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The use of relaxed eddy accumulation to measure biosphere-atmosphere exchange of isoprene and other biological trace gases

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Abstract The micrometeorological flux measurement technique known as relaxed eddy accumulation (REA) holds promise as a powerful new tool for ecologists. The more popular eddy covariance (eddy correlation) technique requires the use of sensors that can respond at fast rates (10 Hz), and these are unavailable for many ecologically relevant compounds. In contrast, the use of REA allows flux measurement with sensors that have much slower response time, such as gas chromatography and mass spectrometry. In this review, relevant micrometeorological details underlying REA are presented, and critical analytical and system design details are discussed, with the goal of introducing the technique and its potential applications to ecologists. The validity of REA for measuring fluxes of isoprene, a photochemically reactive hydrocarbon emitted by several plant species, was tested with measurements over an oak-hickory forest in the Walker Branch Watershed in eastern Tennessee. Concurrent eddy covariance measurements of isoprene flux were made using a newly available chemiluminescence instrument. Excellent agreement was obtained between the two techniques ($r^2 = 0.974$, $n = 62$), providing the first direct com-

parison between REA and eddy covariance for measuring the flux rate of a reactive compound. The influence of a bias in vertical wind velocity on the accuracy of REA was examined. This bias has been thought to be a source of significant error in the past. Measurements of normalized bias (\bar{w}/σ_w) alone would lead us to think that a large potential error exists at this site. However, with our isoprene data and through simulations of REA with fast-response H₂O and CO₂ data, we conclude that accurate REA flux measurements can be made even in the presence of a bias in w .

Key words REA · Oak-hickory forest · Isoprene · Flux · Eddy covariance

Introduction

In recent years, there has been growing interest among ecologists to quantify biologically relevant trace gas fluxes. Currently, most biological fluxes are measured using enclosure techniques at small spatial scales. The use of enclosures such as soil, leaf, and branch chambers is attractive because of their low cost and simplicity, but suffers from a number of disadvantages. These include (1) modification of physical properties such as the light and temperature environment, (2) perturbations to gas concentration gradients and associated diffusion, (3) transport artifacts such as advective transport of gases away from the soil or a leaf, and (4) physical damage to biological structures such as leaves, roots, and symbiotic associations. Micrometeorological techniques offer an alternative approach to measuring biological fluxes that avoids the inherent problems of enclosure methods. Measurements of in situ fluxes are possible at scales that integrate over large areas. These techniques are passive and do not introduce artificial environmental conditions.

In this study, we focus on the micrometeorological flux measurement technique known as relaxed eddy accumulation (REA), which is relatively new and rapidly gaining in popularity. This work is not intended to be an

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exhaustive literature review. However, we feel that this extremely powerful technique needs to be brought to the attention of the ecological community, and with a thorough discussion of relevant literature, we hope that its use among ecologists will become more widespread.

Theory

Several past reviews provide introductions to micrometeorology (e.g., Baldocchi et al. 1988; Businger 1986; Lenschow 1995), including governing equations, critical assumptions, and site selection criteria. Assumptions relevant to eddy covariance (EC) also apply to its variants, eddy accumulation (EA) and REA, and meeting these assumptions is critical to accurate flux measurement. The reader unfamiliar with basic micrometeorology is encouraged to consult these reviews.

EC is based on the following relationship, derived from conservation of mass

$$F = \overline{\rho w' \chi'} \quad (1)$$

where F is the measured flux ($\text{mol m}^{-2} \text{s}^{-1}$), w is the vertical component of wind velocity (m s^{-1}), χ is the mole fraction or mixing ratio of trace gas with respect to dry air (mol mol^{-1}), and ρ is the density of dry air (mol m^{-3}). By convention, an upward flux is considered positive. In this notation, an overbar represents a mean quantity, averaged over the duration of the flux measurement (typically 30 min), and a prime represents deviation from that mean.

Instruments used for EC must be capable of responding to fluctuations of both air motion and air composition at frequencies up to 10 Hz. This rate is not a problem for sonic anemometers (fast-response wind sensors), but the majority of chemical sensors used to measure biological trace gases cannot respond this quickly. This has limited the primary use of EC to measurement of sensible and latent heat, carbon dioxide, and ozone fluxes. In principle, this constraint on sampling frequency can be avoided with a strategy that collects a statistically meaningful sample physically, instead of mathematically. It is on this concept that EA is based (Desjardins 1972, 1977). This technique involves sampling atmospheric air based on the sign and magnitude of w . When $w > 0$, air is collected in an “updraft” reservoir, for $w < 0$, air is sampled into a “downdraft” reservoir. The sampling flow rate is proportional to the magnitude of w . After a suitable averaging period, the flux is determined by (Baker et al. 1992)

$$F = \overline{\rho w' \chi'} = \frac{m_{\text{up}} - m_{\text{dn}}}{\alpha t} \quad (2)$$

where m_{up} and m_{dn} are the total amount (mol) of the trace gas in the updraft and downdraft reservoirs, respectively, α is the pumping coefficient, in volume flow rate per unit of vertical wind speed ($\text{m}^3 \text{s}^{-1} / \text{m s}^{-1}$), and t is the sample period (s). Appealing in principle,

this method suffers from a number of analytical difficulties, which have been discussed in detail by Hicks and McMillen (1984). Among them are (1) the practical difficulty of accurately controlling sample flow rate based on vertical wind speed, and (2) the high chemical accuracy needed to measure the difference in trace gas content in the reservoirs.

Relaxing the constraint that the amount of air sampled be proportional to the magnitude of w , Businger and Oncley (1990) proposed the conditional sampling technique, now more commonly referred to as relaxed eddy accumulation or REA. This technique involves sampling air into updraft and downdraft reservoirs, at constant flow rate, based solely on the sign of w . The flux is expressed as

$$F = \overline{w' c'} = b \sigma_w (\bar{c}_{\text{up}} - \bar{c}_{\text{dn}}) \quad (3)$$

where b is an empirical proportionality coefficient (which is generally in the range 0.3–0.8), σ_w is the standard deviation of w , and \bar{c}_{up} and \bar{c}_{dn} are the average concentrations of the trace gas in the updraft and downdraft reservoirs, respectively. It is intuitively evident that the flux is proportional to the difference in average concentration in updrafts and downdrafts, since atmospheric turbulence is analogous to diffusion of parcels (not molecules) of air, and a concentration gradient is the driving force in a diffusive process. In relaxing the flow rate constraint of EA, this approach sacrifices some information about w , and so the inclusion of the empirical coefficient is not surprising. It is not obvious, however, why σ_w is included. Clearly some parameter describing vertical wind is necessary to describe vertical transport, and σ_w provides good results. It may well be that similar methods involving other turbulence parameters could be derived [e.g., σ_w^2 , w^* , turbulent kinetic energy (TKE); see Stull 1988].

From past studies, and from our own experience, we have learned that a number of details are critical for accurate implementation of REA. Some are obvious, some more subtle, and many are dependent on the trace gas being analyzed. These points are discussed here as a set of guidelines for successful implementation of REA.

Response time and measurement duration

Eddies that contribute significantly to the flux of a scalar generally have a frequency on the order of 5 Hz or less (or alternatively, a time scale of 1/5 s or longer). This cutoff is strongly dependent on measurement height because eddy size decreases as the ground or canopy surface is approached (Kaimal et al. 1972). To adequately sample 5-Hz atmospheric motions while avoiding a discrete sampling effect called aliasing, sampling must be conducted at twice this rate, i.e., 10 Hz. Hence, the generally accepted minimum sampling rate for atmospheric turbulence is 10 Hz, and most EC analyzers have a response time in this range. This is not a strict

criterion, and can often be relaxed through examination of power and cospectra of turbulence at a particular site (see Kaimal and Finnigan 1994; Stull 1988). This limitation also applies to REA sampling – segregation of sample air (valve switching and associated plumbing) must be achieved at or near 10 Hz.

Similarly, to obtain a statistically robust sample of larger eddies (i.e., those with duration of the order of tens of minutes), a flux measurement must be averaged over a suitably long interval. Kaimal et al. (1989) suggest that this interval should be at least ten times the dominant (integral) time scale (T_w) of the process. T_w is the integral of the autocovariance of w (see Kaimal and Finnigan 1994), and corresponds to those eddies (with frequency $1/T_w$) that contribute most to turbulent transport and dominate the cospectra of scalars with w . For many sites this is in the range 20–60 min, and the practically convenient value of 30 min is often used as an averaging time for flux measurement.

Sonic anemometer

Accurate measurement of vertical turbulent air motion is essential for any flux measurement. Currently the best instrument for this purpose is the sonic anemometer, which measures wind speed based on fluctuations in the speed of sound. Sonic anemometers are available commercially in a variety of physical configurations, both one-dimensional (w only) and three-dimensional (u , v , and w ; the three orthogonal wind components). A three-dimensional anemometer is recommended, as knowing all three components provides the capability to align most flux measurements (but not REA) with the mean wind streamlines, forcing \bar{v} and \bar{w} to zero (this is discussed in detail later). This alignment is standard practice for EC measurements, and is needed to perform accurate energy balance analysis. When used for REA, a 3-dimensional sonic allows one to assess the magnitude of problems associated with a bias in w .

Relaxed eddy accumulator

A relaxed eddy accumulator is strictly an air collection device, distinct from the chemical sample analyzer. Air is sampled from as near the sonic anemometer path as possible, but far enough away to avoid distorting the measured wind (typically < 10 cm). Two configurations are typical, depending on whether the pump is located upstream or downstream of the collection reservoirs.

The first type is used with reservoirs that have a single inlet, such as Tedlar or Teflon bags. This design was used in the current study and is shown in detail in Fig. 1. Air is pumped from the inlet through a two- or three-way valve into two or three reservoirs (updraft, downdraft, and sometimes neutral). This system has the advantage of maintaining pressure equilibration

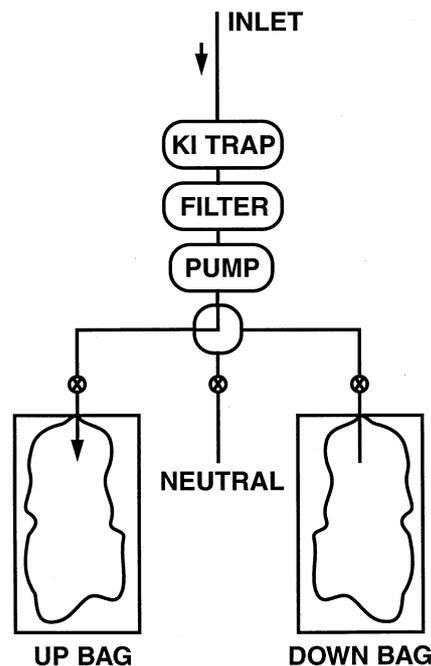


Fig. 1 A pump-upstream relaxed eddy accumulation design, used to measure isoprene fluxes in this study. *Arrows* indicate direction of flow for an updraft. Sample air was drawn from the sonic anemometer (SAT-211/3K, Applied Technologies, Boulder, CO) path through a 94.5×0.64 cm OD length of Teflon tubing, a potassium iodide (KI) ozone trap, and a filter by a Teflon diaphragm pump (NMP-30, KNF Neuberger, Trenton, NJ). Air then flowed through a three-way Teflon manifold solenoid valve (18-53-900, General Valve, Fairfield, NJ), and one of three fine-scale stainless steel needle valves (*circles with crosses*) which were adjusted to match flow rates. Mass flow controllers (MFCs) were not used here since the flow stops and starts at the eddy reversal frequency, much quicker than MFC response time. Sample air then flowed through a 195×0.64 cm OD length of Teflon tubing, and was collected in one of two 8-l Tedlar bags (up and downdraft air) or discarded (neutral air). Control of the three-way valve and communication with the sonic were achieved using custom electronics and software, at a rate of 10 Hz. Sample air was collected using the REA over a 30-min sample period (this was the case for all flux measurements reported here), the bags were manually removed, and analyzed within 2 h. Laboratory and field experiments showed that no sample degradation was detectable in the bags over a period of several hours. Isoprene was determined using GC/FID with cryofocusing using a manual version of the technique of Greenberg et al. (1994). A NIST-traceable isoprene standard (15.59 ppbv isoprene in hydrocarbon-free air) was run several times daily for calibration

between the bags and the atmosphere, useful for maintaining flow rate consistency. The obvious disadvantage is that the sample gas must travel through the pump.

An example of the pump-downstream variety (see Nie et al. 1995; Pattey et al. 1995) is shown in Fig. 2. This design is used with flow-through reservoirs with an inlet and an outlet, such as chemical adsorbent traps or cryogenic collection. The pump is located downstream of the collection reservoirs. This configuration provides the advantage of using two (or three) separate inlet lines and thus avoids problems of separating updraft/downdraft air in the same line. In either system, after collecting for 30 min, the reservoirs are analyzed for trace gas content to get \bar{c}_{up} and \bar{c}_{dn} .

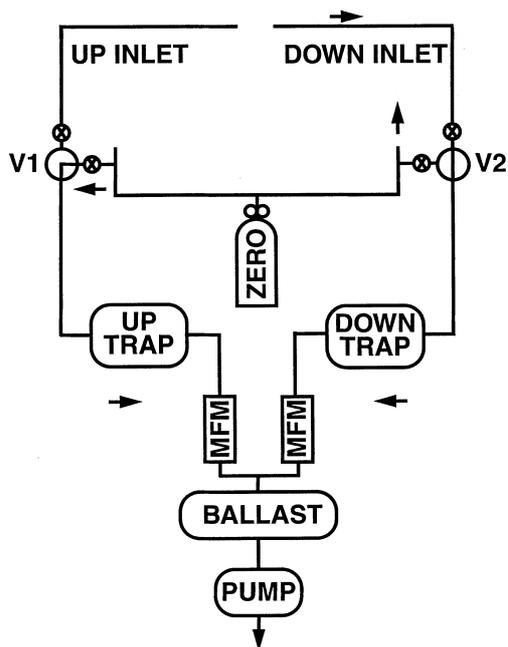


Fig. 2 A general pump-downstream relaxed eddy accumulation design. *Arrows* indicate direction of flow for a downdraft. While downdraft air is being sampled through the *down inlet* line, the *up inlet* line is stagnant. Sample air flows through the *down trap*, while zero air from a compressed-gas cylinder flows through the *up trap*. The reverse is true for an updraft, and zero air flows through both traps during neutral periods. This is controlled by valves *V1* and *V2* which are capable of responding at 10 Hz. Fine-scale needle valves (*circles with crosses*) are used to match flow rates in the zero and sample lines for each side to minimize pressure surges and accompanying flow inconsistencies. Downstream of each trap is a mass flow meter (*MFM*) or controller, whose signal is digitized at 10 Hz, then later parsed to determine up and down sample volumes (crucial for a mole fraction or mixing ratio determination). Accurate volume measurement with this plumbing design is likely to be difficult, as pressure surges upon switching from sample air to zero air or viceversa may not be accurately reflected in the MFM signal – hence these surges must be avoided as much as possible. The purpose of the zero air is to provide a steady flow for the MFM when switching between updrafts and downdrafts. Downstream of the MFMs, there is a *ballast* to minimize pump pressure fluctuations and a small sample *pump*

Regardless of the specific REA design and reservoir type that is used, two criteria must be met. First, sampling must be done at constant flow rate. This is one of the basic tenets of REA. It is crucial to ensure that sampling flow within a given 30-min flux period is constant, otherwise the measurement may be biased toward the beginning or end of the period. Similarly, if resistance to flow is higher in the updraft path than the downdraft path, and the same pump is used for each, then the updraft sample rate will be slower than the downdraft sample rate. Depending on system design this may result in an unknown error in the measured mole fraction or concentration. This is more serious in a pump-downstream system where whole air is not collected.

A related issue is pressure equilibration between each reservoir, and between the reservoirs and the

atmosphere. This is necessary to prevent changes in sample flow rate over the duration of the flux sample period. The use of glass or stainless steel as materials for the updraft and downdraft reservoirs is attractive, as they are relatively chemically inert. However, as sample gas is pumped into a rigid reservoir, the internal pressure of the reservoir will increase, decreasing the sample flow rate. This biases the flux measurement towards the first portion of the measurement period, and most likely also biases towards one reservoir or the other. At the very least this will decrease the concentration difference measured between the two bags, causing an underestimation of the flux. The use of flexible bags or a trap through which sample air can pass while retaining compounds of interest eliminates this problem.

The second critical matter in REA measurements regards accurate timing of sample segregation. This is especially important in systems of the pump-upstream variety (Fig. 1). When a single sample inlet line is used, updraft air and downdraft air reside as adjacent plugs of gas in the sample line, until they reach the segregator valves. These plugs may be fairly small in size, as the updraft/downdraft (eddy) reversal frequency can be a few Hertz (Baker et al. 1992; Beverland et al. 1996c). It takes a finite amount of time for these plugs to traverse the sample line, and so there is a finite and significant delay from the occurrence of an updraft/downdraft transition at the sonic anemometer to the appropriate valve switch. This delay can vary from a few hundred milliseconds to many seconds, and is dependent on sample flow rate and system configuration. Delays of this nature in an eddy covariance system are typically measured by examining the time-lagged cross-correlation of w and c ; the time lag which provides the maximum cross-correlation between the two variables represents the delay time. This is not possible with an REA measurement as the destination for the sample gas is not an analyzer but a reservoir that will be analyzed later.

An additional concern regarding accurate separation of adjacent gas plugs in the inlet tubing involves the properties of the flow in the tubing. The tubing diameter, length, and the sample flow rate must be selected to ensure turbulent and not laminar flow in the sample line. The presence of laminar flow leads to a smearing of turbulent fluctuations in the gas stream, and could in some cases mix updraft and downdraft air before they are segregated (Lenschow and Raupach 1991; Massman 1991; Rannik et al. 1997).

To date, a variety of chemical species have been measured using the REA technique. These have involved a host of system designs and reservoir materials – some dispense with the reservoirs altogether and go straight to the chemical analyzer. These studies are summarized in Table 1. The reader is encouraged to examine these systems to gain an understanding of the wide variety of designs that have been used.

Table 1 Summary of REA measurements to date. Studies which involve REA simulations but no direct measurements are not included. (*IRGA* infrared gas analyzer, *GC* gas chromatograph, *FTIR*

Fourier transform infrared spectroscopy, *TDL* tunable diode laser spectrometer, *NMHC* non-methane hydrocarbons)

Compound	REA type	Reservoir type	Analyzer	Reference
CO ₂	Upstream	Curlam bags	IRGA	MacPherson and Desjardins (1991), Pattey et al. (1993)
		Teflon bags	IRGA	Oncley et al. (1993), Guenther et al. (1996)
	Downstream	Tedlar bags	IRGA	Beverland et al. (1996a–c)
		No reservoir	IRGA	Baker et al. (1992)
H ₂ O	Upstream	No reservoir	IRGA	Baker et al. (1992)
		Mg(ClO ₄) ₂	Gravimetric	Nie et al. (1995)
	Downstream	No reservoir	IRGA	D. Hollinger, USDA Forest Service, personal communication
		Cryogenic	Mass spectrometer	Baker et al. (1992)
Triallate, trifluralin	Downstream	Polyurethane foam plugs	Soxhlet extraction and GC	D. Hollinger, USDA Forest Service, personal communication
		Tenax-TA	GC	Majewski et al. (1993)
Isoprene	Upstream	Teflon bags	GC	Pattey et al. (1995)
		Tedlar bags	GC	Guenther et al. (1996)
Monoterpenes and other NMHCs	Downstream	Tenax-TA	GC	This study
		Various solid adsorbents, including Tenax-TA, Carbotrap	GC	Beverland et al. (1996b)
CH ₄	Upstream	Tedlar bags	GC	Valentini et al. (1997), A. Guenther and B. Baker, NCAR/ACD, personal communication
	Downstream	No reservoir	GC	Beverland et al. (1996b)
N ₂ O	Upstream	Tedlar bags	GC, FTIR, TDL	Beverland et al. (1996b)
				Hargreaves et al. (1996)

***b* coefficient**

For a scalar [such as temperature (T) or water vapor] that can be sampled fast enough for eddy covariance, the *b* coefficient is calculated from measured data by rearranging Eq. 3 to

$$b = \frac{\overline{w'T'}}{\sigma_w(\overline{T}_{up} - \overline{T}_{dn})} \quad (4)$$

To solve Eq. 4, fast temperature data are used to develop ‘virtual’ updraft and downdraft REA samples by simulated sampling of T values for $w > 0$ and $w < 0$, respectively. These simulated samples are then averaged to obtain \overline{T}_{up} and \overline{T}_{dn} . In this manner, Businger and Oncley (1990) in early simulations calculated that the value for *b* was roughly 0.6, and was fairly constant for both temperature and humidity over a wide range of atmospheric stability.

In practice, however, we wish to use REA to measure fluxes of trace gases that we cannot measure fast enough to use Eq. 4 (if we could, EC would be preferred). We often assume that these trace gases are transported by atmospheric turbulence in the same manner as temperature (or some other scalar which can be measured at 10 Hz, such as CO₂ or H₂O), then use these scalars to calculate *b* using Eq. 4. This assumption is called spectral or cospectral similarity (Wyngaard and Coté 1972). The *b* value from temperature

is used for the trace gas of interest, and the flux calculated from Eq. 3.

The actual value for *b* has received a fair amount of attention in the literature. It varies with height (Gao 1995), at least in and near a forest canopy. The statistical nature of the coefficient has been addressed by Baker et al. (1992), Wyngaard and Moeng (1992), and Katul et al. (1996), but we do not yet understand the physical principles that underly its form. Studies in the past have taken two courses – those which regress $\overline{w'c'}$ versus $\sigma_w(\overline{c}_{up} - \overline{c}_{dn})$ for a large number of flux samples, then use a constant *b* (Baker et al. 1992; Beverland et al. 1996a), and those that calculate *b* for each run explicitly, often using a variety of scalars (Guenther et al. 1996; Oncley et al. 1993; Pattey et al. 1993). Katul et al. 1996 investigated the error associated with using *b* calculated from various scalars to calculate the flux of other scalars. When temperature was used to calculate *b*, the associated errors (REA flux compared to EC flux) in calculating the fluxes of H₂O, O₃, and CO₂ were 2.3, 3.3, and 3.9%, respectively. However, the errors associated with the assumption of constant *b* ($b = 0.56$) were only 1.06% (for H₂O), 0.74% (O₃), and 0.23% (CO₂). It was concluded that there is no clear advantage to using one scalar over another, or to regressing a large number of values for the flux. Since temperature fluctuations are generally measured by a sonic anemometer, we recommend using temperature data and Eq. 4 to calculate *b* for each flux measurement period.

Threshold (deadband)

Often, REA sampling involves only two reservoirs: one to collect updraft air and one to collect downdraft air. An alternative sampling strategy that has been used involves collecting, or more commonly disposing, of air in a third reservoir when w is near 0. For $w > w_T$ (where w_T is the threshold value), air is considered an updraft; for $w < -w_T$, a downdraft, and for $-w_T < w < w_T$, neutral. This 'deadband' approach, as it is often called, has the advantage of increasing the scalar concentration difference between the updraft and downdraft reservoirs. Sampling is biased toward larger eddies (those with sufficient vertical velocity to exceed the threshold), which tend to move air from farther along the vertical concentration gradient. Hence that air which is collected represents more extreme samples along this gradient, and results in a larger concentration difference between the reservoirs. This can be exploited to allow flux measurement when precision of the chemical analyzer is limited.

The increase in concentration difference must be balanced by a decrease in b . Businger and Oncley (1990) and Pattey et al. (1993) found an exponential decrease in b with increasing deadband size. The latter study examined the quantitative relationship between deadband and the concentration difference between reservoirs. They found that normalized threshold velocity values (w_T/σ_w) of 0.5 or less maintained an error of less than 1% for 20 simulated, 30-min runs. (Using σ_w to normalize the threshold makes the analysis extendible to periods with different turbulent intensities.) Using a deadband of $w_T/\sigma_w = 0.5$ resulted in a 27% increase in concentration difference between the reservoirs. Pattey and colleagues note that this relationship becomes less predictable for larger deadband values, suggesting a practical limit to the size of the deadband. Until a better understanding of deadband is achieved, the use of a conservative threshold is warranted.

Density fluctuations

The presence of heat or water vapor in sampled atmospheric air can lead to significant error in flux measurements. Warm air is less dense than cool air (i.e., updrafts tend to be warmer on average than downdrafts), and so the density of updrafts tends to be less than that of downdrafts. The water vapor content of air can be a few percent by volume, much greater than the concentration of most trace gases. Since a large H₂O concentration gradient exists in the presence of a latent heat flux, there can be considerable variation in density of sampled turbulent air due to that flux. An analyzer that measures the concentration or mole fraction of a trace gas in ambient air will be influenced by these changes in density. The correction can be as large in magnitude as the measured flux.

Webb et al. (1980) discuss in detail the corrections for density for EC measurements. Pattey et al. (1992) have extended Webb's results for use with REA. They show that the error associated with density fluctuations is dependent on the ratio of the background concentration of a trace gas to its flux. Based on typical values for each, they conclude that density corrections should be significant for REA flux measurements of N₂O, NO, CO₂, CH₄, and O₃, but not for some pesticides (triallate, trifluralin) and hydrocarbons (isoprene, terpenes).

Vertical wind bias

The mean value for vertical wind (\bar{w}) over a sampling period is often, but not always, near zero. When this quantity is non-zero, the total flux is made up of the sum of the advective flux and the eddy flux, $F = \bar{w}\bar{\chi} + \overline{w'\chi'}$. The advective flux represents transport by the mean wind. If a site is horizontally uniform, mean horizontal transport is unimportant; trace gases just move around horizontally until they are transported upwards by turbulence. Further, a horizontally uniform site typically has $\bar{w} = 0$, so mean vertical transport ($\bar{w}\bar{\chi}$) is negligible. With more complex terrain, overall horizontal motion can be translated into small vertical motion as air moves over small hills or slopes. Sensors in the midst of these perturbations will measure a non-zero \bar{w} .

In eddy covariance studies, this error is generally corrected by mathematical rotation of the reference frame of the measurement system to match the mean wind streamlines of the local terrain (e.g., Kaimal and Finnigan 1994, pp. 234–240). Unfortunately, this correction is impossible with REA as air must be collected into separate reservoirs during sampling, and this cannot be undone afterwards. This bias was first discussed by Businger and Oncley (1990) and then by Pattey et al. (1993) as a cause for a potentially large error in REA flux measurements. A bias in w leads to erroneous decisions about the exact nature of updrafts and downdrafts.

We investigated this issue with measurements of carbon dioxide, sensible heat, latent heat, and isoprene fluxes over a mixed oak-hickory forest at the Walker Branch Watershed (in eastern Tennessee) during August 1996. Details of the site can be found in Johnson and van Hook (1989). Isoprene fluxes were measured at 40 m height using REA and EC as described in the captions of Fig. 1 and 5. CO₂ and H₂O fluxes were measured at 37 m using EC as described elsewhere (Baldocchi and Harley 1995; Greco and Baldocchi 1996). REA fluxes reported for CO₂ and latent heat are simulated from 10-Hz data (see the caption of Fig. 3 for details).

We frequently observed a significant non-zero vertical wind bias. Figure 3 shows the flux ratio (biased REA flux/unbiased EC flux) for various values of non-dimensional wind bias, for latent heat and CO₂ and isoprene fluxes. The line was taken from the simulation of Pattey et al. (1993), and shows that data from the two

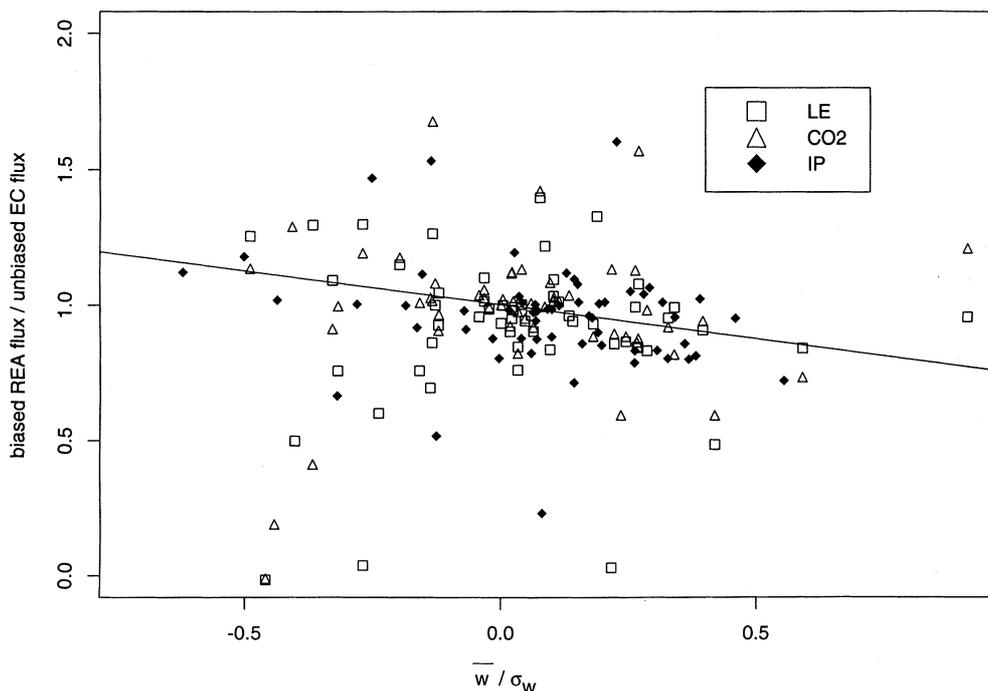


Fig. 3 Flux ratio [biased relaxed eddy accumulation (REA) flux/unbiased eddy covariance (EC) flux] versus normalized bias in vertical wind velocity. The vertical wind bias is normalized by σ_w to compare periods of varying turbulent intensity. The solid line represents $REA/EC = 1 - 0.25(\bar{w}/\sigma_w)$ and was estimated from Pattey et al. (1993, Fig. 10). Isoprene (IP, diamonds) fluxes were measured on 14–23 August 1996. Latent heat (LE, squares) and CO_2 (triangles) EC fluxes were calculated from 10-Hz data during unstable periods ($z/L < 0$) during 19–23 August 1996. Raw time series for u , v , and w were rotated into streamline coordinates based on 30-min means for each following Kaimal and Finnigan (1994). These fluxes are referred to here as “unbiased” EC fluxes because \bar{w} has been forced to zero. The covariance of the rotated w time series with the scalar time series was used to calculate the respective EC fluxes using Eq. 1. Density corrections (Pattey et al. 1992; Webb et al. 1980) were not applied to any of the EC or REA flux values, as exact flux values were not necessary for relative comparison. To simulate REA measurements, the fast scalar time series (H_2O , CO_2) were artificially conditionally sampled based on the raw w time series, which contained non-zero values for \bar{w} over many time periods. This is referred to as the “biased REA” case throughout. The b coefficient was calculated from fast temperature data using Eq. 4, then the flux using Eq. 3. For the “unbiased REA” case, the above coordinate rotation procedure was applied first, then the rotated w time series was used to determine b and segregate into updrafts and downdrafts. Note that this method cannot be used in an actual REA measurement. The unbiased REA simulation approximates the REA flux that we would measure if we could accurately predict coordinate rotation angles for a certain flux period prior to sampling

studies are in agreement. It is apparent that a large error exists in many cases when comparing these fluxes on a ratio basis. However, Fig. 4a–d shows the same LE and CO_2 simulation data plotted on a 1:1 basis, and shows remarkable agreement between the biased REA values and the unbiased EC values. This is particularly true when those values at low sensible heat flux ($H < 10 \text{ W m}^{-2}$) are removed. Note that during conditions of low sensible heat flux, the b coefficient is calculated as the ratio of two small numbers (Eq. 4) and its

value is therefore questionable. Values of b in this study were in the range 0.30–0.85 (0.58 ± 0.09 , mean \pm SD, $n = 63$) for $H > 10 \text{ W m}^{-2}$, and -3.50 – 3.74 (0.43 ± 1.05 , $n = 29$) for $H < 10 \text{ W m}^{-2}$. Clearly, substantial variation in the b coefficient occurs at near-neutral atmospheric stability (small H values).

In the simulation, it was possible to rotate the REA reference frame as with EC after the data were collected, to directly compare the REA fluxes calculated with (Fig. 4a,c) and without (Fig. 4b,d) a bias. Note that the coefficients of determination do improve upon rotation (0.968 to 0.985 for CO_2 , and 0.986 to 0.991 for LE), but not by much. Presumably the lack of perfect correlation between the unbiased REA values and the unbiased EC values is due to lack of perfect cospectral similarity between these scalars and temperature, as temperature data were used to calculate the b coefficients for all these REA fluxes. The robust nature of REA measurements in the face of a bias in w is also apparent in comparisons between measured REA (biased) isoprene flux and measured EC (unbiased) isoprene flux (Fig. 5). Note that excellent linear agreement is evident in this plot, despite the bias in w and the fact that these techniques are founded on different types of measurements. These data show that, on average, remarkable agreement can be obtained in simulated REA flux measurements regardless of the presence of a significant bias in w .

REA investigators in the past have reported a variety of techniques to filter the vertical bias from the w signal during sampling. These include the use of high-pass filters (MacPherson and Desjardins 1991; Majewski et al. 1993; Pattey et al. 1993, 1995), moving average filters (Baker et al. 1992; Nie et al. 1995), moving average filters combined with a deadband based on moving standard deviation (Guenther et al. 1996), and a recursive

Fig. 4 **a** Biased REA CO_2 flux versus unbiased EC CO_2 flux. **b** Unbiased REA CO_2 flux versus unbiased EC CO_2 flux. **c** Biased REA LE (latent heat) flux versus unbiased EC LE flux. **d** Unbiased REA LE flux versus unbiased EC LE flux. **a–d** Units are $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ (CO_2) and W m^{-2} (LE)

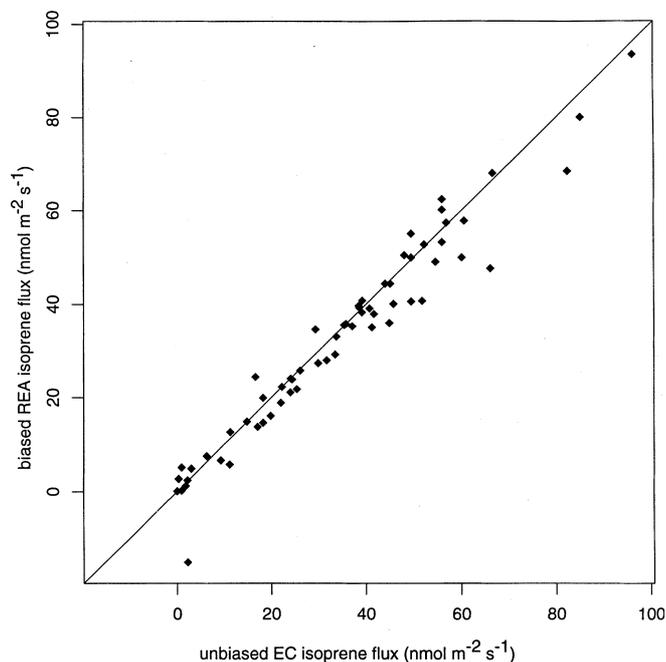
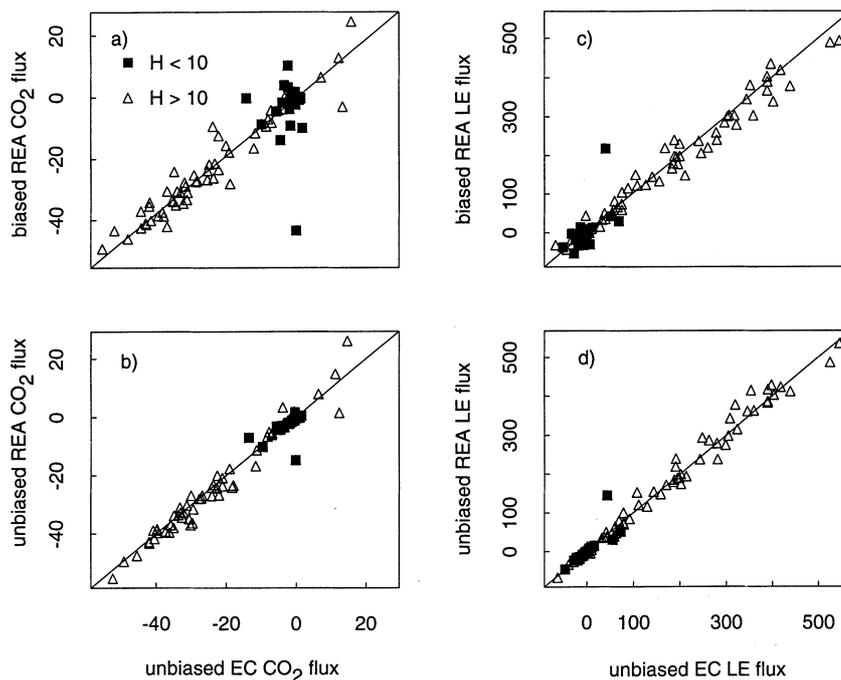


Fig. 5 Measured REA isoprene flux versus measured EC isoprene flux. A 1:1 line is shown for comparison. REA samples were collected as described in Fig. 1. EC fluxes were measured using an ozone-induced chemiluminescence instrument (FIS, Hills Scientific, Boulder, CO) and a sonic anemometer (SAT-211/3K, Applied Technologies, Boulder, CO). Calibrations were performed every 3–4 h throughout the day using a NIST-traceable standard (5.85 ppmv isoprene in N_2 , which was diluted to 1–40 ppbv internally in the instrument). $r^2 = 0.974$, $n = 62$, $P < 0.001$

filter (Beverland et al. 1996 a,b,c). To date the effectiveness of these techniques has not been investigated. Each approach essentially filters the very low frequency

(DC) components from the w signal, which in principle is correct. However, most digital filters (including these) have at best a linear and sometimes a non-linear phase response. This means that the phase of the filtered signal is frequency dependent. We investigated each of the above approaches in early simulations, and found that none provided better results than simply using raw, biased wind data to segregate updrafts and downdrafts. However, none of the methods provided exceedingly poor results, either. As pointed out by Beverland et al. (1996c), a detailed study needs to be carried out to further evaluate these various filters, and if possible design an on-line coordinate rotation scheme that can be used with REA. Perhaps the 10–15% error in these measurements can be reduced with the application of such a technique.

Applications

There are many potential applications for flux measurement using REA. Fluxes of virtually any compound that can be collected and stored in a stable state can be measured. In the studies reported above, we used REA combined with gas chromatography (GC) to measure isoprene fluxes from an oak-hickory forest. Fluxes of other non-methane hydrocarbons from vegetative sources (e.g., monoterpenes, oxygenated hydrocarbons, and alcohols), and methane from wetland sites could be studied using this approach, as they are commonly quantified with GC (Goldan et al. 1993; Helmig and Greenberg 1994; Winer et al. 1992). This would likely involve solid adsorbent or cryogenic trapping. Fluxes of N_2O could be measured using REA coupled with GC with electron capture detection. Biogenic sulfur fluxes

(COS, H₂S, DMS, CS₂) could be measured using REA coupled to GC with flame photometric detection (Fehsenfeld 1995; Goldan et al. 1987; Lamb et al. 1987).

REA also holds promise for measuring fluxes of carbon dioxide over the ocean or freshwater lakes (R. Dissly and P. Tans, NOAA/CMDL, personal communication). There is considerable debate between the micrometeorological and oceanographic communities regarding the validity of EC CO₂ flux measurements over the ocean (Broecker et al. 1986; Crawford et al. 1993). There are locations in the open ocean where conventional EC sensors may lack the necessary sensitivity to measure small fluxes. REA has the potential to resolve this debate by allowing concentration of CO₂ from large air samples (perhaps with a pump-downstream system using cryogenic trapping), which can be followed by high-precision analysis techniques (Thoning et al. 1995; Zhao et al. 1997).

Perhaps the most important potential REA application involves measurement of fluxes of stable isotopes of various compounds. Currently, there is considerable interest in exchange of stable isotopes of CO₂ and H₂O between the atmosphere and the terrestrial biosphere and oceans (Ciais et al. 1995; Tans et al. 1993). Francey and Tans (1987) and Friedli et al. (1987) suggest that the ¹⁸O signature of atmospheric CO₂ may be driven by exchange with the terrestrial biosphere. Recent work indicates that CO₂ fluxes associated with terrestrial photosynthesis and respiration may be separated at the ecosystem scale by close examination of the stable C and O isotopic content of forest CO₂ (Flanagan and Varney 1995; Flanagan et al. 1997; Yakir and Wang 1996). The isotopic signature of soil-respired CO₂ has been measured (Hesterberg and Siegenthaler 1991), and the effects of vegetation on stable isotope signatures of CO₂ are well understood (Farquhar and Lloyd 1993; Farquhar et al. 1993). However, the results of Lloyd et al. (1996) suggest that isotopic differences in updrafts and down-drafts are small, near the limit of current mass spectrometer resolution. Hence, measurement of these fluxes is likely to be difficult.

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