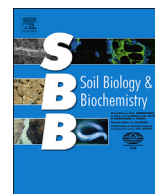




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Hot spots of N₂O emission move with the seasonally mobile oxic-anoxic interface in drained organic soils



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ABSTRACT

N₂O emission from soil is regulated by the more or less sporadic occurrence of anoxic voids within the otherwise oxic soil matrix. Differences in size and density of these voids makes the process highly variable at the microscale. In a search for situations where variation in N₂O emission is at the mesoscale rather than at the microscale we selected a drained and nitrogen rich organic soil incline. N₂O emission rate gradients were observed at the mesoscale (10 m range). Massive N₂O emissions occurred at an interface that may be defined by upslope oxic conditions inducing mineralizing organic nitrogen nitrate production and downslope anoxic conditions inducing the conversion of nitrate into N₂O. This N₂O-producing interface probably contained many small anoxic volumes distributed in the aerated soil matrix. The interface moved uphill in the wet season and downhill in the dry season so the mesoscale pattern also had a clear temporal component. When scaled on a hectare basis, the site with such a hot spot emitted 73 kg N annually as N₂O, indicating the magnitude of this activity.

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1. Introduction

Organic cultivated soils often show high nitrous oxide (N₂O) emission. When organic soils are drained a massive subsidence and decomposition of soil organic matter may be initiated due to increased oxygen access for decomposer microorganisms. In eastern Finland, a drained fen lost 1 cm year⁻¹ during 60 years (Nykanen et al., 1995) and an organic soil in Florida, US, lost 0.7 cm year⁻¹ (Terry, 1980). In a grazed grassland N₂O emission increased by 75% after drainage (van Beek et al., 2010) and in an alder forest site N₂O emission increased by nine times when drained (von Arnold et al., 2005). Under such conditions widespread decomposition of organic matter occurs in the otherwise aerated soil matrix implying large oxygen demands. This potentially creates anaerobic volumes in the aerated soil matrix, which may result in a large interface area between oxic and anoxic conditions per soil surface area. Large N₂O emission from drained organic soils has previously been observed, e.g. 23 kg N ha⁻¹ yr⁻¹ in a boreal site (Maljanen et al., 2004), 23 kg N

ha⁻¹ yr⁻¹ in a Canadian soil (Rochette et al., 2010), 56 kg N ha⁻¹ yr⁻¹ in southern Germany (Flessa et al., 1998), and 97 kg N ha⁻¹ yr⁻¹ in Ohio, US (Elder and Lal, 2008).

Our aim was to investigate the effect of high soil organic matter on N₂O emission along a topographic gradient with varying soil moisture. We selected a toposequence in a Danish arable field with a gradual increase in soil organic matter over a downhill incline. We expected N₂O emission rates along the toposequence to peak at the interface between unsaturated uphill positions where nitrate (NO₃⁻) is produced by nitrification following mineralisation of organic nitrogen (N) and saturated downhill positions where anoxic conditions abound and NO₃⁻ is reduced to N₂O. Moreover, we expected this interface to move uphill when precipitation is greater than evapotranspiration and downhill during dry periods. Finally, we expected denitrification to be more important than nitrification for N₂O release due to the large carbon availability during soil organic matter decomposition at the site.

2. Materials and methods

2.1. The site, soil moisture

A drained organic soil on a slope at Røholte, Sjælland, Denmark,

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stretching uphill 200–500 m from Orup Bæk (Faxe Kommune, municipal stream no. 11, (55° 19' N, 12° 08' E) was selected. The 300-m slope had an average incline of 3% towards the 200 m of horizontal bottom next to a stream. The slope and bottom are farmland grown with grass and maize, respectively. In the 2014 growing season 120 kg ha⁻¹ in NH₄NO₃ was added on the slope and the bottom. The lowest 50 m of the slope and 50 m of the horizontal bottom section adjacent to the slope were studied. The transition between slope and bottom section is denoted 0 m, the distance from the transition along the bottom section is denoted -50 m to 0 m, and the distance uphill on the slope is denoted 0 m to +50 m. Soil profiles from the slope and the bottom were collected down to 70 cm depth on April 10, 2015. At a sampling depth of 0–70 cm down the transect soil pH from was a constant 5.0 with no values differing more than 0.1 units from this average value. Precipitation and potential evapotranspiration data were taken from a local weather station (Brandelev) and Research Center Flakkebjerg located 16 km and 55 km, respectively, from the area investigated (Table 1). Potential evapotranspiration was calculated with the procedure used by the Danish Meteorological institute (DMI, 2001).

2.2. N₂O flux measurement

A PVC plastic tube 10 cm inner diameter, 15 cm long and tapered at one end was hammered 9 cm into the ground. The 6 cm remaining aboveground contained 0.5 L air when closed with a plastic lid. The lid was sealed over a 5-mm thick foam rubber sheet with a metal clamp on the plastic tube when N₂O flux was assessed. Gas samples of 8 mL were collected 0 min and 30 min after sealing and stored in 5.3 mL Exetainers (LabCo, Lampeter, UK). One mL gas from the Exetainers was analyzed on a gas chromatograph (SRI 8610C, Torrance, California, USA) with electron capture detection. Single measurements were taken at between 7 and 16 measurement sites along 55–70 m of the 100 m transect. There were 4–11 m between single sites of measurement.

2.3. N₂O in soil air

Nylon tubing of 6 mm outer diameter and 3 mm inner diameter was inserted at different soil depths between 15 and 95 cm. The tubes were plugged with a butyl rubber septum for gas sampling at the upper end and with a screw at the lower end to prevent soil from filling the tube. Four 1.5-mm holes on the side of the tubing just above the end screw were made. Three replicate tubes were inserted at topographic positions, -16 m, 0 m, and +20 m with a distance of 2–5 m perpendicular to the incline axis. A gas volume similar to the volume inside the tubes was removed before

sampling 8 mL air. These samples were treated and analyzed in the same way as described under N₂O flux measurement.

2.4. N₂O isotopomer measurement

Between 500 mL and 600 mL of sample gas was collected in a 600-mL sampling bag (SupelTM-Inert Multi-Layer Foil bag, Sigma-Aldrich, Brøndby, Denmark) below the lid on the flux chamber. We sampled nine locations along the transect between -22 m and +40 m. We therefore sampled air from the flux chamber and some soil air from below the chamber. To minimize the leakage of gas to and from the sampling bags, the isotopomers (¹⁴N¹⁵N¹⁶O ($\delta^{15}\text{N}^\alpha$) and ¹⁵N¹⁴N¹⁶O ($\delta^{15}\text{N}^\beta$)) and concentration of N₂O was measured within 6 h of sampling. This was done using a Picarro G5131-i analyser (Picarro, Santa Clara, California, USA, Winther et al., 2017). Measurements were performed continuously for 20 min (24 mL min⁻¹) or more to improve the statistical analysis. Park et al. (2011) state that the source of N₂O can be distinguished due to a difference in site preference (SP = $\delta^{15}\text{N}^\alpha - \delta^{15}\text{N}^\beta$) of the two isotopomers, e.g. denitrification leads to SP < 0‰ and nitrification leads to SP > 11‰.

2.5. Potential activity of processes forming N₂O

Soil was sampled at three positions along the transect (-20 m–0 m; 0 m–12 m, and 12 m–46 m) and at two depths (0–10 cm and 30–40 cm) on 10 May 2014. Potential denitrification and potential nitrification were measured on these samples (four replicates per position and depth).

2.5.1. Potential denitrification

Two g of soil (fresh weight) in 117-mL glass flasks was added 5 mL liquid with 1 mM glucose and 1 mM KNO₃. Flasks were sealed with a butyl rubber stopper, headspace evacuated and refilled with N₂ and 10% of the atmosphere replaced with acetylene (C₂H₂). Flasks were mounted on a shaker (at 100 rpm) at room temperature and N₂O concentration in the headspace assessed after 2 h on a gas chromatograph (see above) with electron capture detection (Smith and Tiedje, 1979).

2.5.2. Potential nitrification

Soil slurries were incubated with excess ammonium (NH₄⁺) and production of nitrite (NO₂⁻) followed after amendment with potassium chlorate (NaClO₃) to block the oxidation of NO₂⁻ to NO₃⁻ (Smith and Belser, 1982). Twenty g of soil (fresh weight) in 250-mL glass flasks was added to 100 mL liquid with 0.5 mM (NH₄)₂SO₄ and 10 mM KClO₃ to inhibit oxidation of NO₂⁻ to NO₃⁻ by nitrifying

Table 1
Water balance during the experimental period calculated for the site.

		Precipitation (mm)	Potential evapo-transpiration (mm)	Precipitation excess, minimum (mm)
2014	Feb.	37	16	21
	Mar.	25	39	-14
	Apr.	30	66	-37
	May	38	95	-57
	June	39	115	-76
	July	51	126	-74
	Aug.	91	89	2
	Sept.	66	58	8
	Oct.	106	23	83
	Nov.	37	8	29
	Dec.	110	5	105
	2015	Jan.	71	6
Feb.		22	12	11
Mar.		55	36	20
Apr.		31	72	-41

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