



Nitrous Oxide in Soils: In-Situ Measurements of a Potent Greenhouse Gas

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Abstract

Nitrous oxide (N₂O) is a greenhouse gas that is produced in large quantities in soils throughout the world. Naturally occurring soil bacteria facilitate the production of N₂O. Beginning with ammonium (NH₄⁺), nitrification and denitrification reactions lead to gaseous N₂O as well as N₂ and H₂O. Many soil factors can affect the speed and overall volume of N₂O that is produced. These factors include soil moisture, temperature, texture, organic matter content, and the abundance of available ammonium. In this study, we have used the technique of in-situ quadrupole mass spectrometry to measure real-time levels of N₂O in the soils of various test beds. In addition, soil levels of CO₂, CH₄, and isoprene were also collected. Overall, results indicate that soil moisture levels and soil ammonium content play the largest roles in overall N₂O production.

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Introduction

Nitrous oxide (N₂O), a potent greenhouse gas with a global warming potential nearly 300 times that of carbon dioxide, plays a complex role in soil ecosystems. While essential for certain biological processes, its excessive emission poses significant challenges to both environmental sustainability and climate change mitigation [1-3]. Nitrous oxide is produced primarily through microbial processes in soil, particularly through nitrification and denitrification. Nitrification is the conversion of ammonium (NH₄⁺) to nitrate (NO₃⁻) by bacteria [4], while denitrification is the reduction of nitrate to gaseous nitrogen (N₂), with N₂O as an intermediate product [5]. These processes are crucial for nitrogen cycling, a fundamental process supporting plant growth and ecosystem productivity.

Nitrification is a two-step process involving the oxidation of ammonium (NH₄⁺) to nitrate (NO₃⁻). This process is essential for nitrogen mineralization and plant uptake. Step one in the nitrification process is ammonia oxidation. Bacteria belonging to the genus *Nitrosomonas* and related genera are responsible for the oxidation of ammonium to nitrite (NO₂⁻). The reaction is as follows:

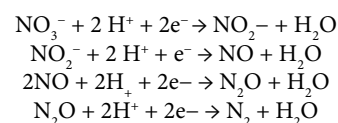


This step is aerobic, requiring oxygen for the oxidation process. Environmental factors such as temperature, soil moisture, soil pH, and oxygen availability significantly influence the rate of ammonium oxidation. High soil oxygen levels favor nitrification, but low oxygen conditions can lead to N₂O production via nitrifier denitrification. Optimal soil pH levels for nitrification are around neutral (6.5-7.5). Extreme pH values can inhibit or slow the nitrification process. Nitrification rates increase with temperature, but excessive heat levels can inhibit microbial activity. Adequate moisture is also necessary for microbial activity, with greater water levels ultimately leading to denitrification and N₂O production.

The second step in the nitrification process is Nitrite oxidation. *Bacteria* belonging to the genus *Nitrobacter* and related genera oxidize nitrite to nitrate. This step is also aerobic and is generally faster than ammonia oxidation. This second reaction is as follows:



Denitrification is the process of reducing nitrate to gaseous nitrogen (N₂), with nitrous oxide (N₂O) as an intermediate product [6]. This process occurs under anaerobic conditions, typically in water containing soils or wet sediments. Denitrification is carried out by a diverse group of facultative anaerobic bacteria, including *Pseudomonas*, *Bacillus*, and *Clostridium*. These bacteria possess the necessary enzymes to reduce nitrate to nitrite, nitric oxide (NO), nitrous oxide (N₂O), and ultimately, dinitrogen gas (N₂). Nitrate serves as an electron acceptor in the absence of oxygen. The reduction of nitrate to nitrogen gas is a stepwise process involving the transfer of electrons. Anaerobic conditions, such as water containing soils or compacted layers, favor denitrification. The availability of organic matter as an electron donor is also essential for the process to occur. Generally, denitrification rates increase with temperature. Combinations of these reactions are shown below, with N₂O production occurring in the third reaction shown.



In addition to the processes and factors listed above, other factors may also affect nitrous oxide emissions from soils [7, 8]. Fine-textured soils with high water-holding capacity tend to have higher N₂O emissions due to increased potential for denitrification. High organic matter content can stimulate microbial activity and N₂O production, but it can also act as an electron donor for denitrification, influencing the N₂O:N₂ ratio. Drought can reduce microbial activity and N₂O emissions, but subsequent rehydration can lead to a rapid increase

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in the production of N_2O . Excessive nitrogen fertilization can also increase N_2O emissions through both nitrification and denitrification pathways. In agricultural applications, reduced tillage can increase soil organic matter and reduce N_2O emissions by minimizing soil disturbance [9,10]. In this study, we have used the technique of quadrupole mass spectrometry to measure nitrous oxide levels in various soils, including bare soil, fertilized soil, grassy fertilized soil, and various soils found in forested areas.

Materials and Method

For this study, we conducted field gas measurements using a custom-designed portable quadrupole mass spectrometer [10]. The essential components of this instrument include a compact quadrupole residual gas analyzer or RGA (Horiba), a miniature diaphragm roughing pump, a 10 l/sec high-vacuum turbomolecular pump (Pfeiffer), and a lithium-ion battery with associated DC-DC converter circuitry for 24-Volt system operation. The system also includes low and high vacuum pressure gauges integrated into the mass spectrometer vacuum system. Control of the instrumentation is managed via a laptop computer connected through a serial port. The gas introduction components of the portable unit use a differentially pumped gas inlet orifice, allowing real-time gas measurements even under fully ambient air pressure conditions. During a typical field measurement at a specific location, we position the system on the ground and activate the roughing diaphragm pump. After a brief rough pumping phase of approximately 10 min., the system attains a pressure of approximately $1^{-3} \times 10^{-3}$ Torr. Subsequently, the turbomolecular pump can be engaged, operating for 15-20 minutes until the total system pressure reaches the low 10^{-6} Torr range or better. Once the system pressure stabilizes within this range, we activate the quadrupole RGA, including the high temperature ionization filaments contained within the high vacuum section of the system.

After setting up the quadrupole measurement system, gas data collection can be conducted at the specific soil location. The gas inlet system, designed with a low-volume probe, is directly inserted into the soil, reaching a depth of approximately two inches. This versatile probe works well in both moist, loose soils and dry, compacted soils. Once the probe is in place, the measurement system reaches equilibrium within a few minutes, allowing real-time monitoring of gas concentrations with part per billion sensitivity. This process can be repeated at different locations until the battery power is depleted, which typically occurs after 2.5 to 3 hours of operation. Figure 1 shows the low-volume soil probe on the ground prior to insertion into plain soil.

Several test beds were constructed that contained identical soil but different plant species, water and fertilizer amounts. These test beds were above ground and contained identical amounts of soil. They also contained identical drainage ports. The soil was commercially available soil that did not contain any additional fertilizer. The fertilizer we used contained a relatively large amount of nitrogen, 20%. One test bed was prepared with only dry soil. This test bed was not watered or fertilized. Additional test beds contained soil that was watered, soil that was watered and fertilized, soil that was watered and fertilized and planted with wildflowers, and soil that was watered and fertilized and planted with Fescue grass. For watering, the beds that received water did so in controlled amounts at two identical times during each day. Measurements of soil gases were also made at identical times of the day to minimize any effects that temperature variations may have on the data.



Figure 1: Photo of low volume soil probe prior to insertion into bare, unfertilized soil.

Results and Discussion

In an electron impact quadrupole mass spectrometer, the primary peaks that appear in the N_2O spectrum occur at 44 and 30 AMU. For our data collection in this study we used the 30 AMU peak to decouple it from the CO_2 peak in the spectrum. In addition, CO_2 sub spectra were also used to help avoid overlap in analysis of these two gas peaks. Figure 2 shows a photo of the commercially purchased local variety wildflowers used in this study. After purchase from a local nursery, the flowers were replanted into our test beds and allowed to grow for approximately 30 days prior to soil N_2O measurements.

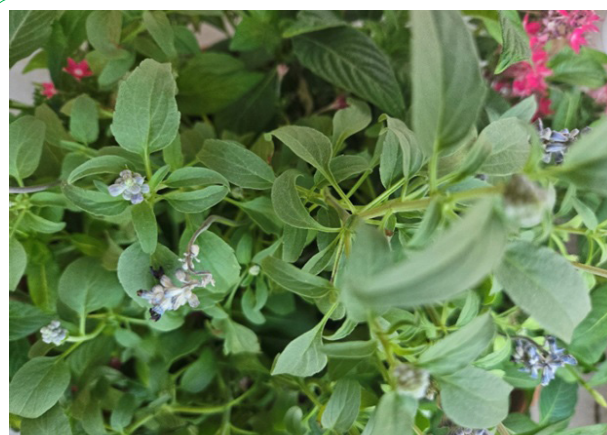


Figure 2: Photo of wildflowers purchased from a local nursery and replanted into a test bed. These flowers were allowed to acclimate to the soil for approximately 30 days prior to soil gas measurements being taken.

In Table 1, we show the results of nitrous oxide measurements and water vapor measurements for the various soil and plant combinations. This data is the average of three separate measurements. The values in the table are all values relative to measurements taken in the ambient air just prior to the soil measurements.

We note that N_2O levels were higher in all of the soil test beds relative to the ambient air. For the soils that were regularly watered such as the grass (Figure 3), the N_2O relative levels were significantly higher than the ambient air or the unwatered soil. We also note that the soil water vapor levels were considerably higher in the watered soils.

	Air	Dry Soil	Fertilized Watered Soil	Fertilized Watered Soil Wildflowers	Fertilized Watered Soil Grass
Nitrous Oxide	1.00	2.22 ± 1%	7.66 ± 1%	10.07 ± 1%	17.01 ± 1%
Water Vapor	1.00	1.12 ± 1%	3.94 ± 1%	4.65 ± 1%	4.87 ± 1%

Table 1: Nitrous oxide and water vapor measurements for the various soil and plant combinations.

These measurements were all taken during the summer months in dry, desert-like environments where the ambient humidity was less than 20%. The water vapor levels measured in the watered soils approach 90% levels or even higher.

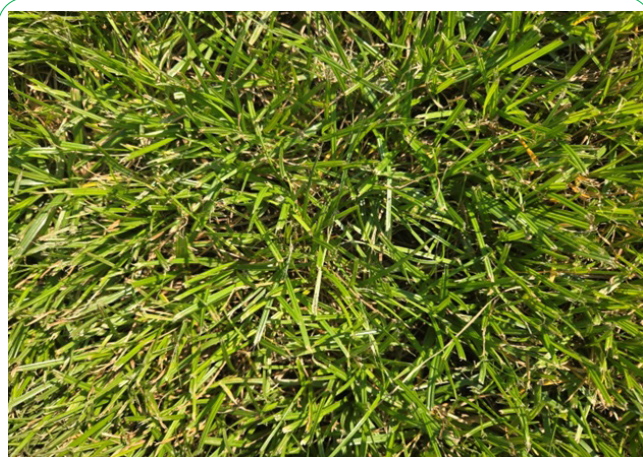


Figure 3. Photo of the fertilized, watered Fescue grass used in this study.

Water plays a critical role in N_2O production in soil [11]. Adequate moisture is essential for the microbial activity driving nitrification and denitrification, both of which contribute to N_2O emissions. However, the relationship is complex. While moderate moisture levels stimulate microbial activity, excessive water can create anaerobic conditions favoring denitrification and increasing N_2O emissions [5]. Conversely, drought can reduce microbial activity and N_2O production, but subsequent rehydration can lead to a flush of N_2O [1]. Understanding this intricate water- N_2O relationship will be crucial for future effective N_2O mitigation strategies. Here, we note that in the test beds where soil water levels are generally high, the measured N_2O levels are also very high relative to what is measured in ambient air. Our measured N_2O levels are very likely exaggerated relative to what would normally occur in farmland soils or naturally occurring soils such as that found in forests owing to the high moisture levels and the similarly high soil nitrogen levels attributable to the fertilizer used.

With regard to fertilizer, it is known that fertilizer application is a primary driver of N_2O emissions from agricultural soils [12]. Nitrogen-based fertilizers, particularly those high in ammonium or nitrate, provide a readily available substrate for soil microbes involved in nitrification and denitrification. These processes convert nitrogen into gaseous forms, including N_2O . Ammonium-based fertilizers can lead to higher N_2O emissions compared to nitrate-based fertilizers,

as ammonium oxidation is often coupled with N_2O production. In this study, we have used an ammonium-based fertilizer with very high nitrogen concentration, about 20%. We believe that this, in conjunction with the higher than normal soil moisture levels is primarily responsible for the high N_2O levels we have measured in our test beds.

There are other factors that may also play an important role in soil N_2O emissions including temperature and soil biomass [13]. Soil temperature significantly influences N_2O emissions. As temperature rises, microbial activity accelerates, leading to increased rates of nitrification and denitrification, the primary processes responsible for N_2O production. However, the relationship is not linear. Extremely high temperatures, however, can inhibit microbial activity, potentially reducing N_2O emissions. Additionally, temperature affects the solubility of gases in soil water, influencing the diffusion of N_2O from the soil to the atmosphere. In our measurements, the ambient temperature was 35°C. This is considered to be a higher temperature that would contribute to generally higher N_2O levels. Soil biomass, particularly microbial communities, is also a critical factor influencing N_2O production. Microorganisms are responsible for the key processes of nitrification and denitrification, which lead to N_2O emissions. The composition and activity of these microbial populations are influenced by various soil properties, including organic matter content. The balance of different microbial groups within the soil ecosystem can significantly impact the ratio of N_2O to other nitrogenous gases produced.

We also took measurements of carbon dioxide (CO_2), Methane (CH_4), and isoprene in the same soils [14]. These values are shown in table 2 below. Again, all values are relative to the same species found in ambient air. The CO_2 soil levels were approximately 1.5 times higher than the value in ambient air. Similarly, the CH_4 and isoprene levels were approximately 1.3 and 1.2 times their ambient levels, respectively. For CO_2 the measured concentrations are similar to those previously found in organic farm produce and fruit tree fields [15]. Here, the CO_2 levels are slightly higher, owing to the higher moisture levels in the soil. The highest concentration of CH_4 is found in the driest soil, with lower concentrations in all of the wet soils. This is consistent with the fact that soils tend to be net producers of CH_4 as they dry out. The largest natural process leading to CH_4 removal in the soils, oxidation of CH_4 , is reduced as the soils dry out. Also, diffusion of CH_4 from lower soil levels is greater in soils that are drier. Isoprene (2-methyl-1,3 butadiene) in these soils is lower in all cases when compared to ambient air. This is similar to levels found in agricultural vegetable fields, but lower than levels we have measured in agricultural tree orchards and natural forest areas [16].

	Air	Dry Soil	Fertilized Watered Soil	Fertilized Watered Soil Wildflowers	Fertilized Watered Soil Grass
Carbon Dioxide	1.00	1.02 ± 1%	1.72 ± 1%	1.77 ± 1%	1.80 ± 1%
Methane	1.00	1.31 ± 1%	1.11 ± 1%	1.16 ± 1%	1.14 ± 1%
Isoprene	1.00	0.96 ± 1%	0.86 ± 1%	0.81 ± 1%	0.78 ± 1%

Table 2: Test bed levels of CO_2 , CH_4 , and isoprene.

Generally, soils act as consumers of isoprene [17, 18]. Microbes in the soil that consume isoprene, include *Arthrobacter*, *Nocardia* and *Rhodococcus* Genera. Bacteria such as *Actinobacteria* and *Alphaproteobacteria* and certain fungal species such as Sordariomycete and Eurotiomycete have also been found to consume isoprene in soils. There are some bacteria, however, that are known to produce isoprene in soils. *Proteobacteria*, *Actinobacteria*, *Firmicutes* and *Bacillus* may produce isoprene, making soil isoprene comparisons more difficult. Higher levels of soil water, which enhance soil CO₂, may be correlated with lower soil oxygen levels and greater anaerobic bacterial activity affecting isoprene levels.

There is little correlation between NO₂ soil levels and soil CO₂, CH₄, and isoprene. Nitrous oxide and CH₄ are both potent greenhouse gases with significant impacts on climate change, but their production pathways in soil are distinct. While both gases can originate from soil, the specific conditions and microbial processes involved in their formation differ. N₂O is primarily produced through nitrification and denitrification, processes driven by aerobic and anaerobic bacteria, respectively. Methane, on the other hand, is produced primarily under anaerobic conditions through methanogenesis by archaea [19, 20]. There is also no currently established direct relationship between N₂O in soil and isoprene. Their production pathways and primary sources are also different. N₂O is primarily produced in soil through microbial processes, while isoprene is emitted by living plants and some soil bacteria. The two compounds have separate biogeochemical cycles.

Conclusions

Agricultural soils typically exhibit high N₂O emissions due to intensive management practices such as fertilizer application, extensive watering, tillage, and crop rotations. These activities can lead to increased nitrogen availability, stimulating microbial processes like nitrification and denitrification that produce N₂O. We have measured N₂O levels in soils under controlled conditions. Both the application of nitrogen containing fertilizer and regular watering cycles lead to potentially very high levels of N₂O in these soils. Further research into N₂O in soils is essential for developing effective greenhouse gas mitigation strategies. Potential areas of focus include improving our understanding of the microbial mechanisms involved in N₂O production and consumption, developing more accurate models to predict N₂O emissions under various soil and climate conditions, and identifying and promoting agricultural practices that effectively reduce N₂O emissions without compromising crop yields.

Competing Interests

The author declares that they have no competing interests.

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