Feasibility of $^{13}\text{CO}_2$ eddy covariance flux measurements using a pulsed quantum cascade laser absorption spectrometer

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Abstract
Better quantification of atmosphere-ecosystem exchange of the isotopologues of CO$_2$ could substantially improve our ability to probe underlying physiological and ecological mechanisms controlling ecosystem carbon exchange, but the ability to make long-term continuous measurements of the isotopic composition of exchange fluxes has been limited by measurement difficulties. Quantum cascade (QC) lasers are a new generation of infrared light sources that offer increased stability and power for absorption spectroscopy applications, including the measurement of atmospheric CO$_2$ isotope ratios, and promise substantial improvements over existing instruments: smaller size, increased robustness, and most significantly for remote or long-term field deployments, no need for cryogenic cooling of laser or detectors. In this paper, we used simulations to test whether the performance of a prototype pulsed QC laser-based isotope-ratio absorption spectrometer (and plausible improvements thereon) is sufficient for making direct eddy covariance measurements of the isotopic composition of CO$_2$ fluxes above a mid-latitude temperate forest (Harvard Forest, in central Massachusetts, USA). We found that the simulated isoflux measurement error associated with the prototype instrument is not more than ~1.5 to 2 times larger than the irreducible “meteorological” noise inherently associated with turbulent flux measurements above this ecosystem (daytime measurement error SD of ~60% of flux versus meteorological noise of 30-40% for instantaneous half-hour fluxes), and that plausible instrument improvements could increase precision to the point where measurement error is comparable to or less than the meteorological noise (measurement error SD reduced to ~ 25% of half-hourly flux; and to ~10% or less of mean 10-day mean hourly flux). This suggests that QCL-based isotope ratio absorption spectroscopy should be able to approach the precision at which sensor error is not a limiting factor in measuring CO$_2$ isotope fluxes via eddy covariance.
1. Introduction

Stable isotope ratios of carbon and oxygen in CO$_2$ have long been recognized as a tool for identifying sources and sinks of atmospheric CO$_2$ and for probing the processes and mechanisms that together control carbon cycling. In particular, the different isotopic composition of CO$_2$ in photosynthetic flux ($F_{\text{photo}}$) versus respiratory flux ($F_{\text{resp}}$) may be used to partition net ecosystem exchange (NEE) of CO$_2$ into these component fluxes, which in turn would allow analysis of the underlying mechanisms controlling these distinct processes (Yakir and Wang, 1996). Appropriate isotopic measurements would allow the simultaneous solution of the pair of equations (1):

\begin{align*}
F_{\text{net}} &= F_{\text{photo}} + F_{\text{resp}} \quad (1a) \\
\delta_{\text{net}} F_{\text{net}} &= \delta_{\text{photo}} F_{\text{photo}} + \delta_{\text{resp}} F_{\text{resp}} \quad (1b)
\end{align*}

where $F_x$ is an ecosystem flux component, and $\delta_x$ is the corresponding isotopic composition of $F_x$, (the subscript being $\text{net}$ for net flux; $\text{photo}$ for photosynthetic flux; and $\text{resp}$ for respiratory flux).

This approach can be employed using measurements of isotopic composition of either the carbon or the oxygen in CO$_2$. Carbon-based partitioning is possible because the carbon isotopic composition of respiring organic matter often differs slightly from the organic matter being concurrently photosynthesized (Bowling et al., 1999). Oxygen-based partitioning is possible because the oxygen isotopic composition of soil water typically differs strongly from that of leaves (Craig and Gordon 1965; Barnes and Allison, 1988; Flanagan et al., 1991). Isotopic exchange between these leaf and soil waters and gas-phase CO$_2$ then means that the air surrounding photosynthesizing leaves will commonly have very different CO$_2$
isotopic composition ($\delta^{18}O_{CO2}$) than does respired CO$_2$ from soils (Farquhar et al., 1993; Tans 1998; Stern et al., 1999). Choosing which tracer to use in such a partitioning involves trade-offs: the end-member pools determining carbon isotopic composition of net CO$_2$ flux may be directly characterized, but their differences are usually very small. The end-member water pools controlling the oxygen isotopic composition of net CO$_2$ flux are almost always very different (potentially leading to easily resolvable differences between flux components), but the relevant water pools are harder to define (Ogee et al. 2004). Prudent research strategy requires continuous measurements of isotopic composition of fluxes of both carbon and oxygen in CO$_2$. It may also be helpful for the CO$_2$ partitioning problem to measure the isotopic composition of the water flux, since this is related to the end member water pools which also influence $\delta^{18}$O of CO$_2$ (Lee et al., in press).

$F_{net}$ is currently measured via eddy covariance continuously at hundreds of sites around the world, as part of the FLUXNET project (http://daac.ornl.gov/FLUXNET/), but measurements of the isoflux ($\delta_{net}F_{net}$) and the end-members $\delta_{photo}$ and $\delta_{resp}$ are more challenging and so far have been almost entirely limited to one-day experiments (Yakir and Wang, 1996; Ogee et al., 2003, 2004), multi-day but limited field campaigns (Flanagan et al. 1997) or long-term but sparse sampling (Bowling et al., 2001; Lai et al, 2003, 2004). Wider usage of stable isotopes in ecosystem exchange studies has been impeded by the complication that existing instrumentation using isotope ratio mass spectrometry (IRMS) – the standard method for determining trace gas stable isotope ratios for many applications other than measuring eddy covariance fluxes – requires samples to be collected in flasks and returned to the laboratory for analysis, a tedious method for measurements that we would like to make continuously. Although recent advances in automated sample collection systems
(Flanagan, et al. 1997; Bowling, et al. 1999; Bowling, et al. 2001; Mortazavi and Chanton 2002; Lai, et al. 2003; Torn, et al. 2003) make IRMS-based applications less cumbersome, tunable infrared laser differential absorption (TILDAS), a broad class of instrumentation which includes tunable diode laser absorption spectroscopy, TDLAS, which has been applied to eddy covariance flux measurements of such trace gases as CH$_4$, N$_2$O, and NO$_2$ (Zahniser et al., 1995; Fowler et al., 1995; Horii et al., 1999; Werle et al., 2001; Kormann et al., 2001), promises simple in situ isotope measurements at high-frequency that IRMS will never match for eddy covariance applications.

Recently, conventional lead-salt tunable diode lasers have been adapted to atmospheric isotope ratio measurements in concentrations of CO$_2$ and H$_2$O vapor, demonstrating the potential and power of technology that can make continuous in situ measurements (Becker et al. 1992; Kerstel et al., 1999; Bowling et al., 2003; Griffis et al., 2004; Castrillo et al., 2005; Lee et al., in press). However, these instruments have not yet been employed in measuring eddy covariance fluxes because the need for frequent drift-correcting calibrations complicates the flux calculations that need to be integrated for as much as 30 min (at least in forest ecosystems). Concentration measurements are sufficient for obtaining gradients and hence estimating fluxes over low-stature ecosystems with aerodynamically smooth vegetation cover such as grasslands and agricultural fields (e.g., Griffis et al., 2004 calculated isotopic fluxes from gradients measured over a soybean field using lead-salt laser technology), but for fluxes over tall vegetation ecosystems such as forests, this approach is logistically difficult because it would require concentration measurements well above the roughness sublayer, typically at an infeasibly high altitude for most tower-based measuring platforms. Hence, in forest ecosystems, the eddy covariance
method is preferable. In addition, lead-salt technology is cumbersome and requires cryogenic cooling of the laser source. These characteristics make such technology less than ideal for taking full advantage of the principle strength of the eddy covariance method as a research tool, which is the ability to integrate continuous fluxes over extended time periods in remote field sites (Barford et al., 2001; Saleska et al., 2003).

A new generation of laser light sources, quantum cascade (QC) lasers, can provide alternative sources of mid-infrared radiation that can overcome some of the difficulties associated with lead-salt diode lasers by providing near room temperature operation, and increased power output. Since QC lasers were first demonstrated (Faist et al., 1994), they have undergone rapid development and can now provide the combination of high precision, long-term stability, and low temperature sensitivity that is needed for good-quality eddy covariance measurements at remote field sites (Nelson et al., 2004; Jimenez et al., 2005). When operated in pulsed mode, quantum cascade lasers overcome the limitations of lead-salt lasers by operating with single mode at near-room temperature and with highly stable mode output. In particular, the power levels are substantially higher than even the best lead-salt lasers, allowing the use of thermoelectrically cooled infrared detectors for a totally cryogen-free operation (Nelson et al., 2004), a significant advantage for field deployment.

In this paper, we test whether the performance characteristics of an existing prototype QC laser-based isotope-ratio TILDAS (and plausible improvements thereon) are sufficient for making scientifically useful direct eddy covariance measurements of the isotopic composition of fluxes above a forest ecosystem. First, we briefly describe the design of the prototype instrument (full details are provided elsewhere (McManus et al., 2005)), and present data characterizing instrument performance in the laboratory in measuring $^{13}\text{C}/^{12}\text{C}$
isotope ratios in CO$_2$ at ambient concentrations. We also characterize the improved performance levels that we expect to achieve in a planned field-deployable isotope ratio instrument, based on current performance of a similar instrument already developed for ambient $^{12}$CO$_2$ concentration measurements from airborne platforms.

Second, we discuss the technical requirements for making eddy covariance measurements of the isotopic composition of net ecosystem exchange of between forest ecosystems and the atmosphere, and propose a specific criterion for judging whether a sensor’s performance is sufficient to achieve the kind of science goals typically pursued by eddy covariance measurements of net ecosystem exchange.

Finally, we test whether the performance level of our QC-TILDAS isotope-ratio sensor (in both prototype and target development forms) meets the proposed criteria. We do this by: (a) simulating the $^{13}\text{C}/^{12}\text{C}$-CO$_2$ isoflux above a real forest ecosystem (Harvard Forest, in central Massachusetts) from existing CO$_2$ eddy covariance measurements and from isotope data derived from flasks (giving a result that for the purposes of sensor evaluation we treat as “true”), (b) sampling from this simulation after adding “measurement error” (where characteristics of the error term are derived from laboratory tests of the sensor) and recalculating the isoflux (giving an estimate of the isoflux that would be “measured” by the proposed sensor), and finally, (c) comparing how closely the “measured” isoflux approaches the “true” (simulated) isoflux in light of the proposed criteria.

2. Instrument and Methods

2.1. QCL spectrometer

2.1.1. Prototype instrument

The design principles and construction details for our prototype QCL spectrometer are discussed in full in McManus et al.[submitted], but we briefly review them here. The
instrument (see schematic, Figure 1) combines a commercially available QC-laser (ALPES Lasers, www.alpeslasers.com) operated in pulse mode, an optical system, and a computer-controlled system that incorporates the electronics for driving the QC-laser along with signal generation and data acquisition. The spectrometer is devised for simultaneous measurement of absorption (sample), pulse normalization (reference) and frequency-lock spectra from the QC-laser. The laser used here can be tuned to the infrared frequencies between 2310 cm\(^{-1}\) and 2315 cm\(^{-1}\). Based on a suite of selection criteria discussed in McManus et al., (2002; 2005), we used a pair of CO\(_2\) absorption lines near 2311 cm\(^{-1}\) (2311.399 cm\(^{-1}\) for \(^{13}\)CO\(_2\) and 2311.105 cm\(^{-1}\) for \(^{12}\)CO\(_2\)), as suggested by Weidmann et al., (2004).

A key feature of the design of the optical system is a dual-path multi-pass cell which compensates for the large (factor of 100) difference in concentration between major and minor isotopologues of CO\(_2\). Our approach, previously implemented with a conventional lead-salt diode laser McManus et al., (2002), uses path lengths that differ by a factor of 74, implemented with a multi-pass astigmatic Herriott cell (base length 0.32 m) in which the different path lengths (0.753 m and 56.08 m) are defined by the number of cell passes (either 2 or 174). This approach overcomes a significant problem in the spectroscopic measurement of isotopic abundances since the measurement of two isotopic species using lines of similar strength but very unequal concentrations leads to low accuracy, with either the minor constituent having too small an absorption depth, or the major constituent having too great an absorption depth. If lines with unequal strength are chosen to compensate for the absorption depth imbalance, then accuracy tends to suffer due to the greater temperature sensitivity of the weaker strength line. Here, the dual path approach greatly lessens the effect of temperature variations in the instrument environment; the temperature stability requirement is virtually negligible (180 K / 0.1 ‰) using the chosen line pairs at 2311 cm\(^{-1}\).
Two data acquisition cards simultaneously measured both species using two InSb photovoltaic detectors. The detectors were LN2 cooled in this prototype unit. The laser was scanned over a 0.5 cm\(^{-1}\) range at 4 kHz. Spectra were co-averaged in real time and fit with our TDLWINTEL (Nelson et al., 2002; 2004) data acquisition software to retrieve continuous mixing ratios of both isotopologues. Although fitting rates of 20 Hz can be obtained, the preliminary data here are reported at 10 Hz. A spectral pair is shown in Figure 2.

Absolute spectroscopic mixing ratios are calculated using the HITRAN data base parameters (Rothman et al. 2003), the measured pressure, temperature, path lengths and the laser line width. The laser line width is convolved with the molecular absorbance model during the fitting to account for non-linear effects at higher optical depths. The isotopologue line strengths in HITRAN are scaled by their nominal natural abundances. For \(^{13}\)CO\(_2\) this scaling factor is 0.01124, the ratio of the Pee Dee Belemnite (PDB) international standard. Directly retrieved mixing ratios are typically within ~5% of true values even with no rescaling or calibration (e.g. Figure 2 shows 345 ppm for \(^{12}\)CO\(_2\) and 333 ppm for \(^{13}\)CO\(_2\)/01124 compared to known value of 350 ppm in reference air). However, high-accuracy applications like those proposed here would require routine calibration for both isotopologues to account for residual uncertainties in the laser line shape and absorption baseline.

2.1.2. Prototype performance

We assessed instrument precision by alternatively sampling gases at 1 Hz from Mylar bags prepared from two sources: an ultra zero air tank containing 350 ppm total \(^{12}\)CO\(_2\) and unknown \(\delta^{13}\)C ("sample") and a "reference" mixture of CO\(_2\) with \(\delta^{13}\)C\(_{\text{PDB}}\) = -49.4 ‰. Reference air was made by diluting gas from a tank of pure CO\(_2\) (\(\delta^{13}\)C\(_{\text{PDB}}\) = -49.4 ‰ as determined by mass spectrometry in the laboratory of Prof. Dan Schrag at Harvard University) with dry N\(_2\) in an airtight Mylar bag to match sample gas \([^{12}\text{CO}_2]\) of ~350ppm.
and the same $\delta^{13}_C$PDB as the reference tank (-49.4 ‰). The reference tank was presumably prepared from combustion of CH$_4$ which is light in $^{13}$C relative to atmospheric CO$_2$.

This assessment (Figure 3) shows that the difference between sample and reference is obtainable with a precision of 0.1‰ ($2\sigma$ standard error of mean of 11 samples) in 10 minutes of analysis time. The SD, 0.18 ‰ with 30 s measurement time shows that this prototype instrument already approaches the best reported literature values using lead-salt TDLs (Bowling et al. 2003).

We evaluated the long term stability of the prototype QCL using the Allan variance technique (Allan 1966; Werle et al., 1993) which distinguishes high frequency random variations in the measurement from systematic variations at longer time scales. To summarize briefly, on a log-log plot in which the variance of repeated measurements of a sample with fixed concentration or isotope ratio is plotted against the averaging time $t$ over which each of those repeated measurements is averaged (called an Allan plot), the variance will generally decrease with time if the measurement error is random, because integrating over longer times will average away random fluctuations. If measurement error is a pure random white noise (with power spectrum that is a constant independent of frequency), the variance ($\sigma^2$) will decrease with $t^{-1}$ ($\sigma$ decreases as $t^{-1/2}$), and a log-log plot of variance versus integration time would be expected to have a slope of -1. If measurement errors are random but correlated, then the measurement variance will still decrease, but not as rapidly (in particular, in the case of so called “pink noise,” which has a power spectrum $\sim 1/f^{0.5}$, where $f$ is frequency, the variance falls with a slope of -1/2). If there are systematic drifts at longer timescales due to temperature, optical instability, or laser instability, then repeated measurements averaged at those time-scales or longer will be systematically different from
each other (because of the drift) and hence have larger and larger variances. The integration
time (called $\tau_{\text{allan}}$) at which the minimum variance occurs (called $\sigma_{\text{allan}}^2$) characterizes
instrument stability and defines a time-scale that divides the time domain into a region in
which random noise fluctuations can be averaged over ($t < \tau_{\text{allan}}$) and a region ($t > \tau_{\text{allan}}$) in
which systematic drift dominates. Measurement errors due to systematic drifts should be
corrected by periodic external calibrations using reference gas with known concentration and
isotope ratio, with $\tau_{\text{allan}}$ useful in choosing an optimal calibration frequency for maintaining
long-term precision.

A 10 Hz time series and Allan plot of the $^{13}\text{CO}_2/^{12}\text{CO}_2$ ratio are shown in Figure 4 for
a 4 hour period with ambient air sealed in the sampling cell at 7 Torr. The time series of the
$^{13}\text{CO}_2/^{12}\text{CO}_2$ ratio has a 0.1 s rms of 1‰ which ideally would decrease to 0.1‰ after 10 s if
measurement error were random white noise. However, the measurement error behaves like
a process intermediate between white noise and $1/f^{0.5}$ “pink” noise, indicating that there
are some correlations in noise sources at time scales of 0.1-100 sec (Figure 4). The variance
has a broad minimum between at 200 and 800 seconds with a minimum corresponding to
$\sigma_{\text{Allan}} = 0.11‰$. There is a greater proportional decrease from 1 s to 200 s for the isotope
ratio than for either of the isotopologues measured separately (not shown), indicating that
some of the contributing noise sources such as laser line width variation and peak position
stability are correlated and cancel when the ratio is taken.

2.1.3. Development target instrument

Figure 3 and Figure 4 together characterize the performance of our prototype isotope
ratio QCL spectrometer. We believe that further modifications to instrument design can
improve on this performance, and we describe here the characteristics of a “development
target” instrument incorporating these improvements. In particular, we note that the existing prototype design has no reference cell. The addition of reference cells (one paired with each path in the sample cell) with column densities roughly equal to that in the corresponding sample path should increase measurement stability and precision. This is because the largest sources of noise in the 1 to 100 second time scales are residual laser frequency fluctuations affecting both the peak position and the laser line width. Since the magnitude of these uncertainties will scale directly with the absorption area, reducing the absorption area by dividing the sample cell spectrum by a reference spectrum obtained from an equal column density reference cell will increase measurement precision.

This technique of reference cell normalization has been employed before in absorption instrumentation (e.g. the widely used Licor CO₂ infrared gas analyzer, though not a spectroscopic instrument, achieves high precision with matched sample and reference cells, and the same principle is used in a commercially-available isotope–ratio spectrometer using conventional lead-salt technology, Bowling et al, 2003; Griffis et al., 2004). We have already implemented this technique in the context of QCL technology with a high-precision ¹²CO₂ QCL sensor currently under development at ARI for deployment on aircraft (Jimenez et al, in prep). This sensor measures only the ¹²CO₂ isotopologue, but the technology is otherwise similar to the prototype isotope ratio instrument discussed above.

The ¹²CO₂ aircraft sensor operates in difference mode using two matched 10 cm cells (one for sample air and one for a known reference) and dividing sample spectrum by reference spectrum before fitting. We plan in future work to apply the same technique to the isotope ratio spectrometer, by adding two 10 cm path cells – one flushed with 0.2% CO₂ reference gas (to balance the short path), and one flushed with 20% CO₂ reference gas (to
balance the long path). Balancing the absorption before spectral fitting will minimize
sensitivity to laser linewidth changes and frequency stability in the lasers. For the purposes
of this paper, we quantify the effects of planned improvements in order to simulate their
effects on measured eddy covariance fluxes.

2.1.4. Development target performance

We quantify the improvement expected from this potential modification by
considering the performance of the existing $^{12}$CO$_2$ QCL sensor (Jimenez et al, in prep). As
discussed above, this sensor is designed to measure absolute $^{12}$CO$_2$ concentrations only, not
isotope ratios, but the technique of reference cell normalization should have comparable
stabilizing effects on $^{13}$CO$_2$ isotopologue. Thus, the characteristics of the existing $^{12}$CO$_2$
QCL instrument allow us to conservatively define the expected performance of a
“development target” isotope ratio spectrometer.

The Allan plot for this sensor (Figure 5) shows a lower 1-sec rms noise (100 ppb
CO$_2$, or about 0.3‰ of ambient), a more rapid initial decrease (along the $t^{-1}$ line between 1 to
30 seconds) and a greater long-term stability (the minimum approached at 200 seconds
remains virtually flat to ~1500 secs) than in the prototype isotope ratio spectrometer (Figure
4). The minimum corresponds to a precision of 20 ppb or 0.05‰ of ambient CO$_2$. Such an
instrument should allow us to obtain an rms precision on isotope ratios of 0.1‰ with 10 s
averaging time, and to push calibration intervals to 1500 s (25 min).

A summary of relevant specifications and performance characteristics in the
prototype and development target spectrometers (compared to the most closely related
commercially available alternative) is in Table I.
2.2. Requirements for Eddy covariance measurements

Eddy covariance measurements of net ecosystem exchange (NEE) of CO₂ (in μmoles m⁻² s⁻¹) are typically calculated as (Goulden et al., 1996):

\[
NEE = \rho w'[CO₂] + \rho \frac{d}{dt} \int_0^h [CO₂](z) dz \quad (2)
\]

where \(\rho\) is molar density of air (moles m⁻³), \(w'[CO₂]\) (in ppm m s⁻¹) is the w-CO₂ covariance (\(w\) being vertical wind in m/s and \([CO₂]\) being molar concentration of carbon dioxide), and the second term on the right is the storage flux, the change in the CO₂ column stored in the canopy air. The primes in the covariance term derive from Reynolds decomposition, by which a series \(x_t\) is written (for some time period) as \(\bar{x} + x'_t\), where \(x'_t\) are the fluctuations from the mean value across the time period. CO₂ is carried when CO₂ fluctuations in one direction are consistently associated with fluctuations in vertical wind (e.g. during nighttime efflux, vertical wind and CO₂ are positively correlated). The storage flux can be especially important in tall vegetation such as forests when attempting to measure the hour-by-hour flux without bias. However, the purpose of this paper is to assess the suitability of a sensor to measure covariances (not to estimate net ecosystem exchange), so we neglect consideration of a storage flux term in what follows.

The isotopic composition of the eddy covariance flux of CO₂, called the isoflux, is defined, for the carbon isotopic composition, as \(\rho w'(\delta^{13}C \cdot [CO₂])\) (units: μmoles CO₂ m⁻² s⁻¹ ‰) (Bowling et al., 2001), and can be thought of as the product of CO₂ flux and its isotopic composition (expressed in δ units). For simplicity in what follows, we neglect the effect of molar air density \(\rho\), and report raw covariances (ppm m s⁻¹ for CO₂ flux, and ppm m s⁻¹ ‰ for isoflux).
Eddy covariance measurements impose strong technical requirements on sensor technology, including: (1) rapid response time (less than one second, sufficient to characterize the high-frequency transport flux); (2) long-term stability (sufficient to integrate continuous measurements for 20-30 minutes without drift), and (3) high precision and resolution (so that the small fluctuations that constitute the eddy flux signal can be quantified). Here we analyze the ability of the prototype and development target instruments to meet these requirements, using the conditions at Harvard Forest in central Massachusetts.

Long-term eddy covariance fluxes at Harvard Forest have typically been acquired at 5 or 10 Hz, but spectral analysis of these data show that 2 Hz sampling is adequate to capture most high-frequency fluctuations (Goulden et al., 1996). Since laser absorption spectroscopy systems routinely acquire data at 10 Hz or more, sensor response time is not a technical hurdle here. Response time in the proposed instrument will be limited as much by flow rates and cell-flushing time as by the speed with which spectra can be acquired, and in any case a sampling rate of 2 Hz or better is not an issue.

Difficulty in achieving sufficient long-term stability has been a limiting factor in lead-salt tunable-diode lasers, but the inherent stability of the QC lasers when drift corrected by matched sample and reference cells (as illustrated by the performance of the $^{12}$CO$_2$ QCL sensor, Figure 5, above) shows that past 200 secs integrating time, the Allan variance for this sensor is flat for integrating times out to at least 1200-1500 sec (20-25 minutes). We anticipate similar performance in the isotope ratio QC laser system, which would allow for uninterrupted eddy covariance integration. Calibrations would be interspersed between each separate eddy covariance integration, to ensure long-term stability in isotopic measurements.
The need for precise high-resolution measurements poses a technical challenge for eddy covariance measurements of isotope ratios, because it is crucial that the differences in atmospheric concentration between updrafts and downdrafts be adequately resolved. To quantify the required sensor resolution, we simulated measurements of $^{13}\text{C}/^{12}\text{C-}\text{CO}_2$ isofluxes from Harvard Forest using existing CO$_2$ eddy covariance measurements and isotope data derived from flasks (simulation methods are described in the next section), and then formulated an objective criterion to judge whether measurement performance was sufficient to achieve the kind of science goals typically pursued by eddy covariance measurements of net ecosystem exchange.

The criterion asks: is the error attributable to the measurement comparable to or less than the inherent meteorological noise associated with turbulence flux measurements? If this criterion is satisfied, it means that the instrument is as good as it needs to be to achieve flux measurements of maximum resolution in a given ecosystem, since further reductions in sensor measurement error cannot give improvements in flux resolution because such improvements are limited by the irreducible noise of turbulent fluxes.

2.3. Simulation methods
2.3.1. Simulating Isoflux and associated measurement error
First, we simulate the $^{13}\text{C}/^{12}\text{C-}\text{CO}_2$ isoflux above a real forest ecosystem (Harvard Forest, in central Massachusetts) from existing CO$_2$ eddy covariance measurements and from isotope data derived from flasks. Net Ecosystem exchange of CO$_2$ (NEE) has been measured by eddy covariance at Harvard Forest since 1991, and the site, measurement methods and analysis are described in detail in other publications (e.g. Goulden et al., 1996; Barford et al., 2001). Periodic measurements of the concentration and isotopic composition of atmospheric CO$_2$ at Harvard Forest are reported in Lai et al. (2004), and exhibit a well-
defined relation, in which $\delta^{13}C$ is proportional to $1/[CO_2]$ (Figure 6A), known as a Keeling plot relation. From the long-term eddy flux dataset and the $\delta^{13}C$ vs. CO$_2$ relation, we simulate the high-frequency carbon isotope ratio time series ($\delta^{13}C_{sim}$) and from this calculate the half-hourly isoflux ($\langle w' \cdot (\delta^{13}C_{sim} \cdot [CO_2])' \rangle$) (Figure 6), following a method used by Ogee et al. (2003), and similar to an approach first used by Bowling et al. (1999), who used a regression linear in [CO$_2$] rather than in $1/[CO_2]$. For the purposes of sensor evaluation we treat this simulated isoflux as “true”.

Next, in order to quantify the effect of sensor error, we simulate the measured isoflux by adding measurement error to the “true” (simulated) $\delta^{13}C_{sim}$ time series:

$$\delta^{13}C_{measured}(t) = \delta^{13}C_{sim}(t) + \varepsilon(t) \quad (2)$$

and then recalculating the isoflux as $\langle w' \cdot (\delta^{13}C_{measured} \cdot [CO_2])' \rangle$. We use four different error time series for $\varepsilon(t)$: $\varepsilon_{prot}(t)$, the actual prototype instrument error (the ratio time series in Figure 4A); $\varepsilon_{develop}(t)$, the error associated with the “development target” instrument (derived from the time series in Figure 5); $\varepsilon_{pink}(t)$, a random “pink noise” time series generated by inverse-Fourier transforming a white noise power spectrum scaled by density $1/f^{0.5}$ into the time domain; and $\varepsilon_{white}(t)$, a random white noise process. The simulated noise series’ $\varepsilon_{pink}(t)$ and $\varepsilon_{white}(t)$ were used in sensitivity analysis to explore the effect of varying magnitudes of 1 second rms noise on the isoflux measurement error.

To generate each half-hourly prototype error series, we first simulated the effect of a 20 second calibration every half-hour by taking the deviations of the ratio time series in Figure 4A from a piecewise straight-line interpolation through the endpoints of each half-hour (where each endpoint was the mean of the ratio series over 20 s). Each half-hourly
\( \varepsilon_{\text{prot}}(t) \) was then set equal to a contiguous half-hour subset of the full 10-hour “calibrated” time series by randomly selecting a starting point.

The “development target” error series \( \varepsilon_{\text{develop}}(t) \) was generated in a similar manner: first, the \( \Delta \text{CO}_2(t) \) time series in Figure 5 was transformed to approximate an isotopologue ratio series:

\[
\varepsilon_{\text{develop}}(t)(\text{raw}) = \sqrt{2} \cdot \frac{[\Delta \text{CO}_2(t) - <\Delta \text{CO}_2(t)>]}{[\text{CO}_2(\text{sample})]}
\]

where \([\text{CO}_2(\text{sample})]\) is the \( \text{CO}_2 \) concentration in the reference tank (close to ambient, \(~375 \text{ ppm}\) ). \( \varepsilon_{\text{develop}}(t)(\text{raw}) \) is expressed as per mil deviation from the mean, relative to the concentration being measured; it is inflated by \( \sqrt{2} \) to account for effect of ratiing with a hypothetical independent \(^{13}\text{CO}_2 \) series with similar noise characteristics; \( \varepsilon_{\text{develop}}(t)(\text{raw}) \) has mean zero and standard deviation 0.42‰ (= 1-sec rms noise). We believe this error series to be a conservative estimate of the likely performance of a dual reference cell \(^{13}\text{CO}_2/^{12}\text{CO}_2 \) QCL spectrometer, because it assumes that errors on the two isotopologues series are independent (hence the \( \sqrt{2} \) inflation of the actually measured series in Figure 5). By contrast, the ratio time series from the prototype sensor exhibits significantly improved noise characteristics relative to the individual time series, apparently due to canceling of correlated errors, but this effect may be smaller in a development target sensor because each individual series will already be the ratio of sample and reference cells. Finally \( \varepsilon_{\text{develop}}(t) \) is derived by “calibrating” \( \varepsilon_{\text{develop}}(t)(\text{raw}) \) according to the same method described above for \( \varepsilon_{\text{prot}}(t) \).

We note that in practice, “calibrating” the noise time series in this way had very little effect on the uncertainty of the calculated isoflux; the main reason for calibration in context
is to maintain long-term accuracy and prevent bias from creeping in to a longer time series of half-hourly isofluxes.

The magnitude of simulated isoflux measurement error was quantified using the “bootstrap” technique, i.e. by repeating the isoflux re-calculation for each of 100 bootstrap resamples on each half hour and taking the standard deviation of the 100 bootstrapped isofluxes, where each resample was generated with an independent realization of the appropriate error time series.

2.3.2 Partitioning Isoflux variation: measurement error vs. sample variation

We compared the magnitude of half-hourly sensor-induced measurement error, using the standard of criterion one, to the magnitude of “meteorological” noise. We quantified meteorological noise as the standard deviation of the “true” isoflux (i.e. without measurement noise) across different half-hours with similar environmental driving variables (photosynthetically active radiation, PAR), where “representative” half hours were taken from within a given day (within 1 hour on either side) and from nearby measurement days (within 5 days on either side).

In addition to simulating half-hourly isoflux measurements on a given day, we also calculated 10-day hourly diurnal patterns of isoflux, a common approach to characterizing ecosystem properties using noisy eddy covariance data (Wilson et al., 2003) that facilitates analysis of how mean flux patterns respond to changes in mean diurnal patterns of driving variables such as moisture, temperature and sunlight. We analyzed the overall variability in simulated measured hourly means across the 10-day averaging period by partitioning the total variability into two components: *sample variation* (the variation in “true” isoflux for a given hour across the 10 measurement days due to day-day variations in environmental
conditions and turbulent noise) and measurement error (the uncertainty on flux for a given single hour, quantified as the variation across 100 bootstrap re-“measurements” of that hour generated according to the method of the previous section). For each hour of the day, total variance on that hour can be partitioned as follows:

$$\sigma^2_{\text{Tot}} \approx \frac{1}{n_{\text{day}} n_{\text{boot}}} \sum_{d,j} (F_{d,j} - \bar{F})^2 = \frac{1}{n_{\text{day}} n_{\text{boot}}} \left[ \sum_{d} \sum_{j} (F_{d,j} - \bar{F}_d)^2 + \sum_{d} n_{\text{boot}} (\bar{F}_d - \bar{F})^2 \right]$$

$$= \frac{1}{n_{\text{day}}} \sum_{d} \sigma^2_{\text{ meas d}} + \frac{1}{n_{\text{day}}} \sum_{d} (\bar{F}_d - \bar{F})^2$$

(4)

where \(F_{d,j}\) is the \(j\)th bootstrap isoflux for that hour on day \(d\), \(\bar{F}_d\) is the mean flux for that hour on day \(d\) (across all bootstrap resamples), and \(\bar{F}\) is the grand mean flux for that hour (across all days and bootstrap resamples); \(n_{\text{day}}\) is the number of days (10), \(n_{\text{boot}}\) is number of bootstrap samples for each hour (100); and we have used the definitions

\(\sigma^2_{\text{ day}} = \frac{1}{n_{\text{day}}} \sum_{d} (\bar{F}_d - \bar{F})^2\) (sample variance across days) and \(\sigma^2_{\text{ meas (d)}} = \frac{1}{n_{\text{boot}}} \sum_{j} (F_{d,j} - \bar{F}_d)^2\) (measurement variance on day \(d\)).

In this way, the standard error for each hour, \(SE_{\text{Tot}} (= \sigma_{\text{Tot}} / \sqrt{n_{\text{day}}})\) is partitioned into

\(SE_{\text{sample}} (= \sigma_{\text{day}} / \sqrt{n_{\text{day}}})\), and \(SE_{\text{meas}} (= \sigma_{\text{meas (d)}} / \sqrt{n_{\text{day}}})\).

3. Results and Discussion

The measured eddy covariance CO₂ flux and the corresponding simulated half-hourly isoflux (Figure 7) show that: (1) the error noise structure associated with the existing prototype instrument (Figure 4A) can generate a time series of half-hour flux measurements (Figure 7) that is unbiased (Figure 8A) but which has an isoflux uncertainty per daytime
half-hour that is somewhat greater than the irreducible “meteorological” noise inherently associated with turbulent fluxes (Figure 8B); but that (2) the “development target” for the isotope ratio QCL sensor (to achieve the performance already demonstrated with the $^{12}$CO$_2$ QCL sensor, Figure 5) would enable isoflux measurements that approach the best precision that can be achieved given the inherent uncertainty introduced by atmospheric turbulence (Figure 8B). Prototype coefficient of variation (CV, the ratio of standard deviation to the mean value) falls close to that produced by a pink noise with the same 1-sec rms, while development target characteristics fall in between white and pink noise.

Note that the uncertainty on the integrated half-hour eddy covariance depends not on the ability to resolve each high-frequency data point separately, but on the uncertainty associated with $\delta^{13}$C (or whatever atmospheric scalar that is being measured) averaged over the full integration period. More precisely, it is the quantity $S_{<w'\delta'>}$ (the uncertainty on the half-hour covariance $<w'\delta'>$, where $w'$ and $\delta'$ are vertical wind and isotope ratio fluctuations, and <> indicates averaging) that must be sufficiently small. In the absence of correlated measurement errors between $w'$ and $\delta'$ (which must be absent for the eddy flux measurement method to work at all), $S_{<w'\delta'>} = <w'> S_{<\delta'>} + <\delta'> S_{<w'>} + S_{<w'>} S_{<\delta'>} = S_{<w'>} S_{<\delta'>}$ (where $S_{<<x>>}$ is the standard error of the mean of quantity x averaged over the integration period; terms like $<x'>' = 0$ by definition of the Reynolds decomposition).

The simulation demonstrates this: development target performance is a 1-sec rms noise of 0.4‰, which is approximately equal to the whole range of isotope data in Figure 6C; clearly no individual high-frequency points could be resolved with this precision. But the reduction in noise from averaging up to the half hour level can improve effective precision.
substantially, in the ideal case of pure random white noise, by a factor of $\sqrt{1800} = 42$; in
the case of random pink noise, by a factor of $1800^{1/4} = 6.51$.

The real strength of eddy covariance measurements (and the adequacy of the
performance of the QCL instrument for such measurements) becomes apparent when
measurements accumulated overall several days are averaged to produce a tightly constrained
mean diurnal curve (simulated for Harvard Forest isofluxes as measured by prototype-quality
or development-target quality instruments, in Figure 9). A dataset of many days or weeks at
a time (difficult or impossible to collect with flasks on an ongoing basis) would allow direct
observation of how such constrained flux patterns respond to variations in driving variables
such as moisture, temperature and sunlight.

In both the individual half-hourly time series (Figure 8B) and in the more relevant
aggregated 10-day diurnal cycle (Figure 9), the portion of the measurement error attributable
to instrument noise characteristics is comparable to the inherent meteorological noise
associated with turbulent fluxes. This suggests that according to the criterion comparing
measurement error to variation associated with turbulent fluxes, the performance of the QCL
isotope ratio spectrometer (in particular, the characteristics of the development target
instrument) is adequate to measure isofluxes at Harvard Forest about as well as they can be
expected to be measured.

Although in this paper we have focused on measuring the $^{13}$C/$^{12}$C ratios of CO$_2$ and
associated isofluxes, we note that the same laser can be tuned to absorption lines for
measuring the oxygen isotopic composition of CO$_2$ as well, with precision expected to be
similar to that obtained for the carbon isotopes. Thus we expect that a field-deployable
version of the prototype discussed here could be used equally well to measure the oxygen
isofluxes of CO$_2$. Indeed, with a dual laser configuration like that outlined in Jimenez et al., (2005), simultaneous high-accuracy measurement of both carbon and oxygen isotope ratios of CO$_2$ in the same sample cell should be possible.

The scientific benefit from the capacity to make continuous high-frequency $\delta^{18}$O$_{CO2}$ measurements and associated isofluxes may well be greater than that from the carbon isotopes, for at least two reasons. First, unlike $^{13}$CO$_2$ (which because of its typically very tightly constrained relation with CO$_2$ – e.g. Figure 6A – is straightforward to estimate by combining eddy flux with flask measurements, just as we have done here to simulate carbon isofluxes), there is virtually no other approach for measuring C$_{18}$OO isoflux above forest ecosystems except for hyperbolic relaxed eddy accumulation (HREA), which adds additional technical complexity to the labor-intensive processing of many flask samples (Bowling et al., 1999). Second, as recently shown in an analysis by Ogée et al. (2004), the long-run potential for effective partitioning of ecosystem CO$_2$ fluxes is likely much greater using oxygen isotopes of CO$_2$ because the isotopic disequilibrium is between $F_{photo}$ and $F_{resp}$ in equation 1 is almost an order of magnitude larger (~12 – 17 ‰) for oxygen than for carbon (~2‰). The limiting factor in using oxygen isotopes for partitioning has been the difficulty in obtaining more accurate $\delta^{18}$O$_{CO2}$ isofluxes. Thus, our preliminary experiments with measuring carbon isotope ratios in CO$_2$ using QCL absorption spectroscopy suggests that this technology shows high potential for oxygen isotopes of CO$_2$, and hence for making significant scientific progress on the CO$_2$ flux partitioning problem.

4. Conclusions
   A pulsed-quantum cascade laser spectrometer operating in the mid-infrared spectral region at 2311 cm$^{-1}$ has sufficient resolution and stability to measure $\delta^{13}$C of atmospheric
CO₂ with the speed and precision needed to enable the calculation of continuous isofluxes by eddy covariance methods. The sensor measurement error in the prototype instrument tested here is slightly larger than the irreducible “meteorological” noise inherently associated with turbulent flux measurements above the Harvard Forest ecosystem, but plausible instrument improvements (especially the addition of matched reference cells) can be expected, based on the high performance of an existing $^{12}$CO₂ sensor in which such improvements have already been incorporated, to increase precision to the point where measurement error is less than this meteorological noise. This suggests that QCL-based isotope ratio absorption spectroscopy should be able to approach the precision at which sensor error is not a limiting factor in making eddy covariance measurements of the isotopic composition of CO₂ fluxes.

The key advantages offered by a field-deployable version of this instrument are: (1) the ability to operate continuously with no need for cryogenic cooling (a significant advantage for deployment in remote field sites); (2) increased temperature stability of the isotopologue line-pairs, reducing the need for precise instrumental temperature control; and (3) increased signal stability, reducing the frequency of calibration required to maintain high precision to once every 25-30 minutes. This last advantage would make such an instrument particularly suitable for eddy covariance applications above tall vegetation, where the covariance needs to be integrated for periods of up to 30 minutes to capture the full spectrum of flux transport.

The performance of this technology in measuring carbon isotope ratios of CO₂ suggests that CO₂ oxygen isotope ratios and associated isofluxes may also be measured. Since oxygen isotopes may present better opportunities than carbon for partitioning net ecosystem fluxes of CO₂ into its photosynthetic and respiratory components, and a significant
limiting factor in oxygen-based CO₂ flux partitioning is the difficulty in accurately measuring isoflux, further development of the QCL-based absorption spectroscopy technology discussed here should present significant opportunities for making progress on the CO₂ flux-partitioning problem.
5. References


Castrillo, A., G. Casa, M. van Burgel, D. Tedesco and L. Gianfrani, First field determination of the 13C/12C isotope ratio in volcanic CO2 by diode-laser spectrometry, Optics Exp. 12, 6515-6523, 2004


Griffis, T.J., J.M. Baker, S.D. Sargent, B.D. Tanner, and J. Zhang, Measuring field-scale isotopic CO2 fluxes with tunable diode laser absorption spectroscopy and


Lee., X., S. Sargent, Ronald Smith, Bert Tanner, In-Situ Measurement of Water Vapor Isotopes for Atmospheric and Ecological Applications, Submitted to Journal of Atmospheric And Oceanic Technology.


Table I. Instrument characteristics of: demonstrated lab prototype, conservatively-estimated development target, and the most closely related commercially available alternative. Key planned development modifications to improve performance of the prototype are shaded in gray, and key advantages for field deployment and eddy-covariance measurements, relative to the current state-of-the-art, are shaded in blue.

<table>
<thead>
<tr>
<th></th>
<th>Lab Prototype (a)</th>
<th>Field-deployable development target (b)</th>
<th>Reference: current commercial state-of-the-art (c)</th>
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<tr>
<td><strong>Laser light source</strong></td>
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<td></td>
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<td>Laser type</td>
<td>Pulsed QC infrared laser</td>
<td>continuous-wave lead-salt diode</td>
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<td>Tuning range</td>
<td>2310 – 2315 cm⁻¹</td>
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<tr>
<td>Absorption lines</td>
<td>$^{13}$CO$_2$: 2314 cm⁻¹ or 2311 cm⁻¹</td>
<td>2308 cm⁻¹</td>
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<tr>
<td>temperature stability</td>
<td>(0.2 K) or (180K) per 0.1‰</td>
<td>(0.006K) / 0.1‰</td>
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<tr>
<td>required for above line</td>
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<tr>
<td>Scan rate</td>
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<tr>
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<td>1.5 m</td>
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<tr>
<td>Matched Reference cell</td>
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<td>Dual</td>
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<tr>
<td><strong>Measurement Performance</strong></td>
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<tr>
<td>1 sec rms noise</td>
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<td>0.4‰</td>
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<tr>
<td>10-sec 1-σ precision</td>
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<td>0.1‰</td>
<td>0.1‰</td>
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<tr>
<td>Allan σ minimum</td>
<td>0.1‰</td>
<td>0.05‰</td>
<td>0.1‰</td>
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<td>Stability, as indicated by</td>
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<td>200 to 1500+ s (flat)</td>
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<td>time to Allen σ² minimum</td>
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<td>(provides an indicator of time interval between calibrations)</td>
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<tr>
<td>response time</td>
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<td>cooling of laser</td>
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<td>LN$_2$</td>
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<tr>
<td>cooling of detector</td>
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Notes:
(a) Prototype performance assessed from data in Figure 4.
(b) Development target characteristics are conservatively estimated based on demonstrated performance (see Figure 5) of a similarly designed Aerodyne QC-TILDAS sensor for aircraft-based CO$_2$ concentration measurements (currently under development).
(c) TDA-100, Campbell Scientific (Logan, Utah). Based on information in Bowling et al. (2003).
Figures

Figure 1. Schematic for prototype isotope ratio QCL absorption spectrometer.

Figure 2. CO$_2$ isotopologue spectra with pulsed QC laser as recorded by TDL-WINTEL software. The cell contains 350 ppm CO$_2$ in air at a total pressure of 7 Torr. The laser line width is 0.01 cm$^{-1}$ hwhm.

Figure 3. Prototype isotope ratio QCL absorption spectrometer measurements of $^{13}$CO$_2$ and $^{12}$CO$_2$, alternating between sample air ([CO$_2$] = 350 ppm, $\delta^{13}$C$_{PDB}$ unknown) and reference air ([CO$_2$] ~ 350 ppm, $\delta^{13}$C$_{PDB}$ = -49.4 ‰), depicted as: raw time series of $^{12}$CO$_2$ and $^{13}$CO$_2$ (bottom panel), $^{13}$CO$_2$/$^{12}$CO$_2$ ratio time series (middle panel), and difference series between each sample interval and the mean of two adjacent reference intervals (top panel). Plots showing reference [12CO$_2$] ~ 345 ppm (bottom panel) and isotope ratio of 0.940 = -60‰ (middle panel) are from directly retrieved (uncalibrated) values, illustrating intrinsic sensor accuracy of ~5% without calibration (high-accuracy applications like that discussed here would require regular calibrations). The flow rate of 0.5 SLPM in a cell volume of 0.5 liters at pressure of 7 Torr corresponds to a cell flushing (1/e) time of 0.6 s. The first 5 s of each 30 s interval were discarded in taking interval means.

Figure 4. Time series (upper plot) and corresponding Allan variance plot (lower) of a 4 hour time series collected by prototype $^{13}$CO$_2$/$^{12}$CO$_2$ QCL sensor with ambient air sealed in the sample cell at 7 torr. Downward sloping straight lines on the allan plot show the theoretical behavior for white noise (slope -1) and pink noise (slope -1/2) processes.

Figure 5. Time series of $\Delta$CO$_2$ (sample tank relative to near-ambient reference tank, sampled at 1 Hz) and corresponding Allan variance plot for $^{12}$CO$_2$ measured by a CO$_2$ QCL sensor (currently in development). This sensor achieves stabilization of drift and noise (compared to the prototype isotope ratio QCL, Figure 4) by operating in difference mode using two matched 10 cm cells (one for sample air and one for a known reference) and dividing sample spectrum by reference spectrum before fitting. Downward sloping straight lines on the allan plot show the theoretical behavior for white noise (slope -1) and pink noise (slope -1/2) processes.

Figure 6. (A) Summer 2003 Harvard forest $\delta^{13}$C vs. [CO$_2$] (above canopy air sampled by flasks, see Lai et al. 2004) gives a relation allowing simulation of high-frequency $\delta^{13}$C from CO$_2$. (B) actual w-CO$_2$ covariance, and (C) simulated w-$\delta^{13}$C covariance (where $\delta^{13}$C is derived from the regression in (A)), illustrating the relatively small range of expected $\delta^{13}$C variation in a typical daytime half-hour (~0.4 ‰). Data in (B) and (C) is from July 2, 2003, 1300-1330 hrs.

Figure 7. (A) Half-hourly measured covariance between vertical wind and CO$_2$ (black points connected by lines), along with photosynthetically active radiation (PAR) on July 15, 2003. (B) Half-hourly simulated isoflux on the same day, including ±1 SD uncertainty due to measurement error in (i) prototype sensor (larger blue error bars), and (ii) “development target” sensor (smaller black error bars).

Figure 8. (A) Simulated half-hourly isoflux (for 1330-1400, July 2, 2003), including ±1 SD uncertainty (simulated from pink noise error series with spectral density ~ $1/f^{0.5}$), versus 1-
sec rms error, and (B) corresponding half-hourly isoflux coefficient of variation (CV = SD/mean) as a function of 1-sec rms error, for both white noise and pink noise processes, and for prototype and development target sensor characteristics. The hatched shaded horizontal bar is the range of uncertainty induced by meteorological fluctuations, and is the irreducible noise inherently associated with turbulent flux measurements.

**Figure 9.** (A) Mean 10-day diel Harvard Forest hourly isoflux ($<w'\cdot (\delta^{13}\text{C}:[\text{CO}_2])'>$ ± SE$_{\text{total}}$, n=10 measurement days) simulated from July 2003 eddy data. SE$_{\text{total}}$ arises from both sample variation (from day-to-day variations and turbulent noise) and from spectroscopic measurement error, simulated here for both prototype and development target sensor characteristics. SE$_{\text{total}}$ is depicted both for measurement error component arising from prototype (larger bars) and from development target (smaller black error bars) sensors. (B) prototype sensor diel SE$_{\text{total}}$ from (A) (black line) partitioned into spectroscopic measurement (orange), and sampling (blue) error components. (C) same as (B), but for development target sensor characteristics. Note that sample variation, which is independent of sensor characteristics, is the same in both (B) and (C).
FIG. 1
FIG. 2

TWO-PASS (0.74 m)  
$^{12}$CO$_2$ (2311.105 cm$^{-1}$)

MULTI-PASS (56 m)  
$^{13}$CO$_2$ (2311.396 cm$^{-1}$)
FIG. 3.
FIG. 4.
FIG. 5.
\[ \delta^{13}C_{CO_2} = -27.3(\pm 0.43) + \frac{7130(\pm 174)}{[CO_2]} \]

\[ R^2 = 0.97 \]

\[ RSE = 0.25 \text{ (on 53 d.f.)} \]

FIG. 6.
FIG. 7.
FIG. 8.
FIG. 9.