

Nitrous oxide emissions from grazing lands

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The nitrous oxide (N₂O) molecule described as the “dominant ozone-depleting substance emitted in the 21st century” [1] is also a potent greenhouse gas [2]. An overview of recent work to understand the processes and drivers governing the formation and loss of N₂O from grazed pastures will be presented, with a focus on ruminant urine patches. Emissions of N₂O occur as the result of nitrogen (N) inputs being transformed by the interactions of chemical, physical and biological processes. These interactions vary over time as soil conditions change. Inputs of N may include excreta from ruminants, both dung and urine, along with fertilisers and biologically fixed N. Ensuing emissions of N₂O are greater when N inputs exceed the pasture plants’ immediate demand for N. This is particularly the case when ruminant urine is deposited onto pasture where urine patches, the pasture area wetted as a consequence of urine deposition, from dairy cattle may typically receive ~600 kg N ha⁻¹ [3]. However, this rate varies widely depending on feed, climate, animal management and behavior [3].

Ruminant urine-N composition is dominated by urea which in high-N containing pastures may result in ruminant urine containing 90% of the urine-N as urea [4]. Upon hitting the soil ruminant urine encounters the ubiquitous enzyme ‘urease’ which transforms the urea contained in the urine to ammonium (NH₄⁺) and carbonate (CO₃²⁻) ions. The ensuing hydrolysis of CO₂ results in bicarbonate, and hydroxyl, ions forming and a rise in soil pH (often > 8.0).

Deposition of ruminant urine-N results in more N in the soil profile than the pasture can immediately use. Consequently, once the NH₄⁺ pool forms there ensues a competition between biological and chemical processes: competitive processes include plants taking up NH₄⁺, the formation of ammonia (NH₃) and ensuing NH₃ volatilisation, nitrifiers beginning the process of nitrification of ammonia to form nitrite (NO₂⁻) and then nitrate (NO₃⁻), and uptake of NH₄⁺ by the soil’s cation exchange surfaces.

The rise in soil pH pushes the chemical equilibrium between NH₄⁺ and ammonia (NH₃) towards NH₃ where upon some of the urine-N is lost via NH₃ volatilisation. Environmental conditions that determine the loss of NH₃ via volatilization will be described. Ammonia provides substrate for the onset of nitrification which under ruminant urine patches is dominated by ammonia oxidizing bacteria (AOB) [5]. Recent studies, that will be discussed, have highlighted the role of NH₃ in preventing the oxidation of NO₂⁻ and demonstrated that a soil’s cation exchange capacity (CEC) plays a pivotal role. Soil CEC influences the contribution of NH₄⁺ within the total ammoniacal-N pool (NH₄⁺ + NH₃) [6]. In conjunction with the soil pH, this CEC thus affects the chemical equilibrium between NH₄⁺ and NH₃, thus the

concentration of NH_3 and therefore the potential for nitrification inhibition. Under urea-affected soils the resulting NH_3 and NO_2^- concentrations have been shown to be strongly linked to the AOB nitrifier gene ratios and consequently the production of N_2O [7], since NO_2^- is a gateway for N_2O producing pathways [8].

These biological and chemical interactions within the urine patch undergo temporal dynamics and these will be discussed and linked to soil physical conditions within a pasture soil. Soil water content has long been recognized as a driver of microbial N transformation processes through its ability to slow down the diffusion of oxygen into soil. More recently relative gas diffusivity, a direct measure of the ability of oxygen to diffuse into the soil, has been demonstrated to be a strong predictor of the soil's ability to generate N_2O [9]. Relative gas diffusivity is a variable that accounts for the interaction of soil bulk density and soil moisture content on gas diffusivity and recent studies examining the interaction of soil biological processes and soil physics will be discussed.

Finally, due to the environmental impacts of the N_2O molecule mitigation options for pasture soils are being intensively explored. Recent developments covering the use of inhibitors and biological nitrification inhibitors will be briefly considered.

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