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CH_4 oxidation and N_2O emissions at varied soil water-filled pore spaces and headspace CH_4 concentrations

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Abstract

Emission of N_2O and CH_4 oxidation rates were measured from soils of contrasting (30–75%) water-filled pore space (WFPS). Oxidation rates of ^{13}C–CH_4 were determined after application of 10 μl ^{13}C–CH_4 l^{-1} (10 at. % excess ^{13}C) to soil headspace and comparisons made with estimates from changes in net CH_4 emission in these treatments and under ambient CH_4 where no ^{13}C–CH_4 had been applied. We found a significant effect of soil WFPS on ^{13}C–CH_4 oxidation rates and evidence for oxidation of 2.2 μg ^{13}C–CH_4 d^{-1} occurring in the 75% WFPS soil, which may have been either aerobic oxidation occurring in aerobic microsites in this soil or anaerobic CH_4 oxidation. The lowest ^{13}C–CH_4 oxidation rate was measured in the 30% WFPS soil and was attributed to inhibition of methanotroph activity in this dry soil. However, oxidation was lowest in the wetter soils when estimated from changes in concentration of $^{12+13}C$–CH_4. Thus, both methanogenesis and CH_4 oxidation may have been occurring simultaneously in these wet soils, indicating the advantage of using a stable isotope approach to determine oxidation rates. Application of ^{13}C–CH_4 at 10 μl ^{13}C–CH_4 l^{-1} resulted in more rapid oxidation than under ambient CH_4 conditions, suggesting CH_4 oxidation in this soil was substrate limited, particularly in the wetter soils. Application of $^{14}NH_4^{15}NO_3$ and $^{15}NH_4^{15}NO_3$ (80 mg N kg soil^{-1}; 9.9 at.% excess ^{15}N) to different replicates enabled determination of the respective contributions of nitrification and denitrification to N_2O emissions. The highest N_2O emission (119 μg $^{14+15}N$–N_2O kg soil^{-1} over 72 h) was measured from the 75% WFPS soil and was mostly produced during denitrification (18.1 μg ^{15}N–N_2O kg soil^{-1}; 90% of ^{15}N–N_2O from this treatment). Strong negative correlations between $^{14+15}N$–N_2O emissions, denitrified ^{15}N–N_2O emissions and ^{13}C–CH_4 concentrations ($r=-0.93$ to -0.95, N_2O; $r=-0.87$ to -0.95, denitrified ^{15}N–N_2O; $P<0.05$) suggest a close relationship between CH_4 oxidation and denitrification in our soil, the nature of which requires further investigation.

Keywords: Denitrification; Methane oxidation; Nitrification; Nitrous oxide; Soil water-filled pore space; Stable isotopes

1. Introduction

During the past few decades atmospheric concentrations of CH_4 and N_2O have been increasing at rates of 0.8 and 0.3% y^{-1}, respectively (Mosier et al., 1998). This is of concern due to the high global warming potentials of these gases (IPCC, 2001) and the involvement of N_2O in the destruction of stratospheric ozone. Agricultural systems are a major source of atmospheric N_2O contributing 6.2 T_g N_2O–N y^{-1} to a total global source strength of 17.7 T_g N_2O–N y^{-1}, mainly as a result of application of inorganic nitrogen fertilisers (Kroeze et al., 1999). Agricultural soils may act as either a source or a sink for atmospheric CH_4 depending on soil type, aeration, environmental variables and N availability (Topp and Pattey, 1997; Chan and Parkin, 2001; Le Mer and Roger, 2001). CH_4 oxidation provides a sink for approximately 30 ± 15 T_g CH_4 y^{-1} of the total atmospheric loading of 598 T_g CH_4 y^{-1} (IPCC, 2001; Le Mer and Roger, 2001). Any change in this sink may result in a net increase in CH_4 emissions and may have a significant effect on global warming.

Net emissions of N_2O and CH_4 from soil are strongly influenced by soil water content. Several processes may contribute to N_2O emission from agricultural soils depending on soil water-filled pore space (WFPS). Emissions following fertiliser N application generally increase with

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increasing soil water content and most rapidly above 70% WFPS where denitrification is thought to predominate (e.g. Dobbie et al., 1999; Abbasi and Adams, 2000; Skiba and Ball, 2002). Nitrification may significantly contribute to N_2O emissions below 70% WFPS (Stevens et al., 1997; Abbasi and Adams, 2000; Wolf and Russow, 2000). CH_4 oxidation is also strongly regulated by soil water content primarily due to the control on diffusion of CH_4 through the soil profile, and activity of methanotrophs (Nesbit and Breitenbeck, 1992; Dunfield et al., 1993; Czepiel et al., 1995; Gulledge and Schimel, 1998; Hütsch, 2001) often resulting in negative correlations between soil water content and CH_4 oxidation rate (Castro et al., 1995; Dobbie and Smith, 1996). However, CH_4 oxidation may be inhibited in dry soils (Striegl et al., 1992; Dobbie and Smith, 1996), and so the effect of soil water content on this process requires verification using recently developed ^{13}C techniques to directly quantify ^{13}C–CH_4 oxidation rates.

Application of fertiliser N has been shown to inhibit CH_4 oxidation in soil (Steudler et al., 1989; Hütsch, 1998; Tlustos et al., 1998; Kravchenko et al., 2002). This inhibition is thought to be either due to competition between NH_3 and CH_4 for methane monooxygenase enzymes (Bédard and Knowles, 1989; Holmes et al., 1995), a non-competitive (toxic) inhibition by NH_2OH or NO_2^- produced during NH_3 oxidation (King and Schnell, 1994), or a general salt effect (Gulledge and Schimel, 1998). This inhibition often results in a net increase in CH_4 emitted from soil (Bronson and Mosier, 1994) and increased oxidation of NH_3 to NO_2^- by methylotrophs (Hütsch, 1998). Inhibition of CH_4 oxidation after fertiliser application is thought to result in N_2O production during NH_3 oxidation by methylotrophs, and thus interactions exist between NH_3 oxidation (nitrification), N_2O production and CH_4 oxidation (Baggs and Blum, 2004). Such interaction may be enhanced by the ability of ammonia oxidisers to oxidise CH_4 (Bédard and Knowles, 1989). Soil water content is likely to affect these interactions, but the extent and nature of any effect is unknown.

The effect of soil WFPS on emissions of N_2O and CH_4, CH_4 oxidation and N_2O production during ammonia oxidation (nitrification) was examined following application of N fertiliser to soil under controlled laboratory conditions. Stable isotope techniques (^{13}C and ^{15}N) were used to directly measure CH_4 oxidation, as opposed to estimating rates from changes in net emissions over time, and to differentiate between N_2O produced during nitrification from that produced during denitrification. We hypothesised that application of fertiliser to soils of low water content (30% WFPS) would inhibit CH_4 oxidation and increase N_2O production during nitrification, but in wetter soil (75% WFPS) the inhibition would be exacerbated as a result of reduced diffusion of CH_4 through the soil, and less N_2O production during nitrification.

2. Materials and methods

2.1. Soil

Soil (0–15 cm depth) was sampled in January 2003 from an arable field on the Imperial College London Estate at Wye that had previously been under cereal cultivation for 10 years. The soil was a brown earth silt loam (17% sand, 68% silt, 15% clay, total carbon 1.9%, total N 0.2%, pH (H_2O) 6.7, CEC 16.6 $Cmol_c$ (+) kg^{-1}, bulk density 1.23 g cm^{-3}) of the Coombe series classified as a Cambisol (FAO classification). Soil was air dried and sieved <2 mm prior to experimental set-up.

2.2. Experimental set-up

The experiment was established in 1 l Kilner jars with gas-tight lids fitted with a gas sampling port. 150 g soil (2% gravimetric water content) was weighed into each jar and soil water content amended to achieve the target water-filled pore space (WFPS) of 30, 45, 60 and 75%. The amount of water required to reach a target WFPS was determined based on the bulk density of the soil with a particle density of 2.65 g cm^{-3}. Soils were conditioned at 20% below their target WFPS for 4 d prior to the experiment to initiate microbial activity and to minimise changes in soil water content at the start of the experiment. On day zero (d 0) soil was fertilised with ^{15}N-labelled NH_4NO_3 in solution at a rate of 80 mg N kg^{-1} soil (150 kg N ha^{-1}). This was applied as either (a) $^{14}NH_4^{15}NO_3$ or (b) $^{15}NH_4^{15}NO_3$ (9.9 at. % excess ^{15}N). Additional distilled water was added to achieve the target WFPS. Each treatment was replicated six times for gas analyses and an additional nine times for soil analyses. All treatments were incubated at 21 °C in the dark for 72 h after fertiliser application, and soil WFPS was maintained on a weight basis.

2.3. Gas sampling and analysis

^{13}C–CH_4 (10 at. % excess ^{13}C) was applied at a concentration of 10 μl l^{-1} to the closed headspace of the Kilner jars of half of the treatment replicates after removing the same volume of air from the headspace. Gas samples were taken immediately (0 h) and at 12, 24, 48 and 72 h from six treatment replicates after time of ^{13}C–CH_4 application. Sample volumes removed for determination of ^{13}C–CH_4 or ^{15}N–N_2O were replaced with the same volume of air immediately after sampling in order to keep the pressure constant within the headspace of the Kilner jars. Samples for $^{12+13}C$–CH_4 and $^{14+15}N$–N_2O analysis were taken using gas-tight syringes, stored in pre-evacuated 12 ml gas vials (Labco), and analysed for CH_4, CO_2 and N_2O on an Agilent 6890 gas chromatograph fitted with a flame ionisation detector, methaniser and electron capture detector (column and detector temperatures 40 and 250 °C, respectively). Samples for ^{13}C–CH_4 and ^{15}N–N_2O determination were