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Resource limitations to nitric oxide emissions from a sagebrush-steppe ecosystem

DAVID R. SMART[1], JOHN M. STARK[2] & VICTORIA DIEGO[3]
[1]*Department of Agricultural Plant Biology, University of California, One Shields Avenue, Davis California 95616-8746, U.S.A.;* [2]*Department of Biology, Utah State University, Logan Utah 84321-5305, U.S.A.;* [3]*Centre de Recerca Ecològica i Applicacions Forestal, Universitat Autonoma de Barcelona, 08091 Bellaterra (Barcelona) Spain*

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Abstract. We monitored soil emissions of NO, NO_2, N_2O, and CO_2 throughout the summer dry season at a remote North American sagebrush-steppe ecosystem following application of several resources, including water, NH_4^+, NO_3^- and sucrose. Despite low levels of soil NH_4^+ (5.60±0.95 mg NH_4^+-N per kg soil, mean ± S.E.), and NO_3^--N (1.34±0.20 mg NO_3^--N per kg soil), NO emissions ranged from about 0.2 to 2.8 ng NO-N m^{-2} s^{-1}, comparable to rates measured from many agricultural, tropical, and other undisturbed ecosystems. Soil wetting increased NO emissions as much as 400-fold when initial gravimetric soil moisture contents were less than about 50 mg kg_{soil}^{-1} and soil temperature was greater than or equal to 20 °C. Wetting treatments with 20 mg NH_4^+-N kg_{soil}^{-1} raised NO emission rates to a level that was nearly an order of magnitude higher than that observed after water addition alone. Wetting treatments with 20 mg NO_3^--N kg_{soil}^{-1}, 240 mg sucrose-C kg_{soil}^{-1}, or NO_3^- plus sucrose had no statistically significant effect upon NO emissions. Soil denitrifying enzyme activity was low at this site, and N_2O emissions in the field were below detection limits. Soil nitrifying enzyme activity was extremely high at this site, indicating that the NH_4^+ released by ammonification would be consumed at least once every 1.7 days. These observations indicate that NO emissions from this undisturbed ecosystem were likely a consequence of high nitrification activity, and that sagebrush-steppe ecosystems may be a more important NO source than has been previously assumed.

Introduction

Nitrogen gas losses from warm arid and semi-arid soils are important in relation to atmospheric chemical processes and nitrogen fertility in desert ecosystems (West & Skujins 1977; West & Skujins 1978; Skujins 1981; Bowden 1986; Peterjohn & Schlesinger 1990). Ammonia (NH_3), nitrous oxide (N_2O), dinitrogen (N_2) and nitric oxide (NO) are among the major forms of nitrogen gas emitted from arid soils. Some important contributions have been made towards a quantitative understanding of the amounts of NH_3

and N_2O released from arid and semi-arid ecosystems (West & Skujins 1977; West & Skujins 1978; Virginia et al. 1982; Matson et al. 1991). Processes that control N_2O emissions have also received some attention (Peterjohn 1991). In comparison to NH_3 and N_2O, very little is known about the quantities and processes that control NO emissions from north temperate arid lands.

There is general agreement that denitrifying bacteria, nitrifying bacteria, and the chemical decomposition of NO_2^- under acid conditions are the major contributors to soil NO production (Firestone & Davidson 1989). The biochemical origins of NO during denitrification, the dissimilatory reduction of NO_2^- and NO_3^- to N_2O and N_2 (Tiedje 1988), are unclear (Conrad 1990), but NO is usually observed as a minor gaseous product (Firestone & Davidson 1989). The amount of NO released by denitrification depends on the total denitrification rate as well as environmental factors that influence the ratio of possible end products (Firestone & Davidson 1989). High rates of denitrification are most often associated with humid climates, anaerobic conditions, and soils or soil microsites that are rich in carbon and nitrogen availability. Arid soils are usually very dry, aerobic, and nitrogen poor. Nevertheless, high denitrification rates have been observed in many desert soils following water addition (Virginia et al. 1982; Peterjohn 1991). Whether denitrification activity following soil wetting results in substantial NO emissions from undisturbed north temperate arid and semi-arid environments, and particularly sagebrush-steppe, has not been established.

Nitrification, the oxidation of NH_4^+ to NO_2^- and NO_3^-, produces NO in relatively large quantities under laboratory conditions (Ritchie & Nicholas 1972; Lipschultz et al. 1981; Anderson & Levine 1986). Nitric oxide is produced as a direct intermediate of NH_2OH oxidation to NO_2^-, as a by-product from an unstable intermediate generated by NH_2OH oxidation, or as a direct product of nitrifier NO_2^- reduction (Hooper 1984). Under field conditions, strong positive relationships have been observed between NO production and extractable soil NH_4^+ contents (Anderson et al. 1988; Skiba et al. 1992; Poth et al. 1995). Strong negative relationships have been observed between NO production and soil moisture contents (Anderson & Levine 1987; Anderson et al. 1988). These observations have led many researchers to conclude that nitrification is the primary biogenic source of NO under field conditions. The possibility of denitrification under apparently aerobic conditions (Lloyd et al. 1987) and/or heterotrophic nitrification would not fully support this conclusion (Conrad 1990). In addition, soil NH_4^+ accumulation is the net result of both NH_4^+ production (mineralization and deposition) and NH_4^+ consumption (nitrification, plant uptake, microbial assimilation, and soil NH_3 volatilization). Hence large NH_4^+ pools might result from a change in any one of the above processes, but would not necessarily indicate heightened

nitrification activity. Nitrification is a highly aerobic process, and arid soils that are mostly warm, dry, and aerobic, might have high nitrification activities. Consequently, it is possible that NO emissions due to nitrification could be significant in these soils.

Among the investigations that have examined soil NO emissions, most have been conducted over agricultural soils (Stohl et al. 1996; Davidson & Kingerlee 1997). As first pointed out by Anderson and Levine (1987) considerably less is known about the rates and controls on NO emissions from unfertilized lands, and this is particularly true for arid ecosystems (Davidson & Kingerlee 1997). Many arid ecosystems subject to distinct wet and dry seasons, including tropical dry forests (Davidson et al. 1991b), tropical savanna (Johansson et al. 1988), short grass prairie (Williams et al. 1987), and chaparral-shrub (Anderson et al. 1988), have been identified as having substantial NO emissions following simulated precipitation events. Like seasonally dry tropical or temperate soils, sagebrush-steppe soils can become extremely dry during the summer and experience dramatic water content changes either at the onset of the wet season, or periodically when precipitation events occur within the dry season. Such water pulses onto dry soils in the Great Basin can result in an immediate release of NO_3^- (Cui & Caldwell 1997). These observations would support that mineralization and particularly nitrification can be stimulated by precipitation during the dry season. Hence, the combination of warm soil temperatures, aerobicity and precipitation onto dry soils may favor NO production in sagebrush-steppe environments.

Here we report on the influence of soil wetting events on NO emissions from a semi-arid sagebrush-steppe ecosystem that we monitored from the beginning of the warm summer season through the onset of the cool wet season. We make an assessment of which resources among water, NH_4^+, NO_3^- and carbon, as sucrose, most strongly limit NO emissions. We then relate these limitations to nitrogen transformation characteristics as determined using ^{15}N isotopic dilution assays and soil nitrifying and denitrifying enzyme contents. Large uncertainties exist in the magnitude of biogenic NO and NO_2 emissions (Ehhalt & Drummond 1982; Crutzen 1983; Davidson & Kingerlee 1997). Information concerning CO_2 emissions from arid soils (Raich & Schlesinger 1992) is likewise sparse. Hence, our observations contribute to a growing body of information concerning carbon and nitrogen gas emissions from soils of arid ecosystems.

Methods

Study site

Our study site was located near Upper Sage Creek Springs at the southeastern end of Bear Lake, Utah, U.S.A., approximately 41°45′ N latitude by 111°15′ W longitude, at an elevation of 2204 m. The site, which is subject to light grazing, is dominated by *Artemisia tridentata* shrubs, with a mix of *Eriogonum* spp., *Koeleria cristata* and *Poa* spp. predominating within the shrub inter-spaces. The soil is a Kearl Loam which is a coarse, loamy, mixed, frigid, Calcic Haploxeroll (USDA 1982). The pH for the top 28 cm of this soil typically averages between 6.6 and 8.4; however, the pH for the top 10 cm at our study site was 6.0±0.2 (mean ± SE, n = 4). The average water holding capacity ranges between 0.14 and 0.18 cm H_2O per cm soil depth. Mean annual precipitation at this site is approximately 30 cm. Average annual temperature is 3.6 °C with the mean July maximum temperature being 27.0 °C and the mean January minimum temperature being −17.9 °C. During the course of this investigation (June to October), the average daily maximum temperature was about 20.9 °C and ranged from 5.0 °C to 30.6 °C, while the average minimum was 4.6 °C and ranged from −8.9 °C to 12.8 °C (Figure 1). There were 11 precipitation events of ≥0.5 cm and 9 such events of less than 0.5 cm during the course of the investigation (Figure 1), each with a duration of less than 24 h.

Soil gas emissions

Soil gas emissions were measured on 8 dates from early July to late October. On the first visit to the site we set a north to south transect. Each day that we visited the site a new 20 m east to west transect was set perpendicular to the main transect and bisected by it. Each east to west transect was established at approximately 5 m further south along the main transect than the previous one. We measured soil NO, NO_2, N_2O and CO_2 emissions at 6 to 9 locations 1 to 2 m apart along the east to west transects. Polyvinylchloride (PVC) rings 25.5-cm in diameter by 12.0-cm in height and sharpened on one edge were placed on the soil surface and then gently rotated about one fourth of a turn to just barely insert them (<1 cm) into the soil surface (Figure 2). The rings were placed about 2.5 to 4 h before any flux measurements were initiated. There was no evidence that placing the rings on the soil had any transient effect on soil gas emissions. Sequential emissions measurements were made at each location without removing the rings from the soil surface.

We used five different soil-wetting treatments that were applied with an amount of water equivalent to a 2-cm precipitation event. This quantity of

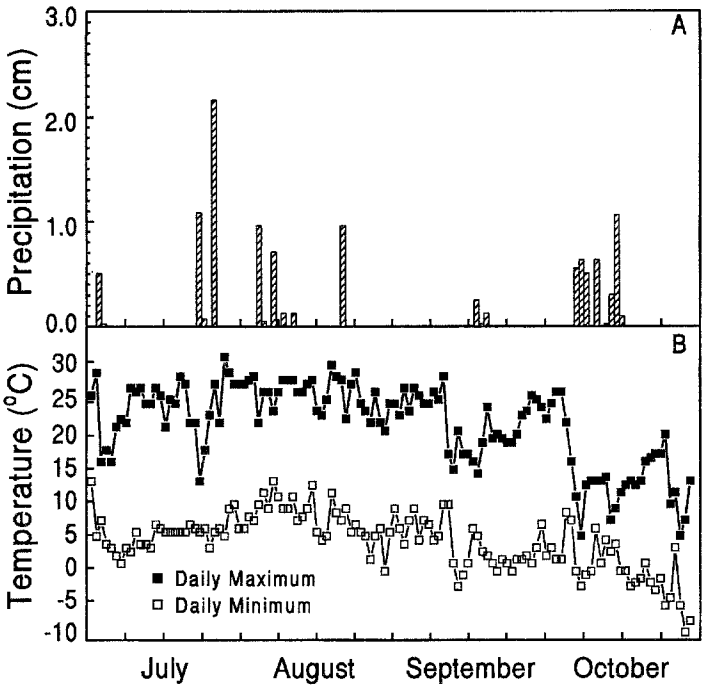

Figure 1. Precipitation (a) and daily maximum and minimum temperatures (b) for the Randolph weather station of the Utah State University Meteorological Survey during the course of time that the investigation was conducted. This weather station is situated within approximately 5 kilometers of the site where our observations were made.

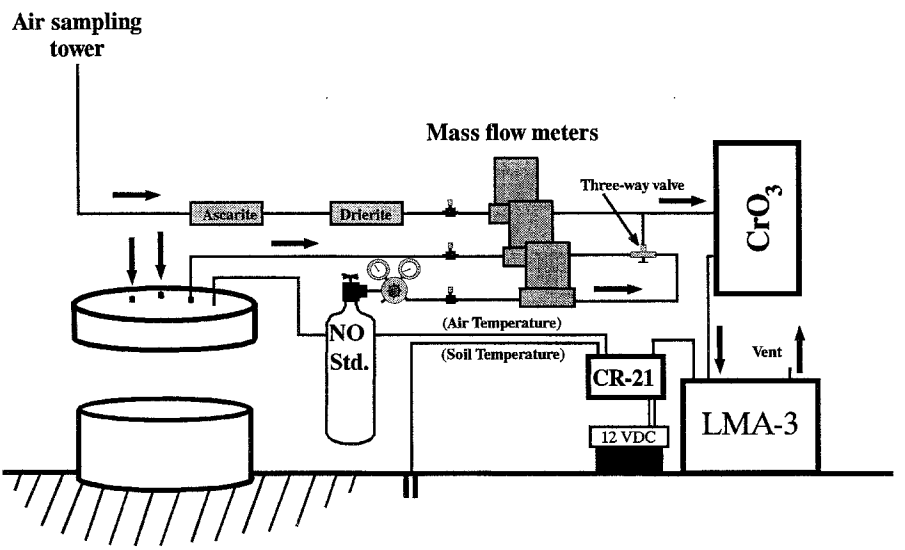

Figure 2. Schematic diagram of the system used for soil NO emissions measurements. Details of the system are provided in the text. Arrows indicate the direction of gas flow through the system. Lines without arrows indicate electrical connections.

water moistened the soil to a depth of about 8 cm. The treatments used in addition to water alone were 1) 3 mM $(NH_4)_2SO_4$; 2) 6 mM KNO_3; 3) 14 mM sucrose; and 4) 6 mM KNO_3 plus 14 mM sucrose. These amounts of NH_4^+-N and NO_3^--N were equal to approximately 20 mg of N per kg of soil, varying slightly with bulk density. We used approximately 240 mg C per kg soil for the sucrose treatments. When this treatment was combined with KNO_3, it gave an added C:N ratio of 12:1. We assumed these quantities of C and N would be sufficient to affect process rates of nitrifying or denitrifying organisms in the desired manner.

The system for measuring NO emissions was modified after that described by Davidson et al. (1991b) (Figure 2). A pressed PVC cover was machined to fit easily over the PVC rings. In order to avoid pressure surges, it was carefully lowered over the top of each ring for measuring soil gas emissions. Air within the chamber was continuously mixed by a 7.5-cm diameter fan blade that was turned by a small 12 V DC motor mounted on the outside of the cover. It was set to rotate at a velocity of about 100 to 150 revolutions min^{-1}. Gas inlet and outlet ports were fixed into the chamber lid using stainless steel and teflon fittings. The inlets (2.76 cm^2) and outlet were situated just outside the perimeter of the diameter path of the fan blades. Even small pressure changes caused by the fan or flow of air through the chamber can lead to overestimates of trace gas emissions (Denmead 1979). For this reason we chose an inlet area versus chamber volume similar to that recommended by Denmead (1979), and a loose unsealed cover rim. These modifications allowed ambient air to easily enter the chamber as air was removed from it by the analyzer (Denmead 1979; Rolston 1982).

We used a Scintrex Ltd. NO_2 analyzer (model LMA-3, Ontario, Canada) to detect NO emissions into the chamber according to the following procedure. An internal pump on the NO_2 analyzer pulled from 700 to 1,000 ml min^{-1} of total air through the system. Sixty to one hundred ml min^{-1} flowed through the chamber while approximately 600 to 900 ml min^{-1} of ambient air was mixed with this amount as it flowed out of the chamber. Carbon dioxide and NO were removed from the ambient air stream using an ascarite filter and moisture removed using a drierite filter. Stainless steel needle valves attached to mass flow meters (Sierra Instruments, model 821-1, Monterey, California, U.S.A.) were used to regulate and accurately monitor gas flow through each pathway. These ancillary instruments were calibrated under laboratory conditions using standard bubble meters. Under laboratory conditions, this instrument had a detection limit of approximately 0.06 ng NO-N m^{-2} s^{-1}.

Dynamic calibrations of the NO_2 analyzer were performed *in situ* using an NO standard containing 0.1017 μl NO per L N_2 (Scott-Marrin Inc., River-

side, California, U.S.A.). NO in the air stream was converted to NO_2 using a CrO_3 filter and NO_2 detected by the chemical luminescence of luminol solution when exposed to NO_2 (Schiff et al. 1986). Hence, the system detects total NO_x ($NO + NO_2$) in its normal operating mode. The CrO_3 filter can be bypassed to detect NO_2 emissions, although some NO_2 emitted into the chamber may be deposited onto the chamber surface (see Johannson et al. 1988). Luminol may be weakly reactive with O_3, CO_2, PAN, and other trace gases emitted by soils. We examined CO_2 interference under laboratory conditions and found that no change in the NO signal was detectable at the concentrations of CO_2 that were observed to accumulate in the chamber during the measurement period (600 to 4000 μl L^{-1} CO_2). In addition, Williams and Davidson (1993) reported that NO detection by the luminol reaction under field conditions was not influenced by NH_3, methylamine, acetonitrile, or N_2O. They also observed that water vapor in the gas stream causes only a slight underestimation of the NO flux. Consequently, the fluxes that we measured following wet-up may slightly underestimate the actual rate due to increased water vapor pressure in the chamber air. At the beginning and end of each day that we made NO emissions measurements, we conducted two tests in which air flowing through the chamber was directly measured without passing it through the CrO_3 filter. All of these tests indicated that the predominant gas measured from the chamber was NO, and that interfering gas species were not present at detectable levels on any occasion. Davidson et al. (1991b) and Williams and Davidson (1993) observed a similar result.

Each day that we measured NO emissions, the instrument was calibrated at the beginning and the end of the day. All of our field calibration data yielded $R^2 \geq 0.93$. The calibration responses at the beginning and the end of the day were very similar, so the data for the beginning and ending calibrations were combined and a single response function used. In general, no significant zero drift was observed during the day, and the NO signal returned to the same zero baseline practically every time the cover was removed from the chamber (see Davidson et al. 1991b). Hence, in spite of a relatively large dilution of chamber air, the NO flux rates into the chamber were large enough not to be biased by signal drift or changes in ambient NO concentration immediately outside the chamber. However, on one day that zero drift was significant, a third calibration was taken at mid-day and the emissions measurements were corrected under the assumption that drift was linear during the time periods between calibrations.

Measurements were initiated 1 min after the chamber lid was placed over a ring and continued for 8 to 12 minutes depending on emission rate. For N_2O and CO_2 emissions, a 20 ml sample (less than 0.2% of the chamber volume) was withdrawn from the chamber at the initiation of a measurement

interval. Then a second sample was withdrawn at either 4 or 6 minutes, and a third sample withdrawn at 8 or 12 minutes, depending on how long the measurement period continued. The gas samples were injected into 13 ml screw-cap culture tubes with butyl rubber septa that were coated with Apiezon-N vacuum grease. The culture tubes were prepared by flushing them three times with N_2 and evacuating. The gas samples were returned to the laboratory and analyzed for N_2O and CO_2 using a Varian Inc. gas chromatograph equipped with electron capture and thermal conductivity detectors (model 3300, Walnut Creek, CA, U.S.A.). After each field measurement, the chamber was removed without disturbing the soil ring and the NO_2 analyzer signal was allowed to return to its zero baseline before a new measurement was initiated. NO emission rates were determined by the rate of NO accumulation in the analyzed gas stream, using the equation described by Davidson et al. (1991b) but modified to account for atmospheric pressure. N_2O and CO_2 emissions were calculated in the same manner as NO, using the rate of N_2O or CO_2 accumulation in the chamber and correcting for the small dilution caused by ambient air being pulled through the chamber. The detection limits for N_2O and CO_2 were 9.6 ng N_2O-N m^{-2} s^{-1} and 2.6 ug CO_2-C m^{-2} s^{-1} respectively.

Soil inorganic nitrogen contents

Soil samples were collected from the upper mineral soil using 5 cm diameter by 8 cm long PVC cores. Twelve locations were sampled on each of two dates in July. The cores were taken at about equal intervals of approximately 1 m along transects where NO emissions were measured. The soil in each sample was well mixed and a sub-sample of approximately 12 to 40 g was immediately placed in 100 ml of 2 M KCl, vigorously shaken and stored on ice. After 24 hours the extraction solution was further shaken and then filtered through Whatman No. 1 filter paper that had been rinsed in 1 M KCl. A second sample of approximately 50 g was weighed and then dried at 105 °C to determine soil moisture content. Ammonium and NO_3^- contents in the extracted solution were determined colorimetrically using a Lachat flow injection autoanalyzer (model QuickChem, Lachat Chemicals, Mequon, WI, U.S.A.). A third subsample of 20 g was finely ground to pass a 160 mesh screen and then two 200 mg sub-samples were combusted in a LECO elemental analyzer to determine total C and N contents (model CHN-1000, St. Joseph, MI, U.S.A.). The filtered material and the material used to determine soil moisture content were wet-sieved and all data expressed on a <2 mm dry soil basis. We also measured soil NH_4^+ and NO_3^- contents at sites used for isotopic dilution analyses that are described below.

Denitrification enzyme assays

During September, six 5 cm diameter by 10 cm long cores were driven into the mineral soil at six randomly selected sites along one transect after gently removing surface litter. The soil in each core was mixed thoroughly and sieved (<2 mm). Four 25 g sub-samples of field moist soil (approximately 0.016 kg water kg^{-1} soil) were taken from each core sample and suspended in 125 ml flasks with 25 ml of water containing 1.0 g L^{-1} chloramphenicol, and either: (1) 1.4 mM KNO_3; (2) 1.67 mM sucrose; (3) 1.4 mM KNO_3 plus 1.67 mM sucrose; or (4) neither KNO_3 or sucrose. A fifth sub-sample was placed in 25-ml of water containing 1.4 mM KNO_3 plus 1.67 mM sucrose but no chloramphenicol. Chloramphenicol is an inhibitor of bacterial protein synthesis. It is normally included in potential denitrification assay solutions to ensure that initial enzyme contents are measured and not synthesis of new enzyme by the denitrifier population during the course of the measurement period. But Pell et al. (1996) recently reported that chloramphenicol directly inhibits activities measured in denitrification assays, thus calling into question its use in such assays. The concentrations of NO_3^- and sucrose were chosen to approximate the amounts of C and N added to soils during field measurements. The headspace gas and nutrient solution were made anaerobic by alternately bringing it under strong vacuum and then flushing with N_2. Ten percent of the head space gas was then replaced with acetylene (C_2H_2). The flasks were incubated on an orbital shaker for 90 min at 23 °C. Gas samples were withdrawn (1-ml) using a nylon syringe at 15, 30, 45, and 90 min. The gas samples were analyzed for N_2O accumulation by gas chromatography as described previously. The total N_2O produced was determined using known solubility constants for N_2O (Wilhelm et al. 1977). Potential denitrification enzyme activity was estimated using the linear regression of N_2O accumulation over time (Tiedje 1982). All of the regressions yielded R^2 values of greater than 0.98.

Nitrification enzyme assays

One hundred milliliters of a weak phosphate buffer containing 1 mM NH_4^+ as $(NH_4)_2SO_4$ was added to approximately 10 g dry weight equivalent of soil in a 250 ml erlenmeyer flask. The slurry was constantly mixed on an orbital shaker for 24 h, and the slurry subsampled. The subsamples were centrifuged and the supernatant frozen until it could be colorimetrically analyzed for NO_3^-, NO_2^-, and NH_4^+ using the Lachat flow injection autoanalyzer previously described. The rate of NO_3^- plus NO_2^- accumulation was determined by linear regression, and expressed per unit soil as mg NH_4^+-N oxidized per kg dry soil per day (Hart et al. 1994).

Nitrogen isotope dilution assays

Five plots were randomly selected within the site on 21 September 1993. Four 4.8 cm diameter by 15 cm long polycarbonate cylinders (inner cores) were driven into the mineral soil at each plot after first removing the surface litter. Larger 10 cm diameter by 15 cm long cylinders (outer cores) were then driven concentrically around each of the inner cores. The soil trapped between the inner and outer cylinders was placed in a plastic bag and thoroughly homogenized. Then a subsample of approximately 15 g moist soil was immediately extracted in 100 ml 2 M KCl and used to estimate the initial NH_4^+ and NO_3^- concentrations in the inner intact core. The remaining soil was sealed into a plastic bag and returned to the laboratory for gravimetric moisture determination.

The cylinders containing the inner cores were capped until solutions enriched in ^{15}N could be injected, about two to three hours later. At that time, eight 2-ml injections of 0.85 mM $(NH_4)_2SO_4$ at 99 atom % ^{15}N were made in two cores from each plot using a syringe with a 15-cm long side-port spinal needle. Identical injections of 1.7 mM KNO_3 at 99 atom % ^{15}N were made in the second pair of cores. For each injection, the needle was inserted to from 0.5 to 1.0 cm above the bottom of the core and withdrawn slowly while injecting. This procedure ensured a uniform distribution of the $^{15}NH_4^+$ and $^{15}NO_3^-$ labels along the length of the core. The eight injections resulted in an increase of from 0.046 to 0.061 kg water per kg of oven dry soil, and from 0.8 to 1.1 mg NH_4^+-N or NO_3^--N kg^{-1} soil depending on bulk density. Because small amounts of $^{15}NH_4^+$ and $^{15}NO_3^-$ become nonextractable immediately upon addition to soil, it was necessary to determine immediate ^{15}N recovery following injection of $^{15}NH_4^+$ or $^{15}NO_3^-$. If not determined, then the initial ^{15}N enrichments will be overestimated and gross rates will be erroneously high (Davidson et al. 1991a). Hence, immediately following injection one inner core that received $^{15}NH_4^+$ and one that received $^{15}NO_3^-$ were removed from the cylinder, homogenized, and a subsample of approximately 15 g moist soil was extracted in 100 ml 2 M KCl. The second intact core from each pair was capped with a thin layer of polyethylene film (15-μm) and placed in an upright position in a 1-L canning jar. The jars containing the core samples were then buried in the soil at their original depth and location. Following 24 h incubations *in situ*, the soils were removed from the cores, homogenized, and subsamples of approximately 15 g were extracted in 2 M KCl.

The 2 M KCl extracts and soils from the outer cores were stored in an ice chest until they could be returned to the laboratory. The containers of 2 M KCl were then re-weighed to determine the quantity of moist soil in the container and the extracts were filtered. The filtrate was colorimetrically analyzed for NH_4^+ and NO_3^- as described previously. The ^{15}N atom percent enrichment of

the extractable NH_4^+ and NO_3^- was determined by first concentrating the N on an acidified filter paper disk using a diffusion technique and then analyzing the N on the disks by direct combustion and mass spectrometry (Stark & Hart 1996).

Gross rates of nitrification were calculated from the rate at which the enriched $^{15}NO_3^-$ pool was diluted with $^{14}NO_3^-$, and gross rates of NO_3^- consumption were calculated from the rate at which ^{15}N disappeared from the $^{15}NO_3^-$ pool (Kirkham & Bartholomew 1954; Hart et al. 1994). Gross rates of ammonification and NH_4^+ consumption were calculated in an analogous manner except that rates of $^{14}NH_4^+$ dilution of the $^{15}NH_4^+$ enriched pool and disappearance of ^{15}N from this pool were used (Hart et al. 1994). Other parameters required for estimating nitrogen transformation rates in the intact cores were calculated from the NO_3^- or NH_4^+ concentration in corresponding outer core samples, the quantity of ^{15}N injected, and the quantity of ^{15}N recovered from the initial extracts of the homogenized samples (Hart et al. 1994).

Results and discussion

Nitrogen transformation characteristics

Total soil N was low at this site (Table 1), and NH_4^+ and NO_3^- contents were relatively low as well (Table 2). More than 84% of the soil samples contained less than 6 mg NH_4^+-N kg^{-1} soil (Figure 3) and more than 75% contained less than 1 mg NO_3^--N kg^{-1} soil (Figure 4). These NH_4^+ and NO_3^- contents were lower than those observed for disturbed agricultural ecosystems evaluated for NO emissions, as well as many undisturbed natural ecosystems evaluated for NO emissions (Anderson et al. 1988; Johansson & Sanhueza 1988; Johansson et al. 1988; Anderson & Poth 1989; Levine et al. 1990; Davidson et al. 1991; Davidson et al. 1993; Poth et al. 1995; Riley & Vitousek 1995; Parsons et al. 1996; Meixner et al. 1997). In addition, annual nitrogen deposition is below 2 kg ha^{-1} y^{-1} (NADP NTN 1996). These data emphasize that this is not a nitrogen rich site.

In spite of low apparent nitrogen availability and nitrogen deposition inputs, potential nitrification enzyme activity (NEA) was extremely high (6.1 mg kg^{-1} d^{-1}, Table 3), indicating that large population densities of NH_4^+ oxidizing microorganisms were present. This observation was supported by the fact that in intact cores following water addition, more than 80% of the NH_4^+ produced by gross ammonification (2.59±1.16 mg kg^{-1} d^{-1}, Table 1), was consumed by nitrification (2.11±1.11 mg kg^{-1} d^{-1}, Table 1). These gross nitrification rates were comparable to rates reported for an ungrazed oak woodland-annual grassland examined for NO emissions and evaluated

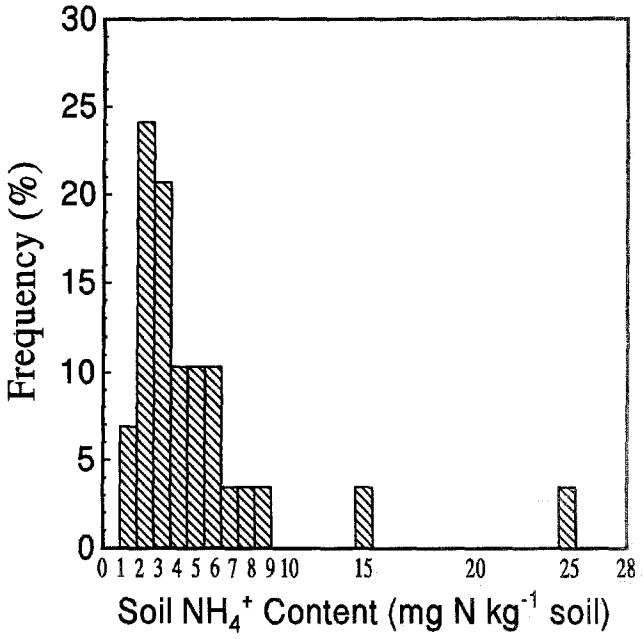

Figure 3. Frequency distribution of soil NH_4^+-N contents.

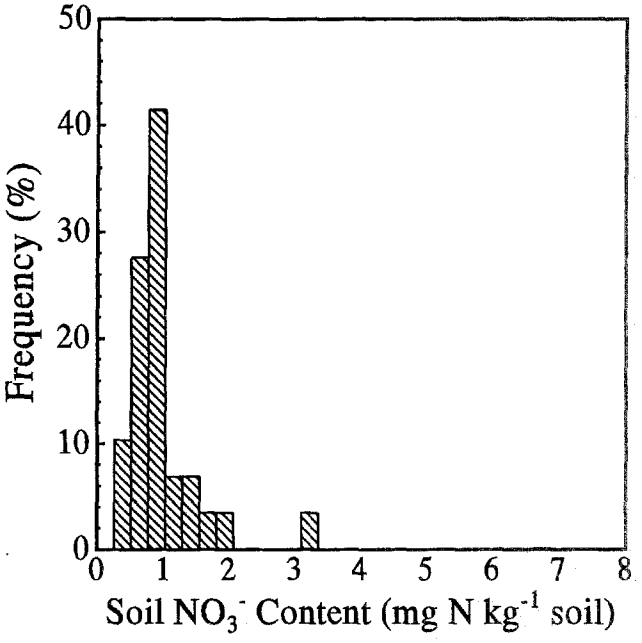

Figure 4. Frequency distribution of soil NO_3^--N contents.

Table 1. Soil phyiscal characteristics and soil nitrogen cycling characteristics for a semi-arid sagebrush-steppe ecosystem. Gross rates of NH_4^+ and NO_3^- consumption, gross rates of NH_4^+ and NO_3^- production and net rates of NH_4^+ and NO_3^- production were determined using $^{15}NH_4^+$ and $^{15}NO_3^-$ pool dilution assays in intact soil cores.

	Mean	S.E.	*n*
Bulk density (Mg m^{-3})	1.07	0.03	5
Total carbon (g kg^{-1})	28.9	1.02	5
Total nitrogen (g kg^{-1})	2.30	0.10	5
pH	6.00	0.20	4
Gross ammonification (mg N kg^{-1} d^{-1})	2.59	1.16	4
Gross NH_4^+ consumption (mg N kg^{-1} d^{-1})	1.89	0.41	4
Net ammonium production (mg N kg^{-1} d^{-1})	1.09	0.71	5
Gross nitrification (mg N kg^{-1} d^{-1})	2.11	1.11	5
Gross NO_3^- consumption (mg N kg^{-1} d^{-1})	1.77	0.60	5
Net NO_3^- productiuon (mg N kg^{-1} d^{-1})	0.34	0.19	5

Table 2. Gravimetric soil water contents, soil inorganic nitrogen contents, and temperature at 5 cm.

Date	Gravimetric soil moisture content (kg kg^{-1})	Soil NH_4^+ content (mg N kg^{-1})	Soil NO_3^- content (mg N kg^{-1})	Soil temperature (°C, 5 cm)		
				Mean	Min.	Max.
July 15	0.042 ± 0.002	6.71 ± 1.45	1.60 ± 0.30	25.51	18.4	28.3
July 18	0.036 ± 0.003	4.93 ± 0.59	1.23 ± 0.13	26.27	19.2	33.1
Sept. 21	0.073 ± 0.004	2.43 ± 0.20	0.54 ± 0.10	23.91	14.3	24.9
Oct. 10	0.184 ± 0.003	N/A	N/A	10.05	2.9	12.6

for nitrogen transformation rates using the same ^{15}N pool dilution methodology, at 2.0 to 2.6 mg kg^{-1} soil d^{-1} (Davidson et al. 1993). They were also comparable to gross nitrification rates for a chronosequence of montane tropical forests, at 1.0 to 4.0 mg kg^{-1} soil d^{-1} (Riley & Vitousek 1995). However, the proportion of NH_4^+ produced by gross ammonification that was consumed by nitrification at the sagebrush-steppe site (81.5%) was greater than that observed for the oak woodland-annual grassland (29 to 65%) or the tropical montane forest chronosequence (5 to 15%). Consequently it appears

that nitrification plays a more important role in the nitrogen economy of this ecosystem (see also Matson et al. 1991).

In comparison to NEA, potential denitrification enzyme activity (DEA) was low in soil samples collected at this site (Table 3). The DEA we measured, at 14.3±6.6 μg N_2O-N kg^{-1} soil hr^{-1} (mean ± S.E., n = 5 for treatments amended with water and chloramphenicol only) was lower than DEA reported for desert systems, at 109.5±40.7 μg N_2O-N kg^{-1} soil hr^{-1} (Peterjohn 1991). Differences in incubation conditions used by Peterjohn (1991), including 25 times higher NO_3^- concentration, 4 times higher carbon concentration, and 1.5 times higher chloramphenicol concentration, may also account for a part of the discrepancy. The DEA data from the sagebrush-steppe site show that denitrification rates were likely limited by carbon rather than NO_3^- supply because addition of NO_3^- did not stimulate denitrification rates, whereas addition of sucrose or sucrose plus NO_3^- resulted in significantly higher denitrification activity (Table 2). Limitation of denitrification activity by carbon availability has been previously observed for soils from desert environments (Peterjohn 1991).

Eliminating chloramphenicol from the assay solution significantly increased DEA (Table 2). Nevertheless, denitrification rates determined between 30 and 45 min in our assays were not significantly higher than the rates measured between 15 and 30 min, regardless of the treatment and whether or not chloramphenicol was present. Thus, the elevated rates observed in the absence of chloramphenicol were not the result of growth, and support that chloramphenicol directly inhibits denitrificaiton (Pell et al. 1996). Although including chloramphenicol in our assays diminished DEA activities, it facilitated comparisons with previous investigations such as those of Peterjohn (1991).

Nitric oxide emissions

Nitric oxide emissions from undisturbed (no wetting treatment applied), relatively dry soils at this site averaged 0.91±0.12 ng NO-N m^{-2} s^{-1} (mean ± S.E.) over the course of the study. Consistently higher rates of NO emission have been observed from undisturbed soils in a few natural systems, including Brazilian rainforest (Kaplan et al. 1988), wet tropical savanna (Johansson & Sanhueza 1988), and chaparral-shrub (Anderson et al. 1988). The chaparral-shrub ecosystem, which is also semi-arid, is situated in an area with extremely high nitrogen deposition inputs, estimated to be at least 20 to 35 kg ha^{-1} y^{-1} (Bytnerowicz & Fenn 1996). At our site, atmospheric inputs are less than 2 kg ha^{-1} y^{-1} (NADP NTN 1996). Such differences in nitrogen deposition inputs may explain why very high emissions rates were consistently observed from the chaparral-shrub site in comparison with sagebrush-steppe. For example,

Table 3. Potential denitrification and nitrification enzyme activities for soils from the 0–10 cm layer of a sagebrush-steppe ecosystem. Assays were conducted using the indicated solutions as treatments. Values are means and standard errors of the means from assays of six soil samples ($n = 6$) collected along a 20-m transect in the case of the denitrification assays and five soil samples ($n = 5$) in the case of the nitrification assays. Values not followed by the same lower case letter differ significantly (Pearsons protected LSD, $\alpha \leq 0.05$).

Treatment	Denitrification enzyme activity (mg N_2O-N kg^{-1} soil d^{-1})	Nitrification enzyme activity (mg N_4^+-N kg^{-1} soil d^{-1})
1.0 mM $(NH_4)_2SO_4$	–	6.10 ± 0.53
Water (+1 g L^{-1} chloramphenicol)	0.34 ± 0.16^a	–
1.4 mM KNO_3 (+1 g L^{-1} chloramphenicol)	0.34 ± 0.13^a	–
1.7 mM sucrose (+1 g L^{-1} chloramphenicol)	0.96 ± 0.11^b	–
1.7 mM sucrose + 1.4 mM KNO_3 (+1 g L^{-1} chloramphenicol)	1.15 ± 0.21^b	–
1.7 mM sucrose + 1.4 mM KNO_3 (no chloramphenicol)	1.85 ± 0.32^c	–

north temperate forests that are affected by nitrogen deposition have very high NO emissions rates in comparison with forests that are not receiving such nitrogen (Valente & Thornton 1993; Butterbach-Bahl et al. 1997). Ecosystems disturbed by burning (Anderson et al. 1988; Levine et al. 1990) or land use changes (Lång et al. 1995) have also shown somewhat higher NO emissions rates, and it is likely that this is a consequence of nitrogen mobilization following such disturbances.

Soil wetting increased the NO emission rate by an average of 15.29±7.64 ng NO-N m^{-2} s^{-1} (Table 4). Extreme variation existed in the soil wet-up effect and it ranged from an increase of 0.59 ng NO-N m^{-2} s^{-1} when soils were cool and moist, up to a high of 139.65 ng NO-N m^{-2} s^{-1} increase when soils were warm and dry. After October 10, when soil temperatures at 5 cm dropped below 5 °C, the wetting effect ceased. The range of rates shown in Table 4 was similar to those reported for undisturbed tropical dry forest soils following wet-up (0.39 ng NO-N m^{-2} s^{-1} to 140.3 ng NO-N m^{-2} s^{-1}, lowest to highest observed increase, Davidson et al. 1991b), tropical savanna soils following wet-up (0.2 to 250 ng NO-N m^{-2} s^{-1}, Johannson et al. 1988), and tropical grassland soils following wet-up (5 to 25 ng NO-N m^{-2} s^{-1}, Poth et al. 1995). It also compares favorably with NO emissions from soils of north temperate short-grass prairie following wet-up (0.028 to 65 ng NO-N m^{-2} s^{-1}, Williams et al. 1987) as well as some unfertilized croplands (see Conrad 1990; Davidson & Kingerlee 1997).

The response to soil wetting appeared to depend most strongly on soil temperature and moisture content (cf. Anderson & Levine 1987). In early July and in mid September, soil wetting increased the rate of NO emission after 1 h by more than 100%. But on two dates in mid-July, when soil temperatures at 5 cm were greater than 20 °C and soil moisture content was less than 5%, simulated precipitation increased NO emissions more than 20 to 80 times the ambient rate (Table 3). This kind of response was consistent with results for other semi-arid subtropical (Slemr & Seiler 1984) and tropical (Davidson et al. 1991b) ecosystems, where soil wetting only strongly stimulated NO emissions during the dry seasons. It has been estimated that up to 24% of the annual NO source may be attributed to such pulsing following precipitation onto dry soils during the transitional period between the dry and the wet season (Yienger & Levy 1995). This generalization appears to be accurate for the sagebrush-steppe ecosystem, although we currently lack information concerning the duration of the post wet-up response.

Spatial variation in NO emissions at our study site was high, as has been observed at many other sites (Yienger & Levy 1995; Davidson & Kingerlee 1997). For example, the highest ambient emission rate we measured occurred in late September, at 2.82 ng NO-N m^{-2} s^{-1}. However, on that same day at

Table 4. Nitric oxide emissions (ng NO-N m^{-2} s^{-1}) and CO_2 emissions (μg CO_2-C m^{-2} s^{-1}) from a sagebrush-steppe ecosystem located in Northeastern Utah, U.S.A., during the summer and fall. Shown are the mean of the emission rate ± one standard error of the mean for 2 to 11 observations that were taken before (0 minutes), 5 minutes following, and 60 minutes following a simulated precipitation event of 2 cm.

Date	*n* (at 0, 5, 60 min)	Time after water application (min) 0	5	60
		NO emissions (ng NO-N m^{-2} s^{-1})		
7/7/93	5, 5, 5	1.86 ± 0.18[1]	2.30 ± 0.65	3.85 ± 0.84
7/9/93	5, 0, 0	0.85 ± 0.24	na[2]	na
7/15/93	8, 3, 3	0.98 ± 0.37	5.41 ± 3.09	24.52 ± 8.99
7/18/93	9, 3, 3	−0.01 ± 0.11	7.42 ± 0.43	81.03 ± 41.64
9/21/93	8, 4, 4	1.11 ± 0.29	1.68 ± 0.95	2.93 ± 1.11
10/10/93	5, 5, 5	0.59 ± 0.04	0.46 ± 0.02	1.19 ± 0.07
10/21/93	7, 2, 2	0.43 ± 0.16	0.40 ± 0.06	0.69 ± 0.29
10/27/93	6, 3, 3	0.32 ± 0.05	0.41 ± 0.04	0.33 ± 0.06
		CO_2 emissions (μg CO_2-C m^{-2} s^{-1})		
7/7/93	5, 5, 0	30.13 ± 8.52[3]	58.83 ± 12.27	na
7/15/93	8, 3, 3	79.34 ± 10.42	420.44 ± 3.15	211.64 ± 110.39
7/18/93	11, 3, 3	27.92 ± 7.01	309.89 ± 9.86	147.98 ± 50.85
9/21/93	6, 4, 4	58.01 ± 10.96	75.71 ± 24.95	384.25 ± 329.98
10/21/93	7, 2, 2	32.92 ± 6.87	79.68 ± 52.87	63.57 ± 4.22
10/27/93	6, 3, 3	20.96 ± 6.04	47.19 ± 10.43	38.01 ± 14.48

[1] the detection limit for NO emissions was 0.06 ng NO-N m^{-2} s^{-1}
[2] data not available
[3] the detection limit for CO_2 emissions was 2.6 μg CO_2-C m^{-2} s^{-1}

another of the four locations along the transect, NO emissions were not within our detection limits. Davidson et al. (1990) have argued that heterogeneity and rapid turnover of the soil NH_4^+ pool may regulate NH_4^+ availability to NH_4^+ oxidizing microorganisms at a microsite scale. Our observations of extreme variability in the soil NH_4^+ pool (Figure 3), variability in NO emissions both before and after water addition, and a strong response of NO emission to NH_4^+ addition (Figure 5) support that NO emissions may be regulated by microsite variation in NH_4^+ or water availability.

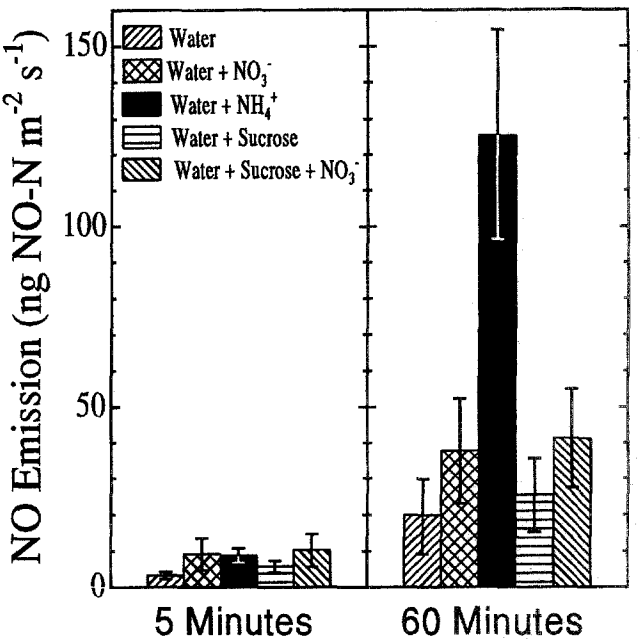

Figure 5. The influence of the addition of water (20 L m^{-2}), NH_4^+ (approximately 20 mg N kg^{-1} soil), NO_3^- (20 mg N kg^{-1} soil), sucrose (240 mg C kg^{-1} soil), and sucrose plus NO_3^- (240 mg C kg^{-1} plus 20 mg N kg^{-1} soil), on soil NO emissions. Shown are the mean and standard error of the mean for measurements at four to six sites that were monitored at approximately 5 minutes and one hour, as indicated, following the application of each treatment.

CO_2 emissions

Soil CO_2 emissions from undisturbed soils at this site did not show strong seasonal variation during the study period (Table 4). The average CO_2 emission rate over all dates was 32.3±3.4 μg CO_2-C m^{-2} s^{-1} (mean ± S.E., n = 44). This rate is in a range previously reported for sagebrush-steppe soils (Caldwell et al. 1977) and also within the range reported for other temperate grassland and desert scrub communities (Raich & Schlesinger 1992).

Carbon dioxide emissions did not respond to simulated precipitation in the same way that NO emissions did. CO_2 emissions initially increased after wetting (at 5 min, Table 4) but did not show any further, statistically significant increase 60 min later. In fact, CO_2 emissions 60 min following water application were higher than the rates measured after 5 min at only 5 of the 44 sites evaluated. Consequently, the increase observed at 5 min likely represents the CO_2 flush caused by water displacement of gas in the soil air space (Norman et al. 1992). Solutions containing NH_4^+, NO_3^-, sucrose and NO_3^-

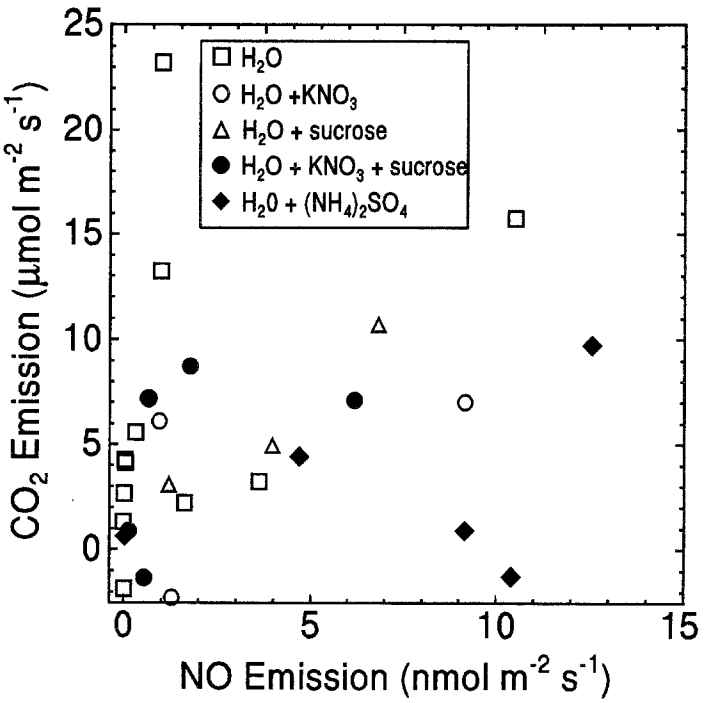

Figure 6. The relationship between changes in soil NO and CO_2 emissions rates one hour following a simulated precipitation event of 2 cm using water alone or solutions of 6 mM KNO_3, 14 mM sucrose, 3 mM $(NH_4)_2SO_4$, or 6 mM KNO_3 plus 14 mM sucrose as indicated.

plus sucrose had no statistically significant effect upon CO_2 emissions. These results suggest that root respiration and not microbial respiratory activity was the major contributor to CO_2 flux. We also found no evidence of correlations between CO_2 and NO emissions (Figure 6) except in the case when NH_4^+ was added with water ($R^2 = 0.67$, $P = 0.024$). Other investigators have found that CO_2 and NO emissions in the field tend to autocorrelate with temperature (Poth et al. 1995).

Resource limitations to NO emissions

Soil NO emissions may be limited by the availability of several resources. If nitrification is the primary source of NO, then soil moisture, O_2 partial pressure, and NH_4^+ availability may exert control on NO production. If denitrification is the primary source of NO, then soil moisture, the availability of reduced C-compounds, and terminal e^- acceptors (O_2, NO_3^-, and NO_2^-) are the resources most likely to exert control on NO production. During denitrification, the ratio of reductant (reduced C-compounds) to oxidant (O_2, NO_3^-, and NO_2^-) also strongly influences the relative amounts of NO, N_2O and N_2

produced (Firestone & Davidson 1989). Generally, at low available carbon to NO_3^- ratios, more NO and N_2O are produced.

We evaluated which resources among NH_4^+, NO_3^- and carbon had the greatest influence on NO emissions rates to use as evidence as to whether nitrification or denitrification was the more important NO source. Addition of a solution containing NO_3^- did not significantly increase NO production relative to addition of water alone (Figure 5). Secondly, addition of carbon (sucrose) did not decrease NO production relative to addition of water or NO_3^-; and addition of solutions containing sucrose plus NO_3^- also had no statistically significant effect on NO emissions as compared with water (Figure 5). These results suggest that denitrification was not responsible for NO production. This conclusion was supported by the fact that we were not able to detect N_2O accumulation in the flux chambers, even when several resources or chemicals that might stimulate N_2O production were applied in the field. These resources included NO_3^-, NO_3^- plus sucrose, or acetylene (data not shown) that blocks conversion of N_2O to N_2. Matson et al. (1991) have also observed low N_2O production in sagebrush-steppe. In contrast, addition of NH_4^+ to wet-up treatments strongly increased NO emission rates above that of water addition alone (P = 0.045, Figure 5). Ammonium increased the rates from a low of 62.56 ng NO-N m^{-2} s^{-1} to a high of 314.46 ng NO-N m^{-2} s^{-1}, and on average this represented a 96.62±29.53 ng NO-N m^{-2} s^{-1} (mean ± SE, n = 6) greater rate than that observed following water addition alone. These data indicated that a primary limitation to NO production in this soil during the dry season was NH_4^+ availability.

Excavation of some of the sites used to measure NO flux revealed that the soil was moistened to a depth of about 8 cm. Hence, the quantity of water that we applied to the wet-up treatments used to measure field NO flux was about five times more than the amount applied to the intact cores used to measure nitrogen transformations by ^{15}N isotope dilution. Both Davidson et al. (1993) and Riley and Vitousek (1995) have searched for relations between gross N transformation rates and NO production under the hypothesis that the quantity of nitrogen being consumed by N transformations determines the amount of NO produced (Firestone & Davidson 1989). In these investigations (Davidson et al. 1993; Riley & Vitousek 1995), intact cores used for the isotope dilution assays received water, but the adjacent sites used for NO flux measurements did not. Our results indicated that when water is made available, both N mobilization and NO release occur at extremely rapid rates. Perhaps the absence of a wetting treatment where the NO flux measurements were taken may help to explain why no apparent relationship between gross

N transformations and NO flux were observed by Davidson et al. (1993) or Riley and Vitousek (1995).

Previous investigators have assumed that positive correlations between elevated NH_4^+ pool sizes and NO emissions (Anderson et al. 1988; Skiba et al. 1992; Poth et al. 1995) or negative correlations between NO emissions and soil moisture contents (Anderson & Levine 1987) indicated NO production by nitrification versus other sources. Results from this investigation show that even when soil NH_4^+ contents are extremely low, NH_4^+ added with water can be consumed by nitrification extremely rapidly. Our results contrast with experiments conducted on moist tropical soils where fertilization with NO_3^- stimulated NO emissions and NH_4^+ had little effect (Johannson et al. 1988; Sanhueza et al. 1990; Cardenas et al. 1993; Rondón et al. 1993). Perhaps denitrification represents a more important source of NO production in warm, humid, tropical soils as compared with the arid soils examined in the present investigation. Finally, it must be noted that production of NO_2^- by nitrification, denitrification or NO_3^- respiration and subsequent chemical decomposition of NO_2^- under acid conditions could produce NO in any of the above environments.

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