

[Home](#) [Search](#) [Collections](#) [Journals](#) [About](#) [Contact us](#) [My IOPscience](#)

Low cost and state of the art methods to measure nitrous oxide emissions

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2013 Environ. Res. Lett. 8 025022

(<http://iopscience.iop.org/1748-9326/8/2/025022>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 192.171.155.204

The article was downloaded on 14/08/2013 at 11:34

Please note that [terms and conditions apply](#).

Low cost and state of the art methods to measure nitrous oxide emissions

Arjan Hensen¹, Ute Skiba² and Daniela Famulari²

¹ Energy Research Centre of The Netherlands, 1755 ZG Petten, The Netherlands

² Centre for Ecology and Hydrology, Bush Estate, Penicuik, EH26 0QB, UK

E-mail: hensen@ecm.nl

Received 4 February 2013

Accepted for publication 30 May 2013

Published 27 June 2013

Online at stacks.iop.org/ERL/8/025022

Abstract

This letter provides an overview of the available measurement techniques for nitrous oxide (N₂O) flux measurement. It is presented to aid the choice of the most appropriate methods for different situations. Nitrous oxide is a very potent greenhouse gas; the effect of 1 kg of N₂O is estimated to be equivalent to 300 kg of CO₂. Emissions of N₂O from the soil have a larger uncertainty compared to other greenhouse gases. Important reasons for this are low atmospheric concentration levels and enormous spatial and temporal variability. Traditionally such small increases are measured by chambers and analyzed by gas chromatography. Spatial and temporal resolution is poor, but costs are low. To detect emissions at the field scale and high temporal resolution, differences at tens of ppt levels need to be resolved. Reliable instruments are now available to measure N₂O by a range of micrometeorological methods, but at high financial cost. Although chambers are effective in identifying processes and treatment effects and mitigation, the future lies with the more versatile high frequency and high sensitivity sensors.

Keywords: chamber methods, infrared analyzers, micrometeorological methods, eddy covariance

1. Introduction

Almost 90% of global N₂O emissions are a result of the microbial processes nitrification and denitrification (e.g. Wrage *et al* 2001) in soils and waters. Emission and production rates are governed by external drivers, principally nitrogen availability, redox potential and temperature (Skiba and Smith 2000). Consequently the agricultural sector, with its high usage of nitrogen, is globally the largest anthropogenic source of N₂O (figure 1). Changes in land use, for example switching from a forest to arable or grassland also affect N₂O emissions; and natural N₂O emitters, such as forests, aquifers, rivers and estuaries are enhanced by nitrogen leaking and deposition mainly from diffuse agricultural sources (Reay *et al* 2012, Skiba *et al* 2012).

Emission rates are typically very variable both in space and time (e.g. Zhu *et al* 2013). Small scale heterogeneity of

physical and chemical soil properties, seasonality (rainfall and temperature) and agricultural management (e.g. fertilization, plowing, irrigation) influence microbial production. In particular grazed fields with urine and dung delivering patches of concentrated nitrogen show large spatial variability in emissions throughout the year (Lesschen *et al* 2011). The temporal structure of the emission pattern is further complicated by fertilizer spreading, the method of spreading and the type of fertilizer used. Significant peaks in the emission can typically occur between 0 and about 21 days after spreading mineral nitrogen, often triggered by rain (Skiba *et al* 2013). For organic compounds (manures, slurries) peaks occur later and are longer lasting as microbial decomposition must precede nitrification and denitrification (e.g. Jones *et al* 2007).

This emission 'scheme', in combination with the measurement methods available, leads to uncertain emission estimates for the measured field. Extra uncertainty is added in the process of upscaling to the national level. Upscaling has to rely on the representativity of a limited set of measured fields for other similar fields together with often insufficient knowledge of the key driving variables that determine N₂O



Content from this work may be used under the terms of the [Creative Commons Attribution 3.0 licence](http://creativecommons.org/licenses/by/3.0/). Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

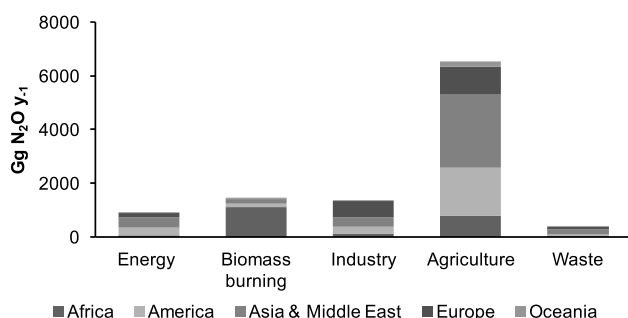


Figure 1. The global anthropogenic N₂O budget, grouped by emission sectors and the continents. Data are from the Emission Database for Global Atmospheric Research (EDGAR) for year 2008 European Commission, Joint Research Centre (JRC)/PBL Netherlands Environmental Assessment Agency. ‘Energy’ includes mobile and stationary fuel combustion, fossil fuel fires, aviation and navigation. Note that the ‘Biomass burning’ sector for Africa is larger than the agricultural sector. ‘Industry’ emissions are mainly from adipic and nitric acid production plants. ‘Agriculture’ includes categories: manure management, manure in pastures, ranges and paddocks, direct soil emissions, diffuse emissions and atmospheric N deposition of NO and NH₃. ‘Waste’ includes solid waste, waste water handling, incineration, other waste.

emission (e.g. soil texture, drainage, bulk density, carbon content, pH, nitrogen availability, temperature, rainfall). Such data is scarce, even in countries where national emission inventories are supported by flux data for a wide range of environments and well documented farm and environmental records. For Europe (EU27) uncertainties of agricultural N₂O emissions were estimated at around 80% (Freibauer 2008) and for a very well documented country as the Netherlands, the contribution of N₂O from fertilized agricultural fields to the total GHG balance still has an uncertainty in the order of 50% (Maas *et al* 2009).

The principal N₂O measurement method is the static chamber and has been used to measure N₂O for almost

40 years. (e.g. Delwiche and Rolston 1976, Matthias *et al* 1978). It is the cheapest most versatile N₂O measurement method, but is not able to provide the high time and spatial resolution required to improve our greenhouse gas budgets and policy making. Technological advancements of principally the laser technology, now enables high temporal and spatial resolution measurements, mainly using micrometeorological methods, at almost affordable prices. The aim of this review is to describe the main chamber and micrometeorological methods used to measure N₂O, identify their pros and cons and make recommendations on appropriate use.

2. Methods for measuring N₂O emissions

The first step to obtain N₂O emissions is to measure N₂O concentrations above atmospheric levels of approximately 0.32 μl l⁻¹. With these data available N₂O flux rates can be derived using several different flux methods. Sensors and methodologies are introduced below.

2.1. Concentration measurements

2.1.1. Gas chromatography. The principle of gas chromatography is the separation of a compound into its molecular constituents. For N₂O the sample is injected through a sample loop (typically 0.25–1 ml) into a carrier gas stream of N₂ (or He) of a gas chromatograph (GC) fitted with an electron capture detector (Wang *et al* 2010, Kelliher *et al* 2013). The volume of sample injected should be at least two times larger than the size of the sample loop. Analysis takes 2–10 min and in near background conditions (around 310 μl l⁻¹) an accuracy of 0.2 μl l⁻¹ can be obtained (e.g. Jones *et al* 2011). Regular (every 30 min) calibration of the system is required to enable corrections for system drift (figure 2) (Loftfield *et al* 1997, Smith and Conen 2004).



Figure 2. The left picture is an example of a typical GC fitted with an electron capture detector for N₂O analysis and a flame ionization detector for CH₄ and CO₂ analysis (left) linked to an autosampler containing the sample vials. Gas samples are usually collected by syringe and stored in either pre-evacuated vials or, as shown in the right picture, by flushing a large sample volume through a small vial. As N₂O is a stable gas vials can be stored for several weeks before analysis.



Figure 3. Infrared N_2O sensors are robust field instruments. This Quantum Cascade Laser spectrometer for CH_4 , N_2O and NH_3 (Aerodyne Instruments, Massachusetts) is deployed in an intensively managed grasslands (NL).

Accuracy of GC measurements varies between laboratories, instruments and operators (Venterea *et al* 2009, Kelliher *et al* 2013). We would recommend that each operators perform regular reproducibility tests to refine and establish accuracy. It is also necessary to test all GC detectors for possible contamination with O_2 (Parkin and Venterea 2010) or CO_2 (Zheng *et al* 2008).

2.1.2. Infrared techniques. Infrared detection (IR) techniques exploit the ability of gases (e.g. H_2O , CO_2 , CH_4 , N_2O and NH_3) to absorb infrared light at unique wavelengths. Sample gas is either pumped into a measurement cell where the IR beam is illuminating the sample (closed path system) or the IR beam can be used in the outside air (open path system). To date, only closed path measurement systems are used for N_2O , although open path systems are currently under development. Commonly used IR detectors are (1) Fourier transform infrared spectrometers (FTIR), which use a broadband thermal system to scan through the IR spectrum, and thereby measure a whole suit of gases simultaneously (Galle *et al* 1994, Schäfer *et al* 2011); (2) photo-acoustic instruments, combining opto-acoustics with a broadband IR source (Iqbal *et al* 2013); (3) laser-based systems tuned to the unique absorption line of a specific trace gas, such as tunable diode laser (TDL) (Mammarella *et al* 2010) or quantum cascade laser (QCL) spectrometers and cavity ring-down systems (CRD) (Kroon *et al* 2007, 2010) (figure 3).

2.1.3. Pros and cons of GC and IR systems. Gas chromatographs used for soil N_2O flux measurements are easy to use and affordable laboratory instruments. They require a continuous supply of high purity carrier gases and have a much poorer detection limit than most IR systems. Gas samples can be collected in small vials and shipped abroad for analysis, if locally GC are not available (e.g. Hergoualc'h *et al* 2008).

Infrared systems are considerably more expensive than GCs and require experienced maintenance. However, they

perform measurements at frequency up to 20 Hz at a sensitivity >500 times better than by GC. For example the CEH GC autochamber system has a detection limit of $0.2 \mu\text{l l}^{-1}$ for N_2O compared to a detection limit of $0.001 \mu\text{l l}^{-1}$ of the tunable diode laser (Jones *et al* 2011) and of $0.00003 \mu\text{l l}^{-1}$ for a 2010 Aerodyne quantum cascade laser (Famulari 2013).

2.2. Flux measurement methods

2.2.1. Chamber methods. Chamber measurements have the main advantage that the concentration signal is amplified significantly so that smaller emissions can be evaluated with a given, low instrumental precision. Sensors used for chamber measurements do not need to be fast response sensors. Gas chromatographs and opto-acoustical instruments (Innova, Bruel & Kjaer, DK) are universally used to measure soil respiration rates, CH_4 and N_2O fluxes (e.g. Flechard *et al* 2005). The term 'fluxes' describes both emission and uptake; for N_2O emissions tend to be more important. Manual chambers are cheap to make, do not require electricity except small batteries in some cases and are easily transported to remote areas (figure 4). Some authors suggest that it is essential to (i) mix air inside the chamber using a small fan, (ii) install a vent hole or tube to avoid effects of pressure differences between in- and outside conditions, (iii) a proper sealing to the sub-surface is required and (iv) the temperature and humidity inside the chamber should not be allowed to increase too much; so insulation or water trapping inside the enclosed chamber might be needed. Recommendations can be found in Hutchinson and Mosier (1981), Parkin and Venterea (2010), Christiansen *et al* (2011), Rochette (2011), Clough *et al* (2013).

Chamber fluxes (F) are calculated from the increase in concentration (dC) during chamber closure (dt) and the volume of the chamber (V) enclosing surface area (A).

$$F = dC/dt \cdot V/A.$$

Most chamber studies in the past assumed a linear increase in concentration over time, however, assuming linearity may underestimate fluxes by 20–40% (Kroon *et al* 2008, Kutzbach *et al* 2007). Calculating fluxes from several concentration measurements (3–5) during chamber closure using non-linear or best-fit-model approaches (Pedersen *et al* 2010, Levy *et al* 2011, Venterea *et al* 2013) would reduce some of the uncertainty.

With chambers a small area ($< \text{m}^2$) of the ecosystem can be studied without interference from other sources. Measured flux rates can be linked to environmental variables measured at the same location and time, for example soil temperature, nitrate availability, water table depth or pH, which facilitates the development of process models. Chamber measurements do, however, have a problem covering the fast temporal and spatial inhomogeneity (figure 5) of, for example, N_2O emissions from a grazed field (Velthof *et al* 1996, Flechard *et al* 2007). Chamber studies are in danger of missing main peak events after rainfall or fertilization, because the experimentalists are not in the field on a particular day and

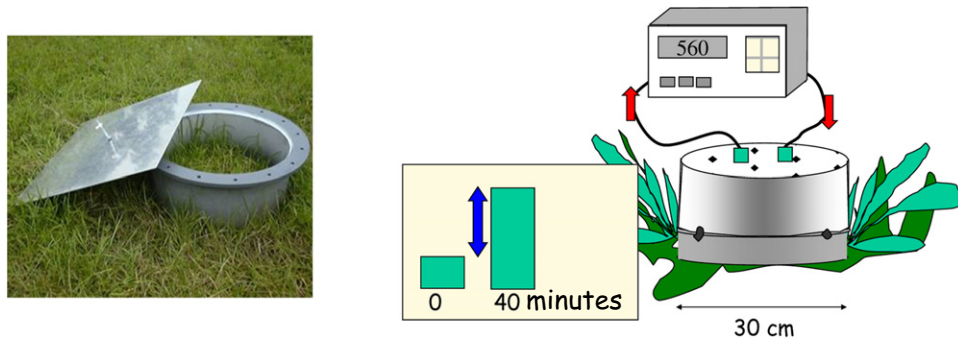


Figure 4. Chamber measurement methods measure the increasing (or decreasing) concentration inside a chamber, preferably a number of times after closing the chamber. The photo on the left is of a low cost static manual chamber, made from commercially available drainpipe (40 cm diameter), flange and an aluminum lid and used for manual sampling of the air into glass vials for subsequent analysis by gas chromatography (figure 2). The schematic diagram on the right shows a chamber connected to a photo-acoustic analyzer, the air is re-circulated between analyzer and instrument, and the increase in N₂O concentration is measured once a minute. CO₂ and H₂O have to be scrubbed from the gas flow in order to get useful N₂O data.

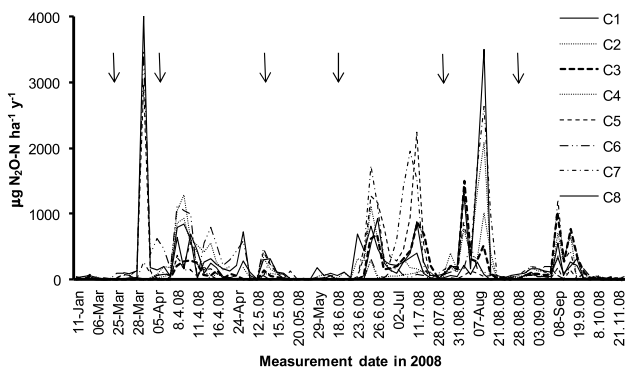


Figure 5. Spatial and temporal variability of N₂O fluxes measured by eight static chambers (C1–C8) from a grazed grassland in the UK (Skiba *et al* 2013). The arrows denote dates of N fertilizer application (52 kg N ha⁻¹ yr⁻¹ in March, May, June, July, 69 kg N ha⁻¹ yr⁻¹ in April and 35 kg N ha⁻¹ yr⁻¹ in August). The onset and magnitude of fertilizer induced N₂O emission peaks was different for each chamber and each fertilizer event.

capable of flux measurements every few hours (figure 6) (e.g. Smith and Dobbie 2001, Grace *et al* 2013). However, spatial coverage is likely to be even smaller than for manual chambers, due to their much higher costs.

The combination of chambers with a fast response infrared sensor can help to significantly increase the number of measurements that can be one on a single field (Hensen 2012). The fast chamber method uses 10 Hz instruments for this application so that, in general, chambers only need to be enclosed for a few minutes. Air is re-circulated between chamber and TDL or QCL and fluxes are calculated from concentration increases recorded every second. Such high frequency records of N₂O accumulation allow a much more accurate flux calculation than possible from the 3–5 points available for GC analysis. With this method, a high temporal resolution of the emission landscape can be obtained (figure 6).

chambers can only be sealed a limited number of times per day in order not to alter the microclimate inside. Some of these issues can be resolved by using automated chamber systems,

2.2.2. Micrometeorological methods. Micrometeorological methods have some advantages over enclosure methods: measurements are on a larger scale, they do not interfere with the micro-environment, and they have a very high

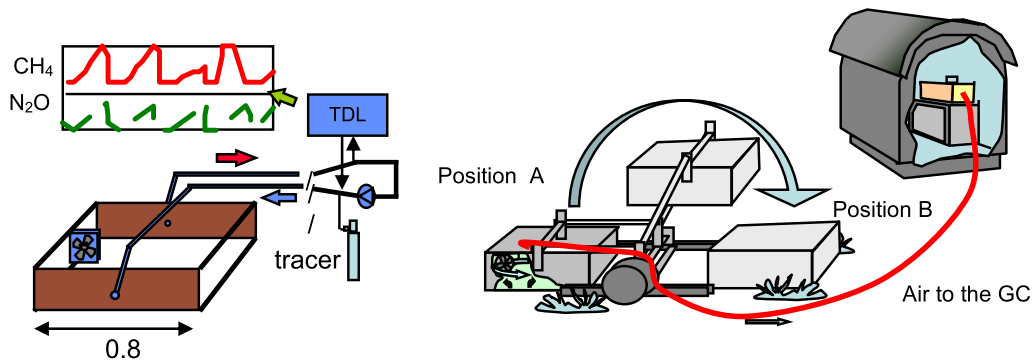


Figure 6. Two chamber methods setups used to overcome the spatial and temporal variability problems associated with soil N₂O fluxes. The fast chamber method (left), using the TDL or QCL as a sensor, allows many measurements at different locations in a short period of time. On the right the automatic chamber that alternates between two positions and is connected to a GC and enables many measurements from the same locations throughout a day.



Figure 7. Eddy covariance flux measurements at Zegveld (NL) over a manured field. Left: mast with an ultra-sonic anemometer and sample inlet line. Right: the sample line is connected to a TDL housed inside the electrically powered mobile laboratory.

temporal resolution. These methods integrate fluxes over large plots (>10 m²) up to regional scales. There are however disadvantages to micrometeorological methods as well: they require large, uniform surfaces, and fast response infrared sensors, which are often expensive; they are introduced below. The data capture for these methods is also constrained by the atmospheric stability, which can sometimes affect measurements during night time, for example; overall, a micrometeorological system will have better temporal coverage than any enclosure system.

2.2.2.1. Eddy covariance (EC). The eddy covariance (EC) method is widely used since a few decades (e.g. Aubinet *et al* 2000, Baldocchi 2003); the emission/deposition flux (F_C) of a gas is defined as the covariance between the vertical wind speed (w) and the gas concentration (C) itself measured at one point as follows:

$$F_C = \overline{w' \cdot C'}$$

Eddies very efficiently mix high concentration air from nearby sources with background air, and a correlation (or anti-correlation) between vertical wind and concentration indicates up- or down-ward transport of the gas (e.g. Stull 1988). To apply EC, fast sensors are required for both wind (ultra-sonic anemometers) (e.g. Kaimal and Gaynor 1991) and concentrations (see section 2.1): this means the costs for equipment and expertise are relatively high.

Eddy covariance measurements of N₂O were made possible by the development of fast response laser instruments, the tunable diode lasers, which have mostly been superseded by quantum cascade laser, as these are more robust, easier to use and have higher sensitivity. Examples of measurements for N₂O with TDL's are described in Jones *et al* (2011) or Laville *et al* (1997) and of QCL measurements including a discussion on uncertainties in EC measurements can be found in Kroon *et al* (2007, 2010). EC measurements have been mainly used to study fieldscale N₂O fluxes from agricultural fields, see figures 7 and 8 (Wienhold *et al* 1994, Laville *et al* 1997, Kroon *et al* 2007, Neftel *et al* 2010), and for above canopy N₂O flux measurements in forests (Shaw *et al* 1998, Pihlatie *et al* 2005).

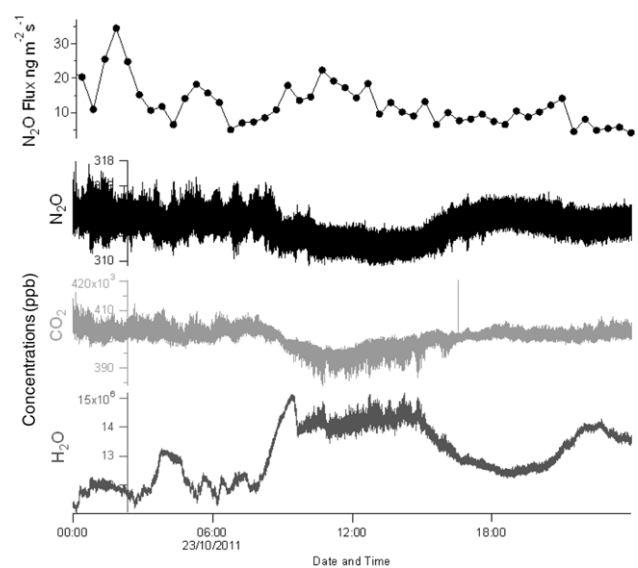


Figure 8. An example day of mixing ratios (1 ppb = 1 ng l⁻¹) of N₂O, CO₂ and H₂O recorded at 10 Hz by the QCL (three bottom traces), and calculated N₂O fluxes (top trace). These measurements were made from a grassland in England fertilized with slurry.

2.2.2.2. The relaxed eddy accumulation (REA) method. REA is a conditional technique (Businger and Oncley 1990) that has been widely used in the past two decades for a range of gases, including N₂O (e.g. Pattey *et al* 2006); unlike EC it allows slow response concentration analyzers. In that sense, REA is the ‘cheap version’ of EC: it uses the same sonic anemometer to measure the vertical wind speed w , but sampling air into updraft and downdraft reservoirs (e.g. Tedlar bags for non-reactive gases), at constant flow rate, based on the sign of w . The flux is expressed as:

$$F = \beta \sigma_w (c_{up} - c_{dn})$$

where β is an empirical proportionality coefficient (generally in the range 0.3 ± 0.8), σ_w is the standard deviation of w , and c_{up} and c_{dn} are the average concentrations (over 30 min) of the trace gas in the updraft and downdraft reservoirs, respectively. The gas samples of N₂O can then be analyzed by GC, or IR.

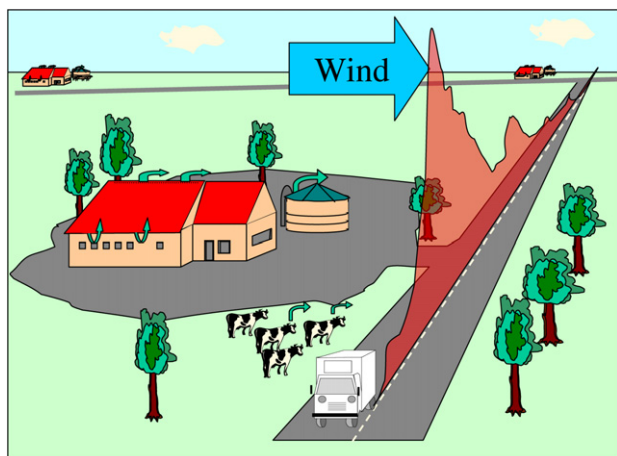


Figure 9. Mobile plume measurements: the van houses a fast N₂O sensor and sonic anemometer and travels at a constant speed downwind of N₂O plumes originating from various farm source.

2.2.2.3. *Aerodynamic gradient method (AGM).* This technique has been widely applied on a large variety of gases in the past fifty years, as it can rely on slower sensors than EC. Vertical profiles of temperature, wind speed and trace gas concentration (*C*) are used to calculate the flux (*F_C*), according to:

$$F_C = K_C \frac{\partial C}{\partial z}$$

where *z* is the height above the ground; the term *K_C* represents the eddy exchange coefficient, and it is derived by similarity from the vertical profiles of wind and temperature (see e.g. Fowler and Duyzer 1989, Dyer and Hicks 1970, Wagner-Riddle *et al* 1996). In a very turbulent atmosphere (e.g. strong winds or convection during sunny days) the surface layer is well mixed and the gradients will be small. In a very stable atmosphere with hardly any turbulence (e.g. during nights with low wind speed) the differences between the measurement heights will be much larger.

2.2.2.4. *Mass balance and plume methods.* For source areas that have a clear border (a manure heap, a housing system, a test field), spatial integrating measurements are possible with either mass balance or plume measurement techniques.

Similar to the gradient technique, the mass balance technique has been used widely in the past few decades also for N₂O (e.g. Denmead 2000): it uses concentration (*C*) measurements versus height, in combination with the vertical gradient of wind (*U*). The flux is calculated as *U · C* for all heights and integrated horizontally (e.g. Fowler and Duyzer 1987, Denmead *et al* 1998). This method is applied for finite sources that only stretch out about 4–5 times the height of the measurement tower in the upwind direction, and it is the bridge between micrometeorological techniques and plume measurements that rely on advection as well.

The plume method evaluates the concentration plume that originates at the source and is transported by the wind (Czepiel *et al* 1996, 2003, Trégourès *et al* 1999, Hensen and Scharff 2001). Typical distances between source and

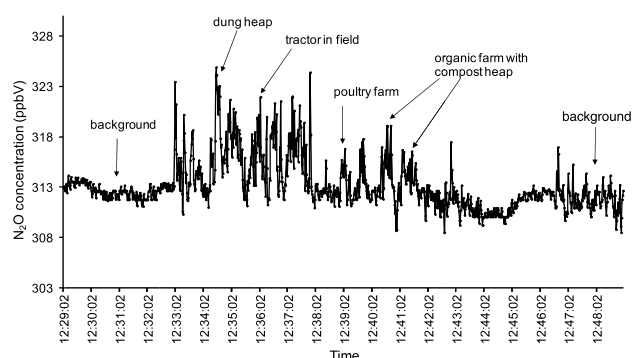


Figure 10. Typical trace of mobile plume measurements in an agricultural area using a TDL to detect N₂O fluxes at 10 Hz recorded in spring on a 33 ha flat region in UK, containing crops, a small poultry farm, dung heaps and an organic farm. The average concentration increase was 2.6 ± 2.7 ppb (1 ppb = 1 ng l⁻¹). Results suggest that for this period the N₂O emission rate was 290 ng N₂O m⁻² s⁻¹.

measurement transects are 50 m⁻² km (figure 9). Wind speed, wind direction, turbulent parameters are needed to calculate the emission flux using a transport model. The plume technique can either use a mobile measurement system or an array of stationary samplers. Examples of a mobile system are shown in figures 9 and 10.

Both the plume and mass balance method can use relatively low cost sampling systems. With a focus on relevant sources (high emitters) relatively slow opto-acoustical sensors or GC analyses can provide the concentration data. In addition these methods require meteorological instrumentation. A dispersion model is needed to translate the measured concentration levels into emission levels. This can be a Gaussian model, but new backward Lagrangian models are now available that bring improvement on the modeling part of this type of emission evaluations (Loubet *et al* 2010).

No model is required when a tracer release is used (Scharff and Hensen 2009), provided that the tracer source distribution can sufficiently mimic the actual N₂O source distribution.

2.2.2.5. *Tall tower measurements.* High resolution measurements at a single site with elevation over 100 m on a tower, a high building or a mountain can also be used to evaluate emissions. The measurements detect N₂O passing the tower. Concentration peaks above background contain information on the sources upwind. With inverse modeling techniques, wind fields can be used to calculate the backward trajectories of air parcels that show where the air mass originated. On the European scale this technique is already used to evaluate country scale emissions these are then compared to the standard ‘bottom up’ method of emission inventories. Bergamaschi *et al* (2010) discuss how already national emission data has been updated based on this kind of analyses.

2.2.2.6. *Boundary layer budget approach.* Polson *et al* (2011) showed how the N₂O budget for the UK can be

evaluated using measurements from an airplane that flew around the UK, sampled airflow entering and exiting the country. During the flight air samples were collected into Tedlar® gas sample bags, to be analyzed when back on the ground for a range of gases, including N₂O by TDL. Fluxes were calculated using inverse modeling techniques and compared to the UK national emission inventory. Smaller fluxes were reported by the bottom up inventory compared to the aircraft measurements for N₂O, implying that the UK's annual N₂O emission inventory using the International Panel on Climate Change methodology (IPCC 2006) may underestimate emissions.

3. Different research questions require different methods and sensors

The data produced by the observational systems described above are required to determine (i) which sources are important; (ii) the relative contribution of these sources; (iii) where and how to mitigate; (iv) how to extrapolate to the regional, national scale. It is important that appropriate tools are selected to address the above knowledge items.

Ecosystem or km² scale budget studies aim to show what the large sources are and what their relative importance is (addressing (i) and (ii)). Comparison of source systems is based on annual area integrated data. The spatial integrating methods can provide this information.

In order to mitigate N₂O emissions however insight is required into the processes that lead to or affect N₂O exchange patterns (iii).

In order to understand the drivers of emission for example chambers are well suited. They can be used to evaluate different treatments in the field (e.g. Jones *et al* 2007) and in controlled environment laboratory studies (e.g. Sánchez-Martín *et al* 2008). Key is that all possible variables likely to influence the N₂O flux are measured at the same time. Mechanistic models are data hungry and it is advisable to discuss data requirements with the modeler at the experimental design stage. High quality comprehensive data sets are the panacea for sensible model outputs. Widely used mechanistic models for N₂O are DNDC (Li *et al* 1992) and DAYCENT (Parton *et al* 2001).

Upscaling to the national scale can be done in several ways. The most basic method to calculate annual N₂O emissions from agricultural soils, the Tier 1, IPCC emission factor approach, is universally applicable, but with an uncertainty of >400% (IPCC 2006). The tall tower measurements linked with inverse modeling can provide a means for emission verification in an independent way. Across Europe a network of tall towers for GHG flux measurements is currently emerging in order to provide long-term observations of GHG and monitor change (Integrated Carbon Observation Systems (ICOS) www.icos-infrastructure.eu/).

Figure 11 shows how different measurement methods provide data on different spatial and temporal scales. The available measurement methods provide the knowledge at these different scales in time and space.

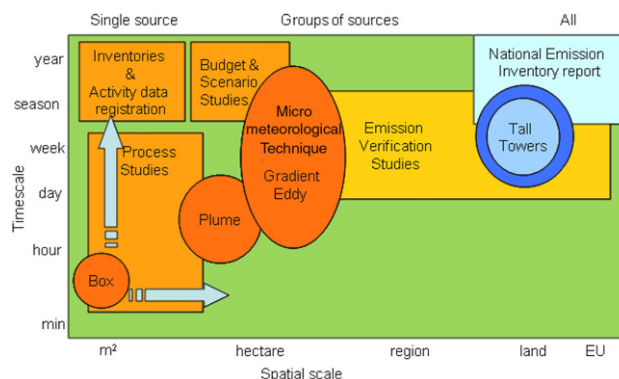


Figure 11. The role of different methods used in view of the spatial and temporal variability.

4. Final remarks and recommendations

In the scientific arena, in Europe, North America or new Zealand/Australia there is a clear trend towards the use of space integrating EC technique. This technique however need not be the first option for countries starting a programme of N₂O research, or may not even be appropriate, as large uniform fields may not be characteristic of the agricultural landscape. When the starting point is a minimum in available research infrastructure, low cost techniques are certainly the first option.

Chamber, plume and gradient methods can be done low cost and can provide emission data on different source systems. Chambers are the most obvious choice to start with, they provide valuable information on N₂O fluxes when used properly. It is important to follow guidelines on chamber design, sampling, flux calculation, replication in space and time etc.

Chamber and mass balance technique seem so simple that there is a danger to miss some of the warning signs that can be found in literature. Taking the latest recommendations for these methods into account however, might rapidly increase the price of the low cost setup and available budget might impose a limit on what is possible.

Chambers allow for off line sample analyses by GC, which can even be done abroad when conditions would not allow having a N₂O monitor on the site or within the country. However, having an analyzer close to the measurement site would provide much faster information of temporal changes in flux rates and allows optimization of the measurement strategy (e.g. length of chamber closure, frequency of chamber measurements) in response to changed environmental or management conditions.

The most recent laser systems, top end of the market, are definitely the best option in terms of performance: stability, precision, accuracy. They will allow both for chamber and the much more demanding eddy covariance or tall tower observations to be carried out. Even though the initial price of latest generation IR systems (circa 100 kEuro) is about a factor of two above a complete GC system. However, they are becoming more competitive as the lower operational costs may pay back in the long run. With the laser spectrometers there is no need for carrier gases and only limited need for

calibration gases. The latest laser spectrometers no longer need liquid nitrogen, and do not have the safety limitations of the radioactive GC–ECD sensors. Important is the need to use inlet filters since optical systems and especially the highly reflective mirrors in the measurement cell can get damaged by particles.

A limitation for field deployment of IR laser spectrometers will be power requirements. Small air samples (~1 l) can be collected manually into gas tight bags or vials using a large syringe or small vacuum pump from chambers, mass balance, gradient or stationary plume measurements. For eddy covariance however, the measurement cell has to be flushed at a high flow rate whilst maintaining low pressure in the cell. In practice that requires 1–4 kW pumps to be used. Running these systems on, for example, solar or wind power can be a problem. It is to be expected that in the coming years low power open path systems will be developed that can circumvent these limitation.

In fact the choice what to do right now is not so much what instrument to use but what method to use. That mainly depends on the questions asked. For a regional emission validation, use the tall tower (for example a telecommunication tower) with inverse modeling technique. For process understanding small chambers and for field scale evaluation or multiple plot emission surveys the mass balance, gradient, plume or eddy covariance methods are suitable approaches.

With the current speed of developments in optical measurement techniques low cost versions of the laser systems will become available that might cost 5–20 kEuro but have a 10 or 100 fold reduction of the resolution in concentration. These systems would be able to do chamber measurements or mass balance/plume measurements close to high emitters, but not allow for the micromet or tall tower techniques.

Acknowledgments

We wish to thank our national funding authorities (Natural Environment Research Council (NERC) and—Department for Environment, Food and Rural Affairs (DEFRA) in the UK and government funding in the NL) for support through several contracts over the years; and the EU for financing collaborative research through the FP7 integrated projects CarboEurope IP, NitroEurope IP and before that GreenGrass and Midair.

References

Aubinet M, Moncrieff J and Clement R C 2000 Estimates of the annual net carbon and water exchange of forests: the EUROFLUX methodology *Adv. Ecol. Res.* **30** 113–75

Baldocchi D 2003 Assessing the eddy covariance technique for evaluating carbon dioxide exchange rates of ecosystems: past, present and future *Glob. Change Biol.* **9** 479–92

Bergamaschi P et al 2010 Inverse modeling of European CH₄ emissions 2001–06 *J. Geophys. Res.* **115** D22309

Businger J A and Oncley S P 1990 Flux measurement with conditional sampling *J. Atmos. Ocean. Technol.* **7** 349–52

Christiansen J R, Korhonen J F J, Juszcak R, Giebels M and Pihlatie M 2011 Assessing the effects of chamber placement, manual sampling and headspace mixing on CH₄ fluxes in a laboratory experiment *Plant Soil* **343** 171–85

Clough T J, Rochette P, Thomas S M, Pihlatie M, Christiansen J R and Thorman R E 2013 *Global Research Alliance on Agricultural Greenhouse Gases: Nitrous oxide chamber methodology guidelines, Version 1.0* ed C de Klein and M Harvey, chapter 2 (Chamber Design) (www.globalresearchalliance.org/research/livestock/activities/nitrous-oxide-chamber-methodology-guidelines/)

Czepiel P, Shorter J H, Mosher B, Allwine E, McManus J B, Harriss R C, Kolb C E and Lamb B K 2003 The influence of atmospheric pressure on landfill methane emissions *Waste Manag.* **23** 593–8

Czepiel P M, Mosher B, Harriss C, Shorter J H, McManus J B, Kolb C E, Allewine E and Lamb B K 1996 Landfill methane emissions measured by enclosure and atmospheric tracer methods *J. Geophys. Res.* **101** 16711–9

Delwiche C C and Rolston D E 1976 Measurement of small nitrous oxide concentrations by gas chromatography *Soil Sci. Soc. Am. J.* **40** 324–7

Denmead O, Leuning R and Griffith D W T 2000 Nitrous oxide emissions from grazed pastures: measurements at different scales *Chemosphere: Global Change Sci.* **2** 301–12

Denmead O T, Harper L A, Freney J R, Griffith D W T, Leuning R and Sharpe R R 1998 A mass balance method for non-intrusive measurements of surface–air trace gas exchange *Atmos. Environ.* **32** 3679–88

Dyer A J and Hicks B B 1970 Flux gradient relationships in the constant flux layer *Q. J. R. Meteorol. Soc.* **96** 715–21

Famulari D 2013 personal communication

Flechard C, Neftel A, Jocher M, Ammann C and Fuhrer J 2005 Bi-directional soil/atmosphere N₂O exchange over two mown grassland systems with contrasting management practices *Glob. Change Biol.* **11** 2114–27

Flechard C R et al 2007 Effects of climate and management intensity on nitrous oxide emissions in grassland systems across Europe *Agric. Ecosyst. Environ.* **121** 135–52

Fowler D and Duyzer J H 1989 Micrometeorological techniques for the measurement of trace gas exchange *Exchange of Trace Gases Between Terrestrial Ecosystems and the Atmosphere* ed M O Andreae and D S Schimel (New York: Wiley) pp 301–12

Freibauer A 2008 Designing an observation strategy for N₂O *The Continental-Scale Greenhouse Gas Balance of Europe (Ecological Studies vol 203)* ed A J Dolman and R Valenti (New York: Springer) pp 135–51

Galle B, Klemetsson L and Griffith D W T 1994 Application of a Fourier transform IR system for measurements of N₂O fluxes using micrometeorological methods, an ultralarge chamber system, and conventional field chambers *J. Geophys. Res.* **99** 16575–83

Grace P, van der Weerden T J, Kelly K, Rees R M and Skiba U M 2013 *Global Research Alliance on Agricultural Greenhouse Gases: Nitrous Oxide Chamber Methodology Guidelines, Version 1.0* ed C de Klein and M Harvey, chapter 5 (Automated Greenhouse Gas Measurement in the Field)

Hensen A 2012 Methods for observation and quantification of trace gas emissions from diffuse sources *PhD Thesis* VU Amsterdam

Hensen A and Scharff H 2001 Methane emission estimates from landfills obtained with dynamic plume measurements *Water Air Soil Pollut.* **1** 455–64 (Focus)

Hergoualc’h K, Skiba U, Harmand J-M and Henault C 2008 Fluxes of greenhouse gases from Andosols under coffee in monoculture or shaded by *Inga densiflora* in Costa Rica *Biogeochemistry* **89** 329–45

Hutchinson G L and Mosier A R 1981 Improved soil cover method for field measurement of nitrous oxide fluxes *Soil Sci. Soc. Am. J.* **45** 311–6

- IPCC 2006 *IPCC Guidelines for National Greenhouse Gas Inventories, Prepared by the National Greenhouse Gas Inventories Programme* ed H S Eggleston *et al* (Hayama: IGES)
- Iqbal J, Castellano M J and Parkin T B 2013 Evaluation of photoacoustic infrared spectroscopy for simultaneous measurement of N₂O and CO₂ gas concentrations and fluxes at the soil surface *Global Change Biol.* **19** 327–36
- Jones S K, Famulari D, Di Marco C F, Nemitz E, Skiba U, Rees R M and Sutton M A 2011 Nitrous oxide emissions from managed grassland: a comparison of eddy covariance and static chamber measurements *Atmos. Meas. Tech. Discuss.* **4** 1079–112
- Jones S K, Rees R M, Skiba U and Ball B C 2007 Influence of organic and mineral N fertiliser on N₂O fluxes from a temperate grassland *Agric. Ecosyst. Environ.* **121** 74–83
- Kaimal J C and Gaynor J E 1991 Another look at sonic thermometry *Bound.-Lay. Meteorol.* **56** 401–10
- Kelliher F M, Sherlock R, Clough T J, Premaratne M, Laughlin R J, McGeough K L, Harvey M J, McMillan A M S, Reid A and Sagar S 2013 Air sample collection, storage and analysis *Global Research Alliance on Agricultural Greenhouse Gases: Nitrous Oxide Chamber Methodology Guidelines, Version 1.0* ed C de Klein and M Harvey, chapter 4
- Kroon P S, Hensen A, Jonker H J J, Ouwensloot H G, Vermeulen A T and Bosveld F C 2010 Uncertainties in eddy covariance flux measurements assessed from CH₄ and N₂O observations *Agric. Ecosyst. Environ.* **150** 806–16
- Kroon P S, Hensen A, Jonker H J J, Zahniser M S, van 't Veen W H and Vermeulen A T 2007 Suitability of quantum cascade laser spectroscopy for CH₄ and N₂O eddy covariance flux measurements *Biogeosciences* **4** 715–28
- Kroon P S, Hensen A, van den Bulk W C M, Jongejan P A C and Vermeulen A T 2008 The importance of reducing the systematic error due to non-linearity in N₂O flux measurements by static chambers *Nutr. Cycl. Agroecosyst.* **82** 175–86
- Kutzbach L, Schneider J and Sachs T E A 2007 CO₂ flux determination by closed-chamber methods can be seriously biased by inappropriate application of linear regression *Biogeosciences* **4** 1005–25
- Laville P, Henault C, Renault P, Cellier P, Oriol A, Devis X, Flura D and Germon J C 1997 Field comparison of nitrous oxide emission measurements using micrometeorological and chamber methods *Agronomie* **17** 375–88
- Lesschen J, van den Berg M, Westhoek H, Witzke H and Oenema O 2011 Greenhouse gas emission profiles of European livestock sectors *Anim. Feed Sci. Technol.* **166/167** 16–28
- Levy P E, Gray A, Leeson S, Gaiawyn J, Kelly M P C, Cooper M D A, Dinsmore K J, Jones S K and Sheppard L J 2011 Quantification of uncertainty in trace gas fluxes measured by the static chamber method *Eur. J. Soil Sci.* **62** 811–21
- Li C, Frolking S and Frolking T A 1992 A model of nitrous oxide evolution from soil driven by rainfall events: I. model structure and sensitivity *J. Geophys. Res.* **97** 9759–76
- Lofthfield N, Flessa H, Augustin J and Beese F 1997 Automated gas chromatographic system for rapid analysis of the atmospheric trace gases methane, carbon dioxide, and nitrous oxide *J. Environ. Qual.* **26** 560–4
- Loubet B, Générumont S, Ferrara R, Bedos C, Decuq C, Personne E, Fanucci O, Durand B, Rana G and Cellier P 2010 An inverse model to estimate ammonia emissions from fields *Eur. J. Soil Sci.* **61** 793–805
- Maas C W M *et al* 2009 *Greenhouse Gas Emissions in the Netherlands 1990–2007* (PBL Report 500080012/2009) (Bilthoven: Planbureau voor de Leefomgeving)
- Mammarella I, Werle P, Pihlatie M, Eugster E, Haapanala S, Kiese R, Markkanen T, Rannik Ü and Vesala T 2010 A case study of eddy covariance flux of N₂O measured within forest ecosystems: quality control and flux error analysis *Biogeosciences* **7** 427–40
- Matthias A D, Yarger D N and Weinbeck R S 1978 A numerical evaluation of chamber methods for determining gas fluxes *Geophys. Res. Lett.* **5** 765–8
- Neftel A, Ammann C, Fischer C, Spirig C, Conen F, Emmenegger L, Tuzson B and Wahlen S 2010 N₂O exchange over managed grassland: application of a quantum cascade laser spectrometer for micrometeorological flux measurements *Agric. Forest Meteorol.* **150** 775–85
- Parkin T B and Venterea R T 2010 Chamber-based trace gas flux measurements *Sampling Protocols* ed R F Follett chapter 3 (www.ars.usda.gov/research/GRACENet)
- Parton W J, Holland E A, Del Grosso S J, Hartman M D, Martin R E, Mosier A R, Ojima D S and Schimel D S 2001 Generalized model for NO_x and N₂O emissions from soils *J. Geophys. Res.* **106** 17403–19
- Pattey E, Strachan I, Desjardins R, Edwards G, Dow D and Macpherson J 2006 Application of a tunable diode laser to the measurement of CH₄ and N₂O fluxes from field to landscape scale using several micrometeorological techniques *Agric. Forest Meteorol.* **136** 222–36
- Pedersen A R, Petersen S O and Schelde K 2010 A comprehensive approach to soil atmosphere trace-gas flux estimation with static chambers *Eur. J. Soil Sci.* **61** 888–902
- Pihlatie M, Rinne J, Ambus P, Pilegaard K, Dorsey J R, Rannik Ü, Markkanen T, Launiainen S and Vesala T 2005 Nitrous oxide emissions from a beech forest floor measured by eddy covariance and soil enclosure techniques *Biogeosciences* **2** 377–87
- Polson D *et al* 2011 Estimation of spatial apportionment of greenhouse gas emissions for the UK using boundary layer measurements and inverse modelling technique *Atmos. Environ.* **45** 1042–9
- Reay D S, Davidson E A, Smith K A, Smith P, Melillo J M, Dentener F and Crutzen P J 2012 Global agriculture and nitrous oxide emissions *Nature Clim. Change* **2** 410–6
- Rochette P 2011 Towards a standard non-steady-state chamber methodology for measuring soil N₂O emissions *Anim. Feed Sci. Technol.* **166/167** 141–6
- Sánchez-Martín L, Vallejo A, Dick J and Skiba U 2008 The influence of soluble carbon and fertilizer nitrogen on nitric oxide and nitrous oxide emissions from two contrasting agricultural soils *Soil Biol. Biochem.* **40** 142–51
- Schäfer K, Böttcher J, Weymann D, von der Heide C and Duijnisveld W H M 2011 Evaluation of a closed tunnel for field-scale measurements of nitrous oxide fluxes from an unfertilized grassland soil *J. Environ. Qual.* **41** 1383–92
- Scharff H and Hensen A 2009 Further development of a cheap and simple methane emission measurement method *Proc. Sardinia 2009, 12th Int. Waste Management and Landfill Symp. (S. Margherita di Pula, Cagliari, Oct. 2009)*
- Shaw W J, Spicer C W and Kenny D V 1998 Eddy correlation fluxes of trace gases using a tandem mass spectrometer *Atmos. Environ.* **32** 2887–98
- Skiba U, Jones S, Dragosits U, Drewer J, Fowler D, Rees R, Pappa V, Cardenas L, Chadwick D and Yamulki S 2012 UK emissions of the greenhouse gas nitrous oxide *Phil. Trans. R. Soc. B* **367** 1175–85
- Skiba U, Jones S K, Drewer J, Helfter C, Anderson M, Dinsmore K, McKenzie R, Nemitz E and Sutton M A 2013 Comparison of soil greenhouse gas fluxes from extensive and intensive grazing in a temperate maritime climate *Biogeosciences* **10** 1231–41
- Skiba U and Smith K A 2000 The control of nitrous oxide emissions from agricultural and natural soils *Chemosphere* **2** 379–86
- Smith K A and Conen F 2004 Measurement of trace gases I: gas analysis, chamber methods and related procedures *Soil and Environmental Analysis, Modern Instrumental Techniques* 3rd edn, ed K A Smith and M S Cresser (New York: Dekker)
- Smith K A and Dobbie K 2001 The impact of sampling frequency and sampling times on chamber-based measurements of N₂O emissions from fertilized soils *Glob. Change Biol.* **7** 933–45

- Stull R B 1988 *An Introduction to Boundary Layer Meteorology* (Dordrecht: Kluwer Academic)
- Trégourès A *et al* 1999 Comparison of seven methods for measuring methane flux at a municipal solid waste landfill site *Waste Manag. Res.* **17** 453–8
- Velthof G L, Jarvis S C, Stein A, Allend A G and Oenema O 1996 Spatial variability of nitrous oxide fluxes in mown and grazed grasslands on a poorly drained clay soil *Soil Biol. Biochem.* **28** 1215–25
- Venterea R T, Parkin T B, Cardenas L, Petersen S O and Pedersen A R 2013 *Global Research Alliance on Agricultural Greenhouse Gases: Nitrous oxide chamber methodology guidelines, Version 1.0* ed C de Klein and M Harvey, chapter 6 (Data Analysis Considerations) www.globalresearchalliance.org/research/livestock/activities/nitrous-oxide-chamber-methodology-guidelines/
- Venterea R T, Spokas K A and Baker J M 2009 Accuracy and precision analysis of chamber-based nitrous oxide gas flux estimates *Soil Sci. Soc. Am. J.* **73** 1087–93
- Wagner-Riddle C, Thurtell G W, Kidd G E, Edwards G C and Simpson I J 1996 Micrometeorological measurements of trace gas fluxes from agricultural and natural ecosystems *Infrared Phys. Technol.* **37** 51–8
- Wang Y, Wang Y and Hong L 2010 A new carrier gas type for accurate measurements of N₂O by GC-ECD *Adv. Atmos. Sci.* **27** 1322–30
- Wrage N, Velthof G L, van Beusichem M L and Oenema O 2001 Role of nitrifier denitrification in the production of nitrous oxide *Soil Biol. Biochem.* **33** 1723–32
- Wienhold F G, Frahm H and Harris G W 1994 Measurement of N₂O fluxes from fertilized grassland using a fast response tunable diode laser spectrometer *J. Geophys. Res.* **99** 16557–67
- Zheng X *et al* 2008 Quantification of N₂O fluxes from soil–plant systems may be biased by the applied gas chromatograph methodology *Plant Soil* **311** 211–34
- Zhu J, Mulder J, Wu L P, Meng X X and Wang Y H 2013 Spatial and temporal variability of N₂O emissions in a subtropical forest catchment in China *Biogeosciences* **10** 1309–21