Wyoming alpine site.

The differences between CH_4 fluxes in the wet and dry meadows are not surprising. In an 8 year record of growing season soil moistures on Niwot Ridge, Walker et al. (1994) reported average soil moisture contents of 63.1% and 133.9% (Table 1). Bulk densities for the dry and wet meadows average 0.63 g/cm^3 and 0.54 g/cm^3 (wet meadow bulk density: DA Walker, unpublished data) yielding an average water filled pore space (WFPS) of 52% for the dry meadow and 90% for the wet meadow (Table 1). The greater soil water content of the wet meadow relative to the dry meadow favors the development of the anaerobic conditions required for CH_4 production. It is also possible that higher rates of net primary production (NPP) and the higher total soil organic matter (SOM) in the wet meadow plots relative to the dry meadow plots (Bowman et al. 1993) results in increased availability of the carbon substrates needed for methanogenesis (Valentine et al. 1993). However, the lack of a significant difference in CH_4 production in wet meadow fertilized and non-fertilized plots, despite higher NPP and SOM in the fertilized wet meadow, suggests that moisture exerts primary control over CH_4 production and consumption on Niwot Ridge.

Nitrous oxide

N_2O emissions from control plots on Niwot Ridge are low relative to fluxes from soils of tropical and temperate forests (Keller et al. 1983) but are similar to fluxes measured in Colorado grasslands (Mosier et al. 1991). Daily mean N_2O fluxes from dry meadow plots decreased through the summer until August 17, when fluxes were measured within 24 hours following a rainstorm (Fig. 3). Similar results have been described by several investigators who have documented a significant pulse of N_2O following the wetting of dry soils (Davidson et al. 1993; Hao et al. 1988; Garcia-Mendez et al. 1991).

Fertilization increased mean summer emissions of N_2O from the nitrogen amended dry meadow plots by approximately 22 fold relative to control plots (Table 1). Likewise, N_2O fluxes from fertilized wet meadow plots were 45 times larger than those in the unfertilized wet meadow plots (Table 1). The

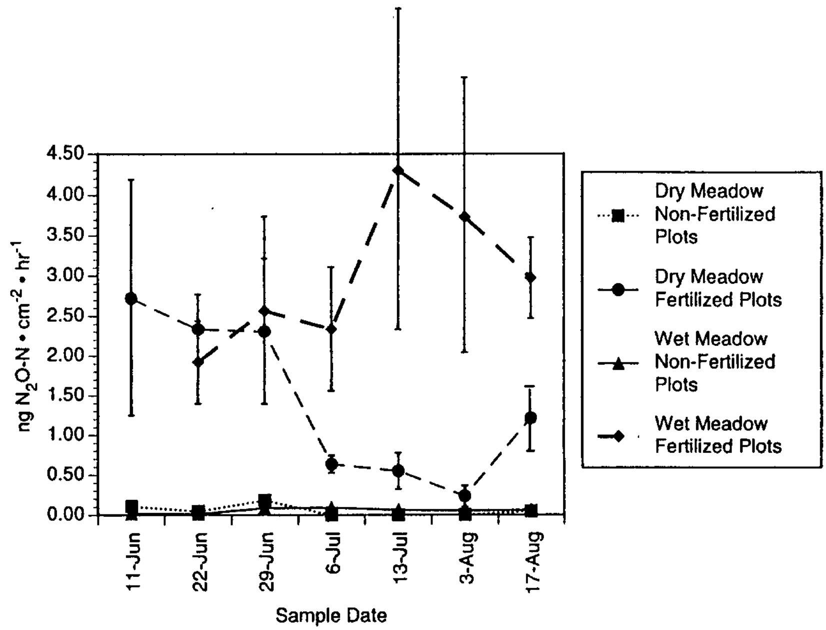

Fig. 3. Nitrous oxide fluxes from fertilized and control plots in wet and dry meadow communities on Niwot Ridge, Colorado, USA, 1992. No samples were taken in the wet meadow on June 11, 1992. Error bars represent standard errors (on average $n = 5$).

increases in N_2O emissions following nitrogen fertilization are considerably larger than the small increases found in temperate forest soils by Bowden et al. (1991). However, the enhancement of dry meadow N_2O production in fertilized plots is similar to the results of Matson et al. (1992) for the second year of fertilization in a Rocky Mountain Douglas fir forest.

The significantly higher N_2O fluxes from fertilized plots relative to control plots suggests that nitrogen availability plays a major role in controlling the production of N_2O in alpine wet and dry meadows. Although net N mineralization rates in the dry meadow during the period from June to July were not significantly different between control and fertilized plots, higher nitrification rates in the fertilized plots may have contributed directly to increased losses of N_2O to the atmosphere. As with methane fluxes, measurements of extractable soil N were not significantly correlated to N_2O emissions.

The differences in fluxes of N_2O from dry and wet meadow fertilized plots are striking and may be due to different pathways of N_2O production in the two sites. The wet meadow soils are likely to be anaerobic and thus denitrification may play a more important role in wet meadow N_2O production, while nitrification (an aerobic process) dominates dry meadow N_2O production (Firestone & Davidson 1989).

In 1992, 0.08% and 0.18% of the previous two year's fertilization N inputs were emitted as N_2O-N from the dry and wet meadows respectively. This calculation applies the mean emission rates in Table 1, a 4 month growing season with annual losses of 0.04 and 0.09 g m^{-2} yr^{-1} for the dry and wet meadow plots. The small proportion of added N released as N_2O suggests that only a small portion of anthropogenically deposited N will be returned to the atmosphere as N_2O from this very nitrogen limited system. The 25 g m^{-2} yr^{-1} of fertilizer applied in this experiment is considerably larger than the current 0.73 g m^{-2} yr^{-1} rate of atmospheric nitrogen deposition and occurred in a large pulse instead of the low and chronic inputs associated with atmospheric deposition (Sievering et al. 1992). However, the N_2O fluxes in this experiment occurred two years after the initial fertilization and the impact of the added N was likely mediated by plant uptake and N turnover in soils. Bowman (1994) documented higher foliar and litter N concentrations in the fertilized plots of both the wet and dry meadows; these higher concentrations may have increased decomposition and may be responsible for the increased N turnover and N_2O fluxes observed in this experiment.

Conclusions

The addition of nitrogen to alpine tundra communities significantly decreased dry meadow CH_4 uptake and increased both wet and dry meadow N_2O release. However, changes in both CH_4 and N_2O fluxes following fertilization varied at the end-points of a gradient of soil moisture and net primary productivity. Fertilization increased N_2O fluxes and decreased CH_4 consumption in dry meadow communities characterized by low soil moisture and low NPP. These changes were accompanied by increased rates of net N mineralization and net nitrification. In wet meadow soils with higher soil moisture, fertilization increased N_2O emissions but did not significantly affect the net production of CH_4 through the summer growing season.

As the Niwot Ridge alpine ecosystem experiences long term chronic deposition of N, changes in nitrogen cycling may result. This experiment demonstrates that alpine trace gas fluxes can potentially be affected by changes in nitrogen inputs but that these effects will not be uniform across the alpine landscape.

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