Two Automatic Chamber Techniques for Measuring Soil-Atmosphere Exchanges of Trace Gases and Results of their use in the OASIS Field Experiment

C.P. (Mick) Meyer, Ian E. Galbally, Yingping Wang, Ian A. Weeks
CSIRO Atmospheric Research

and

Ian Jamie, David W.T. Griffith
Chemistry Department, University of Wollongong

CSIRO
Atmospheric Research

CSIRO Atmospheric Research Technical Paper No. 51

Two Automatic Chamber Techniques for Measuring Soil-Atmosphere Exchanges of Trace Gases and Results of their use in the OASIS Field Experiment

Meyer, C.P., Galbally, I.E., Wang, Y.P., Weeks, I.A.,
CSIRO Atmospheric Research

Jamie, I. and Griffith, D.W.T.
Chemistry Department, University of Wollongong

CSIRO Atmospheric Research Technical Paper No. 51

National Library of Australia Cataloguing-In-Publication Entry

Meyer, C.P., Galbally, I.E., Wang, Y.P., Weeks, I.A., Jamie, I. and Griffith, D.W.T.

Two Automatic Chamber Techniques for Measuring Soil-Atmosphere Exchanges of Trace Gases and Results of their use in the OASIS Field Experiment

Bibliography.
ISBN 0-643-06645-4

1. Soil air - Analysis. 2. Air sampling apparatus. 3. Gases - Analysis - Equipment and supplies. 4. Plant-atmosphere relationships. I. Meyer, C. P. (Mick). (Series : CSIRO Atmospheric Research technical paper).

631.43

Address and contact details: CSIRO Atmospheric Research
Private Bag No. 1., Aspendale Victoria 3195 Australia
Ph: (+61 3) 9239 4400; fax: (+61 3) 9239 4444
email: chief@dar.csiro.au

CSIRO Atmospheric Research Technical Papers may be issued out of sequence.

TWO AUTOMATIC CHAMBER TECHNIQUES FOR MEASURING SOIL-ATMOSPHERE EXCHANGES OF TRACE GASES AND RESULTS OF THEIR USE IN THE OASIS FIELD EXPERIMENT

C.P. (Mick) Meyer, Ian E. Galbally, Yingping Wang,
Ian A. Weeks
CSIRO Atmospheric Research
Aspendale, Victoria, Australia
and
Ian Jamie, David W.T. Griffith
Chemistry Department, University of Wollongong
Wollongong, New South Wales, Australia

Abstract

Two techniques for measuring soil/plant/atmosphere exchange fluxes of stable trace gases are presented. The first technique involves an automatic chamber capable of running at remote, unpowered, unattended sites. The air samples collected from individual flux measurements are progressively added to holding volumes, essentially averaging the concentrations in the accumulated air samples before their chemical analysis. This technique allows the continuous measurement of trace gas exchange at multiple distant remote sites to be carried out by one or two persons operating from a central laboratory housing the analytical facilities. The scientific advantages of this method are that emission measurements are automated, integrated day and night, and can be carried out at remote locations without mains power. The second technique involves continuous online analysis of the chamber headspace once per minute by Fourier Transform Infrared (FTIR) spectrometry. This technique provides simultaneous measurement of CO_2, N_2O and CH_4, is suitable for use at well supported measurement sites, and allows the continuous, automated determination of trace gas exchange measurements on a half hourly or hourly basis. The underlying theoretical and experimental basis of the use of chambers to measure trace gas exchange over soil/plant surfaces is presented. Measurements are presented from the OASIS (Observations At Several Interacting Scales), field experiment. The temperature and soil moisture responses of soil/plant respiration, N_2O emissions and CH_4 uptake are observed and quantified. Both approaches produced comparable results for CO_2 fluxes. While for the most part N_2O fluxes were also equivalent, there were some differences due principally to minor differences in chamber operating conditions.

1. Introduction

Analysis of chamber measurements is based on the application of the equation of conservation of mass for the trace gas within the chamber. Chamber measurements are particularly useful for studies of the soil and plant processes involved in this trace gas exchange. The particular requirements for accurate chamber measurements (Galbally and Roy, 1980; Galbally et al., 1985; Businger, 1986) are:

- a realistic and quantified boundary layer resistance within the chamber,
- adequate turbulent mixing of the free volume within the chamber,
- the inertness of the material making up the chamber wall,
- the equality of ambient pressure within and outside the chamber,
- minimal interference of the chamber with key soil and plant environmental variables; and
- a quantified rate of flow of air into and out of the chamber.

In the OASIS project (Leuning et al., 1997), measurements of trace gas exchange were made with different systems that measured on scales varying from a leaf to a landscape scale. This paper presents details about the chamber technique that makes individual measurements on patches of < 1 m^2 at multiple sites in a field. Two differently configured systems for measurement of the trace gas concentrations have been used with these chambers. One is a bag-sampling system for integrated flux measurements suitable for use at remote locations in the absence of electrical power, the other is a continuous system for use at well-supported field sites. Examples of the system performance are drawn from the OASIS fieldwork along with previous studies using this instrumentation.

2. Equipment and site description

2.1 Automatic flux chamber design

Each automatic flux chamber used in this experiment consisted of an open base unit that was pressed into the soil to a depth of 75 to 100 mm and a moveable box. The moveable boxes were constructed from anodised aluminium, have a volume of ca. 100 L and cover a ground area of 0.35 m^2 (0.7 m by 0.5 m). The roof of each chamber was fitted with a glass window to maintain some natural lighting, along with a lid that closes or opens with a double-acting gas piston using compressed air from a small gas cylinder. The box unit fitted over the base and sealed with a silicone rubber O-ring compressed between two flanges (Fig. 1).

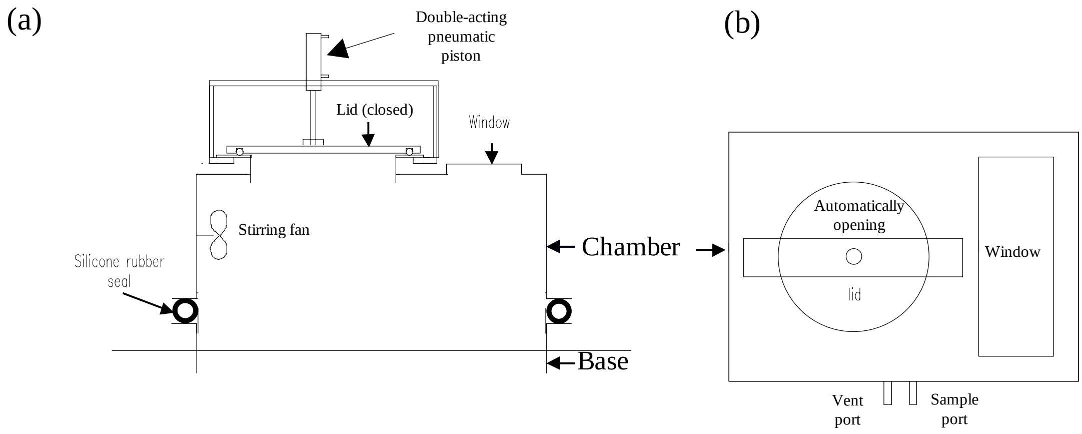


Figure 1 Schematic diagram of the chamber in (a) elevation and (b) plan.

Air within the chamber was continually stirred with an instrument fan to maintain a boundary-layer conductance determined as approximately 0.02 m s^{-1}. Pressure within the chamber was maintained at ambient at all times by a vent consisting of a 3-mm bulkhead union and 100-mm Teflon tube of internal diameter 2 mm. The operation of the chambers was controlled by a programmable microprocessor and all operations (i.e. digital output states, battery voltage, sample manifold pressure) and key environmental variables including chamber temperature, ambient (external) windspeed, and wind direction were logged at 30-s intervals.

When measurements were made over crops that are taller than the height of the standard chamber (0.3 m), an extension was fitted to the sides of the chambers doubling or tripling its height.

In the integrated method, air samples were drawn from the chamber by a 12 V Teflon pump (Model MPU487-NO5, KNF Neuberger, NJ, USA) powered by a regulated 12 V DC/DC converter to ensure a constant flow rate. The sample stream was then directed via one of five Teflon valves (Biovalve 1101461, Furon, USA) to either one of four Tedlar sample bags (8 litre or 11 litre, Cole Parmer, USA) or to the sample vent.

In the continuous method, air was circulated at 15 L min^{-1} through a closed loop from the chamber through approximately 30 m of 12-mm copper and Teflon tubing to the measurement cell in the FTIR spectrometer, and returned via an oil-free diaphragm pump (Thomas OD5) to the chamber.

The controller/logger and gas sampling equipment were housed in a weather-proof field housing. The logger/controller was based on an Intel 80552 microprocessor. The entire system was powered by a 12 V, 60 ampere-hour deep-cycle battery, which stored sufficient charge for 4 days' operation. When in automatic mode, the microprocessor programme accessed an event table specifying the required sequence of timed events. Communication with the logger/controller was via an RS232 interface to an ASCII terminal, usually a laptop PC, which was connected to the logger/controller to download the data during a daily maintenance visit to the site.

2.2 Operation and gas analysis

2.2.1 *Integrating method - gas chromatography*

The concentrations of N_2O, CH_4 and CO_2 in the integrated samples contained in Tedlar bags were measured on an automated analysis system. Carbon dioxide concentration was measured by a non-dispersive infra-red gas analyser (NDIR, Licor 6251, Licor, Nebraska, USA); methane concentration was measured by a gas chromatograph with a flame ionisation detector (Dani Model 6500, DANI, Italy) on molecular sieve 5A with nitrogen carrier gas; nitrous oxide was measured with a gas chromatograph equipped with an electron capture detector (Hewlett Packard model 5890, Palo Alto, USA) on Porapak QS with 5% methane in argon carrier gas. Both gas chromatographs (GCs) were operated with backflush. Compounds with retention times greater than that of required species were retained on the pre-column and backflushed to the atmosphere in order to minimise the time required and improve the quality of each analysis. Water vapour was removed from all samples by a semi-permeable membrane drier (Nafion, Dupont, USA) prior to analysis. Methane and nitrous oxide concentrations of the air samples were determined by comparison with a clean air working standard prepared by CSIRO GASLAB using standard protocols linked to the international scales for CO_2, N_2O and CH_4 (Francey et al., 1993). Multipoint calibrations were performed occasionally to quantify the detector responses over the range of gas concentrations encountered during the experiment. The flame ionisation detector was linear for methane concentration. While the electron conductivity detector was non-linear for nitrous oxide concentration. The analysis system was controlled and logged by a microcomputer. Analytical precision was 0.2% for N_2O, 0.6% for $CH_{4,}$ and 0.2% for CO_2.

In operation, a flux measurement cycle was initiated by closing the chamber lid. In the integrating mode, gas samples (about 1 litre volume) were withdrawn from the chamber at specified times after closure (commonly 5, 15, 25 and 45 minutes) and accumulated in Tedlar gas sampling bags. One bag was allocated to each of the sampling times. The lid was then opened 2 minutes after the final sample was collected and the chamber was rapidly flushed with ambient air. The lid remained open until the next flux measurement was initiated, when another set of samples were added to the accumulating bags. In the case where a 24-hour average was required, chamber closures were triggered every four hours, and therefore at the end of a 24-hour measurement period each of the four sample bags contained approximately six litres of air. In this study the rate of change in average gas concentration was estimated by either the difference in concentration over one time interval, or by least squares regression of concentration against time where four separate sampling times were used.

2.2.2 Continuous mode – FTIR spectrometry

Infrared spectra were measured at 1 cm^{-1} resolution using a Bomem MB104 FTIR spectrometer fitted with a globar source, InSb detector and 22-m path, 8-L volume White cell (IR Analysis, Anaheim Ca.) housed in a thermostatted enclosure in a mobile laboratory 20 m from the chamber sites. Cell pressure and temperature were monitored and logged along with each spectrum measured. Air from the chamber was circulated continuously through the cell, and spectra were collected continuously and accumulated in 1-minute (20 scans) groups. The entire operation was fully automated under the control of a single Array Basic program running in the GRAMS (Galactic Industries, New Hampshire) spectrometer operating environment. The spectrometer details and methods are similar those described in detail by Esler et al. (2000).

FTIR spectra were analysed by Classical Least Squares (CLS) using calculated calibration spectra as described in detail by Griffith (1996). Measured concentrations could be corrected for cell temperature, pressure and water vapour concentration also retrieved from the FTIR spectra to provide dry air mixing ratios when required. This analysis provided a working calibration scale was related to the GASLAB scale by daily measurements of the clean air working standard used in the GC analyses described above. Analytical precision was better than 0.5ppbv for N_2O and 1 ppmv for CO_2 for a 1-minute average based on replicate measurements of a single air sample. The analysis showed a small cross-sensitivity of measured N_2O to CO_2 concentration, of the order of 1 ppbv N_2O per 100 ppmv CO_2, due to spectroscopic overlap not fully accounted for by the CLS analysis. This was quantified by measurements where CO_2 was added to the chamber-cell volume at constant N_2O concentration and used to correct all N_2O measurements. There is also a similar cross sensitivity to water vapour, but this was less significant because water vapour was close to saturation at all times and normally did not vary significantly throughout a 30 minute measurement cycle.

Each flux measurement cycle commenced with five minutes of air measurement with the chamber lid open to establish the ambient trace gas concentration. The chamber lid was then closed, and the trace gas concentrations were recorded at 1-minute intervals for the next 20 minutes. The sequence was completed by reopening the chamber for five minutes to flush the chamber with ambient air before the next cycle. In the OASIS experiment the FTIR was switched between two chambers on alternate half hours using a pair of solenoid gas valves under the control of the program (Fig. 2). Thus a flux measurement was made on each chamber each hour, 24 hours per day except for a 0.5-1 hour maintenance break for calibration and data backup.

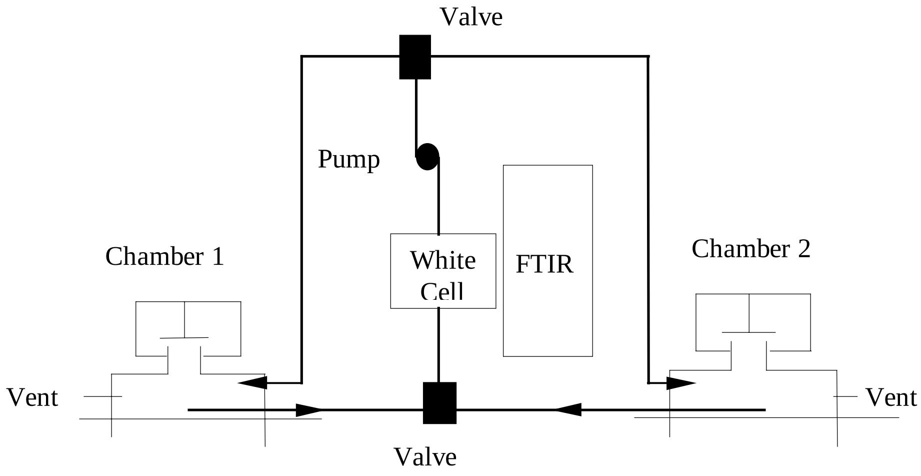


Figure 2 Schematic diagram of the FTIR gas circuit

2.3 Site description

The continuous and the integrating methods were used to measure fluxes of CO_2, CH_4 and N_2O in two agricultural fields in October 1994 and October 1995 as part of the OASIS campaigns. In both 1994 and 1995, one set of measurements was made in a 15 ha lucerne pasture at the Charles Sturt University farm, near Wagga Wagga, New South Wales (35°4'S, 147°21'E, altitude 219 m). Approximately 70% of the surrounding district is assigned to pasture for grazing sheep and cattle, and the rest is used for crops. Soil at the site grades from a fine sandy loam at the surface (23 g kg^{-1} clay) to a mild clay (55 g kg^{-1} clay) at 0.6 m with a band of fine iron-manganese nodules (Poss et al., 1995). The second set of measurements was made in an adjacent 15-ha instrumented field to the east planted with oats in 1994 and *Triticale* in 1995.

Six chambers were deployed during each campaign, three in each crop. In order to reduce disturbance to crop growth during the time course of the campaigns, each chamber was supplied with two adjacent bases. The chamber box units were moved to their alternate base each morning ensuring that the measurement sites were covered for a maximum of 24 hours before returning to ambient conditions.

The first season, October 1994, was very dry supporting limited crop growth. Only 154 mm of rain fell in the six months from the beginning of April until field measurements commenced in October, well below the climatic average of 383 mm. Leaf area indices (LAI) were < 0.5 for the pasture and ≈1 for the crop in 1994.

For the second season, October 1995, rainfall was above average. Rainfall in the preceding six months was 434 mm, while from 11 to 29 October, LAI increased from 0.6 to 1.5 for the pasture and from 3.1 to 3.8 for the crop.

Significant rainfall events occurred during both the campaigns. In 1994, rainfall occurred on the 27th October, at the end of the campaign. The 1995 campaign encompassed a drying cycle spanned by rainfall events on 13th and 22nd October.

In 1994, only CH_4 and CO_2 exchange was measured. In 1995, N_2O was included in the measurement suite. Additionally, in 1995 the chamber windows were covered with aluminium foil, and therefore the CO_2 exchange observed during the day was entirely due to soil and plant respiration.

3. The chamber trace gas exchange measurement technique

3.1 Principles and assumptions

3.1.1 Chamber mass balance

Fluxes of trace gases are often measured by the closed chamber technique (e.g. Galbally and Roy, 1980; Galbally et al., 1985; Businger, 1986; Kirstine et al., 1998). The principles of the technique, and the artifacts to which it is sensitive, have been reviewed by a number of authors (Denmead, 1979; Hutchinson and Mosier, 1981; Jury et al, 1981; Galbally et al., 1985; Livingston and Hutchinson, 1995; Healy et al., 1996). In brief, the flux of a gas is calculated from the initial rate of change in concentration of the gases of interest when the chamber volume is sealed from the ambient air.

Conservation of mass is applied to the chamber:

$$F = \frac{V}{A} . \frac{dC_t}{dt} + \frac{v_g}{A}(C_t - C_a) + \upsilon_d C_t \qquad (1)$$

where:

F	is the flux of the trace gas (g $m^{-2}s^{-1}$)
C_t	is the concentration of the trace gas in the chamber at time t (g m^{-3}),
	C_a is the concentration of the trace gas in ambient air (g m^{-3}),
t	is the time after closure of the chamber (s),
V	is the volume of the closed chamber (m^3),
A	is the area of ground surface area enclosed by the chamber,
v_g	is the volumetric rate of loss of air from the chamber (m^3 s^{-1}), described here as the gross rate of loss of air from the chamber,
u_d	is the deposition rate of the gas on the chamber, plant and soil surfaces, (m s^{-1}).

The subscripts *i* and *f* represent initial and final states respectively.

The gross rate of loss of air from the chamber can be represented by its constituent parts as:

$$v_g = v_s + v_e \tag{2}$$

v_s is the rate at which air is deliberately withdrawn from the chamber usually for sampling,

v_e is the natural ventilation or leakage rate of air from the chamber.

A key feature of this analysis is that the deliberate removal of air and natural leakage of air from the chamber is small such that it makes only a minor contribution to Eq. 1. Choice of a small value of t_f helps this by minimising C_t. Sealing the chamber well to minimise natural ventilation is also important.

3.1.2 Characterisation of natural air leakage from chambers

The natural ventilation (leakage) rate of the chambers was determined in tests using CO_2 as an inert tracer gas. In these tests, the chambers were located over a sealed anodised aluminium base. A pulse of CO_2 was injected into the chamber immediately after closure of the chamber lid, and the ventilation rate was calculated from the rate of change in the CO_2 concentration in the chamber.

From an analysis of the chamber mass balance, the relationship between the natural ventilation and the time course of tracer concentration can be derived (Marynick and Marynick, 1975; Kimball, 1990), viz.

$$\frac{v_e}{V} = \frac{\ln(C_i / C_f)}{(t_f - t_i)} - \frac{v_s}{V} \tag{3}$$

Measurements of v_e/V were conducted with all chambers. The results for chamber 5 are presented in Fig. 3 and demonstrate that ambient windspeed has a substantial influence on v_e/V. It can be demonstrated by applying a mass balance analysis to the chamber via Eq. 1 (Galbally et al., 1985) that a leakage rate of $v_g/V = 0.1\ h^{-1}$, when neglected, leads to an error in the flux of 3.5% for a 45-minute chamber closure. In this study, all fluxes have been corrected for leakage assuming an average chamber leakage rate of $0.2\ h^{-1}$.

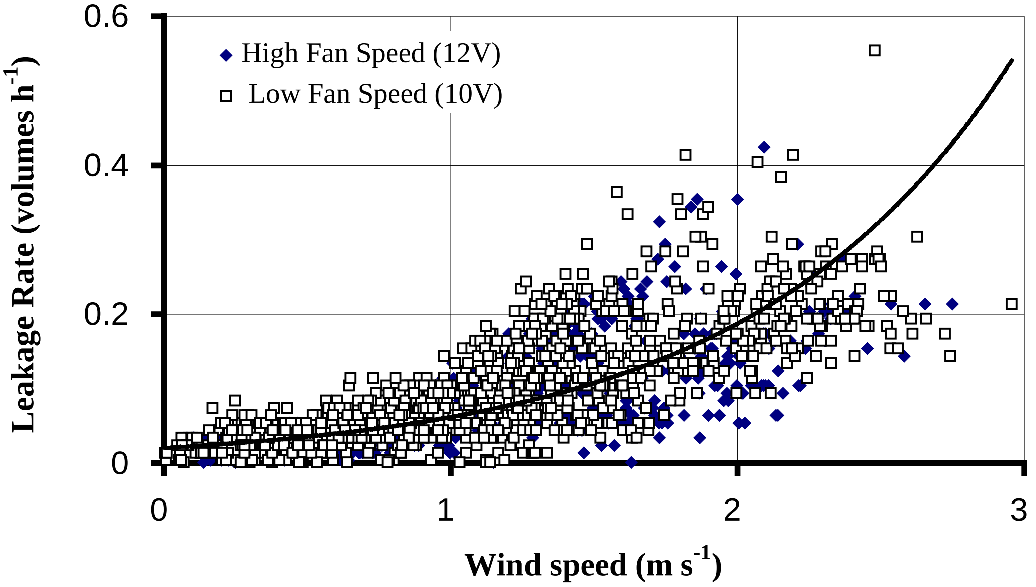


Figure 3 The effect of ambient wind speed on the chamber's leakage rate.

The boundary-layer resistance of these chambers was calculated from measurements of the rate of water evaporation from an underlying fully wet surface into dry air in the chamber, and averaged 88 s m^{-1}. It can be shown (Thom and Oliver, 1977) that an aerodynamic resistance of this magnitude is equivalent to a windspeed of 3 m s^{-1} at 2 m above a uniform free water surface.

The chambers were also tested for artefact fluxes. The exchanges of trace gases observed over a solid aluminium base, typically 0.02 ± 0.03 ng N m^{-2} s^{-1} N_2O, – 0.22 ± 0.20 ng C m^{-2} s^{-1} CH_4 and 0.8 ± 0.3 µg m^{-2}s^{-1} CO_2, are negligible compared with the real fluxes observed when there is an open soil/plant surface beneath the chamber. An emission from the soil to the atmosphere is defined as a positive flux.

3.1.3 The effect of a deep canopy in the chamber on the concentration time course

Commonly, it is assumed in chamber studies that the air space is well mixed. This assumption will not apply to the case of measurements over a deep dense crop. To our knowledge this situation has not been studied. Consequently, we have undertaken a study using a numerical model of the mixing in the chamber, described in the Appendix, and the results of the modelling are presented here.

Using the theory of Raupach (1987) the variation of both the turbulent diffusion coefficient D and aerodynamic resistance r_a with height was calculated for a dense canopy of 1-m depth with similar characteristics to the *Triticale* crop (Fig. 4). This demonstrates that the turbulent diffusion coefficient decreases rapidly towards the bottom of the canopy and approaches the value of the molecular diffusion coefficient of N_2O in ambient air (=1.5x10^{-5} m^2 s^{-1}) at the bottom of the canopy. About half of the integrated aerodynamic resistance between the soil surface and the air above the canopy is in the 0.02-m layer above the soil. Therefore N_2O emitted from soil is likely to build up to a much higher concentration at the bottom of the canopy than in the other part.

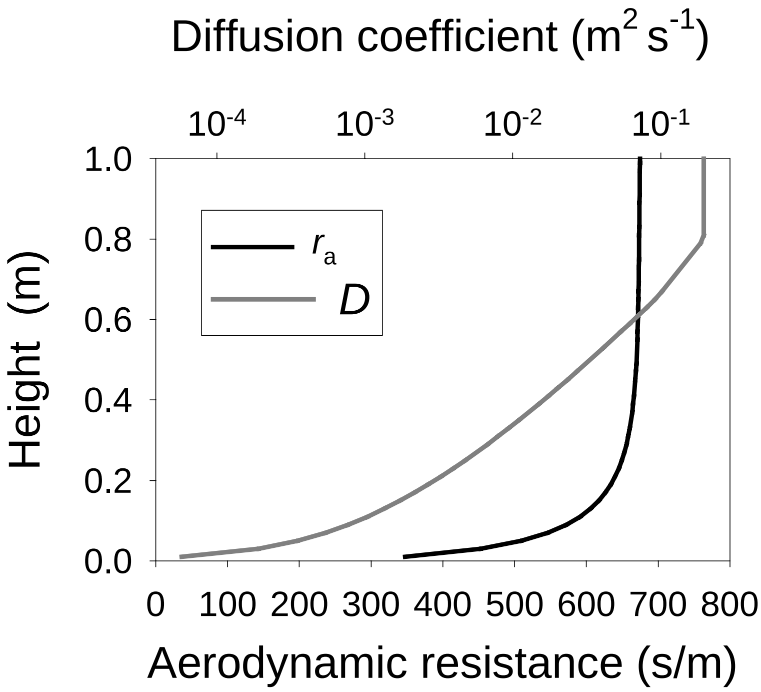


Figure 4 Variation of the turbulent diffusion coefficient and the total canopy resistance from the surface as a function of canopy height for a dense crop of 0.8 m height and leaf area index of 4.

Fig. 5 shows the N_2O concentration at three different heights within the canopy after the chamber is closed assuming a constant flux of 10 ng N m^{-2} s^{-1} from the soil at the lower boundary of the canopy. A non-linear increase in N_2O concentration is most evident at the bottom layer during the first 30 seconds after the chamber closure, because of the poor turbulent mixing. About 60 seconds after the chamber closure, N_2O concentration within the canopy increases linearly with time and at an equal rate at all heights, therefore flux calculated from air samples taken at 600 and 1800 seconds after chamber closure will provide an unbiased estimate of the soil N_2O emission. This result is also valid if the soil N_2O flux at the bottom of the canopy varies with time, as long as it is not directly dependent on N_2O concentration at the surface through metabolic feedback mechanisms. Therefore trace gas transport through the canopy is unlikely to introduce errors into the flux estimates despite the occurrence of a significant concentration gradient. Thus complete mixing within the air space of the chamber is not always a necessary condition for valid chamber measurements.

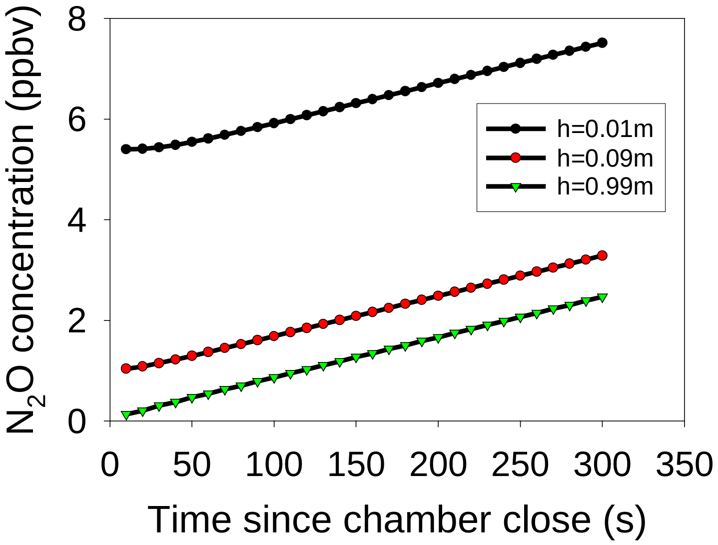


Figure 5 Simulated time course of trace gas concentration near the soil surface, at 0.01m, 0.09 m and at 0.99 m above the soil surface for an N_2O flux of 10 ng N m^{-2} s^{-1} into a static chamber for a dense crop of 1m and leaf area index 4. In the real word these concentrations would represent the perturbations of nitrous oxide concentration above the prevailing ambient concentration.

The details presented so far show that the flux chamber method has a rigorous basis and is constructed so that the soil/plant/atmosphere exchange processes in the chamber mimic those in the outside world as closely as possible. The system has operated successfully in the field on many occasions providing extended periods of continuous trace gas exchange measurements for CO_2 from respiration, N_2O and CH_4 (Meyer et al., 1997, Wang et al., 1997).

3.2 Integrated and continuous flux measurement methods

When there is no loss of the gas to the chamber itself and no back reaction with the source on earth, then the rate of change in trace gas concentration is:

$$F = \frac{V}{A}\frac{dC}{dt} + \frac{v_g}{A}(C_t - C_a)\,. \tag{4}$$

Equation 4, in time transformed units, is used for the derivation of fluxes. This equation can only be fitted to the data using non-linear techniques (Galbally et al., 1985). An alternative to this is a solution to Eq. 4 that corrects for chamber leakage (e.g. Marynick and Marynick, 1975), by modifying time *t* using the transform

$$t' = \frac{(1 - e^{-tv_g V^{-1}})}{v_g V^{-1}} \tag{5}$$

where t' is the leak-corrected time. This transform collapses the second term from the right-hand side of Eq. 4 into the first term on the right-hand side. The formulation used involves the linear regression of C versus $t^{'}$ Under these circumstances Eq. 4 can be reduced to a simple derivative or finite difference form:

$$F = \frac{V}{A} \cdot \frac{dC}{dt^{'}} = \frac{V}{A} \cdot \left(\frac{C_f - C_i}{\Delta t^{'}} \right) \tag{6}$$

where the subscripts $\Delta t^{'}$ is the time interval, (Δt = t_f - t_i,) expressed in transformed units. The values of t_i and t_f are commonly 5 and 45 minutes. This approach is used for the continuous method.

The following provides the basis of the integrating method. The mean daily flux rate $\overline{F}$, calculated from n individual flux measurements, F_j is

$$\overline{F} = \left[\sum_{j=1}^{j=n} F_j \right] / n \,. \tag{7}$$

If the sampling times for each individual measurement ($t_{i,}$ t_f) are constant throughout the experiment (as is the case with automatically controlled chambers), and a constant air mass is withdrawn from the chamber at each sampling (as is approximately the case with voltage regulated pumps and small ambient temperature variation), then substituting Eq. 6 into Eq. 7 gives

$$\overline{F} = \frac{V}{A\Delta t} \left(\frac{\sum_{j=1}^{j=n} C_{fj}}{n} - \frac{\sum_{j=1}^{j=n} C_{ij}}{n} \right) \tag{8}$$

or

$$\overline{F} = \frac{V}{A\Delta t^{'}} \left(\overline{C}_f - \overline{C}_i \right) \tag{9}$$

where $\overline{C}_f$ and $\overline{C}_i$ are, respectively, the average concentrations of the n initial and n final air samples. In turn, $\overline{C}_f$ and $\overline{C}_i$ can each be calculated either from n individual chemical analyses or, if the n samples are of equal mass and are mixed prior to analysis, from a single analysis of the bulked air sample. Thus the average flux obtained from the set of individual flux values can be obtained from the measurement of the average concentrations as represented by the accumulated initial and final air samples. This is the basis of the integrated chamber technique. There were no 24-h (4 bag) timecourses recorded using the integrating method over equilibrated soil sites in the OASIS study; however a typical example of a timecourse measured using the integrated method in related study conducted in a Eucalyptus forest in southern Victoria (Meyer et al.; 1997) is shown in Fig. 6.

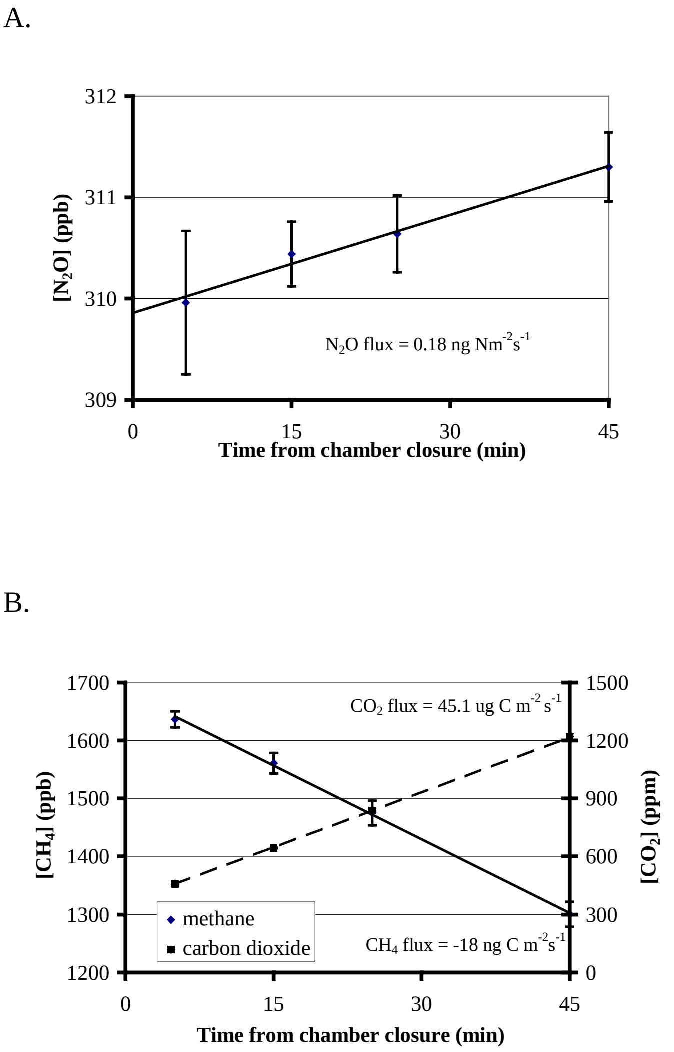
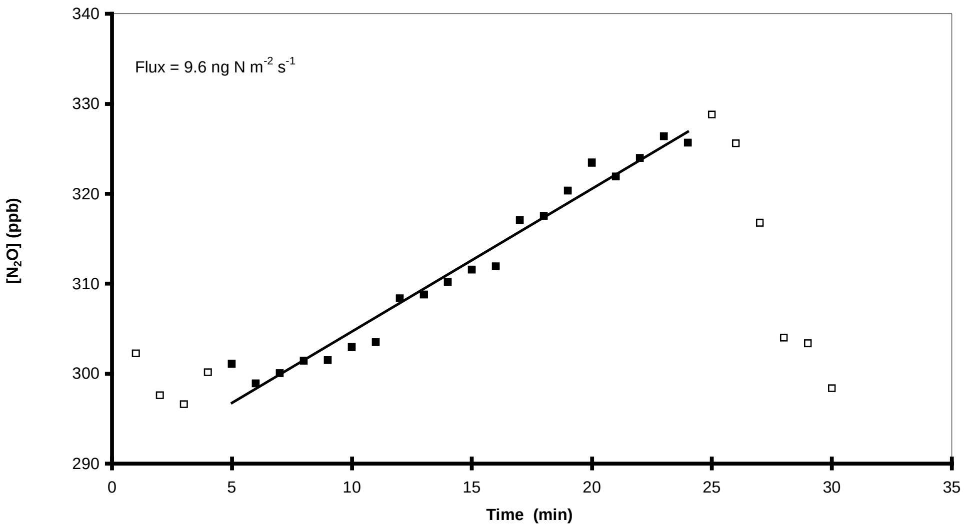


Figure 6. Time-course of (a) N_2O concentration and (b) CH_4 concentration (diamonds) and CO_2 concentration (squares) in the chamber headspace during the 24-h mean soil-atmosphere flux measurement in a Eucalyptus forest near Spargo Creek, Victoria. The data points are mean ± standard errors of the mean for five replicate analyses of the bulked air samples. In the case of CO_2 the standard error bars are smaller than the data points. The lines are the least-squares linear regressions.

Typical examples of N_2O and CO_2 concentration time courses measured by FTIR using the continuous method are shown in (Fig. 7). In all cases, the time courses were linear. Though in principle methane fluxes can also be determined by FTIR, in practice the variability in the methane concentration observed by FTIR was too large for the calculation of meaningful methane fluxes. Measurements with the FTIR when the chamber remained closed for 7 hours (transformed time) showed no non linearity in the rates of change of N_2O and CO_2 concentration, see (Fig. 8).

A.



B.

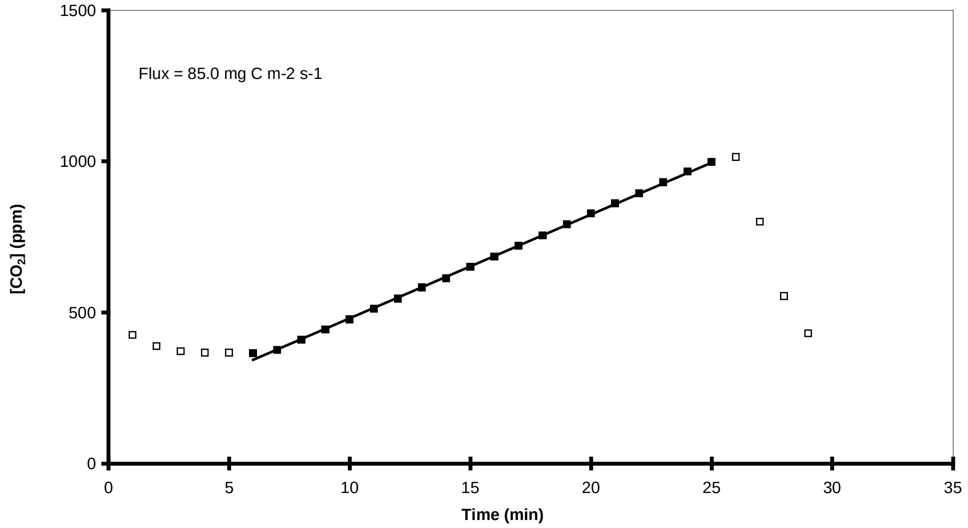


Figure 7 Time course of trace gas concentration and derived emission rates on 24 October 1995 at 1430 local time measured by FTIR. Chamber open, open symbols; chamber closed, closed symbols. (a) N_2O (b) CO_2

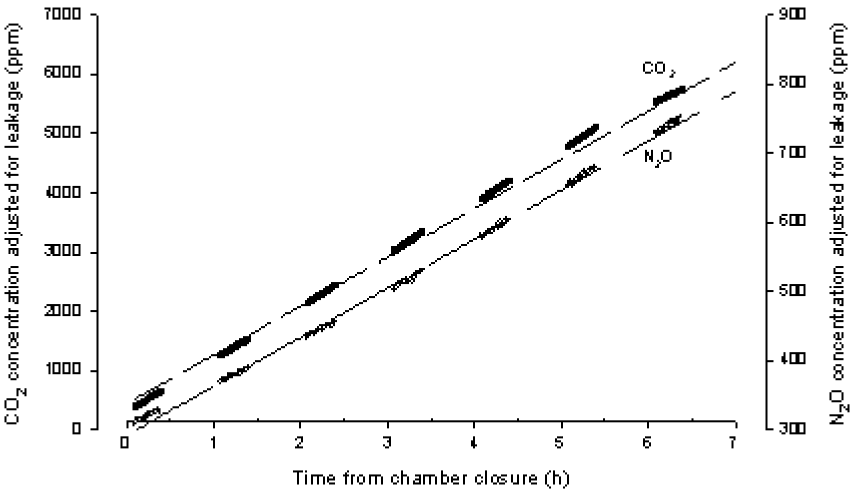


Figure 8 Timecourse of CO_2 and N_2O concentration during a chamber flux measurement over lucerne pasture. The flux chamber remained closed for seven hours. Times are corrected for a chamber air exchange rate of 0.2 $h^{-1.}$

4. Field observations

4.1 Time series of CO_2, N_2O and CH_4

4.1.1 Integrating method

The average daytime, night-time and daily fluxes of CO_2, CH_4 and N_2O observed during the 1994 and 1995 campaigns are summarised in Table 1. Respiratory carbon dioxide fluxes observed in 1995 were more than double those observed in 1994 and showed a strong diurnal variation with significant differences between the pasture and *Triticale* crop, Figs. 9a and 10a. Night-time fluxes averaged 35 and 44 µg C m^{-2} s^{-1} in the lucerne and *Triticale* paddocks respectively while daytime soil plus plant respiration averaged 58 and 94 µg C m^{-2} s^{-1} in the lucerne and *Triticale* respectively. The night-time and day-time fluxes of CO_2 and N_2O observed during 1995 using the integrating method are shown in Fig. 10. The difference between day-time and night-time fluxes increased between the two rain days, 13th and 22nd October, in concert with air temperature. This was particularly apparent for the *Triticale* crop where the daytime respiratory CO_2 flux exceeded the night-time flux by a factor of 1.2 to 3.5 in contrast to the lucerne pasture where the diurnal variation ranged from a factor of 1.1 to 2. There was no indication of any stimulation in respiration immediately following rain, suggesting that soil and plant respiration were not water limited. This contrasted with 1994 when a minor rainfall event stimulated a 3 to 4-fold increase on CO_2 emission from both oats and pasture (data not presented). Site-to-site variability for CO_2 exchange was small, which implies that the averaged fluxes should give reasonably good comparative estimates for each crop.

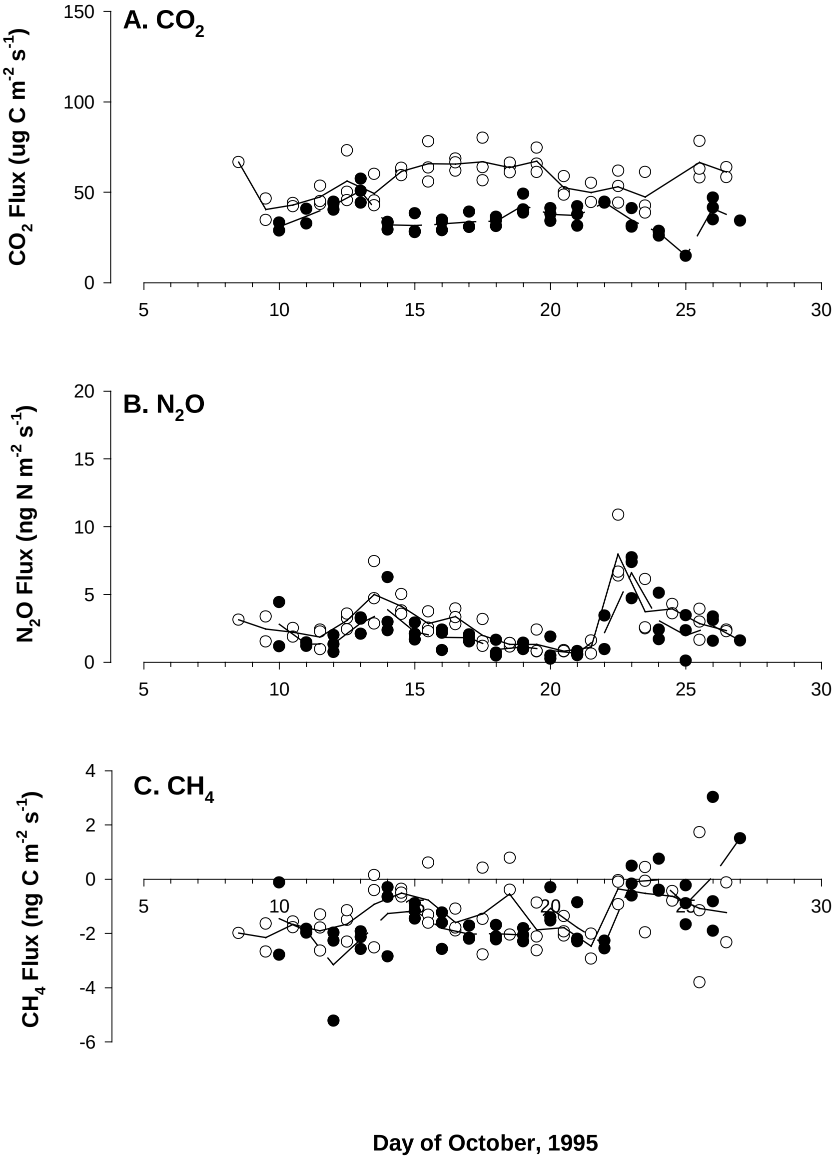


Figure 9 Time course of (a) CO_2 soil plus plant respiration, (b) N_2O and (c) CH_4 soil emission measurements from the lucerne pasture using the integrating method. Individual chamber measurements are shown as points and averages for all chambers are shown as lines for daytime (open symbols, solid line) and night-time (closed symbols, dashed line) fluxes.

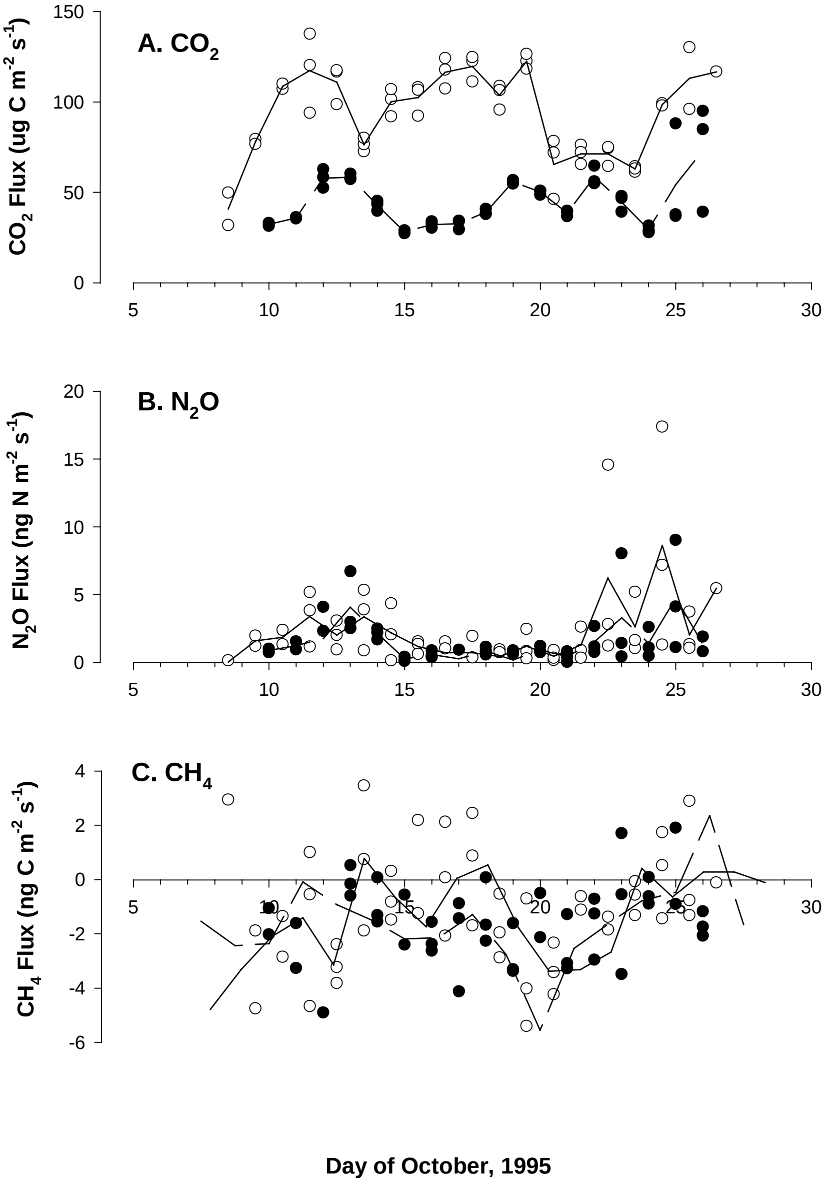


Figure 10 Time course of (a) CO2 soil plus plant respiration, (b) N2O and (c) CH4 soil emission measurements from the Triticale crop using the integrating method. Individual chamber measurements are shown as points and averages for all chambers are shown as lines for daytime (open symbols, solid line) and night-time (closed symbols, dashed line) fluxes.

Table 1 Average daily fluxes of CO_2, CH_4 and N_2O from all soil sites measured during the OASIS campaigns in October 1994 and October 1995. The CO_2 fluxes constitute soil plus plant respiration only. Means ± standard errors of the mean. By definition, a positive flux is an emission from the soil to the atmospere.

Crop		**Day-time**	**Night-time**	**24-hour**
	1994			
Lucerne	CO_2 flux (µg C m^{-2} s^{-1})	-	17 ±4	-
	CH_4 flux (ng C m^{-2} s^{-1})	-4.9 ±1.1	-4.1 ±0.5	-5.5 ± 0.9
Oats	CO_2 flux (µg C m^{-2} s^{-1})	-	29 ± 6	-
	CH_4 flux (ng C m^{-2} s^{-1})	-3.9 ±0.8	-5.9 ± 0.5	-5.3 ± 0.4
	1995			
Lucerne	CO_2 flux (µg C m^{-2} s^{-1})	60 ± 2	38 ± 1	48 ± 3
	CH_4 flux (ng C m^{-2} s^{-1})	-1.4 ± 0.2	-1.4 ± 0.3	-1.5 ± 0.2
	N_2O flux (ng N m^{-2} s^{-1})	3.1 ± 0.4	2.3 ± 0.4	2.9 ± 0.4
Triticale	CO_2 flux (µg C m^{-2} s^{-1})	100 ± 6	48 ± 3	77 ± 4
	CH_4 flux (ng C m-^{2} s^{-1})	-1.5 ± 0.4	-1.7 ± 0.4	-1.5 ± 0.3
	N_2O flux (ng N m^{-2} s`)	2.5 ± 0.5	1.6 ± 0.4	2.1 ± 0.4

The nitrous oxide fluxes exhibited considerable day-to-day variation, with maximum emission rates occurring immediately after rainfall, followed by a slow decline during the subsequent 10 days as the soil dried, Fig. 9b and Fig. 10b. The maximum 12-h N_2O flux observed from the lucerne pasture was 11 ng N m^{-2}s^{-1} following rain on 22nd October rising from a minimum of 1 ng N m^{-2}s^{-1} on 21st October. The N_2O fluxes from the *Triticale* crop on average were approximately 25% lower than the fluxes from the lucerne pasture and followed a similar time course. The maximum N_2O flux observed in the *Triticale* was 18.1 ng N m^{-2}s^{-1} on 24th October. The *Triticale* sites showed far greater variability in response of N_2O flux to the second rainfall event than was apparent in the lucerne with little response evident in chamber 4, a similar response to the lucerne shown in the chamber 5 sites, and a delayed response observed in the chamber 6 sites. This variability, which was not mirrored in either the CH_4 or CO_2 fluxes, indicates greater heterogeneity in the distribution of anaerobic soil sites in the *triticale* crop than in the lucerne crop, possibly a consequence of the greater water demand by the *Triticale* crop. Daytime N_2O fluxes were slightly larger than the night-time fluxes, particularly on the fine days following the rain on the 13th October.

Methane fluxes in 1995 were 75% lower than those recorded from the same sites during the drought year of 1994, Table 1, averaging approximately 1.5 ng C m^{-2}s^{-1} with little difference between daytime and night-time fluxes. Further there was considerable day-to-day variation in methane oxidation rate particularly in the second wetter year, 1995. In both the *Triticale* and lucerne paddocks, methane uptake rate was smallest immediately following rain and largest at the end of the drying cycle.

4.1.2 *Continuous measurements.*

The time course of hourly measurements of carbon dioxide exchange for a single chamber in the lucerne pasture, (Fig. 11), reveals a daily cycle of large amplitude that was highly correlated with temperature, as shown in (Fig. 12). A simple exponential relationship explains most of the variability (r^2 = 0.83 for lucerne and 0.92 for *Triticale*), which supports the conclusion drawn earlier from the integrated flux measurements that respiration was controlled principally by temperature and was not limited by soil water.

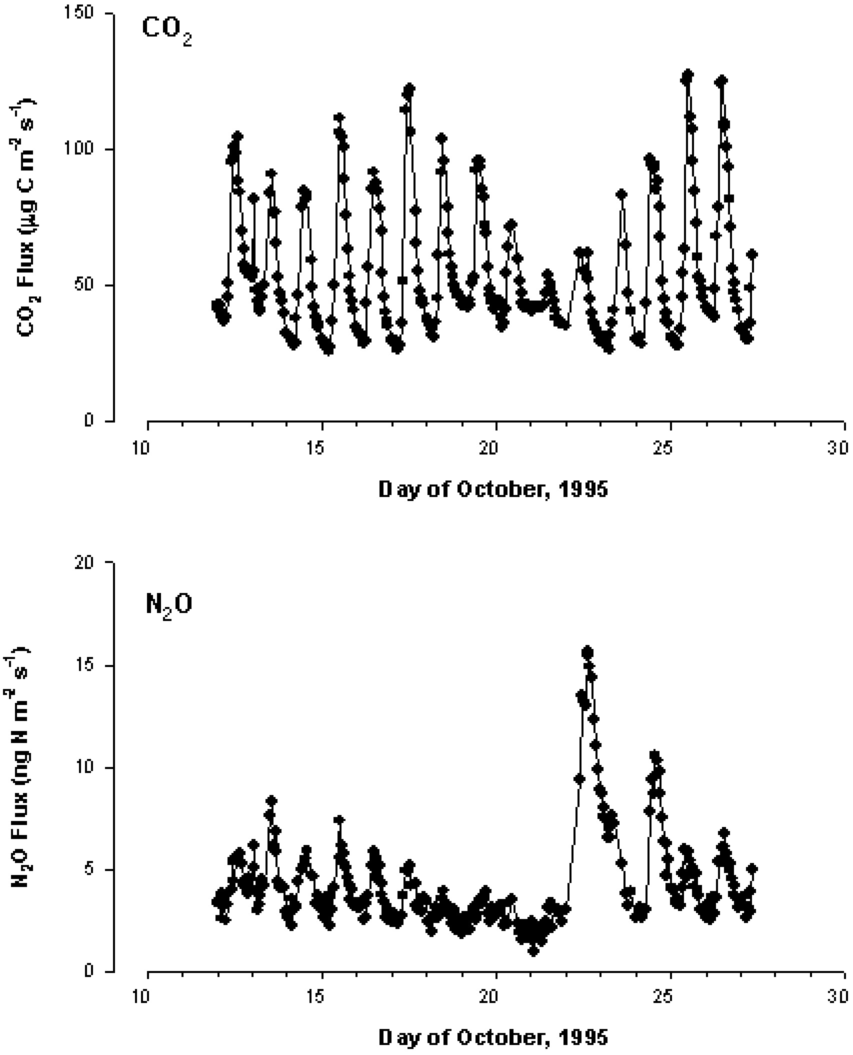


Figure 11 Time course of (a) CO_2 soil plus plant respiration and (b) N_2O soil emission measurements from the lucerne pasture using the continuous mode chamber method coupled to FTIR gas analysis.

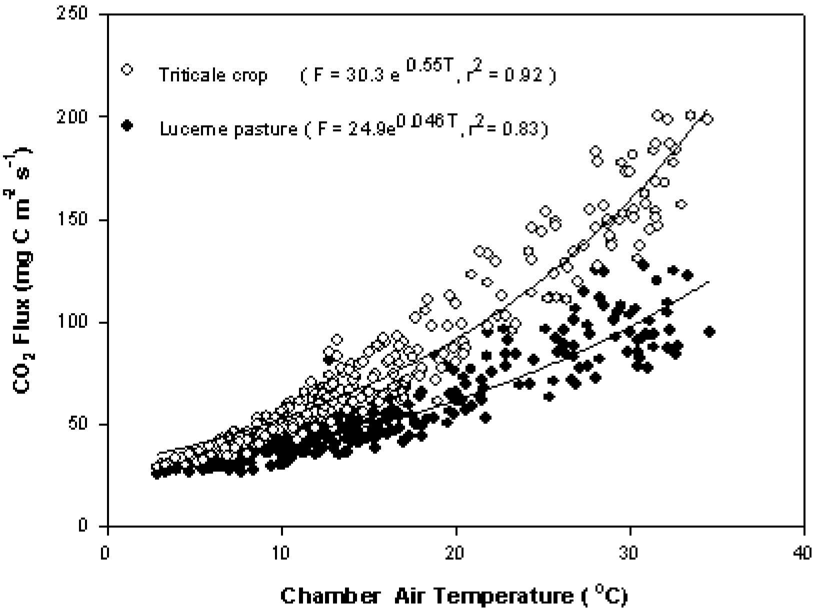


Figure 12 Relationship between soil plus plant dark respiration and air temperature. Hourly fluxes, measured by FTIR. Open symbols, *Triticale* crop; closed symbols, lucerne pasture both for October 1995.

The time course of hourly nitrous oxide flux from the lucerne pasture site is also shown in (Fig. 11). Both rainfall events on October 13 and 22 clearly stimulated a pulse of N_2O emission and increased the sensitivity of this N_2O emission to diurnal temperature variation. However, these effects were transient, and within 7 days N_2O emission had declined to a constant basal rate. Large but transient responses to rainfall are well known properties of denitrification events and suggest that the short-term variability in N_2O emission is due mainly to denitrification.

4.1.3 Discussion of time series

The salient features of these chamber measurements may be summarised as follows. When both crop and pasture paddocks had adequate soil moisture, respiratory CO_2 fluxes were significant, and controlled largely by temperature. Nitrous oxide fluxes were dependent on both rainfall events and temperature, though the temperature sensitivity appeared to be moisture dependent. Methane oxidation rate responded inversely to soil moisture content, with the rate of change greatest as the soil moisture level approached field capacity.

The fluxes observed at Wagga are broadly consistent with observations from other agricultural systems in Australia, and comparable nitrogen limited systems in the USA. The night-time CO_2 fluxes were similar to those observed in natural temperate forest soils in southern Australia and grazed pasture near Wagga Wagga (Galbally et al., 1995; Wang et al., 1997). The nitrous oxide fluxes observed in this experiment were also consistent with the rates of 1-2 ng N m^{-2} s^{-1} reported from several agricultural sites in south eastern Australia and tended toward the lower end of the emission rates reported from regularly fertilised cropland in Europe and USA (Bouwman, 1990).

Recently, there has been considerable interest in the effect on methane exchange of soil disturbance by agricultural activities. Where direct comparisons can be made between natural and agricultural systems, there is clear evidence that the conversion of undisturbed lands to agricultural activity may suppress the methane uptake (Mosier et al., 1991, 1993, 1997; Ojima et al., 1993; Willison et al., 1995) or even reverse it (Keller and Reiners, 1994; Steudler et al., 1996). Ojima et al. (1993) estimated that in the USA conversion of natural soils to agriculture coupled with nitrogen fertilization has reduced methane uptake by soils by 30 to 75%, and that, globally, agriculture has reduced the methane sink by 30%. A comparison between the methane fluxes found in this study (1.5 to 5.5 ng C $m^{-2}s^{-1}$) and those from temperate forests (10 to 16 ng C $m^{-2}s^{-1}$) is consistent with this conclusion.

The comparison between the temperature dependence of respiration in the two crops suggests that the *Triticale* crop was more sensitive to air temperature than the lucerne pasture. The relationship between carbon dioxide flux and air temperature yields Q10 values, (i.e. the ratio of the respiration rates at 10^o C intervals) of 1.6 and 1.8 for the lucerne pasture and the *Triticale* crop respectively. These values, though consistent with measurements in other ecosystems (e.g. Rayment and Jarvis, 1997), are lower than the value of 2 that is characteristic of purely metabolic processes. The lower values indicate the presence of some physical constraints.

The cause of the difference in temperature sensitivity between the two crops may be the difference in plant biomass. The above-ground biomass in the *Triticale* crop was considerably larger than the lucerne in the pasture and therefore above-ground respiration contributes a greater proportion of the total CO_2 flux in the *Triticale* than in the pasture. Above-ground plant respiration is strongly coupled to air temperature. Soil and root respiration rates are determined by soil temperature. However, since the amplitude of the daily temperature cycle is increasingly attenuated with soil depth, using air temperature as a surrogate for soil temperature will tend to underestimate the temperature dependence of soil respiration. Hence pasture, in which soil and plant respiration contribute significantly to the total respiratory fluxes, will apparently be less sensitive to air temperature changes than crops in which above-ground plant respiration is more dominant.

Soil porosity is perhaps the most important of the factors affecting nitrous oxide production and methane oxidation rate (Keller and Reiners,1994; Castro et al., 1995; Mosier et al., 1996; Steudler et al., 1996). Rainfall events that partially saturate soil pore space create the anaerobic conditions required for denitrification. At the same time, methane oxidation rate is reduced by an increase in the resistance to methane diffusion from atmosphere to the oxidation sites in the soil. Both the difference in methane oxidation rate between 1994 and 1995 and the variation in methane flux during the drying cycle of 1995 are consistent with the difference in soil water content.

In general, therefore, the first two requirements for validation have been met, at least qualitatively. The magnitude of the fluxes observed with both techniques are consistent with the fluxes observed independently in comparable agricultural systems, and the short-term responses to environmental drivers are consistent with the known behaviour of soil microbial and physical processes.

4.2 Comparison of the continuous method with the integrating method

During the 1995 OASIS campaign both techniques were run alternately using the same two chambers on the same soil/plant plots. The continuous mode flux measurements alternated with the integrated mode measurements, every 30 minutes. The high frequency FTIR trace gas exchange measurements were averaged to produce fluxes for the same integration period as the integrated measurements. The two systems should give identical results if the following requirements are met:

- air mixing in the chambers is adequate;
- the system is inert to trace gases;
- the differential air pressure between the chamber and ambient is identical in each configuration;
- the effect of the chamber on the soil/plant environment is identical;
- the air flows out of the chamber are accurately determined;
- the volumes of both systems are accurately determined;
- both trace gas measurement systems are calibrated against a common standard;
- the responses of the two chemical analytical instruments are identical for the matrix of chamber air that contains the gases being analysed; and
- the time bases for the both sets of measurements are identical.

A detailed examination suggests that all of these requirements were met in the current system configuration. The major difference between the systems was the recirculating pump in the FTIR circuit.

The issue of mixing deserves comment; because there is a physical difference in the characteristics of all mixing in the two chambers. The continuous mode includes an air return of 15 l min^{-1}. This emerges from an orifice of 0.1 cm cross-section with a velocity of more than 20 m s^{-1}. This air flow will create an additional source of turbulent mixing and stirring within the chamber. The CO_2 emissions arise from the soil and plants and, in a deep canopy, the above ground plant tissue is probably the major source. In contrast, the N_2O fluxes derive from the soil. Therefore, the characteristics of CO_2 and N_2O transport through the canopy to the chamber headspace might differ. However, as previously discussed in Section 3.1.3, incomplete mixing in the chamber does not bias the flux measurements.

In practice, though the two methods yielded largely consistent results, there were some differences. The average day and night CO_2 fluxes measured by the integrating and the continuous methods are compared in Fig. 13a and Table 2. The analysis using a reduced major axis regression, shows no significant differences between the two methods with either the small chamber on the lucerne crop or the large chamber on the *Triticale* crop. The intercepts are less than 10% of the mean fluxes and are not significantly different from zero.

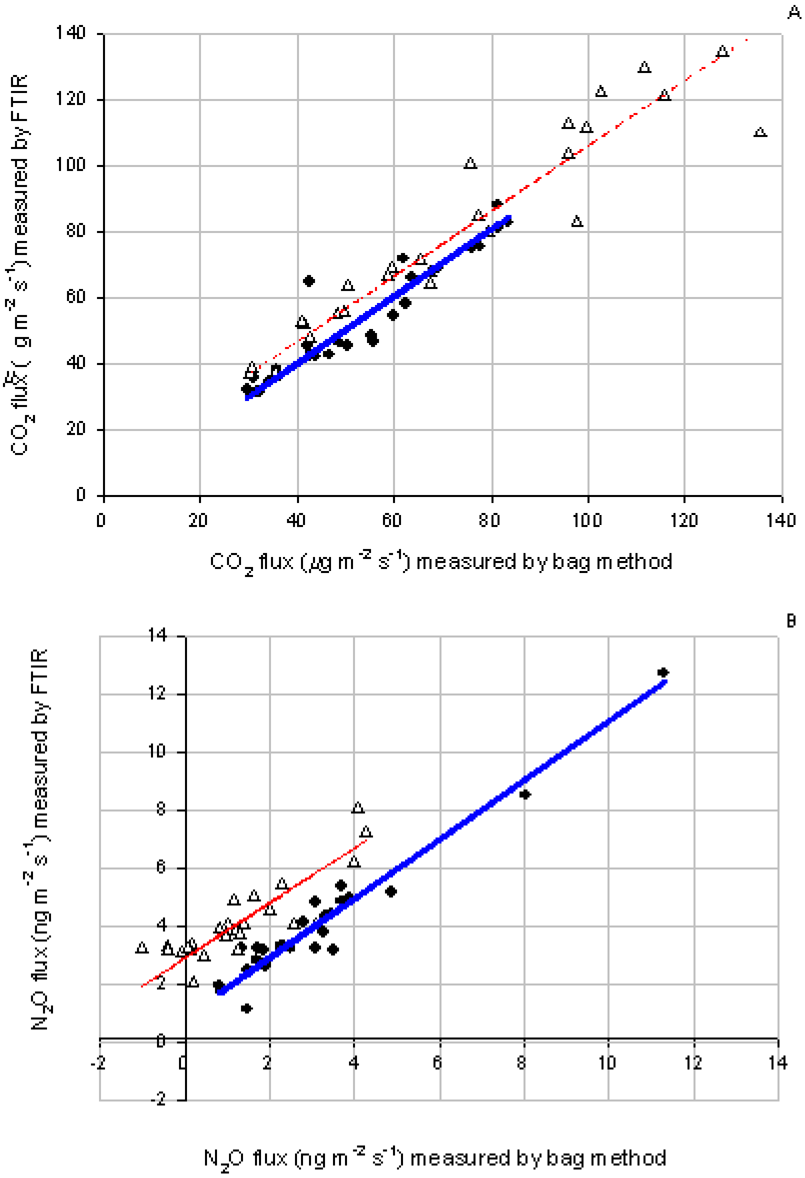


Figure 13 Comparison measurements of (a) CO_2 fluxes and (b) nitrous oxide fluxes by the integrating method and by the continuous method averaged over comparable time intervals. Closed symbols and solid line, lucerne pasture; open symbols and dashed line, *Triticale* crop, both for October 1995.

Table 2 Regression coefficients for a reduced major axis regression between the flux estimates of CO_2 and N_2O made by the integrating (bag) method and the continuous (FTIR) method averaged over identical time intervals.

Crop	**CO_2 flux***		**N_2O flux***	
	(μg C m^{-2} s^{-1})		**Ng N m^{-2} s^{-1}**	
	Slope	**Intercept**	**Slope**	**Intercept**
Lucerne Pasture	1.02 ± 0.13	-0.7 ± 7.8	1.03 ± 0.0.10	0.85 ± 0.38
Triticale	0.99 ± 0.13	7.2 ± 10.4	0.95 ± 0.20	2.9 ± 0.38

* coefficient ± 95% confidence limits.

The comparison between the N_2O flux measurements by the two methods Fig. 13b, shows that the integrating method underestimated the flux by 20% with the small chamber on lucerne pasture and 60% with the larger chamber on the *Triticale* crop relative to the FTIR/continuous method, for mid-range fluxes of about 5 ng N m^{-2} s^{-1}. These differences were due entirely to a significant positive offset between the two methods. This offset was larger with the larger chamber used on the *Triticale* crop i.e. 2.9 ± 0.4 ng N m^{-2} s^{-1} compared with 0.9 ± 0.3 for the small chamber on the lucerne crop (Table 3). In both cases the offset is significant relative to the average fluxes observed during the experiment.

There are several plausible explanations for the differences between the two methods. These include:

1. The mixing in the chamber in the dense high crop (T*riticale*) may be inadequate in the case of the integrated system, but better due to the return flow in the continuous mode. (The chamber was not designed to hold such a crop, and the mixing under such conditions is unknown). If the mixing was inadequate in the integrated system the emissions of N_2O and CO_2 could be suppressed by the build-up of high concentrations of these gases in the bottom of the chambers.
2. The GC and FTIR are subject to cross sensitivity particularly for gases such as CO_2 and N_2O. Though the FTIR was explicitly calibrated for cross sensitivity between N_2O and both CO_2 and H_2O, the issue deserves further investigation.
3. If, despite the vent, there was significant pressure variation in the chamber caused by circulating air through the FTIR gas circuit, then the trace gas fluxes might be increased by the effect of pressure pumping on the mass transport of trace gas from the soil. This phenomenon is distinct from the diffusive and turbulent transport within the canopy discussed in section 3.2. It has been reviewed in detail by Livingston and Hutchinson (1995), has been modelled by several authors (e.g. Massman et al., 1997) and studied both experimentally and theoretically by Gao and Yates (1998a, 1998b), and has been shown to increase apparent flux rates significantly.

The first explanation is unlikely because suppression of trace gas emission from the soil due to an increasing concentration in the atmosphere would lead to a nonlinear time course of the trace gas concentration. The concentration time courses for CO_2 and N_2O recorded with the continuous method, after correction for a leakage rate of 0.2 h^{-1}, were always linear, even on one occasion when, due to a timing error, the chamber remained closed for seven hours. The concentration changes during this event, 2500 ppm CO_2 and 100 ppb N_2O, were very much greater than the concentration gradients that might be supported by a dense canopy, see Fig. 5, and yet there was no indication that the flux of either species was suppressed by the increasing concentration in the chamber headspace. Our modelling study, section 3.2, and the Appendix show that on its own, turbulent and diffusive transport through a canopy will not induce non-linearities or biases in the concentration timeseries that might lead to errors in flux determinations.

Cross sensitivity between N_2O and another unidentified trace gas emitted by the canopy gases could lead to an offset proportional to canopy size. While cross sensitivities can occur in the FTIR analytical technique, known cross sensitivities were entirely accounted for in the analysis of the residuals. There were no other gases that absorbed significantly in the region of the infra red spectrum used for N_2O and CO_2 detection.

While it is probable that the continuous method induced pressure fluctuations in the chamber by the return flow from the pump, it would be expected that a larger chamber volume would dampen the fluctuations to a greater extent than a smaller chamber volume and therefore the offset in fluxes measured by the two methods would be inversely proportional to chamber volume. However, the offset appeared to increase with increasing chamber volume. On the other hand, the pressure fluctuations might also significantly enhance the diffusion of trace gas through the plant canopy and upper layers of the soil profile. This process was not included in our model in section 3.2, or in the analyses of Healy et al. (1997) and Hutchinson et al. (2000). The deep and dense canopy of the *Triticale* crop would be affected to a greater extent than the smaller lucerne canopy. Further, CO_2 and N_2O diffusion might be affected differently because a significant proportion of the CO_2 flux derives from leaves in the upper layers of the canopy, in contrast to N_2O, which is produced exclusively in the soil. Massman et al. (1997) modelled the influence of pressure pumping on trace gas diffusion though a snowpack overlying soil and concluded that the effects of pressure pumping diminished with the magnitude of the concentration gradient, and were essentially transient. Gao and Yates (1998a, 1998b) have shown for continuous flow chambers that the flux can be perturbed to either a lower or higher flux value, in some cases differing by a factor of 5 from the static chamber observed value and the theoretically estimated value. We surmise that some unknown aspect of the flow generated the systematic differences in fluxes observed here in the FTIR observations.

5. Conclusions

The integrating method and the continuous-mode static chamber methods have been used during the OASIS experiment to provide a comprehensive estimate of N_2O, CH_4 and respiratory CO_2 fluxes for comparison with coincident measurements made by micrometeorological methods. The theoretical and experimental basis of these chamber techniques is presented.

Qualitatively, the CO_2, N_2O and CH_4 flux rates observed during the OASIS experiment by the two independent chamber methods appear to be consistent in magnitude to rates measured in other similar agricultural systems. The variation in fluxes in response to major environmental factors also appears to be consistent with well described soil metabolic processes, and will be analysed quantitatively in a subsequent study.

The comparison between the two flux methods showed that for the most part the results were comparable. That is, the CO_2 emission rates were equivalent and the comparison of the N_2O emission showed that the two techniques differed by a constant that was independent of N_2O flux. The cause of the offset was not identified, however several possibilities were investigated and eliminated. These included: restrictions to diffusive transport through a dense canopy, cross sensitivity in the FTIR between N_2O and an other known trace gases, and time lags caused by the large volume of the FTIR cell. However, one potential artefact could not be eliminated was disturbance to the trace gas concentration profile in the soil by small pressure fluctuations induced by recirculating analysis air. This possibility justifies further investigation.

The systematic offset between the two methods with respect to N_2O flux is significant because the size of the offset is similar to the size of the average fluxes being measured. We consider that this systematic offset most probably results from an artefact in the continuous method, and therefore the integrating method delivers a better estimate of the absolute fluxes. Nevertheless, direct comparison of the N_2O fluxes between the crops remains difficult until the source of the offset is unequivocally established. Fortunately both methods deliver the same response to change in N_2O flux (i.e. the slope of the regression is 1), therefore conclusions about the relative variation of N_2O exchange within each crop can be made with confidence. Similarly if comparisons are confined to the relative variation in flux rate, then the two methods also deliver complementary spatial and temporal information for N_2O exchange. Further comparison of flux measuring techniques is desirable.

6. Acknowledgements:

We thank the CSIRO Atmospheric Research Electronic Design and Mechanical Laboratories for implementing the design and construction of these chambers. CSIRO Atmospheric Research GASLAB prepared the trace gas working standards. The field studies were conducted with funding from the Rural Industrial Research Development Council, National Greenhouse Gas Inventory Committee and National Greenhouse Advisory Committee. This work was conducted as part of the CSIRO Climate Change Research Program.

References

Businger, J., 1986. Evaluation of the accuracy with which dry deposition can be measured with current micrometeorological techniques. *Journal of Climate Applied Meteorology,* **25**, 1100-1124.

Butterbach-Bahl, K., Gasche, R., Breuer, L., and Papen, H., 1997. Fluxes of NO and N_2O from temperate forest soils: impact of forest type, N deposition and of liming on the NO and N_2O emissions. *Nutrient Cycling in Agroecosystems* **48,** 79-90.

Bouwman, A.F., 1990. Exchange of greenhouse gases between terrestrial ecosystems and the atmosphere. In: *Soils and the Greenhouse Effect*. ed. A.F. Bouwman, John Wiley and Sons Ltd, pp. 63–127.

Carslaw, H.S. and Jaeger, J.C. 1959. *Conduction of heat in solids* Clarendon, Oxford. U.K.

Castro, M.S., Steudler, P.A., Melillo, J.M., Aber, J.D., and Bowden, R.D., 1995. Factors controlling atmospheric methane consumption by temperature in forest soils. *Global Biogeochemical Cycle* ***9***, 1–10.

Denmead, O.T., 1979. Chamber systems for measuring nitrous oxide emission from soils in the field. *Journal of the Soil Science Society of America* **43**, 89-95.

Esler, M.B., Griffith, D.W.T. Wilson, S.R. and Steele, L.P., 2000. Precision trace gas analysis by FT-IR spectroscopy 1. Simultaneous analysis of CO_2, CH_4, N_2O and CO in air, *Analytical Chemistry* **72**, 206-215.

Francey, R.J., Steele, L.P., Langenfelds, R.L., Lucarelli, M.P., Allison, C.E., Beardsmore, D.J., Coram, S.A., Derek, N., De Silva, F.R., Etheridge, D.M., Fraser, P.J., Henry, R.J., Turner, B., Welch, E.D., Spencer, D.A., and Cooper, L.N., 1993. Global Atmospheric Sampling Laboratory (GASLAB): supporting and extending the Cape Grim trace gas programs. In: *Baseline Atmospheric Program Australia*. 1993 ed. R. J. Francey, A. L. Dick and N. Derek (editors). [Melbourne]: Department of the Environment, Sport and Territories, Bureau of Meteorology in cooperation with CSIRO Division of Atmospheric Research. p. 8-29.

Gao, F., and Yates, S.R., 1998a. Laboratory study of closed and dynamic flux chambers: Experimental results and implications for field application, *Journal of Geophysical Research,* **103**, 26,115-26,125.

Gao, F., and Yates, S.R., 1998b. Simulation of enclosure-based methods for measuring gas emissions from soil to the atmosphere, *Journal of Geophysical Research,* **103**, 26,127-26,136.

Galbally, I.E., Roy, C.R., Elsworth, C.M., and Rabich, H.A.H., 1985. *The measurement of nitrogen oxide (NO, NO_2) exchange over plant/soil surfaces* CSIRO Division of Atmospheric Research, Aspendale, Australia. Technical Paper 8. 23 pp. (plus microfiche).

Galbally, I.E. and Roy, C.R., 1980. Destruction of ozone at the earth's surface. *Quarterly Journal of the Royal Meteorological Society* **106**, 599–620.

Griffith, D.W.T., 1996. Synthetic calibration and quantitative analysis of gas-phase FTIR spectra. *Applied Spectroscopy* **50**, 59-70.

Healy, R.W., Striegl, R.G., Russell, T.F., Hutchinson, G. L., and Livingston, G. P., 1996. Numerical evaluation of static chamber measurements of soil-atmosphere gas exchange: identification of physical processes. *Journal of the Soil Science Society of America* **60**, 740-747.

Hutchinson, G.L. and Mosier, A.R., 1981. Improved soil cover method for field measurements of nitrous oxide fluxes, *Journal of the Soil Science Society of America* **45**, 311-316.

Hutchinson, G.L., Livingston, G.P., Healy, R.W., and Striegl, R.G., 2000. Chamber measurement of surface-atmosphere trace gas exchange: Numerical Evaluation of Dependence on soil, interfacial layer, and source/sink properties. *Journal of Geophysical Research* **105**: 8865-8875.

Jury, W.A., Letey, J. D., and Collins, T., 1981. Analysis of chamber methods used for measuring nitrous oxide production in the field. *Journal of the Soil Science Society of America* **46,** 250-256.

Keller, M., and Reiners, W.A., 1994. Soil-atmosphere exchange of nitrous oxide, nitric oxide, and methane under secondary succession of pasture to forest in the Atlantic lowlands of Costa Rica. *Global Biogeochemical Cycles **8***, 399–409.

Kimball, B.A., 1990. Exact equations for calculating air leakage rates from plant growth chambers. *Agronomy Journal* **82**, 998–1003.

Kirstine, W., Galbally, I. E., Ye, Y. and Hooper, M. A., 1998. Emissions of volatile organic compounds (primarily oxygenated species) from pasture. *Journal of Geophysical Research* **103**, 10605-10619.

Leuning, R., Denmead, O. T., Griffith, D. W. T., Jamie, I. M., Isaacs, P., Hacker, J. M., Meyer, C. P., Galbally, I. E., Cleugh, H. A., Raupach, M. R., and Essler, M. B., 1997. *Assessing sources and sinks of greenhouse gases at three interlinking scales: final report to NGAC*. [Canberra], CSIRO Land and Water, Canberra, Australia. (Consultancy report; 97-56). 1 v.

Livingston, G.P., and Hutchinson, G.L., 1995. Enclosure-based measurement of trace gas exchange: applications and sources of error. In P.A. Matson and R.C. Harriss Eds, *Biogenic Trace Gases* Measuring Emissions from Soil and Water. Blackwell Science Ltd., Oxford, U.K., pp. 14-51.

Marynick D.S., and Marynick M.C., 1975. A mathematical treatment of rate data obtained in biological flow systems under non-steady state conditions. *Plant Physiology* **56**, 680–683.

Massman, W.J., Sommerfeld, R.A., Mosier, A.R., Zeller, K.F., Hehn, T.J. and Rochelle, S.G., 1997. A model investigation of turbulence-driven pressure pumping effects on the rate of diffusion of CO_2, N_2O and CH_4 through layered snowpacks, *Journal of Geophysical Research* **102**, 18851 - 18863.

Meyer, C. P., Galbally, I. E., Wang, Y. P., Weeks, I. A., Tolhurst, K. G., and Tomkins, I. B., 1997. *The Enhanced emissions of greenhouse gases from soil following prescribed burning in a southern eucalyptus forest, final report to the National Greenhouse Gas Inventory Committee*. CSIRO Division of Atmospheric Research, Aspendale, Australia. 66 pp.

Mosier, A., Valentine, D., Bronson, K., and Parton, W., 1991. Methane and nitrous oxide fluxes in native, fertilised and cultivated grasslands. *Nature* **350**, 330–332.

Mosier, A.R., Klemedtsson,L.K., Sommerfeld, R.A., and Musselman, R.C., 1993. Methane and nitrous oxide flux in a Wyoming subalpine meadow. *Global Biogeochemical Cycles* **7,** 771-784.

Mosier, A.R., Parton, W.J., Valantine, D.W., Ojima, D.S., Schimel, D.S., and Delgado J.A., 1996. CH_4 and N_2O fluxes in the Colorado Short Grass Steppe: I impact of landscape and nitrogen addition. *Global Biogeochemical Cycles* **10**, 387-399.

Mosier, A.R., Parton, W.J., Valantine, D.W., Ojima, D.S., Schimel, D.S. and Heinmeyer, O., 1997. CH_4 and N_2O fluxes in the Colorado Short Grass Steppe 2. long-term impact of land use change. *Global Biogeochemical Cycles* **11**, 29-42.

Ojima, D.S. Valantine, D.W., Mosier, A.R., Parton, W.J. and Schimel, D.S., 1993. Effect of land use change on methane oxidation in temperate forest and grassland soils. *Chemosphere* **26,** 675-685.

Poss, R., Smith, C.J., Dunin, F.X. and Angus, J.F., 1995. Rate of soil acidification under wheat in a semi-arid environment. *Plant and Soil* **177**, 85-100.

Raupach, M.R., 1987. A Lagrangian analysis of scalar transfer in vegetation canopies. *Quarterly Journal of the Royal Meteorological Society* **113**, 107-120.

Rayment, M.B. and Jarvis, P.G., 1997. An improved open chamber method for measuring soil CO_2 effluxes in the field, *Journal of Geophysical Research* **102**, 28779-28784.

Steudler, P.A., Melillo, J.M., Feigl, B.J., Neil, C., Piccolo, M.C. and Cerri, C.C., 1996. Consequences of forest to pasture conversion on CH_4 fluxes in the Brazilian Amazon basin *J. Geophys. Res.,* **101,** 18547–18554.

Thom, A.S. and Oliver, H.S., 1977. On Penman's equation for estimating regional evaporation. *Quarterly Journal of the Royal Meteorological Society* **103**, 345-357.

Wang, Y. P., Meyer, C. P., Galbally, I. E. and Smith, C. J., 1997. Comparisons of field measurements of carbon dioxide and nitrogen oxide fluxes with model simulations for a legume pasture in southeast Australia. *Journal of Geophysical Research*, **102,** 28013-28024.

Willison, T.W., Webster, C.P., Goulding, K.W.T. and Powlson, D.S., 1995. Methane oxidation in temperate soils: effects of land use and the chemical form of nitrogen fertilizer. *Chemosphere* **30**, 539-546.

Appendix: The effect of a dense plant canopy in the chamber on the concentration time course

As shown in Eq. 1 the closed chamber provides a measurement of the flux from the soil through a measurement of the time rate of change of the volume-averaged concentration of gas under consideration in the chamber.

It is assumed that the canopy aerodynamic resistance was much smaller than the soil resistance and so does not have significant effect on the flux measurements. This is generally the case for the relatively sparse vegetation in a small chamber. However large chambers, which completely enclose a crop canopy or forest ground cover, are now being commonly used in trace-gas-emission studies from crops and natural ecosystems. (1989; Butterbach-Bahl et al., 1997). Even in well-stirred chambers, the plant canopy might constitute a major diffusive barrier, and therefore might introduce additional errors to flux estimation. We have investigated the influence on the measured trace gas flux of a deep canopy contained within a closed static chamber.

The concentration of a trace gas within a plant canopy can be described by the diffusion equation as follows:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial z}\left(D\frac{\partial C}{\partial z} \right) = -\frac{\partial F}{\partial z} \tag{10}$$

where C is the gas concentration at a height z above the soil surface (m), t is time (s), D is the turbulent diffusion coefficient within the canopy ($m^2\ s^{-1}$), F is the volumetric vertical trace gas flux within the canopy ($m^3\ m^{-2}\ s^{-1}$) and z is the height above the soil surface (m). The following boundary conditions are applicable for this study: $F = F_0$ when $z = 0$; $C = C_a$ when $z = 0$;$C = C_a$ when $z = h$ (canopy height) and the chamber is open, where C_a is the ambient trace gas concentration; $D = 0$ when $z = h$ and chamber is closed.

Eq. 10 can be solved either analytically or numerically. The analytical solution can be formulated using the above boundary conditions for constant D (see p. 113, Carslaw and Jaeger, 1959). When D varies with z and the chamber is open, the steady state solution of Eq. 1 is given by

$$C(z) = C_a + F_0 \int_z^h \frac{dz}{D(z)}. \tag{11}$$

The term $\int_z^h \frac{dz}{D(z)}$ is the total aerodynamic resistance between height z and h. Variation of D with z is calculated using the theory developed by Raupach (1987). A numerical solution is required for the time dependent solution after the chamber lid has closed. Information from this solution for the example of N_2O is provided in Fig. 4 and Fig. 5. The canopy height is 0.8 m. Turbulence is assumed to be patterned on a plane mixing layer rather than a surface boundary layer above the canopy, therefore the diffusivity is roughly constant.

CSIRO Atmospheric Research, Technical Paper

(Series title changed from CSIRO Division of Atmospheric Research Technical Papers at number 38)

No. 1 Galbally, I.E.; Roy, C.R.; O'Brien, R.S.; Ridley, B.A.; Hastie, D.R.; Evans, W.J.F.; McElroy, C.T.; Kerr, J.B.; Hyson, P.; Knight, W.; Laby, J.E. Measurements of trace composition of the Austral stratosphere: chemical and meteorological data. 1983. 31 p.

No. 2 Enting, I.G. Error analysis for parameter estimates from constrained inversion. 1983. 18 p.

No. 3 Enting, I.G.; Pearman, G.I. Refinements to a one-dimensional carbon cycle model. 1983. 35 p.

No. 4 Francey, R.J.; Barbetti, M.; Bird, T.; Beardsmore, D.; Coupland, W.; Dolezal, J.E.; Farquhar, G.D.; Flynn, R.G.; Fraser, P.J.; Gifford, R.M.; Goodman, H.S.; Kunda, B.; McPhail, S.; Nanson, G.; Pearman, G.I.; Richards, N.G.; Sharkey, T.D.; Temple, R.B.; Weir, B. Isotopes in tree rings. 1984. 86 p.

No. 5 Enting, I.G. Techniques for determining surface sources from surface observations of atmospheric constituents. 1984. 30 p.

No. 6 Beardsmore, D.J.; Pearman, G.I.; O'Brien, R.C. The CSIRO (Australia) Atmospheric Carbon Dioxide Monitoring Program: surface data. 1984. 115 p.

No. 7 Scott, J.C. High speed magnetic tape interface for a microcomputer. 1984. 17 p.

No. 8 Galbally, I.E.; Roy, C.R.; Elsworth, C.M.; Rabich, H.A.H. The measurement of nitrogen oxide (NO, NO2) exchange over plant/soil surfaces. 1985. 23 p.

No. 9 Enting, I.G. A strategy for calibrating atmospheric transport models. 1985. 25 p.

No. 10 O'Brien, D.M. TOVPIX: software for extraction and calibration of TOVS data from the high resolution picture transmission from TIROS-N satellites. 1985. 41 p.

No. 11 Enting, I.G.; Mansbridge, J.V. Description of a two-dimensional atmospheric transport model. 1986. 22 p.

No. 12 Everett, J.R.; O'Brien, D.M.; Davis, T.J. A report on experiments to measure average fibre diameters by optical fourier analysis. 1986. 22 p.

No. 13 Enting, I.G. A signal processing approach to analysing background atmospheric constituent data. 1986. 21 p.

No. 14 Enting, I.G.; Mansbridge, J.V. Preliminary studies with a two- dimensional model using transport fields derived from a GCM. 1987. 47 p.

No. 15 O'Brien, D.M.; Mitchell, R.M. Technical assessment of the joint CSIRO/Bureau of Meteorology proposal for a geostationary imager/ sounder over the Australian region. 1987. 53 p.

No. 16 Galbally, I.E.; Manins, P.C.; Ripari, L.; Bateup, R. A numerical model of the late (ascending) stage of a nuclear fireball. 1987. 89 p.

No. 17 Durre, A.M.; Beer, T. Wind information prediction study: Annaburroo meteorological data analysis. 1989. 30 p. + diskette.

No. 18 Mansbridge, J.V.; Enting, I.G. Sensitivity studies in a two- dimensional atmospheric transport model. 1989. 33 p.

No. 19 O'Brien, D.M.; Mitchell, R.M. Zones of feasibility for retrieval of surface pressure from observations of absorption in the A band of oxygen. 1989. 12 p.

No. 20 Evans, J.L. Envisaged impacts of enhanced greenhouse warming on tropical cyclones in the Australian region. 1990. 31 p. [Out of print]

No. 21 Whetton, P.H.; Pittock, A.B. Australian region intercomparison of the results of some general circulation models used in enhanced greenhouse experiments. 1991. 73 p. [Out of print]

No. 22 Enting, I.G. Calculating future atmospheric CO2 concentrations. 1991. 32 p.

No. 23 Kowalczyk, E.A.; Garratt, J.R.; Krummel, P.B. A soil-canopy scheme for use in a numerical model of the atmosphere — 1D stand- alone model. 1992. 56 p.

No. 24 Physick, W.L.; Noonan, J.A.; McGregor, J.L.; Hurley, P.J.; Abbs, D.J.; Manins, P.C. LADM: A Lagrangian Atmospheric Dispersion Model. 1994. 137 p.

No. 25 Enting, I.G. Constraining the atmospheric carbon budget: a preliminary assessment. 1992. 28 p.

No. 26 McGregor, J.L.; Gordon, H.B.; Watterson, I.G.; Dix, M.R.; Rotstayn, L.D. The CSIRO 9-level atmospheric general circulation model. 1993. 89 p.

No. 27 Enting, I.G.; Lassey, K.R. Projections of future CO2. with appendix by R.A. Houghton. 1993. 42 p.

No. 28 [Not published]

No. 29 Enting, I.G.; Trudinger, C.M.; Francey, R.J.; Granek, H. Synthesis inversion of atmospheric CO2 using the GISS tracer transport model. 1993. 44 p.

No. 30 O'Brien, D.M. Radiation fluxes and cloud amounts predicted by the CSIRO nine level GCM and observed by ERBE and ISCCP. 1993. 37 p.

No. 31 Enting, I.G.; Wigley, T.M.L.; Heimann, M. Future emissions and concentrations of carbon dioxide: key ocean/atmosphere/land analyses. 1994. 120 p.

No. 32 Kowalczyk, E.A.; Garratt, J.R.; Krummel, P.B. Implementation of a soil-canopy scheme into the CSIRO GCM — regional aspects of the model response. 1994. 59 p.

No. 33 Prata, A.J. Validation data for land surface temperature determination from satellites. 1994. 40 p.

No. 34 Dilley, A.C.; Elsum, C.C. Improved AVHRR data navigation using automated land feature recognition to correct a satellite orbital model. 1994. 22 p.

No. 35 Hill, R.H.; Long, A.B. The CSIRO dual-frequency microwave radiometer. 1995. 16 p.

No. 36 Rayner, P.J.; Law, R.M. A comparison of modelled responses to prescribed CO2 sources. 1995. 84 p.

No. 37 Hennessy, K.J. CSIRO Climate change output. 1998. 23 p.

No. 38 Enting, I. G. Attribution of greenhouse gas emissions, concentrations and radiative forcing. 1998. 29 p.

No. 39 O'Brien, D.M.; Tregoning, P. Geographical distributions of occultations of GPS satellites viewed from a low earth orbiting satellite. 1998. 23 p.

No. 40 Enting, I.G. Characterising the temporal variability of the global carbon cycle. 1999. 23 p.

No. 41 [In preparation]

No. 42 Mitchell, R.M. Calibration status of the NOAA AVHRR solar reflectance channels: CalWatch revision 1. 1999. 20 p.

No. 43 Hurley, P.J. The Air Pollution Model (TAPM) Version 1: technical description and examples. 1999. 41 p.

No. 44 Frederiksen, J.S.; Dix, M.R.; Davies, A.G. A new eddy diffusion parameterisation for the CSIRO GCM. 2000. 31 p.

No. 45 [In preparation]

No. 46 Prata, A.J. Global Distribution of Maximum Land Surface Temperature Inferred from Satellites: Implications for the Advanced Along Tracking Scan Radiometer. 2000. 30 p. Electronic edition only.

No. 47 Prata, A.J. Precipitable water retrieval from multi-filtered shadowband radiometer measurements. 2000. 14 p. Electronic edition only.

No. 48 [In preparation]

No. 49 [In preparation]

No. 50 [In preparation]

A complete list of CSIRO Atmospheric Research Technical papers can be found at www.dar.csiro.au/info/TP.htm

Address and contact details: CSIRO Atmospheric Research
Private Bag No. 1 Aspendale, Victoria 3195 Australia
Ph: (+61 3) 9239 4400; fax: (+61 3) 9239 4444
email: chief@dar.csiro.au