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Spatial variation in soil pH controls off-season N_2O emission in an agricultural soil

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ABSTRACT

Experiments with soils have provided ample evidence that soil pH controls the $N_2O/(N_2O + N_2)$ ratio of denitrification, which increases with decreasing pH, most probably because low pH interferes with the expression of N_2O reductase in denitrifying bacteria. In contrast, the N_2O/NO_3^- product ratio of nitrification appears to be unaffected by soil pH within the range relevant for agricultural soils (pH 5.5–7.0). We hypothesized that local pH variations in cultivated soil may control *in situ* N_2O emissions during periods of active denitrification. To test this hypothesis, we identified three plots with slightly different soil pH (5.4–5.9) within an agricultural field under spring ploughed cereal cropping, and placed four frames within each plot for measuring N_2O emissions throughout autumn and spring. Soil samples were taken from each frame after the experiment to characterize the kinetics of NO, N_2O and N_2 production by anoxic incubation. The data were used to calculate an N_2O index, I_{N2O}, which is an inverse measure of the capacity of the denitrifying community to effectively express N_2O reductase under anoxia and hence a proxy for the soil's propensity to emit N_2O under denitrifying conditions. N_2O emissions were greatest during spring thaw, intermediate in autumn and low in late spring. Emissions during autumn and spring thaw were inversely related to soil pH, supporting the hypothesis that soil pH influences N_2O emissions when denitrification is the main source of N_2O. During these periods, emissions were positively correlated with I_{N2O}, further substantiating the idea that soil pH affects denitrification product ratios *in situ*. Total organic carbon and nitrate content were negatively correlated with soil pH, thus co-varying with N_2O emissions. However, the relationship of N_2O emission to TOC and nitrate appeared weaker than to pH. Off-season emissions dominate N_2O budgets in many regions. If the pH relationship holds at greater scales, careful soil pH management by precision liming could be a viable tool to reduce N_2O emissions.

1. Introduction

Long before N_2O emissions from soils became an environmental issue, Wijler and Delwiche (1954) and Nommik (1956) observed that the production of nitrous oxide (N_2O) relative to dinitrogen (N_2) during denitrification is higher in acid than in neutral soil. This phenomenon was rediscovered several times throughout the next five decades (Simek and Cooper, 2002). The reason for the higher $N_2O/(N_2O + N_2)$ product ratio in acid soils remained obscure, however, and the functional relationship between the product ratio of denitrification, soil pH and N_2O emissions has not been assessed systematically for the more narrow pH range of cultivated soils or across different soil types.

We recently conducted a series of studies in which a variety of soils from long term agronomic experiments were screened for denitrification product ratios using a robotized incubation system for high-resolution measurement of NO, N_2O and N_2 production in batch incubations (Molstad et al., 2007; Liu et al., 2010; Raut et al., 2012; Qu et al., 2014; Obia et al., 2015). These investigations demonstrated that the $N_2O/(N_2O + N_2)$ product ratio is strongly controlled by soil pH, decreasing linearly with increasing pH within the normal pH range of temperate agricultural soils (4.0–7.0), irrespective of soil type. The underlying mechanisms were investigated by studying gene transcription and enzyme activities during transition from oxic to anoxic respiration in the model organism *Paracoccus denitrificans* (Bergaust et al., 2010) and in suspensions of bacteria extracted from soils (Liu et al., 2014; Brenzinger et al., 2015). These studies showed that the making of functional N_2O reductase was increasingly difficult with declining pH within the

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range of pH 6.0–7.5, while enzymes expressed at pH 7.0 were fully functional at low pH. These results suggest that soil pH controls the product ratio at the cellular level by obstructing or delaying the expression of N_2O reductase. An alternative explanation is that pH affects the product ratio indirectly by controlling the species composition of the denitrifying soil community, as suggested by Jones et al. (2014), based on a screening of agricultural soils. Their interpretation has been questioned, however (Bakken et al., 2015), and the observation that the N_2O product ratio responds immediately to manipulation of the soil pH suggests that the direct effect of pH is more important than community composition (Cuhel and Simek, 2011; Qu et al., 2014).

Whatever mechanism being at work, we may expect that soil pH affects N_2O emission rates, increasing with decreasing pH, all other factors held constant. Even though there is circumstantial evidence for this in meta-studies summarizing field flux observations (Stehfest and Bouwman, 2006; Shcherbak et al., 2014), it is not trivial to test this hypothesis, since N_2O emissions under field conditions vary grossly in response to fluctuating soil moisture, temperature, mineral nitrogen and carbon substrate availability. Another factor which may blur the effect of pH on N_2O emission rates is nitrification. Nitrification is the main source of N_2O under oxic conditions (Smith, 1997), but there is no straightforward relationship between nitrification rate and soil pH (Booth et al., 2005). The N_2O yield (N_2O/NO_3^-) of nitrification is only marginally affected by soil pH within the normal pH range of agricultural soils (Mørkved et al., 2007). Therefore, it is unlikely that N_2O emissions deriving primarily from nitrification correlate with soil pH. Despite the shortcomings and pitfalls of field experiments, studies of N_2O emissions within natural ecosystems with large spatial variations in soil pH have demonstrated declining emission with increasing soil pH, both for a riparian ecosystem (Van den Heuvel et al., 2011) and a forest on drained peat (Weslien et al., 2009; Rütting et al., 2013). To our knowledge, no such study has been carried out within agricultural fields, in which the soil pH is expected to vary within a more narrow range.

The objective of the present study was to explore N_2O emissions along marginal pH gradients in a cereal cropping field outside the vegetation period. Off-season was chosen to avoid confounding effects of fertilization, root activity and strong fluctuations in soil moisture content, all of which may influence N_2O emissions directly, or indirectly via modifying soil pH locally. As a test location, we chose a spring wheat field in Southeast Norway, previously used in a four-year fertilizer trial (Øvergaard et al., 2010, 2013a, b), in which we identified three plots from the same fertilization treatment and with similar soil properties but with marginally different soil pH (5.4–5.8). We installed four permanent frames in each plot for N_2O chamber measurements and monitored N_2O emissions in all 12 frames during autumn (post-harvest until snow cover) and during two periods in the spring (snowmelt and late spring prior to tillage). At the end of the field experiment, we took soil samples from each frame and determined potential oxic and anoxic respiration, along with the kinetics of NO, N_2O and N_2 production during denitrification in laboratory assays.

2. Materials and methods

2.1. Field trial

2.1.1. Experimental site and soil pH measurements

Measurements were conducted between September 2010 and May 2011 in the stubble of a spring wheat (*Triticum aestivum* L.) field, previously used in a four-year (2007–2010) experiment aimed at estimating yields by proximal and remote sensing (Øvergaard et al., 2010, 2013a, b). The field is located at NIBIO Apelsvoll (60°42′ N, 10°51′ E, 250 m above sea level) in Southeast Norway, on an imperfectly drained brown earth (Gleyed melanic brunisoils, Canadian System of Soil Classification) with dominantly loam and silty sand textures. For the period 2000–2014, mean annual precipitation was 693 mm and mean annual temperature 5.1 °C. Based on a soil survey performed in 2001 (Øvergaard et al., 2013a), we selected three 2 m × 8 m large plots with comparable texture but with differences in soil pH (Table 1). Measurements of pH were repeated with higher spatial resolution at the end of the field experiment, as described below. In each of the three plots, four micro plots for flux measurements were established in September 2010 by pressing 50 × 50 × 20 cm aluminium frames a minimum of 7 cm into the soil. Each two frames were placed next to each other (about 20 cm apart), one pair in each end of the plots, about 50 cm from the edge of the plot (Fig. S1). The frames served as bases for chamber measurements of N_2O emissions (see below).

At the end of the field experiment in spring 2011, three equally spaced soil samples (0–20 cm) were taken from the inside of each frame along a diagonal transect. Soil sample were taken with a soil auger (18 mm diameter). For every position along the transect, three cores were taken and mixed by hand. pH was measured after dispersing 10 g of soil from each sample in 0.01 M $CaCl_2$ (Seven Multi, Mettler-Toledo). As expected, pH_{CaCl2} values measured in 2011 were lower than pH_{H2O} values measured in 2001, but when averaging the values for each of the three plots ($n = 12$), the ranking of plots for pH remained: pH_{CaCl2} in frames of plot 1 was higher than in plot 2 and 3, despite the high variability between frames within each plot, particularly in plot 1 (Table 2). All selected plots had been fertilised with 200 kg N ha^{-1} during the cropping season in 2010 (Øvergaard et al., 2013a); half of the dose was given at sowing as compound fertilizer (9.6% NO_3–N, 11.0% NH_4–N, 9.6% K and 3.6% P) and the reminder as calcium nitrate (14.5% NO_3–N, 1.1% NH_4–N and 18.8% Ca) top dressed at the beginning of stem elongation (BBCH-stage 31, Lancashire et al., 2008). Meteorological data were obtained from the meteorological station at Apelsvoll, located approx. 150 m from the experimental site. Soil temperature and volumetric moisture content were measured continuously by sensors (5TE, Decagon Devices, Inc.) permanently installed at depths of 5, 20 and 35 cm in each plot, one set for each pair of frames (Fig. S1).

2.1.2. N_2O flux measurements

N_2O emissions were measured by a static chamber method (Rochette and Bertrand, 2008), placing 51 × 51 × 20 cm large aluminium chambers equipped with a 3-way sampling port and a 3 mm diameter pressure equilibration tube (15 cm long) on the preinstalled frames. The frames had a 3 × 3 cm open groove on top, which was filled with water prior to deployment to secure airtight connection. Samples (~15 ml) were taken from the chambers 0, 15, 30 and 45 min after deployment with a 20 ml polypropylene syringe. Before taking a sample, the air in the chamber was mixed by pulling and pushing the plunger of the syringe three to four times. The samples were transferred to pre-evacuated 12.5 ml glass vials (Chromacol) top crimped with butyl rubber septa. Temperature outside and inside one chamber in each plot was recorded by a handheld digital thermometer after the last sampling. Measurements were carried out once a week from end of September (after harvest) until the field was covered with snow in mid of November. In order to explore the potential effect of diurnal temperature variation around the freezing point,