Influence of pore size distribution and soil water content on N_2O response curves

Tony van der Weerden[A], Cecile de Klein[A] and Francis Kelliher[B,C]

[A]AgResearch, Invermay Agricultural Centre, Mosgiel, New Zealand, Email tony.vanderweerden@agresearch.co.nz
[B]AgResearch, Lincoln, New Zealand, Email frank.kelliher@agresearch.co.nz.
[C]Lincoln University, Department of Soil and Physical Sciences, Lincoln, New Zealand.

Abstract
A laboratory study was conducted to determine nitrous oxide (N_2O) response curves against water filled pore space, volumetric water content and volumetric gas content using intact cores collected from two soils with contrasting drainage characteristics. While both soils had similar total porosities, the soil considered to be poorly drained was found to have a higher macroporosity (pores > 30 μm) mainly due to a larger volume of very large (>100 μm) pores, resulting in this soil draining more rapidly at low tensions. Consequently, pore size distribution had a significant effect on the drainage characteristics. Volumetric water content was found to be the independent variable that related best to the measured N_2O emissions. An empirical relationship between N_2O emissions and volumetric water content, rather than water filled pores space, is applicable to soils with different bulk densities. This may provide a method for predicting N_2O emissions from a soil water balance model at a national level.

Key Words
Volumetric water content, water filled pore space, gas diffusivity, intact cores, emission factors, nitrous oxide inventory.

Introduction
Urine deposition onto pasture is New Zealand's largest source of nitrous oxide (N_2O) emissions, representing *c*. 80% of the N_2O emissions inventory including direct and indirect emissions. Presently, an IPCC Tier 1 methodology is followed, where a single country-specific emission factor (EF_3) of 1%, an average weighted according to soil drainage classes, is used for estimating emissions from excreta deposited onto grazed pastures within the national N_2O inventory (Ministry for the Environment 2009). However, a series of seasonal EF_3 field trials has shown that EF_3 varies throughout the year (Kelliher *et al*. 2005a) primarily due to varying soil water status at the time of field experiments. The development of seasonal and regional EF_3 values that reflect differences in soil water status will provide an important step towards a Tier 2 methodology for national N_2O inventory reporting.

Beneath a urine patch, where soil N concentrations are high, oxygen diffusion has a dominant influence on N_2O emissions. As oxygen diffusion rate in soils is difficult to measure, soil water content is often used as a proxy. Water filled pore space (WFPS) has been widely used to express soil water content in incubation and field studies. However, soils with different bulk densities will have different volumes of air and water at any given value of WFPS, resulting in considerable variation in relationships based on WFPS and N_2O fluxes. Thus it may be more appropriate to use other descriptors such as volumetric water content (VWC) or volumetric gas content (VGC) for estimating N_2O emissions across landscapes with varying bulk densities (Farquharson and Baldock 2008).

In a previous study, a water balance model was combined with an empirical relationship between N_2O emissions and soil gas content to develop a method to estimate N_2O emissions in the field from weather data (Kelliher *et al*. 2005b). This approach provides a potential method for determining spatial and temporal EF3 values for a Tier 2 inventory structure. In their study, the relationship between N_2O and soil gas content was determined in a laboratory study using re-packed cores from a single soil type. The aim of this trial was to determine which measure of soil water may be most suitable for predicting N_2O emissions from intact soil cores using two soils with contrasting soil physical properties.

Methods
Experimental design
The main treatment of the experimental design was 5 different soil water tensions (-0.5 kPa, -1 kPa, -3 kPa, -5 kPa and -10 kPa), with a sub-treatment of soil type (well drained and poorly drained) and nitrogen addition

(0N and +N). A poorly drained Otokia silt loam (Fragic Perch-gley Pallic soil, NZ soil classification) and a well drained Wingatui silt loam (weathered Fluvial Recent soil, NZ soil classification) were used for this laboratory study, as these soils have been extensively studied in previous seasonal EF3 field trials (e.g. de Klein *et al*. 2004, Sherlock *et al*. 2003). The physical nature of these soils is of interest because in some trials higher N_2O emissions were observed from the well-drained Wingatui soil compared to the poorly-drained Otokia soil. Sixty intact soil cores (5 cm height, 10 cm diameter) were collected from each site using stainless steel rings. Soil bulk density, moisture release curves and the pore size distribution were determined for each core in addition to volumetric water and gas contents and WFPS. Cores were trimmed and the top soil surface "peeled" off to provide an unsmeared natural soil surface. The bottom of the cores were trimmed evenly and fitted with a fine gauze cloth. Earthworms were extracted from the cores using several approaches including saturation of cores, placing black plastic over cores and applying a mild electric shock to the cores for 15 seconds using a 9 V battery.

The trial was designed so that N_2O emission and moisture release data would be collected in parallel. This was accomplished as follows: 1) as soil water tension increased from 0 kPa to -10 kPa, all cores were weighed at each critical tension for determining moisture release curves; 2) as each batch of cores reached its assigned moisture tension for N_2O measurements, nitrogen treatments would be applied to the core surface and cores were allowed to equilibrate at the prescribed tension prior to the first N_2O emission measurement. 3) on completion of measurement of gas fluxes (at about 8 weeks after application of N), collection of moisture release data continued until all cores had reached -10 kPa. As denitrification is considered the primary source of N_2O emissions from pastoral land in New Zealand, nitrogen was applied to the "+N" cores as dissolved potassium nitrate at a rate equivalent to 500 kg N/ha. The "+N" and "0N" treatments were replicated 8 and 4 times, respectively.

Nitrous oxide measurements

N_2O emissions were measured on six occasions from each core, until emissions from '+N' treatments returned to levels measured from the '0 N' treatments. Emissions were determined by removing soil cores from the tension table and placing them in a plastic container. Headspace gas sample volumes of either 1 or 2 ml were removed from the container via rubber septa positioned in the lid. Gas samples were collected at 30 and 60 minutes following closure, while background air samples were used to represent 0 minutes. Gas samples were injected into 6 mL Exetainer vials containing ambient concentrations of N_2O at atmospheric pressure, resulting in a pressurised vial containing 1 or 2 mL of container headspace air and 6 mL of ambient air. This allowed dilution of the sample, necessary due to the high headspace concentrations. The variation in the actual volume collected was required to adjust sample dilution. Following gas sampling, cores were weighed and returned to the appropriate tension. Gas samples were analysed for N_2O concentrations by gas chromatograph using a SRI 8610 automated gas chromatograph.

The N_2O fluxes were calculated for each container from the increase in head space N_2O concentrations over the sampling time. The hourly N_2O emissions (mg N /m^2/h) were calculated as follows:

$$N_2O\,flux = \frac{\delta N_2O}{\delta T} * \frac{M}{Vm} * \frac{V}{A}$$

where, δN_2O is the increase in head space N_2O concentrations over time (μL/L); δT is the enclosure period (hours); M is the molar weight of N in N_2O; Vm is the molar volume of gas at the sampling temperature (L/mol); V is the headspace volume (m^3); and A is the area covered (m^2).

N_2O response curves against increasing WFPS, VWC and VGC were generated for each soil type and for combined soil data and analysed using Genstat 10.

Results

Pore size distribution

Total porosity was similar for the two soils while pore size distribution differed (Table 1) due to the Wingatui soil having a higher measured clay content of 37% compared to 32% for the Otokia soil. Soil bulk density was also higher for the Wingatui soil, at 0.88 Mg/m^3 compared to 0.82 Mg/m^3. Micropores (pores less than 30 μm) represented 43% and 50% of the total soil volume for the Otokia and Wingatui soils, respectively. Consequently, the macropores (pores greater than 30 μm) represented a larger soil volume in the Otokia (25%) than in the Wingatui (16%) mainly due to a greater proportion of very large pores (>100 μm, equivalent to 0.1 mm) (Table 1). Because of this, Otokia soil will drain readily thereby decreasing the water content more rapidly with increasing tension during a drying phase following saturation.

Table 1. Pore size distribution of the Otokia and Wingatui soils.

Porosity and pore size distribution (% of soil volume)	Otokia	Wingatui
Total porosity	68.4	66.1
Microporosity	43.3	50.4
Macroporosity	25.1	15.7
pores between 30 & 60 µm	4.6	4.1
pores between 60 & 100 µm	2.6	1.7
pores between 100 & 300 µm	7.6	3.5
pores > 300 µm	10.2	6.0

N_2O response curves

N_2O emissions were greatest from the first gas sampling, conducted 4 days following equilibration at the prescribed moisture tension. Emissions declined rapidly as the moisture tension increased from -0.5 to -3 kPa, with emissions from the Otokia soil initially declining more rapidly compared to the Wingatui soil, presumably due to the Otokia soil containing a larger volume of very large pores (>300 µm; Table 1) which drain rapidly.

N_2O response curves to soil water or gas content were most distinct when data was restricted to the first gas sampling occasion from the "+N" cores when nitrogen was not limiting. An analysis of the scatter grams of N_2O emissions against increasing water or gas content revealed that the data better fitted a broken line model rather than a curvilinear model. When relating WFPS, soil water or gas content to N_2O emissions across both soils, the strongest relationship was obtained when VWC was the independent variable (R^2 = 79%, P < 0.0001; Figure 1). The intersection of the two lines occurs at 0.55 cm^3/cm^3 (s.e.m. = 0.006). There was no significant difference in the relationships based on VWC for each soil type, allowing the data to be combined. The associated residual variance was 140, while the corresponding residual variance for VGC and WFPS was more than double, at 397 and 375, respectively, suggesting weaker relationships against N_2O emissions. Furthermore, in contrast to VWC, using either WFPS or VGC as a proxy of oxygen diffusion rates revealed significantly different broken line models for each soil type, which made impossible to combine the data for the two soil types.

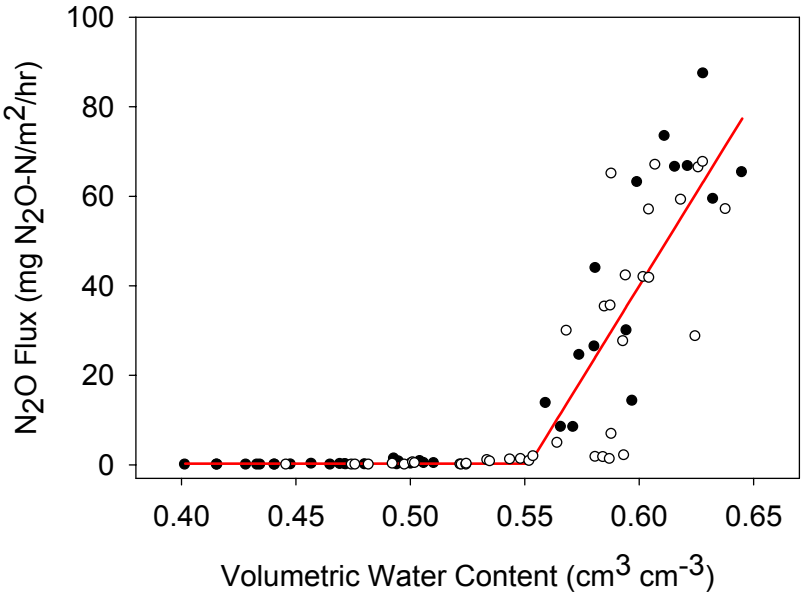

Figure 1. Scattergram of volumetric water content plotted against N_2O emissions, where ● = Otokia soil and ○ = Wingatui soil. Data is limited to emissions measured on first sampling occasion only. Broken line model fitted to pooled data has R^2 = 79% (P < 0.0001). Y-intercept of the straight line = 0.3 mg N_2O-N/m^2/hr (sem = 1.9) while the slope of the increasing line = 831 (sem = 88) and the intersection of the two lines occurs at 0.55 cm^3 water /cm^3 soil (sem = 0.006).

Discussion

While both soils exhibited similar total porosities with values of approximately 66-68% v/v, it is the distribution of the pore size that influences the soil gas content of these soils above field capacity. The large proportion of very large pores in the Otokia soil will drain rapidly following rainfall or irrigation events resulting in a more rapid increase in soil gas content during a drying phase. This will allow greater oxygen diffusion which, in turn, will reduce N_2O production via denitrification. In practice this suggests that when the Otokia and Wingatui soils are subjected to the same tension during a drying phase following rainfall, the Wingatui soil will remain wetter for a longer duration, which may partly explain the higher N_2O emissions observed from this soil during earlier field trials.

The slower drainage and associated higher N_2O emissions from the Wingatui soil suggest that, in the top 50 mm, this soil is a poorer draining soil than the Otokia soil. However, the 'poorly drained' soil drainage classification for the Otokia soil relates to the whole soil profile, which is characterised by water perching on a slowly permeable subsurface fragipan restricting drainage to lower depths. This suggests that the current use of soil drainage status for weighting a national EF3 value may not be appropriate, considering the majority of N_2O production occurs in the topsoil and that previous studies using these soils have shown N_2O emissions from the 'well drained' Wingatui soil are often greater than those measured from the 'poorly drained' Otokia soil.

Volumetric water content was found to be the best independent variable relating to the measured emissions. This work has also demonstrated that, in contrast to WFPS and VGC, employing VWC as a key variable to potentially predict N_2O emissions allows data from soils with different bulk densities to be pooled to develop an empirical relationship that is applicable across soil types. For predicting emissions, this is currently one of the limitations of WFPS, a term that is used universally by many researchers studying N_2O emissions from soils. These results provide support to the suggestion that VWC may be a more appropriate predictor of N_2O emissions due to denitrification (Farquharson and Baldock 2008).

Conclusion

While total porosity was similar for the two soils, the Otokia soil was found to have a higher macroporosity, mainly due to a larger volume of very large (>100 μm) pores, resulting in this soil draining more rapidly at low tensions. Consequently, pore size distribution had a significant effect on the drainage characteristics in the top 50 mm (core height). VWC was found to be the independent variable that related best to the measured N_2O emissions: this was also the only variable where data from the two soils types could be combined. An empirical relationship between N_2O emissions and volumetric water content is applicable to soils with different bulk densities. Combined with a water balance model this may provide a method for predicting N_2O emissions at a national level

References

de Klein CAM, Li Z and Sherlock RR (2004) Determination of the N_2O emission factor from animal excreta or urea, following a winter application in two regions of New Zealand. Report for MAF Policy, Wellington, New Zealand.

Farquharson R, Baldock J (2008) Concepts in modelling N_2O emission from land use. *Plant and Soil* **309,** 147-167.

Kelliher FM, de Klein CAM, Li Z, Sherlock RR (2005a) 'Review of nitrous oxide emission factor (EF3) data'. Client report prepared for MAF.

Kelliher FM, Scotter DR, Li Z, de Klein CAM (2005b) Water filled pore space and the direct nitrous oxide emission factor for excreta deposited by grazing animals onto pastoral soils. Report to the Ministry of Agriculture and Forestry.

Ministry for the Environment (2009) New Zealand's Greenhouse Gas Inventory 1990-2007. Submitted to the United Nations Framework Convention in Climate Change. Publication number ME 928. Wellington.

Sherlock RR, de Klein CAM, Li Z (2003) Determination of the N_2O and CH_4 emission factor from animal excreta, following a spring application in 3 regions of New Zealand. Report for MAF Policy, Wellington, New Zealand.