Enhancing confidence in extrapolating emission measurements

MAF Technical Paper No: 2011/88

Report prepared for Ministry of Agriculture and Forestry
By NIWA (CC MAF POL_0708-66)
September 2008

Authors: M Harvey, J Laubach, D Giltrap, N Hudson, D Wheeler

ISSN 2230-2794 (online)
ISBN 978-0-478-38740-7 (online)

October 2011

Ministry of Agriculture and Forestry
Te Manatū Ahuwhenua, Ngāherehere

BIOSECURITY NEW ZEALAND

NEW ZEALAND FOOD SAFETY AUTHORITY

Disclaimer

The information in this publication is not government policy. While every effort has been made to ensure the information is accurate, the Ministry of Agriculture and Forestry does not accept any responsibility or liability for error of fact, omission, interpretation or opinion that may be present, nor for the consequences of any decisions based on this information. Any view or opinion expressed does not necessarily represent the view of the Ministry of Agriculture and Forestry.

Publisher

Ministry of Agriculture and Forestry
PO Box 2526
Pastoral House, 25 The Terrace
Wellington 6140
www.maf.govt.nz

Telephone: 0800 008 333

Facsimile: +64 4 894 0300

© Crown Copyright October 2011 – Ministry of Agriculture and Forestry

Enhancing Confidence in Extrapolating Emission Measurements

NIWA Client Report: WLG2008-71
July 2008

NIWA Project: MAF08309

Enhancing Confidence in Extrapolating Emission Measurements

Objective 2:
Mike Harvey (NIWA)
Johannes Laubach (Landcare)
Donna Giltrap (Landcare)
Neale Hudson (NIWA)
David Wheeler (AgResearch)

Prepared for

MAF Policy Ministry of Agriculture and Forestry

Climate Change — Agricultural Inventory Programme 2007/08

NIWA Client Report: WLG2008- 71
September 2008

NIWA Project: MAF08309
MAF Contract: CC MAF POL_0708-66 (INVENT-10A)

National Institute of Water & Atmospheric Research Ltd
301 Evans Bay Parade, Greta Point, Wellington
Private Bag 14901, Kilbirnie, Wellington, New Zealand
Phone +64-4-386 0300, Fax +64-4-386 0574
www.niwa.co.nz

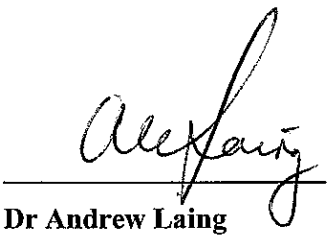
© All rights reserved. This publication may not be reproduced or copied in any form without the permission of the client. Such permission is to be given only in accordance with the terms of the client's contract with NIWA. This copyright extends to all forms of copying and any storage of material in any kind of information retrieval system.

Contents

Reviewed by:

Dr. Andrew McMillan

Approved for release by:



Dr Andrew Laing

Executive Summary

This document aims to provide a comprehensive update on upscaling methodologies that can provide verification for the inventory calculation of agricultural greenhouse gas emission. With a focus on recent work in New Zealand, we consider:

i. existing measurement methods for the quantification of N_2O by chamber and micrometeorological methods (for both CH_4 and N_2O), their pros and cons and some novel techniques including remote sensing methods that will give new insights in the future at larger (regional) scales, particularly for methane.

ii. existing modelling methods, from simple disaggregation (which can be applied to both CH_4 and N_2O) through to semi-empirical and process-based modelling techniques (for N_2O) that could provide a method in the future for a higher (more complex) tier of inventory calculation as well as a basis for testing scenarios and management practices designed to minimise N_2O emission.

iii. a brief discussion around uncertainties associated with upscaling and some recommendations for development of the current measurement and modelling research

There are several motivating factors that stimulated production of the report which included – firstly advances in paddock-scale techniques for CH_4 and N_2O emission in recent years which have developed to the point where they can provide a reliable non-intrusive source of continuous and spatially averaged data at the paddock-scale for both gases although advances in N_2O are more recent and have come about through the deployment of high-precision optical (tuneable diode laser) technology. Secondly, at the paddock-scale and beyond, a number of model frameworks for greenhouse gas accounting through to full simulation continue to be developed and can now benefit from a wider range of verification data. It is through model-based upscaling that there is the potential to produce an inventory of higher tier (using IPCC terminology). We briefly discuss uncertainty aspects of this and the constraints of additional data requirements. A final motivation is the increasing interest on both inventory and measurement down at the paddock-scale. This comes about through the need to test the efficacy of mitigation treatments (nitrification inhibitors) at larger scales designed to reduce greenhouse gas emission and provide other co-benefits and through the design period of an emissions trading scheme that has been considering emissions down at farm-scale.

1 Introduction

The update follows from the previous report of Harvey et al. (2005); in the 3 years since the previous review there have been significant advance in technologies available and in the application of methods for paddock and regional scale assessment.

As a back-drop to the report, Figure 1 shows a typical upscaling framework, here with a focus on nitrous oxide.

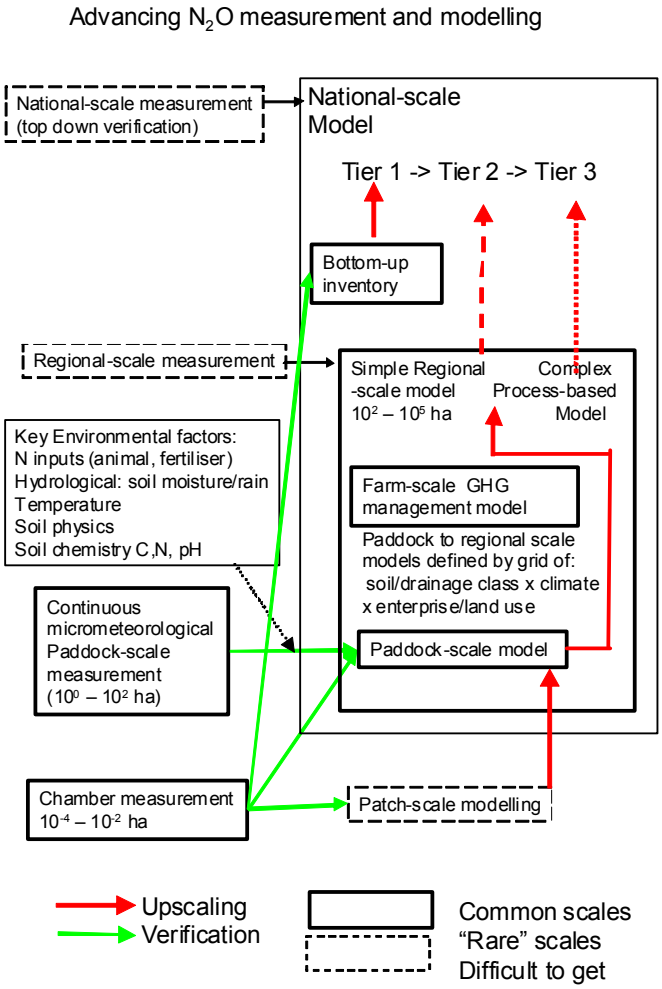


Figure 1: Upscaling framework e.g. for nitrous oxide. Commonly available scale in measurement and modelling are shown in bold boxes. Scales where measurement and modelling is much more difficult are shown as dotted boxes.

Measurements have typically made at small scales (chambers) to provide verification for models at larger scales (from paddock scale process models through to verification

of bottom-up Tier 1 inventory estimates based on emission factors for particular N_2O emission processes. In recent years, paddock-scale measurements have become possible through the use of high precision optical detectors (e.g. tuneable diode lasers) and these measurements can be used as a basis for model development and verification at the same scale. Through upscaling techniques, particularly model-based upscaling it is possible to take models verified in a particular environment at paddock- or farm-scale and extrapolate to larger scales. Through this type of model-based upscaling, it is possible to extend emission estimates to the national scale and potentially form the basis for a more complex or high tier inventory methodology. The major limitation of this approach is the much greater data requirement required to verify the extended modelling with a well quantified uncertainty.

1.1. Review of direct measurement techniques

A comprehensive review is presented of techniques as applied in New Zealand for methane and nitrous oxide emission assessment on-farm. The use of micrometeorology for emission factor verification is discussed as well as recommendations on future research and application of these techniques. Consideration is given to novel techniques.

The accurate determination of rates of emission or uptake of greenhouse gases (GHG) or volatile materials from area sources such as agricultural paddocks, anaerobic treatment ponds, feedlot pads and compost windrows requires careful application of measurement techniques. There are two approaches to measurement that are commonly adopted:

- Chapter 2 considers enclosures: intrusive sampling devices, where a chamber, hood or wind tunnel, is deployed on an emitting surface. The device may be static (sealed or vented) or dynamic (flushed with contaminant-free carrier at a known velocity or flow rate). The emission rate is calculated as the rate of concentration increase in the static case or product of concentration and airflow through the device in the dynamic case [e.g.(Balfour et al. 1987, Conen & Smith 1998, Eklund, B. 1992, Eklund, B.M. et al. 1985, Fukui & Doskey 1996, Gholson et al. 1989, Gholson et al. 1991, Peu et al. 1999, Raich et al. 1990)].

- Chapter 3 considers non-intrusive micrometeorological techniques, including novel approaches where the emission rate is calculated from concentrations measured across the plume of emitted material along with local meteorological data, specifically horizontal and vertical wind

velocity profile data or from the direct high-frequency measurement of concentration and eddy transport velocity within a uniform flux field [e.g. (Christensen et al. 1996, Denmead et al. 2000a, Kim et al. 2005, Magliulo et al. 2004, Yamulki et al. 1996)].

The conclusions of a review of techniques conducted two decades ago by Wesely (1989) are still relevant today and "point out that there is no single system or technique for flux measurement that is universal. Rather a combination of techniques must be used, depending on environmental conditions and the technology of species measurement." An update on techniques for measuring fluxes of nitrous oxide and methane at various scales has been recently produced by Denmead (2008). This excellent review provides a broad overview of the various techniques, and summarises many of their recognised benefits and disadvantages.

Beyond the common approaches, Chapter 4 reviews current and future remote sensing prospects.

1.2. Review of modelling techniques

Whilst soil N_2O emissions can be estimated at the small scale using chambers, and spatially integrated measurements can be made at the paddock-scale using micrometeorological techniques, it would be impractical (in terms of cost) to establish a network with the sampling intensity needed to provide national emission estimates based solely on measurements without use of models for extrapolation. Chapter 5 in this review considers modelling approaches that have been pursued in New Zealand and have great promise as upscaling methodologies. The review includes potential Tier 2 methodologies (IPCC 2006) where a framework is developed to re-aggregate the results of spatially and otherwise disaggregated emissions factors. This could potentially provide a national estimate of lower uncertainty than under Tier 1 although this is by no means certain. Beyond that, there are semi-empirical approaches such as the Boundary-Line technique (Conen et al. 2000) that is of intermediate complexity between an emission factor based approach and a full-process-based model. Two process-based models: DayCent and NZ-DNDC are considered. The process-based approach (Giltrap et al. 2007, Saggar et al. 2007a) could form the basis of a complete Tier 3 methodology following significant model calibration and validation over a range of landscapes and farming systems. Chapter 6 presents some initial discussion of the challenges and uncertainties of model-based upscaling. Chapter 7 provides some conclusions and recommendations to take the measurement and modelling work forward.

2 Direct measurements: chamber-scale techniques

This chapter discusses soil chamber and paddock wind-tunnel measurement, with a particular emphasis on quantifying nitrous oxide emissions. Chambers (sometimes referred to as animal calorimeters) can also be used to enclose and study individual animal emissions. This report does not consider this type of measurement. We note that facilities for ruminant methane measurement have developed significantly recently through the extension of the animal calorimetry facility at AgResearch Grasslands, Palmerston North, with the aim of producing a premier research facility for the rapid and highly accurate measurement of methane emissions from forage fed sheep and cattle.

2.1 Chamber description

Chambers provide a convenient method for measuring the rate of emission or flux of volatile materials from a particular surface of interest. Chambers are placed on a surface, and the motion of the overlying air is controlled so that the fluxes of gases lead to measurable changes in concentration within the chamber volume over time. The emission (or deposition) rate can be calculated from the time-dependent changes in headspace concentration.

Chambers are specifically designed to obtain emission rates from "area sources", but are not suitable for determining emission rates from volume sources (such as poultry sheds, piggery buildings and other animal housing), or point sources, such as stacks. Other techniques are used for sampling from volume and point sources.

A wide range of chamber designs and methodologies have been developed. The differing approaches reflect (1) a desire to sample at a sufficient spatial and temporal frequency to adequately characterize the emission rates from the surface of interest; (2) to avoid artefacts associated with the enclosure of the overlying air or placement of the chamber; (3) obtain concentrations or samples within the chamber that can be measured with the analytical device. Below, we discuss the range of physical characteristics of chambers, and the various operation modes employed in the field.

2.1.1 Physical characteristics

The principal physical characteristics of chambers are: shape of the area enclosed (chamber footprint); the dimensions of the area enclosed (footprint area); the volume of the chamber (chamber height divided by the footprint area).

In a recent review, Hudson and Ayoko (2008) considered 92 different emission devices and chambers, selected from the literature. While the review focused on use of these devices from the perspective of collecting samples of odorous air, most of the devices were used to collect samples of other volatile materials, including greenhouse gases.

Twenty-seven of the devices selected were categorised as cylindrical, while the remaining 65 were rectangular.

Figure 2: Static chambers: left: 100 mm diameter machined PVC ring – semi permanent collar as receptacle for CO_2 flux chamber, right: 300 mm diameter static chamber with removable lid for N_2O measurement – (design – Landcare Research)

Diameters of the cylindrical devices included in the review ranged from 76 mm to 325 mm, and internal volumes from 2.2 L to over 66 L. The area covered by the cylindrical devices was quite small, the largest being 0.33 m^2.

Rectangular devices were more diverse in size and shape. The area of the chamber footprint ranged from 0.01 m^2 to 113 m^2. Internal volumes were also more diverse, ranging from 0.1 L to 512 000 L

Rochette and Eriksen-Hamel (2008) recently reviewed use of chamber measurements of N_2O emissions. Part of their review focused on the physical dimensions of the various chambers used for these measurements. They were of the view that an area: perimeter ratio greater than about 100 mm was required to ensure that leakage did not adversely influence the measurements. This publication is reviewed extensively in Section 2.7 Uncertainty discussion, because it draws attention to many aspects of chamber design, operation, sampling and measurement that must be addressed to ensure good quality data are obtained. Pape et al. (2008) provide a list of details for a number of chamber designs as well. Their paper is also included in this review.

2.1.2 Operating Principles

Chambers can be broadly categorized as flow-through or closed. Flow-through (also known as "open") chambers allow a constant flow of outside air to exchange with the headspace whereas closed chambers allow no, or very little, exchange with the atmosphere. Flow-through chambers require that the concentration is measured both at the inlet and outlet of the chamber whereas closed chambers require a measurement only within the headspace volume. A wind tunnel is a type of flow-through chamber in which the air flow is large, and intended to simulate external aerodynamic conditions.

Closed chambers can be further categorised into static chambers and dynamic chambers. With static chambers, the headspace volume is enclosed and not circulated over the enclosure period. Typically, a series of grab samples are removed from the headspace volume at known intervals, and stored for off-line analysis. For example, gas syringe samples can be extracted and analysed at a later stage by gas chromatography.

With dynamic chambers, the headspace volume is continually monitored for concentration using an in-line analytical sensor. This requires that the headspace volume is re-circulated in a closed loop between the volume overlying the surface and the analytical sensor. A common configuration for measuring soil CO_2 fluxes is an automatically opening and closing chamber that is in line with a closed path infra-red gas analyser (IRGA) and a pump. The pump returns analyzed air back to the chamber headspace. These systems allow immediate determination of flux rates and are able to detect when headspace concentrations become sufficiently high to inhibit further upward flux via interference of concentration gradients. Some sophisticated systems incorporate scrubbing columns to remove emitted CO_2 thereby avoiding this artefact.

2.1.3 Literature describing use of chambers

A number of generic descriptions exist to guide practitioners in the collection of samples of volatile materials. For instance, Gostelow (2003) describe the use of wind tunnels and flux chambers for the collection of samples of odorous air, Klenbusch (1986) and Gholson et al. (1989, 1991) describe use of the dynamic emission chamber for characterising emissions of volatile organic compounds from contaminated soils and storage lagoons. Matson and Harriss (1995) describe chamber methods for measuring soil gas emissions.

In New Zealand and Australia, a draft standard was recently open for public comment (Standards Australia and Standard New Zealand 2008). It was prepared to describe best practice use of two chamber devices and a wind tunnel for the collection of odour samples. While no single standard or approved method exists for sampling emissions of GHG using chamber methods (de Klein, pers. comm. Keith & Wong 2006 referring to measurement of CO2 efflux from soils), the recent literature provides many examples of techniques in common use. Many recent uses of chambers follow the calculation protocols published by Hutchinson and Mosier (1981). The recent critical review of Rochette and Eriksen-Hamel (2008) should be considered by anyone currently using or intending to use a non flow through, non steady state chamber device. Rochette and Eriksen-Hamel (2008) identify a number of useful publications summarising use of non-steady-state devices for sampling soil gases. Pape et al. (2008) provide a useful list a number of publications where dynamic chambers were used for measurement of reactive gases (particularly NO and NO_2). Table 4 of their paper summarises materials of construction, flushing air used and basic quality control procedures. This Table also provides an indication of the very different conditions likely to result from the chamber volumes, flushing rates and closure times used. Seven of the 25 publications reviewed made use of automated systems that closed the chamber prior to measurement.

2.2 Sampling methodology

When using a chamber device for determining emission rates, the following actions are necessary: (1) selection of sample area; (2) insertion of chamber or chamber base; (3) sealing between the chamber and the surface; (4) sample collection or concentration measurement; (5) collection of ancillary measurements.

2.2.1 Selection of sample area

An area representative of the entire emitting surface is selected, on which the device is then deployed [often this selection process is subjective, based on visual appearance

(e.g. wet vs. dry, which in an agricultural context may be urine versus non-urine affected patches)];

2.2.2 Insertion of chamber or chamber base

In most cases, the chamber is inserted into the emitting surface as far as possible [e.g. (Parkin 2008)], hopefully creating a leak tight seal, or it may be placed on top of this surface. However, insertion of the chamber can disturb the ground and enhance diffusion rates and/or release gases stored temporarily within the soil [e.g. (Gerlach et al. 2001)].

To minimize disturbance of the surface, a steel ring or rim can be inserted into the emitting surface to provide a semi-permanent "collar", on which the device may be mounted during a sampling.. This approach is often used when it is necessary to collect a series of samples from a location, for instance over a growing season, or over a rainfall event, or as an applied nutrient is utilised by a crop. Following initial collar installation, the site needs to be left for a period before sampling is initiated.

2.2.3 Sealing between the chamber and the surface

It may be necessary to improve the seal (i.e. reduce or eliminate leakage of air) between the chamber, or the collar, and the surface through placement of suitable material, such as a clean, dry sand, around the outside of the chamber [the quality of the seal is generally presumed, not determined experimentally]. Sealing between the collar (if used) and the chamber can be achieved by use of soft rubber seals or threaded seals. Alternatively, a guttering around the top edge of the collar can be filled with distilled water, and the bottom edge of the chamber fitted into this guttering. The ~2 cm depth of water forms a gas tight seal around the base of the chamber. This design is particularly well suited for methane flux measurements because of the low solubility of methane in water.

2.2.4 Sample collection or concentration measurement

Sample collection or concentration monitoring should proceed immediately following chamber placement. When using a dynamic device, a stabilisation period ensues, during which flushing of the device takes place (typical stabilisation periods are between five and 20 minutes duration).

2.2.5 Ancillary measurements

Depending on the measurement and calculation protocols followed by the practitioner, other data can be collected during the period of enclosure. Typically these data include the air temperature inside and outside the chamber, soil temperatures at specified depths, pressure within the chamber etc.

Figure 3: University of New South Wales style wind tunnel and US EPA flux chamber in feedlot. Note the use of clean sand to improve seal between device and emitting surface

2.3 Typical chamber protocols

2.3.1 Chamber Selection and Placement

De Klein et al.(2003) provide an example of "best practice" use of chamber methods under New Zealand conditions. Two slightly different methods of chamber deployment were described by De Klein et al. (2003), necessitated by the differences between field- and laboratory-scale emission measurements. During field sampling, the chambers were placed on the same position on each sampling occasion. The

chambers were inserted 30 mm into the emitting surface to achieve a seal. Thirty minutes following chamber placement, the two ports providing access to the chamber headspace were sealed and sampling commenced. For the laboratory measurements, a gas tight top was placed on the chamber and sampling commenced immediately.

Other researchers [e.g. Skiba et al. (1998)], utilise slightly different techniques. In order to measure N_2O emissions from a grazed paddock, a collar was inserted permanently into the emitting surface. On each sampling occasion, the chamber was placed on the collar 60 minutes prior to sampling. Commencement of sampling followed immediately on from sealing the ports into the chamber headspace. Where livestock was not an issue, the chamber walls were left in place permanently. The chambers were sealed following placement of a Perspex lid. Either of these techniques minimised soil disturbance, known to bias emission rates [e.g. (Keith & Wong 2006)].

Manual chamber techniques similar to those used by Skiba et al. (1998) were used in project GREENGRASS, where exchange fluxes of N_2O were monitored over a three-year period at 10 locations in eight European countries. A range of climate, soil and environmental conditions were included (Flechard et al. 2007). Automated chambers were also utilised to enable more intensive monitoring.

Smith et al. (1995) describe use of “closed” and “open” (flow-through) chambers. The closed chambers were very similar to those described by Skiba (1998) and de Klein (2003). The “open” chambers are in fact closed, but continuously ventilated to enable analysis of NO; under these circumstances, it is necessary to concentrate the diluted N_2O sampled from the headspace using molecular sieve traps.

Parkin (2008) described use of a series of four automatic static chambers. The chamber lid was open unless measurement was in progress. The chamber was vented to allow pressure equilibration. Measurements took place four times daily. Extensive data collection included within and external air temperature measurement, soil temperature at four depths and differential pressure (chamber headspace vs. ambient pressure).

Large volume chambers may also be used to measure soil gas emissions. They have larger footprint, thereby reducing the effects of spatial variability. Their use was briefly described by Smith et al. (1995). In this application, a chamber measuring about 2 m in width by up to about 30 m in length was formed using polyethylene sheet and plastic hoops. The volume of the chamber thus formed was between 40 and 47 m^3, significantly larger than those typically used.

2.3.2 Measurement of concentrations

Two basic approaches exist when chamber devices are used to estimate emission rates:

- On-site measurement of concentrations, or
- Off-site measurement of concentration, either
  - in whole samples collected in suitable containers and taken as such to a laboratory facility, or
  - analysis of volatile constituents which have been trapped on a solid phase sorbent, or within a liquid trapping solution.

2.3.2.1 On-site measurements

On-site measurement obviously requires all analytical and sampling equipment to be present on site. While it can present logistical challenges with certain applications, it offers the benefit that data are potentially available immediately, allowing the sampling campaign or analysis to be modified as required. More frequent monitoring is also likely – significant infrastructure is deployed, making automation of all aspects of the emission measurement process more attractive.

An increasing array of options is available for on-site determination of chamber concentrations. For CO_2 flux rates, closed path IRGAs are widely available, relatively inexpensive, easy to operate, portable, and can be powered by batteries. They are rapid response and have sufficient sensitivity to detect small fluxes. Several vendors offer integrated systems that incorporate the IRGA, one or more chambers, and the associated plumbing and pumping apparatus. PP Systems Ltd (Hitchin, UK) produce a small portable chamber, covering an area of 0.008 m^2 (Soil respiration chamber: SRC-1 chamber) coupled to an infrared gas analyser (EGM-4 IRGA) system http://www.ppsystems.com/co2_gas_analyzers.htm. For longer term deployment Licor Biosciences produce the Automated Soil CO_2 Flux System (LI 8100 http://www.licor.com/env/Products/li8100/8100.jsp) with an rugged IRGA and environmental logger which can be coupled to a single automatic chamber or network of up to 16 multiplexed chambers to provide spatial averaging.

An array of dynamic chambers can be connected to a single analyser, via a sample manifold/pumping system. When coupled with mass flow controllers and automation software, a series of measurements may be made from a number of devices

sequentially, allowing trends over both space and time to be assessed. While this approach is not as readily applicable to non-steady state devices, where the measurement must commence immediately following deployment of a sealed or vented chamber on the emitting surface, examples do exist in the literature. Pape et al. (2008) described an automated dynamic chamber system, capable of simultaneous measurement at up to six discrete locations. In this application, the chambers were intermittently closed, with measurement taking place over a 12-minute period during each hour. The intermittent closure minimised the interference to natural conditions, unavoidable when a chamber system is used. The Licor Biosciences LI-8100 follows this approach.

While on-site concentration determinations with flow-through or closed-dynamic chamber systems are most frequently applied only to CO_2 exchange, recent advances have made it possible to quantify other greenhouse gases. A range of other, more specific analysers are also available to allow measurement of one or more GHG, utilising a range of analytical techniques, mainly based on spectroscopic methods[1]. Denmead (2008) describes a system where concentrations inside an array of automated dynamic chambers were sequentially analysed for CH_4, N_2O and CO_2 by an on-site Fourier Transform Infra-red (FTIR) spectrometry.

2.3.2.2 Off-site measurements

Off-site measurements are often the only option for materials present in low concentrations, or where sophisticated analysis is required, possibly involving pre-concentration and/or chemical derivatization prior to measurement. Samples usually have to be concentrated, requiring sorbent traps. An extended sampling interval is often required to collect sufficient sample (typically 30 to 60 minutes), and may constrain the numbers of samples that may be collected.

The analytical requirements of trace gases such as CH_4 and N_2O are more demanding and it is generally more practical to measure their concentrations off-site. Gas chromatography (GC) is the most common form of analysis. The GC detection system varies according to the concentration and the detection requirements of the gases of interest. For high concentration samples, e.g. CO_2 and CH_4 in biogas, thermal conductivity detectors (TCD) are useful because they are inexpensive and can measure the concentration of multiple gases simultaneously. In most situations, the concentration changes of CH_4 and N_2O are too small for detection by GC-TCD, and separate GC systems must be used for each gas. CH_4 concentrations are measured

[1] e.g. CO_2 - http://www.thermo.com/com/cda/product/detail/1,,10120732,00.html, Multiple GHG - http://www.thermo.com/com/cda/product/detail/1,,10142250,00.html, http://www.picarro.com/docs/datasheet_measurement_trace_gases.pdf

using a flame ionisation detector (FID) and N_2O concentrations are measured using an electron capture detector (ECD). While GC-FID determination of CH_4 is relatively straightforward, GC-ECD determination of N_2O requires reasonably complex flow splitting and venting to avoid exposure of the ^{63}Ni in the detector to excessive concentrations of oxygen. Multiple detector GC methods have been developed to simultaneously determine CO_2, CH_4 and N_2O (Sey et al. 2008).

For CH_4 and N_2O off-site analysis, the concentration of gas collected at different intervals from within the chamber volume is sufficient to allow direct injection directly into a GC without the need for pre-concentration. Therefore the sampling procedure simply requires removing grab samples from the chamber and storage until analysis. Grab samples can be removed the chamber using a gas-tight syringe, or by pumping into a Tedlar bag or evacuated sampling canister. The air may be transferred from the syringe to a container with better storage characteristics if the analysis is not immediate.

De Klein et al (2003) utilised simple rubber-stoppered, evacuated glass vials for both collection and storage of samples prior to analysis of N_2O. A sample volume of 6 mL was withdrawn at three specific times following chamber placement or sealing. At other sites, 50 mL volume of air was withdrawn from the headspace using a syringe and transferred to a 6 mL evacuated tube. Skiba et al. (1998) withdrew sample volumes of 500 mL twice following chamber placement or sealing using large syringes. These samples were then transferred to Tedlar bags for transport and storage prior to determination of N_2O concentrations. In the case of de Klein et al. (2003), the discrete samples represented about 0.1% of the headspace volume. For the two chambers used by Skiba et al., the individual samples represented about 2% and 0.15% of the headspace volume respectively.

2.4 Calculation of emission rates or flux

The control of the headspace air differs between different chamber designs, leading to different relationships between the flux and the time-dependent concentration changes. Consequently, the formulae for calculating the fluxes have different forms.

2.4.1 Closed or static chamber devices

The flux of a gas measured in a closed path chamber is:

$$f = \frac{V}{A}\left(\frac{d\rho_g}{dt}\right) = h\left(\frac{d\rho_g}{dt}\right) \qquad \text{Equation 1}$$

Where f is the flux of the gas of interest, V is the volume of the chamber, A is the area covered by the chamber, h is the headspace height and $\left(\frac{d\rho_g}{dt}\right)$ is the change in the headspace gas density (mass/volume) as a function of time. This latter term can be calculated from linear or non-linear regression, or by finite difference. In practice, GC measurements of the grab samples provide a volumetric mixing ratio (e.g. volume per unit volume) rather than a mass density (ρ_g, mass per unit volume). Using the ideal gas law, the molar weight of the gas and a temperature or pressure measurement inside the chamber, the mixing ratio is converted to a mass density. Ideally this correction is done at each sample removal since pressure or temperature may change during the course of enclosure.

The major disadvantage of the static chamber approach is that large concentrations of gases can accumulate within the headspace, decreasing the vertical concentration gradient and potentially inhibiting the physical and biological processes contributing to the flux. This problem implies that linear fits to the concentration time series are probably inappropriate and non-linear models may better describe concentration changes inside the chamber.

Hutchinson and Mosier (1981) proposed the use of Equation 2 to correct the error in the flux determination due to the decrease in the concentration gradient over the course of chamber enclosure, requiring a correction.

$$f_0 = \left(\frac{V(C_1 - C_0)^2}{At_1(2C_1 - C_2 - C_0)}\right)\ln\left(\frac{C_2 - C_0}{C_2 - C_1}\right) \qquad \text{Equation 2}$$

where C_0, C_1 and C_2 represent concentration measurements at three different times. The rate of change of headspace concentration is used to determine the emission rate, which is then corrected to provide a flux estimate at t_0, the time of chamber placement.

Other non-steady state diffusion models have been developed to address this problem, and were recently discussed by Livingston et al. (2006). Livingston et al. (2006) demonstrated that linear models, as well as more complex quadratic models, probably introduce errors into the estimation process. They also drew into question the basic design of many of the non–steady-state chambers; the dimensions of many the devices

were optimised to promote apparent linearity of headspace concentrations with time. While they proposed that a time-dependent diffusion model offered advantages, they also indicated that performance of the model needed to be validated experimentally.

2.4.2 Dynamic chamber devices and wind tunnels

Concentration inside dynamic closed chambers and flow-through chambers can either be measured either on-site or off-site. For both types of chamber, a period of equilibration occurs immediately after chamber deployment. Once conditions have stabilized to approximately steady state conditions, determination of flux rates can proceed. The flushing rate of the headspace must be known, and can either be set at a known and controlled rate, or measured over the duration of the enclosure. For dynamic closed chambers, the flushing rate is typically in the range of 1 to 20 L/min, but for flow-through chambers, such as wind tunnels, much larger flushing rates are used, ranging from hundreds to thousands of L/min.

Once the concentration of the gas is known, the calculation of the emission rate is straightforward and an equation of the form in Equation 3 is used (Pape et al. 2008):

$$f = \left(\frac{Q}{A}\right)\rho_d \left[\mu_{out} - \mu_{in}\right] \qquad \text{Equation 3}$$

Where Q is the chamber flushing rate (typically L/min), ρ_d is the molar density of dry air and $\mu_{out} - \mu_{in}$ is the concentration difference between flushing air leaving and entering the chamber (if cylinder gas, e.g. instrument grade air is used, μ_{in} is typically zero for N_2O or methane).

2.5 Short term versus automated long-term chambers

Much of the above discussion has to be considered each time a chamber is placed for a measurement. However, considerable effort has been made to establish a number of long-term measurement sites with semi-permanent chamber installations with automated operation, data collection and telemetry. The Department of Primary Industries, Australia, has established two sites in Victoria on grazed (Hamilton) and cropped (Horsham, Figure 4) land to follow emissions from specific treatment plots over entire years or growing seasons. The chambers at these sites are designed to open or flush and minimise environmental disturbance of the structure. In addition to their long-term measurement capability, the chambers are also designed to provide data from a number of replicated treatment plots. Having this capability with chambers for a well-defined patch or plot is complex but less “equipment-intensive” than trying to

achieve the same replicated experimental plot result with a micrometeorological approach.

Figure 4: "Open top" automated chambers in Horsham, VIC

2.6 General advantages and drawbacks of chambers and tunnels for emission measurements

2.6.1 Potential advantages

Wind tunnels and flux chambers offer a number of benefits over other techniques used to measure emission rates.

- The process is conceptually and computationally simple.
- With a large gas concentration headspace in the chamber, they have two orders of magnitude lower detection limit on flux compared with micrometeorological approaches
- The numbers of variables requiring control or management is limited (generally only flushing rate).

- The devices are generally quite simple to manufacture, and therefore moderately priced.

- The technique allows multiple emission devices to be connected to a single analytical unit, allowing trends over time and space to be assessed. This is often a very cost effective method to overcome the potential bias introduced by spatial inhomogeneity.

2.6.2 Potential disadvantages

- Both chambers and wind tunnels cover relatively small areas. In agricultural systems, greenhouse gas emissions may occur over large areas of the landscape, e.g. from an entire paddock or farm, from a large treatment pond, or from a wetland. It is unlikely that the area selected for chamber placement will represent the average emission from an area source, thereby introducing bias into the emission rate estimate. To overcome this issue, it is necessary to make a sufficiently large number of replicate measurements, which in turn is tedious and requires significant resources.

- Deployment of chambers, no matter how carefully, disturbs the system from which the sample is being derived. Perturbations that have been documented include:

    - Altering the solar radiation to which the emitting surface was subject;

    - Altering the temperature in the air immediately above the emitting surface;

    - Altering the rate and distribution of rainfall to the surface;

    - Altering the influence of turbulent atmospheric processes, e.g. almost eliminating the wind speed within a static chamber, altering the turbulence within the headspace of a dynamic chamber, but in a non-uniform fashion, altering the wind speed and turbulence characteristics above the emitting surface within a wind tunnel;

    - Altering the pressures within both wind tunnel and chambers relative to the adjacent, uncovered emitting surface.

Figure 5: Relative size of wind tunnel and flux chamber to a typical anaerobic treatment pond

- The composition of the air within both wind tunnel and flux chamber is altered relative to that above the adjacent, uncovered emitting surface:
    - For a static chamber, the rate of change of headspace concentration is used to determine the emission rate, i.e. the technique depends on the fact that the system being assessed will be altered.
    - In the static chamber, the increase is non-linear and asymptotically approaches a maximum value.
    - In the case of a dynamic chamber, the headspace is also altered. Typically, the headspace concentrations of the variables of interest are increased, but to new, equilibrium-like values (i.e. the concentrations do not continue to increase over time).

- When used on liquid surfaces and very moist soils, condensation within the device can be an issue, particularly for reactive gases [e.g. (Pape et al. 2008)].

Figure 6: Condensation occurring within the headspace of a flux chamber

- Increasing headspace concentration decreases the concentration driving force that is fundamental to all mass-transfer processes. The likely impact would be a tendency to depress emission rates. The increase in concentration is however often viewed as a benefit, because it may make the detection and analysis of volatile compounds easier. Bekku et al. (1997) utilised static, dynamic and flow-through chambers to measure rates of emission of carbon dioxide from soils. They confirmed that emission rates could be depressed by increases in concentrations of carbon dioxide in the headspace of static chambers. They were able to minimise the impact on measured carbon dioxide emission rates by limiting the chamber placement period.

- A wind tunnel is likely to introduce other effects. The large flushing rate may decrease the concentration of the variable of interest relative to the air above adjacent, uncovered surfaces, making analysis of the sample more difficult.

- Absence of guidelines or standards in the design and operation of the many different wind tunnels and flux chambers must also be regarded as disadvantageous.

Many of these issues remained largely unresolved. For example, the debate regarding optimal chamber design and utilisation was reviewed by Hutchinson and Livingston (2001). They identified that for non-steady state devices (i.e. static chambers), a properly designed and installed vent tube is vital for performance; leakage at the interface between the chamber and the emitting surface remained a significant source of potential error. Pressure fluctuations were shown to be quite large, potentially exerting a significant effect on flux measurements made soon after chamber deployment. While recommendations were provided regarding best design and installation of a vent tube in order to reduce pressure effects, validation is still required.

More recently, Livingston et al. (2006) indicated that the curve fitting procedure used to calculate GHG emission rates using results from static chambers was probably a significant source of error. Livingston et al. (2006) recommended using a non-linear model. This recommendation is important – previous uses of linear model to fit headspace concentration data encouraged the construction of relatively tall devices, which were then used over long placement and measurement periods. The sensitivity of such chambers to pressure effects was also illustrated. Once more, a properly designed and installed vent tube was regarded as a solution to this problem.

Limited comparisons of emission rates using static chambers and device-independent methods have been undertaken. Smith et al. (1994) compared flux measurements made with chambers with those derived from two micrometeorological methods. Fluxes determined from chamber measurements (210 to 300 ng N_2O-N m^2/s) were over a factor of two higher than fluxes determined from micrometeorological measurements (43 to 85 ng N_2O-N m^2/s). Christenson et al. (1996) observed better agreement between chambers and micrometeorological approaches. Because of natural spatial and temporal variability in emission, it is **especially important** that a true comparison is conducted with (i) identical plots of land being measured (i.e. the same flux footprint) (ii) during concurrent times for both the chambers and micrometeorological techniques. For N_2O emission in New Zealand, some initial comparisons between chamber measurement, atmospheric and process-based model predictions were made by Saggar et al. (2005a). This paper gives some insight into the challenges faced in

comparison of quite different techniques and the potential for errors to multiply in upscaling estimates.

2.7 Uncertainty discussion: physical aspects

The uncertainty discussion is divided between errors arising from (1) physical aspects of chamber measurement and (2) errors arising from the difficulty of capturing spatial and temporal variability in flux in an inhomogeneous flux field. This difficulty is particularly pertinent to emissions of N_2O from pastoral agriculture which are characterised by significant areal variability and is dealt with below in 2.8 Uncertainty discussion: Areal variability.

2.7.1 Physical aspects: Reliability of chamber nitrous oxide emission estimates

Following their review consideration of 356 published studies of N_2O emission, Rochette and Eriksen-Hamel (2008) concluded that the results of flux estimates in only about 40% of all studies should be regarded to have better than a medium confidence score (as defined in Table 1), and 60% of the results should be regarded with "low confidence".

Table 1: Confidence level definitions

Confidence level	Underestimation of flux (%)
High	0 to 10
Medium	0 to 30
Low	10 to 50
Very low	20 to 60

The quality of most of the published measurements of N_2O flux was regarded as poor. The criteria they developed to assess the quality of these results are useful for generally evaluating emission estimates making use of chambers. When compiling their criteria, they identified binary characteristics and numeric characteristics. In general errors arising from measurement practice were generally additive, and would lead to a cumulative under-estimation of N_2O flux. These were summarised in Table 1 of their paper, which is summarised below in Table 2:

Table 2 **Criteria for evaluating best practice N_2O flux measurement using non-steady state chambers [from (Rochette & Eriksen-Hamel 2008)]**

Chamber characteristic	Unit for numeric criteria	Rating			
		Very poor	Poor	Good	Very good
Type of chamber			Push-in, single piece		Base and chamber
Insulation			No		Yes
Vent			No		Yes
Pressurised, fixed volume sample			No		Yes
Quality control sample		No			Yes
Time zero sample collected			No		Yes
Non-linear model considered		No			Yes
Zero slope tested			No	Yes	
Temperature correction			No		Yes
Sample container		Plastic syringe	Glass syringe	All other vials	Exetainers®, Vacutainers®, on-site measurement
Height of chamber	cm	<10	10 to <20	20 to <40	≥40
Chamber base insertion	cm	<5	5 to <8	8 to <12	≥12
Area/perimeter ratio	cm	<2.5	2.6 to <6.25	6.26 to <10	≥10
Duration of deployment	min	>60	>40 to 60	>20 to 40	≤20
Number of samples	no.	1	2	3	>3
Duration of storage					
Plastic syringe	day	>2	1 to 2	<1	
Glass syringe	day	>4	>2 to 4	1 to 2	<1
Other vessel	day	>90	>45 to 90	>15 to 45	≤15

2.7.2 Interpretation of key criteria – binary characteristics

Quality control

Samples of reference gas should be collected using the same procedures used for chamber samples, stored under identical conditions, and analysed in the same manner as chamber samples.

Use of non-linear model

This criterion was discussed extensively by Livingston et al. (2006). Use of non-linear models allows compensation for the immediate depression in emission rate likely to result from the chamber placement.

Sample container

Proprietary, fixed volume evacuated glass containers are recommended because of proven performance (low leakage).

2.7.3 Interpretation of key criteria – numeric characteristics

Chamber height

Chamber height must be considered in association with the resulting chamber placement time (placement time likely to increase with chamber height). The reviewers consider that it was not possible to accurately determine the flux with a 20 cm-high chamber over a 30-minute deployment period.

Chamber insertion

Chamber insertion depths were related to the duration of chamber deployment and soil porosity. Unless the emitting surface was likely to provide saturated conditions, chamber insertion-time values greater than 12 cm/h were recommended.

Area/perimeter relationship

As the area of the chamber increases, the ratio of area to perimeter decreases, effectively reducing the relative loss of material by leakage at the perimeter. Chamber diameters greater than 40 cm were recommended.

Duration of deployment

The perturbation of natural conditions (inhibition of emission, increased headspace humidity and temperature relative to ambient conditions) increases with chamber placement time. Chamber placement periods of less than 40 min duration were recommended.

Numbers of samples collected during chamber placement period

The technique relies on a curve-fitting procedure; the accuracy of this fit increases with sample number, and collection of at least four samples was recommended.

2.7.4 Other factors influencing accuracy

Rochette and Eriksen-Hamel (2008) identify the inter-relationship of a number of factors as important in determining the overall accuracy of emission estimates.

Chamber design

Soil disturbance should be minimised as far as possible, and use of two-piece base and chamber designs was encouraged. Reduction of radiant heating (through insulation) and reducing pressure effects (through well-designed vent tubes) is necessary.

Seal on the emitting surface

Leakage is minimised through use of a two piece base and chamber design, where the base is inserted an adequate depth into the soil (determined in part by the soil porosity), and where the ratio of perimeter to area exceeds about 10.

2.7.5 Recommendations for non-flow-through, non-steady-state chambers

1. Devices should be of two-part design, with separate base and chamber;

2. Chambers should be insulated and vented appropriately;

3. Chamber heights should be greater than 10 cm;

4. Chamber insertion depths should exceed 5 cm;

5. Pressurised, fixed volume storage containers should be used;

6. At least three discrete air samples should be collected over the chamber placement period, starting at time zero;

7. Non-linear techniques should be used to determine the change in headspace concentration over time.

2.7.6 Between-device variability, chambers and wind tunnels

A specific issue which has not received widespread attention relates to the actual emission rates derived from different devices, placed side-by-side on a surface, and used to collect paired samples simultaneously. Very few, truly paired comparisons of emission rates have been undertaken and reported in the literature.

Research undertaken jointly by the Department of Primary Industries and Fisheries, Queensland (DPI&F), and Queensland University of Technology (QUT) has generated a substantial body of work that defines the differences in emission rate produced by two devices commonly used to determine odour emission rates.

A series of measurements were made on a selection of area sources of odour (anaerobic treatment ponds, feedlot pads and permeable pond covers). Samples of odorous air were collected from a University of New South Wales wind tunnel and US EPA flux chamber placed side by side on a range of emitting surfaces, as shown in Figure 3. Replicate samples from each device were submitted to the DPI&F dynamic olfactometer for assessment. The results of this series of measurements were recently published (Hudson et al. 2008). Wind tunnel emission rates were consistently greater than those derived from flux chambers.

It is interesting to note that in their review of over 350 uses of chamber techniques to determine N_2O fluxes, Rochette and Eriksen-Hamel (2008) did not identify any paired comparison trials, which could provide estimates of uncertainty in flux estimates resulting from use of different types of devices. This is an area that deserves some attention. Unless the between-device variability can be estimated, it will be very difficult to separate the variability in flux associated with the device from variability arising from spatial or environmental factors.

2.7.7 Chamber flux errors caused by gas diffusion impacts

In a discussion of errors arising from the intrusive nature of chamber measurements, Davidson et al. (2002) found the build up of gas in the chamber headspace will affect the diffusion gradient in the soil below and is likely to lead to an increasing underestimate of the flux as time progresses. Livingston et al. (2005) estimated that chambers typically underestimate emission rates by 15 – 25% by ignoring this effect

Diffusion gradient alone is not the only source of error. Other researchers have demonstrated a clear relationship between wind speed and emission rate, including:

- Zhang et al. (2002) concluded that when measuring mercury emission rates, "high flushing flow rates are therefore a prerequisite for more accurate flux estimations and are strongly recommended whenever practical";

- Cobos et al. (2002), who demonstrated that conditional sampling substantially overcame this problem, offering the promise of greatly improved measurements of mercury flux, particularly at the landscape scale;

- Reicosky et al. (2008), who identified that wind and associated aerodynamic pressure fluctuations affect gas exchange from soils, implying that molecular diffusion alone was not responsible for mass transfer, and that use of sealed chambers may underestimate CO_2 exchange. In a similar vein, others have demonstrated similar dependence of measured emission rate on atmospheric turbulence (i.e. wind speed) [e.g. (Lee et al. 2004, Rathbun & Tai 1987)]. It is therefore clear that sampling techniques used to assess greenhouse gas emissions should also have regard for this dependency.

2.7.8 Dependence of emission rate on ventilation rate or flushing rate

Another issue with steady-state (i.e. dynamic, or flushed) flux chambers that has received inadequate consideration is the role of flushing rate. The original work describing use of the US EPA flux chamber indicated that the relationship between ventilation rate and emission rate was weak for the flux chamber (Klenbusch 1986). Research undertaken in Queensland indicated a strong dependence of emission rate for both wind tunnel and flux chamber, as indicated in Figure 7. Data included in the review by Denmead (2008) confirms that GHG flux measurements are similarly subject to wind speed effects (Figure 3).

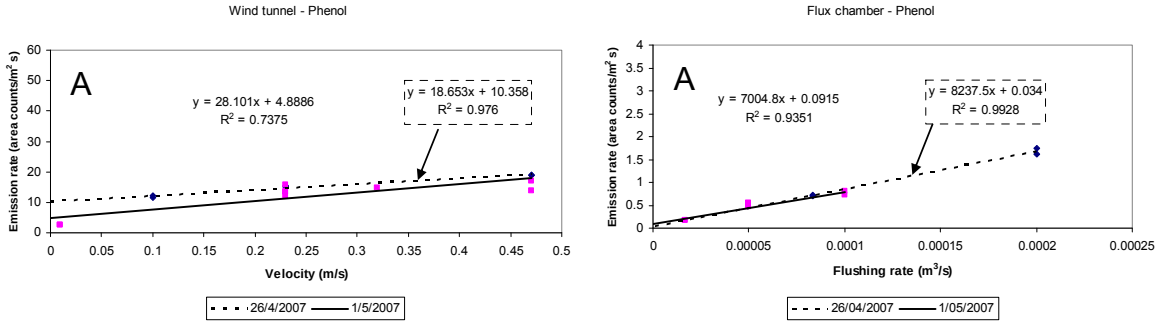


Figure 7: Relationship between emission rate and velocity (wind tunnel, left) and flushing rate (US EPA flux chamber, right) from Hudson and Ayoko (2008)

The limited number of published comparisons of wind tunnel derived emission rates with those derived from device-independent techniques indicate that wind tunnels are possibly more representative of emissions under "real-world" conditions. The previously discussed dependence between emission rate and wind speed or flushing rate deserves particular consideration.

When measuring ammonia emission rates under field conditions Ryden and Lockyer (1985) compared emission rates derived from a large wind tunnel and an independent micrometeorological method. Measurements were made over periods of 15 and 17 days respectively. When the tunnel wind speed was maintained at 1 m/s, the emission rate differed from values obtained by mass balance by factors of two to five, with the wind tunnel method consistently underestimating ammonia loss relative to the mass balance method. When the tunnel wind speed was maintained as close to ambient wind speed as possible, no significant difference in emission rates provided by the two methods was observed. Emission rates calculated from wind tunnel studies required a correction based on wind speed to produce values consistent with those derived under undisturbed conditions.

Smith & Watts (1994) used a simple Gaussian back-calculation model to estimate odour emission rates from feedlot pads. These values were then compared with emission rates derived from two different wind tunnels (Smith, K.A. et al. 1995, Smith, R.J. & Kelly 1996, Smith, R.J. & Watts 1994). A good relationship was demonstrated between emission rates derived from the two methods. This reasonably close relationship between wind tunnel estimates of emission rate, and those derived from device-independent back-calculation, was subsequently confirmed by Galvin et al. (2004), using a large number of odour samples collected from a range of anaerobic treatment ponds over a 14-month period.

The results of Galvin (2004) and Smith et al. (1995) when measuring odour emission rates appear to be consistent with the use of backward Lagrangian stochastic (bLs) dispersion techniques, discussed by Denmead (2008). In the bLs procedure, the concentrations of samples collected downwind of the source are projected backward to the source itself, while simultaneously accounting for atmospheric turbulence and height, to predict the flux from the surface.

2.8 Uncertainty discussion: Areal variability

2.8.1 Capturing spatial variability with chambers

The small size of chambers makes them suitable for measurement of flux from small areas, or from multiple sites within a large area. Applications of this capability may include estimating fluxes from soils subject to specific treatments (e.g. denitrification inhibitors), waste application (areas of pasture subject to manure or urine application), or when undertaking replicated trials of these or other treatments.

The spatial limitations restrict the usefulness of these devices when measuring GHG fluxes from larger areas, or where a high degree of spatial variability is likely. The impact of spatial variability may be reduced by deployment of multiple devices [e.g. (Denmead 2008, Pape et al. 2008)]. There are practical limits to the number of devices that may be deployed. On pastoral land, there will be significant spatial variability in emission (especially for nitrous oxide) associated with spatial variability of dung and urine deposition. It is difficult to quantify the spatial average emission estimate with small randomly placed chambers and it is likely that quite a high density grid of chambers is required to give an accurate spatial average. An experiment to study of spatial variability without the influence of patchy nitrogen deposition by Ambus and Christenson (1994) suggested a minimum grid size of about 7 m to detect variability attributed to soil moisture and that small scale variability may be important to account for denitrifying microsites. (Folorunso & Rolston 1984) on cropped land estimated the need for 3 chambers m^2 to estimate the spatially averaged N_2O flux to within 10%. There has been little published work investigating this for New Zealand pastoral systems.

Ambus and Christenson (1994) also caution that even results from mega-chambers (upwards of 50 m) designed to capture spatial variability, should be interpreted with caution. Mega-chambers are also prone to other difficulties including problems in getting a good chamber perimeter seal and in ensuring adequate mixing of the chamber atmosphere (usually assisted by air circulation fans).

2.8.2 Capturing temporal variability with chambers

Estimates of the errors in integrated flux introduced by discrete sampling with chambers have been made by Parkin (2008). In his study, sampling at relatively frequent intervals i.e. once every three days, produced estimates within ±10% of expected values. This range widened to between +60 and -40% when sampling every 21 days. However, some pastoral systems in New Zealand are highly likely to be subject to highly episodic fluxes (because of episodic deposition with grazing rotation and episodic triggers with irrigation).

The current authors have also observed large (factor of 2) differences in flux estimates between chambers and micrometeorological approaches in the same campaign. We present here some details of further work we are developing to compare a grid of chambers sampling within the fetch of a flux-gradient micrometeorological tower during FarmGas2006 (Harvey et al. 2008) to investigate the cause of these initial differences. If significant episodes of emission are not adequately captured in the chamber sampling then emission rates can be significantly underestimated. To perform the comparison, experimental sites have been set up with a grid of chambers (~40 chambers in the case of FarmGas2006 upwind of the micrometeorological flux measurement tower (Figure 8 and Figure 9). The footprint of the measurement tower was calculated using the parameterisation of Kljun et al. (2004). For periods of spatial overlap between the micrometeorological flux footprint and the chamber plot, fluxes from the two approaches were compared (Figure 10)

.

Figure 8: FarmGas2006 experimental site.

Figure 9: **Chamber/tower micrometeorological comparison experiment (red hatched area – fenced off from cattle; green hatched area – chamber plot; blue lines – irrigator wheelings)**

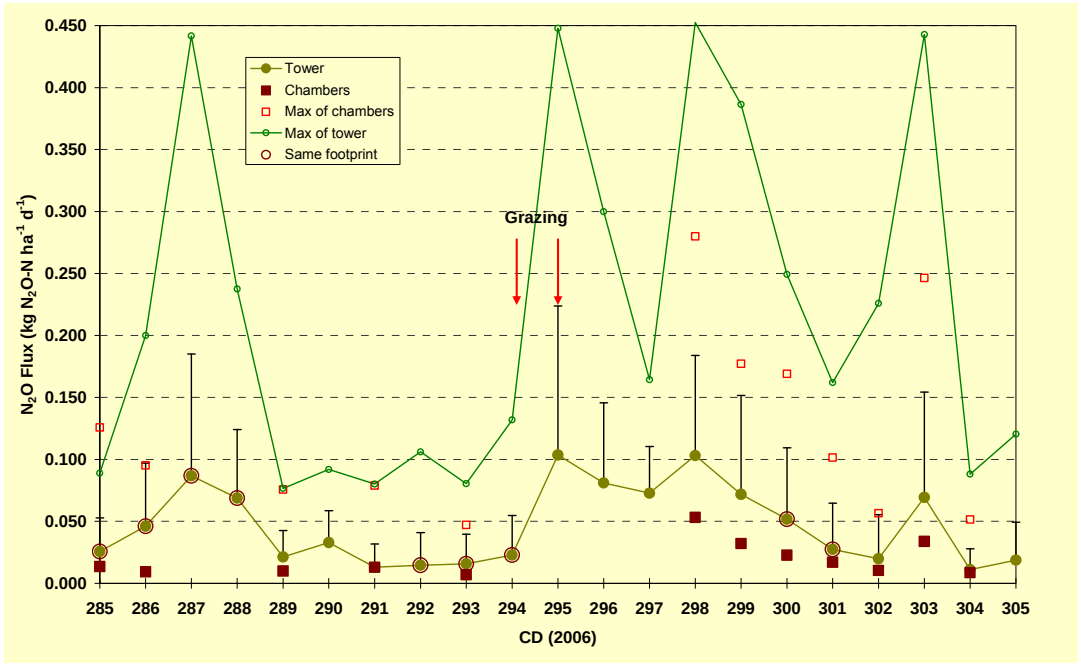


Figure 10: **Chamber/tower micrometeorological comparison experiment**

Several interesting features are apparent in the comparison of Figure 10 showing daily integrated values from discrete chamber measurements versus continuous micrometeorological measurement: (1) similar trends were apparent in both the chambers and the micrometeorological measurements; (2) the maximum fluxes from the tower were always greater than the maxima of the chambers; (3) except during quiescent periods (e.g. day 289 and 291) when they were equal and (4) the average of the tower measurements were also always greater than the average of the chambers except during the quiescent periods. Integrated data are summarised in Table 3. The result of chambers not capturing bursts of high emission was that their emission estimate was about half of that from the continuous micrometeorological techniques. For this trial (Figure 11) there was a significant "tail" in the log normal distribution of emission where half of the total emission occurred in only 10-15% of the time and much of this episodic emission was not captured by the chambers.

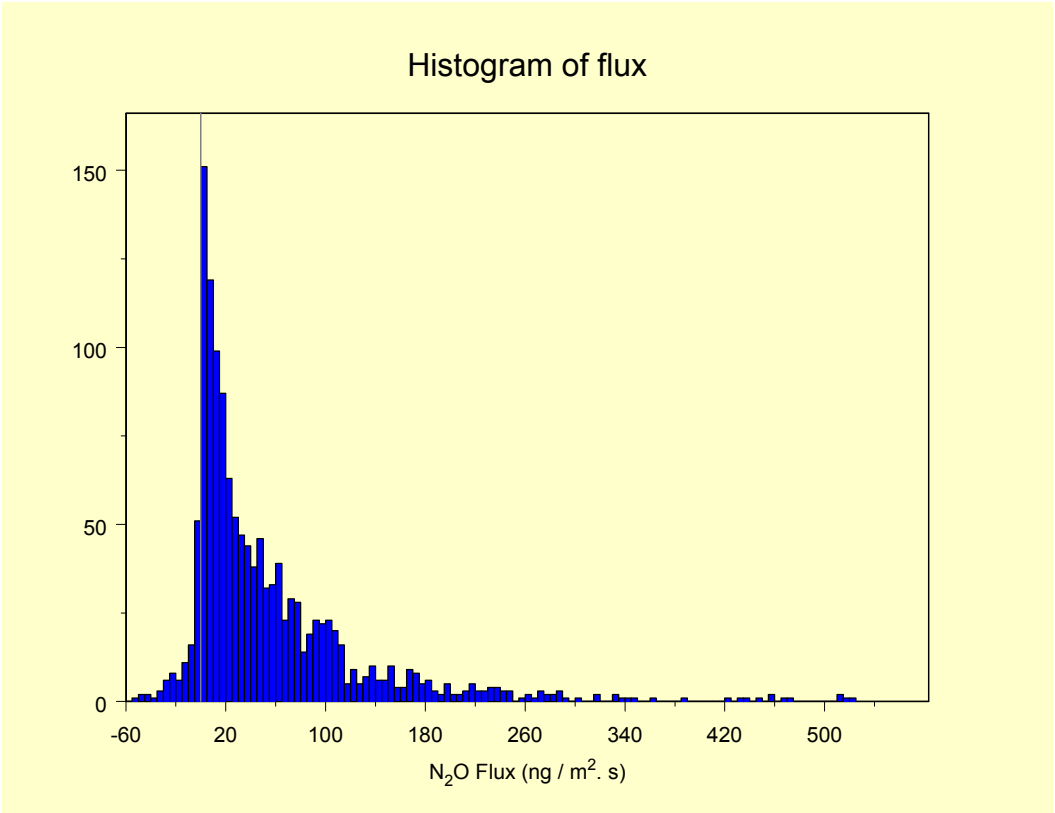


Figure 11: Histogram of emission during FarmGas2006. The episodic nature of emission at this time was characterised as half of the total emission occurring in 10-15% of the time

Table 3: Calculated N_2O emission flux kg ha^{-1} in 10 days for 3 techniques in FarmGas2006

Treatment	Measurement technique		
	Gradient TDL	Gradient GC	Chambers
Pre-Grazing	0.31	0.22	0.10
Post-Grazing	0.56	0.55	0.25
Baseline	0.13	0.06	

2.9 Implications regarding use of chambers to measure greenhouse gas emissions

Static and dynamic chambers, and wind tunnels, all influence the source and conditions within which the emission measurement is taking place. These influences include alteration of the headspace concentration within the device, which may feedback to affect diffusion from the within soil atmosphere (particularly with static chambers), increase in the humidity of air within the device (particularly static chambers and low-flushing rate dynamic chambers), reduction in the effect of turbulent atmospheric processes (specifically wind speed and pressure differences) – particularly for static and low-flushing rate dynamic chambers. Dynamic devices such as wind tunnels appear to offer advantages when determining the emission rate or flux of a variety of volatile substances and soil gases.

All chamber and wind tunnel devices cover a very small proportion of the emitting surface – single or low numbers of discrete measurements are unlikely to provide an accurate assessment of the actual emission from the surface. Device-independent techniques therefore appear better-suited to measurement of greenhouse gas emissions at the paddock and landscape scale.

Chamber and wind tunnel devices do have an important role in the measurement and management of greenhouse gas emissions. Micrometeorological techniques are not well suited to determining spatial differences over small scales (say of the order of metres to tens of metres). Such measurements are particularly useful when determining the impact of specific actions at the small scale on emission processes, e.g. small trial plots examining use of nitrification inhibitors, impact of manure or effluent application to soils, impact of soil moisture on emission processes etc. Insights into all of these effects may be conveniently obtained by undertaking replicate, small-scale laboratory and field-scale trials. In addition, replicated experiments are more practical to conduct with chambers compared to the paddock scale. At paddock scales, exact replication of the environment and soil condition is not practical to achieve.

Consideration of spatial, temporal and environmental factors (i.e. soil moisture, wind speed and temperature) and the requirement to estimate greenhouse gas emissions indicates strongly that static and dynamic chambers, wind tunnels and device independent techniques are complementary, rather than exclusive. Selection of the measurement technique should be made on the basis of the information required. Overall, upscaling emission measurements should have particular regard for atmospheric processes such as wind speed, pressure and solar heating. As such, more dynamic techniques, that emulate natural processes, such as wind tunnels, should be regarded as better suited to the task than static chambers, where a number of natural influences are substantially altered.

Micrometeorological techniques eliminate many of the spatial variability issues by effectively averaging variability over areas of hundreds to thousands of m^2, but do not allow estimates at very finite spatial scale (tens of m^2). These techniques can include the use of long-path length devices, often capable of high speed measurement (e.g. 10 Hz). This allows very short-term variability to be assessed. In addition, the measurement is automated and takes place over periods of days to weeks at very high resolution. This in turn allows assessment of the influence of diurnal variability, rainfall and other meteorological factors to be estimated. Such assessment is not really practical for most chamber measurement strategies. The table that follows provides some guidance regarding the relative strengths and weaknesses of the various techniques.

Table 4 Comparison of features, strengths and weaknesses of various techniques used for GHG measurements

Factor	Technique			
	Chamber	Mass-balance	backward Lagrangian stochastic	Micrometeorological
Temporal variability	Limited – less than 24 measurements/ day	High	High	High
Spatial scale	m^2	Tens to thousands m^2	Tens to ten thousands m^2	Tens of thousands m^2
Suitability for estimating spatial variability	Yes, repeated measure	Yes, through averaging	Yes, through averaging, or operation at small scale	Yes, through averaging
Complexity	Low	High	High	Very high
Cost	Low[1]	High	High	High
Portability	High (provided bases are established prior to measurement period)	Low	Low	Low
Relative sensitivity	High	High	High	Variable (gas dependent)
Inhibition effects	Yes	None	None	None
Pressure sensitivity	Yes	None	None	None
Leakage sensitivity	Yes	None	None	None
Subject to solar heating effects	Yes[2]	None	None	None
Subject to atmospheric turbulence and wind speed effects	No[3]	Yes	Yes	Yes
Subject to rainfall	Yes	Yes	Yes	Yes

Notes

[1] Low cost only applies to simplest application – less than about 4 measurements/day

[2] Regarded as limitation – perturbation of emitting environment, probably increasing flux.

[3] Regarded as limitation – perturbation of emitting environment minimises one of the principal factors determining mass transfer.

3 Direct measurements: Paddock-scale techniques

3.1 General remarks and terminology

This section reviews a range of techniques that use knowledge of the airflow near the earth's surface to infer gas emissions from a grazing animal herd (for CH_4) or a grazed or fertilised paddock (for N_2O), therefore called paddock-scale techniques. Their main advantages over animal-scale or chamber techniques are that they take measurements only outside the grazed area, thus do not affect the animals' behaviour, and that they sample emission rates representative of the whole herd, not a subset of preselected animals. The techniques are complementary to chambers or enclosures where replicated treatment plots or animals can be studied in a carefully controlled environment. At the paddock-scale, the individual animal is substituted by a herd and any study of treatment plots is at the 50 m x 50 m scale or beyond. The environment is not controlled and the methods are non-intrusive.

The review classifies the techniques into four groups: mass-budget, vertical-flux, backward-Lagrangian, and tracer-ratio techniques. For each group there is one subsection describing the concepts and requirements of the techniques, the suitability for either trace gas, and recent studies where they have been applied. It is no coincidence that these studies are almost exclusively from Australia, Canada and New Zealand (and one from Ireland), since it is these countries where the interest in quantifying the greenhouse gas emissions from pastoral agriculture is largest, partly due to the large ratio of farm-animal population to human population and partly due to widespread practice of outdoor grazing. The four sections describing the techniques are followed by two brief synthesis sections, one comparing the advantages and limitations of the techniques, the other discussing their uncertainties.

All techniques reviewed here require the measurement of windspeed, some at one height, others at multiple heights, and wind direction. They also require the measurement of either the gas density or the mixing ratio (more casually, called "concentration", C) of the gas of interest downwind of the emission sources. Some of them require the measurement of upwind (background) concentration, C_b, too.

We denote the emission rate (source strength) per surface area by Q. The surface area in which emissions occur is the area grazed by the animals, i.e. the paddock. For N_2O, Q is the immediate quantity of interest, because the gas emanates from the soil surface. Q can be converted into the emission rate per head, E, by $E = Q/N$, where N is the stock density (No. of animals per paddock area). For CH_4, the immediate quantity of interest is E; assuming that, over time, the animals' positions during grazing are

evenly spread across the paddock, their emissions can be considered equivalent to the areal source strength, or "surface flux", Q, which is the quantity determined by the paddock-scale techniques.

3.2 Mass-budget techniques

Two variants of micrometeorological mass-budget techniques are available at the paddock scale, in the following denoted as IHF (integrated horizontal flux) technique and NBL (nocturnal boundary-layer budget) technique. Both establish the budget of the trace gas of interest within an air volume above the paddock, in the horizontal limited by the paddock dimensions and in the vertical reaching from the ground to a height z_b. The difference of the fluxes of the gas into the volume and out of the volume (through all faces of the budget volume) equals the change of gas contents within the air volume. Both techniques then derive the flux of interest at the ground-air interface, Q, from quantifying the other terms in the budget equation, the fluxes through the air-air interfaces and the change of contents within the volume. The two techniques make different assumptions which of these terms are negligible.

The **NBL technique** is based on the idea that during stable stratification (at night-time) the vertical exchange is completely suppressed at the top of the nocturnal boundary layer (defined as the inversion height z_i). Hence, the budget volume has a natural lid at $z_b = z_i$. It is further assumed that there is no mean wind, so horizontal exchange of air is slow and fluxes through the sides of the budget volume are small compared to the surface flux of the gas of interest. The surface flux therefore causes the concentration of the gas in the budget volume to increase over time. This increase is measured along a vertical profile, which must reach higher than z_i. This typically being a few tens of metres, small masts are not sufficient as instrument platforms. Tethered sondes or radiosondes can be employed for this purpose. The largest weakness of the technique is the uncertainty about the extent of the surface that the budget represents. It is thus unknown what fraction of the measured concentration build-up over time is caused by distant sources. Even if there are no distant sources, it is poorly known to what horizontal distance the air mass in the NBL contributes to the dilution of the gas emitted from the local sources of interest. Strictly speaking, the simple NBL budget assumption requires an infinitely large homogeneous source area; for typical paddock sizes, this is a poor assumption. The situation is further complicated by the occasional occurrence of intermittent turbulence in the NBL, which then renews the air mass in which the gas has accumulated (Harvey, M.J. et al. 2002). Denmead et al. (1998) used the NBL technique to measure CH_4 emissions from sheep, finding agreement with other techniques within a factor of 2. Given the principal difficulties as mentioned before, it is unlikely that the accuracy of the method can be improved much, except for rare cases of ideal conditions.

The **IHF technique** assumes that horizontal windspeed is strong enough to exchange the air in the budget volume rapidly, hence the net contents change is assumed zero and fluxes into the volume are balanced by fluxes out of the volume. The height z_b is chosen as the height where the concentration drops to its background value ($C = C_b$), i.e. where the air does not contain any gas emanated from the sources beneath. This means the vertical flux through the top face of the air volume is zero, and the surface flux is given as the difference of the vertically-integrated horizontal fluxes downwind and upwind of the paddock. In two dimensions (vertical and alongwind, assuming that crosswind fluxes balance to zero), the budget can be written as:

$$Q = \frac{1}{r_{up} - r_{dn}} \int_0^{z_b} < u \left(C_{dn} - C_{up} \right) > dz$$

where u is the horizontal windspeed, r_{up} and r_{dn} are the alongwind coordinates of the upwind and downwind paddock boundaries, C_{up} and C_{dn} are the upwind and downwind concentrations, and brackets <…> indicate a time average. The time-averaged horizontal flux consists of two contributions, one with the mean flow and one with the turbulent fluctuations:

$$<u\ (C_{dn} - C_{up})> = <u>\ (<C_{dn}> - <C_{up}>) + (<u'\ C_{dn}'> - <u'\ C_{up}'>)$$

where the prime (') indicates the difference of the instantaneous value from the time average. The mean term (first on right-hand side) is the horizontal flux that can be measured. The turbulent term (second on right-hand side) is of opposite direction to the mean term ("backflow"). It cannot be measured directly and needs to be parameterised.

The IHF technique was originally applied on small plots grazed by a handful of animals, where it was possible to measure vertical concentration profiles on all four horizontal sides with a single instrument, via a switching system that included 16 intake tubes (for N_2O: (Harper et al. 1999), for CH_4 from cattle: (Leuning et al. 1999), for CH_4 from sheep: (Laubach & Kelliher 2004)). Because profiles on all four paddock sides were measured, no footprint considerations were needed. The turbulent backflow term was assumed a fixed proportion (10 or 15 %) of the mean-flow horizontal flux. These studies provided proof of concept, but for the purpose of testing inventory predictions of emissions, larger animal numbers are required

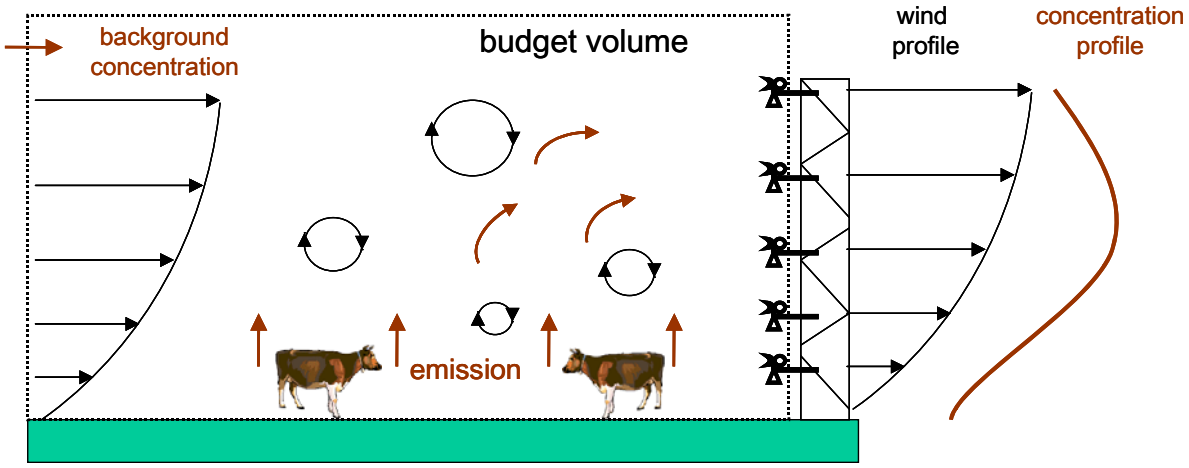


Figure 12: **Schematic of the IHF technique. Gas emitted from the animals or the ground (brown arrows) is transported in the vertical by turbulent eddies (black circles), and in the horizontal by the mean wind (profile shown as black arrows on left and right). A measurement mast with five sampling heights is placed downwind of the grazed paddock. An exemplified concentration profile is shown on the right. Upwind concentration is assumed to be constant with height and equal to the background value.**

Laubach and Kelliher (2004) modified the technique for realistic paddock sizes in New Zealand, of 1 to 10 ha, grazed by a few hundred animals. In their approach, shown schematically in Figure 12, only one vertical profile is measured, in a location anticipated to be downwind of the paddock for much of the experiment duration. It is assumed that $C_{up} = C_b$, which is measured in one or two separate locations. Wind direction determines which cross-section of the paddock is upwind of the profile mast, hence the actual source area varies over time. Laubach and Kelliher (2004) derived how this depends on paddock geometry and wind direction. They also derived a parameterisation of the turbulent backflow term and estimated its uncertainty.

3.3 Vertical flux techniques

The vertical gas flux, F, at some location downwind from the gas sources, is related to the emission rate via $Q = F/S$, where S is the source area weight function, or "footprint" function. This function quantifies the fraction that the limited paddock area would contribute to the vertical flux of a hypothetical tracer that was uniformly released everywhere at the upwind surface, inside and outside the paddock. S depends on the setup geometry (paddock coordinates and measurement location), the meteorological conditions (wind vector and stability) and the roughness of the upwind surface. Methods to measure F, as described in the following, usually collect the data necessary to estimate S anyway, hence they are suited to determine Q.

There are two principal ways to measure the vertical flux: either directly as the correlation product of vertical wind and concentration fluctuations, or indirectly, by relating the flux to the vertical concentration gradient, which is easier to measure. The direct technique is called eddy covariance (EC), the indirect is called flux-gradient (FG) technique. A "semi-direct" technique: relaxed eddy accumulation (REA) exists that partitions gas according the measurement of vertical velocity and accumulates samples typically over half hour periods, eliminating the need for fast response gas sensing

The setup geometry for EC and FG is shown in Figure 13.

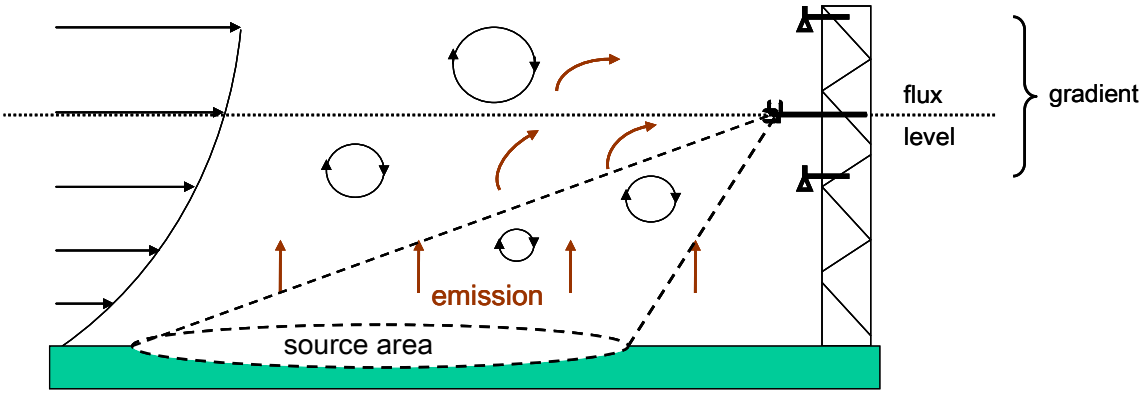


Figure 13: **Schematic of the vertical flux techniques. Emitted gas, turbulent eddies and wind profile are shown as in Figure 12. The horizontal dotted line marks the height at which the vertical turbulent flux is measured, either directly by eddy covariance (EC) instruments at that level, or indirectly from the concentration gradient between the measurement heights above and below. The elliptical "source area" is the area from which the gas emissions contribute most strongly (up to a prescribed fraction of the total, e.g. 50 % or 90 %) to the measured flux.**

The basic equation of the **EC technique** is:

$F = \langle w'C' \rangle$

where w is vertical windspeed. Both w and C need to be measured at the same location at high time resolution (> 5 Hz sampling rate). Fast measurements of w can readily be provided by sonic anemometers. While over the last 20 years or so measurements of the fluxes of heat, water vapour and CO_2 by the EC technique have become routine, a serious limitation to its application for trace gases has been a lack of suitable gas sensors. This is because for practically all methods measuring gas concentrations, resolution and precision decrease with decreasing integration time. First prototypes for

CH_4 and N_2O were tried in the early nineties (Fowler et al. 1995, Wienhold et al. 1995). Nowadays, tuneable diode lasers (Edwards et al. 2003) have become commercially available, though they are bulky, expensive, sensitive to vibrations and require cooling with liquid nitrogen, which makes them challenging to run under field conditions. They have so far been applied to N_2O emissions from grazed pasture only by Scanlon & Kiely (2003). A new compact CH_4 instrument, based on off-axis spectroscopy, is now commercially available (Hendriks et al. 2008) but has not been applied to measure animal emissions yet.

The basic EC equation, above, is a special case of the budget equation for the gas of interest. To be valid, it requires stationary and horizontally homogeneous flow, thus flat terrain without obstacles or major roughness changes. Also, in practice there are further assumptions (e.g. of zero mean vertical wind, co-location of *w* and *C* measurement, perfect instrument response etc.) that are never fully met and may need correction procedures. These are extensively discussed by Pattey et al (2006).

The relaxed eddy accumulation **REA technique** described by Businger and Oncley (1990) is a technique in which wind turbulence is measured in the same way as with the EC technique and this is used to separate upwardly moving (up-draft) air from down-draft air through fast response solenoid valves. The REA flux is given by:

$$F = A\sigma_w(\overline{\rho N_2O^+} - \overline{\rho N_2O^-})$$

Where σ_w is standard deviation of vertical velocity, ρN_2O^+ is mean gas density of updraft + air (ng m^{-3}) and A is the REA empirical coefficient. Gas is collected at the same height as the wind measurement and accumulated into updraft + and downdraft – samples. An advantage/motivation for the use of REA is that measurement of the gas can be offline and can be made with slow-response gas detectors within the typical 30 minute micrometeorological run time.

An alternative that is technically less demanding is the **FG technique**. Its basic equation is:

$$F = -K\,\frac{\partial C}{\partial z}$$

where *K* is the turbulent diffusivity of the gas of interest. In practice, the concentration gradient is approximated by concentration differences between two measurement heights. These differences must be measured with high precision, but no fast response is needed. The validity of the flux-gradient equation is based on Similarity Theory, which requires the same assumptions of stationarity and homogeneity as the EC

technique. The gas diffusivity K must be parameterised, usually assuming that (again, according to Similarity Theory) it almost equals the diffusivity of either momentum or heat, except for a stability-dependent factor, φ, of magnitude 1. The diffusivity of momentum can be obtained from the wind profile (aerodynamic method) or from the momentum flux measured with a sonic anemometer. The diffusivity of heat can be obtained from simultaneous measurements of temperature and humidity profiles (Bowen ratio method) or from a temperature profile and the sensible heat flux measured by a sonic anemometer. The experimentally simplest method is the one using momentum flux; the sonic anemometer data also provide the stability parameter on which the φ factor depends.

There is ongoing debate regarding the similarity assumptions of the diffusivities (see Laubach & Kelliher 2004). Yet, the accuracy of the momentum diffusivity is limited by the measurement error of momentum flux, and the accuracy of the diffusivity for heat is limited by the combined errors of sensible heat flux and temperature gradient. In both cases, 10 to 20 % relative error is realistic. Within these error margins, the similarity assumption usually holds, except for very stable or very unstable stratification, when either the fluxes (stable) or the gradients (unstable) become small and error-prone, for which reason alone the FG technique does not work reliably in very stable or very unstable conditions. Note that the relative error of K accounts only for part of the technique's uncertainty; more see in the separate section below. Trace gas emissions from animals can successfully be measured with the FG technique, as demonstrated e.g. by Judd et al. (1999) for CH_4 and by Phillips et al. (2007) and Harvey et al. (2008) for N_2O.

3.4 Backward-Lagrangian simulation technique

Lagrangian stochastic models simulate the flight paths of individual air parcels, provided the windspeed and turbulence statistics of the flow are known. Such models can be used forward or backward in time. In the forward case, the air parcels travel from a given starting point; this can then be used to predict how a trace gas (added to the air at the starting point) will disperse downwind. In the backward case, the air parcel's origin is determined from a given observation point; this information can then be used to infer the unknown strength of a gas source located upwind. For a few years now, a backward-Lagrangian stochastic (BLS) model for the atmospheric surface layer (Flesch et al. 1995) has been commercially available under the trade name WindTrax (Thunder Beach Scientific, Halifax, Nova Scotia, Canada). It is described comprehensively by Flesch et al. (2004). WindTrax assumes a flat surface of homogeneous roughness, free of flow obstacles. It requires the following inputs: at least one measurement of windspeed, one measurement of concentration downwind of the gas source, C, background (upwind) concentration, C_b, and the horizontal

coordinates of the source area, here the paddock. (For area sources, the emission is always assumed to be at ground level). Turbulence statistics can be provided (e.g. from sonic anemometer data), otherwise they are set to default values known from Similarity Theory. Further wind and concentration input data can be added, providing redundancy and thus reducing uncertainty of the simulations. The model tracks, for each set of input data, a user-defined number (many thousands) of air parcels backwards from the location(s) of the concentration measurements. The flight path of each air parcel is a random manifestation of the turbulent interaction between air parcels (Figure 14). These interactions are parameterised with probability functions that depend on the windspeed and turbulence statistics. The model counts how many of the simulated air parcels touch the ground within the paddock area, and how many originate from outside the paddock ("touchdown" statistics). Knowing that only the former air parcels contribute to the measured ($C - C_b$), the touchdown statistics then provide the relationship that converts ($C - C_b$) to the emission rate, Q.

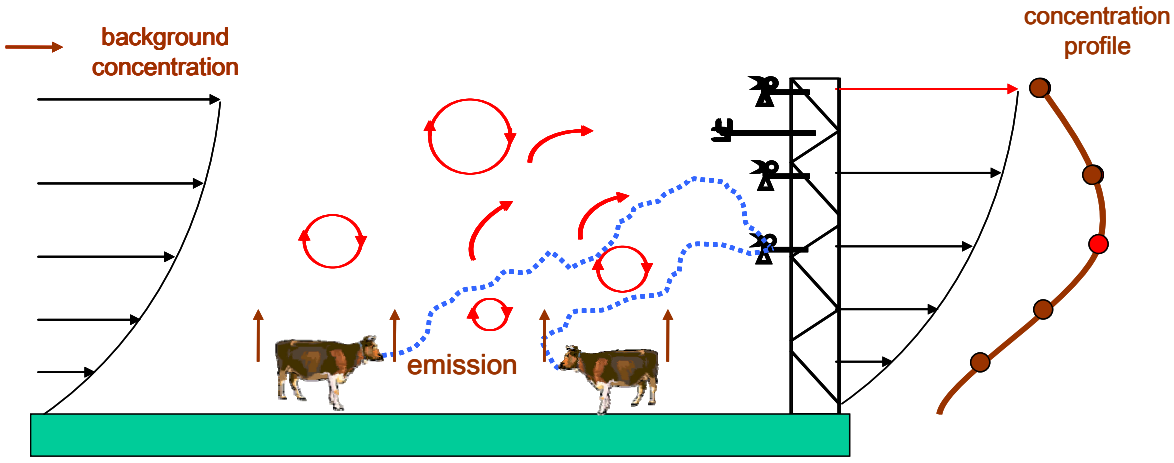


Figure 14: **Schematic of the BLS technique. Emitted gas, turbulent eddies, wind and concentration profile are shown as in Figure 12. The blue dotted lines are two examples of air parcel trajectories which are calculated backwards from the point of measurement. The minimum requirement is to measure windspeed and concentration at one height each (indicated in red). The emission rate is calculated from the "touchdown" statistics of many thousands of simulated air parcels.**

3.5 Tracer ratio techniques

If two gases are released from the same locations, then in a turbulent flow field they will be transported downwards by the same air parcels and will be dispersed equally. If their concentrations are measured at the same downwind location, the concentrations will be elevated above their upwind (background) concentrations in the same ratio as the ratio of the emission rates:

$$Q_1 / Q_2 = (C - C_b)_1 / (C - C_b)_2$$

where subscripts 1 and 2 distinguish the two gases. This simple equation is exploited by so-called tracer ratio techniques, where one of the gases, the "tracer", is artificially released at a known rate Q_1, and the concentrations are measured simultaneously, ideally by the same instrument. The method does, in principle, not need to measure any meteorological parameters, which keeps the number of error sources small. Crucial requirements are to know Q_1 accurately, which requires a reliable release mechanism, to know the upwind (background) concentrations of both gases, and to match the release locations of the tracer as closely as possible with the expected source locations of the gas of interest. Tracer release can be at the paddock surface, as successfully applied by Galle et al. (2000) to measure NH_3 emissions from a fertilised plot (the same setup could potentially be applied to N_2O), and by Griffith et al. (2008) to quantify CH_4 emissions from cattle. In the latter case, the release locations of the tracer and CH_4 were not really co-located, rather, it was assumed that release of the tracer from the fenceline upwind of the animals was close enough to the CH_4 sources. An obvious improvement over this setup would be to release the tracer from containers carried by the animals, to effectively measure E_1/E_2 instead of Q_1/Q_2. The group led by D.W.T. Griffith (Univ. of Wollongong) intend to conduct three field campaigns in 2008 to test this approach, at sites in Australia and New Zealand, and compare it to other paddock-scale techniques.

A variant of the tracer ratio techniques is the NBL ratio technique (Kelliher et al. 2002). There, CO_2 respired from the grass surface was used as a natural tracer to determine the N_2O emissions from the same surface. This was done in the stable nocturnal boundary layer (NBL), when it could be expected that the gases would not be carried away by the wind and accumulate in the NBL. Instead of the concentration difference between upwind and downwind, the concentration changes over time were recorded for both gases, and assumed that their ratio equalled the ratio of the emission rates. The underlying assumptions of the NBL characteristics are the same as for the

NBL budget technique (see section on mass-budget techniques), but the realisation is much simpler because the concentrations need to be measured at only one height and NBL depth does not need to be known. It is not even necessary to measure the gas concentrations in situ: collection of air samples and subsequent lab analysis is possible, however, care must then be taken that the air sample represents a long enough period or large enough volume to be representative of the average concentration (at sampling height) in the NBL. The main drawbacks of the technique are, again, the restriction to calm nights and the uncertainty about the horizontal extent of the surface area influencing the concentration measurements. In a pastoral agricultural setting, there is the potential for error in the derived flux if animal respired CO_2 as opposed to surface respired CO_2 has contributed significantly to the boundary-layer mass budget. However, if the area of co-located gas emissions is large and homogeneous and the measurement height kept low, then this uncertainty should be much smaller than for the NBL budget technique.

3.6 Comparison of advantages and limitations of the techniques

All techniques require wind (minimum speed of order 2 m/s at 2 m above ground), except for the NBL budget and NBL ratio techniques, which rely on the build-up of stable stratification in weak-wind conditions. In theory, the latter two techniques thus appear to be good complements to the other techniques. In practice, though, the applicability of both is severely restricted, as discussed further below. For the other techniques, the dependence on wind forces the experimenter to design the setup so that it works for either a large range of wind directions, or at least the most likely wind directions. This can be done in a number of ways, e.g. by duplication of instruments, by quick relocation of instrumentation as the wind changes, by placing instruments in the centre of the grazing area, or simply by depending on wind direction forecast and allowing enough field campaign time to wait through periods of unsuitable wind direction – all of these approaches have their advantages and disadvantages which cannot be discussed in detail here. For N_2O, the instrumental setup can be stationary and optimised to one location, because the intention is usually to record the temporal pattern of emissions from the ground for a period around a grazing or fertilising event. For CH_4, the logistics are more challenging, because the practice of rotational grazing requires that the instruments are relocated, at least every few days, in order to follow the herd from one paddock to another.

Mass-budget techniques do not make assumptions about the flow. The most critical assumption is that of a closed volume dependent on the extent of the paddock and its distance from the point of measurement, the measured profiles may not reach high enough and extrapolation may be needed. In addition, the IHF technique requires a turbulent backflow correction, which can be estimated from additional measurements (Laubach & Kelliher 2004). Otherwise it is very versatile: it does not require fast

concentration sensors, is sensitive to precision only for the upwind-downwind concentration difference, but not within the downwind profile, and it tolerates moderate flow disturbances by obstacles or roughness changes. Compared with CH_4, for N_2O, the precision in upwind-downwind concentration difference presents a more significant limitation with the technique. In most pastoral settings, there will be a significant background flux from adjacent paddocks that is likely to exhibit similar temporal variability to the measurement area. As pointed out by Denmead et al. (2000b) this presents a limitation because the residual concentration used to determine the fluxes is a small value calculated as the difference between two much larger numbers.

The NBL budget technique is severely restricted in its applicability, to suitably shallow stably stratified boundary layers, which occur only at night-time, and not every night. Further, it is seriously limited by the uncertainty of the horizontal extent of the budget volume, which in strongly stable stratification can extend for several km. Therefore, the NBL budget technique is not discussed further.

Tracer ratio techniques, like the mass-budget techniques, do not make assumptions about the flow. There, the crucial assumption is that the sources of the gas of interest and the tracer are co-located. This is never perfectly true. For tracer release at the surface, it is likely that the tracer emission rate is homogeneous across the release area, but the sources of the gas of interest are often inhomogeneously distributed. For tracer release from the animals, the emission rates per animal for the gas of interest and the tracer will each vary between animals in an unpredictable and uncorrelated fashion. For the gas of interest, its source strength depends on the animal's physiology and behaviour. For the tracer, there is variability because of manufacturing tolerance in the release mechanism. The tracer techniques have higher labour and material costs than the other techniques, because of the tracer release system. An exception is the NBL ratio technique (Kelliher et al. 2002) when it uses a natural tracer (respired CO_2). Ideally, the NBL ratio technique would require a suitable paddock area surrounded by non-respiring surfaces. This is rarely found in practice. If the surrounding area contains living soil and/or vegetation of different kind to that in the paddock, then this technique is subject to the same kind of footprint uncertainty as the NBL budget technique (though to a lesser degree).

The vertical-flux techniques make assumptions on the nature of the flow: they are valid for flat, homogeneous terrain without major obstacles, such as trees or buildings, and without major changes in surface roughness. The flux-gradient technique, in addition, needs to parameterise the turbulent diffusivity, which is done with Similarity Theory. This theory works well for moderately stable to moderately unstable stratification. It is invalid for strongly convective conditions (fine-weather daytime)

and strongly stable conditions (weak-wind night-time). Similar limitations apply to most of the available footprint models, which are required for all vertical-flux techniques. Finally, these techniques require precise measurements of small concentration differences: measurement error of concentration differences is often a significant contributor to overall uncertainty.

The BLS technique, in the practical realisation that has become popular (WindTrax software, Flesch et al. 2004, Flesch et al. 1995) makes the same assumption of homogeneous flow over flat terrain as the vertical-flux techniques. It also uses Similarity Theory, in order to provide consistent relationships between the wind profile shape and turbulent flow parameters (surface roughness, friction velocity and stability), which are needed to model the vertical and lateral movements of air parcels. It is therefore applicable with similar restrictions as the flux-gradient technique. In principle, it would be possible to apply the BLS technique with different flow models that can account for obstacles, roughness changes, or strongly convective conditions; however, combinations of BLS with such models are not readily available to date (Vesala et al. 2008). An advantage of the BLS technique over the flux-gradient technique is that it is less sensitive to measurement precision of the concentrations.

The techniques are not mutually exclusive: a particular instrumental setup often allows more than one method of source strength computation, which provides consistency checks. In particular, IHF, FG and BLS (using a vertical concentration profile) can be carried out with the same suite of instruments, as realised by Laubach and Kelliher (2005a) and Laubach et al. (2008). They found that the Q estimates from the three techniques generally co-varied from one run to the next, which enhanced the overall confidence in the results.

Tracer ratio methods can also make use of the same instrumentation if the tracer release system and a vertical profile of tracer concentration measurements are added to the setup. The EC technique, however, cannot be included in such a multi-technique approach, because a separate gas sensor of fast-response capability is required, in combination with a sonic anemometer (which is useful but not essential for the other techniques). Finally, BLS with path-averaging also requires separate concentrations measurements. This technique is attractive because of its better coverage of the footprint and lower dependence on wind direction, compared to the other techniques.

3.7 Line averaged versus point averaged tower measurement

A number of single or multi-height techniques can be used with line-averaging sensors, as opposed to single point micrometeorological tower measurements. Typically the single point measurements are made with closed-cell instrumentation, the line-averaged measurements are made by both closed-cell – connected to a

spatially extensive plumbing array or by an open-path optical sensor (typically a Fourier transform spectrometer or a tuneable diode laser instrument). Line-averaging has two advantages: first, the footprint is extended in the horizontal (parallel to the path orientation), which means a larger fraction of the paddock (ideally, all of it) is included in the footprint, and second, a given sampling geometry covers a larger range of wind directions.

There are a number of micrometeorological mass balance experiments that have enclosed paddock areas, e.g. a rectangular area with sides typically less than 100 m. We have discussed the small enclosed plot measurement in Section 3.2 Mass-budget techniques. The enclosure leads to a well defined footprint. Line-averaging open systems for integrated horizontal flux (IHF) assessment (which all four sides of the plot are not enclosed) have been deployed for ruminant methane emission using open-path lasers (Desjardins et al. 2004, Laubach & Kelliher 2005b). The BLS technique can also be used with both vertical concentration profiles (Laubach & Kelliher 2005a) or with line-averaging sensors (Flesch et al. 2004, Laubach & Kelliher 2005b, McGinn et al. 2006). Suitable line-averaging sensors (laser systems) are available for CH_4 but not for N_2O. In principle, this technique could be realised for many trace gases, including both CH_4 and N_2O, with open-path Fourier-Transform Infrared Spectroscopy (FTIR see Griffith & Jamie 2000), but this has not been tried yet so the achievable accuracy is unknown. Some research groups are attempting to develop open path measurement of N_2O and some activities are discussed in Section "3.10 Novel techniques and mapping technologies".

3.8 Uncertainty discussion

Each technique has its own measurement uncertainty, which varies considerably with the particular circumstances of each experiment. The discussion below quotes some typical values that have been published, and finds them generally corroborated by comparisons between techniques. As a general rule, errors of mean windspeed and setup coordinates are assumed small (< 1 %) and can be neglected compared to other error sources (concentration measurements, turbulence measurement or parameterisation, idealised assumptions not being met in practice).

The uncertainties quoted here apply to typical individual sampling periods, of order 30 min. For mean emission rates from whole field campaigns, smaller uncertainties may be achieved by virtue of averaging many sampling periods; this will be discussed at the end of the section.

For the **NBL budget technique**, the variability of the uncertainty with particular circumstances is probably enormous, and very little data are available. Harvey et al.

(2002) compared CH_4 emissions from the NBL budget technique to the SF_6 tracer (animal-scale) technique and obtained 20 % difference in some nights and 100 % in others. This uncertainty is so large and variable that the NBL budget method is not likely to contribute to future inventory improvements.

An inevitable contributor to the uncertainty of the **IHF technique** is the error of the upwind-downwind concentration difference ($C - C_b$). Further, dependent on windspeed, stability, and distance r_{up}, it can occur that the top measurement level is not high enough to reach z_b. For such cases, Laubach and Kelliher (2004) used an extrapolation procedure and estimated that it adds about 10 % of Q to the uncertainty of Q. In subsequent experiments Laubach and Kelliher (2005b) and Laubach et al. (2008) used smaller paddocks (< 2 ha) and increased the top measurement height from 5 to 7 m, with the result that the extrapolation procedure was rarely needed. They showed, both from propagation of estimated measurement errors and from comparison to other techniques, that the uncertainty of the IHF technique (without vertical extrapolation) is **about 10 %**, provided that a turbulent backflow correction is applied. Flesch et al. (2002) arrived at the same result. Comparison by Griffith et al (2008) to the tracer ratio technique suggests that this is a realistic estimate. Specifically for N_2O, in a comparison of techniques, Denmead et al. (2000b) estimate also that a mass balance approach can provide the most precise answer, and in the case of their study with a standard error of around 30% of the daily mean flux.

When the **FG technique** works reliably, in neutral and moderately unstable or stable stratification, its uncertainty combines the relative errors of K (10 to 20 %, already discussed above), of the footprint S (which is of similar magnitude, since it depends on the same parameters as K), and of the concentration difference (which may be similar to the first two, or smaller). Laubach and Kelliher (2004) estimated the error of Q in their experiment as 27 to 48 %; Phillips et al. (2007) gave 15 to 45 % for theirs. It seems thus warranted to quantify the uncertainty of the FG technique as **of order 20 to 50 %**.

Despite the simple basic equation, flux measurements with the **EC technique** are subject to a large variety of error sources, some of which are corrected for in complex procedures (Pattey et al. 2006). The error of an EC-measured gas flux is typically given as 10 to 20 %. (For example, Hendriks et al. (2008) found 20 % difference between CH_4 fluxes measured by EC and with a chamber technique. Of course, errors of both techniques combined to explain this difference.) For measurements with a confined source area, requiring a footprint correction factor S, the error of the emission rate, Q, is then likely to be **15 to 30 %**. This is slightly better than FG but, given that both EC and FG are less accurate and less versatile than IHF, the latter appears preferable.

Errors in **REA technique** estimates result from similar sources to the **EC technique** with a similar range of likely error. It is possible to minimise errors due to air density differences between up and down draft by pre-drying the air and running the pumping system at constant temperature. If this configuration is impractical, then air density corrections associated with sensible and latent heat fluxes are required. The density corrections have been described by Webb et al. (1980) and a detailed analysis and development of correction expressions for REA has been described by Pattey et al (1992).

The uncertainty of the **BLS technique** is extensively discussed by Laubach and Kelliher (2005a). They found that propagation of measurement errors resulted in a statistical uncertainty of **about 20 %**. This estimate was supported by the degree of correlation with the IHF technique found by these authors, and it agrees with Flesch et al. (2004) who tested the BLS technique with a CH_4 laser system in a controlled-release experiment and found the calculated Q to vary ±22 % around the known release rate. This uncertainty estimate does not include possible errors of the turbulent parameterisation used in the BLS model. If such errors exist, they are likely to produce a bias. Flesch et al. (2004) found a bias of only 2 % (not significant). However, Laubach et al. (2008) found the BLS technique to systematically exceed IHF by 15 % and FG by 25 % (Figure 15). The causes of this are still under investigation. BLS does not achieve the same accuracy as IHF, but where its accuracy is sufficient, it can be a useful alternative because it requires fewer instruments.

The measurement uncertainty of the **tracer ratio technique** depends only on the precision of the concentration measurements of the two gases and the accuracy of the tracer release rate. Using closed-path Fourier Transform Infrared Spectroscopy (FTIR), with N_2O as the tracer and CH_4 as the gas of interest, Griffith et al. (2008) achieved about 5 % error of the CH4 emission rate. This error estimate did not include, though, the effect of the two gas sources not being co-located in that experiment. A bias of order 10 % resulted from that (estimated with the BLS technique). The tracer ratio technique is thus potentially the most accurate of the reviewed techniques. However, to realise this potential, one requires high-precision instrumentation for two gases instead of one only (FTIR instruments have the virtue of measuring a range of different gases simultaneously), and one needs to install a reliable and accurate release apparatus for the tracer, at additional cost and effort.

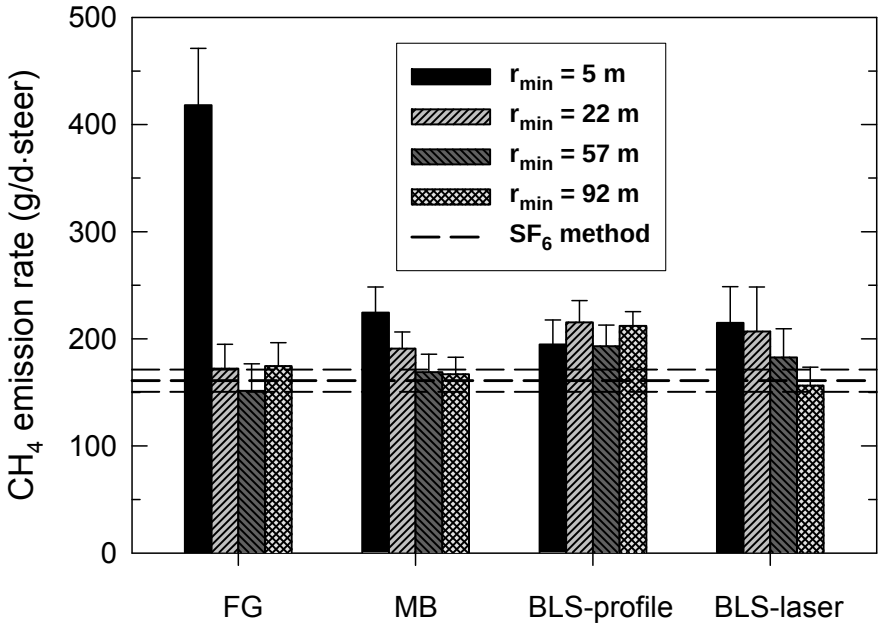


Figure 15: **Results from comparison experiment at Aorangi Farm, 28 Oct – 14 Nov 2006. Methane (CH_4) emission rates according to four paddock-scale methods, averaged for four classes of minimum distance between the cattle and instruments (r_{min}). FG: flux-gradient, MB: mass-budget, BLS: backward-Lagrangian stochastic model, "-profile": same CH_4 input data as for FG and MB from vertical profile (5 heights), "-laser": using CH_4 data from tunable-diode-laser paths up- and downwind of the herd. The error bars indicate 95 % confidence intervals. Dashed horizontal lines represent the mean (± 95 % confidence) of nine daily herd averages obtained with the SF_6 technique (from Laubach et al. 2008).**

The error of the **NBL ratio technique** consists of the same error as the tracer ratio technique (dependent on gas measurement precisions and accuracy of the tracer's emission rate), plus a footprint error that is poorly known because available footprint models are not valid in windless stable stratification. Kelliher et al. (2002) gave the relative error of the N_2O emission rate as 21 %, but this result is experiment-specific and cannot be generalised. The NBL ratio technique may occasionally complement the other paddock-scale methods, because it works when these fail, but because of its restricted applicability, it is unlikely to become a technique of relevance to inventory improvements.

3.9 Instrumentation advances

The range of gas chromatographic detectors used discussed under the chambers Section "2.3.2 Measurement of concentrations" is also suitable for adaption to continuous monitoring and paddock-scale micrometeorological measurement (e.g. (Judd et al. 1999) for methane and (Harvey, M. et al. 2008) for N_2O).

However, optical sensors, in general provide a faster-response instrument with higher measurement precision. The flux measurement of N_2O is most challenging because of its low yet wide-ranging flux densities (Figure 16). However, it is also the case that for N_2O, the measurement precision by tuneable diode laser is typically an order of magnitude better then by GC. Some typical measurement precision estimates for concentration and flux of N_2O are given in Table 5.

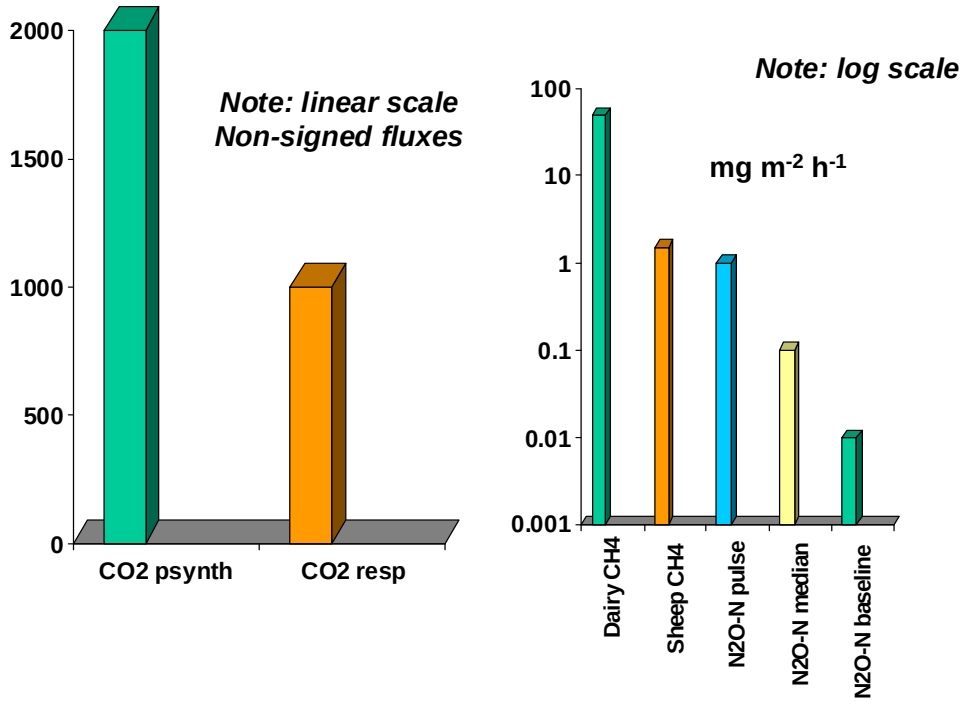


Figure 16: "Typical" greenhouse gas flux densities in pastoral agricultural systems. (The N_2O baseline emission estimate has been provided by van der Weerden and de Klein (pers. comm.)

Table 5: "Typical concentration and flux measurement capability for both GC and TDL.

Instrument	N_2O Ppb	~Flux magnitude mg N_2O-N/m^2/hr	~Flux magnitude kg N_2O-N/ha/yr
GC	0.1 (0.03%)	0.1	6.0
TDL	0.01 (0.003%)	0.01	0.6

3.9.1 Tuneable diode laser (TDL)

TDL consists of a small laser source that can be tuned across a relatively small wavelength range. These are typically set up to scan across a single absorption line of the gas to be measured. Many different configurations are possible from small hand-held units with closed cells, to open path systems using either fixed paths with retro-reflectors or open paths that rely on backscatter from some target for the return signal.

One commercially available configuration is the TGA-100A (Campbell Scientific Inc., Logan Utah http://www.campbellsci.com/tga100a) which uses a 1.5 metre internal cell, and operates as a comparator between sample and a reference gas cell. A single laser is chosen to monitor the gas of interest, but the instrument can be purchased with a second laser available for a different gas, or there are modes where a single laser can be chosen to include two gases or isotopes of the same gas within its limited scan range, allowing them to be recorded with one laser (albeit at a lower precision than when each laser is optimally selected for a single target gas). This model of instrument was successfully deployed in New Zealand in a pastoral agricultural setting in the FarmGas06 campaign (Harvey et al. 2008). A recent article reviewing various methods available for the determination of agricultural trace gas fluxes over a wide range of agro-ecosystems in Canada demonstrates the versatility of this instrument, used with a wide variety of measurements strategies (Pattey et al. 2007). The absorption line for methane is in the 3.3 micron band (at 3018 cm^{-1}) and sensitivity/noise amounts to 7 ppb with differences at little as 140 ppt resolvable in 30 minute averages. Another line at longer wavelength is possible to use in to measure methane in combination with N_2O but is 3 times worse in precision for methane. The measurement rate can be as high as 10 Hz allowing eddy covariance measurements.

Another commercially available TDL unit applicable in this context is a Boreal Gasfinder http://www.boreal-laser.com/. This can be set up to make a (multiple) open path measurement with a retro-reflector at the far end. For methane the laser is tuned to 1.653 micron and sensitivity is 1 ppm – metre. Over a path length of 200m this translates to 5 ppb, comparable with the Campbell instrument. This type of system has been deployed in New Zealand by Laubach and Kelliher (2005b) monitoring along

the four fence-lines of a grazed paddock. The system can be configured with multiple measurement heads, connected by optic fibre to the central unit to allow up to 8 open paths to be monitored. The optics required for the open path are simpler than those required for an open-path FTS instrument.

3.9.2 Fourier Transform Spectrometer (FTS)

Fourier transform spectrometers can be used in a number of configurations. Optimal absorption wavelengths for methane exist in bands at 1.6 and 3.3 micron, with the latter being far stronger. The light path through the measured gas typically needs to be of the order of a hundred metres or more, in order to get sufficient sensitivity. This can either be a long open path, or achieved with some sort of path folding, such as a multi-reflection system, or a more compact multi-path White cell.

Analysis is by fitting either synthetic absorption spectra for the gases of interest, or by fitting measured spectra of reference gases with known concentrations, with a least squares fitting process, to match the measured spectrum. One advantage of an FTS system is that it can measure multiple gases as easily as a single gas. This means that a single instrument can be applied to a variety of different applications or campaigns. Also, it can allow the identification of parameters that are related to the emission processes being studied. For example CO_2 measurement can indicate the effects of plant to animal respiration in the test area even when the target gas is N_2O or CH_4. A long-term FTS in situ measurement system has been installed at NIWA Lauder, in support of a carbon-column measurement programme and collaboration between NIWA and University of Wollongong. The system, designed by the University of Wollongong, consists of a commercial 1 cm Bruker FTS, White cell, manifold for the switching of calibration gases, and operating and analysis software. The White cell arrangement carries the advantage of compactness and that the measured reference gas spectra are measured under nearly identical conditions to the sample spectra. The sampling manifolds, and enclosure this system is fitted with, make it unsuited to open path applications. However, the configuration means that measurements of concentration can be made with higher precision, amounting to around 0.1%.. Fourier-transform spectroscopic measurement can also be made with open-path designed instruments as discussed in Section “3.7 Line averaged versus point averaged tower measurement” and in the section following for more novel approaches. Beyond small enclosed plots, an open path measurement is likely to be of lower precision than one used with a closed cell system, because the uncertainty, in knowing temperature along the measurement path and turbulence. Precisions for individual measurements are typically an order of magnitude lower than for closed-cell configuration.

3.10 Novel techniques and mapping technologies

This chapter has reviewed methodologies that have been deployed to date, many in New Zealand, and essentially involve point or line averaged profiles to determine emission source strength within an area enclosed by an open-path detector system or measurement of concentration coupled with application of turbulent diffusion theory to relate the measured concentration back to emission source strength within the local footprint. Novel techniques, some of which are described below, extend these techniques with vertical or horizontal concentration sectioning (tomography).

3.10.1 Ground-based tomography (aka environmental computer assisted tomography (cat)

As an extension to the micrometeorological open-path techniques, such as closed plot micrometeorological mass balance techniques the integrated horizontal flux (IHF) discussed in Section 3.2 Mass-budget techniques, Hashmonay et al. (1999) used a mapping approach with open multiple-path FTS to map gas concentration and then applied a mathematical inversion of the across-plume concentration map to estimate emission rate using a plume dispersion model. The technique, using near-infrared open-path tuneable diode laser has been refined further by Thoma et al. (2005) to determine the emissions of source regions of both ammonia and methane. Interestingly, as with the estimates in this report Section "3.8 Uncertainty discussion for the accuracy IHF," Thoma et al. (2005) estimate 10% as the flux measurement accuracy of their open-path measurements through a vertical flux plane downwind of the emission region where the entire plume is sampled or a plume extrapolation is performed where required above max measurement height.

Todd et al. (2001) have been able to quantify non-homogeneous emission of ammonia at the "paddock scale" (i.e. 100 – 200 m) with a horizontal grid of open-path FTS to measure a tomographic (2-dimensional) concentration map, in this case over a lagoon. The concentration map has been converted to an emission map using a ratiometric approach of simultaneous measurement of a tracer from the release of a known flux of gas-tracer. A quite different spatially integrating approach has been trialled recently using acoustical tomography (akin to large-scale sonic anemometry). Schleichardt et al. (2008) have developed a 1000 m^2 spatial mapping of eddy diffusivity with a plan to combine this with N_2O measurements to develop the capability for spatial mapping of N_2O flux. These are multi-open path techniques. As a further alternative method for generating tomographic surface concentration plots for use in determining emission fluxes, Liley (pers. comm.) has investigated the theoretical potential for using a single horizontal scanning laser instrument operated as a steerable lidar for methane mapping of a herd at the paddock scale. Initial studies of modelled emissions under idealised

conditions from a cattle herd indicate that a lidar tuned for methane would be able to detect and map methane emissions at the paddock scale.

3.10.2 On-line paddock-scale isotope flux measurements

Both Fourier transform spectroscopy and tuneable diode laser based sensors have the potential to make high-resolution isotope flux measurements and there is particular interest in $^{13}CO_2$ measurement for improving knowledge of biosphere-atmosphere exchange processes in the carbon cycle. Compared with conventional isotope ratio mass spectrometry (IRMS) these optical techniques achieve a slightly lower precision (~0.2 ‰) but with a very high sample throughput. Field deployable FTS measurement has been recently discussed by (Mohn et al. 2007) and a fast response eddy covariance measurement of $\delta^{13}CO_2$ has been developed by Griffis et al (2008).

3.11 Conclusions

It appears thus that the most accurate paddock-scale methods have a measurement uncertainty of about 10 % (Table 6) for the individual run (typically 30 min). Over the course of a field campaign, the run-to-run variability is usually larger than that: for CH_4, the s.d. is typically 50 % of the mean Q (e.g. Laubach & Kelliher 2004) and for N_2O, the s.d. is often >100 % of the mean, with strongly skewed distribution (e.g. Harvey et al. 2008). This indicates that there is significant real variation in the emission rates.

Table 6: Summary in uncertainty of flux estimate across paddock-scale techniques

Technique	Uncertainty estimate	Gas /ref	Comments
Tracer Ratio	~ 5%	(FTS multigas) / (Griffith et al. 2008)	Requires release of second (GH) gas
Integrated horizontal flux (IHF)	~ 10%	CH_4 / (Laubach & Kelliher 2004)	Least uncertainty in small plot line-sampling enclosures. Residual to background a critical limitation for N_2O
Backward Lagrangian Stochastic (BLS)	~ 20%	CH_4 / (Laubach & Kelliher 2005a)	(perhaps biases) Uncertainty reduced through increased (over-determined) sampling. Residual to background a critical limitation for N_2O
Flux gradient (FG)	20 – 50%	CH_4/N_2O / (Laubach & Kelliher 2004, Phillips et al. 2007)	
Eddy covariance (EC)	15 – 30%	CH_4/N_2O (Hendriks et al. 2008, Pattey et al. 2006)	Error corrections need to be carefully applied (Burba & Anderson 2008)
NBL budget	20 – 100%	CH_4 / (Harvey, M.J. et al. 2002)	Limited and indirect technique where high-precision is not available

3.11.1 Paddock-scale measurement of CH_4

In the case of CH_4, where animals are the sources, variability in emissions results both from animal behaviour and animal-to-animal variability. Since CH_4 emissions originate from ruminating activity, spatial and temporal variations in animal behaviour will cause temporal variations in CH_4 flux. This temporal variability cannot be resolved by the animal-scale (SF_6) technique, which integrates over many hours, but it can potentially be captured with paddock-scale techniques. Animal-to-animal variability of emissions, combined with the random selection of which individual

animals are inside the footprint for the current wind direction will also result in temporal and spatial variations in CH_4 flux. For any given run, it is possible that the animal density within the footprint is larger or smaller than the average animal density in the paddock. The key assumption that needs to be approximately fulfilled is that, over time, the animals spread homogeneously across the paddock. For free-grazing cattle, this is usually true; for sheep, this assumption is more frequently violated.

3.11.2 Paddock-scale measurement of N_2O

In the case of N_2O, one cause of variability is the patchiness of the emission sources. Paddock-scale techniques integrate naturally over this patchiness, better than chamber techniques where chamber locations are critical, but it must be assumed that the emitting patches are reasonably evenly spread across the paddock. In the same way that the animal density within the footprint varies for CH_4, the urine patch density within the footprint varies for N_2O. If it is not evenly distributed, then it will depend on wind direction statistics during the campaign if the average emission rate is biased or not. Another, more critical, cause of variability is the occurrence of specific events, like rainfall, irrigation or fertilising, that dramatically increase N_2O emissions for a limited time period. Such events cause large skewness and large range. of the probability distribution of *Q*.

A further very important consideration for N_2O is consideration of the background emission, especially for the IHF and BLS techniques where it is the difference from background or atmosphere upwind of the experimental plot that is required for accurate assessment of emission from the plot of interest. In an agricultural setting with neighbouring paddocks, environmental drivers (especially rainfall) are likely to cause bursts (episodes) of N_2O emission in both the upwind (background) paddocks as well as the experimental plots. By comparison, the impact of plumes of methane from nearby animals can usually be avoided through careful experimental design. We therefore recommend careful upwind measurement in IHF and BLS configurations and consideration be given to an "over-determined" design for BLS measurement.

Because of the large real variability between runs, the measurement uncertainties compiled above are not critical and any technique with up to, say, 30 % error will yield useful statistics of *Q*. The key to getting meaningful paddock-scale emission rates is therefore to average a large enough number of runs, from campaigns of at least several days duration, or better, a few weeks. Care must be taken to ensure that the averaging procedure is not biased towards particular times of day (for CH_4) or around particular events (for N_2O).

4 Direct Measurements: Satellite-based mapping of greenhouse gas column and surface flux estimates

The surface fluxes of the greenhouse gases can be inferred from the spatial and temporal fluctuations in the atmospheric column amounts. For CO_2 and the relatively long-lived CH_4 these variations are small and superimposed on a large atmospheric background modulated by natural processes. For N_2O the total signal and variations are smaller still. At this point in time, there is rapid advance in technology and the next generation of satellite-borne instruments is about to be deployed. It is anticipated that this will have a dramatic impact on carbon-cycle research. The current surface-based monitoring network for greenhouse gases provides accurate measurements, but is very sparse. The much greater temporal and spatial coverage possible from space will allow significant progress in understanding of the sources and sinks of carbon dioxide and methane that is a prerequisite to allowing reliable predictions about their future atmospheric concentrations and hence future climate of the planet. In the longer-term, greenhouse gas monitoring from space should be able to provide an objective verification of greenhouse gas emission reporting within the UNFCCC and under the Kyoto protocol and subsequent international agreements governing environmental policy.

4.1 Satellite sensors

For nadir (or glint) viewing sensors, there are 3 sensing approaches that produce operational or research data products or are under development as summarised in Table 7.

4.1.1 Thermal emission sounders:

a/ The NASDA National Space Development Agency, Japan with "Interferometric Monitor for Greenhouse gases" IMG on ADEOS http://www.eorc.jaxa.jp/AtmChem/IMG/ measured mid-tropospheric greenhouse gases between 1996-97.

b/ The Measurement of Pollution in the Troposphere MOPITT package of the Canadian Space Agency on the NASA Terra satellite http://terra.nasa.gov/About/MOPITT/about_mopitt.html has measured distributions of CO and CH_4 since 1999. Focus has been on CO, there is a potential for release of monthly averaged 1% column precision 1° by 1° resolution gridded CO & CH_4 data.

c/ The TIROS Operational Vertical Sounder (TOVS) has been flown aboard the National Oceanic and Atmospheric Administration (NOAA) polar meteorological

satellites since 1978. Retrievals of mid-tropospheric greenhouse gas concentrations have been developed from the data of this package of instruments (Chédin et al. 2002). Analyses are typically at low spatial resolution (e.g. 15° x 15°) and the standard deviation of CO_2 in the retrieval is around 1% (Chédin et al. 2003). At lower resolution, these measurements can provide a basis for analysis of long-term trends, as well as seasonal and interannual variability.

d/ The NASA Atmospheric Infrared Sounder (AIRS) on the Aqua spacecraft http://www-airs.jpl.nasa.gov/index.cfm since 2002 has measured mid-tropospheric CO_2 distribution at 100 km resolution to a high (1.2 ppm) precision with data planned for public release this year. Other species being researched include CH_4 distribution, CO column O_3 vertical distribution.

Table 7: Remote sensing of greenhouse gases

Method	Thermal infra-red emission	Near-Infra red scattering	Lidar
Method	Passive	Passive	Active
Vertical column weighting (averaging kernel)	Above 3 km (mid-troposphere – a function of T, H_2O O_3)	Total column average from surface	Total column average from surface
Age of air	Weeks to months	Variable with height	Variable with height
Vertical resolution	>10km	>10km	1km
Horizontal resolution	1- 10's km	1- 10's km	1 km
Frequency	High	Daytime only	High
Current instruments	IMG.ADEOS (1996) TOVS,AIRS, IASI	SCIAMACHY	
Planned instruments		OCO 2009 GOSAT 2009	A-SCOPE ~2015
Precision target	CO_2: ~2ppm CH_4 ~20ppb N_2O 10% (not routine)	OCO – 1 ppm CO_2	0.5 – 1.5 ppm CO_2

d/ The European Space Agency Infrared Atmospheric Sounding Interferometer IASI is a recent FTS sensor series mounted on MetOp series of European operational meteorological polar-orbit satellites http://smsc.cnes.fr/IASI/ launched in 2006. Data products are under development including planned including CO_2, CH_4, CO, and N_2O column measurement to 50 km resolution with CH_4 to better than 5% N_2O to better than 10%.

All these thermal emission instruments are weighted towards the mid-troposphere in the vertical (around 3-5 km) and do not provide detailed information on surface concentration. Multiple gas measurement is a powerful feature. For example: CO can be used to help distinguish combustion sources (fossil or biomass) from other sources/sinks in methane and carbon dioxide analysis and both CO and O_3 can potentially contribute to improved transport modelling.

4.1.2 Near-infra red instruments (SCIAMACHY)

Of the near infra-red sensors, the SCanning Imaging Absorption spectroMeter for Atmospheric CartograpHY SCIAMACHY on the European ENVISAT http://www.sciamachy.org since 2003 is the first, and at this time, the only satellite instrument capable of measuring the column of the greenhouse gases of CO_2 and CH_4 from the top of the atmosphere down to the Earth's surface. The capability to measure at the surface, where the source and sink trace gas signal is largest and collocated with the source is clearly of major interest to research in detecting anthropogenic emissions and the associated biological feedbacks, which are far more uncertain than the anthropogenic emissions themselves. For CH_4, SCIAMACHY has provided the first high quality maps of global amount and distribution showing regions of enhanced concentration, for example, those over Asia attributed to rice production, livestock farming, and coal mining in China and India. The instrument will run in parallel with the next generation of near-infra red sounders between 2009-14. Details of operational and research data products and links to validation literature are available at http://www.sciamachy.org/products.

Horizontal resolution is 30 x 60 km2. Vertical columns of: CO_2 have shown quite systematic low bias of 1.5%, single pixel precision of 1-2%, and agreement with reference data within 1-3% for 2003-05 data. Vertical columns of CH_4 have shown a low bias of 2%, single pixel precision of 1-2%, and agreement with reference data within 1-2%

N_2O can be measured to 10% target precision. Dils et al. (2006) felt that it would be possible to gain future improvements to this with more research effort and that it was clear that the current data quality of column average dry air mole fraction X[N_2O] needs improvement before it becomes useful for research users.

4.1.3 The next generation of near-IR instruments

There is great anticipation in the research community with the impending launch of the next generation of satellite sensors in 2009, the US Orbiting Carbon Observatory (OCO) http://oco.jpl.nasa.gov/ high resolution spectrograph for measurement of the

column burden of CO_2 and the Japanese consortium "Greenhouse gases Observing SATellite" (GOSAT) http://www.jaxa.jp/projects/sat/gosat/index_e.html http://www.gosat.nies.go.jp/index_e.html.

The OCO is targeting a design specification of 1 ppm CO_2 in the column. The precision (0.3-0.5%) aims to resolve regional scale processes against the 8ppm pole to pole column-averaged CO_2 dry air mole fraction X[CO_2] gradients and similar magnitude X[CO_2] differences found in the seasonal cycle in the Northern Hemisphere. Overall, this should reduce error in surface CO_2 flux estimates by an order of magnitude. The instrument will have a 16-day repeat cycle, facilitating monitoring X[CO_2] variations on semi-monthly time scales. The research programme includes a comprehensive ground-based validation and correlative measurement program to ensure accuracy and precision. The instrument does not have a good ability to discriminate in the vertical (Connor et al. 2008) although retrievals are made of vertical atmospheric profiles of temperature, CO_2 and water vapour as well as aerosol content and scalar measures of albedo, surface pressure and X[CO_2] The "Level 3" data product will map global X[CO_2] at one part per million (ppm) accuracy over the Earth's surface in bins of 1° by 1°. From that data inversion routines will give the geographic distribution of CO_2 sources and sinks over a planned two annual cycles of sensor operation.

The Greenhouse gases Observing SATellite (GOSAT) plans a rapid orbital repeat cycle of 44 orbits over 3 days. The mission aims to map the global distribution of both CO_2 and CH_4 with flux estimates for 64 sub-continental (several thousand kilometres square) regions. Target precisions of around 1% are proposed for near-IR X[CO_2] retrievals, and 2% for near-IR X[CH_4] retrievals.

4.1.4 Future prospects for very-high resolution mapping

Other "active" lidar-based remote sensing instruments are in development as a potential observational method for monitoring CO_2, CH_4 and N_2O from space. Like the near-infrared sensors they have high surface sensitivity with added advantages of no interference from thin cloud layers and aerosols and the ability to measure day and night with very high spatial resolution. One proposed instrument is the "**A**dvanced **S**pace **C**arbon and Climate **O**bservation of **P**lanet **E**arth" A-Scope lidar planned for the ESA Earth explorer mission around 2015. The design target precision is 0.5 – 1.5 ppm of CO_2, with the ability to resolve 0.02 $PgCO_2$-C/yr at a spatial resolution of 106 km^2.

5 Model-based upscaling

5.1 Introduction

The New Zealand national inventory for N_2O is calculated with a "Tier 1" level of complexity. That is, the simplest possible level with the incorporation of country specific emission factors where there is evidence to support a country specific value. In summary, the tiers of complexity for inventory range from 1 to 3:

Tier 3	More detailed or country-specific methods:
	- empirical models
	- process based models
	To provide a more accurate estimate these need robust calibration / validation over the grid of possible climatic/soil/land-use categories
Tier 2	- disaggregated-specific emission factor
Tier 1	-simplest method
	- activity data available to all countries

There range of complexity in model-based approaches to upscaling follows these tiers. The first level of complexity is a refinement of the current (Tier 1) inventory with a greater degree of disaggregation in emission factor (by e.g. season, soil drainage, land use, excretal dung and urine) to what then becomes a Tier 2 level of complexity. There are increased data requirements for verification of a larger number of emission factors and their uncertainties. Greater disaggregation may not lead to lower uncertainty and this is discussed further in Chapter 6. However, one significant area of inventory advance where there is a need to disaggregate further is in capturing the benefit in inventory of lowering of emission through mitigation treatments (such as nitrification inhibitors) that have a seasonally specific reduction. There may be need in the future in disaggregation down to the farm-level, if farm-level emission were to be the point of obligation of the future Emissions Trading Scheme (ETS). In considering practical frameworks through which regional or farmscale emission

assessment could be aggregated, we consider the use of the OVERSEER® nutrient budget model with its GHG emission capability. This management tool for use at the farm-level incorporates an estimation of GHG emission using IPCC methodology. We consider some generic issues in 5.2 Disaggregation and budgeting techniques with OVERSEER®, important for a tool such as OVERSEER® if used to form the basis for more refined (disaggregated) farm-scale emissions calculation as a possible Tier 2 inventory approach and/or as an enterprise level ETS calculator. Following that, we comment on 5.3 Semi-empirical methods and finish with greater detail in Section 5.4. Recent progress with process-based modelling, with a focus on the DayCent and DNDC models.

5.2 Disaggregation and budgeting techniques with OVERSEER®

The OVERSEER® Nutrient Budgets model developed at AgResearch combines nutrient budgets with indices derived from these nutrient budgets, to provide users with a tool to examine the impact of nutrient use and flows within a farm (as fertiliser, effluent, supplements or transfer by animals) on nutrient use efficiency and possible environmental impacts. The model also provides a means to investigate mitigation options to reduce the environmental impact of nutrients within a land use. The comments here are based on experience in having the OVERSEER® nutrient budget model used as a tool to implement regional council policy, and in implementing National Inventory greenhouse gas emission methodology in OVERSEER®. The model is available at http://www.agresearch.co.nz/overseerweb/

5.2.1 Scaling issues

Like all models, when upscaling the user needs to consider the scale of the model and the scale of the data. It is generally unreasonable to expect the summation of model outputs from a small-scale model to equal the output from a larger scale model. However, it can be expected that the differences will be smaller if the data and model are independent of scale (fractal data). This is rare in human systems.

There are usually differences in interpretation of data when it is collected at different scales. For example, the national inventory methodology for methane emissions is based on animal numbers, an animal intake model and methane emission factors. If exactly the same animal intake model and methane emission factors are used in a farm and national scale model, the summation may not be the same if individuals classify or report animal numbers differently, or if in the national statistics, assumptions about animal classes are made that are not valid.

5.2.2 Disaggregation

In applying models at different scales, it is important to consider whether decoupling or integration of model parameters has occurred. For example, if the emission factor for nitrous oxide from urine is a weighted value across drainage classes for the national inventory, should the farm scale model be based on the weighted average, or should a "disaggregated" emission factor that better describes the value for the drainage condition on the farm be used, if indeed it is available.

5.2.3 Model Boundary issues

Clearly defining boundary conditions and the data that resides within the boundary can be important. For example, with nitrous oxide emissions, should indirect emissions be included in the farm scale model (as they are sourced from the farm), or separated? With supplement movements between farms within New Zealand, should the cost be borne by the farmer making the supplement or receiving the supplement? The National Inventory ignores animal transfers between farms as the animals are within New Zealand, but animal movements between farms would be important in a farm scale model. Hopefully, the sum of animal movements should be zero. In defining boundaries for the model, it is important to ensure that outputs are not doubly accounted for, or conversely outputs are not omitted.

5.2.4 Model data inputs

The source of the data to drive the models should also be considered. For example, the OVERSEER® nutrient budget model was set up to use information that the farmer knew, or could readily obtain, or with suitable defaults where available. This put some constraints of the how the model was developed, for example, including process-orientated models are problematic due to the type of data required. For example, drainage models require knowledge of the hydraulic conductivity parameter ksat, which is highly variability and difficult to measure. Most farmers have an idea of whether there farms are poor draining or not, and sometimes their soil type. Thus the OVERSEER® nutrient budget model was developed around concepts familiar to the farmer.

5.2.5 Model application

Models can be configured to account for absolute emissions or to quantify relative change (e.g. 20% reduction). In many applications, relative change may be preferred and is usually considered more accurate. This is the approach that some regional councils have used to get a reduction in nitrate leaching from farms. However, this approach does require benchmarking and setting of protocols so that the baseline is relatively fixed over time. Greenhouse gas emissions are more likely to be required as absolute estimates because the baseline without farming activity is negligible for the majority of circumstances. To achieve this is going to require models either where all the inputs are verifiable and measureable, or where there a protocols written to ensure that information is used in a similar manner.

5.2.6 Spatial scaling

There is an expectation that modelling at smaller scales results in better estimates of total losses. The impact of spatial modelling scales has been examined and little information was found to support or reject this hypothesis. What did come out of this project was an understanding that process-orientated models frequently need to be calibrated to a given site to get 'reasonable' predictions of absolute losses, and that there is an interaction between data availability and model complexity. It is probable that in many cases simple data plus simple model can be as accurate as a complex data and complex models.

5.2.7 Temporal scaling

Much work has focused on spatial scale, but the temporal scale should also be considered. OVERSEER® nutrient budget model is a quasi-equilibrium model that predicts the average loss if the system entered in the model had been place for several years. It does not try to predict loss for a given year for a given climate pattern. Clear definition of the temporal scale is important for processes such as nitrous oxide emissions from urine leaching, where the amount emitted in a given year depends on the climate and the animal management systems (which are also influenced by climate). It is important that the temporal scales of the model are consistent with the purpose the model is being used for, and when upscaling, the temporal scales are the consistent through the scales.

5.2.9 Recommendations for tailoring requirement in model design

The above has highlighted that there can be many problems with upscaling data and models, and that many of these issues are frequently forgotten in the process. I believe that the way forward is to focus on the outcome that is desired, and design a system around that outcome. There have been instances where regional council policy has been set without consultation with model developers or field staff. If a model is used as a tool for implementation of policy, then the outcome may not be optimised. It can also result in mundane issues around backwards compatibility, dealing with model changes over time, and model naming and version numbering.

It is important that the users of a model have a clear understanding of what the model is aiming to achieve, that is, the model is fit for purpose. For example, a specifically modified version of Overseer could be used as part of an ETS scheme that supplies estimates that are 'fair' for individual farms. This may mean that the national inventory methods are modified to achieve this. Whilst the approach may be suitable for ETS accounting, it may be unsuitable for UNFCCC inventory reporting. It has been interesting to note that farmers are frequently happy with OVERSEER® nutrient budget outputs provided that they see how it applies to their particular farm. This relationship between confidence in model outputs and the model structure does require further exploration, particularly if applied to a farm-scale ETS scheme.

In contrast, a modified version of Overseer could apply the national inventory method strictly, such that the sum of farms across New Zealand adds up to the national emission estimates. This model may give a reasonable estimate of national inventory emissions, but may not be suitable for ETS as it is seen as being unfair, and may not allow for mitigation options or practices that could result in reduced greenhouse gas emissions.

5.2.10 Importance of model calibration/validation

In implementing sub-models in the OVERSEER® nutrient budget, one problem that has frequently occurred is that representative data or parameterisation is not available for the whole spectrum of conditions being modelled, i.e. any research data applies to a narrow range of conditions. Research work on selected locations is important for understanding the principles but is not necessarily conducive to New Zealand wide modelling. We would suggest that more research work is directed to locations or situations such that extremes are included, and the work is deliberately focused to calibrating and strengthening a model that has been selected to achieve the desired outcomes. That is, the research program for supporting a model may look different from that required to understand or determine whether a process is important. Development of the OVERSEER® nutrient budget model has resulted in the

identification of key research areas in terms of enhancing and strengthening this model. The future calibration/validation requirements should be tailored towards reducing uncertainties for the application/question being addressed.

5.2.11 Recommendations

We have outlined here some potential pitfalls that need to be avoided in the use of the OVERSEER® nutrient budget model to assess greenhouse gas emissions. Before any widespread application, we recommend an initial design/evaluation stage is undertaken, to identify any significant gaps/uncertainties that could potentially impact on accuracy of an up-scaled emission. This design/evaluation should consider the linkages between the desired policy outcome, methods of policy implementation, and the model that is used.

5.3 Semi-empirical methods

Semi-empirical approaches such as the Boundary-Line technique (Conen et al. 2000) are of intermediate complexity between an approach based on emission factors and a full-process-based model. Process-based models, such as DNDC and DAYCENT (see next section), attempt to simulate the physical and biogeochemical processes that ultimately lead to N_2O emissions. These models are of medium to high complexity, and require a reasonable level of information on soil environmental physics and chemistry as input. Consequently, scaling to regional or national levels is often limited by the availability of input data at these scales. Boundary line predictive models such as described by Conen et al. (2000) are empirical models driven by fewer and simpler input datasets. In addition, the datasets involved are available at regional scales and over long time periods. Boundary-line predictive models are developed by deriving separate relationships between the response variable of interest, N_2O emissions, and each of the important environmental drivers, such as water-filled pore space (WFPS) and soil mineral-N content. Functions can be fitted to the most extreme values of the response (boundary line functions) in the scattergrams drawn between the response variable and each of the important environmental drivers. The boundary line functions can then be incorporated into a single Boundary Line Predictive Model equation for N_2O emission.

A study by Sherlock et al. (2005) used the Boundary Line approach to create a predictive model based on analysis of MAF-commissioned N_2O emission trials. Boundary-line functions were generated for 4 environmental drivers: Water-Filled Pore Space, total soil mineral nitrogen content, soil temperature, and rainfall amount within the last 48 hours. The final form of the Boundary-Line Predictive Model was:

$FN_2O_{pred} = FN_2O_{max}$ x [f(WFPS) x f(Min-N) x f(Temp) x f(Day#) x f(Rain48)]

where FN_2O_{max} is a site-specific maximum observed N_2O flux, Day# is the days following N application and each f(x) is a dimensionless multiplier function determined by the Boundary Line equations for water-filled pore space, mineral-nitrogen, soil temperature and rainfall in last 48 hours. Sherlock et al. (2005) recommended that the Boundary Line Predictive Modelling approach continue to be explored and tested, and viewed it as promising for nationwide implementation. Geospatial data for input variables would form the basis of the mapping of N_2O emission potential or with accurate geospatial information on mineral-nitrogen, the mapping of N_2O emission flux would be possible at regional or a finer scale level.

5.4. Recent progress with process-based modelling

Process-based models attempt to simulate the actual chemical/physical/biological processes within a system. As the processes that produce greenhouse gas fluxes within agricultural soils are complex, with many interactions, it is difficult to develop an empirical model with sufficient flexibility to cover the full range of management practices, and soil and climate conditions found in New Zealand's grazed pasture systems.

New Zealand currently uses the IPCC default methodology (with country specific emission factors) in its emissions inventory to determine the N_2O emissions from agricultural soils. The IPCC default methodology is relatively simple to apply but has some disadvantages. First, there is a high degree of uncertainty in the predicted emission. In 2005 the uncertainty in the direct N_2O emissions from agricultural soils had a 95% confidence interval from -42% to +73% (Ministry for the Environment 2007). Most of this uncertainty was due to the high degree of variability in the emission factor $EF_{3(PR\&P)}$ with weather and soil type. The second disadvantage of the IPCC methodology is that it is unable to capture the effects of management strategies (e.g. the use of nitrification inhibitors) that reduce N_2O emissions.

A robust process-based model of N_2O emissions could be used to improve New Zealand's greenhouse gas inventory in a number of ways. A process-based model could be used to disaggregate the emission factor by (for example) region, farm type, soil type or climate regime. Alternatively, the process-based model could provide independent verification of the national inventory. Finally, a well-proven and internationally accepted model could be used as the inventory methodology.

5.4.1 Development of process-based modelling in New Zealand

An evaluation of process-based models suitable for estimating nitrous oxide emissions from New Zealand grazed pastures was conducted by van der Weerden (2002). Four process-based models (DNDC, DayCent, NOPAS, ExpertN) were identified as suitable for evaluation, although ExpertN was not assessed due to lack of availability and funding constraints. The other three models were modified for New Zealand conditions (the modified version of DNDC is referred to as NZ-DNDC) and tested against field measurements of soil mineral N, WFPS and N_2O emissions on three different soils. The NOPAS model had the disadvantage that it did not predict soil mineral N and water-filled pore space (WFPS) and needed to be integrated with another model (such as NZ-DNDC or DayCent). The report recommended (among other things) that the ExpertN be evaluated at a later date. However, according to the ExpertN website (http://www.helmholtz-muenchen.de/en/iboe/expertn/) as of March 2008, there was still no version of ExpertN available for download.

A later study (Harvey, M. et al. 2005, Saggar, S. et al. 2005b), compared NZ-DNDC and DayCent predictions with N_2O emissions from a Canterbury dairy farm. NZ-DNDC and DayCent predicted EFs of 0.022 and 0.015 respectively for non-irrigated conditions, and 0.041 and 0.032 with irrigation (compared to 0.01 from the median atmospheric measurements). However, the lack input data such as irrigation schedules, soil ammonium and nitrate levels and grazing schedules prior to the campaign period limited the usefulness of these validations. Both models were found to give satisfactory results given the high degree of uncertainty in some of the required input variables. Recommendations included improving the soil moisture balance of NZ-DNDC and changing DayCent so that management practices such as grazing and fertiliser application could be scheduled on a daily time scale and that more than one event per month could be modelled.

5.4.2 NZ-DNDC

NZ-DNDC is based on the DNDC (Denitrification-Decomposition) model of Li et al. (1992a, 1992b, 1994), with modifications for New Zealand's grazed pastoral conditions.

DNDC is a process-based model that can simultaneously predict soil emissions of N_2O, CH_4 and CO_2. The model can be run at field or regional scale and has been applied internationally to a wide range of systems in a number of countries including Australia (Kiese et al. 2005), Belgium (Beheydt et al. 2007), China (Li et al. 2004, Xu-Ri et al. 2006), Germany (Butterbach-Bahl et al. 2004, Neufeldt et al. 2006), India (Babu et al. 2006), New Zealand (Giltrap, D.L. et al. 2007, Saggar, S. et al. 2004,

Saggar, S. et al. 2007b), UK (Brown et al. 2002), USA (Farahbakhshazad et al. 2008, Li et al. 1996). The model was also used in the NitroEurope project, an integrated research project aimed at addressing core aspects of reactive nitrogen in the atmosphere (Sutton et al. 2006).

Recently a Global DNDC Researchers Network has been established to facilitate the exchange of information and ideas between the widely dispersed users of the DNDC model. This network includes an email list hosted by Landcare Research (http://info.massey.landcareresearch.co.nz/mailman/listinfo.cgi/dndcmodel) and plans to establish a website and to hold regular workshops.

Model description

DNDC consists of four sub-models: thermal-hydraulic, decomposition, denitrification and plant growth. The thermal-hydraulic sub-model uses input climate data to simulate soil temperature and moisture for each soil "layer". The denitrification sub-model is based on the kinetic processes of N_2O production and is activated when the soil WFPS exceeds a threshold level. These processes are moderated by soil temperature, WFPS and substrate availability. The decomposition sub-model uses four carbon pools decomposable residues, microbial biomass, humads and stable humus (which is assumed not to interact with the active pools over the time period of the model simulation). Each of the active pools has a number of sub-pools each with characteristic C:N ratios and turnover times. The decomposition rate is influenced by soil texture (clay content), moisture and temperature. The plant growth sub-model accumulates above and below ground biomass subject to sufficient daily water and N availability in the root zone.

Modification for New Zealand conditions

The original DNDC model was developed for cropping systems in the USA. New Zealand's grazed pasture systems and climate are quite different from most countries (24 hour, year-round grazing) with soils that are distinctive and diverse within short distances and have higher organic C contents than the world average (Saggar, S. 2001).

The NZ-DNDC model was initially developed by modifying DNDC version 6.7. The changes made are described in Saggar et al. (2004). The modifications made were:

- Adding a multiplicative factor to plant growth to account for variations in daylength throughout the year.

- Reversing the order that the model performed the water infiltration and drainage operations (so that drainage occurred before infiltration).

- Replacing the air-soil temperature relationship to better fit New Zealand conditions. The New Zealand specific relationship was:

$T_{surface} = T_{air} + 1.3$

- Increasing the threshold at which denitrification occurs from 35% WFPS to WFPS at field capacity.

- Adding N inputs from grazing animals. The mean N excreted by a dairy cow was calculated to be 0.29 kg per day split 60:40 between urine and dung. These inputs were calculated based on the number of grazing animals and time grazed and entered using the manure-input mechanism.

The modified NZ-DNDC model was found to make reasonable predictions of N_2O emissions when compared with field measurements from two different dairy-grazed soils (Saggar, S. et al. 2004). NZ-DNDC was also used in an upscaling case study on a Canterbury dairy farm (Harvey, M. et al. 2005). In both simulations the N_2O predictions were reasonable, although Saggar et al. (2004) found that the model did not predict a very high emission peak following a summer rainfall and Harvey et al. (2005) found that the predictions of WFPS and soil mineral-N could be improved.

In 2004, the NZ-DNDC model was updated from the Unix-based, command line interface DNDC6.7 to the Windows-based DNDC8.6K with a graphical user interface. The modifications listed above were made to the DNDC8.6K source code. The updated model also included some new features (such as automatically calculating dung and urine inputs from grazing animals).

Saggar et al. (2007a) describes further modifications made to the NZ-DNDC model:

- A new crop type, perennial pasture, was added based on observed seasonal growth curves in New Zealand.

- Excretal N for sheep set to 40g N/head/day.

- DNDC used the Thornthwaite formula to calculate potential evapotranspiration. However, Coulter (1973) found that the Thornthwaite equation did not generally produce good results in New Zealand. Therefore

NZ-DNDC was updated to give the option to use the Priestly and Taylor method using the parameters developed by Scotter et al. (1979) when solar radiation data were available.

- Previously DNDC had been unable to simulate the soil saturation conditions that occurred in grazed dairy pastures. One possible explanation was that the soil compaction caused by animal treading was affecting water flow through the soil profile. To simulate this, the "water retention layer" feature was used. This water retention layer is a user definable layer within the soil profile below which the soil hydraulic conductivity is greatly reduced. This modification improved the model's ability to predict both soil moisture and N_2O emissions.

Other minor modifications include the ability to specify the start date and the option to assume that animals receive sufficient additional feed when pasture production does not meet their food requirements.

Model application in New Zealand

The NZ-DNDC model has been tested against field data in a number of different experiments. These field experiments have included a number of different farming systems (dairy-grazed, sheep-grazed), measurement techniques (chambers, boundary layer micrometeorology) and greenhouse gases (N_2O, CH_4 and CO_2).

Saggar et al. (2004) compared the N_2O emissions predicted with NZ-DNDC to field measurements from two dairy-grazed pastures on contrasting soil types (a well-drained sandy loam and a poorly-drained silt loam). The model predictions of N_2O emissions compared reasonably well to the measured results, although the model did fail to predict a large emission event that occurred after heavy rainfall in summer.

A sensitivity analysis demonstrated that NZ-DNDC was sensitive to changes in climate, soil properties and farm management (such as fertiliser application amount, splitting fertiliser applications and grazing regimes (Saggar, S et al. 2007a). N_2O emissions were found to be particularly sensitive to rainfall, quantity and frequency of N inputs (both from fertiliser and animal excreta) and initial soil organic carbon levels.

The NZ-DNDC model was also tested against measurements of soil N_2O and CH_4 fluxes in a sheep-grazed pasture (Saggar, S. et al. 2007b). Initially the model over-predicted the soil uptake of CH_4. The model was then modified to account for the reduced CH_4 uptake when the WFPS at the soil surface restricted diffusion. This modification the NZ-DNDC model simulated effectively the general pulses and trends in both N_2O and CH_4 fluxes.

NZ-DNDC has also been tested against chamber measurements of N_2O and CO_2 fluxes from a dairy-grazed pasture (Giltrap, D.L. et al. 2008). The NZ-DNDC predictions of CO_2 production were highly sensitive to the initial allocation of soil organic carbon (SOC) to the three pools. N_2O emissions were less sensitive to the initial SOC allocation. An initial allocation of 2% of the SOC to the highly decomposable pool gave reasonable predictions of both CO_2 and N_2O emissions. However, the chamber measurements of CO_2 flux will also include CO_2 from plant above ground respiration, which is currently not simulated by NZ-DNDC.

NZ-DNDC has been used to estimate agricultural N_2O emissions for the Manawatu-Wanganui region (Giltrap et al. 2007). The modelled N_2O emissions were consistent with the IPCC calculations. However, there was still a high degree of uncertainty in the model estimate due to uncertainty in the soil organic carbon. The model also demonstrated that using climate data from different years produced different emission factors and could change the total regional N_2O emissions by about 20%.

Some preliminary research has been done on modelling the effects of nitrification inhibitors on N_2O emissions (Giltrap et al. 2006). It was found that simply reducing the nitrification rate by 60-80% when nitrification inhibitors were used produced good agreement with the field measurements. However, further work is needed to account for the differences in nitrification inhibitor lifetime and effectiveness in different soil types.

Summary

NZ-DNDC has the potential to simultaneous predict fluxes of N_2O, CH_4 and CO_2 from agricultural system as well as other environmental/economic impacts such as crop production and nitrate leaching. The model has been tested in a number of field trials, although increasing the range of soil and farm types tested will increase confidence in the model's predictions. Future work is needed to incorporate the effects of mitigation strategies, such as nitrification inhibitors, into the model. An expansion of the model to include an enteric methane component and validating the nitrate leaching

predictions would allow calculations of net biological greenhouse gas emissions from agriculture at paddock, farm and regional scale.

5.4.3 DAYCENT

DayCent (Del Grosso et al. 2001) is a daily time-step version of the CENTURY ecosystem model (Parton et al. 1994).

Model description

The structure of DayCent is similar to DNDC with sub-models for plant productivity, land surface parameters, soil organic matter (SOM) decomposition, and N gas fluxes. The plant productivity sub-model simulates plant growth while the land surface sub-model simulates evapotranspiration and soil moisture and temperature for the various soil layers. The decomposition sub-model includes three SOM pools as well above- and below- ground litter pools and a surface microbial pool with different potential decomposition rates (adjusted by soil moisture and temperature factors). The N gas sub-model predicts N_2O and NO_x emissions from nitrification and denitrification based on WFPS, pH, labile C availability, O_2 availability and soil concentrations of nitrate and ammonium.

Modifications for New Zealand conditions

Major modifications made to DayCent for New Zealand conditions were (van der Weerden et al. 2002):

- Changing plant production so that it was primarily driven by short-wave radiation rather than temperature.
- Adding dynamic allocation of net primary production (NPP) to roots or shoot depending on soil nutrient and moisture status.
- Using a soil moisture factor (moisture held in air-dry soil) instead of clay percentage as the key driving variable affecting soil organic matter stabilisation.
- Using an alternative algorithm (Woodward et al. 2001) for potential evapotranspiration.
- Minor changes to the soil temperature, water and grazing routines.

- Model parameterised to satisfactorily model pasture production on an irrigated Lismore soil.

Model application in New Zealand

DayCent was used in a pilot study comparing the performance of three different process-based models (NZ-DNDC, DayCent and NOPAS) in predicting soil mineral N, WFPS and N_2O emissions using data from three New Zealand sites (van der Weerden et al. 2002). In this study DayCent gave poor predictions of WFPS for all soils, but reasonable predictions of NH_4^+-N and NO_3^--N in most cases. In most cases the predicted N_2O fluxes were of the correct magnitude, although the daily dynamics were not well simulated.

Harvey et al. (2005) and Saggar et al. (2005b) compared the predictions of DayCent and NZ-DNDC with N_2O measurements made using chambers and micrometeorological methods. The results of this study have been described in an earlier section.

Stehfest & Müller (2004) tested DayCent's predictions of N_2O produced by nitrification and denitrification processes. The model predictions were compared to data from a one year field experiment near Lincoln using synthetic urine to simulate the effects of sheep grazing. The fraction of N_2O from nitrification was determined from a separate field that received the same urine treatments but the acetylene inhibition method was used to suppress denitrification reactions. DayCent predicted the general pattern of N_2O emissions relatively well but over predicted the observed emissions by more than three times. This was attributed to an overestimation of nitrification related N_2O emissions.

Summary

DayCent has produced reasonable predictions of N_2O emissions in New Zealand grazed pasture systems. However, it has been noted that the model needs to be modified so that all processes (such as fertiliser/urine addition and plant nutrient uptake) can be simulated at a daily time step and that more than one event per month can be simulated. Recently there has been less work on developing DayCent in New Zealand compared to NZ-DNDC.

5.4.4 Modelling uncertainty discussion

Saggar et al. (2007a) performed a sensitivity analysis of the paddock-scale NZ-DNDC model with respect to the effects of a number of soil, climate and management factors on pasture production and N_2O emissions. While stocking rate and fertiliser addition were important factors in net N_2O emission other factors such as SOC, rainfall and temperature also had noticeable effects on the annual N_2O predicted.

Giltrap et al. (2007) used NZ-DNDC to predict the agricultural N_2O emissions for the Manawatu-Wanganui region for the year ended June 2003. The model predicted net agricultural N_2O emissions for the region of 4.6 ± 1.5 Gg N_2O-N. The uncertainty in this number was due to uncertainties in the SOC values only. This methodology used the most extreme values of SOC within each polygon so it may be possible to improve the methodology (e.g. use a weighted mean SOC) to reduce the uncertainty. However, other sources of uncertainty such as variations in stocking rates and other management practices were not assessed. From Saggar et al. (2007a) the N_2O emissions were reasonably linear with respect to stocking rates and fertiliser inputs, so using average rates should not have affected the overall emissions significantly. However, assumptions made about the relative amounts of fertiliser applied on different farm types and the timing of the fertiliser applications may have introduced some bias.

The Manawatu-Wanganui study also found that rerunning the same soil and farm management data using the climate data for the year ended June 2004 resulted in a 20% reduction in the net N_2O emissions. This indicates that interannual variations in climate can have a significant impact on the predicted emissions.

6 Uncertainty with upscaling

Overall uncertainty in the national total anthropogenic N_2O emission from agriculture has been assessed for the national inventory report by Monte Carlo simulation following recommendations of Chapter 3 of Inventory Good Practice Guidance ((IPCC 2006) bearing in mind that uncertainty is inherent and non-normally distributed because of the biogenic origin of the gas. The inventory with its Tier 1 complexity is highly uncertain. For 2006, the annual emission is 41.1 Gg per annum N_2O with the 95% confidence interval of 23.8 to 71.5 Gg per annum (Ministry for the Environment 2008). The majority (90%) of this uncertainty is attributed to $EF_{3(PR\&P)}$ reflects natural variance in EF_3 described as "determined largely by the vagaries of the weather and soil type".

If the inventory were to be developed beyond "Tier 1", we cannot assume that uncertainty will be reduced as a result in what would be determined by the effect of combined disaggregated uncertainties in $EF_{3(PR\&P)}$, whether it be disaggregation by dung and urine, geographic/climatic region or soil type because uncertainty in each of the disaggregated $EF_{3(PR\&P)}$. The data verification requirements are significant.

In moving to a higher tier (more disaggregated or geospatially modelled emission) the contribution to uncertainty in the up-scaled emission estimate of all the input components needs to be assessed. With satellite-based methods discussed in Chapter "4 Direct Measurements: Satellite-based mapping of greenhouse gas column and surface flux estimates" data exist for top-down verification of methane emissions from space. The quality of these will improve over time. However, it is unlikely in the short term that methods beyond the paddock-scale will become available for N_2O emission assessment. Therefore, it is through model-based upscaling that there is greatest promise for climate-responsive regional to national N_2O emission assessment. "Section 5.4. Recent progress with process-based modelling" includes discussion of initial work on model-based regional upscaling for N_2O by Giltrap (2007). As this regional work develops, there will be a need for careful consideration of uncertainty with upscaling. Of relevance to model-based upscaling of N_2O emission in New Zealand is the study of van Bodegom et al (2002) for CH_4 from rice paddies in Java. The uncertainty framework for CH_4 in the context of this study and N_2O in New Zealand are similar. These authors consider in detail the range of component uncertainties that contribute to upscaled uncertainty. The four uncertainty source categories considered are:

- uncertainty in actual GHG emission measurement (including underlying verification)

- uncertainty in model input parameters
- uncertainty introduced through model parameterisation / simplification
- uncertainty in process-based understanding or drivers of GHG production

van Bodegom et al found that for the reasonably heterogeneous methane source, the influence of data on the uncertainty in geostatistical upscaling was a major component of the overall uncertainty of the upscaled emission estimate compared against the uncertainty introduced from the process-based modelling. They conclude that without significant increase in (verification) data across the range of environmental variables, it will be difficult to reduce uncertainty in emission estimates.

In spite of the degree of uncertainty in absolute model emission estimates, their use in predicting trends or changes in emission for the entire basket of gases with both climate-change related changes in environmental drivers or changes in management practices (affecting e.g. available nitrogen inputs) is another important capability of (particularly process-based) models. Li et al (2004) provide a good example of this type of model application, exploring some what if? sensitivity analysis.

7 Conclusions and recommendations

In this chapter we briefly summarise aspects where paddock-scale measurement and modelling approaches in the near-term will be of greatest utility in advancing confidence in the national inventory. Referring back to Figure 1, both measurement and models have now developed to the stage where they can be usefully deployed at paddock-scale, measurements should be possible with sufficient accuracy to form a good basis for model verification and through model-based upscaling, there is a potential methodology for development of higher tier inventory that can respond to climate and ultimately could form a good framework for testing system-response to mitigation treatments

7.1 Verification strategy

Verification of models of various degrees of complexity with accurate field measurements of emission will be a critical aspect to refinement and development of both national inventory and farmscale inventory if this becomes a point of obligation under the Emissions Trading Scheme. At the paddock scale, micrometeorological methodologies for flux measurement require specialised equipment and knowledge and the high-precision optical instrumentation is not cheap and therefore widespread deployment at the present time is impractical. With limited resources, it is therefore of critical importance that careful strategic consideration is given to the "where and when" of measurement programmes. Amongst farm-systems, intensively farmed pastures such as dairy are likely to have highest emissions, there has been a focus on study of these systems and that should continue. There is merit also in looking at less intensively farmed areas such as rolling hill country which also accounts for a significant amount of land area.

7.2 Options to enhance confidence of CH4 inventory

7.2.1 Measurement

With high-deployment cost, the paddock-scale techniques are not suitable for routine application to a large number of farms. They will always need to be applied as well-planned experiments in limited case studies. Such case studies can, nevertheless, make important contributions to increase the confidence of the national CH_4 inventory. In at least three ways such contributions are feasible, as follows:

1. Paddock-scale techniques can provide independent confirmation of the animal-scale SF_6 technique, by using both approaches simultaneously. This would be complementary to animal chamber trials because it works outdoors, on larger animal numbers. Past experiments of this kind have found good agreement (Laubach & Kelliher 2004, Laubach et al. 2008).

2. Paddock-scale techniques can assess a herd's response to a change in food quantity or quality. Such studies can be specially designed (e.g. using feedlot scenarios) to assess the CH_4/DMI emissions factor that is used in the national inventory. Landcare Research and AgResearch plan such an experiment for November 2008.

3. Paddock-scale techniques will be useful to assess a herd's response to future mitigation techniques. Again, it is an important feature of these techniques that they work outdoors, on larger animal numbers, while these animals are subjected to normal farm management routines (with and without the mitigation technique to be tested). Subject to the uncertainty limits as discussed above, the effect of the mitigation technique can then be quantified.

7.2.2 Modelling

New Zealand currently uses a Tier 2 approach to calculate enteric CH_4 emissions (Ministry for the Environment 2008). This approach uses a detailed livestock population and productivity model to calculate the required feed intake which is then used to derive the enteric CH_4 produced. This calculation is currently performed independently of the soil N_2O emissions. In reality there are feedbacks between pasture growth and quality, animal productivity and excretal-N inputs to the soil. Therefore including these feedbacks in a process-based model would enable the impacts of enteric CH_4 mitigation options on soil N_2O emissions (and vice versa) to be assessed.

7.3 Options to enhance confidence of N_2O inventory

7.3.1 Measurement

In addition to enhancing confidence in the CH_4 inventory, paddock-scale techniques can contribute to enhancing confidence in the N_2O inventory, as follows.

1. Paddock-scale techniques can be used, in case studies, to assess paddock emissions prior, during and after being grazed by a herd (and same can be done for fertiliser application). They can establish the time trajectory of the

emissions over a few weeks and, by integration, the total emission related to the grazing (or fertilising) event. The emissions can then be compared to inventory-based predictions, thereby assessing the suitability of the emission factors used in the inventory. Examples of such case studies are Harvey et al. (2008) and Phillips et al. (2007).

2. These case studies also allow us to improve our understanding of the processes controlling N_2O emissions, because relevant parameters like soil temperature or soil moisture can be measured simultaneously. That way, the emission factors can not only be tested, but their parameterisation can be improved, leading to better inventory predictions.

3. Like for CH_4, paddock-scale techniques will be useful to assess the efficacy of mitigation techniques for N_2O. Subject to the uncertainty limits, the effects of the tested mitigation technique can then be quantified.

4. Longer-term studies to assess the seasonal variability of emission factors for N_2O are possible, too. For example, Scanlon and Kiely (2003) found, in an 8-month long experiment over grazed and fertilised pasture in Ireland, that the emission factor there did not show a significant seasonal variation. Given that result, and considering the required long-term commitment of expensive equipment and labour, this is perhaps of lower priority than studies to assess the variability with type of farming activity and soil properties (see 2).

7.3.2 Modelling

Modelling is always going to be required for New Zealand's N_2O inventory as national scale measurements will not be practicable. Process-based modelling can contribute to the improvement of the national inventory in the following ways:

1. Assessing the efficacy of mitigation strategies such as nitrification inhibitors and stand-off pads in reducing emissions.

2. Assessing the variability in N_2O emissions caused by variations in soil properties, climate and management regimes.

3. Providing independent verification of the national inventory following extensive calibration/validation.

4. Aiding disaggregation of emission factors by (for example) region, farm type, soil type or climate regime.

5. Examining the long term impacts of climate change and management strategies on agricultural greenhouse gas emissions.

6. A well-proven and internationally accepted model could be used directly or aid the development of a Tier III inventory methodology.

It is important that the models used can account for all three greenhouse gases (CH_4, N_2O and CO_2) as in some situations reductions in one gas may be offset by an increase in another gas. Process-based models can be particularly useful for identifying such risks as they incorporate many of the complex feedback mechanisms.

Models will be needed that can operate at paddock scale (for comparison with experimental results), farm scale (to develop best management practices and/or enable farmers to assess their greenhouse gas emissions) and regional/national scale (for inventory purposes and scenario testing).

8 Acknowledgements

The authors thank Ben Liley and Stephen Wood, NIWA Lauder for discussion of ground-based mapping in 3.10 Novel techniques and mapping technologies, and thank Vanessa Sherlock, NIWA Wellington for input and discussions on the atmospheric remote sensing Chapter 4 Direct Measurements: Satellite-based mapping of greenhouse gas column and surface flux estimates.

9 References

Ambus, P.; Christensen, S. (1994). Measurement of N2O emission from a fertilised grassland: an analysis of spatial variability. *Journal of Geophysical Research 99(D8)*: 16549-16555.

Babu, Y.J.; Li, C.; Frolking, S.; Nayak, D.R.; Adhya, T.K. (2006). Field validation of DNDC model for methane and nitrous oxide emissions from rice-based production systems of India. *Nutrient Cycling in Agroecosystems 74*: 157-174.

Balfour, W.D.; Schmidt, C.E.; Eklund, B.M. (1987). Sampling approaches for the measurement of volatile compounds at hazardous waste sites. *Journal of Hazardous Materials 14*: 135-148.

Beheydt, D.; Boeckx, P.; Sleutel, S.; Li, C.; van Cleemput, O. (2007). Validation of DNDC for 22 long-term N2O field emission measurements. *Atmospheric Environment 41*: 6196-6211.

Bekku, Y.; Koizumi, H.; Oikawa, T.; Iwaki, H. (1997). Examination of four methods for measuring soil respiration. *Applied Soil Ecology 5(3)*: 247-254.

Brown, L.; Syed, B.; Jarvis, S.C.; Sneath, R.W.; Phillips, V.R.; Goulding, K.W.; Li, C. (2002). Development and application of a mechanistic model to estimate emission of nitrous oxide from UK agriculture. *Atmospheric Environment 36(6)*: 917-928.

Burba, G.G.; Anderson, D.J. (2008). Introduction to the Eddy Covariance Method: General Guidelines and Conventional Workflow. http://www.licor.com. LI-COR Biosciences. 141 p.

Businger, J.A.; Oncley, S.P. (1990). Flux measurement by conditional sampling. *Journal of Atmospheric and Oceanic Technology 7*: 349-352.

Butterbach-Bahl, K.; Kesik, M.; Miehle, P.; Papen, H.; Li, C. (2004). Quantifying the regional source strength of N-trace gases across agricultural and forest ecosystems with process based models. *Plant and Soil 260(1-2)*: 311-329.

Chédin, A.; Hollingsworth, A.; Scott, N.A.; Serrar, S.; Crevoisier, C.; Armante, R. (2002). Annual and seasonal variations of atmospheric CO2, N2O and CO concentrations retrieved from NOAA/TOVS satellite observations. *Geophysical Research Letters 29(8)*: 110-111 - 110-114.

Chédin, A.; Serrar, S.; Scott, N.A.; Crevoisier, C.; Armante, R. (2003). First global measurement of midtropospheric CO2 from NOAA polar satellites: Tropical zone. *Journal of Geophysical Research D: Atmospheres 108(18)*: ACH 7-1 - ACH 7-13.

Christensen, S.; Ambus, P.; Arah, J.R.M.; Clayton, H.; Galle, B.; Griffith, D.W.T.; Hargreaves, K.J.; Klemedtsson, L.; Lind, A.M.; Maag, M.; Scott, A.; Skiba, U.; Smith, K.A.; Welling, M.; Wienhold, F.G. (1996). Nitrous oxide emission from an agricultural field: comparison between measurements by flux chamber and micrometeorological techniques. *Atmospheric Environment 30(24)*: 4183-4190.

Cobos, D.R.; Baker, J.M.; Nater, E.A. (2002). Conditional sampling for measuring mercury vapor fluxes. *Atmospheric Environment 36(27)*: 4309-4321.

Conen, F.; Dobbie, K.E.; Smith, K.A. (2000). Predicting N2O emissions from agricultural land through related soil parameters. *Global Change Biology 6*: 417-426.

Conen, F.; Smith, K.A. (1998). A re-examination of closed flux chamber methods for the measurement of trace gas emissions from soils to the atmosphere. *European Journal of Soil Science 49*: 701-707.

Connor, B.J.; Boesch, H.; Toon, G.; Sen, B.; Miller, C.; Crisp, D. (2008). Orbiting Carbon Observatory: Inverse method and prospective error analysis: doi:10.1029/2006JD008336. *Journal of Geophysical Research 113*: D05305.

Coulter, J.D. (1973). Prediction of evapotranspiration from climatological data. *In*: Proceedings of the Soil and Plant Water Symposium, pp. 38-45.

Davidson, E.A.; Savage, K.; Verchot, L.V.; Navarro, R. (2002). Minimising artifacts and biases in chamber-based measurements of soil respiration. *Agricultural and Forest Meteorology 113(1)*: 21-37.

de Klein, C.A.M.; Barton, L.; Sherlock, R.R.; Li, Z.; Littlejohn, R.P. (2003). Estimating a nitrous oxide emission factor for animal urine from some New Zealand pastoral soils. *Australian Journal of Soil Research 41*: 381-399.

Del Grosso, S.J.; Parton, W.J.; Mosier, A.R.; Hartman, M.D.; Brenner, J.; Ojima, D.S.; Schimel, D.S. (2001). Simulated interaction of carbon dynamics and nitrogen trace gas fluxes using the DAYCENT model. *In*: Shaffer, M.J.; Ma, L.; Hansen, S. (eds). Modeling Carbon and Nitrogen Dynamics for Soil Management, pp. 303-332. CRC Press.

Denmead, O.T. (2008). Approaches to measuring fluxes of methane and nitrous oxide between landscapes and the atmosphere. *Plant and Soil 309*: 5-24.

Denmead, O.T.; Harper, L.A.; Freney, J.R.; Griffith, D.W.T.; Leuning, R.; Sharpe, R.R. (1998). A mass balance method for non-intrusive measurements of surface-air trace gas exchange. *Atmospheric Environment 32*: 3679-3688.

Denmead, O.T.; Leuning, R.; Griffith, D.W.T.; Jamie, I.M.; Esler, M.B.; Harper, L.A.; Freney, J.R. (2000a). Verifying inventory predictions of animal methane emissions with micrometeorological measurements. *Boundary-Layer Meteorology 96(1/2)*: 187-209.

Denmead, O.T.; Leuning, R.; Jamie, I.M.; Griffith, D.W.T. (2000b). Nitrous oxide emissions from grazed pastures: measurements at different scales. *Chemosphere - Global Change Science 2*: 301 - 312

Desjardins, R.L.; Denmead, O.T.; Harper, L.; McBain, M.; Masse, D.; Kaharabata, S. (2004). Evaluation of a micrometeorological mass balance method employing an open-path laser for measuring methane emissions. *Atmospheric Environment 38(39)*: 6855-6866.

Dils, B.; De Mazière, M.; Müller, J.F.; Blumenstock, T.; Buchwitz, M.; de Beek, R.; Demoulin, P.; Duchatelet, P.; Fast, H.; Frankenberg, C.; Gloudemans, A.; Griffith, D.; Jones, N.; Kerzenmacher, T.; Kramer, I.; Mahieu, E.; Mellqvist, J.; Mittermeier, R.L.; Notholt, J.; Rinsland, C.P.; Schrijver, H.; Smale, D.; Strandberg, A.; Straume, A.G.; Stremme, W.; Strong, K.; Sussmann, R.; Taylor, J.; van den Broek, M.; Velazco, V.; Wagner, T.; Warneke, T.; Wiacek, A.; Wood, S. (2006). Comparisons between SCIAMACHY and ground-based FTIR data for total columns of CO, CH4, CO2 and N2O. *Atmos. Chem. Phys. 6(7)*: 1953-1976.

Edwards, G.C.; Thurtell, G.W.; Kidd, G.E.; Dias, G.M.; Wagner-Riddle, C. (2003). A diode laser based gas monitor suitable for measurement of trace gas exchange using micrometeorological techniques. *Agricultural and Forest Meteorology 115(1-2)*: 71-89.

Eklund, B. (1992). Practical guidance for flux chamber measurements of fugitive volatile organic emission rates. *Journal of Air & Waste Management Association 42*: 1583-1591.

Eklund, B.M.; Balfour, W.D.; Schmidt, C.E. (1985). Measurement of fugitive volatile organic emission rates. *Environmental Progress 4(3)*: 199-202.

Farahbakhshazad, N.; Dinnes, D.L.; Li, C.; Jaynes, D.B.; Salas, W. (2008). Modeling biogeochemical impacts of alternative management practices for a row-crop field in Iowa. *Agriculture Ecosystem and Environment 123*: 30-48.

Flechard, C.R.; Ambus, P.; Skiba, U.; Rees, R.M.; Hensen, A.; van Amstel, A.; Dasselaar, A.v.d.P.-v.; Soussana, J.F.; Jones, M.; Clifton-Brown, J.; Raschi, A.; Horvath, L.; Neftel, A.; Jocher, M.; Ammann, C.; Leifeld, J.; Fuhrer, J.; Calanca, P.; Thalman, E.; Pilegaard, K.; Di Marco, C.; Campbell, C.; Nemitz, E.; Hargreaves, K.J.; Levy, P.E.; Ball, B.C.; Jones, S.K.; van de Bulk, W.C.M.; Groot, T.; Blom, M.; Domingues, R.; Kasper, G.; Allard, V.; Ceschia, E.; Cellier, P.; Laville, P.; Henault, C.; Bizouard, F.; Abdalla, M.; Williams, M.; Baronti, S.; Berretti, F.; Grosz, B. (2007). Effects of climate and management intensity on nitrous oxide emissions in grassland systems across Europe. *Agriculture, Ecosystems & Environment 121(1-2)*: 135-152.

Flesch, T.K.; Prueger, J.H.; Hatfield, J.L. (2002). Turbulent Schmidt number from a tracer experiment. *Agric. For. Meteorol. 111*: 299-307.

Flesch, T.K.; Wilson, J.D.; Harper, L.A.; Crenna, B.P.; Sharpe, R.R. (2004). Deducing Ground-to-Air Emissions from Observed Trace Gas Concentrations: A Field Trial. *J. Appl. Meteorol. 43*: 487-502.

Flesch, T.K.; Wilson, J.D.; Yee, E. (1995). Backward-Time Lagrangian Stochastic Dispersion Models and Their Application to Estimate Gaseous Emissions. *Journal of applied Meteorology 34(6)*: 1320-1332.

Folorunso, O.A.; Rolston, D.E. (1984). Spatial variability of field-measured denitrification gas fluxes. *Soil Science Society of America Journal 48*: 1214-1219.

Fowler, D.; Hargreaves, K.J.; Skiba, U.; Milne, R.; Zahniser, M.S.; Moncrieff, J.B.; Beverland, I.J.; Gallagher, M.W. (1995). Measurements of CH4 and N2O fluxes at the landscape scale using micrometeorological methods. *Philosophical transactions of the Royal Society of London Series A: Physical sciences and Engineering 351(1696)*: 339-356.

Fukui, Y.; Doskey, P.V. (1996). An enclosure technique for measuring nonmethane organic compound emissions from grasslands. *Journal of Environmental Quality 25*: 601-610.

Galle, B.; Klemedtsson, L.; Bergqvist, B.; Ferm, M.; Törnqvist, K.; Griffith, D.W.T.; Jensen, N.O.; Hansen, F. (2000). Measurements of ammonia emissions from spreading of manure using gradient FTIR techniques. *Atmos. Environ. 34*: 4907-4915.

Galvin, G.; Lowe, S.; Smith, R. (2004). The Validation Of A Simple Gaussian Dispersion Model For Determining Odour Emission Rates From Area Sources. *Developments in Chemical Engineering & Mineral Processing 12(5/6)*: 1-14.

Gerlach, T.M.; Doukas, M.P.; McGee, K.A.; Kessler, R. (2001). Soil efflux and total emission rates of magmatic CO2 at the Horseshoe Lake tree kill, Mammoth Mountain, California, 1995-1999. *Chemical Geology 177(1-2)*: 101-116.

Gholson, A.R.; Albritton, J.R.; Jayanty, R.K.M. (1989). Evaluation of the flux chamber method for measuring volatile organic emissions from surface impoundments. 79 pp p.

Gholson, A.R.; Albritton, J.R.; Jayanty, R.K.M. (1991). Evaluation of an enclosure method for measuring emissions of volatile organic compounds from quiescent liquid surfaces. *Environmental Science & Technology 25(3)*: 519-524.

Giltrap, D.; Saggar, S.; Singh, J.; Li, C. (2006). "Modelling the effects of nitrification inhibitors on nitrous oxide emissions from grazed pastures." Presented at the New Zealand Soil Science Society Conference, Rotorua.

Giltrap, D.L.; Saggar, S.; Li, C.; Wilde, H. (2007). Using the NZ-DNDC model to estimate agricultural N2O emissions in the Manawatu-Wanganui region. *Plant and Soil*: DOI: 10.1007/s11104-11007-19527-11107.

Giltrap, D.L.; Saggar, S.; Singh, J. (2008). Measured and modelled carbon dioxide fluxes from a grazed dairy pasture. *In*: Proceedings of the Fertilizer and Lime Research Workshop, pp. (In press).

Gostelow, P.; Longhurst, P.J.; Parsons, S.A.; Stuetz, R.M. (2003). Sampling for measurement of odours. IWA Scientific and Technical Report No. 17. p.

Griffis, T.J.; Sargent, S.D.; Baker, J.M.; Lee, X.; Tanner, B.D.; Greene, J.; Swiatek, E.; Billmark, K. (2008). Direct measurement of biosphere-atmosphere isotopic CO_2 exchange using the eddy covariance technique. doi:10.1029/2007JD009297. *Journal of Geophysical Research D: Atmospheres 113*: D08304.

Griffith, D.W.T.; Bryant, G.R.; Hsu, D.; Reisinger, A.R. (2008). Methane emissions from free-ranging cattle: Comparison of tracer and integrated horizontal flux techniques. *Journal of Environmental Quality 37(2)*: 582-591.

Griffith, D.W.T.; Jamie, I.M. (2000). Fourier Transform Infrared Spectrometry in Atmospheric and Trace Gas Analysis. *In*: Meyers, R.A. (ed.). Encyclopedia of Analytical Chemistry, pp. 1979-2007. John Wiley & Sons, Chichester.

Harper, L.A.; Denmead, O.T.; Byers, F.M. (1999). Direct Measurements of Methane Emissions from Grazing and Feedlot Cattle. *Journal of Animal Science 77(6)*: 1392.

Harvey, M.; Pattey, E.; Saggar, S.; T., B.; Dow, D.; Kotkamp, M.; Martin, R.; Moss, R.; Singh, J. (2008). Verification techniques for N2O emission at the paddock scale in New Zealand: FarmGas 2006. *Aust. J. Exp. Agric. 48*: 138-141.

Harvey, M.; Saggar, S.; Metherell, A.K.; Andrew, R.M.; Giltrap, D.; Gimson, N.; Porteous, A. (2005). Upscaling agricultural N2O emission estimates through process-based modelling. *NIWA Client Report WLG2004-48,* Report to Ministry of Agriculture and Forestry. 111 p.

Harvey, M.J.; Brailsford, G.W.; Bromley, A.M.; Lassey, K.R.; Mei, Z.; Kristament, I.S.; Reisinger, A.R.; Walker, C.F.; Kelliher, F.M. (2002). Boundary-layer isotope dilution/mass balance methods for measurement of nocturnal methane emissions from grazing sheep. *Atmospheric Environment 36*: 4663-4678.

Hashmonay, R.A.; Yost, M.G.; Mamane, Y.; Benayahu, Y. (1999). Emission rate apportionment from fugitive sources using open-path FTIR and mathematical inversion. *Atmospheric Environment 33(5)*: 735-743.

Hendriks, D.M.D.; Dolman, A.J.; van der Molen, M.K.; van Huissteden, J. (2008). A compact and stable eddy covariance set- up for methane measurements using off-axis integrated cavity output spectroscopy. *Atmos. Chem. Phys. 8*: 431-443.

Hudson, N.; Ayoko, G.A. (2008). Comparison of emission rate values for odour and odorous chemicals for two sampling devices. *Atmospheric Environment Submitted for publication*.

Hudson, N.; Ayoko, G.A.; Dunlop, M.; Duperouzel, D.; Burrell, D.; Bell, K.; Gallgher, E.; Nicholas, P.; Heinrich, N. (2008). Comparison of odour emission rates measured from various sources using two sampling devices. *Bioresource Technology Accepted for publication, 10.1016/j.biortech.2008.05.043(10.1016/j.biortech.2008.05.043)*.

Hutchinson, G.L.; Livingston, G.P. (2001). Vents and seals in non-steady-state chambers used for measuring gas exchange between soil and the atmosphere. *European Journal of Soil Science 52*: 675-682.

Hutchinson, G.L.; Mosier, A.R. (1981). Improved Soil Cover Method for Field Measurement of Nitrous Oxide Fluxes. *Soil Science Society of America Journal 45(2)*: 311-316.

IPCC. (2006). IPCC Guidelines for National Greenhouse Gas Inventories. *In*: Eggleston, H.S.; Buendia, L.; Miwa, K.; Ngara, T.; Tanabe, K. (eds). Prepared by the National Greenhouse Gas Inventories Programme, pp. IGES, Japan.

Judd, M.J.; Kellier, F.M.; Ulyatt, M.J.; Lassey, K.R.; Tate, K.R.; Shelton, I.D.; Harvey, M.J.; Walker, C.F. (1999). Net methane emissions from grazing sheep. *Global Change Biology 5(6)*: 647-657(611).

Keith, H.; Wong, S.C. (2006). Measurement of soil CO2 efflux using soda lime absorption: both quantitative and reliable. *Soil Biology and Biochemistry 38(5)*: 1121-1131.

Kelliher, F.M.; Reisinger, A.R.; Martin, R.J.; Harvey, M.J.; Price, S.J.; Sherlock, R.R. (2002). Measuring nitrous oxide emission rate from grazed pasture using Fourier-transform infrared spectroscopy in the nocturnal boundary layer. *Agricultural and Forest Meteorology 111*: 29-38.

Kiese, R.; Li, C.; Hilbert, D.W.; Papen, H.; ButterbachBahl, K. (2005). Regional application of PnET-N-DNDC for estimating the N2O source strength of tropical rainforests in the Wet Tropics of Australia. *Global Change Biology 11(1)*: 128-144.

Kim, K.H.; Kim, M.Y.; Kim, J. (2005). Application of micrometeorological approaches to measure methane exchange in a dry paddy field in the western coast of Korea. *Chemosphere 59*: 1613-1624.

Klenbusch, M.R. (1986). Measurement of gaseous emission rates from land surfaces using an emission isolation flux chamber. 60 pp p.

Kljun, N.; Calanca, P.; Rotach, M.W.; Schmid, H.P. (2004). A Simple Parameterisation for Flux Footprint Predictions. *Boundary Layer Meteorology 112(3)*: 503-523.

Laubach, J.; Kelliher, F.M. (2004). Measuring methane emission rates of a dairy cow herd by two micrometeorological techniques. *Agricultural and Forest Meteorology 125*: 279-303.

Laubach, J.; Kelliher, F.M. (2005a). Measuring methane emission rates of a dairy cow herd (II): results from a backward-Lagrangian stochastic model. *Agric. For. Meteorol. 129*: 137-150.

Laubach, J.; Kelliher, F.M. (2005b). Methane emissions from dairy cows: Comparing open-path laser measurements to profile-based techniques. *Agricultural and Forest Meteorology 135(1-4)*: 340-345.

Laubach, J.; Kelliher, F.M.; Knight, T.; Clark, H.; Molano, G.; Cavanagh, A. (2008). Methane emissions from beef cattle – a comparison of paddock- and animal-scale measurements. *Aust. J. Exp. Agric. 48*: 132-137.

Lee, J.F.; Chao, H.P.; Chiou, C.; Manes, M. (2004). Turbulence effects on volatilization rates of liquids and solutes. *Environmental Science & Technology 38*: 4327-4333.

Leuning, R.; Baker, S.K.; Jamie, I.M.; Hsu, C.H.; Klein, L.; Denmead, O.T.; Griffith, D.W.T. (1999). Methane emission from free-ranging sheep: a comparison of two measurement methods. *Atmospheric Environment 33*: 1357-1365.

Li, C.; Frolking, S.; Frolking, T.A. (1992a). A model of nitrous oxide evolution from soil driven by rainfall events: 1. Model Structure and Sensitivity. *Journal of Geophysical Research 97((D9))*: 9759-9776.

Li, C.; Frolking, S.; Frolking, T.A. (1992b). A Model of Nitrous Oxide Evolution From Soil Driven by Rainfall Events: 2. Model Applications. *Journal of Geophysical Research 97*: 9777-9783.

Li, C.; Frolking, S.; Harriss, R. (1994). Modeling carbon biogeochemistry in agricultural soils. *Global Biogeochemical Cycles 8*: 237-254.

Li, C.; Mosier, A.; Wassman, R.; Cai, Z.; Zheng, X.; Huang, Y.; Tsuruta, H.; Boonjawat, J.; Lantin, R. (2004). Modeling greenhouse gas emissions from rice-based production systems: Sensitivity and upscaling. *Global Biogeochemical Cycles 18*: GB1043, doi 1010.1029/2003GB002045.

Li, C.; Narayanan, V.; Harriss, R.C. (1996). Model estimates of nitrous oxide emissions from agricultural lands in the United States. *Global Biogeochemical Cycles(2)*: 297-306.

Livingston, G.P.; Hutchinson, G.L.; Spartalian, K. (2005). Diffusion theory improves chamber-based measurements of trace gas emissions (DOI 10.1029/2005GL024744). *Geophysical Research Letters 32(24)*: L24817.

Livingston, G.P.; Hutchinson, G.L.; Spartalian, K. (2006). Trace gas emission in chambers: A non-steady-state diffusion model. *Soil Science Society of America Journal 70(5)*: 1459-1469.

Magliulo, V.; Alterio, G.; Peressotti, A. (2004). Experimental and Numerical Test of the Micrometeorological Mass Difference Technique for the Measurement of Trace Gas Emissions from Small Plots. *Environmental Science and Technology 38(9)*: 2693-2700.

Matson, P.A.; Harriss, R.C. (1995). Biogenic trace gases: measuring emissions from soil and water. *Methods in ecology.* Blackwell Science Limited, Oxford. p.

McGinn, S.M.; Flesch, T.K.; Harper, L.A.; Beauchemin, K.A. (2006). An approach for measuring methane emissions from whole farms. *J. Environ. Qual. 35*: : 14-20.

Ministry for the Environment (2007). New Zealand Greenhouse Gas Inventory 1990-2005 and Common Reporting Format. p.

Ministry for the Environment (2008). New Zealand Greenhouse Gas Inventory 1990-2006 and Common Reporting Format. 44 p.

Mohn, J.; Werner, R.A.; Buchmann, B.; Emmenegger, L. (2007). High-precision $\delta^{13}CO_2$ analysis by FTIR spectroscopy using a novel calibration strategy. *Journal of Molecular Structure 834-836(SPEC. ISS.)*: 95-101.

Neufeldt, H.; Schafer, M.; Angenendt, E.; Li, C.; Kaltschmitt, M.; Zeddies, J. (2006). Disaggregated greenhouse gas emission inventories from agriculture via a coupled economic-ecosystem model. *Agriculture, Ecosystems and Environment 112*: 233-240.

Pape, L.; Ammann, C.; Nyfeler-Brunner, A.; Spirig, C.; Hens, K.; Meixner, F.X. (2008). An automated dynamic chamber system for surface exchange measurement of non-reactive and reactive trace gases of grassland ecosystems. *Biogeosciences Discussion 5*: 3157-3219.

Parkin, T.B. (2008). Effect of Sampling Frequency on Estimates of Cumulative Nitrous Oxide Emissions. *Journal of Environmental Quality 37(4)*: 1390-1395.

Parton, W.J.; Ojima, D.S.; Cole, C.V.; Schimel, D.S. (1994). A general model for soil organic matter dynamics: sensitivity to litter chemistry, texture and management. *In*: Quantitative Modeling of Soil Forming Processes. SSSA, Spec. Pub. 39, pp. 147-167.

Pattey, E.; Desjardins, R.L.; Boudreau, F.; Rochette, P. (1992). Impact of density fluctuations on flux measurements of trace gases: implications for the relaxed eddy accumulation technique. *Boundary-Layer Meteorology 59*: 195-203.

Pattey, E.; Edwards, G.; Strachan, I.B.; Desjardins, R.L.; Kaharabata, S.; Wagner Riddle, C. (2006). Towards standards for measuring greenhouse gas fluxes from agricultural fields using instrumented towers. *Canadian Journal of Soil Science 86*: 373 - 400.

Pattey, E.; Edwards, G.C.; Desjardins, R.L.; Pennock, D.J.; Smith, W.; Grant, B.; MacPherson, J.I. (2007). Tools for quantifying N2O emissions from agroecosystems. *Agricultural and Forest Meteorology 142(2-4)*: 103-119.

Peu, P.; Beline, F.; Martinez, J. (1999). A floating chamber for estimating nitrous oxide emissions from farm scale treatment units for livestock wastes. *Journal of Agricultural Engineering Research 73*: 101-104.

Phillips, F.A.; Leuning, R.; Baigent, R.; Kelly, K.B.; Denmead, O.T. (2007). Nitrous oxide flux measurements from an intensively managed irrigated pasture using micrometeorological techniques. *Agricultural and Forest Meteorology 143(1-2)*: 92-105.

Raich, J.W.; Bowden, R.D.; Steudler, P.A. (1990). Comparison of two static chamber techniques for determining carbon dioxide efflux from forest soils. *Soil Science Society of America Journal 54*: 1754-1757.

Rathbun, R.E.; Tai, D.Y. (1987). Volatilization of ethylene dibromide from water. *Environmental Science & Technology 21(3)*: 248-252.

Reicosky, D.C.; Gesch, R.W.; Wagner, S.W.; Gilbert, R.A.; Wente, C.D.; Morris, D.R. (2008). Tillage and wind effects on soil CO2 concentrations in muck soils. *Soil and Tillage Research 99(2)*: 221-231.

Rochette, P.; Eriksen-Hamel, N.S. (2008). Chamber Measurements of Soil Nitrous Oxide Flux: Are Absolute Values Reliable? *Soil Science Society of America Journal 72*: 331-342.

Ryden, J.C.; Lockyer, D.R. (1985). Evaluation of a system of wind tunnels for field studies of ammonia loss from grassland through volatilisation. *Journal of Science of Food and Agriculture 36*: 781-788.

Saggar, S. (2001). Soil Science at the cross roads – Norman Taylor Memorial Lecture 2001. *New Zealand Soil News 49(6)*: 132-139.

Saggar, S.; Andrew, R.M.; Tate, K.R.; Hedley, C.B.; Rodda, N.J.; Townsend, J.A. (2004). Modelling nitrous oxide emissions from New Zealand dairy grazed pastures. *Nutrient Cycling in Agroecosystems 68*: 243–255.

Saggar, S.; Giltrap, D.L.; Hedley, C.B.; Lambie, S.M.; Tate, K.R.; Li, C. (2005a). Nitrous oxide emissions from grazed perennial pastures in New Zealand. *In*: Amstel, A.v. (ed.). Non-CO2 Greenhouse Gases (NCGG-4), pp. 113 - 121. Millipress, Rotterdam, The Netherlands.

Saggar, S.; Giltrap, D.L.; Li, C.; Tate, K.R. (2007a). Modelling nitrous oxide emissions from grazed grasslands in New Zealand. *Agriculture, Ecosystems and Environment 119*: 205 - 216.

Saggar, S.; Harvey, M.; Giltrap, D.; Metherell, A.K.; Andrew, R.M. (2005b). Simultaneous examination of nitrous oxide emissions using chamber and paddock scale measurements, and process-based models in grazed pastures. *Environmental Sciences 2(2-3)*: 117-131.

Saggar, S.; Hedley, C.B.; Giltrap, D.L.; Lambie, S.M. (2007b). Measured and modelled estimates of nitrous oxide emission and methane consumption from a sheep-grazed pasture. *Agriculture Ecosystems and Environment 122(3)*: 357-365.

Scanlon, T.M.; Kiely, G. (2003). Ecosystem-scale measurements of nitrous oxide fluxes for an intensely grazed, fertilised grassland. *Geophysical Research Letters 30(16)*: 1852.

Schleichardt, A.; Barth, M.; Schäfer, K.; Raabe, A. (2008). A 100 m x 10 m Sonic to observe area averaged wind and temperature data in comparison to FTIR line integrated measurements. doi:10.1088/1755-1307/1/1/012056. *Earth and Envrironmental Science 1*: 012056.

Scotter, D.R.; Clothier, B.E.; Turner, M.A. (1979). The soil water balance in a Fragiaqualf and its effect on pasture growth in central New Zealand. *Australian Journal of Soil Research 17*.

Sey, B.K.; Manceur, A.M.; Whalen, J.K.; Gregorich, E.G.; Rochette, P. (2008). Small-scale heterogeneity in carbon dioxide, nitrous oxide and methane production from aggregates of a cultivated sandy-loam soil. *Soil Biology and Biochemistry In Press, Uncorrected Proof*.

Sherlock, R.R.; Li, Z.; De Klein, C.A.M. (2005). Boundary Line analysis of the autumn, summer, spring and winter N2O emission factor trial data. *Report to Ministry of Agriculture from NzONet study*. 42 p.

Skiba, U.M.; Sheppard, L.J.; MacDonald, J.; Fowler, D. (1998). Some key environmental variables controlling nitrous oxide emissions from agricultural and semi-natural soils in Scotland. *Atmospheric Environment 32(19)*: 3311-3320.

Smith, K.A.; Clayton, H.; Arah, J.R.M.; Christensen, S.; Ambus, P.; Fowler, D.; Hargreaves, K.J.; Skiba, U.; Harris, G.W.; Wienhold, F.G.; Klemedtsson, L.; Galle, B. (1994). Micrometeorological and chamber methods for measurement of nitrous oxide fluxes between soils and the atmosphere: Overview and conclusions. *Journal of Geophysical Research 99(D8)*: 16541-16548

Smith, K.A.; Clayton, H.; McTaggart, I.P.; Thomson, P.E.; Arah, J.R.M.; Scott, A.; K.W.T., G.; Monteith, J.L.; Phillips, V.R. (1995). The measurement of nitrous oxide

emissions from soil by using chambers. *Philosophical Transactions: Physical Sciences and Engineering 351(1696)*: 327-338.

Smith, R. (1995). A gaussian model for estimating odour emissions from area sources. *Mathematical Computer Modelling 22(9)*: 23-29.

Smith, R.J.; Kelly, J. (1996). "A comparison of two methods for estimating odour emissions from area sources." Presented at the.

Smith, R.J.; Watts, P.J. (1994). Determination of odour emission rates from cattle feedlots: Part 2, Evaluation of two wind tunnels of different size. *Journal of Agricultural Engineering Research 58*: 231-240.

Standards Australia and Standard New Zealand (2008). Stationary source emissions. Part 4: Area source sampling - Direct measurement techniques (Draft for public comment). Draft for public comment. 13 p.

Stehfest, E.; Müller, C. (2004). Simulation of N2O emissions from a urine-affected pasture in New Zealand with the ecosystem model DayCent (doi: 10.1029/2003JD004261. *Journal of Geophysical Research 109*: D03109.

Sutton, M.; Reis, S.; Beier, C.; Butterbach-Bahl, K.; Cellier, P.; Cotrufo, M.F.; Erisman, J.W.; Nemitz, E.; Skiba, U.; de Vries, W. (2006). The nitrogen cycle and its influence on the European greenhouse gas balance. *IGACtivities Newletter 34*: 11-18.

Thoma, E.D.; Shores, R.C.; Thompson, E.L.; Harris, D.B.; Thorneloe, S.A.; Varma, R.M.; Hashmonay, R.A.; Modrak, M.T.; Natschke, D.F.; Gamble, H.A. (2005). Open-path tunable diode laser absorption spectroscopy for acquisition of fugitive emission flux data. *Journal of the Air and Waste Management Association 55(5)*: 658-668.

Todd, L.A.; Ramanathan, M.; Mottus, K.; Katz, R.; Dodson, A.; Mihlan, G. (2001). Measuring chemical emissions using open-path Fourier transform infrared (OP-FTIR) spectroscopy and computer-assisted tomography. *Atmospheric Environment 35(11)*: 1937-1947.

van Bodegom, P.M.; Verburg, P.H.; Denier van der Gon, H.A.C. (2002). Upscaling methane emissions from rice paddies: problems and possibilities doi: 10.1029/2000GB001381. *Global Biogeochemical Cycles 16(1)*: 1014.

van der Weerden, T.J.; S., S.; Metherell, A.K.; Andrew, R.M.; S., F.G. (2002). Evaluation of process-based models for predicting nitrous oxide emissions – final report. *Report prepared for MAF policy,* Crop & Food Research Confidential Report No. 762. 72 p.

Vesala, T.; Kljun, N.; Rannik, Ü.; Rinne, J.; Sogachev, A.; Markkanen, T.; Sabelfeld, K.; Foken, T.; Leclerc, M.Y. (2008). Flux and concentration footprint modelling: State of the art. *Environmental Pollution 152*: 653-666.

Webb, E.K.; Pearman, G.I.; Leuning, R. (1980). Correction of Flux Measurements for Density Effects due to Heat and Water Vapor Transfer. *Quarterly Journal of the Royal Meteorological Society 106*: 85-100.

Wesely, M.L.; Lenschow, D.H.; Denmead, O.T. (1989). Flux measurement techniques. *In*: Hicks, B.B.; Lenschow, D.H. (eds). Global Tropospheric Chemistry: Chemical Fluxes in the Global Atmosphere, pp. 31 - 46. The National Aeronautics and Space Administration and the National Oceanic and Atmospheric Administration, Washington, DC.

Wienhold, F.G.; Welling, M.; Harris, G.W. (1995). Micrometeorological measurement and source region analysis of nitrous oxide fluxes from an agricultural soil. *Atmos. Environ. 29*: 2219-2227.

Woodward, S.J.R.; Barker, D.J.; Zyskowski, R.F. (2001). A practical model for predicting soil water deficit in New Zealand pastures. New Zealand. *Journal of Agricultural Research 44*: 91-110.

Xu-Ri, H.; Niu, H.-S.; Li, C.-S.; Wang, Y.-S.; Wang, M.-X. (2006). Uncertainties in up-scaling N2O flux from field to 1° x 1° scale: A case study for Inner Mongolian grasslands in China. *Soil Biology & Biogeochemistry 38*: 633-643.

Yamulki, S.; Harrison, R.M.; Goulding, K.W.T. (1996). Ammonia surface-exchange above an agricultural field in southeast England. *Atmospheric Environment 30(1)*: 109-118.

Zhang, H.; Lindberg, S.E.; Barnett, M.O.; Vette, A.F.; Gustin, M.S. (2002). Dynamic flux chamber measurement of gaseous mercury emission fluxes over soils. Part 1: simulation of gaseous mercury emissions from soils using a two-resistance exchange interface model. *Atmospheric Environment 36*: 835-846.