Workshop Report

Nitrous Oxide Chamber Methodology Guidelines

9-10 May 2011
Lincoln, New Zealand

Draft Report June 2011

Cecile De Klein
Mike Harvey
Selai Letica

New Zealand Government

GLOBAL RESEARCH ALLIANCE
International Workshop
9-10 May 2011
Lincoln, New Zealand

Compiled by Cecile de Klein[1], Selai Letica[1] and Mike Harvey[2]
[1] AgResearch Invermay, Private Bag 50034, Mosgiel, New Zealand
[2] NIWA, P.O. Box 14-901, Kilbirnie, Wellington, New Zealand

Funding sources
New Zealand Government to support the goals and objectives of the Global Research Alliance on Agricultural Greenhouse Gases

Acknowledgements
Contributions to the content of this report include information and photos from Philippe Rochette, Canada; Rod Venterea, U.S.A.; Tim Parkin, U.S.A.; Tom Misselbrook, United Kingdom; Marta Alfaro, Chile; HJ Di, New Zealand; Kevin Kelly, Australia; Lehna Rodhe, Sweden; Takashi Osada, Japan; Tom Denmead, Australia as well as contributions made by the workshop delegates and participants:

Invited delegates:

Name	Institution	email
Cecile de Klein (facilitator)	AgResearch, N. Z.	cecile.deklein@agresearch.co.nz
Mike Harvey (facilitator)	NIWA, N. Z.	m.harvey@niwa.co.nz
Marta Alfaro	National Institute for Agricultural Research, Chile	malfaro@inia.cl
Keith Cameron	Lincoln University, N. Z.	Keith.cameron@lincoln.ac.nz
David Chadwick	Rothamsted Research, United Kingdom	David.chadwick@bbsrc.ac.uk
Tim Clough	Lincoln University, N. Z.	clought@lincoln.ac.nz
Hong Di	Lincoln University, N. Z.	Hong.di@lincoln.ac.nz
Peter Grace	Queensland University of Technology, Australia	Pr.grace@qut.edu.au
Frank Kelliher	AgResearch, N. Z.	frank.kelliher@agresearch.co.nz
Kevin Kelly	Department of Primary Industries, Australia	Kevin.kelly@dpi.vic.gov.au
Søren Petersen	Aarhus University, Denmark	Soren.O.Petersen@agrsci.dk
Philippe Rochette	Agriculture and Agri-Food Canada	Philippe.Rochette@AGR.GC.CA
Surinder Saggar	Landcare Research, N. Z.	Saggars@landcareresearch.co.nz
Rob Sherlock	Lincoln University, N. Z.	Rob.sherlock@lincoln.ac.nz
Tony van der Weerden	AgResearch, N. Z.	Tony.vanderweerden@agresearch.co.nz
Rod Venterea	USDA-ARS Soil & Water Management Research Unit, U. S. A.	Rod.Venterea@ARS.USDA.GOV

Other participants:

Selai Letica	AgResearch, N. Z.	selai.letica@agresearch.co.nz
Andrew McMillan	NIWA, N. Z.	a.mcmillan@niwa.co.nz
Steve Thomas	Plant and Food Research, N. Z.	Steve.Thomas@plantandfood.co.nz

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BACKGROUND

There are two broad categories of methodology used for measurement and in-situ verification of (nitrous oxide) trace gas emissions at landscape scale: chamber (enclosure) methods and micrometeorological methods (Denmead, 2008). Chamber methods are the most widely used, are relatively low cost and simple to deploy and are the focus of this workshop. A recent review of N_2O emissions studies using chamber methodologies from around the world highlighted that there is large variation in chamber design, deployment and data analysis (Rochette and Ericksen-Hamel, 2008). Using specific criteria for chamber design, deployment and data analysis, these authors concluded that more than half of the 356 studies were of poor or very poor quality. This has implications for the reliability of N_2O emission factors that are derived from these data. Through the development of internationally applicable guidelines and standards, it will be possible to improve both the quality of measurements that support national inventory verification and international intercomparability of these data.

A workshop attended by over 50 international experts in 2010 (Banff, Canada) discussed a wide range of chamber methodology topics. The main conclusion of the workshop was that there is a need for international good practice guidelines on all aspects of chamber design, chamber deployment, sample handling and data analysis.

The New Zealand Government in support of the goals of the Global Research Alliance funded a follow-up workshop in May 2011 in Lincoln (New Zealand). Leading international experts in the field of N_2O chamber and sampling methodologies from the countries represented at the original workshop were invited to the workshop. Of these, seven experts from six different countries were able to attend the workshop. They were joined by nine New Zealand delegates and three NZ participants to discuss:

- Current understanding and considerations of all aspects of chamber methodologies,
- Uncertainty and error estimates of different steps in N_2O emissions measurements using chambers
- The proposed format, outline and time table for the agreed guidelines.

This report provides an overview of the aims, agenda and attendees of the Lincoln workshop, and provides a proposed outline for each chapter, a list of the lead authors and contributors and a timeline for the completion of the Guidelines. The report also and describes, for each Guideline chapter, the key recommendations and considerations that were made prior to[1], and revised at, the workshop.

[1] Discussion document

OVERVIEW OF WORKSHOP

Aims

The aims of the May 2011 workshop were to:

- Provide an overview on the current state of understanding about the different aspects of N_2O chamber methodologies,
- Outline a table of contents to develop international guidelines for N_2O chamber methodology,
- Assign authors to chapters that will develop the guidelines for publication,
- Agree on Editor, Lead- and Co-authors, and on time-line for completion

Agenda

Day 1 (Monday 9 May)	
9.00	*coffee/tea available*
9.15 – 9.45	Introductions, purpose, agenda
9.45 – 10.00	*Scene setting talk:* Experiences with implementing standards *Rodney T. Venterea, USDA-ARS Soil & Water Management Research Unit on GRACEnet*
10.00 – 11.30	**Topic1**: Chamber design (e.g. materials, size, venting, base, automation) Discussion lead: *Cecile DeKlein, AgResearch, Invermay*
11.30 – 12.30	**Topic 2**: Sample collection – part 1 (e.g. enclosure period, number of samples per flux, time of day, over-pressurising, storage issues) Discussion lead: *Søren O. Petersen, Aarhus University Denmark* Including experimental design and gas sampling strategy, and the appropriateness of extended chamber deployment if a non-linear flux estimation method is adopted.
12.30 – 13.30	*Lunch*
13.30 – 14.30	Visit lysimeter and GC lab at Lincoln University (*Hosted by Hong Di*)
14.30 – 15.00	*tea/coffee*
15.00 – 17.00	**Topic 2:** Sample collection – part 2, and Sample analysis (e.g. real time analysis, lab analysis, gas standards, QA/QC procedures) *Frank Kelliher, Rob Sherlock and Tim Clough*
Day 2 (Tuesday 10 May)	
8.30 – 9.00	recap day 1 *Mike Harvey, Cecile de Klein*
9:00 – 9:20	*Scene setting talk:* Known problems with chamber flux determination *Philippe Rochette*
9.20 – 10.40	**Topic 3:** Chamber deployment (e.g. replication, grazing, randomisation, frequency of sampling during measurement period, supporting data/measurements) *Peter Grace*
10.40 – 11.00	*tea/coffee*

11:00 -11:20	**Topic 3:** System specific deployment issues *a/ Grazed systems* *b/ Cropping systems*
11.20 – 12.30	**Topic 4:** Data analysis (e.g. flux integration method, statistical analysis, heterogeneity, negative fluxes) *Discussion lead: Rodney T. Venterea, USDA-ARS Soil & Water Management Research Unit* Including focus on Flux calculation schemes pros and cons of the various options
12.30 – 13.30	*Lunch*
13.30 – 14.30	Agree on editor, authors and time-line *Discussion lead: Cecile de Klein*
14.30 – 16.30	Uncertainty and error estimates associated with chamber methodologies *Discussion lead: Frank Kelliher*
16.30 – 17.00	*Wrap-up*

OUTCOMES OF THE WORKSHOP

Table of Contents for the Guidelines

During the workshop each topic of the draft Table of Contents that was included in the workshop discussion document[2], was introduced by a lead expert in that particular field (see agenda above). Each lead expert summarised the current understanding of the topic and then led the discussion on what delegates agreed were either i) agreed minimum requirements, ii) site specific requirements or iii) 'evolving' requirements, i.e. those that delegates did not necessarily agree on and for which more information or analysis was required. There were some minimum requirements everybody agreed (e.g. material and size of the chamber). Delegates also agreed that a number of requirements are 'site-specific'. A relatively larger number of requirements were identified as 'evolving' as these provoked a lot of discussion and different points of view. Some examples of these 'evolving' requirements were as basic as, whether or not the chambers should be vented during the enclosure period, the number of samples that need to be taken during the enclosure period, the frequency of sampling, and the flux calculation methods. These issues clearly require further discussion and analysis.

Following these presentations and discussions, the delegates agreed on a revised Table of Contents and the authors for the Guidelines (see below). The delegates also agreed that the Guidelines should be as succinct and clear as possible, so that they would be of use to a wide audience. It is intended that the Guidelines will be written as a cook-book style manual with i) minimum requirements, ii) site-specific requirements and iii)'evolving requirements.
The delegates did not discuss or agree on the length of each chapter, but based on 8-10 pages per chapter (including diagrams and photos), the approximate length of the Guidelines could be between 55 and 70 pages. The editors will review and discuss this further with MAF and the GRA once the authors have finalised the extended outlines are completed.

[2] Discussion document

Agreed Table of Contents:

CONTENT/CHAPTERS	**LEAD**	**TEAM**
Introduction and editing	Cecile de Klein/ Mike Harvey (NZ)	Selai Letica (NZ)
Chamber design	Tim Clough (NZ)	Philippe Rochette (Can) Mari Pihlatie (Finland) Jesper Riis Christiansen (DK) Steve Thomas (NZ)
Deployment protocols	Philippe Rochette (Can)	Dave Chadwick (UK) Sören Petersen (Denmark) Keith Cameron/ HJ Di (NZ) Mari Pihlatie (Finland) Jesper Riis Christiansen (DK)
Sample collection, handling & analysis	Frank Kelliher (NZ)	Surinder Sagar (NZ) Mike Harvey/Andrew McMillan (NZ) Catherine Watson (UK)
Data analysis	Rod Venterea (US)	Tim Parkin (US) Sören Petersen (Denmark) Asger Pedersen (Denmark) Peter Levy (UK) Laura Cardenas (UK)
Automated systems	Peter Grace (Aus)	Tony vd Weerden (NZ) Kevin Kelly (Aus) Bob Rees (UK)
Data reporting	Marta Alfaro (Chile)	Donna Giltrap (NZ) UK people (names tbc) Cecile de Klein (NZ)
Health & Safety	Dave Chadwick (UK)	All

Proposed content/outline for each chapter in the guidelines

1. Chamber design

Author[3]: Tim Clough[1], Philippe Rochette[2], Mari Pihlatie[3], Jesper Riis Christiansen[4], Steve Thomas[5]

- **Chamber materials**

Considerations:
- Inertness, i.e. non-reactive material
- Robustness according to climate, stock and machinery effects
- Light infiltration, i.e. allowing light in for plant growth but reducing temperature rise in the chamber headspace during deployment. Light requirements within the chamber headspace will be unique to the objectives of individual trials.

Existing recommendations:
- Stainless steel, aluminium, PVC, polypropylene, polyethylene (Parkin & Venterea, 2010)
- Plexi-glass (Rochette et al)

Examples of commonly used materials:
- Steel: e.g. de Klein et al., Rhode et al. 2009,
- PVC/Plastic: e.g. Alfaro et al., Chen et al., Huggins et al., Misselbrook et al., Rhode et al. 2006
- Aluminium and Perspex: e.g. Kelly et al.
- Smoked and clear plexi-glass e.g. Grace et al., Rochette et al.
- Reflective foils for diffuse light e.g. Grace et al.
- Styro-foam e.g. Sherlock et al.

Workshop recommendations: Use (and test) inert materials. Plexiglass is cheap, reasonably light, easily cut to shape and does not require specialist manufacturing. For transparent chamber designs, reflective foils or smoked plexi-glass allow in diffuse light and are effective at reducing significant temperature increases (> 5 °C) over the duration of the enclosure periods .2 – 1 h, except in extreme climates. Stainless steel designs that minimize hoof damage are effective in grazing systems where stock have access to plots.

- **Chamber size**

Footprint

Considerations:
- Balance between ensuring adequate mixing (better in smaller chambers) *versus* minimising spatial variability (better with larger chambers)
- Size of expected 'hot-spots' such as urine patches, crop rows, manure heaps, manure application/injection. Therefore the appropriate size to capture variability of N_2O emissions at the soil surface is often determined by the system where gas measurements are taken.

[1]Lincoln University, New Zealand, Clought@lincoln.ac.nz [2]Agriculture and Agri-food, Canada [3]University of Helsinki, Finland [4]University of Copenhagen, Denmark [5]Plant and Food, New Zealand

- An increase in chamber size will increase risk issues associated with adequate sealing at the soil surface and/or the base to cover, as well as increase the time and resources required to move chambers

Existing recommendations:
- Between 0.1 – 0.2 m^2 however some are larger (up to 2 m^2) according to trial and system requirements
- 182 cm^2 (Parkin & Venterea, 2010)

Examples of common chamber sizes:
- 0.25 m^2
- 0.36 m^2
- 0.64 m^2
- Some > 2 m^2

Workshop recommendations: The size of the chambers should be adequate to capture the variability that exists within a treatment plot due to soil variables. This issue can be approached using larger chambers, or more small chambers. Tests to ensure adequate seal to the soil surface and the base to cover should be performed for chambers >1 m^2 and methodologies to do so should be outlined by authors. Chambers with a footprint >2 m^2 also need to be tested to ensure that there is suitable gas mixing and that sample location(s) within the headspace are adequate. Methodologies for testing should be outlined by authors. Large chambers (i.e. > 2 m^2 or headspace volume > 100 L) require mixing. The effects of mixing/non-mixing in large headspace volumes have also been identified as an area of chamber design that requires further research attention.

Height (pasture, cropland, manure piles)
Considerations:
- Balance between being high enough to minimise very high N_2O concentrations that could increase risk of leakage and of diffusion constraints *versus* low enough to allow i) detection of concentration increase, and ii) adequate mixing of the headspace.
- Crop height might dictate chamber height
- What is the effect of plants within the chamber on gas mixing?
- Does the crop volume in the headspace effect gas concentrations?
- Should crop volume be measured and corrected for in flux calculations?
- Should samples be taken from various locations within the chamber headspace (e.g. Venterea et al.)
- Headspace variance increases as height increases (e.g. modification of the gas gradient with height)
- Long term deployment issues (e.g. chamber height extension for tall crops)

Existing recommendations:
- between 20 and 40 cm height (Rochette, 2011)
- 15 cm height (Parkin & Venterea 2010)

Examples of commonly used chamber heights:
- 10, 15 and 25 cm

Workshop recommendations: Chamber height < 15 cm is problematic to accurately measure headspace volume which will introduce error into flux calculations. Low chamber heights require very accurate chamber volume measurements. Plant volume in headspace < 15 cm is likely to become a significant factor in the headspace calculation. Plants may also affect gas mixing.

- **Chamber venting**

Considerations

- Vented chambers are meant to ensure natural pressure fluctuations occur inside the chamber, so that pressure-induced mass flow of the gas from the soil is maintained.
- Vented chambers are meant to avoid convective fluxes related to pressure gradients
- Balance between maintaining natural pressure fluctuations and pressures inside a vented chamber *versus* risk of 'leakages' or risk of over-estimation of fluxes due to Venturi effect (particularly in windy conditions).
- Samples may be 'lost' in high wind conditions due to wind entering through vent
- In porous soils venting has a significant effect. The effect of a vent is not significant in finer textured soils

Existing recommendations:

- Properly designed vents should be fitted (e.g. Rochette 2011; Parkin & Venterea 2010)
- Caution should be taken with vents as they may create large errors (e.g. Conen & Smith 1998)
- Size: 10 cm long, 4.8 m diameter (Parkin & Venterea)
- Or circular vent (Xu et al 2006)

Examples of commonly used venting systems:

- Both vented and non-vented chambers

Workshop recommendations: A review and summary of the literature is necessary to gain a consensus. There is currently not enough evidence to conclusively support or reject the use of vents in static chamber design, therefore more experimental work is required in this area. It is agreed that a sealable vent should remain open as the chamber lid is being closed to prevent pressure increases within the chamber headspace at this time. A good vent design is to have the vent tube point downwards towards the soil surface as wind velocity and air movement through the vent is reduced in this way. It is expected that withdrawing headspace samples of 20 mL from a headspace volume of 20 L are not big enough to create a vacuum effect through a vent.

- **Chamber insulation**

Considerations:

- Insulation or reflective material/paint will minimise artificial increase in temperature inside the chamber during the enclosure period.
- It is well-accepted that insulation and or reflective material should be used

Existing recommendations:

- Chambers should be insulated to avoid temperature rises

Examples of commonly used materials:

- Reflective foil: e.g. de Klein et al., Chen et al.
- Foam: e.g. de Klein et al.
- White PVC: e.g. Misselbrook et al.

Workshop recommendations: The type of insulation used may be determined by the requirements of the trial.

- **Base and cover**

Considerations:

- Covers need to be able to be adequately sealed to bases/collars
- Cover shape
- Base design can affect the micro-climate inside the chamber, particularly if base sides are high

Existing recommendations:

- Bases/collars should be able to be inserted at least 5 cm into the soil (Rochette & Eriksen-Hamel 2008)

Use rubber, water, or soil for base to cover seals

Commonly used seals and insertion depths:

- Water seal: e.g. Di et al. 2010, de Klein et al. 2011, Misselbrook et al., Rhode et al. 2006.
- Rubber seal: e.g. Alfaro et al., Chen et al., Misselbrook et al., Rhode et al. 2009.
- Soil seal: e.g. Huggins et al.

Workshop recommendations: For *in situ* grazing trials the base design should be made of robust material. Bases should be as flush as possible to the ground to avoid hoof damage, as well as base damage and to minimise the rain/sun shadow effect in the chamber. Covers should be flat, rather than 'salad bowl' shaped.

2. Deployment protocols

Author:[4] Philippe Rochette[1], David Chadwick[2], Søren Petersen[3], Hong Di[4], Keith Cameron[4], Mari Pihlatie[5], Jesper Riis Christiansen[6]

- **Replication and placement**

Considerations:

- Large spatial variability of N_2O emissions (CVs commonly exceeding 100%).
- Some spatial variability can be accounted for by using larger chambers. However, generally a large number of replicate measurements per treatment is required.
- Different scales of spatial variability – e.g. landscape units, soil types, hot spots (e.g. in grazed pasture) – require different sampling designs and chamber replication.
- Chambers need to be placed in such a way that they adequately represent the system to be measured (e.g. crop rows and furrows, grazed system).
- What confidence limits are acceptable for flux estimates?

Existing recommendations:

- As many chambers as possible!
- In plot scale studies, a minimum of 2 chambers per plot (Parkin & Venterea 2010).
- In row-crop systems, place chambers both in rows and inter-rows (Parkin & Venterea 2010).
- Use permanently installed bases (e.g. Rochette 2011, Parkin & Venterea 2010)

[1]Agriculture and Agri-Food, Canada, Philippe.Rochette@AGR.GC.CA [2]Rothamsted Research, United Kingdom [3]Aarhus University, Denmark [4]Lincoln University, New Zealand [5]University of Helsinki, Finland [6]University of Copenhagen, Denmark

Commonly used numbers of replicates:

- Between 2 and 6 for plot studies.
- Between 6 and 18 chambers randomly placed in grazed pastures (e.g. de Klein et al 2006; Saggar et al. 2004).

Workshop recommendations: The number of chambers should be adequate to capture the variability that exists within a treatment plot due to soil variables. This issue can be approached using larger chambers, or a larger number of smaller chambers.

- **Installation**

Considerations:

- Insertion depth should be at least 0.4 cm per minute of deployment (Rochette 2011)
- Separate bases or collars that are installed permanently into the soil can minimise soil disturbance at each sampling event
- Inserting chambers into the soil can cause soil disturbance and pressure fluctuations that can affect the gas emissions.
- Chamber bases/collars may impact on the microclimate of the measurement area (e.g. shading, impairment of lateral water flow causing flooding) and they may need to be moved.
- Permanently installed bases/collars cannot always be used, e.g.in grazed pastures
- Permanent collars can change pre-measurement conditions to affect N_2O production and diffusion rates; factors such as soil water content, water flow, energy balance, redox potential and substrate availability
- Soil disturbances (i.e. cracks, crust, root damage) affect the soil-atmosphere N_2O transfer also

Existing recommendations:

- Install bases/collars at least 24 hours prior to flux measurement (Parkin & Venterea 2010)
- Move bases/collars if the microclimate inside the base is affected.
- 3-5 , 5, 10, 15, 20 cm insertion depth
- Space filler around the inside of the chamber to soil interface where gaps exist due to soil type/conditions

Workshop recommendations: The base should be inserted 24 h before sampling begins to avoid elevated T_0 measurements, to a depth of at least 10 cm. Deeper base insertion is best for longer chamber enclosure periods and for soils with high air filled pore space (AFPS). The time between base insertion and gas sampling may be shortened following grazing, as the effect of grazing is expected to be greater than the effect of base insertion. A summary of the literature to determine the impact of base insertion on plant roots is needed. There are theoretical guidelines available for the effect of insertion on air filled pore space (AFPS), however more experimental data is required to understand this interaction with base insertion over time. Crushed local soil or an inert space filler material can be used for cracks that affect the quality of the seal/contact between soil and chamber base.

- **Sampling frequency**

Considerations:

- N_2O emissions are temporally variable.
- Temporal variability occurs at different scales, e.g. seasonal, diurnal, events-driven (e.g. following rainfall, grazing, fertiliser application, ploughing).
- The frequency of sampling and the sampling pattern may impact on the accuracy of the estimated total N_2O emissions

- Should measurements be made at regular intervals or in response to 'events'?
- Parkin (2008) and Smith & Dobbie (2001) used subsets of automated measurements to assess impact of sampling frequency. They concluded that a when the sampling frequency was once every 3-7 days, the estimated fluxes were within ±10-14% of the 'automated' fluxes.

Existing recommendations:
- Characterise the diurnal N_2O and temperature pattern and if needed use a Q10 correction procedure to adjust the measured flux to a daily average flux (de Klein et al. 2003, Parkin & Venterea 2010).
- In N_2O emission factor studies, the measurement period should capture the entire treatment-induced emission envelope (de Klein et al. 2003).

Commonly used approaches:
- Daily for the first week after treatment application, then 3 times per week for next fortnight, then weekly (Alfaro pers. comm.).
- 2 to 3 times per week for the first 4 to 6 weeks after treatment application, then weekly with extra sampling following 'events' (de Klein pers. comm.; Misselbrook pers. comm.).
- Twice per week (Chen pers. comm.)
- When once per day sampling, measurements are typically made between 11 am and 2 pm.

- **Supporting measurements**

Considerations:
- Ancillary measurements are used to aid interpretation of the measured N_2O fluxes and to drive models.
- Some ancillary measurements will be required at different frequency to others. E.g. soil bulk density, pH, total C and total N content may only be required to be measured once. Others, e.g. soil mineral N, soil WFPS, may be required as often as resources allow. Soil and air temperature and rainfall may be required on a daily or hourly basis.

3. Sample collection, handling and analysis

Author:[5] Frank Kelliher[1], Mike Harvey[2], Andrew McMillan[2], Surrinder Saggar[3]

Sample collection

Considerations:
- Storage in vials or syringes?
- Evacuated *versus* non-evacuated vials?
- Over-pressurising vials when collecting the headspace sample in the field and then returning sample to ambient pressure just prior to analysis in the lab provides QA/QC procedure for samples that are transported and/or stored prior to analysis.
- Time of day samples are collected

Existing recommendations:
- Use 5 to 30 ml evacuated vials and over-pressurise the vial (Parkin & Venterea 2010).
- Over-pressurise samples and avoid storage in plastic syringes as they are leaky (Rochette and Eriksen-Hamel 2008).

[5] [1]AgResearch, New Zealand, frank.kelliher@agresearch.co.nz 2 NIWA, New Zealand [3]Landcare Research, New Zealand

- Sample between the hours of 12 and 2pm

Commonly used approaches:

- Exetainers are widely used vials for N_2O flux measurements (glass with butyl rubber stoppers).
- Over-pressurised glass vials.
- Glass vials at ambient pressure.
- Syringes (plastic or glass).

Workshop recommendations: The time of day samples are taken should represent the average daily flux for a 24 h period. This is generally between 10 am and 2 pm, however tests should be done to determine the exact period for each system. However, time of day is not critical if an appropriate model is used to determine gas flux. It's also important to consider that soil temperature influences N_2O release from soil solution. Workers need to explain what T_0 is for their protocol.

- **Enclosure period and number of headspace samples per period**

Considerations:

- The enclosure period is a balance between long enough to allow detection of significant increase in N_2O concentration and short enough to avoid negative feedback of N_2O concentration on N_2O flux.
- The linearity of the increase in N_2O concentration can be tested if 3 or more headspace samples are taken per enclosure period.
- The cost of extra headspace samples per enclosure period needs to be balanced against using the resources to increase the number of replicates and/or the frequency of sampling.
- Do you introduce more error the more sampling times per enclosure period?
- N_2O is generally produced in 0-5 cm soil depth, however may be produced deeper, however does this N_2O have time to get to the surface in the deployment period? Or is it being consumed on the way up the soil profile?

Existing recommendations:

- The enclosure period should be less than 30 minutes (Rochette 2011).
- The enclosure period should be less than 60 minutes (Parkin & Venterea 2010)
- A minimum of 3 headspace samples should be taken (Rochette and Eriksen-Hamel 2008, Parkin & Venterea 2010).
- The increase in N_2O concentration is commonly linear, particularly when the magnitude of the flux increases, and it is sufficient to take 2 headspace samples. This saves on resources which are better used to increase chamber replication (de Klein et al 2003).

Workshop recommendations: 3 gas samples as a minimum, however there is evidence to suggest that 5 measurements over an enclosure period are optimal. There are however theoretical reasons that some soils are suitable for 2 gas samples, rather than 3. This literature needs to be explored more. Enclosure periods should be no more than 1 hr to avoid pressure changes and formation of gas gradients in the environment under the cover.

- **Length of storage**

Considerations:

- Storage of headspace samples can affect sample integrity.
- Logistics and the number of samples may require samples to be stored prior to analysis

- If samples are over-pressurised, a QA/QC check can be done to ensure leakage has not occurred during storage

Existing recommendations:
- Limit sample storage to less than 45 days (Rochette and Eriksen-Hamel 2008)
- Over-pressurise samples that need to be stored (see above).
- Bring over-pressurised samples back to ambient pressure using a double ended needle in a glass beaker (de Klein et al 2003).

Workshop recommendations: Sample viability can be determined by testing for pressure (if the vials were over-pressurised at the time of sampling). Store standards with samples.

- **Real time and laboratory analysis**

Considerations:
- What are the pros and cons of real-time versus laboratory gas analysis systems?
- What are the pros and cons for different real-time approaches (e.g. GC, FTIR, TDALS, photo – acoustic)?
- ECD preservation and vulnerability to CO_2 or water vapour levels interfering with N_2O peaks
- What is the level of analytical precision of equipment? This will impact on detection of flux.

Existing recommendations: adding magnesium perchlorate will dry samples to preserve ECD from water vapour damage, or putting a scrubber or water trap in the system will eliminate vapour and CO_2. CO2 is a good tracer gas to check instrument integrity.

Commonly used analytical techniques:
- GC most common

Workshop recommendations:

- **Quality Assurance / Quality Control procedures**

Considerations:
- Gas sample preparations and GC injection procedure
- Standard gases and calibration curve
- Order of gas sample analysis
- Inter-lab/GC calibration
- Sampling and storage equipment
- Assigning error to gas sampling method *versus* gas analysis
- Instrument drift

Existing recommendations (Parkin & Venterea 2010):
- GC should be fitted with sample valve
- Samples from individual chambers are run in sequence (e.g. t0, t1, t2,) rather than segregating all the samples by time
- Standards are run periodically throughout the sample run (e.g. every 10 to 20 samples).

Workshop recommendations: Different batches of sample vials and lids have shown variation. Tests should be conducted to check the seals and absorbency of exetainer lids at regular intervals. Pressurising sample vials ensures that sample integrity can be checked at the time of analysis. There is a need to quantify variability in all steps of the gas sampling and analysis procedures. More regular and rigorous inter lab/GC checking needs to be done. Also need to know and regularly check the error of gas standards. Lab standards should be verified across labs also and travelling standards should be introduced to check error. Closer attention to instrument drift. Need to decide (and state in methods) on an error level to accept/reject samples on a trial basis.

4. Data analysis

Author:[6] Rodney Venterea[1], Timothy Parkin[1], Søren Petersen[2] Asger Pedersen[2], Peter Levy[3]

- **Flux calculation**

Considerations:

- An hourly flux is calculated from the increase in N_2O concentration in the headspace.
- Linear, curvi-linear (Hutchinson & Mosier 1981) and quadratic approaches (e.g. Wagner et al 1997) are used, with the latter accounting for a possible negative feedback of the increase in N_2O concentration on the N_2O diffusion gradient and the resulting flux.
- Recently, Pedersen et al., (2010) developed a technique designated as the HMR model, which is a modification of the Hutchinson/Mosier technique to account for horizontal gas diffusion and/or chamber leaks
- We integrate and accumulate studies to produce numbers representative of the total flux for a given system for EFs, however there is always error in flux estimates.
- Inadequate determination of dc/t
- Greater flux = greater linearity. Characterising low fluxes requires sensitive and accurate equipment
- What is the effect of air temperature (i.e. heating and cooling) and humidity on headspace volume? How do we calculate the change for T_0, T_2, T_3 etc for these factors?
- Low porosity soils accumulate less N_2O, which will change to gradient of the flux calculation. Linear calculations are not suited to this type of data. Therefore flux calculations may be determined by soil type/conditions.
- Interrogation of existing data to assess linearity of flux calculations.

Commonly used approaches:

- Most researchers measure (or assume) a linear increase in N_2O emissions particularly as the magnitude of the flux increases (e.g. de Klein et al 2003).

- **Integration method**

Considerations:

- To estimate the total N_2O loss over a measurement period, the hourly measurements need to be integrated over time.
- When a sampling frequency is 'events' based (see above) should the integration method be adjusted during and after peak events (compare graphs below)?
- Grazed pasture systems have 2 different sources of FN_2O populations: urine and inter-urine. These need to be defined separately.
- Diurnal variation needs to be taken into account when integrating data

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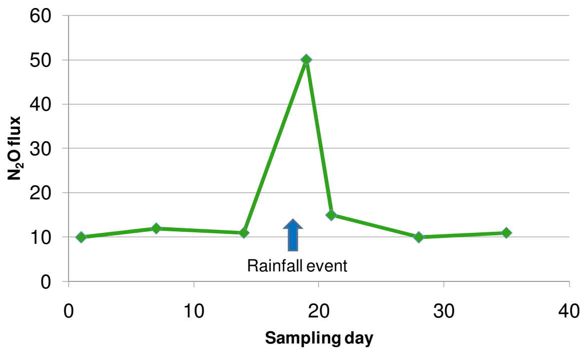
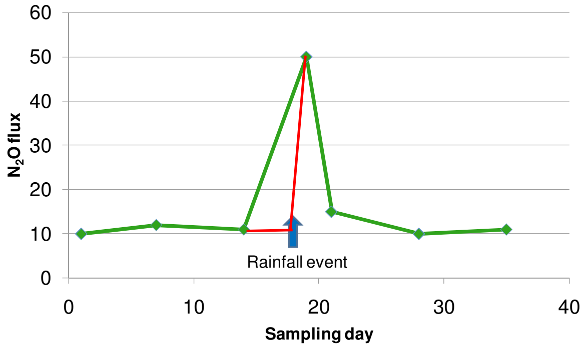
[6] [1]USDA-ARS Soil and Water Management Research Unit, USA, Rod.Venterea@ARS.USDA.GOV [2]Aarhus University, Denmark [3]Centre for Ecology and Hydrology, UK





Commonly used approaches:

- Trapezoid/linear integration method

- **Averaging and statistical methods**

Considerations:

- N_2O fluxes are commonly log-normally distributed and the method used to averaging replicates may influence the 'mean' value (e.g. arithmetic mean, geo-metric mean, median etc).
- Results are often log-transformed to normalise variances and thus allow statistical comparisons.
- Averaging daily fluxes for each treatment and then integrating daily averages over time *versus* integrating daily flux of each individual chamber over time and then averaging the integrated fluxes per treatment.
- How to take into account trampling affects at different soil moisture levels?
- To estimate mean flux we can use arithmetic mean for normally distributed data, geomeans for log-normal distributions, or cluster means for 'groups' of flux data.

Existing recommendations:

- Integrate daily flux of each individual chamber over time and then average the integrated fluxes per treatment (de Klein et al 2003).

What are special considerations for heterogeneous/patchy surfaces?

- **Negative fluxes**

Considerations:

- Are negative fluxes truly negative or are they a result of experimental error?
- Experimental error of GC analysis can be estimated; other experimental errors (e.g. sampling errors are difficult to determine).
- Negative emissions cannot be log-transformed, and an alternative transformation method is needed to normalise variances.

Existing approaches:

- Negative daily fluxes are not adjusted, but integrated over time 'as is'.
- Negative integrated fluxes are adjusted using log (N_2O flux + *a*) approach, where *a* is determined by maximum likelihood based on existing data (van der Weerden et al 2011)

Does anybody have a computer programme they could make available to do the calculations??

5. Automated systems

Author:[7] Peter Grace[1], Tony van der Weerden[2], Kevin Kelly[3]

Considerations:

- Advantages of automated chambers and sampling systems e.g.:
  - More frequent (near-continuous) sampling without increase labour intensity;
  - Characterisation of diurnal variability;
  - Sampling of remote sites;
  - Large data-sets for modelling
- Disadvantages e.g.:
  - Higher costs;
  - Less replication;
  - Complexity;
  - Requires more rigorous QA/QC;
  - Less mobile
- What are key principles of automated systems?
- What are similarities and differences between manual and automated systems?

Workshop recommendations: Issues are generally the same for automated and manual chambers. The air flow/pumping rate in the automated system will determine how many samples are taken per enclosure period. Pumping rate should not affect chamber pressure, and should be verified. The detection limits of the system will determine sampling frequency and pumping rate etc.

6. Data Reporting

Author:[8] Marta Alfaro[1], Donna Giltrap[2], Cecile de Klein[3], UK experts[4]

Considerations:

- This chapter is included as experts agreed there is a need for guidance on the minimum requirements of trial information to i) allow the soundness/robustness of the results to be verified ii) allow other researchers to repeat the work, and/or iii) the results to be able to be included in the emission factor data-base
- What information should be included in reports and papers?
- How should data be reported?

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[7] [1]Queensland University, Australia, pr.grace@qut.edu.au [2]AgResearch, New Zealand [3]Department of Primary Industries, Australia

[8] [1]National Institute for Agricultural Research, Chile, malfaro@inia.cl [2]Landcare Research, New Zealand [3]AgResearch, New Zealand [4]tbc

7.
Health and Safety

Author:[9] David Chadwick[1]

NEXT STEPS

The workshop participants agreed that the development of standardised guidelines is urgently needed to provide consistency, transparency and, probably most importantly, reliability of the measured emissions.

THE participants also agreed that because of the need for this reliability, the development of the guidelines requires more than a literature review and summary of currently adopted approaches. Instead, a critical analysis and thorough discussion of all the issues involved with chamber methodologies is required to ensure the guidelines are credible, pass the scrutiny of the wider science community, and when adopted, provide the best possible emissions estimates.

The next step is for those experts who have indicated their interest in this project, whether it is as an author, lead author or editor, to seek appropriate resources from their national institution to enable them to participate.

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[9] [1]Rothamsted Research, United Kingdom

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