Modification of the relaxed eddy accumulation technique to maximize measured scalar mixing ratio differences in updrafts and downdrafts

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Abstract. A modification to the relaxed eddy accumulation (REA) flux measurement technique is proposed which maximizes the scalar mixing ratio difference in updrafts and downdrafts. This technique was developed with the goal of measuring the stable isotope $({}^{13}C/{}^{12}C$ and ${}^{18}O/{}^{16}O)$ ratios of updraft and downdraft air and thus the net fluxes of $^{13}C^{16}O_2$ and $^{12}C^{18}O^{16}O$. Current mass spectrometer precision is small relative to measured isotopic gradients in CO2 in the Earth's boundary layer, and the conventional REA approach is likely to be ineffective. The new technique, which we refer to as hyperbolic relaxed eddy accumulation (HREA), uses the conditional sampling concept of hyperbolic hole analysis to control sampling of air during only those turbulent events which contribute most strongly to the flux. Instead of basing updraft/downdraft sampling decisions strictly on vertical wind velocity, CO₂ mixing ratio ([CO₂]) fluctuations or those of another scalar are also used. Simulations using 10-Hz data show that a wind-based/ scalar-based sampling threshold can achieve a factor of 2.7 increase in scalar updraft/downdraft [CO₂] differences over simple REA. During midday periods with strong photosynthetic fluxes, up/down [CO₂] differences with HREA of 8–10 ppm are possible, compared with 3–5 ppm for the best conventional REA case. Corresponding isotopic differences can likely be resolved with current mass spectrometers using this approach.

1. Introduction

Measurements of isotopic fluxes of carbon dioxide and water vapor are likely to provide valuable insight into the terrestrial carbon cycle. Previous work [*Francey and Tans*, 1987; *Friedli et al.*, 1987; *Farquhar et al.*, 1993] has illuminated two biological processes which have a strong controlling influence on the ¹⁸O signature of atmospheric CO₂. First, CO₂ respired by roots and soil microbes is slow to diffuse out of the soil and equilibrates isotopically with soil water [*Hesterberg and Siegenthaler*, 1991; *Amundson et al.*, 1998]. Second, during photosynthesis, CO₂ that diffuses into leaves but is not fixed photosynthetically will diffuse back out, after equilibrating isotopically with water in the leaf via the enzyme carbonic anhydrase [*Farquhar et al.*, 1993]. Evaporation at the internal leaf surfaces substantially enriches leaf water (and thus CO₂) in ¹⁸O relative to soil water.

The carbon 13 content of atmospheric CO_2 is also influenced by the biosphere. Photosynthesis discriminates against the heavier ¹³C isotope [*Farquhar et al.*, 1989], leaving the air relatively enriched in ¹³C relative to leaves. Respired CO_2 in ecosystems originates both from recently fixed photosynthates and from very recalcitrant organic substrates [*Trumbore*, 1993; *Schimel et al.*, 1994]. Thus a portion of soil respiration reflects

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the ¹³C signature of an earlier atmosphere, in which the δ^{13} C of CO₂ was different from the present [*Keeling et al.*, 1989]. (In the present paper we use δ notation to describe isotope ratios relative to a standard, where δ^{13} C (or δ^{18} O) = ($R_{\text{sample}}/R_{\text{standard}} - 1$) × 1000, where *R* is the molar ratio of heavy to light isotope. Here δ is expressed in per mil (% σ).)

Therefore CO₂ associated with photosynthesis and with respiration contains different isotope ratios, and at most locations these isotope ratios also differ considerably from background atmospheric CO₂. These natural labels will in principle allow us to partition net CO₂ flux into its gross respiratory and photosynthetic components [*Farquhar et al.*, 1993; *Yakir and Wang*, 1996; *Lloyd et al.*, 1996; *Flanagan et al.*, 1997]. Further, measurements of surface fluxes of ¹³C¹⁶O₂ and ¹²C¹⁸O¹⁶O will provide an additional and very valuable constraint on global-scale inversion models [*Ciais et al.*, 1997a, b] and increase our understanding of terrestrial versus oceanic influences on atmospheric CO₂.

Observed $[CO_2]$ variation in surface and mixed layer profiles is of the order of 10–15 ppm, and the measured isotope ratio range in a given profile is about 1% for both δ^{13} C and δ^{18} O in CO₂, depending on latitude [*Nakazawa et al.*, 1997; *Lloyd et al.*, 1996]. Keeling-type mixing measurements at a variety of latitudes and ecosystem types [e.g., *Keeling*, 1958, 1961; *Lancaster*, 1990; *Flanagan et al.*, 1996, 1997; *Buchmann et al.*, 1997] suggest that these small isotopic variations are fairly representative. At present, the best published mass spectrometer precisions for δ^{13} C and δ^{18} O in CO₂ are 0.03% and 0.05%, respectively [*Trolier et al.*, 1996]. *Lloyd et al.* [1996] show with a mass balance model that isotope ratio differences in updrafts and downdrafts (which we wish to measure using relaxed eddy accumulation) are of the order of tenths of per mil. Resolution

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of such small isotopic differences presents quite a measurement challenge.

The flux-gradient technique has been used with success to partition net CO₂ flux into photosynthetic and respiratory components over several crops [Yakir and Wang, 1996]. Strong vertical gradients (a few per mil within tens of meters for δ^{13} C and δ^{18} O) in the CO₂ isotope ratio have been observed within and below forest canopies [e.g., Sternberg et al., 1989; Buchmann et al., 1997; Flanagan et al., 1996, 1997]. However, the standard flux-gradient approach is difficult to use close to (or within) a tall forest canopy, as the flux-profile relationships on which it is based are only valid in the surface layer, above the roughness sublayer [Cellier and Brunet, 1992]. Isotopic gradients in the surface layer over forests are much smaller $(<0.05\% \text{ m}^{-1})$ [Lloyd et al., 1996]. To successfully use the flux-gradient approach, large measurement height differences would be necessary, leading to associated flux footprint heterogeneity concerns [Schmid, 1994]. Although the eddy covariance technique can be used to measure total CO₂ fluxes [e.g., Goulden et al., 1996], it cannot be used to measure isotopic CO₂ fluxes since fast response mass spectrometers are unavailable for CO2. Thus relaxed eddy accumulation is the most promising flux measurement technique presently available for measuring isotopically differentiated fluxes of CO₂ in forest ecosystems.

In this paper we examine the usefulness of the REA technique to measure net fluxes of ${}^{13}C^{16}O_2$ and ${}^{12}C^{18}O^{16}O$ over a deciduous forest in eastern Tennessee. We begin with relevant REA theory and present a modification to the standard sampling strategy. Then, using simulations with fast (10 Hz) data sets for wind, CO₂, H₂O, and isoprene, we examine how far we can extend the appropriate sampling threshold in each case to maximize the difference in scalar mixing ratios in updrafts and downdrafts. We conclude with a discussion of the potential for measurement of stable isotope fluxes of CO₂ using relaxed eddy accumulation.

2. Theory

The relaxed eddy accumulation (REA) technique [Businger and Oncley, 1990] allows flux measurement for many scalars for which fast instruments (i.e., 5- to 10-Hz sampling rate) are not available. This involves sampling turbulent air based on vertical wind fluctuations (w'), collecting updraft air in one reservoir and downdraft air in another, at a constant flow rate. After a suitable sampling interval the reservoirs are analyzed with slower instruments, and the scalar flux is related to the mixing ratio difference in the two reservoirs by

$$F = \overline{\rho w' c'} = \rho b \,\sigma_w (\overline{c_{\rm up}} - \overline{c_{\rm dn}}) \tag{1}$$

where $F = \rho w'c'$ = flux (g m⁻² s⁻¹), ρ is air density (g m⁻³), b is a theoretical or empirical coefficient (dimensionless), σ_w is the standard deviation of w (m s⁻¹), and \bar{c}_{up} and \bar{c}_{dn} are the average mixing ratios of the scalar in updrafts and downdrafts, respectively. Here b has a theoretical value of 0.627 if the joint probability distribution between w and c is Gaussian [Baker et al., 1992]. Often a wind threshold is used to extend the mixing ratio difference in the reservoirs [e.g., Pattey et al., 1993], with a corresponding decrease in b; only larger updrafts (w' > threshold) and downdrafts (w' < -1 × threshold) are sampled, and air near w' = 0 is discarded. In this paper we follow the standard convention that an overbar represents time (Reynolds) averaging and a prime represents deviation from that average.

To illustrate the REA sampling concept, consider Figure 1, which is a two-dimensional frequency distribution of water vapor fluctuations versus vertical wind fluctuations, collected over a deciduous forest in eastern Tennessee (see section 3). We follow the convention that an upward flux is positive. Notable in this figure is the correlation between normalized water vapor fluctuations (q'/σ_a) (in this paper, σ_x refers to the standard deviation of x, calculated over a 30-min measurement period) and w'/σ_w . Those periods with $w'/\sigma_w > 0$ tend to also have $q'/\sigma_q > 0$ (quadrant 1), and those with $w'/\sigma_w < 0$ generally have $q'/\sigma_q < 0$ (quadrant 3). Points in these quadrants contribute to the upward water vapor flux in a positive way, that is, upward moving air is generally more humid and downward moving air is drier. Both cases are examples of instantaneous water vapor movement with the mean concentration gradient. Most points in Figure 1 fall in these quadrants. However, some sampled air falls into quadrants 2 and 4, which correspond to moist air moving downward or dry air moving upward, i.e., against the mean concentration gradient. This effect in fact diminishes the water vapor flux, and thus air that is sampled using REA during these turbulent events diminishes the measured mixing ratio difference in updrafts and downdrafts. If this mixing ratio (or isotope ratio) difference is already small relative to the analyzer precision (as it is for isotope ratios), we are unlikely to resolve it correctly.

The standard, no-threshold REA sampling approach would collect all updraft air (all points with $w'/\sigma_w > 0$ in quadrants 1 and 4) and all downdraft air ($w'/\sigma_w < 0$, quadrants 2 and 3) in separate reservoirs. The inclusion of air from the countergradient quadrants (2 and 4) limits the mixing ratio difference in the reservoirs.

The dashed lines in Figure 1 represent a wind velocity threshold of $0.6\sigma_w$, which was recommended by *Oncley et al.* [1993] to maximize signal (mixing ratio difference) to noise (measurement uncertainty) ratio. Sampled air in quadrants 1 and 4 with wind velocity exceeding this threshold is considered a significant updraft and is considered in quadrants 2 and 3 a significant downdraft. Since scalar mixing ratio is correlated with *w*, using a large velocity threshold generally improves the mixing ratio difference in updrafts and downdrafts. However, note that there is still a large contribution from the countergradient flux quadrants; minimizing this contribution is our goal.

The REA technique was developed to measure scalar fluxes for which no fast instruments are available. For CO_2 , however, we have the advantage that we can measure turbulent fluctuations at 10 Hz. This additional information enables us to sample only those events which contribute strongly to the CO_2 flux, thus collecting air at either end of the CO_2 mixing ratio range. By using measurements of total CO_2 as a proxy for isotope ratio, we can maximize the difference in isotope ratio in collected updrafts and downdrafts.

Various conditional sampling approaches have been used in the past [e.g., Antonia, 1981; Coppin et al., 1986; Bergstrom and Hogstrom, 1989; Duncan and Schuepp, 1992] to analyze turbulence structure in the surface layer. A common approach is to exclude a "hole" in velocity-scalar space, defined by two hyperbolas [e.g., Shaw et al., 1983; Shaw, 1985; Baldocchi and Meyers, 1988]. We define the threshold for hyperbolic relaxed eddy accumulation (HREA) sampling using

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Figure 1. A two-dimensional frequency distribution of water vapor fluctuations (q') versus vertical wind velocity (w') fluctuations, collected over a 30-min period at the Walker Branch Watershed in eastern Tennessee. Both quantities are normalized by their respective standard deviations and are dimensionless. Shading indicates frequency of occurrence. Dashed lines show an relaxed eddy accumulation (REA) sampling threshold of $0.6\sigma_w$, as described in the text.

$$H = \left| \left(\frac{w'}{\sigma_w} \right) \left(\frac{c'}{\sigma_c} \right) \right| \tag{2}$$

where *H* is an arbitrary dimensionless threshold referred to as hole size and *c* is the mixing ratio or concentration of the scalar. Note this formulation differs from the traditional approach used for momentum flux by *Shaw et al.* [1983] (*H* = $u'w'/\overline{u'w'}$) in that the threshold is scaled by σ_w and σ_c instead of the total flux (i.e., the two methods differ by the correlation coefficient *r* since by definition $\overline{a'b'} = r\sigma_a\sigma_b$). HREA differs from REA only in the additional use of scalar concentration to define the sampling threshold. As with conventional REA, sampling must be achieved at constant flow rate, and (1) is used to calculate the flux.

Figure 2 shows a frequency distribution of w'/σ_w and $-\text{CO}'_2/\sigma_{\text{CO}_2}$. This photosynthetic (downward) CO₂ signal has been inverted to maintain consistency with Figure 1. Thus quadrants 1 and 3 remain associated with fluxes along the mean concentration gradient instead of against it. The dashed lines show the hyperbolic threshold defined by H = 1.1. (The dotted line threshold is explained in section 3.) The center region is the hole, which is excluded from sampling. Any air in

quadrants 1 and 4 which has a product of w'/σ_w and CO'_2/σ_{CO_2} with magnitude sufficient to exceed the hyperbolic threshold H is considered a significant updraft, and air outside the threshold in quadrants 2 and 3 is a significant downdraft. (Recall that w' is positive in quadrants 1 and 4 (updrafts) and negative in quadrants 2 and 3 (downdrafts).) Note that there are very few points in the countergradient quadrants (2 and 4) that fall outside the threshold; without explicitly ignoring these quadrants, we can effectively remove the influence of them on HREA air collection. Thus HREA sampling allows the existing concentration gradient in the atmosphere to be more fully exploited than does REA (by focusing on the most significant instantaneous flux events).

The HREA method requires that means and standard deviations for w and CO_2 or other scalars be known at the time of sampling. This is impossible in a true Reynolds average sense, as the statistics of the flow can only be computed after the fact. However, digital recursive filters are now routinely used to compute means for turbulence statistics [McMillen, 1988; Shuttleworth et al., 1984; Baldocchi and Meyers, 1991], and thus this requirement should present no problem.

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Figure 2. Normalized two-dimensional frequency distribution of CO'_2 (multiplied by -1) versus w'. Dashed lines indicate a hyperbolic REA (HREA) sampling hole size of 1.1, and the dotted line indicates the change of threshold in quadrant 3 associated with the asymmetric HREA approach.

We also borrow from hole analysis the concept of time fraction. For a given hole size a certain amount of air is excluded from analysis. This means that only a fraction of a given flux measurement period will be sampled as updrafts or downdrafts. The fractions of 10-Hz samples actually collected for updrafts and downdrafts, relative to the total number of samples in the measurement period, are referred to as updraft and downdraft time fractions, respectively. As hole size increases, time fractions will decrease, and volume of sampled air will also decrease (since sampling flow rate must remain constant). Thus there is a practical analytical limit to hole size, which we must determine in order to maximize updraft/downdraft differences.

3. Methods

We investigated the limits of standard REA thresholds and HREA hole sizes with a series of simulations. Fast (10 Hz) turbulent data were collected for a variety of scalars, and these time series were analyzed with simulated REA and HREA sampling. With these simulations we examined how far the thresholds can be extended to maximize mixing ratio differences in updrafts and downdrafts. We also examined the effectiveness of the HREA technique when an easily measured scalar (such as virtual temperature) is substituted for the scalar of interest in making updraft/downdraft decisions.

3.1. Site Description

This study was conducted August 14–23, 1996, at the Walker Branch Watershed, a mixed deciduous forest representative of the Eastern deciduous biome. The watershed is located on the United States Department of Energy Reservation near Oak Ridge, Tennessee (35°57'30" latitude, 84°17'15" longitude), at 365 m elevation. The forest is composed of uneven stands of oak (*Quercus* spp.), hickory (*Carya* spp.), red maple (*Acer rubrum*), and scattered pine (*Pinus echinata* Mill. and *Pinus virginiana* Mill.). Mean annual precipitation and temperature are 1.39 m and 14.5°C, respectively. Further site details are given by Johnson and van Hook [1989].

Flux measurements were made from a 44-m instrument tower located at the site. The mean height of the forest canopy during this experiment was 26 m.

3.2. Instrumentation

Sensible heat, latent heat, and carbon dioxide fluxes were measured at 37 m using the eddy covariance (EC) technique, as described by *Baldocchi and Harley* [1995]. Briefly, CO_2 and H_2O vapor fluctuations were measured with an open-path,

infrared absorption gas analyzer [*Auble and Meyers*, 1992]. Wind velocity and virtual temperature fluctuations were measured using a triaxial sonic anemometer (SWS-211/3K, Applied Technologies, Inc., Boulder, Colorado) with a 15-cm path length. Virtual heat fluxes were converted to sensible heat fluxes [*Schotanus et al.*, 1983]. Humidity measurements for this conversion were obtained using an HMP-35A sensor (Vaisala, Inc., Woburn, Massachusetts). All flux measurements during this study were made over a sample period of 30 min, and all turbulent data were collected at 10 Hz.

The EC technique was also used to measure isoprene fluxes, at 40 m. A second triaxial sonic anemometer (SAT-211/3K, Applied Technologies, Inc., Boulder, Colorado) was located at this height. Isoprene mixing ratio was measured using a commercially available ozone-induced chemiluminescence instrument called a fast isoprene system (FIS) (Hills Scientific, Boulder, Colorado). A recent study demonstrated that this instrument is suitable for eddy covariance measurements [Guenther and Hills, 1998]. Sampled air for the FIS was pumped from within 10 cm of the sonic anemometer path through a 460-cm length of 0.64-cm OD Teflon tubing to a reaction cell, where it was reacted with 4% ozone produced by a high-voltage discharge ozonizer. This reaction produces excited-state products, which emit light that is detected with a photomultiplier tube. Delay time through the sample inlet was calculated by examining the cross correlation between isoprene and vertical wind for each 30-min sample period. Calibrations were performed several times daily using a NIST-traceable standard (5.85 ppmv isoprene in N_2) that was diluted to 0-40ppb using internal mass flow controllers.

3.3. REA and HREA Simulations

From the larger data set, all unstable (defined following convention as z/L < 0, where z is measurement height (meters) above zero plane displacement and L is Obukhov length (meters)) 30-min periods were selected from August 20, 21, and 22, 1996, when turbulent data were available for CO_{2} , H_2O , temperature (T), and isoprene, a total of 60 periods in all. During the majority of periods the net CO₂ flux was photosynthetic (downward), but a few unstable early morning periods exhibited net respiratory fluxes. Coordinate rotations were performed for each period [e.g., Kaimal and Finnigan, 1994] to align measurements with the mean wind, forcing \bar{v} and \bar{w} to zero. This rotation is not possible during an actual REA measurement, as air must be sampled before all the data for the rotation are available. However, Bowling et al. [1998] show that rotation errors in measured REA fluxes at this site are minimal. Density corrections [Webb et al., 1980; Pattey et al., 1992] were not applied, as our purpose was simply to compare REA, HREA, and EC fluxes, for which the corrections will not differ.

Five types of simulations were performed. The first was standard REA sampling with a constant w threshold (w_t) , varying from 0.0 to 0.6 m s⁻¹. For a scalar c, any sample with $w' > w_t$ was considered an updraft, and these updraft samples were mathematically averaged over the 30-min period to get \bar{c}_{up} in equation (1) (vice versa for downdrafts). Sonic virtual temperature (T) was sampled in the same fashion, and the b coefficient for the period was calculated by rearranging (1) as

$$b = \frac{w'T'}{\sigma_w(\bar{T}_{up} - \bar{T}_{dn})}$$
(3)

Note that we use an empirical rather than theoretical [Businger and Oncley, 1990; Baker et al., 1992; Pattey et al., 1993] approach, based on our own REA measurements of isoprene [Bowling et al., 1998] and CO₂ fluxes [Oncley et al., 1993], as well as the simulation results of Katul et al. [1996]. This scalar similarity approach assumes that the b value calculated for T can be used for other scalars (CO₂, H₂O, and isoprene), an assumption that we address later in this paper. The values for b, \bar{c}_{up} , and \bar{c}_{dn} for all REA and HREA simulations in this paper were calculated using this approach. The definitions of updrafts and downdrafts, however, differed for each of the five simulations.

The second simulation involved REA sampling with a threshold dependent on σ_w (calculated for each 30-min period), where w_t ranged from $0.2\sigma_w$ to $1.4\sigma_w$, with $w' > w_t$ for updrafts and $w' < -w_t$ for downdrafts.

The third sampling method was HREA, with hole size (*H*) varying from 0.25 to 1.50. Samples with $|(w'/\sigma_w)(c'/\sigma_c)| < H$ were always rejected, those with $|(w'/\sigma_w)(c'/\sigma_c)| > H$ and w' > 0 were considered updrafts, and those with $|(w'/\sigma_w)(c'/\sigma_c)| > H$ and w' < 0 were considered downdrafts.

The fourth simulation involved HREA with an asymmetric hyperbola in quadrant 3 only, which was found to be necessary to keep downdraft time fractions close to updraft time fractions, a consequence of the skewness of the probability density distributions of the scalars (see section 4 for details). The only difference in HREA and asymmetric HREA is that for the latter, the portion of the hyperbola that lies in quadrant 3 is moved toward the origin from its original location. This is illustrated by the dotted line in Figure 2. Since for REA or HREA our sampling protocol is arbitrary anyway, this has the desired effect of maintaining more constant downdraft time fractions. Again, samples with $|(w'/\sigma_w)(c'/\sigma_c)| < H$ were always rejected, and those with $|(w'/\sigma_w)(c'/\sigma_c)| > H$ and w' > 0 were considered updrafts. A sample in quadrant 2 was considered a downdraft if $|(w'/\sigma_w)(c'/\sigma_c)| > H$, and in quadrant 3 downdrafts were defined by $|(w'/\sigma_w)(c'/\sigma_c)| >$ H/2.

The fifth simulation was identical to the fourth except in quadrant 3, where H/m was used as the cutoff instead of the arbitrary H/2. The parameter *m* is based on skewness of the probability density distribution for each scalar as described in section 4.

4. Results and Discussion

Results for the simulations with CO₂ fluxes are shown in Table 1. The basic REA case with no threshold shows an average difference in CO₂ mixing ratio (Δ CO₂) in updrafts and downdrafts for all 60 periods of 1.87 ppm. The 60 periods represent fluxes throughout the day, so this average is not a physically or biologically meaningful value. However, we can use it to compare the relative effectiveness of these techniques. The lack of perfect correlation between REA and EC fluxes is due to lack of perfect scalar similarity between T and CO_2 , since the *b* value for REA was calculated from temperature data (equation (3)). As the threshold size increases, ΔCO_2 increases, with a corresponding decrease in time fractions and b. Note the correlations remain high but the fit to the 1:1 line degrades (i.e., $\Sigma d_{YX}^2 / \Sigma y^2$ increases). There is an important practical limit to the size of the threshold, as enough air must be collected for analysis. Assuming (1) a constant sampling flow rate of 350 cm² min⁻¹, (2) a volume requirement for

Table 1. Results of Simulation of REA and HREA Sampling Techniques for CO₂ Fluxes at the Walker Branch Watershed

Method	Hole Size,	Up Time Fraction	Down Time Fraction	ΔCO_2 ,	h	r ²	$\sum d^2 - \sum v^2$
	111-5	Taction	Traction	ррш	υ	/	$\Delta u_{YX'} \Delta y$
REA							
	0.0	0.49(0.04)	0.51(0.04)	1.87 (1.05)	0.58(0.10)	0.983	1.06
	0.1	0.38(0.05)	0.41(0.06)	2.18 (1.23)	0.48(0.07)	0.992	0.53
	0.2	0.29(0.08)	0.31 (0.08)	2.48 (1.46)	0.43 (0.04)	0.996	0.30
	0.3	0.23 (0.09)	0.23 (0.08)	2.71 (1.87)	0.38 (0.04)	0.973	1.67
	0.4	0.17(0.08)	0.16(0.08)	2.98 (2.14)	0.33 (0.12)	0.983	1.03
	0.5	0.13 (0.07)	0.11(0.07)	3.27 (2.08)	0.31 (0.11)	0.928	4.74
	0.6	0.10(0.06)	0.08(0.05)	3.54 (1.88)	0.28 (0.16)	0.951	3.23
REA							
	$0.2\sigma_w$	0.41 (0.03)	0.43 (0.04)	2.18 (1.20)	0.49 (0.07)	0.989	0.73
	$0.4\sigma_w$	0.33 (0.03)	0.35(0.03)	2.44 (1.35)	0.44(0.05)	0.993	0.45
	$(0.6\sigma_w)$	(0.27(0.03))	(0.28(0.03))	(2.68 (1.49))	(0.40(0.03))	(0.996)	(0.24)
	$0.8\sigma_w$	0.21 (0.02)	0.21 (0.02)	2.91 (1.62)	0.37 (0.02)	0.997	0.16
	$1.0\sigma_w$	0.17(0.02)	0.15(0.02)	3.11 (1.77)	0.35 (0.04)	0.996	0.22
	$1.2\sigma_w$	0.12(0.02)	0.11(0.01)	3.26 (1.92)	0.34 (0.12)	0.988	0.78
	$1.4\sigma_{w}$	0.09(0.02)	0.07(0.01)	3.37 (2.08)	0.41(1.07)	0.766	3.23
HREA	w						
	0.25	0.29(0.03)	0.30(0.04)	2.99 (1.60)	0.36(0.05)	0.985	0.97
	0.50	0.21(0.02)	0.20(0.04)	3.77 (1.96)	0.30 (0.05)	0.977	1.48
	0.75	0.16(0.02)	0.13(0.03)	4.42 (2.21)	0.24(0.05)	0.966	2.29
	1.00	0.13(0.03)	0.09(0.03)	4.92 (2.44)	0.22(0.05)	0.949	3.57
	1.25	0.11(0.03)	0.06(0.02)	5.31 (2.69)	0.21(0.09)	0.841	10.9
	1.50	0.09(0.02)	0.04(0.02)	5.60 (3.05)	0.22(0.13)	0.732	23.3
HREA $(H/2)$							
	0.25	0.29(0.03)	0.35(0.04)	2.98 (1.53)	0.36(0.05)	0.987	0.83
	0.50	0.21(0.02)	0.27(0.05)	3.76 (1.79)	0.28(0.05)	0.978	1.32
	0.75	0.16(0.02)	0.22(0.04)	4.42 (2.00)	0.24(0.05)	0.965	2.20
	1.00	0.13 (0.03)	0.18(0.04)	4.94 (2.18)	0.22(0.05)	0.952	3.07
	(1.10)	(0.12(0.03))	(0.16(0.04))	(5.11(2.26))	(0.21(0.05))	(0.947)	(3.40)
	1.20	0.11 (0.03)	0.15 (0.04)	5.27 (2.35)	0.21 (0.05)	0.942	3.68
	1.25	0.11(0.03)	0.14(0.03)	5.35 (2.39)	0.20(0.05)	0.941	3.79
	1.50	0.09(0.02)	0.12(0.03)	5.68 (2.65)	0.20(0.08)	0.918	5.18
	1.75	0.08(0.02)	0.10(0.03)	5.99 (2.91)	0.17(0.12)	0.896	7.36
HREA (H/m)	11/0	0.00 (0.02)	0110 (0100)	(1))	(0112)	0.020	100
(11,)	0.5	0.21(0.02)	0.21(0.06)	3.58 (2.22)	0.31(0.52)	0.796	29.32
	0.75	0.16(0.02)	0.15(0.06)	4.17 (2.64)	0.19(0.63)	0.846	17.86
	1.0	0.13(0.03)	0.11(0.05)	4.70 (3.13)	0.35(0.89)	0.825	17.88
	1.0	0.12(0.03)	0.09(0.04)	4 88 (3 33)	0.29(0.44)	0.850	15.61
	1.1	0.12(0.03)	0.09(0.01)	5.03 (3.54)	0.25(0.11)	0.484	143.4
	1.2	0.11(0.03)	0.08(0.04)	5 11 (3 62)	0.25(0.37)	0 464	172.7
	1.25	0.09(0.02)	0.06(0.04)	541(3.02)	0.25(0.51) 0.26(0.42)	0.409	425.7
	1.0	0.09 (0.02)	(+0.0) 00.0	5.71 (5.77)	0.20 (0.72)	0.702	743.7

Data are from 60 unstable 30-min sampling periods over 3 days in August 1996 and are presented as means (standard deviation). ΔCO_2 is the average magnitude of the difference in $[CO_2]$ in updrafts and downdrafts; r^2 is the coefficient of determination of a least squares linear regression between REA (or HREA) fluxes and EC fluxes. The error statistic in the rightmost column is the ratio of the unexplained to explained sum of squares (multiplied by 100), a measure of goodness of fit to a 1:1 line [Sokal and Rohlf, 1995]. Other terms are as defined in the text. The REA threshold recommended by Oncley et al. [1993] and the asymmetric HREA hole size selected in this study (H/2) are shown in the two rows of values in parentheses.

analysis of 1 L of air, and (3) a 30-min sampling period, a time fraction of 0.10–0.15 seems an appropriate minimum (maximum threshold of 0.5 m s⁻¹; Table 1). Thus the standard constant-threshold REA technique can only improve ΔCO_2 by 3.54 ppm/1.87 ppm or a factor of 1.8 over the simple REA case with no threshold.

If instead we allow the threshold to change between 30-min periods (but remain constant within any given period) by making it a function of σ_w , we can improve ΔCO_2 to 3.26 ppm or so ($w_t = 1.2\sigma_w$; Table 1) and still sample enough air for analysis. This is not an improvement for ΔCO_2 over the simple REA case, but note that the time fractions (and thus sampled volumes) become much more consistent, a benefit which is desirable from an analytical standpoint. The r^2 values and the 1:1 fit are also much better. The first row of values in parentheses in Table 1 shows the threshold of $0.6\sigma_w$ which optimizes both the signal-to-noise ratio and statistical sampling uncertainty [Oncley et al., 1993]. Our results suggest that this threshold may be more conservative than necessary.

The results for HREA simulations are also shown in Table 1. As hole size is increased, time fractions decrease as well, but not equally for updrafts and downdrafts. Downdraft time fractions are consistently less than those for updrafts, limiting H with our sampling volume criterion to about 0.75. ΔCO_2 increases as expected to 4.42 ppm, but the low downdraft time fractions force a more conservative hole size.

This is a consequence of the fact that updrafts and downdrafts are not symmetric with respect to scalar mixing ratio in the presence of a vertical concentration gradient. Mean probability density distributions for all 60 periods for w and the scalars are shown in Figure 3. The density for w is fairly symmetric, as has been noted by many workers at z/h near 1.5 and greater (see *Raupach et al.* [1996] for review). However, the distributions for the scalars are all fairly skewed to the left



Figure 3. Probability density distributions of w, CO₂, q, T, and isoprene (IP) at Walker Branch, scaled so each has an area of 1. Lines drawn are average probability densities of sixty 30-min periods.

(q, T, and isoprene) or to the right for those scalars with net sinks at the surface (CO₂). The skewness of a random variable *x* is defined as [*Kaimal and Finnigan*, 1994]

$$Sk_x = \overline{(x')^3} / \sigma_x^3 \tag{4}$$

Average skewness for these variables was w (0.06), CO₂ (-0.16), q (0.37), T (0.90), and isoprene (1.09). Skewed probability distributions for wind velocity have been observed at many sites, including the Walker Branch [Baldocchi and Meyers, 1988], and have also been noted for temperature [Maitani and Shaw, 1990; Amiro, 1990; Katul et al., 1997b]. For T, q, and isoprene, there tend to be more samples below the mean value than above, and the distribution has a very sharp cutoff on the low (left) side of Figure 3. These are minimum values for each scalar, representing the effect of the well-mixed boundary layer above, and are associated with downdrafts. Updrafts tend to carry air with higher mixing ratios, as the sources for these scalars (T, q, and isoprene) are the vegetation canopy below the instruments. For CO₂, photosynthetic drawdown diminishes mixing ratios in the canopy, and thus updrafts carry less CO₂ than downdrafts. Hence the distribution is skewed to the right. Air in the convective boundary layer above the instruments is well-mixed and represents the background [CO₂] that mixes with biologically influenced CO₂ from below.

This skewness in the CO_2 distribution is apparent in Figure 2 as a strong concentration of points in quadrant 3 (recall CO_2 was inverted in this figure). When using a symmetric hyperbolic sampling threshold, it is clear that this skewness results in lower downdraft time fractions than updraft time fractions, and thus with a minimum sampling volume criterion we are forced to use a smaller hole size.

For this reason we modified the sampling criterion in quadrant 3, arbitrarily moving the hyperbola toward the origin (the H/2 method), to bring the time fractions closer together. From the results in Table 1 we see that an asymmetric hole size of H = 1.25 provides average time fractions of 0.11 and 0.14 for updrafts and downdrafts, respectively, while extending ΔCO_2 to 5.35 ppm. These time fractions are averages of all 60 periods; examination of the full data set (not shown) suggests that the more conservative hole size of H = 1.1 will achieve a factor of 2.7 improvement over simple REA while providing time fractions that are greater than 0.1 for virtually every run. An important limitation is introduced upon using an asymmetric hole: The direction of the flux must be assumed a priori. This is a potential problem for a scalar such as CO_2 over a forest that exhibits both upward (respiratory) and downward (photosynthetic) fluxes over a diurnal cycle. However, at present it is unlikely that isotope ratio differences will be discernible except under the strongest midday flux conditions (see Figure 7), so this limitation is not serious.

In principle, it would be preferable to base the change in quadrant 3 on some measure of skewness rather than choose an arbitrary value such as H/2 as done here. Various studies have shown that the difference in time fraction in quadrants 1 and 3 can be related directly to the skewness of either horizontal wind velocity (for momentum flux [*Nakagawa and Nezu*, 1977; *Nagano and Tagawa*, 1988]) or scalars (for scalar flux [*Katul et al.*, 1997a]). On the basis of a third-order cumulant expansion of the joint probability density function for w and a scalar c, *Katul et al.* [1997a] derive the relationship

$$D_{\text{sweep}} - D_{\text{eject}} = \frac{Sk_c}{3\sqrt{2\pi}}$$
(5)

where Sk_c is the skewness of the scalar distribution and D_{sweep} and D_{eject} are the time fractions in quadrants 3 and 1, respectively (the fractions of total samples that fall in quadrants 3 or 1, without considering a hyperbolic hole). Dividing both sides by D_{eject} and rearranging terms, we get

$$D_{\text{sweep}} = \left(\frac{Sk_c}{3D_{\text{eject}}\sqrt{2\pi}} + 1\right) D_{\text{eject}}$$
(6)

Figure 4. The parameter *m* as a function of the skewness of the probability density distributions for CO_2 , *T*, *q*, and isoprene (IP). Both quantities are dimensionless. The skewness for CO_2 has been multiplied by -1 for consistency with the other scalars (which are generally directed upward), since the time periods represented here are predominantly photosynthetic (downward). Each point represents a single 30-min flux measurement period.

Let

$$m = \frac{Sk_c}{3D_{\text{eject}}\sqrt{2\pi}} + 1 \tag{7}$$

and then

$$D_{\rm sweep} = mD_{\rm eject} \tag{8}$$

So rather than using H/2 as the asymmetric hole size in quadrant 3, we can use H/m, where *m* is a function of the skewness for the scalar of interest. The relationship between *m* and Sk_c for each scalar in this study is shown in Figure 4. Note that the majority of points fall between m = 1 (the symmetric HREA case) and m = 2 (the arbitrary value chosen earlier) and that there is a nearly linear relationship except under cases of extreme skewness. The skewness for a Gaussian distribution (which is symmetric about the mean) is zero, for which *m* approaches 1.

We repeated the HREA simulations for CO₂ flux using this strategy, and the results are shown in Table 1. At first glance this method seems inferior to the H/2 method, with poor r^2 and $\sum d_{YX}^2/\sum y^2$ values and lower ΔCO_2 for a given hole size. Recall that we have assumed a downward CO₂ flux, which is clearly in error early in the morning and late in the day. The distribution for CO₂ at these times is skewed far to the left (positive skewness, shown inverted in Figure 4 for consistency)) instead of to the right, as shown in Figure 3. During these periods, *m* approaches zero and the time fraction outside the hyperbola H/m in quadrant 3 becomes too small to adequately reconstruct the flux. These points contribute to the poor results shown in Table 1. When the five points with m < 0.5 are removed for the H = 1.1 case, ΔCO_2 improves to 5.35 ± 2.17 ppm (1 standard deviation), r^2 improves to 0.902, and $\sum d_{YX}^2 / \sum y^2$ improves to 5.77. This is not a substantial improvement in ΔCO_2 over the H/2 method but is based on a physical flow parameter and is thus more appealing.

However, the value for the hole size H remains arbitrary at this stage, regardless of how we treat the asymmetry in quadrant 3. We cannot compute the skewness for a scalar distribution in a given measurement period until after the fact, and it is unlikely that skewness for the previous sample period would be an acceptable substitute. A "running-skewness" computation for use in controlling REA valves during actual sampling could be accomplished using recursive filters as described earlier but would add additional computation time to sampling decisions and may not be feasible within the 100-ms (10 Hz) time window available. Further, since this method does not perform as well as the H/2 method in all cases, we feel it is an unnecessary complication for practical application of this technique. On the basis of this analysis, we choose the H/2 asymmetric sampling strategy with H = 1.1 as our best threshold and examine these simulations further.

In Figure 5, plots of HREA flux using this hole size versus eddy covariance flux are shown for CO2, latent heat, and isoprene for all 60 periods, with 1:1 lines for comparison. For the simulations in the left panels we used w and each particular scalar (CO₂, H₂O, and isoprene in Figures 5a, 5c, and 5e, respectively) as the basis for sampling decisions. The comparison is good for CO₂ and latent heat but poor for isoprene. Updraft and downdraft mixing ratios for isoprene measured during this experiment using REA with gas chromatography [Bowling et al., 1998] ranged from 0.9 to 10.1 ppb, the lower values associated with downdrafts. The isoprene sensor used has a detection limit of about 1 ppb isoprene, and so downdraft mixing ratios were often obscured by instrument noise. Since the HREA method biases the sampling to extreme values along the concentration gradient, it performs rather poorly. This is a measurement artifact but illustrates one limitation of the HREA technique.

For the simulations in Figures 5b, 5d, and 5f we used w and sonic virtual temperature (instead of each scalar) as the basis for sampling decisions. Such an approach would be necessary if the HREA technique was applied to scalars which cannot be measured fast enough for eddy covariance. Although the fit is tight, in each case the HREA technique underestimates the flux under strong flux conditions. This is especially true for isoprene. It is under these conditions that the probability density distributions for these scalars are most skewed, and often the skewness for temperature is the most pronounced (data not shown). Baldocchi et al. [1999] have shown the importance of differing source footprints in this forest for isoprene and CO_2 flux. Since the sources of isoprene (strictly oak species), water vapor (transpiration from all trees and understory plants, and soil evaporation) and sensible heat (the entire forest) are different, differences in probability distribution for these scalars are not surprising. If the HREA sampling pattern is based on the structure of the probability density function for temperature, we are unlikely to sample correctly a scalar with a different distribution. Thus using temperature and wind as a sampling basis for HREA measurements is likely to lead to an underestimate of the true flux.

This calls into question our assumption of scalar similarity. The open circle and the triangle in Figure 5a correspond to time periods August 20, 1230–1300 local standard time (LST) and August 21, 1200–1230 LST, respectively. Figure 6 shows





Figure 5. Simulation results (asymmetric HREA flux (H/2 method) versus eddy covariance flux) for CO₂ (Figures 5a and 5b), latent heat (LE) (Figures 5c and 5d), and isoprene (Figures 5e and 5f) flux. HREA sampling decisions for the left panels were based on w and CO₂ (Figure 5a), H₂O (Figure 5c), or isoprene (Figure 5e). Those in the right panels were based on w and sonic virtual temperature (T). Hole size = 1.1 for all six panels. Each data point represents a single 30-min flux. The open circle and triangle in Figure 5a correspond to time periods in Figure 6. In all cases, b values were calculated from the T time series using equation (3) for each 30-min time period.

the probability density distributions for CO₂ (inverted for comparison) and temperature for these periods. The open circle in Figure 5a falls on the 1:1 line, and the distributions are very similar. However, the relationship (triangle) deviates substantially from the line when the distributions differ (Figures 6c and 6d). In fact, removing those periods in Figure 5a where the skewness parameters for CO₂ and *T* differ in sign improves the r^2 value from 0.947 (n = 60) to 0.972 (n = 43). Thus, during those periods when the scalar similarity assumption between CO₂ and *T* is valid, the HREA technique works well and is less robust when the assumption is false. This is manifested as low HREA fluxes when wind and virtual temperature are used to make sampling decisions for other scalars (Figures 5b, 5d, and 5f).

For the purposes of simulation we used sonic temperature to calculate *b* from (3). This has been successful with actual REA measurements of isoprene [*Guenther et al.*, 1996; *Bowling et al.*, 1998] and CO₂ [*Pattey et al.*, 1993] and for other scalars in simulations [*Katul et al.*, 1996]. However, we stress that calculating *b* from sonic temperature data is unnecessary for actual experimental use of HREA to measure CO₂ or H₂O fluxes, as we can calculate *b* directly from the 10-Hz data sets for these



Figure 6. Probability density distributions for (a) $-1 \times CO_2$ and (b) *T* for August 20, 1230–1300 LST, the point denoted by the open circle in Figure 5a, and for (c) $-1 \times CO_2$ and (d) *T* for August 21, 1200–1230 LST, denoted by the triangle in Figure 5a. Distributions are scaled to have an area of 1.

scalars. (Had we done this in our simulations the relationships in Figure 5 would be exactly 1:1.) Thus the scalar similarity assumption is not a concern for actual use of this technique in the field for these scalars.

However, our goal is to collect updraft and downdraft air for isotope analysis and calculate the net fluxes of ${}^{13}C^{16}O_2$ and ${}^{12}C^{18}O^{16}O$. To do this using (1), we must assume scalar similarity between total CO₂ and these isotopic forms. For a measured difference in isotope ratio between extreme updrafts and downdrafts in an HREA sample to be the correct difference in total updrafts and downdrafts, the isotope ratio of CO₂ must be linearly related to $[CO_2]$ during any sampling period, at all timescales relevant to a flux measurement (100 ms to 30 min). There is some evidence to support this assumption at the longer timescales in this range. Traditionally, δ^{13} C in whole air samples has been regressed versus 1/[CO2], and this relationship is linear [*Keeling*, 1958], implying δ^{13} C is hyperbolic with [CO₂]. However, during a given 30-min flux measurement period, the existing vertical gradient in [CO₂] is small, and a linear fit between isotope ratio and [CO2] is reasonable [Flanagan et al., 1996]. At present, there is no evidence to address the validity of this assumption at very short timescales, as required by the HREA technique. However, it can be tested experimentally by constructing a plot of δ^{13} C versus [CO₂] for updraft and downdraft samples collected using hyperbolic REA and comparing it with the relationship for whole air samples collected at longer timescales (minutes to hours).

Indeed, if this linear relationship can be established with sufficient confidence, we can calculate isotope fluxes of CO_2 using eddy covariance combined with this mathematical relation. However, this slope is likely to change over a season for ¹³C and ¹⁸O and over the diurnal cycle for ¹⁸O [*Buchmann et al.*, 1997], as the influence of evaporative enrichment in leaves is most pronounced at midafternoon and absent at night. Thus such an approach would require an extensive flask sampling protocol combined with eddy covariance measurements and would likely be limited to a few days of measurements at most.

Numerous studies have demonstrated the linearity of the Keeling relationship [*Keeling*, 1958, 1961; *Yakir and Wang*, 1996; *Buchmann et al.*, 1997; *Trolier et al.*, 1996; *Lloyd et al.*, 1996; *Friedli et al.*, 1987; *Flanagan et al.*, 1997], and from these we take a general average slope for the δ^{13} C versus [CO₂] relationship to be -0.05% ppm⁻¹ for δ^{13} C and -0.03% ppm⁻¹ for δ^{18} O. Figure 7 summarizes the difference in CO₂ mixing ratio in updrafts and downdrafts from our REA and HREA simulations versus time over the 3 days of simulations.



Figure 7. Difference in simulated CO₂ mixing ratios in updrafts and downdrafts for the 60 measurement periods versus time. Squares denote REA sampling with no threshold, crosses indicate REA with a wind threshold of $1.2\sigma_w$, and solid circles indicate asymmetric HREA (H/2 method) based on w and CO₂, with a hole size of 1.1. The axes on the right are expected isotopic differences in updrafts and downdrafts assuming slopes of $-0.05\%_0$ ppm⁻¹ for δ^{13} C and $-0.03\%_0$ ppm⁻¹ for δ^{18} O. Solid bars on the isotope axes show the mass spectrometer precision of *Trolier et al.* [1996] for each.

The axes on the right use the above slopes to predict the corresponding difference in isotope ratio. The bars on the isotope axes correspond to published values for mass spectrometer precision [*Trolier et al.*, 1996] for each. It is clear that the simple REA case does not provide much of a signal above instrument uncertainty and that the best ($w_t = 1.2\sigma_w$) REA case is not much better. However, the asymmetric HREA simulation results suggest that during conditions of strong midday CO₂ flux, differences in isotope ratio between updrafts and downdrafts may be large enough to resolve using current mass spectrometers with confidence.

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References

- Amiro, B. D., Comparison of turbulence statistics within three boreal forest canopies, *Boundary Layer Meteorol.*, 51, 99–121, 1990.
- Amundson, R., L. Stern, T. Baisden, and Y. Wang, The isotopic composition of soil and soil-respired CO₂, Geoderma, 82, 83–114, 1998.
- Antonia, R. A., Conditional sampling in turbulence measurements, Annu. Rev. Fluid Mech., 13, 131–156, 1981.
- Auble, D. L., and T. P. Meyers, An open path, fast response infrared absorption gas analyzer for H₂O and CO₂, *Boundary Layer Meteorol.*, 59, 243–256, 1992.
- Baker, J. M., J. M. Norman, and W. L. Bland, Field-scale application of flux measurement by conditional sampling, *Agric. For. Meteorol.*, 62, 31–52, 1992.
- Baldocchi, D. D., and P. C. Harley, Scaling carbon dioxide and water vapour exchange from leaf to canopy in a deciduous forest, II, Model testing and application, *Plant Cell Environ.*, 18, 1157–1173, 1995.
- Baldocchi, D. D., and T. P. Meyers, Turbulence structure in a deciduous forest, *Boundary Layer Meteorol.*, 43, 345–364, 1988.
- Baldocchi, D. D., and T. P. Meyers, Trace gas exchange above the floor of a deciduous forest, 1, Evaporation and CO₂ efflux, *J. Geophys. Res.*, 96, 7271–7285, 1991.
- Baldocchi, D. D., J. D. Fuentes, D. R. Bowling, A. A. Turnipseed, and R. K. Monson, Scaling isoprene fluxes from leaves to canopies: Test cases over a boreal aspen and a mixed-species temperate forest, *J. Appl. Meteorol.*, in press, 1999.

Bergstrom, H., and U. Hogstrom, Turbulent exchange above a pine

- forest, II, Organized structures, *Boundary Layer Meteorol.*, 49, 231–263, 1989.
- Bowling, D. R., A. A. Turnipseed, A. C. Delany, D. D. Baldocchi, J. P. Greenberg, and R. K. Monson, The use of relaxed eddy accumulation to measure biosphere-atmosphere exchange of isoprene and other biological trace gases, *Oecologia*, 116, 306–315, 1998.
- Buchmann, N., J.-M. Guehl, T. S. Barigah, and J. R. Ehleringer, Interseasonal comparison of CO₂ concentrations, isotopic composition, and carbon dynamics in an Amazonian rainforest (French Guiana), *Oecologia*, 110, 120–131, 1997.
- Businger, J. A., and S. P. Oncley, Flux measurement with conditional sampling, J. Atmos. Oceanic Technol., 7, 349–352, 1990.
- Cellier, P., and Y. Brunet, Flux-gradient relationships above tall plant canopies, Agric. For. Meteorol., 58, 93–117, 1992.
- Ciais, P., et al., A three-dimensional synthesis study of δ^{18} O in atmospheric CO₂, 1, Surface fluxes, *J. Geophys. Res.*, 102, 5857–5872, 1997a.
- Ciais, P., et al., A three-dimensional synthesis study of δ^{18} O in atmospheric CO₂, 2, Simulations with the TM2 transport model, *J. Geophys. Res.*, *102*, 5873–5883, 1997b.
- Coppin, P. A., M. R. Raupach, and B. J. Legg, Experiments on scalar dispersion within a model plant canopy, II, An elevated plane source, *Boundary Layer Meteorol.*, 35, 167–191, 1986.
- Duncan, M. R., and P. H. Schuepp, A method to delineate extreme structures within airborne flux traces over the FIFE site, J. Geophys. Res., 97, 18,487–18,498, 1992.
- Farquhar, G. D., J. R. Ehleringer, and K. T. Hubick, Carbon isotope discrimination and photosynthesis, *Annu. Rev. Plant Physiol. Plant Mol. Biol.*, 40, 503–537, 1989.
- Farquhar, G. D., J. Lloyd, J. A. Taylor, L. B. Flanagan, J. P. Syvertsen, K. T. Hubick, S. C. Wong, and J. R. Ehleringer, Vegetation effects on the isotope composition of oxygen in atmospheric CO₂, *Nature*, 363, 439–443, 1993.
- Flanagan, L. B., J. R. Brooks, G. T. Varney, S. C. Berry, and J. R. Ehleringer, Carbon isotope discrimination during photosynthesis and the isotope ratio of respired CO₂ in boreal forest ecosystems, *Global Biogeochem. Cycles*, 10, 629–640, 1996.
- Flanagan, L. B., J. R. Brooks, G. T. Varney, and J. R. Ehleringer, Discrimination against C¹⁸O¹⁶O during photosynthesis and the oxygen isotope ratio of respired CO₂ in boreal forest ecosystems, *Global Biogeochem. Cycles*, 11, 83–98, 1997.
- Francey, R. J., and P. P. Tans, Latitudinal variation in oxygen-18 of atmospheric CO₂, *Nature*, 327, 495–497, 1987.
- Friedli, H., U. Siegenthaler, D. Rauber, and H. Oeschger, Measurements of concentration, ¹³C/¹²C and ¹⁸O/¹⁶O ratios of tropospheric carbon dioxide over Switzerland, *Tellus, Ser. B*, 39, 80–88, 1987.
- Goulden, M. L., J. W. Munger, S.-M. Fan, B. C. Daube, and S. C. Wofsy, Measurements of carbon sequestration by long-term eddy covariance: Methods and a critical evaluation of accuracy, *Global Change Biol.*, 2, 169–182, 1996.
- Guenther, A. B., and A. J. Hills, Eddy covariance measurement of isoprene fluxes, *J. Geophys. Res.*, *103*, 13,145–13,152, 1998.
- Guenther, A. B., et al., Isoprene fluxes measured by enclosure, relaxed eddy accumulation, surface layer gradient, mixed layer gradient, and mixed layer mass balance techniques, *J. Geophys. Res.*, *101*, 18,555–18,567, 1996.
- Hesterberg, R., and U. Siegenthaler, Production and stable isotopic composition of CO₂ in a soil near Bern, Switzerland, *Tellus, Ser. B*, 43, 197–205, 1991.
- Johnson, D. W., and R. I. van Hook (Eds.), Analysis of Biogeochemical Cycling Processes in Walker Branch Watershed, 401 pp., Springer-Verlag, New York, 1989.
- Kaimal, J. C., and J. J. Finnigan, Atmospheric Boundary Layer Flows, Their Structure and Measurement, 289 pp., Oxford Univ. Press, New York, 1994.
- Katul, G. G., P. L. Finkelstein, J. F. Clarke, and T. G. Ellestad, An investigation of the conditional sampling method used to estimate fluxes of active, reactive, and passive scalars, *J. Appl. Meteorol.*, 35, 1835–1845, 1996.
- Katul, G., C.-I. Hsieh, G. Kuhn, D. Ellsworth, and D. Nie, Turbulent eddy motion at the forest-atmosphere interface, J. Geophys. Res., 102, 13,409–13,421, 1997a.
- Katul, G., G. Kuhn, J. Schieldge, and C.-I. Hsieh, The ejection-sweep character of scalar fluxes in the unstable surface layer, *Boundary Layer Meteorol.*, 83, 1–26, 1997b.
- Keeling, C. D., The concentration and isotopic abundances of atmo-

spheric carbon dioxide in rural areas, Geochim. Cosmochim. Acta, 13, 322–334, 1958.

- Keeling, C. D., The concentration and isotopic abundances of atmospheric carbon dioxide in rural and marine air, *Geochim. Cosmochim. Acta*, 24, 277–298, 1961.
- Keeling, C. D., R. B. Bacastow, A. F. Carter, S. C. Piper, T. P. Whorf, M. Heimann, W. G. Mook, and H. Roeloffzen, A three-dimensional model of atmospheric CO₂ transport based on observed winds, 1, Analysis of observational data, in *Aspects of Climate Variability in the Pacific and Western Americas, Geophys. Monogr. Ser.*, vol. 55, edited by D. H. Peterson, pp. 165–236, AGU, Washington, D. C., 1989.
- Lancaster, J., Carbon-13 fractionation in carbon dioxide emitting diurnally from soils and vegetation at ten sites on the North American continent, Ph.D. thesis, Univ. of Calif., San Diego, 1990.
- Lloyd J., et al., Vegetation effects on the isotopic composition of atmospheric CO₂ at local and regional scales: Theoretical aspects and a comparison between rain forest in Amazonia and a boreal forest in Siberia, *Aust. J. Plant Physiol.*, 23, 371–399, 1996.
- Maitani, T., and R. H. Shaw, Joint probability analysis of momentum and heat fluxes at a deciduous forest, *Boundary Layer Meteorol.*, 52, 283–300, 1990.
- McMillen, R. T., An eddy correlation technique with extended applicability to non-simple terrain, *Boundary Layer Meteorol.*, 43, 231– 245, 1988.
- Nagano, Y., and M. Tagawa, Statistical characteristics of wall turbulence with a passive scalar, J. Fluid Mech., 196, 157–185, 1988.
- Nakagawa, H., and I. Nezu, Prediction of the contributions to the Reynolds stress from bursting events in open-channel flows, J. Fluid Mech., 80, 99–128, 1977.
- Nakazawa, T., S. Sugawara, G. Inoue, T. Machida, S. Makshyutov, and H. Mukai, Aircraft measurements of the concentrations of CO₂, CH₄, N₂O, and CO and the carbon and oxygen isotope ratios of CO₂ in the troposphere over Russia, *J. Geophys. Res.*, *102*, 3843–3859, 1997.
- Oncley, S. P., A. C. Delany, T. W. Horst, and P. P. Tans, Verification of flux measurement using relaxed eddy accumulation, *Atmos. Environ.*, 27A, 2417–2426, 1993.
- Pattey, E., R. L. Desjardins, F. Boudreau, and P. Rochette, Impact of density fluctuations on flux measurements of trace gases: Implications for the relaxed eddy accumulation technique, *Boundary Layer Meteorol.*, 59, 195–203, 1992.
- Pattey, E., R. L. Desjardins, and P. Rochette, Accuracy of the relaxed eddy-accumulation technique, evaluated using CO₂ flux measurements, *Boundary Layer Meteorol.*, 66, 341–355, 1993.
- Raupach, M. R., J. J. Finnigan, and Y. Brunet, Coherent eddies and turbulence in vegetation canopies: The mixing-layer analogy, *Bound*ary Layer Meteorol., 78, 351–382, 1996.
- Schimel, D. S., B. Braswell, E. Holland, R. McKeown, D. Ojima, T. Painter, W. Parton, and A. Townsend, Climatic, edaphic, and biotic controls over storage and turnover of carbon in soils, *Global Biogeochem. Cycles*, 8, 279–293, 1994.
- Schmid, H. P., Source areas for scalars and scalar fluxes, *Boundary Layer Meteorol.*, 67, 293–318, 1994.
- Schotanus, P., F. T. M. Nieuwstadt, and H. A. R. De Bruin, Temperature measurement with a sonic anemometer and its application to heat and moisture fluxes, *Boundary Layer Meteorol.*, 26, 81–93, 1983.
- Shaw, R. H., On diffusive and dispersive fluxes in forest canopies, in *The Forest-Atmosphere Interaction*, edited by B. A. Hutchinson and B. B. Hicks, pp. 407–419, D. Reidel, Norwell, Mass., 1985.
- Shaw, R. H., J. Tavangar, and D. P. Ward, Structure of the Reynolds stress in a canopy layer, J. Clim. Appl. Meteorol., 22, 1922–1931, 1983.
- Shuttleworth, W., et al., Eddy correlation measurements of energy partition for Amazonian forest, Q. J. R. Meteorol. Soc., 110, 1143– 1162, 1984.
- Sokal, R. R., and F. J. Rohlf, *Biometry*, 887 pp., W. H. Freeman, New York, 1995.
- Sternberg, L. S. L., S. S. Mulkey, and S. J. Wright, Ecological interpretation of leaf carbon isotope ratios: Influence of respired carbon dioxide, *Ecology*, 70, 1317–1324, 1989.
- Trolier, M., J. W. C. White, P. P. Tans, K. A. Masarie, and P. A. Gemery, Monitoring the isotopic composition of atmospheric CO₂: Measurements from the NOAA Global Air Sampling Network, J. Geophys. Res., 101, 25,897–25,916, 1996.
- Trumbore, S. E., Comparison of carbon dynamics in tropical and temperate soils using radiocarbon measurements, *Global Biogeochem. Cycles*, 7, 275–290, 1993.

- Webb, E. K., G. I. Pearman, and R. Leuning, Correction of flux measurements for density effects due to heat and water vapour transfer, *Q. J. R. Meteorol. Soc.*, *106*, 85–100, 1980.
- Yakir, D., and X.-F. Wang, Fluxes of CO₂ and water between terrestrial vegetation and the atmosphere estimated from isotope measurements, *Nature*, 380, 515–517, 1996.

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