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MEASURING BIOSPHERE–ATMOSPHERE EXCHANGES OF BIOLOGICALLY RELATED GASES WITH MICROMETEOROLOGICAL METHODS

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ABSTRACT

Ecologists are expected to play an important role in future studies of the biosphere/atmosphere exchange of materials associated with the major biogeochemical cycles and climate. Most studies of material exchange reported in the ecological literature have relied on chamber techniques. Micrometeorological techniques provide an alternative means of measuring these exchange rates and are expected to be used more often in future ecological studies, since they have many advantages over the chamber techniques. In this article we will provide an overview of micrometeorological theory and the different micrometeorological techniques available to make flux measurements.

Key words: gas exchange; micrometeorology.

INTRODUCTION

Anthropogenic emissions of pollutant gases are feared to be modifying the major biogeochemical cycles (e.g., Likens et al. 1981) and climate (e.g., Ramanathan et al. 1985). The discipline of ecology forms the intersection of the biological, physical, and chemical processes that operate in the biosphere. It is anticipated that ecologists will play a greater role in evaluating the impact of man on his environment (see Mooney et al. 1987) through their studies of the biosphere/atmosphere exchange of materials associated with the major biogeochemical cycles and climate.

Most studies of biosphere/atmosphere exchange in the ecological literature have relied on chamber techniques or cuvettes (e.g., Edwards and Sollins 1973, da Costa et al. 1986, Keller et al. 1986). These methods are inherently limited since they alter the local environment about the subject under study, thus making it unrepresentative of its population. Due to logistical problems, it is often difficult to employ chambers for long-term, continuous measurements or to deploy enough chamber replicates to obtain statistically reliable results.

Micrometeorological techniques provide an alternative means for measuring exchanges of chemicals between the biosphere and the atmosphere. Micrometeorological techniques have many advantages. First, they are in situ and do not disturb the environment around the plant canopy. Second, these techniques allow continuous measurements. And third, time-averaged micrometeorological measurements at a point provide an area-integrated, ensemble average of the exchange rates between the surface and the atmosphere.

Relatively few studies in the ecological literature have employed micrometeorological techniques to examine mass exchanges between ecological communities and the atmosphere (e.g., Coyne and Kelly 1975, Allen and Lemon 1976, Jarvis et al. 1976, Houghton and Woodwell 1980, Baldocchi et al. 1987*a*). Yet we foresee increased use of these techniques by the ecological community due to their advantages and due to advances in instrumentation and data acquisition systems. It is therefore important to communicate to this scientific community the underlying theory, strengths and limitations of micrometeorological methods. In this special feature we present an overview of micrometeorological techniques used to measure canopy–atmosphere gas exchange.

MICROMETEOROLOGICAL THEORY

The conservation equation provides the basic framework for measuring and interpreting micrometeorological flux measurements. In concept, the conservation equation states that the time rate of change of the mean mixing ratio (concentration) of a chemical constituent at a fixed point in space (I) is balanced by the mean horizontal and vertical advection (II), by the mean horizontal and vertical divergence or convergence of the turbulent flux (III), by molecular diffusion (D), and by any source or sink (S). The conservation equation is expressed as:

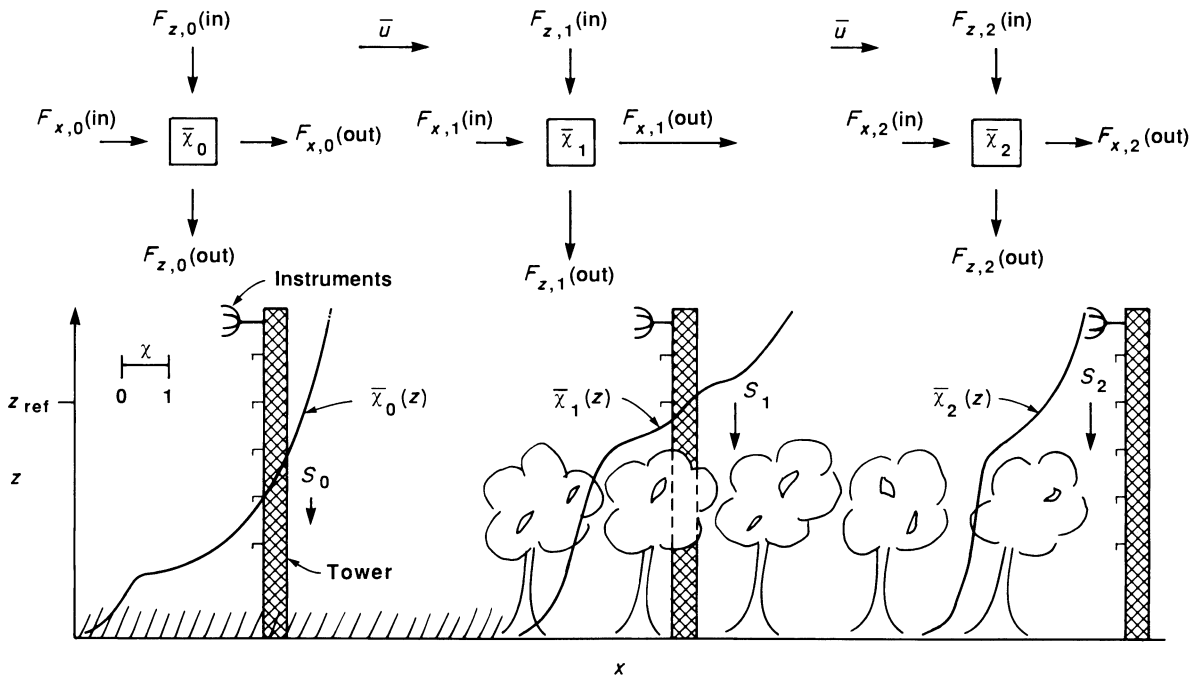

FIG. 1. A schematic description of the continuity equation, as viewed when a parcel of air flows from a well-developed boundary layer over a short, smooth, vegetation surface to the boundary layer over a tall, rough vegetation surface. The balance of fluxes (F) entering and leaving a controlled volume are denoted for three locations (subscripts 0, 1, and 2) and in the vertical (z) and horizontal directions (x). The lengths of the vectors entering and leaving the controlled volume denote the relative magnitudes of the fluxes and wind speed, u. At locations 0 and 2 the surface boundary layer is in relative equilibrium with the underlying surface. Therefore fluxes entering and leaving the controlled volume are in balance. At the transition to the new surface (location 1), the aerodynamic roughness and sink strength (S) of the underlying surface change. This alters the mixing ratio (concentration) χ at the reference height (z_{ref}) from that upwind and results in a horizontal gradient in χ, advection, and flux divergence.

$$\underbrace{\partial\bar{\chi}/\partial t}_{\text{(I)}} = \underbrace{-\bar{u}\,\partial\bar{\chi}/\partial x - \bar{v}\,\partial\bar{\chi}/\partial y - \bar{w}\,\partial\bar{\chi}/\partial z}_{\text{(II)}} \underbrace{- \partial\overline{u'\chi'}/\partial x - \partial\overline{v'\chi'}/\partial y - \partial\overline{w'\chi'}/\partial z}_{\text{(III)}} + D + S, \quad (1)$$

where χ is the mixing ratio of a chemical constituent (mass of constituent per unit mass of dry air) and u, v, and w are the streamwise, lateral, and vertical wind velocity components, respectively, that operate in the respective longitudinal (x), lateral (y), and vertical (z) directions. The mean covariances between wind velocity components and χ represent turbulent fluxes. D is molecular diffusion and S is a source/sink term. Overbars denote time averaging and primes (′) denote fluctuations from the mean. We base this expression in terms of the mixing ratio instead of absolute density, since the former is a conserved quantity whereas the latter varies with pressure and temperature.

It is appropriate to explain the terms used in Eq. 1 with the aid of a schematic (Fig. 1). The mixing ratio in a controlled volume will remain unchanged if the flux of material entering it equals that leaving it. On the other hand, the occurrence of advection and flux divergence will act to alter the mixing ratio in a controlled volume. Advection is defined as the mean transport of an atmospheric property by the mean motion of the atmosphere, and occurs when the spatial gradient of χ is nonzero and is transported along the mean wind. Flux convergence occurs when material is accumulating in a controlled volume because the flux entering the volume is greater than that leaving it; flux divergence represents the opposite situation. Molecular diffusion results from the motion of molecules due to random thermal motion; in the atmosphere this term is usually negligible in comparison to turbulent transfer. The source/sink term represents the net rate that the material of interest is being created or destroyed per unit volume. The rate of photosynthesis and respiration per unit volume of leaf area are examples of a sink and source for CO_2, respectively. For other discussions of the conservation equations, as related to micrometeorological measurements, the reader is referred to the work of Kanemasu et al. (1979) and Businger (1986).

Ideal conditions require that the surface is horizontally uniform and level (resulting in no advective effects), no sources or sinks exist in the atmosphere above the surface, and the concentration of the constituent does not vary significantly with time. With these assumptions, Eq. 1 reduces to:

$$\partial\overline{w'\chi'}(z)/\partial z = D = -\nu\,\partial^2\bar{\chi}(z)/\partial z^2, \quad (2)$$

where ν is molecular diffusivity. Since molecular diffusion in the surface boundary layer is negligible in comparison to the turbulent flux, integration of Eq. 2 with respect to height, z, yields:

$$\overline{w'\chi'}(z) = F = -\nu\,\partial\bar{\chi}(0)/\partial z. \quad (3)$$

Eq. 3 implies that the mean vertical turbulent covariance (F) is constant with height in a well-adjusted, internal boundary layer (the layer of air that is adjacent to and affected by the underlying surface) and equals the molecular, gradient-diffusion flux at the surface.

From Eq. 3, the mean vertical turbulent flux of material over a horizontally homogeneous surface under steady-state conditions is:

$$F = -\,\overline{\rho_a}\;\overline{w'\chi'}, \quad (4)$$

where ρ_a is the density of dry air. This flux is directed downward when $F < 0$ and is directed upward when F is positive.

Why does the turbulent covariance in Eq. 4 equal the mean vertical turbulent flux of material? The instantaneous amount of material passing through a horizontal plane of unit area per unit time is equal to $\rho_a w\chi$. Since the atmosphere is turbulent we must form a temporal average of this instantaneous product in order to estimate the mean transfer of material. This mean product is computed from the decomposed forms of the instantaneous values of ρ_a, w, and χ, which are each the sum of the mean and fluctuating components.

$$\begin{aligned}\overline{(\bar{\rho}_a + \rho_a')(\bar{w} + w')(\bar{\chi} + \chi')} = {} & \bar{\rho}_a\bar{w}\bar{\chi} + \overline{\rho_a w\chi'} + \overline{\rho_a w'\chi} \\ & + \overline{\rho_a w'\chi'} + \overline{\rho_a' w\chi} \\ & + \overline{\rho_a' w\chi'} + \overline{w'\rho_a'}\,\bar{\chi} \\ & + \overline{\rho_a' w'\chi'}. \end{aligned} \quad (5)$$

According to Reynolds' averaging procedures, the average of fluctuations about a mean and the mean vertical velocity over a horizontal, homogeneous extended surface are zero. Furthermore, the mean turbulent flux of dry air ($\overline{w'\rho_a'}$) and $\overline{\rho_a' w'\chi'}$ are zero. Applying these averaging criteria to Eq. 5 ultimately yields Eq. 4.

Measurement criteria

The natural environment is rarely ideal. Geophysical variability restricts the level of accuracy with which one can measure a turbulent flux to ≈10–20% (see Wesely and Hart 1985) under the best of conditions. And the spatial variability of underlying vegetation is at best on the order of 10–20%. Consequently, considerable error must be accepted during field measurements of surface exchanges.

The degree to which one can deviate from the assumptions of steady-state conditions and horizontal homogeneity and still make reasonable flux measurements can be investigated by examination of the conservation equation. First, let us define the limits about which ambient conditions can vary from ideal steady-state conditions. Under nonsteady state but horizontally homogeneous conditions, Eq. 1 reduces to:

$$\partial\bar{\chi}/\partial t = \partial F/\partial z. \quad (6)$$

Eq. 6 can be modified to express the temporal change in χ that occurs with a relative variation in F:

$$\Delta\chi/\Delta t = F\,\Delta F/(F\,\Delta z). \quad (7)$$

As an example we examine the acceptable temporal variability associated with a flux measurement of CO_2 in air. If we assume that the acceptable relative error in F (i.e., $\Delta F/F$) due to flux divergence is 10%, the sampling period (Δt) is 30 min, Δz is 3 m, and F is 1.00 mg·g^{-1}ms^{-1}, a typical midday value for CO_2 exchange of a vegetated canopy (Baldocchi et al. 1987*a*), the resulting tolerable temporal variation in $\chi(\Delta\chi/\Delta t)$ is ≈ 33 μg·g^{-1}·s^{-1}. Assuming that the ambient CO_2 mixing ratio in air is ≈ 524 mg/g, a 10% relative error in the flux estimate of CO_2 results from an 11% temporal variation in CO_2 mixing ratio over one-half hour. During daytime periods the CO_2 mixing ratio rarely varies by this much. However, larger changes in CO_2 may occur at dusk and dawn (Brown and Rosenberg 1970) and make flux measurements during these periods unreliable.

Advective effects are manifested when the internal boundary layer has not fully adjusted. Readjustment of the internal boundary layer occurs when two adjacent fields differ in aerodynamic roughness or in rates of surface exchanges (see Fig. 1), e.g., an actively transpiring alfalfa field next to desert vegetation, or a lake adjacent to a forest. As a rule of thumb, 100 m of fetch is needed to readjust the internal boundary layer for each 1 m above the effective surface (Monteith 1973, Businger 1986). A simple technique derived by Gash (1986) shows that the effective fetch for a 90% adjustment of the internal boundary layer in neutral stability can be computed as:

$$x_f = \frac{z[\ln(z/z_0) - 1 + z_0/z]}{k^2\ln(0.90)}, \quad (8)$$

where z_0 is the roughness length (defined as $\approx$ 10% of the canopy height), z is the measurement height, and k is von Karman's constant (0.4). Estimates based on Eq. 8 agree to within 20% of estimates derived from a more complex model developed by Dyer (1963). The actual estimate of the fetch-to-height ratio is more complex, being influenced by atmospheric stability and surface roughness; a transition from a rough to smooth surface requires a greater fetch-to-height ratio than does the reverse.

Complex terrain and sloping hills can cause a divergence or convergence of the streamlines of air flow over the surface and flow separation in the lee of a hill, negating the validity of the one-dimensional framework used to measure turbulent fluxes (see Finnigan 1983). A more complex experimental design than the one-dimensional framework discussed above is required to make flux measurements in such situations.

When measuring fluxes over tall, rough canopies, the concept of a constant flux layer for scalar quantities becomes unreliable as one approaches the top of the canopy (Garratt 1978, 1980, Raupach et al. 1980, Raupach and Legg 1984). This is because considerable wake turbulence is generated by the interaction between the turbulence and the tree crowns. Flux measurements should therefore be made above the zone affected by these obstruction-generated, turbulent eddies. From wind tunnel studies, Raupach et al. (1980) found that the height of the zone affected by turbulent wakes over a uniform, artificial canopy is about $h + 1.5L_t$, where h is canopy height and L_t is the transverse element length scale, which is typically on the order of a tree crown width for a closed forest canopy. Under more extreme conditions, Garratt (1978) shows that flux measurements over widely scattered trees in a savannah must be made at a height 3-4 times the height of the trees to avoid wake effects.

When measuring the exchange rates of chemical compounds, rapid reactions among other reactive species may occur between the point of measurement and the surface (Lenschow 1982, Fitzjarrald and Lenschow 1983), causing chemical disequilibria among the reactant chemical constituents and introducing a source/sink term into Eq. 1. Such chemical effects are important if the time scales of the chemical reactions are comparable to or less than the time scales associated with turbulent mixing. Consequently, fluxes of the primary constituent and the other reacting compounds at two levels, as well as the uptake of the chemical of interest, must be measured to account for flux divergence caused by the chemical reactions (Fitzjarrald and Lenschow 1983). The photochemical triad, O_3-NO-NO_2, is an example of a case where photochemistry affects the source/sink term of the conservation equation.

Measurement corrections

The assumption of horizontal homogeneity causes the mean vertical velocity, $\bar{w}$, to equal zero. Over uniform surfaces with active exchanges of heat and water vapor, this assumption is not always true. The exchanges of these entities lead to fluctuations in the density in dry air, which introduces a small but significantly nonzero mean vertical velocity (Webb et al. 1980). Ignoring this effect can result in a substantial error in the in situ flux measurement of many trace species, unless these entities are measured as mixing ratios or the air sample is dried and brought to a common temperature. Following Webb et al. (1980), the corrected vertical turbulent flux (F_c), when measured in terms of concentrations (c), is:

$$F_c = \overline{w'c'} + 1.61(\bar{c}/\bar{\rho}_a)\, E + (1 + 1.61\bar{q})H\bar{c}/(\bar{\rho}_a C_p \bar{T}_k), \quad (9)$$

where E is the mass flux of water vapor, H is sensible heat flux, C_p is the specific heat of air, q is the specific humidity, and T_k is the absolute temperature. To account for the effects of density fluctuations, any experiment measuring the exchange of a trace species must include measurements of the water vapor and sensible heat flux. Density fluctuations can cause errors as large as 40% in the measurement of CO_2 exchange (Leuning et al. 1982). These corrections are not needed for sensible heat flux (Webb et al. 1980) and are generally small for water vapor and for constituents relatively low in concentration such as SO_2 (see Matt et al. 1987).

Under certain circumstances, modifications in the application of the Webb et al. (1980) corrections need to be made. In some experiments air is drawn through a long sample line and brought to a chemical analyzer. Under these conditions, temperature fluctuations are dampened and the correction for heat flux need not be applied. Similarly, measurement of some constituents requires that the air sample be introduced to a flame, and the correction of flux covariance for heat flux does not apply.

Micrometeorological Measurement Techniques

Eddy correlation method

Evaluation of Eq. 4 forms the basis of the eddy correlation method. Although this equation seems simple, pitfalls associated with sensor time response, the separation distance between sensors, the measurement height above the surface, the length of the sampling period, sensor tilt and orientation, sensor noise, and sampling rates must be avoided in order to measure the vertical turbulent flux correctly. Treatment of these problems is discussed below.

To eliminate the need to store large quantities of

instantaneous data, digital low-pass recursive filters can be used to compute a real-time running mean and thus turbulent fluctuations and covariances (Lloyd et al. 1984). This concept is based on an analog approach introduced by Dyer et al. (1967). The real-time running mean is computed as:

$$\bar{c}_i = \alpha \bar{c}_{i-1} + (1 - \alpha)c, \tag{10}$$

where $\bar{c}_i$ and $\bar{c}_{i-1}$ are the new and old running means and c is the new instantaneous value. The constant, α, is computed as:

$$\alpha = \exp(-\Delta t/\Gamma), \tag{11}$$

where Δt is the time interval between samples and Γ is a time constant.

There is no prescribed value for the time constant Γ. The original analog application of the filtering technique relied on an RC (resistance-capacitance) filter with a 100-s time constant (Dyer et al. 1967). Longer time constants (400–1000 s) have gained favor in recent years (Lloyd et al. 1984, Shuttleworth et al. 1984, Verma et al. 1986). For example, Shuttleworth et al. (1984) report that time constants on the order of 300 s result in reduced flux estimates, compared with a 1000-s time constant. On the other hand, it can be argued that these long time constants (1000 s) may be excessive and impractical, since a long time is needed to initiate the filter. Eq. 11 represents a low-pass filter, and spectral studies show that eddies with periods on the order of 100 s contribute significantly to the variance of scalars and vertical velocity fluctuations (Kaimal et al. 1972). Thus, running means computed with exceedingly long time constants may not reflect all of the important turbulent events that contribute to the expected mean. Furthermore, Dyer et al. (1970) show that little improvement occurs in the computation of $\overline{u'w'}$ by increasing the filter time constant from 100 to 1000 s. We conclude that it is more important to specify an optimal value for the ratio $\Delta t/\Gamma$, than a specific Γ value.

It is often impossible to orient the vertical velocity sensor so that the mean velocity is nearly zero, or find a perfectly flat experimental site. The influence of sensor tilt or terrain irregularities can contaminate the computation of the flux covariance by causing an apparent mean vertical velocity (Kaimal and Haugen 1969, Hyson et al. 1977, Dyer 1981). If one is measuring fluxes with the eddy correlation technique in gently sloping terrain, it is often adequate to rotate the coordinate system of the three wind velocity components, making the vertical and lateral velocity components equal to zero, and proceed with computing the turbulent flux perpendicular to the streamlines (Hyson et al. 1977). As a rule of thumb, it is assumed that reliable turbulent flux measurements can be made, after appropriate coordinate rotation, when the slope of the terrain is $< \approx 8$–15%. This scheme is not valid when flow separation on the lee side of a hill occurs; the critical slope for flow separation is $\approx 20°$ (Taylor et al. 1987), but varies with properties such as surface roughness. Dyer (1981) reports that the tilt error in tangential momentum stress, $\overline{u'w'}$, is $\approx 14\%$ per degree of tilt. Tilt error for scalar flux covariances is smaller, $\approx 3\%$ per degree of tilt.

We recommend that the three wind velocity components be measured with a three-dimensional anemometer when using the eddy correlation technique, so that tilt or terrain effects can be corrected through coordinate rotation computations. Generally it is adequate to perform only a two-dimensional rotation. The first rotation is about the z axis and aligns u into the x direction on the x-y plane. The second rotation is about the x axis and aligns w into the z direction, yielding w and $v = 0$. The turbulence flux covariance, rotated about two axes, can be computed as:

$$\overline{w'c'} = \overline{w'c'}_i \cos\theta - \overline{u'c'}_i \sin\theta \cos\Sigma - \overline{v'c'}_i \sin\theta \sin\Sigma, \tag{12}$$

where $\overline{w'c'}_i$, $\overline{u'c'}_i$ and $\overline{v'c'}_i$ are flux covariances computed in the original coordinate system of the anemometer. The cosines and sines are computed in terms of the original measurements of u, v, and w:

$$\cos\theta = (\bar{u}^2 + \bar{v}^2)^{0.5}/(\bar{u}^2 + \bar{v}^2 + \bar{w}^2)^{0.5}$$
$$\sin\theta = \bar{w}/(\bar{u}^2 + \bar{v}^2 + \bar{w}^2)^{0.5}$$
$$\cos\Sigma = \bar{u}/(\bar{u}^2 + \bar{v}^2)^{0.5}$$
$$\sin\Sigma = \bar{v}/(\bar{u}^2 + \bar{v}^2)^{0.5}.$$

Under more complex situations the products $\overline{u'v'}$ and $\overline{v'w'}$ are nonzero. Consequently, a third rotation must be introduced about the z-y plane, making $\overline{v'w'} = 0$ (see Wesely 1970).

Additional errors in measuring turbulence velocities and momentum stress can be introduced by flow distortion by the instrumentation and supporting structure. An analysis by Wyngaard (1981) shows that coordinate rotations do not account for the effects of flow distortion created by the instrumentation, which contrasts the arguments of Dyer (1981). In a more recent analysis, Wyngaard (1988) states that flow distortion effects can be minimized through designing a sensor array that is vertically symmetrical.

When conducting an experiment with the eddy correlation technique, the length of the sampling period must be carefully chosen to ensure that the sampling period accounts for the spectrum of eddies that contribute to the transfer processes. The sampling duration for measuring turbulent statistics in geophysical flow depends on the statistical moment being measured (Lumley and Panofsky 1964). The sampling duration

for the measurement of the $\overline{w'c'}$ covariance in near-neutral conditions can be approximated as:

$$T = 200(z - d)/(a^2u), \quad (13)$$

where a is the desired accuracy of the measurement and d is the zero plane displacement, which is on the order of 60 - 80% of canopy height. Assuming a measurement height ($z - d$) of 3 m and a wind speed (u) of 3 m/s yields $T = 2000$ s or 33 min when the sampling error of the measurement is 10%. Although longer sampling periods (>2 h) are desired from sampling theory, they can introduce dynamic effects due to the diurnal variation in solar radiation and the biological source or sink; thus, excessively long sampling periods should not be used.

To ensure that the highest frequency eddies, which contribute to the turbulent flux, are being detected, the appropriate frequency response of the instrument and its sampling rate need to be determined. Cospectra for CO_2, water vapor, and sensible heat exchange over a deciduous forest (Anderson et al. 1986) show that the nondimensional, cutoff frequency for the exchange of these scalars ($f_c = n_c(z - d)/u$) is on the order of $\approx$5–10, where n_c is the natural cutoff frequency. The time constant of an instrument should, therefore, be less than: $(z - d)/(f_c u)$. The sensor should be able to respond to eddies as small as $(z - d)/(2\pi f_c)$; a factor of 2π is introduced to avoid spectral attenuation due to spatial sampling (Kaimal 1975, Businger 1986). On the other hand, given an instrument with a known frequency response, one can invert the relationship of the desired instrument response and compute the height at which to place the instruments for given wind speed regimes. Higher frequencies are associated with turbulence measured during nocturnal, stable conditions, and proper adjustments should be made in instrument placement and design.

It is not always possible to obtain or manufacture an instrument with ideal spectral response characteristics for the conditions in which it is to be used. Imperfections in the spectral response of instruments and spectral attenuation caused by the finite path length of the instrument can be compensated for by introducing spectral transfer functions (Hicks 1972, Businger 1986, Moore 1986). However, with proper experimental design, the error attributed to these problems is often < 10% and these corrections can be ignored.

Modern computerized data acquisition systems require that the electronic analog signal be digitized. Digitizing an analog signal at discrete intervals introduces a problem called aliasing (see Hamming 1983). Aliasing occurs when a high-frequency signal appears as a lower frequency signal, since harmonic components of the high-frequency signal are folded back onto lower frequency signals; the reverse rotation of wagon wheels on forward moving wagons in Western movies is attributed to aliasing. Aliasing results in spurious energy or power being attributed to lower frequency eddies. In order to minimize aliasing, the sampling rate should be at least 2–3 times the highest frequency of interest. Further reduction in aliasing can be attained by additional filtering of the analog signal with an electronic low-pass filter whose cutoff frequency is equal to the highest frequency of interest.

Many instruments used to measure eddy fluxes of trace gases have relatively small signal-to-noise ratios. Noisy instruments distort the power spectra and cospectra and increase the run-to-run variability of turbulent flux measurements (Wesely and Hart 1985). Consequently, flux measurements from individual experimental runs, obtained with noisy instruments, often are not precise. Wesely and Hart (1985) recommend averaging data from many sampling periods to obtain a reliable flux estimate with a noisy instrument.

Field installation of an array of instrumentation introduces problems associated with lateral and longitudinal separation of the instruments. The desired separation distance between two sensors should be less than the length scale of the smallest eddy to be detected, because the signals of two sensors become increasingly uncorrelated with increasing separation distance. Kristensen and Fitzjarrald (1984) recommend that the separation between two sensors be $< \approx (z - d)/5$. Transfer functions correcting for lateral and longitudinal separation can also be applied to compensate for this effect (Hicks 1972, Moore 1986).

Flux-gradient theory

Flux-gradient theory assumes that turbulent transfer is analogous to molecular diffusion; the turbulent flux is proportional to the product of the mean vertical mixing ratio gradient and an eddy diffusivity (K): $F = -K(z)\, d\bar{\chi}/dz$. Gradient techniques are attractive for measuring fluxes of trace species for which no fast response chemical instrumentation is available. However, flux-gradient techniques should not be used to measure fluxes inside plant canopies because countergradient transport occurs, which violate the assumptions on which this technique is based.

Two of the more popular techniques for computing eddy exchange coefficients are the aerodynamic method and the Bowen-ratio, energy-balance technique (see Kanemasu et al. 1979). The aerodynamic method is based on the momentum flux equation and the wind speed gradient relationship. The exchange coefficient for momentum transfer (K_m) is computed as:

$$K_m = k^2(z - d)^2\, du/dz\, \Phi_m^{-2}, \quad (14)$$

where Φ_m is the dimensionless wind shear function and is a function of atmospheric stability. Several empirical

relationships describing the dependence of Φ_m on atmospheric stability are available in the literature. Most notable are those of Dyer and Hicks (1970), Webb (1970), Businger et al. (1971), and Pruitt et al. (1973).

The Reynold's analogy assumes that the eddy exchange coefficient for momentum transfer is equal to those for heat and mass exchange. Many boundary layer studies in the early 1970s found this not to be the case (Dyer and Hicks 1970, Businger et al. 1971, Pruitt et al. 1973). Relationships correcting for the differences between K_m and K_c must also be applied when using the aerodynamic method to compute exchange rates of mass and energy.

Typical errors associated with the aerodynamic method range between 10 and 30% (Verma and Rosenberg 1975). These errors are associated with uncertainties in the empirical stability formulae and are greatest during periods with low wind speeds.

The energy balance method is based on the energy balance relationship over a surface:

$$R_n = H + LE + S + G + P_s \qquad (15)$$

where R_n is net radiation, LE is latent heat flux, S is soil heat flux, G is the canopy heat storage term, and P_s is the energy consumed via photosynthesis. Assuming that the K's for mass and energy are equal, Eq. 15 becomes:

$$K = -\frac{(R_n - S - G)}{\rho_a(C_p\,\partial T/\partial z + L\,\partial v/\partial z + \psi\,\partial C/\partial z)}, \qquad (16)$$

where v and C are the mixing ratios of water vapor and CO_2, respectively, and ψ is the energy equivalent of CO_2 fixation. The energy balance technique is fairly reliable, typically yielding errors in flux estimates on the order of 10–15% (Sinclair et al. 1975, Verma and Rosenberg 1975). However, errors exceeding 40% can occur when the magnitude of R_n and the values of the water vapor and temperature gradients are small. Large errors also occur when S and G are large, since these terms are difficult to measure.

The sensor requirements for gradient measurements are quite rigorous. For example, field experiments show that gradients of temperature and humidity over forests can be quite small due to the effective mixing provided by the rough forest canopy (Jarvis et al. 1976). In general, sensor precision in the range of 0.02 to 0.5% is required to resolve small gradients (Hicks et al. 1980, Businger 1986, Hicks et al. 1988).

The precision and resolution of most instruments are often better than their accuracy. Thus, it is recommended that the gradients be measured differentially or by sampling the air at two or more levels, using a single instrument.

A shorter sampling period is required to measure a mean value than a covariance (Lumley and Panofsky 1964). On the other hand, the accuracy required to deduce gradients from mean values measured by separate instruments is more stringent. The sampling period for a mean is:

$$T = \frac{20(z - d)\bar{c}'^2}{\bar{u}a^2\bar{c}^2}. \qquad (17)$$

Assuming 1% accuracy ($a = 0.01$), $(z - d) = 3$ m, $u = 3$ m/s, and $\overline{c'^2}/\bar{c}^2 = 0.01$, then the required sampling period is 2000 s or 33 min.

The effects of nonlevel terrain on flux-gradient measurements cannot be treated via coordinate rotation. Yet, under these non-ideal conditions advective effects are manifested and result in errors in the flux measurement based on a one-dimensional framework. To compensate for advective effects, an array of instrument masts must be employed to account for advection, via the framework established in Eq. 1 (see Kanemasu et al. 1979).

Alternative approaches

Over the past few years, several alternative techniques have been developed to estimate fluxes. These include the variance, eddy accumulation, mass balance, and inferential modeling techniques.

a) Variance technique.

The turbulent flux covariance can also be expressed as:

$$F = r_{wc}\sigma_w\sigma_c, \qquad (18)$$

where r_{wc} is the correlation coefficient between w and c and σ is the standard deviation. By assuming that the correlation coefficient for w and temperature, r_{wT}, or water vapor, r_{wv}, equals r_{wc} (Hicks et al. 1980), F becomes:

$$F = H\sigma_c/\sigma_T = LE\sigma_c/\sigma_v. \qquad (19)$$

To minimize the effects of sensor noise and different instrument response characteristics, it is recommended that σ_T and σ_c be computed from data subjected to a band-pass filter. If estimates of H or LE are not possible, then a value for r_{wt} must be assumed. Unfortunately, this is a source of considerable potential error. A major disadvantage of this technique is that it provides no information on the direction of the flux; this must be known a priori.

b) Eddy accumulation.

The eddy accumulation technique has been proposed as a possible means of measuring the flux of constituents for which no fast response sensor is available. The technique involves the collection of upward and downward transported material in two separate con-

tainers at rates proportional to the vertical wind speed (Hicks and McMillen 1984, Speer et al. 1985). The flux is evaluated as the difference in concentration accumulated over the sampling period. Unfortunately, the practical difficulties of measuring small concentration differences in the accumulators and sampling the air according to vertical wind velocity have proven unsurmountable with present technology (see Hicks and McMillen 1984); attempts to implement the eddy accumulation technique in the field successfully have so far failed (Speer et al. 1985).

c) Mass balance technique.

The mass balance technique has been to measure fluxes of ammonia from small fields (Denmead et al. 1977, Wilson et al. 1982, 1983). The computation of F is derived from Eq. 1.

$$F = 1/x \int_0^{z_r} \bar{u}\bar{c}\, dz, \qquad (20)$$

where x is the horizontal distance from the upwind edge of the field and z_r is the top of the air layer influenced by the emission of the gas.

Eq. 20 assumes that the mean horizontal turbulent flux ($\overline{u'c'}$) is much smaller than the mean, horizontal, advective flux ($\overline{uc}$). z_r is a function of stability and surface roughness, but can generally be estimated as $z_r = 0.1x$ (Denmead 1983). Denmead (1983) recommends that concentrations and wind speeds be measured at five levels at least. The horizontal distance, x, must be known precisely. Therefore, to minimize the effects of changing wind direction on x, it is recommended that experiments, based on Eq. 20, be conducted in a circular plot with the instrument array in the center.

d) Inferential modeling technique.

At present it is impractical to apply micrometeorological methods for extended periods. An alternative approach, promoted by the Atmospheric Turbulence and Diffusion Laboratory (Baldocchi et al. 1987*b*, Hicks et al. 1987) involves computing fluxes with an inferential model based on routine chemical and meteorological measurements.

The framework of the model depends on the system and trace gas being measured. For the deposition of SO_2 and O_3 to vegetation, a simple resistance-analog model has proven to be successful (Matt et al. 1987, Meyers and Baldocchi, 1988). Fluxes are determined as the product of the concentration and the deposition velocity. The deposition velocity is the reciprocal of the sum of the aerodynamic, quasi-laminar boundary layer and surface resistances. Under other circumstances where the surface is not a perfect sink and gaseous emissions occur from the soil, modifications in the modeling routines must be incorporated (see Hicks and Matt, 1987).

TABLE 1. Summary of chemical sensors and micrometeorological techniques used to measure turbulent fluxes (adapted from Hicks et al. (1988). EC,G, and MB represent the eddy correlation, flux-gradient, and mass balance techniques, respectively.

Chemical species	Sensor	Technique
H_2O	Lyman-alpha hygrometry	EC
	Infrared absorption	EC, G
CO_2	Infrared absorption	EC, G
	Chemical absorption	G
SO_2	Flame photometry	EC
	Ultra-violet absorption	EC
	Bubblers	G
NO	O_3 luminescence	EC
NO_2	O_3 luminescence	EC
	Luminal	EC
O_3	NO luminescence	EC
	Bubblers	G
HNO_3	Nylon filters	G
NH_3	Absorption Traps	G
		MB
CH_4	Grab-bag air sample	G
	Bubblers	G

Applications

Due to editorial constraints on the scope of this paper, we cannot survey, in detail, the chemical sensors and micrometeorological techniques commonly used to measure turbulent fluxes of specific chemical compounds. However, to summarize current capabilities, we present Table 1. This table does not include new evolving technologies such as tunable diode lasers and fast Fourier transform infrared radiometers.

CONCLUSIONS

Reliable flux measurements can be made with micrometeorological techniques, as long as the user works within the theoretical framework discussed in this paper. Due to the interdisciplinary nature of studying biosphere–atmosphere exchange, a closer cooperation between atmospheric scientists and ecologists should produce meaningful results. It is our hope that this article will encourage ecologists to initiate or participate in cooperative micrometeorological studies of gas exchange between the biosphere and atmosphere and we look forward to fruitful results.

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