Developments in Flux Measurements of Greenhouse Gases
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Abstract

The paper reviews methods for measuring the exchanges of trace gases between soil-plant systems and the atmosphere, with emphasis on the greenhouse gases CO₂, CH₄ and N₂O. The methods vary in scale from chambers covering < 1m² to convective boundary layer budgets for regions of 100 to 1000 km². They should be seen as complementary rather than alternatives, each having a special role.

New micrometeorological approaches are filling gaps in our measurement capabilities: less demanding mass balance techniques, new laser-based gas analysers, and convective boundary layer budget methods which permit estimates of trace gas fluxes on regional scales from relatively simple measurements.

1. Introduction

Much of our uncertainty about the greenhouse effect derives from deficiencies in our ability to measure the surface-to-air exchange rates of the main greenhouse gases, carbon dioxide, methane and nitrous oxide, and to extrapolate those measurements to larger scales. This paper gives a brief overview of methods for measuring exchanges of the greenhouse gases between soil-plant systems and the atmosphere. A more extensive review has been given recently by Denmead and Raupach (1992).

2. Chambers

Almost all our present knowledge of emissions of CH₄ and N₂O comes from chamber measurements. Chambers offer high sensitivity, portability, versatility, and relative simplicity. The operating principle is to restrict the volume of air with which gas exchange occurs, thereby magnifying changes in the concentration of the emitted (or absorbed) gas in the head space. In closed chamber systems there is no replacement of air in the head space and the gas concentration changes continuously. In open systems a constant flow of air through the head space is maintained and the gas concentration attains a steady difference from the background concentration in the ambient air. Closed systems are used more commonly because a larger concentration change occurs and they are mechanically simpler.

In closed systems, the rate of concentration change in the head space is used to calculate the gas flux to or from the soil system:

$$F_g = (V/A) dp_g/dt \quad (1)$$

where F_g is the flux density of the gas, V is the volume of the head space, A is the area of land enclosed, p_g is the gas density within the chamber, and t is time. (Of course, precautions must be taken to prevent changes in the gas concentration within the chamber from influencing the flux.) In open systems, the flux is calculated from:

$$F_g = v (\rho_g - \rho_b) / A \quad (2)$$

where v is the gas flow rate and ρ_b is the background gas concentration. In practice, v is adjusted so as to keep $(\rho_g - \rho_b)$ small.

Tables 1 and 2 set out some operating requirements for chambers and conventional micrometeorological methods and convective boundary layer (CBL) budgets. The tables indicate that for chambers, not only can gas sensors be of relatively slow response, but they also can be of much lower precision. For CH_4 and N_2O , for instance, the precision required to estimate the flux within 10% is at least 100 times less than for conventional micrometeorological approaches. Put another way, for comparable sensor precision, chambers are 100 times more sensitive. (The advantage is not so large for measuring CO_2 assimilation by vegetation in chambers because of the need to prevent depletion of CO_2 in the chamber and the consequent need to ventilate rapidly.)

Table 1 suggests another advantage of chambers: they require small land areas for their deployment, and so permit detailed process studies and allow experiments with various land treatments on scales which cannot be contemplated with alternative micrometeorological approaches. Their disadvantages include the facts that they necessarily interfere with the microclimate, they sample only a small area of the surface, and the sampling periods are usually short, often less than 1 hour. Detailed discussions of these problems are given elsewhere, e.g. Wesely et al. (1989) and Denmead and Raupach (1992). There is a need to complement chamber measurements with methods which integrate over larger areas and longer time scales. Micrometeorological techniques are one such alternative and CBL budgets are another. They are discussed below.

3. Micrometeorological Methods Gradient Techniques

These are based on the proposition that in the unobstructed air layer above the surface of interest, gas transport occurs by a process of turbulent diffusion along the gradient of mean concentration. Practical applications of these and eddy correlation techniques are limited to situations in which the air has blown over a homogeneous exchange surface for a long distance so that equilibrium is established and the vertical flux density of the gas is constant with height in the air layers close to the ground. The depth of the air layer in which the flux is constant with height is between 1/100 and 1/200 of the fetch i.e. the distance the wind has travelled over the treated area. It is evident that experimental areas need to be hundreds of metres in extent.

Following Webb et al. (1980), we can write for the vertical flux density of the gas:

$$F_g = - \bar{\rho}_a K_g \partial \bar{s} / \partial z \quad (3)$$

where ρ_a is the density of dry air, K_g is an eddy diffusivity, $s (= \rho_g / \rho_a)$ is the mixing ratio of the gas with respect to dry air, z is height, and the overbar denotes a time average. The eddy diffusivity depends on wind speed, surface roughness, height above the surface, and atmospheric stability. It is usual to infer its value *in situ* from flux-gradient relationships like Eq. (3), written for some other tracer entity whose flux is known and whose concentration gradient is measured simultaneously. Heat, water vapour, and momentum are the tracers used most commonly. Appropriate procedures and formulations for these various approaches are contained in many publications, e.g. Denmead (1983).

Focussing on the gases of interest here, we note that gradient techniques were developed for measuring CO_2 fluxes more than thirty years ago and are now used commonly. With good technique, differences in atmospheric CO_2 concentration smaller than 0.1 ppmv can be detected by on-line infrared gas analysis, a resolution which is sufficient for most applications in agricultural and forest systems (Table 2). The situation

for N_2O and CH_4 is not as satisfactory because of sensor limitations. Table 2 shows that for the flux densities of N_2O common in agriculture and forestry, which are about four orders of magnitude less than for CO_2 , resolutions of hundredths of a ppb will be required to define the vertical profile of atmospheric N_2O concentration accurately. Such resolution appears to be still on the edge of what can be achieved with gas chromatography and beyond what can be accomplished with on-line infrared gas analysis. It appears, however, that this resolution might now be achieved with laser systems.

For CH_4 , we are aware of only one reported application of gradient methods in an agricultural system, a preliminary account by Denmead (1991) of measurements of emissions from a rice field, which employed on-line infrared gas analysis to measure the concentration gradient and measurements of the profile of horizontal wind speed to infer K_g . The approach is a feasible alternative to chambers, and refinements in technique promise to make it a very useful tool for making nondisturbing, continuous measurements of CH_4 emissions on horizontal scales of 100 m or more. As for N_2O , new laser systems appear to offer a more accurate measurement of the atmospheric CH_4 gradient.

Eddy Correlation

While often regarded as the best micrometeorological option because it is a direct measurement requiring few assumptions, eddy correlation has its own difficulties when applied to some trace gases. First, there is a need for a fast-response sensor (Table 1) so that the gas concentration of the transporting eddies can be sensed instantaneously. Other problems arise because of the need to apply corrections to the apparent eddy flux to account for density effects associated with simultaneous fluxes of heat and water vapour (Webb et al., 1980).

The instantaneous vertical flux density of a gas is simply the product of the vertical wind speed w and the gas density ρ_g . The mean flux density F_g is given by

$$F_g = \overline{w\rho_g} \quad (4)$$

where the bar denotes an average over an appropriate measuring period. Both w and ρ_g can be represented as sums of means, $\bar{w}$ and $\bar{\rho}_g$, and fluctuations about those means, w' and ρ'_g . Thus,

$$F_g = \bar{w} \bar{\rho}_g + \overline{w'\rho'_g} \quad (5)$$

As explained by Webb et al. (1980), the second term on the right is the apparent eddy flux usually measured by eddy correlation systems, while the first term, $\bar{w} \bar{\rho}_g$, is a correction to the apparent flux, which can be calculated from simultaneous measurements of the flux densities of heat H and water vapour E . For trace gases with small background concentrations and relatively large fluxes, such as ammonia, it is unimportant, but for all of CO_2 , CH_4 , and N_2O it will usually be very important. Wesely et al. (1989) tabulate typical magnitudes, based on published estimates of gas fluxes. For CO_2 , $\bar{w} \bar{\rho}_g$ is typically between 0.3 and 0.7 of the true flux, F_g . For CH_4 , it varies from 0.04 to 0.56 and for N_2O , from 0.25 to 10.5.

Webb et al. (1980) point out that if gas concentrations are measured relative to dry air and at a common temperature, no corrections for the density effects are necessary. Usually, this will not be entirely possible in eddy correlation systems, but pre-conditioning

the air streams to remove water vapour and attain constant temperature is almost always possible when fluxes are calculated by gradient methods. For a gas like N_2O where the corrections for eddy correlation can be very large, it may be preferable to use a gradient method as a matter of course, even though the sensor has a fast response.

Finally, we note that the situation regarding gas sensors is the same for eddy correlation as for gradient methods: the precision required is about the same, and while adequate fast-response sensors for CO_2 are available commercially (both open- and closed-path), fast-response sensors for N_2O and CH_4 are still expensive and under development.

Eddy Accumulation

The technique has been described by a number of workers, e.g. Desjardins et al. (1984). Theoretical and practical difficulties exist, but these are being overcome and it seems likely that eddy accumulation or a variant, conditional sampling (Businger and Oncley, 1990), will eventually be used widely for measuring trace gas fluxes. Instead of a fast-response sensor, these techniques use fast sampling. Air associated with updrafts and downdrafts is sampled into each of two bins at a rate proportional to the vertical velocity. Slow-response, but high-resolution sensors can then be used to measure the mean concentrations of the gas in the "up" and "down" bins at the end of a sampling period. (In connection with Table 1, it should be noted that a response time of about 0.1 s is still required for sensing the vertical wind speed.) The resolution required in measuring gas concentrations will be much the same as for eddy correlation or gradient methods, but the measuring instrument can be remote and operated under ideal laboratory conditions. The system has another advantage over *in situ* eddy correlation: the air samples can be pre-conditioned to avoid the corrections associated with heat and water vapour fluxes.

Mass Balance

When discussing chambers, we pointed to the very large spatial and temporal variability usually found in gas fluxes from soils and suggested that there was a need for non-disturbing techniques that integrate over larger space and time scales than is possible with chambers. Wilson et al. (1982) and Denmead (1983) describe a small-plot, micrometeorological, mass balance technique which meets these criteria, but does not require the large fetches needed for gradient and eddy correlation approaches. Plot dimensions are typically tens of meters instead of the hundreds of meters required for the last. As well, the instrumentation requirements can be quite simple, particularly when trapping techniques can be used to concentrate the gas, as for N_2O which can be trapped on molecular sieve.

The method equates the flux of gas into the atmosphere from a treated area of limited upwind extent with the rate at which it is transported by the wind across the downwind edge. The conservation of mass gives:

$$F_g = \frac{1}{X} \int_0^Z \overline{u(\rho_g - \rho_b)} dz \quad (6)$$

where X is the upwind fetch, Z is the height of the air layer substantially affected by the emission (about $1/10 X$), and, as before, ρ_b is the upwind, background concentration. Here, the aim is to measure gas concentration profiles right through the boundary layer developed over the plot rather than just in the much smaller, equilibrium layer close to the surface. Unlike the micrometeorological methods described so far, this technique is most

successful when the fetch is small so that Z is also conveniently small. When X is 10 to 20 m, Z is around 1 to 2 m, its actual magnitude depending on fetch, surface roughness and atmospheric stability.

A difficulty is that the fetch X must be known precisely in order to calculate F_g . As discussed by Wilson et al. (1982) and Denmead (1983), this complication can be overcome by working with a circular plot and measuring $\bar{u}$ and $\bar{\rho}_g$ at its centre. Regardless of compass direction, the wind will always blow towards the centre, and X will always be equal to the plot radius.

Apart from its suitability for small plots, this method has some distinct advantages over the equilibrium methods discussed previously. It has a simple theoretical basis, requires no special form for the wind profile, and the instrumentation is relatively simple. It needs neither to be of exceptionally fast response nor to have high precision. Jarvis (1990) describes an application to measurements of N_2O emissions from grassland soils.

4. CBL Budget Methods

By day over land, when surface heating generates buoyant convection, the planetary boundary layer consists typically of a progressively deepening layer of strong convective turbulence, often more than 1 km deep by evening, known as the convective boundary layer, CBL. The turbulence mixes the bulk of the CBL very efficiently, producing uniform average (potential) temperatures and concentrations of other scalar entities such as water vapour and trace gases except in a thin surface layer, a few tens of meters deep. The CBL is bounded above by a sharp, capping inversion. The capping inversion height, and hence the CBL depth, increases during the day because of the warming of the entire CBL by daytime solar radiation. This deepening is associated with entrainment of the overlying atmosphere into the CBL.

There are substantial diurnal fluctuations in the concentrations of greenhouse gases near the surface of the earth over land. During the night, CO_2 concentrations build up to large values, typically 100 ppm above the ambient (large-scale average) concentration, because respired CO_2 is trapped in the shallow, stably-stratified, nocturnal boundary layer. By day, photosynthesis by the vegetated surface causes a CO_2 "drawdown", typically 20 to 40 ppm. Diurnal variations in the concentrations of other trace gases are not so well documented, but Denmead and Raupach (1992) report a distinct diurnal cycle in the ambient N_2O concentration after widespread rain, and Wofsy et al. (1988) show clear diurnal variation in ambient CH_4 concentrations above an Amazonian forest.

Here we sketch how measurements of diurnal concentration variations can be used to infer trace gas fluxes at the surface of the earth on a regional scale (100 to 1000 km²). This is a budget method for flux measurement which amounts to using the CBL as a large "natural chamber". Its bulk properties are independent of small-scale surface heterogeneities, so it acts as a natural integrator of surface fluxes over heterogeneous terrain (Raupach et al., 1992). The distance over which the CBL carries some "memory" of conditions upwind, its "footprint", is typically 5 to 30 km.

Following Raupach et al. (1992), the conservation equation for scalars in the CBL can be written in simplified form as

$$\frac{dC}{dt} = \frac{F_c}{h} + \frac{C_s - C}{h} \frac{dh}{dt} \quad (7)$$

where C is the mean scalar concentration in the CBL, t is time, h is the CBL depth, and

C_+ is the value of C just above h . The first term on the right hand side of (7) accounts for the change in C due to the surface flux, and the second for the change due to entrainment (or encroachment) of air at the top of the CBL. Rearranging Eq. (7) leads to an expression for the regional flux:

$$F_c = h \frac{dC}{dt} - (C_+ - C) \frac{dh}{dt} . \quad (8)$$

Raupach et al. (1992) refer to the evaluation of F_c through Eq. (8) as the "differential" CBL budget method. It requires detailed knowledge of changes in the gas concentration and the height of the CBL.

With some simplifying assumptions, Raupach et al. (1992) also derive an integrated form of Eq. (8), which allows direct calculation of the total gas flux over periods of several hours, viz.,

$$I_g(t) = - h(t)(C_+ - C(t)) \quad (9)$$

where I_g is the cumulative gas flux over time t . The only data required are the height of the CBL and the gas concentration within it after time t . Further, it can be seen from Table 2 that for this technique, C need not be known as precisely as for conventional, micrometeorological approaches; a precision 5 to 10 times less is adequate.

To explore the utility of these approaches, regional fluxes of CO_2 , CH_4 and N_2O have been estimated from observations of the diurnal variation in their near-surface concentrations, and calculations or measurements of h and dh/dt . In the calculations C_+ was chosen to be the free-atmosphere base-line values for CO_2 , CH_4 , and N_2O at the times of observation. In each case, the estimated regional fluxes are compared with locally measured fluxes.

CO_2

The observations were made in an investigation of the CO_2 flux over a wheat crop at Wagga Wagga, NSW in the spring of 1991. The free atmosphere CO_2 concentration was 353 ppmv. Details of the local flux measurements and calculations of the regional flux by both Eq. (8) and Eq. (9) are given in Raupach et al. (1992). The fluxes from the CBL budget methods were mostly smaller than those measured over the wheat crop (by 30% on average), but that was expected, because the crop was dense and high yielding. Given the simplifying assumptions made in the analysis, the agreement is very encouraging.

CH_4

Our example is based on the excellent observations of Wofsy et al. (1988) for the Amazon Basin. Application of Eq. (9) to their data gives a mean daytime F_{CH_4} of $1.5 \mu\text{g m}^{-2} \text{s}^{-1}$. This is near the average of values given by Bartlett et al. (1988) for various communities in the Amazon Basin (flooded forests, $2.2 \mu\text{g m}^{-2} \text{s}^{-1}$; floating grass mats, $2.8 \mu\text{g m}^{-2} \text{s}^{-1}$; open water lakes, $0.3 \mu\text{g m}^{-2} \text{s}^{-1}$), although about ten times larger than their estimate for the average CH_4 emission over the whole of the Amazon drainage area, which encompasses $7 \times 10^6 \text{ km}^2$.

N_2O

The observations were made over grassland at Canberra. The local flux

measurements, were made with open chamber systems. The corresponding atmospheric N₂O concentrations, were measured at 1.5 m above the grass surface by continuous infrared gas analysis. The surrounding countryside is predominantly grazed pasture. Details of the analysis are given in Denmead and Raupach (1992). Using the differential form of the CBL budget, Eq. (8), they estimated the average regional flux of N₂O from 0700 to 1030 to be 140 ng m⁻² s⁻¹. The chamber measurements gave an average local N₂O flux of 37 ng m⁻² s⁻¹, 26% of the regional estimate. Allowing for the crudeness of the assumptions and the large spatial variability of soil fluxes, the fact that the regional estimates and the spot measurements are of the same order of magnitude is encouraging.

It is evident that CBL budget methods hold much promise. In its simplest form, the general CBL approach appears to offer a very useful survey tool, giving order of magnitude estimates. The indications from Raupach et al. (1992) are that at best, the method could be a practical way to obtain detailed hour by hour information on regional trace gas fluxes over long time periods. Validation with aircraft data is highly desirable.

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Table 1. Characteristics of various methods for measuring trace gas fluxes

Method	Footprint	Required instrument response time
Chamber	1m ²	100s
Mass balance	1,000m ²	100s
Gradients	10ha	100s
Eddy accumulation	10ha	100s
Eddy correlation	10ha	0.1s
Convective boundary layer	100km ²	100s

Table 2. Sensor precision required for measuring fluxes to within 10%

Gas	Surface	Typical flux	Method	Required precision	Reference
CO ₂		kg m ⁻² s ⁻¹		ppb	
	Forest	10 ⁻⁶	Open chamber	150	Denmead et al. (1993)
	Forest	10 ⁻⁶	Micrometeorology	30	Denmead et al. (1993)
	Wheat	10 ⁻⁶	Micrometeorology	300	Raupach et al. (1992)
CH ₄	Wheat	10 ⁻⁶	CBL	3000	Raupach et al. (1992)
	Rice field	10 ⁻⁹	Closed chamber	200	Seiler et al. (1984)
	Rice field	10 ⁻⁹	Micrometeorology	2	Denmead (1991)
	Rice field	10 ⁻⁹	CBL	10	Raupach et al. (1992)
N ₂ O	Soil	2 x 10 ⁻¹⁰	Closed chamber	80	Matthias et al. (1980)
	Grassland	3 x 10 ⁻¹¹	Open Chamber	3	Denmead et al. (1979)
	Grassland	3 x 10 ⁻¹¹	Micrometeorology	0.02	Denmead (1979)
	Grassland	3 x 10 ⁻¹¹	CBL	0.1	Denmead and Raupach (1992)