

Review of Nitrous Oxide Emission by Denitrification in Subsurface Soil Environment

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(Manuscript received 20 November 1999)

심층토에 있어서 탈질화에 의한 N₂O 방출의 평가

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(접수 1999년 11월 20일)

요 약

현재 지구상에서 농업에 기인하여 배출되는 N₂O의 80% 정도가 지구의 온난화 뿐만 아니라 오존층 파괴에까지 영향을 미친다. 토양에서 수분함량 등과 관련한 유기태 탄소는 지하수면의 계절적 변화에 따라 탈질화를 결정하는 주요 요인이 되기도 하며 심층토의 탈질화 활동은 토양내 유기물을 분해하여 유기태 질소를 일시적으로 토양에 축적시키기도 한다. 그리고 토양의 관리방법, 폐기물의 토양처리, 질소질 비료의 사용 등이 N₂O 증가에 결정적 요인이 되기도 한다. 그러나 이러한 효과의 정도는 거의 알려져 있지 않을 뿐만 아니라 질산화나 탈질화와 같은 상반되는 과정과 제한 요소와 관련하여 범용적으로 적용할 수 있는 N₂O 방출을 예측하는 측정 계수와 같은 연구는 매우 미미한 상태이다. 그러므로 농업 토양에서 비료와 유기물 사용 등에 의해 발생하는 토양의 N₂O 배출을 효율적으로 관리하기 위하여 심층토에서의 동적 역학적 N₂O 배출 측정과 관리 방법을 개발하여야 한다.

Key words : denitrification, subsurface soil, N₂O

I. INTRODUCTION

Nitrous oxide, implicated for its possible deleterious effects on global warming and the catalytic destruction of stratospheric ozone, is naturally produced in soils by microbial processes during denitrification. Denitrification below the active root zone in the subsurface environment is one possible source of atmospheric N₂O while biological activity has been considered negligible below the active root zone.

Generally, the subsurface soil profile can be divided into two zones such as the subsurface soil and the underlying intermediate vadose zone, which is the unsaturated layer between the active root zone and the saturated layer. Most biological measurements are made in the active root zone, generally in the top 30 to 60 cm of the soil profile.

In subsurface soils and the intermediate vadose zone, disappearance of NO₃⁻ and decreasing NO₃⁻/Cl⁻ ratios are the most common indirect indicators of subsurface soil denitrification. This assumption may be reasonable below the active root zone, where plant uptake is not a major mechanism of NO₃⁻ removal. Thus, most of individual factors that regulate the efflux of N₂O and NO_x by the processes of nitrification and denitrification are known, significant knowledge gaps in understanding of these processes limit our ability to accurately control emission of these gases in agricultural soils.

Therefore, field experiments documented in agriculture, soil science, other scientific journals were reviewed as a preliminary step in assessing and managing the atmospheric burden of N₂O and economic loss of N sources in agriculture.

II. Process Investigation at Field and Landscape Scales

In spite of tremendous efforts, knowledge to explain and predict variation in soil NO or N₂O exchange within and across landscapes, or even in small plot studies, remains troublesome. For example, we know that NH⁴⁺ availability is an important controller of nitrification, as is NO₃⁻ availability for denitrification, but we lack a universally applicable assay for soil N availability. Robertson and Tiedje (1984) found that a net nitrification assay correlated well with N₂O production in intact cores of forest soils, while a good correlation between a net mineralization assay and N₂O flux from tropical forest soils was reported. In NO emission studies, Williams and Fehsenfeld (1991) found that soil NO₃⁻ concentration was a good predictor of the differences in emission rates of widely varying ecosystem types, but Hutchinson *et al.* (1992) reported that emissions from a grass pasture on sandy soil in humid region were much more strongly related to soil NH⁴⁺ than soil NO₃⁻ concentration. However, no single predictive parameter or suite of parameters has emerged as applicable across all sites and studies. Failure to find common predictors probably arises from several confounding factors. First, two very different processes are involved, i.e. nitrification and denitrification. Second, other process-limiting factors that interact with N availability may be more important at some sites than others. In addition, the scale chosen for investigation influences the nature of the predictors likely to be found useful. The relation of NO emissions to soil NO₃⁻ concentration at the larger scale reflects that this ion generally accumulates when N availability in the system exceeds C availability, resulting in a leaky N cycle. The rate of N cycling may actually be higher in fertile forest sites than in tilled agricultural fields, but high C availability in temperate forest soils usually results in a conservative N cycle, little NO₃⁻ accumulation, and low emission of gaseous N oxides.

Of all the factors known to affect soil NO and N₂O exchange rates, these two are probably the most critical to understand the variation of N oxide emissions within a cropped field, such that the distributions of plant roots, crop residues, bands of fertilizer, and small-scale topographic features must be considered, because they contribute to determining the local N

and O₂ supplies. To understand variation within a landscape, soil texture and drainage class have proved useful, presumably as surrogates of O₂ availability.

III. Fate of Nitrous Oxide in Soil Environment

To have an impact on atmospheric concentrations, N₂O produced in subsurface environments obviously must be released to the atmosphere. Nitrous oxide may diffuse upward to the soil surface, or N₂O dissolved in the water may be transported along hydrologic gradients. The source of diffused N₂O when it evolves from the soil surface cannot be easily identified, especially if underlying subsurface soils or groundwaters are contaminated and producing significant quantities of N₂O. Dissolved N₂O in the water also may be transported from the site of production. During transport through the intermediate vadose zone or along the hydrologic gradient of the aquifer, N₂O may be further reduced to N₂. The N₂O in the aquifer may diffuse upward into the vadose zone and potentially to the soil surface. Dissolved N₂O in the aquifer also may be eventually released to the atmosphere through outgassing at interfaces with surface water or from wells (Bowman and Bormann, 1986).

Ronen *et al.* (1988) observed that drainage water from organic soils in New York contained 200 to 900 mL N₂O/L, which was 900 to 4200 times greater than expected from water in equilibrium with the atmosphere. Seeps from harvested forest watersheds contained dissolved N₂O two orders of magnitude greater than expected, and the N₂O rapidly degassed 10m from the seep (Bowden and Bormann, 1986). They suggested that outgassing of transported dissolved N₂O in shallow aquifers may be a major source for atmospheric N₂O. Locating and quantifying these sources of N₂O release may be important, because the gas may be transported from the site of production.

IV. The Vadose Zone and Subsurface Soils

Decreased concentration of NO₃⁻ and changing ratios of NO₃⁻/Cl⁻, demonstrated by Gast *et al.* (1974) demonstrated are the most common indirect indicators of denitrification below the active root zone, where plant uptake is not a major mechanism of

NO₃⁻ removal.

More direct evidence for denitrifying activity is provided by measurement of denitrifying activity or incubation of samples to measure the nitrogenous gas products. McGarity and Myers (1968) demonstrated that significant denitrifying activity was stratified and variable within the soil profile, but the increased activity was associated with the beginning of the Bt horizon. Significant subsurface soil denitrifying activity was attributed to transitory accumulations of organic C in the subsurface soil by leaching of highly available soluble organic C from the overlying surface horizons (Myers and McGarity, 1971). In a silt loam soil, denitrifying activity might be stratified within the soil profile. The stratification was probably associated with physical changes, such as bulk density and increased clay in the subsurface soil (Rice and Rogers, 1991). Not all subsurface soils demonstrate significant denitrification. Unstratified coarse textured soils generally do not exhibit significant denitrification apparently because of the lack of organic C or anaerobic conditions (Lund *et al.*, 1974; Devitt *et al.*, 1976; Parkin, 1989; Rice and Rogers, 1991). Fine textured soils also may not have significant subsurface soil denitrification apparently because of the lack of NO₃⁻ or organic C moving into the subsurface soil (Gast *et al.*, 1974).

Based on observations of subsurface soil denitrification, one of the most important variables creating conditions conducive for denitrification is stratification of morphological properties within the soil profile. Changes in soil physical properties create discontinuities that impede water and solute movement. Layers that impede water movement allow the soil above the discontinuity to have higher soil moisture contents, resulting in decreased O₂ diffusion and increased potential for anaerobic microsites. The morphological characteristics that result in these discontinuities include textural changes (Lund *et al.*, 1974; Devitt *et al.*, 1976) and bulk density. Lund *et al.* (1974) reported a good relationship between the average clay content and NO₃⁻ concentration in the control section (1.8 to 8 m depth) of the soil profile. Significantly lower NO₃⁻ concentrations than expected based on the clay content were found in two soils that had variable textures within the control section or contained a duripan. These two situations impede water movement, thus enhancing subsurface soil denitrification. Devitt *et al.* (1976) similarly con-

cluded that subsurface soil denitrification was possible in coarse-textured soils that contained a subsurface layer of higher clay content. Saturation does not always indicate conditions favorable for denitrification. During high-intensity precipitation events, denitrification was apparently repressed by transport of dissolved O₂ with the infiltrating water (Gambrell *et al.*, 1975).

Organic C with respect to water content in soils was the primary factors determining the presence of denitrification in the zone of a seasonal changes of water table. Soluble organic C and NO₃⁻, accrued from the application of manure or chemical fertilizer can be accumulate at the zones of restricted water movement. McGarity and Myers (1968) reported a good correlation between total organic C and denitrification in the surface horizons but a lack of fit in subsurface soils, Myers and McGarity (1971) latter concluded that the transitory nature of denitrifying activity in the subsurface soil was supported by transport of soluble organic C from the or organically rich surface horizons. The accumulation of dissolved organic C at zones of restricted water movement also may create anaerobic microsites within an aerobic soil (Rice *et al.*, 1988).

The amount of subsurface soil denitrification that will result in N₂O production is not known. The ratio of N₂O/N₂ is variable because it is affected by NO₃⁻ concentration, diffusion, and other factors (Firestone, 1982). Most studies have focused on total denitrification, because the primary focus has been the removal of NO₃⁻ to maintain groundwater quality. The indirect indicators for denitrification, NO₃⁻ disappearance, NO₃⁻/Cl⁻ ratios, and redox potentials, do not measure the gaseous products. Lind and Eiland (1989) measured N₂O production to a depth of 20 m with samples that were anaerobically incubated. The addition of a C source enhanced N₂O production in the subsurface environment, which indicates the potential for N₂O production. Reports of N₂O concentrations in soil profiles in situ are rare. Rolston *et al.* (1976) measured N₂O concentrations of a repacked Yolo loam. Maximum concentrations up to 32β¹ N₂O N mL⁻¹ soil air were reported at 85 cm. In the field, N₂O concentrations of 9.6β¹ N₂O-N mL⁻¹ soil air were greatest near the soil surface and declined with depth. The authors also indicated that the peak N₂ concentration occurred 4 days after the peak N₂O concentration. These results suggest the

potential for N₂O to be removed from the site of denitrification by diffusion or leaching of dissolved N₂O before it is further reduced to N₂. Rice and Rogers (1991) measured N₂O concentrations in an undisturbed soil profile of a silt loam. The N₂O profile demonstrates: (i) a significant amount of gaseous N₂O throughout the soil profile, and (ii) an increase in N₂O at certain zones related to stratified soil layers. Because N₂O is soluble in water, the dissolved N₂O is susceptible to downward movement, Bowden and Bormann (1986) measured a 10 to 100 fold increase in N₂O concentrations up to 300β¹ N₂O-N mL⁻¹ in the soil water after tree harvest in a forested watershed.

Further research is, therefore, required to properly depict the extent of N₂O production in subsurface environments to better estimate its potential contribution to atmospheric N₂O.

V. SUMMARY

Subsurface environments, including the intermediate vadose zone and aquifers, may be contributing to increased atmospheric concentrations of N₂O. Denitrification appears to be the major source of N₂O in the subsurface environment. In the intermediate vadose zone, the level of denitrifying activity is dependent on the soil morphology, particularly stratified layers within the soil profile, which impede water and solute movement and create conditions favorable for denitrification. Movement of organic C from the soil surface appears to support denitrifying activity by providing an energy source and increasing the consumption of O₂. Denitrification and N₂O production have been observed in aquifers but appear to be of greatest significance in shallow unconfined aquifers. The lack of organic C, NO₂, or anaerobiosis is often a limiting factor for activity but seems to be site specific. The presence of denitrifying bacteria does not appear to be a major limitation, based on published results, but the ubiquity of denitrifiers in subsurface environments needs to be confirmed. The fate of the N₂O produced in subsurface environments is unknown. Transport of N₂O by up ward diffusion, by outgassing at contacts with surface waters, and by ground water use need to be quantified to determine the contribution to atmospheric N₂O. Contamination of subsurface environment with NO₃⁻ and organics has the potential for

increasing the contribution to atmospheric N₂O by enhancing denitrification.

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