Soil moisture and N_2O fluxes along a toposequence in Tennessee Valley, California

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Abstract The emissions of nitrous oxide (N_2O) from soils are an important source of this greenhouse gas, which has a global warming potential 300 times greater than carbon dioxide. This study explored one of the major documented controls of soil N_2O fluxes, soil moisture. Four sites forming a soil toposequence on a hill slope in northern California were monitored over five months for soil moisture and N_2O fluxes. In this soil toposequence, factors affecting soil formation other than landscape properties were unchanged between sites, allowing for a subsurface moisture gradient without changing precipitation inputs. The major objectives were to identify whether subsurface moisture conditions regulated by topography correlated with N_2O flux rates, and to determine the extent to which N_2O flux rates displayed significant seasonal variability. Soil moisture was quantified using subsurface probes at each site. N_2O fluxes were sampled using static gas flux methods and quantified using gas chromatography. While N_2O flux rates varied significantly over time, there was no significant correlation between soil moisture and N_2O flux rates. Soil moisture levels did not follow a consistent ranking by topographical position as predicted and were lower in magnitude than hypothesized. While this result conflicts with previous research, it suggests the importance of temporal variation in soil moisture, as well as seasonal precipitation and temperature patterns, in regulating soil N_2O fluxes.

Introduction

Nitrous oxide (N_2O) is a greenhouse gas with the ability to absorb infrared radiation about 300 times more effectively than carbon dioxide. This gas contributes nearly six percent to the enhanced radiative forcing associated with global warming. Over the past century, the concentration of N_2O in the atmosphere has increased by about twelve percent to a current level of 320 parts per billion (IPCC 2001). Additionally, N_2O oxidation to NO_X aids in the destruction of stratospheric ozone, which shields the surface of the Earth from the most damaging solar wavelengths of ultraviolet radiation (Rochette et al. 2000). Nearly two-thirds of the total natural N_2O emissions (fluxes) are derived from soils as a result of the microbe-driven anaerobic processes of nitrification and denitrification (Davidson et al. 1991). This flow of N_2O is of comparable scale to the N_2O released from all anthropogenic activities; these include biomass incineration, cattle feed lots, and other industrial emissions (Reth et al. 2005).

Concern over the fluxes of N_2O from soil has intensified because of the potential for ecological feedback mechanisms that may dampen or amplify the initial climate forcing. Because an increased N_2O concentration in the atmosphere may warm the Earth through the greenhouse process, average soil moisture may decrease (Reth et al. 2005). This change in soil moisture would presumably affect N_2O fluxes, but not in a universal fashion (Niklinska et al. 1999). Moreover, an enhanced greenhouse effect may not only increase the average temperature at the surface of the Earth, but also alter global precipitation patterns. Currently, many climate projections predict increased precipitation in the middle and high latitudes of the Northern Hemisphere (Walther et al. 2002). A changing global precipitation distribution due to greenhouse warming may significantly alter N_2O emission patterns as a result of changes in a number of soil properties including soil moisture, nutrient concentrations, and erosion rates (Berhe et al. 2005). Any climate-induced changes in soil N_2O fluxes will be in addition to anthropogenic soil alterations such as tillage activity and fertilizer application, both of which increase the total stock of nitrogen available to soil microbes (Rochette et al. 2000).

A number of studies have explored the variables that influence soil N_2O flux rates. In regards to soil properties, Skiba et al. (1998) demonstrated that the most important factors that influence N_2O fluxes from soil are nitrogen content, temperature, and moisture. In general, the amount of water in soil controls how much gas escapes from it in a relationship that is often approximated using linear models (Neill et al. 2005). Stark and Firestone (1995) showed that soil moisture content had a direct effect on the productivity of denitrifying bacteria and, as a result, N_2O fluxes. Concerning the relationship between precipitation and N_2O fluxes, Holtgrieve et al. (2006) found that mean annual precipitation and soil N_2O flux rates were at first directly correlated, until the Hawaiian soil became saturated with water (greater than 75% volumetric moisture content) and trace gas flux rates were at or below detection limits. In a Brazillian forest, N_2O fluxes only occurred in significant magnitude from soil with a volumetric water content of at least 30% (Neill et al. 2005).

While the dynamics of the nitrogen cycle are well documented, the interactions of variables influencing soil N_2O flux rates are still poorly understood (Del Grosso et al. 2005). Additional study was necessary in order to determine how soil moisture and landscape topography interacted to control N_2O emissions in localized ecosystems and distinct climate regimes, as well as the importance of soil moisture in creating an anaerobic environment for microbes while still permitting gas emissions. This study explored a single soil type in Tennessee Valley, California to determine whether N_2O fluxes differed significantly across a topographic gradient. In this soil toposequence, factors affecting soil formation other than landscape slope, aspect, and position were unchanged between sites (Brady and Weil 2002). A hill slope in a coastal prairie ecosystem in northern California was an ideal study area because of little variation in precipitation received at different elevations, but an observed gradient in soil moisture due to the concave nature of the land in a stream convergence zone (Dietrich et al. 1995).

The objective of this study was to identify whether subsurface moisture conditions regulated by topography significantly influenced N_2O flux rates on this hill slope. As a secondary objective, this study aimed to determine the extent to which N_2O flux rates displayed significant seasonal variability. These findings could aid in the determination of current and future global N_2O stocks and flows and contribute needed regional data to global N_2O modeling efforts. Specifically this study explored how N_2O emissions vary along four sites on a hill slope (with a range in soil water content) using static gas flux methods (Brumme et al. 1999). This study follows similar work conducted by Nobre et al. (2001) and Holtgrieve et al. (2006) in the tropical climates of Costa Rica and Hawaii, which examined loamy soils derived from weathered volcanic ash.

There were several hypotheses regarding the relationship between soil moisture, topography, and N_2O flux rates: first, that flux rates at the four sites would be directly correlated with soil moisture ratio up to a threshold between 40-60% volumetric soil moisture content, at which point N_2O fluxes would begin to decrease with increasing moisture, in a quadratic fashion. This hypothesis was based on the findings of Holtgrieve et al. (2006) while recognizing the tendency for soil at this site to become saturated with water for extended periods of time, causing a hypothesized plateau in N_2O fluxes (Yoo et al. 2005). Second, N_2O flux rates would be greatest in magnitude in the middle of the hill slope due to moderate soil moisture content by volume, and would be significantly less at low and high elevations due to generally high and low soil moisture levels at these sites, respectively. Lastly, it was expected that N_2O flux rates would display seasonal variability, with significantly higher flux rates at all sites during winter months than in the fall. This seasonal change would be driven by precipitation and soil temperature patterns: hot, dry fall months would limit sufficient moisture inputs for N_2O-producing microbes, while the cooler and wetter winter months would provide these microbes with adequate moisture. In general, differences in soil temperature, nitrogen, and precipitation inputs among the four study sites were not expected not to be significant.

Methods

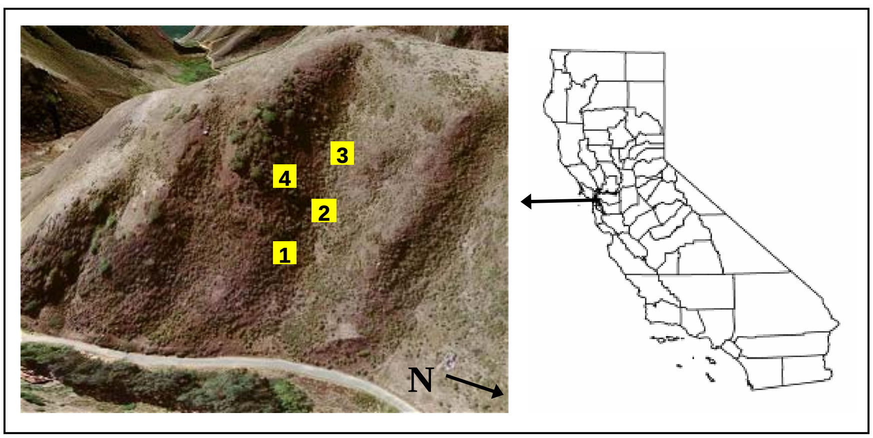

Figure 1: Four sites on a hill slope in Tennessee Valley, California (Google Earth).

Study Site Data collection was conducted at the Marin Headlands in Tennessee Valley, California from October 2006 to February 2007. Tennessee Valley is part of the Golden Gate National Recreation Area on the southern peninsula of Marin County (37.85° N 122.54° W). Area topography was uniquely suited for this research, with a convergence zone in soil moisture as rainfall flows downhill towards a narrow stream channel (Dietrich et al. 1995, see Fig. 1). As a result, while soil temperature and precipitation patterns tend to vary only slightly at different elevations, the distribution of soil water content spans a large gradient. The soil on this hill slope is a lithic haplustol, a type of mollisol (thick with organic matter), that overlies sandstone parent material (Yoo et al. 2005). This soil toposequence is classified within an ustic moisture regime, as it is dry and microbially inactive for more than three consecutive months of the year, typically between May and October. Four sites, each with an area of approximately 16 m^2, were randomly selected within four distinct ranges of elevation to capture documented variability in soil volumetric water content (Yoo et al. 2005). These sites were monitored over five months for variation in soil moisture and N_2O flux rates. Although trails at Tennessee Valley are publicly accessible, the study site was relatively isolated and the major biotic soil disturbance was from a small population of pocket gophers (*Thomomys bottae* Eudoux & Gervais) (Berhe et al. 2005).

Data Collection: Automated Sampling Soil moisture conditions were monitored at randomized locations within each of the four sites by use of subsurface probes and data loggers. Continuous automated sampling was preferable to instantaneous sampling because of the need to quantify soil moisture for a fixed time period preceding each sampling bout (Brady and Weil, 2002). While moisture likely varied within each site, financial constraints prevented the installation of replicate probes. Previous soil research in this area has suggested that variations within these sites are generally smaller than variations among sites (Yoo et al. 2005).

Decagon ECH_2O EC-5 soil moisture probes were placed at depths of 15 cm at random locations within each site, then covered with existing soil and overlying vegetation to document the variation in soil moisture between sites. Volumetric soil moisture was derived from the soil dielectric constant, measuring rate of change of voltage applied to the subsurface probes (Holtgrieve et al. 2006). A Decagon Em5b data logger was connected to the moisture probes at each site using 5 m cables and programmed to record data on an hourly basis over the five month study period. These data loggers were enclosed within several sealed plastic bags to avoid damage from rain, wind, and biological disturbance. Soil moisture readings were periodically downloaded to a laptop computer for data processing and analysis.

Data Collection: Manual Sampling N_2O fluxes at each of the four sites were quantified using conventional static gas flux methods (Holtgrieve et al. 2006) during four sampling trips. Three replicate plastic chambers with open bottoms were positioned randomly within each site. After securing chambers to the ground with plastic collars, chambers equilibrated with the soil for five minutes. Gas was then sampled from the chambers five times at ten minute intervals. Twenty-five mL of gas were drawn into a 30 mL plastic syringe inserted into a small slit on the top of each chamber. Gas from the syringe was then injected into vacuum-evacuated and sealed 35 mL glass vials. Vials for all four sites (60 total per sampling trip) and standards of known gaseous composition were analyzed for N_2O concentrations using a Shimadizu GC-14A gas chromatograph in the Silver Lab, UC Berkeley. N_2O concentrations were plotted against the times (in seconds) at which the chambers were sampled, and the slope of this line was the raw gas flux rate (dN_2O/dt). This flux rate was corrected for chamber dimensions, air pressure and temperature (recorded at each site during each gas sampling) according to the ideal gas law:

$$N_2O \text{ flux rate } (\mu\text{mol } N_2O/m^2/s) = \frac{\frac{dN_2O}{dt} \times V \times P}{A \times R \times T}$$

V = Chamber volume (0.0084 m^3)*
P = Air pressure (1 atm)*
A = Land area covered by chamber (0.049 m^2)*
R = Ideal gas constant (8.21 x 10^{-5} m^3 atm/mol K)
T = Air temperature (K)
* Assumed constant over time for all chambers.

The units of the N_2O flux rate reflect micromoles of the gas emitted per square meter of land area per second (Skiba et al. 1998).

Data Analysis Regression analysis was employed to identify relationships between the volumetric soil moisture level and N_2O flux rate at each site. Soil moisture readings were continuous, but the four gas sampling trips occurred at single time points. As a result, soil moisture for the 36 hours preceding a sampling trip was averaged to a single volumetric soil moisture percentage. This time period accounted for the biological response of soil microbes to precipitation inputs, as well as the ability of soils to drain water (Stark and Firestone 1995). Soil moisture percentages were paired with the average of the three N_2O flux rates and plotted together by sampling trip. An F-test was executed to determine the best correlation model between these two variables. In order to detect significance in the seasonal variation of fluxes, a two-factor ANOVA (N_2O fluxes by sampling date and site) was performed along with a post-hoc Tukey test to identify any such significance.

Results

Average N_2O flux rates for the replicate chambers were paired with corresponding average soil moisture readings (Table 1). While site 4 was always among the wettest, and site 3 among the driest, the sites did not display a consistent soil moisture ranking over time. These moisture patterns contradicted the hypothesis that soil moisture would decrease with altitude.

Table 1: N_2O flux rates and soil moisture for four sampling trips.

Site	October 24		November 28		December 15		February 16	
	Average N_2O flux (10^6 µmol/m^2/s) ± S.E.M.	Average Soil Moisture (%) ± 3.0	Average N_2O flux (10^6 µmol/m^2/s) ± S.E.M.	Average Soil Moisture (%) ± 3.0	Average N_2O flux (10^6 µmol/m^2/s) ± S.E.M.	Average Soil Moisture (%) ± 3.0	Average N_2O flux (10^6 µmol/m^2/s) ± S.E.M.	Average Soil Moisture (%) ± 3.0
1	0.70 ± 0.37	6.0	19.84 ± 16.24	28.3	10.22 ± 2.17	35.2	6.61 ± 2.17	36.1
2	5.41 ± 1.04	8.1	19.24 ± 8.98	11.1	8.12 ± 2.71	14.2	5.41 ± 2.08	14.3
3	13.52 ± 2.70	5.0	10.22 ± 3.66	4.2	14.43 ± 1.80	8.4	9.32 ± 4.24	17.4
4	2.89 ± 0.72	9.3	18.64 ± 8.73	12.7	16.24 ± 9.94	30.8	4.90 ± 3.47	26.9

Correlation analysis of soil moisture and N_2O flux rate data did not suggest the predicted correlation between the two study variables. The highest soil moisture level was only 36.1%, indicating a lower range in soil moisture than had been anticipated. Nevertheless, the expected linear relationship at this part of the larger quadratic curve between soil moisture and N_2O fluxes to a threshold of 40-60% water content was not observed (Fig. 2, r^2=0.0152). Log, square, and square-root transformations of flux rates

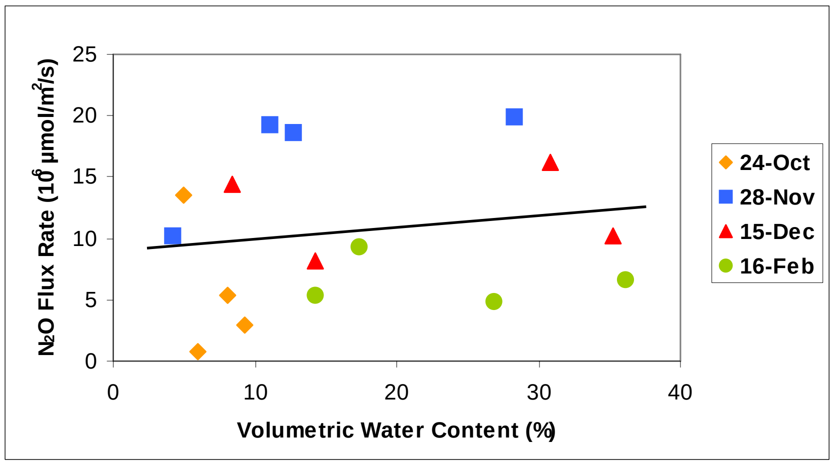

Figure 2: Soil moisture percentages and N_2O fluxes for all sites (r^2 = 0.0152).

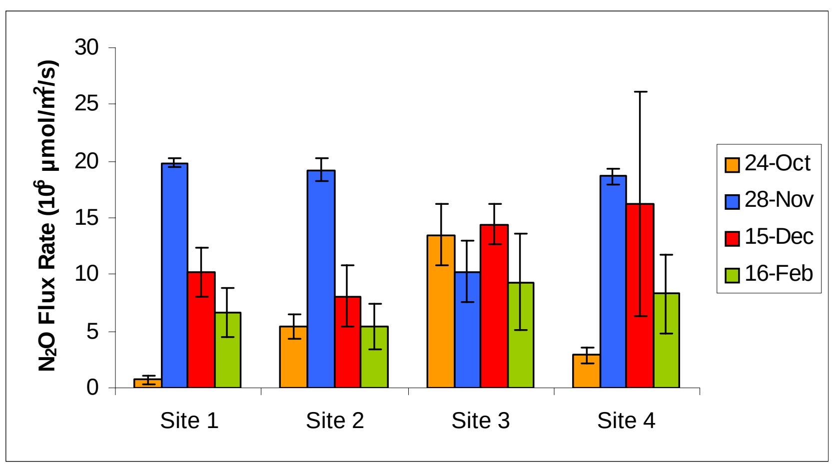

Figure 3: N_2O flux rates measured at four separate times.

did not result in a stronger relationship. An F-test demonstrated the minimum adequate model as the mean, as soil moisture did not explain a significant amount of the variation in N_2O fluxes ($F=0.353$, $df_n=1$, $df_d=14$, $p=0.562$).

Fluxes of N_2O spanned roughly an order of magnitude, suggesting seasonal variation due to climate patterns (Fig. 3). At sites 1, 2, and 4, fluxes were lowest on October 24, highest on November 28, and declined on December 15 and further on February 16. In contrast, site 3 displayed less variation in its N_2O flux rates. Overall, N_2O flux rates displayed significant seasonal variability as a two-factor ANOVA detected significant variation in N_2O flux rates by sampling date ($p=0.025$), but not by site ($p=0.803$). A post-hoc Tukey test identified significantly higher N_2O flux rates on November 28 compared to October 24 ($p<0.05$).

Discussion

While subsurface moisture levels varied among four sites, these differences did not strongly correlate with N_2O flux rates. In particular, N_2O flux rates were expected to be highest at sites with moderate (40-60%) moisture, but in fact the three highest N_2O flux rates occurred between 11.1% and 28.3% volumetric water content. Soil moisture along the toposequence did not vary as greatly as anticipated, ranging from 4.2% to 36.1%, less than half of the anticipated moisture gradient. The low variation in flux rates at site 3 may have been due to consistently low moisture levels.

Although these results appear inconsistent with the Holtgrieve et al. (2006) observation that N_2O flux rates decline as soil becomes more saturated with water, it should be noted that the pervious study only observed this decline above a volumetric water content of 50%. In contrast, none of the moisture levels in this study exceeded 36.1%. Furthermore, the Holtgrieve study served as a snapshot of N_2O flux rates on four days over one year, in contrast to the use of four sampling bouts over this five-month study.

While the results of this study appear to complicate the relationship between soil moisture and N_2O flux rates, it is possible that the clear correlation observed in the Holtgrieve et al. (2006) Hawaii study was not a universal pattern, but rather unique to a particular ecosystem and precipitation pattern. Furthermore, the existence of strong storm events in both Hawaii and California suggests that the cumulative effect of soil moisture saturation may play a role in the regulation of N_2O fluxes. That is, depending on when a site is sampled for N_2O after a storm,

N_2O fluxes may display more immediate variability than soil moisture, especially when the soil is at or near field capacity (water saturation). A more frequent sampling of flux rates could potentially capture temporal variability in emissions. In a wider sense, the inconclusive results of this study may suggest that soil moisture-N_2O relationships are not universally applicable, and that certain soil types, with specific capacities for moisture retention, may permit unique N_2O emission patterns. It may be too simple to generalize the relationship observed in Hawaii to a region with distinct soil properties, nitrogen inputs, and precipitation rates.

A number of problems that occurred during data collection may have introduced experimental error. Chambers were not always sufficiently sealed to the soil surface, permitting the entry of outside air and changing the concentration of N_2O in sampling vials. Furthermore, chamber volumes were assumed to be constant even though vegetation under the chambers did not occupy a constant volume. Also, soil moisture probes may have become dislodged from tight soil contact during strong storms, and as a result may not have recorded true soil moisture content. Assumptions regarding the similarity of temperature and nitrogen inputs among all sites may not have been justified, thus confounding results. The relative infrequency of N_2O sampling inhibited the development of a detailed seasonal overview of N_2O fluxes out of soils.

Study of the relationship between soil moisture and N_2O fluxes warrants additional attention, particularly into the temporal variation of both soil moisture and N_2O fluxes, and the effects of strong storm events, which saturate the soil with water, on flux rates over a time period of hours and days, instead of weeks and months. While this study did not identify a significant correlation between soil moisture and N_2O fluxes, the demonstration of significant seasonal variation in N_2O emissions suggests that seasonal patterns such as moisture and temperature inputs may play an important role in regulating how much N_2O escapes from soil. As the Earth warms, further examination of the interaction between these two variables will be vital in shaping effective land management strategies and mitigating soil N_2O fluxes to the atmosphere.

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