Nitrate Exposure: A metric to describe the influence of soil NO_3^- on N_2O emissions.

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Introduction

Nitrate (NO_3^-) concentration is an important aspect of the soil biological environment. It is a source of nitrogen for biosynthesis in plants and other organisms, a terminal electron acceptor in anaerobic respiration and transportable anion. Because it is the most oxidized form of nitrogen, it accumulates in aerobic soil systems. NO_3^- is the first terminal electron acceptor used in denitrification and the dominant source of nitrous oxide (N_2O) in humid agroecosystems. The influence of NO_3^- is not only expressed in real-time as a result of its participation in various chemical and biological reactions, it also has a longer term effect as it influences biological growth and expression. Here we define an extensive variable, nitrate exposure (NE), which provides the opportunity for integration of NO_3^- over space and/or time, reflecting the longer term influence of NO_3^- on soil biological processes, supporting growth, poising the redox and influencing gene expression.

Objective

To examine the ability of the parameter nitrate exposure (NE), a spatially and temporally integrated measure of soil NO_3^- content, to explain the variation in cumulative N_2O emissions.

Methodology

The results of 8 studies conducted over the past 10 years in the Canadian provinces of NS, NB, PE and MB (Table 1) were used to examine the relationship between NO_3^- and N_2O emissions. These studies all used similar analytical methods but span a range of soil and climatic conditions.

Table 1. Studies considered in the evaluation of the relationship between NO_3^- and N_2O emissions.

Crop	Years	Location	*n**
1. Potato	2002-2003	Fredericton, NB	380
2. Barley	2004-2005	Fredericton, NB	324
3. Corn	2004-2005	Woodstock, NB	320
4. Potato-Barley-Red Clover	2001-2004	Charlottetown, PE	180
5. Corn	2006-2007	Berwick, NS	510
6. Canola	2008-2009	Truro, NS	800
7. Wheat	2000-2002	Brandon, MB	308
8. Wheat	2000-2002	Winnipeg, MB	780

•N = treatments x replications x dates

N_2O flux measurements were made using vented, non-steady-state chambers. Deployment times were kept to 30 minutes with samples being collected at 0, 10, 20 and 30 minutes. N_2O concentrations were determined using gas chromatography. Cumulative emissions were estimated by linear interpolation between sampling dates during the monitoring periods.

Soil NO_3^- was determined on soil samples collected from the surface layer, adjacent to the chambers on the same day that flux measurements were taken. NO_3^- content of KCl extracts were determined colorimetrically. NE was calculated as the area under the nitrate concentration (mg N/kg soil) vs. time (d) curve (Eq. 1) and has the units of mg N d/kg soil. It is an extensive parameter expressing the magnitude and duration of exposure of soil organisms to NO_3^- (a concept similar to that of heat units).

$$NE = \sum_{i=1}^{n} [NO_3^-]_i * \left(\frac{d_{i+1} - d_{i-1}}{2} \right) \qquad \text{Eq. [1]}$$

The relative ability of temporal integration vs. spatial integration to improve the relationship between NO_3^- and N_2O emissions was evaluated. Temporal integration was achieved by calculating NE (Eq. 1). Spatial integration was achieved by calculating the arithmetic mean of replicate measurements.

Results & Discussion

The relationship between NE and cumulative N_2O emissions was always much better (mean R^2 0.32) than the relationship between daily soil NO_3^- concentration and N_2O flux (mean R^2 0.04; Fig. 2; Table 2). The coefficient of determination was often, but not always, improved when mean daily NO_3^- was regressed against mean N_2O (mean R^2 0.06) relative to individual plot data (mean R^2 0.02) . When NE and Cumulative N_2O emissions were calculated from treatment mean values, rather than replicate data, the R^2 was substantially greater (mean R^2 0.51; Table 1).

Figure 2: Relationship between N_2O emissions (g N_2O-N ha^{-1} d^{-1}) and soil nitrate content (ug N g^{-1} soil) for individual observations (A) and mean values (B); cumulative N_2O emissions over the monitoring period (kg N_2O-N $ha^{-1}$and nitrate exposure (gN d kg^{-1} soil) for individual observations (C) and mean values (D).

Relationships between daily $[NO_3^-]$ and daily N_2O flux often showed numerous outliers (Fig. 2). This is consistent with the episodic nature of the denitrification process where relationship between N_2O flux and $[NO_3^-]$ might be expected to change from day to day. The correlation between mean daily $[NO_3^-]$ and mean N_2O flux for each treatment was only marginally better. If the influence of $[NO_3^-]$ were simply instantaneous, we would not expect these relationships to improve with temporal integration.

Relationships between NE and cumulative N_2O emissions demonstrated considerably larger R^2 values (Table 1) and seldom demonstrated significant outliers (Fig. 2C) suggesting a more predictable relationship between these two parameters. The relationship between treatment mean NE values and cumulative N_2O emissions was stronger than for the individual replicate data (Fig. 2D; Table 2).

Table 2: Coefficient of determination (R^2) for the relationship between daily N_2O emissions and soil nitrate concentration (Daily), daily treatment NO3- concentrations and N_2O emissions (Daily Mean), NE and cumulative N_2O emissions (NE) and NE and cumulative N_2O emissions calculated from treatment means (NE on Mean).

Study	Year	Daily	Daily Mean	NE	NE on Mean
1	2002	0.00	0.00	0.01	0.73
	2003	0.04	0.07	0.29	0.87
2	2003	0.04	0.10	0.01	0.90
	2004	0.01	0.01	0.18	0.34
	2005	0.00	0.00	0.59	0.90
3	2004	0.08	0.25	0.00	0.46
	2005	0.08	0.19	0.16	0.69
4	2001	0.01	0.01	0.07	0.32
	2002	0.11	0.16	0.15	0.50
	2003	0.05	0.02	0.65	0.90
	2004	0.00	0.01	0.08	0.68
5	2006	0.02	0.07	0.31	0.70
	2007	0.00	0.00	0.12	0.48
6	2008	0.01	0.02	0.02	0.35
	2009	0.00	0.16	0.05	0.09
7	2000	0.00	0.03	0.13	0.76
	2001	0.00	0.01	0.20	0.42
	2002	0.01	0.03	0.06	0.24
8	2000	0.01	0.03	0.01	0.00
	2001	0.00	0.00	0.03	0.32
	2002	0.00	0.00	0.00	0.29

Temporal integration of $[NO_3^-]$ by the calculation of NE demonstrated a much stronger relationship with N_2O emissions (Fig. 2; Table 2). This suggests that the influence of NO_3^- on N_2O emissions is not simply expressed as the instantaneous concentration of NO_3^- at the time of sampling. This is not a particularly surprising statement. It is well known that the previous exposure to NO_3^- influences the growth, nitrogen content and gene expression of soil microbial community as well as impacting plant growth and root exudation. Therefore it is also not surprising that a temporally integrated measure of the exposure of the population to NO_3^- might be a better descriptor of NO_3^-'s influence on biological processes.

The value of a temporally integrated parameter such as NE is that, because it is a composite of multiple sampling times, it provides a better description of the influence of NO_3^- over the observation period. Instantaneous observations are not only more variable, but more importantly they fail to reflect reflect past conditions that may influence the biological events occurring at the time of observation. This may explain why we have such difficultly modeling the effect of NO_3^- on N_2O emissions on a daily time step, but N fertilizer application rate is a relatively good predictor of annual emissions (e.g., IPCC emission coefficients).

The influence of spatial integration is less clear and less consistent. Spatial integration of NO_3^- concentrations and N_2O emissions may better reflect the central tendency of the system and be less influenced by the extreme spatial variability that is characteristic of $[NO_3^-]$ and denitrification. This may also be due, in part, to the soil samples used to determine NO_3^- concentration being collected in proximity to the flux chamber but not within it. Spatial integration was most effective when combined with temporal integration.

Integration of point measurements in time and/or space resulted in a reduction in the variance of the data set, removing local scale variability, emphasizing variability at greater spatial or temporal scales. The appearance of greater correlation at higher levels of organization is often interpreted as evidence of an emergent property. A spatially and temporally integrated parameter such as NE may better reflect the complex direct and indirect influences of NO_3^- on the soil biological environment, the ability of the system to compensate over time and the spatial interdependence of processes such as mineralization, nitrification, denitrification and NO_3^- movement in the landscape.

Conclusion

- ✓ Temporal integration of NO_3^- availability (nitrate exposure) resulted in greater correlation with N_2O emissions.
- ✓ Spatial averaging of NO_3^- and N_2O emissions also resulted in greater correlation.
- ✓ Both observations suggest that the impact of NO_3^- on N_2O emissions occurs at and temporal scales greater than a single point in time and space. The relationship between NE and cumulative N_2O emissions may reflect an emergent property of the system.

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