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Measurements of carbon sequestration by long-term eddy covariance: methods and a critical evaluation of accuracy

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Abstract

The turbulent exchanges of CO2 and water vapour between an aggrading deciduous forest in the north-eastern United States (Harvard Forest) and the atmosphere were measured from 1990 to 1994 using the eddy covariance technique. We present a detailed description of the methods used and a rigorous evaluation of the precision and accuracy of these measurements. We partition the sources of error into three categories: (1) uniform systematic errors are constant and independent of measurement conditions (2) selective systematic errors result when the accuracy of the exchange measurement varies as a function of the physical environment, and (3) sampling uncertainty results when summing an incomplete data set to calculate long-term exchange.

Analysis of the surface energy budget indicates a uniform systematic error in the turbulent exchange measurements of -20 to 0%. A comparison of nocturnal eddy flux with chamber measurements indicates a selective systematic underestimation during calm (friction velocity < 0.17 m s⁻¹) nocturnal periods. We describe an approach to correct for this error. The integrated carbon sequestration in 1994 was 2.1 t C ha⁻¹ y⁻¹ with a 90% confidence interval due to sampling uncertainty of ±0.3 t C ha⁻¹ y⁻¹ determined by Monte Carlo simulation. Sampling uncertainty may be reduced by estimating the flux as a function of the physical environment during periods when direct observations are unavailable, and by minimizing the length of intervals without flux data. These analyses lead us to place an overall uncertainty on the annual carbon sequestration in 1994 of -0.3 to +0.8 t C ha⁻¹ y⁻¹.

Keywords: deciduous forest, eddy correlation, micrometeorology, NEP, net ecosystem production, photosynthesis, respiration

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Introduction

Long-term measurements of the exchange of CO2 between natural vegetation and the atmosphere have the potential to markedly improve understanding of the role terrestrial ecosystems play in the global carbon cycle. Eddy covariance is a micrometeorological technique that allows a non-invasive measurement of the exchange of CO2 between the atmosphere and a several hectare area of forest, shrubland, or grassland (Baldocchi et al. 1988). Recent technical advances have made long-term eddy covariance measurements practical (Wofsy et al. 1993), opening the possibility of a global network of field stations for monitoring biosphere-atmosphere CO2 exchange (Baldocchi et al. 1996). However, investigators must first establish that the accuracy and precision of eddy covariance is sufficient to allow a reliable assessment of carbon sequestration over time scales ranging from hours to decades.

We have used the eddy covariance technique throughout the last four years to monitor the net exchanges of CO2 and H2O above the Harvard Forest, an aggrading deciduous forest in the northeastern United States. The observations span a range of climatic conditions, allowing a quantitative assessment of the physical and biological controls on whole-forest activity. In this paper we (i) describe the methods in use at Harvard Forest (ii) sum-
marize the observations of carbon flux, and (iii) evaluate the precision and accuracy of these measurements.

We partition the sources of error into three categories, and proceed by assessing each category separately. (1) **Uniform systematic errors** are constant and independent of measurement conditions (e.g. an error in the span of a gas analyser). A **uniform error of 15%** in the hourly measurements results in a 15% error in the calculation of long-term carbon sequestration. (2) **Selective systematic errors** result when the accuracy of the exchange measurement varies as a function of the physical environment. Because carbon sequestration reflects the difference between two larger fluxes, respiratory efflux during the night and photosynthetic uptake during the day, a small **selective underestimation of nocturnal flux** can cause a large overestimation of long-term sequestration. (3) **Sampling uncertainty** occurs when summing an incomplete data set to estimate long-term exchange. The observations at Harvard Forest are interrupted for maintenance, equipment failure, and unsuitable atmospheric conditions. Day-to-day variability in carbon balance creates uncertainty in the calculation of long-term flux.

**Methods**

**Site description**

The measurements are made on the Prospect Hill tract of the Harvard Forest, near Petersham, Massachusetts (42°32' N, 72°11' W, elevation 340 m), an area typical of rural New England (Foster 1992). The forest is 50-to-70-years old, dominated by red oak and red maple, with scattered stands of hemlock, and white and red pine. The canopy height is 20–24 m. Nearly continuous forest extends for several km to the south-west and the north-west of the site, the dominant wind directions. The site is centred in a small level drainage, with a stream running west of the site, the dominant wind directions. The site extends for several km to the south-west and the north-west (5° facing north). Soil type, soil drainage, and a gentle upward slope for several hundred meters from the north-west to the east within 50 m of the tower, is centred in a small level drainage, with a stream running west of the site, the dominant wind directions. The site extends for several k

urban areas are 100 km east (Boston) and 100 km southwest (Hartford). Additional site details are included in Munger et al. (1996), Moore et al. (1996), and Wofsy et al. (1993).

**Tower measurements**

The eddy fluxes of sensible heat, latent heat, CO₂, and momentum are measured at 30 m on the tower. Wind and temperature are measured with a 3-axis sonic anemometer (Applied Technologies, Boulder CO) pointed into the prevailing wind direction (west). The mixing ratios of CO₂ and H₂O are monitored by sampling 6–8 standard litre min⁻¹ (slpm) through an inlet located 0.5 m behind the vertical axis of the anemometer. The error due to separation of the inlet from the anemometer should be small at 30-m altitude (1–2% during unstable periods, Lee & Black 1994). The sample is drawn down the tower in a 50-ml 0.5-cm inner diameter (id) Teflon tube and through a CO₂/H₂O infrared gas analyser (IRGA; Model 6262, LiCor, Lincoln NE) located in the instrument hut. A 2-µm, 47-mm diameter Teflon filter at the inlet on the tower is changed every 2–4 weeks, and a second filter immediately before the IRGA is changed every 6 months. The inner surface of the sampling tube is cleaned periodically using a moist cotton ball. The pressure immediately after the IRGA is monitored and actively controlled at 60 kPa using a variable valve (MKS Instruments, Andover MA). The sample stream reaches an equilibrium temperature before entering the IRGA, removing the effects of coincident sensible heat flux (e.g. Webb et al. 1980). The effects of coincident water vapor fluctuations are removed by the IRGA software. The gain of the IRGA is automatically determined every 5 h by addition to the main sample stream near the inlet of 1% CO₂ gas mixture at 30 standard ml min⁻¹ (scm). The response time of the IRGA to a step change in CO₂ is also determined during this procedure.

The data acquisition and control systems are fully automated, allowing extended periods of unattended operation. The system records outputs from the sonic anemometer and the IRGA at 4 Hz. A spectral analysis of data collected at 10 Hz revealed no appreciable underestimation of flux due to 4 Hz sampling (Moore et al. 1996). The data are stored on disk at the site and transferred every two to four days for processing. Eddy CO₂ flux is calculated as the 30 minute covariance of vertical wind velocity (w') and CO₂ concentration (c'). The CO₂ record is detrended using a linear least squares fit. The time lag required to draw air down the tower is determined by maximizing the correlation between w' and c'. The lag is extremely consistent due to the active pressure control at the IRGA. The flux is rotated to the plane where the mean vertical wind is zero (McMillen 1988).

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The closed-path IRGA and long sampling tube result in a small underestimation of CO$_2$ flux due to the damping of high-frequency fluctuations (Leuning & King 1992). The magnitude of underestimation varies with atmospheric stability, creating a possible selective systematic error. We determine the magnitude of this underestimation by recalculating the sensible heat flux after numerically slowing the response of the temperature detector to simulate the slower response of the CO$_2$ analyser (exponential time constant = 0.2 s as determined by CO$_2$ addition on the tower). We then increase the calculated CO$_2$ flux by the ratio of the fast-response heat flux to the slow-response heat flux. The response-time correction is determined for each 30 minute run, and is typically 0–2% during the day and 0–5% during the night.

We use a second IRGA (Binos, Hanau Germany) to sequentially measure the mixing ratio of CO$_2$ at 8 levels through the canopy (0.05, 0.85, 2.8, 6.2, 9.5, 18.2, and 30.8 m). The hourly change in CO$_2$ beneath 30 m (storage, Wofsy et al. 1993) is calculated by interpolation through space and time to synchronize the profile and eddy observations. The eddy flux and storage observations are added to calculate the hourly net ecosystem exchange (NEE, Wofsy et al. 1993). The flux of photosynthetically active photons (PPFD) to the forest is measured with a silicon quantum sensor (LiCor, Lincoln NE). The net radiation at 30 m is measured with a thermopile net radiometer (REBS Q*6, Seattle WA). Air temperature and water vapor content are measured at the top of the tower with an aspirated thermistor and solid-state humidity probe (Vaisala, Woburn MA). Soil temperature is measured with an array of thermistors buried at the base of the litter layer. Soil water content is measured hourly by time domain reflectometry using six 15-cm and two 50-cm sets of wave guides placed vertically (Campbell Scientific, Logan UT).

Chamber measurements

We used a multiplexing gas exchange system to measure the efflux of CO$_2$ from soil, stems, and leaves over diel courses during summer 1992. The system sequentially sampled 10 open chambers (Field et al. 1989; Mosier 1989) deployed in a semi-circle, completing a circuit every 2 h. The system was moved among 10 sites around the tower, allowing measurements at 50 soil and 50 stem locations.

The soil chambers consisted of a 27-cm id by 10-cm long by 0.5-cm thick polyvinyl chloride (PVC) collar with a removable solid PVC lid. The collars were inserted to a depth of 2–4 cm during June 1992. Air was drawn at $\approx 5$ slpm from a sample port on the chamber top through the sample cell of a differential infrared gas analyser (LiCor 6251, Lincoln NE). Ambient air entered the chamber through a 10-cm tall, 4-cm id chimney on the side of the lid opposite the sample port. A subsample from the chimney was drawn through the reference cell of the IRGA at $\approx 0.5$ slpm. A measurement was made over a 12 minute period by (i) selecting a chamber with a solenoid valve (Skinner Valves, New Britain CT), (ii) measuring flow through the chamber with a mass flow meter (MKS Instruments, Andover MA), and (iii) measuring the difference in CO$_2$ between the inlet and outlet of the chamber.

The data were recorded and the system managed using a data logger (Campbell Scientific, Logan UT). The IRGA and mass flow meter were zeroed every 2 h, and the ambient concentration of CO$_2$ entering a chamber determined after each observation. Soil temperature at 2-cm and 5-cm depth was measured within each chamber using type T thermocouples. The chambers remained in place between measurements and flow was maintained at 5 slpm. The system was moved to a new site every one to four days, and the chamber tops removed when the system was deployed at other sites. Five soil collars were measured at least once at each of the 10 sites.

We established the analytical accuracy of the system with a series of standard additions. When a small flow of 1% CO$_2$ was metered into a chamber, the increase in flux matched the rate of CO$_2$ addition to within 5%. Errors caused by aspirating air from the soil are a particular problem with open-type chambers (Mosier 1989). We checked for this possibility by measuring the resistance to mass flow from the soil. When combined with the expected pressure drop through the chimney ($10^{-3}$ Pa at 5 slpm) these observations indicate a forced flow from the soil at the leakiest collars of a few sccm. Assuming a soil CO$_2$ concentration of 4000 $\mu$L L$^{-1}$ the maximum overestimation due to aspiration is 0.2 $\mu$mol m$^{-2}$ s$^{-1}$.

The stem respiration chambers consisted of 0.01-cm polyethylene sheet wrapped around 500–3000 cm$^2$ of stem. The chambers were placed at a height of 1–2 m, and sealed around the trunks using caulkign compound and tape. The sample port consisted of a perforated 1-to-4-m length of tubing wrapped around the stem within each chamber. Ambient air entered a chamber through an opening in the sheet held open by an inlet tube (4-cm id). A subsample from the inlet tube was drawn through the reference cell of the IRGA. The respiration of five stems representing various species was measured at each of the 10 sites. The absolute rates of CO$_2$ efflux from the 50 stems were well correlated with both the volumes and
the areas enclosed within the chambers. The relationship between enclosed area and CO₂ efflux was linear with a large zero offset such that small diameter stems had a greater flux per area, whereas the relationship between volume and efflux was linear with a zero intercept such that flux per volume was constant over a range of diameters. Respiration was therefore calculated on a volume basis and converted to ground area based on a survey of wood volume in 40 10-m radius plots within 500 m of the tower. Most of the stem respiration measurements were made after the period of maximum secondary growth (April through June), and the observed flux is likely dominated by maintenance respiration.

Leaf respiration in the canopy was measured by deploying branch chambers from a pair of 20-m tall scaffolding towers. The branch chambers consisted of 50-cm long by 30-cm diameter by 0.01-cm thick polyethylene bags held open by a frame of 0.64-cm outer diameter coated aluminium tube (Dekoron, Aurora OH). The chambers enclosed 20-50 leaves. Sample air was drawn through a series of perforations in the Dekoron frame. Measurements were made on a total of 10 branches representing 3 species during two nights in August 1992. Respiration was calculated per leaf and converted to ground area based on leaf litter collections in autumn 1992.

**Results: Measurements of turbulent exchange**

**Turbulence measurements**

The tilt of the mean wind at the top of the Harvard Forest tower generally does not vary by more than a few degrees from a fixed horizontal plane, indicating that flow distortion due to local topography or tower shadowing is minor (Fig. 1). The rotation angle varies as a function of wind direction in a manner consistent with a simple 2° offset between the plane through the u and v axes of the anemometer and the local topography (McMillen 1988). The relationship between rotation angle and wind direction is consistent from day to night, summer to winter, and calm to windy periods. The rotation angle is relatively variable when wind is blowing from behind the tower (45-135°), suggesting the possibility of modest distortion despite the tower's small cross section. The ratio of σw to u* is consistent as a function of direction with a modest increase in variability from 45 to 135°, also suggesting the possibility of modest tower shadowing (Moore et al. 1996). Fortunately wind from behind the tower is infrequent (= 14% of the time). We do not remove these periods from the main data set as they are often associated with cloud cover and we do not want to introduce a bias.

Spectral analyses of the fluctuations in atmospheric CO₂, T, and H₂O associated with turbulent transport provide a useful tool for assessing the reliability of flux measurements (Kaimal et al. 1972). Under ideal circumstances the shapes of the w’CO₂’, w’T’, and w’H₂O’ cospectra should be similar (Ohtaki 1985). An incomplete resolution of small eddies, a common error when making eddy covariance measurements, is indicated by the loss of power at high frequencies (Leuning & King 1992). The power spectrum of the CO₂ time series, the cospectrum of vertical wind and CO₂, and the cospectrum of vertical wind and air temperature, indicate that the closed-path IRGA records nearly all of the fluctuations in CO₂ associated with turbulent transport (Fig. 2). The CO₂ spectrum decreases through the subinertial range at the expected 2/3 power to a frequency of 1 Hz (Fig. 2a). The cospectrum of w’CO₂’ is similar to that of w’T’ (Fig. 2b). Both cospectra indicate that large eddies with frequency less than 0.1 Hz dominate flux (cf. Hollinger et al. 1994). The cospectrum of w’H₂O’, also measured with the closed-path IRGA, shows a nearly complete lack of flux at n > 0.2 Hz, and a modest underestimation of flux at n > 0.01 Hz (data not shown). The damping of high frequency water vapor fluctuations, which presumably is due to adsorption and desorption on the walls of the sample tube, results in an underestimation of evaporation by 20%.

**CO₂ exchange at Harvard Forest**

Measurements of CO₂ exchange were made during 20 300 of the 35 000 hours from Oct. 1990 to Oct. 1994 (Fig. 3), with interruptions for calibration, data transfer, maintenance, rain, and equipment failure. Notable gaps occurred when an IRGA failed repeatedly in spring 1991, when a
MEASURING CARBON SEQUESTRATION BY EDDY COVARIANCE

Fig. 2 (a) Spectrum of CO₂ with dash line showing −2/3 slope, (b) Co-spectrum of vertical wind and CO₂ (solid line), and co-spectrum of vertical wind and T (dashed line). Curves are composite averages of 52 individual spectra calculated during light periods in September 1991.

tape drive failed in May 1991, and following lightning damage in June 1992, August 1993, and July 1994. The seasonal course of CO₂ exchange was similar each year, with a midday uptake of 20–30 µmol m⁻² s⁻¹ from June through August, a peak nighttime efflux of 5–10 µmol m⁻² s⁻¹ from June through August, and an efflux during both day and night of 0–5 µmol m⁻² s⁻¹ from October through April. A more detailed look reveals several differences between years including a notable increase in efflux from Dec. 1992 to Feb. 1993 (Fig. 3; Goulden et al. 1996).

A typical summer day of turbulent fluxes is shown in Fig. 4. Respiratory efflux of 3–5 µmol m⁻² s⁻¹ during the first night was followed by photosynthetically driven net uptake of 14–19 µmol m⁻² s⁻¹ during the day and respiratory efflux of 0–1 µmol m⁻² s⁻¹ during the second night (Fig. 4a). The difference in flux between nights was associated with a difference in turbulence; the first night was windy whereas the second night was calm with a friction velocity that often approached zero (Fig. 4b). Carbon dioxide storage was quite variable from hour to hour, with a general increase at night and a general decrease during the morning (Fig. 4a). Nocturnal storage was not well correlated with turbulence, and the difference in eddy flux between nights was not offset by storage. The relationships between eddy flux, CO₂ storage, and turbulence on calm nights are discussed further in the section on selective systematic errors. The sum of sensible and latent heat was 100 W m⁻² less than net radiation as the forest warmed in the morning, and 0–50 W m⁻² less than net radiation in the afternoon and early evening (Fig. 4c). The outgoing radiation at night exceeded the influx of sensible heat by 25–75 W m⁻², and summed over the 24-hour period the turbulent fluxes were within 10% of the net radiation.

Nocturnal NEE over a whole year was exponentially related to surface soil temperature with Q₁₀ = 2.1 (Fig. 5; Wofsy et al. 1993; Hollinger et al. 1994; Fan et al. 1995). Similarly, soil CO₂ efflux measured with an automated chamber was tightly correlated with temperature at 2 cm depth (Fig. 6a), and bole respiration measured with a chamber was tightly correlated with temperature averaged over the outer 2 cm of stem (Fig. 6b). The complete set of soil chamber measurements was exponentially related to the soil temperature monitored at the tower with Q₁₀ = 2.2 ($n = 2450$, data not shown). The chamber measurements were made over diel cycles, and most of the range in soil temperature was due to the difference between days and nights. The Q₁₀ observed with the chambers is therefore appropriate for extrapolating nighttime observations of respiration to daytime as a function of soil temperature at the tower.

The relationship between nocturnal NEE and soil temperature allows a separation of the processes that contribute to daytime NEE. Net ecosystem exchange at night should equal the combined rates of autotrophic and heterotrophic respiration. During the day NEE should equal the combined rates of rubisco carboxylation and oxygenation (gross ecosystem production, GEP), and autotrophic respiration and heterotrophic respiration. We separate daytime NEE into respiration and GEP by first determining the exponential fit with Q₁₀ = 2.2 between NEE during well-mixed nocturnal periods (see section on selective systematic errors) and soil temperature within time blocks that include 100 h of valid nocturnal observations (2–4 weeks). We then calculate GEP as the difference between NEE and the respiration estimated from soil temperature. Our sign convention is that a flux addition of CO₂ to the atmosphere is a positive flux and hence GEP is negative. However, we discuss all processes, including photosynthesis and carbon sequestration, as positive.

Hourly GEP during the summer was well correlated with incident light (Fig. 7; Wofsy et al. 1993). The slope at low light indicated a quantum yield of 0.055 µmol C per µmol incident photon. The maximum photosynthetic rate was 20–25 µmol m⁻² s⁻¹, with moderate saturation
Fig. 4 Typical diel course of (a) carbon exchange, (b) friction velocity, and (c) energy exchange above Harvard Forest. Observations were made 31 Aug. 1992 to 2 Sept. 1992. Lines connect hourly averages.

beginning around 400 \mu\text{mol} \text{ photons m}^{-2} \text{ s}^{-1}. The relationship between photosynthesis and light was very tight, with an absolute scatter similar to that observed at night, approximately \pm 5 \mu\text{mol m}^{-2} \text{ s}^{-1} (Fig. 7, Fig. 5). This fidelity is remarkable since a range of phenomena, including measurement variability due to the finite sampling interval (Baldocchi et al. 1988), physiological processes that modulate photosynthesis, variability in the respiration flux (Fig. 5), and spatial heterogeneity in photosynthesis, could lead to high variance in daytime flux. The simple and tight relationship between light and photosynthesis indicates that secondary limitations to photosynthesis such as drought are typically of minor importance at Harvard Forest. The relationship also supports the use of 'big-leaf' and long-time-step models to describe canopy carbon uptake (Monteith 1972; Sinclair et al. 1976; Jarvis & Leverenz 1983).

Effects of turbulence on CO$_2$ exchange

Turbulence may affect CO$_2$ efflux in several ways. During calm periods turbulence limits the transport of CO$_2$ through the atmosphere as discussed in the section on selective systematic errors. During windy periods turbulence appears to affect the movement of CO$_2$ out of the soil as discussed in this section. The winter observations of whole-forest exchange indicate a positive correlation between efflux and friction velocity during very windy periods (Fig. 8, $u^* > 0.8 \text{ m s}^{-1}$). This correlation likely reflects the aspiration of CO$_2$-rich air from soil and snow pore space, rather than a short-term increase in CO$_2$ production. The increase in CO$_2$ efflux during windy periods was especially pronounced in winter 1993 (Fig. 3; Goulden et al. 1996). Rates of efflux exceeding 10 \mu\text{mol m}^{-2} \text{ s}^{-1} were repeatedly observed when the friction velocity exceeded 0.8 \text{ m s}^{-1} (Fig. 9a). The enhanced efflux was observed only when the tower sampled regions to the north-west, a poorly drained area dominated by a maple bog and old stands of hemlock. Fluxes of CO$_2$ to the south-west, an upland area of oaks and maples, were similar to those in other winters. The fluxes of latent and sensible heat (Fig. 9b), the response and gain of the CO$_2$ analyser, and the flow through the CO$_2$ analyser, did not give any indication of experimental problems during these periods.

The soil chambers were designed to allow the entry of static pressure fluctuations associated with overlying
Fig. 5 Nocturnal CO₂ efflux measured by the tower as a function of soil temperature during 1992. Points are hourly averages during periods with $u^* > 0.17 \text{ m s}^{-1}$. Flux (μmol m⁻² s⁻¹) = \exp(0.129 + 0.073 \times T (°C)), $n = 1800$.

Fig. 6 Typical diel course of (a) soil respiration measured with an automated chamber (b) stem respiration of a 34-cm diameter beech measured with an automated chamber, and (c) friction velocity measured at 30 m. Circles are temperature (a) at 2-cm soil depth in the chamber and (b) averaged over outer 2 cm of trunk in the chamber. Respiration curves are individual measurements at 2 hour intervals connected by lines, friction velocity is hourly average connected by lines.

turbulence, a property that we confirmed by measuring the pressure within a chamber (data not shown; Sigmon et al. 1983). Contrary to the pattern observed in winter, and also to reports suggesting that fluctuations in static pressure increase gas exchange from forest soils (Baldocchi & Meyers 1991), we found no consistent relationship during the summer between CO₂ efflux into the soil or stem chambers and above-canopy turbulence (Fig. 6a, b, c). Similarly, we have not observed a tight correlation between eddy CO₂ flux and friction velocity during windy summer periods ($u^* > 0.17 \text{ m s}^{-1}$). The difference from winter to summer in the sensitivity of efflux to strong turbulence may be a consequence of the canopy. The canopy may reduce ground-level turbulence in summer, preventing it from reaching the intensity where aspiration occurs.

Discussion: accuracy of the measurements

Long-term precision

Based on instrument specifications and calibration protocols we estimate a long-term precision for the eddy covariance measurements of better than ±5%. Similar infrared gas analysers have been used for the flux measurements since April 1991. The performance of the IRGA is monitored closely with a calibration every 5 h to determine both instrument gain and response time. The CO₂ standard used in the calibration has been replaced twice during the study, with an intercomparison between standards to within 1%. The zero offsets of the mass flow meters used in the calibration are determined every 2-4 days, and the meters are calibrated at least once every year. Similar sonic anemometers have been used throughout the study, with only a modest change in the on-line shadowing correction, providing long-term stability of
Fig. 7 Gross exchange as a function of incident photosynthetically active photon flux density (PPFD). Points are hourly means from 10 June 1992 to 16 Sept. 1992. Gross exchange was calculated as the difference between measured net exchange and respiration estimated from soil temperature. Flux (\(\mu\text{mol m}^{-2}\text{s}^{-1}\)) = \(1.4 + (-32.9 + \text{PPFD})/ (587 + \text{PPFD})\), \(n = 1350\).

Uniform systematic errors: Accuracy of daytime measurements

Experience has shown that eddy covariance works best during windy periods. Errors during these periods are presumably uniformly systematic (e.g. inaccurate concentrations of calibration gases), and should apply equally to all periods. An analysis of the surface energy budget provides a useful approach for evaluating the measurements of latent heat, sensible heat, and, based on spectral similarity (Fig. 2b), \(\text{CO}_2\) flux. A convincing closure of the energy budget at Harvard Forest is difficult due to the underestimation of latent heat flux revealed by the spectral analysis, and also due to uncertainty in the rate of heat storage. When these factors are taken into account (Verma et al. 1986; Moore 1986; Leuning & King 1992) good agreement is obtained between the loss and storage of energy at the surface, and the net flux of radiation to the forest (Fig. 10). The comparison indicates a tendency for the turbulent fluxes to underestimate exchange by 5–10%. An additional ±10% should be added to account for uncertainties in the measurement of net radiation, in the calculation of heat storage, and in the correction of latent heat flux. The confidence interval for the measurement of daytime turbulent exchange is −20 to 0%.

Additional analyses support this conclusion. The daily evaporation at the site measured by eddy covariance during 20 summer days in the later stages of drying cycles was 0.14 cm day\(^{-1}\), while the evaporation estimated from time domain reflectometry in the top 50 cm of soil was 0.16 cm day\(^{-1}\) (data not shown). The mean photosynthesis at the site measured by eddy covariance...
Fig. 9 (a) CO₂ exchange (solid line) and \( u^* \) (dashed), and (b) net radiation (fine dash), sensible plus latent heat flux (course dash), and soil temperature (solid) from 17–19 January 1993 showing high CO₂ efflux during turbulent periods.

During three summer afternoons was 15.5 µmol m\(^{-2}\) s\(^{-1}\), while the canopy photosynthesis estimated by aggregating leaf-chamber observations was 12.5 µmol m\(^{-2}\) s\(^{-1}\) (Wofsy et al. 1993).

Selective systematic errors: Underestimation of nighttime flux

Selective systematic errors, which result when there is a correlation between the direction of surface exchange and the accuracy of the exchange measurement, represent a serious problem when summing short-term measurements (hourly NEE) to longer intervals (annual carbon sequestration). Of particular concern is the possibility that nocturnal exchange may be underestimated. The reliability of the daytime flux measurements is not surprising; the methods in use at Harvard Forest are comparable to those used with success above other forested sites (Denmead & Bradley 1985; Verma et al. 1986; Kellilher et al. 1992). In contrast, the applicability of eddy covariance during nocturnal periods has not been completely established (Fig. 4; Fitzjarrald & Moore 1990). Nocturnal periods include conditions that may challenge otherwise reliable methods. These include cold air drainage, sporadic mixing, a spectral shift towards high-frequency eddies, fluctuations in vertical wind too small to be
resolved by the sonic anemometer, and increased importance of storage.

The observations of nocturnal CO₂ exchange at Harvard Forest indicate a selective underestimation of flux during calm periods. There is a reduction in the measured vertical flux of CO₂ at 30 m during poorly mixed periods (u* < 0.17 m s⁻¹, Fig. 11a) that is not due to a reduction in the flux of CO₂ from the soil (Fig. 11c). This discrepancy cannot be explained entirely by increased storage. The rate of CO₂ accumulation during calm periods is only 20–30% of the eddy flux during windy intervals (Fig. 11a). The flux of CO₂ at 30 m immediately following the resumption of mixing is not unusually high (Fig. 11b) as would be expected with flushing of accumulated CO₂. Carbon dioxide evidently escapes from the forest during poorly mixed periods by an undetected route. Similar patterns have been observed in boreal forests (M.L. Goulden, personal observation; T.A. Black, personal communication; P.G. Jarvis, personal communication). However, Grace (J. Grace, personal communication) observed that storage quantitatively offset the reduction in eddy flux during calm nocturnal periods in a tropical forest.

The cause of flux underestimation during stable periods has not been identified. One possibility is that CO₂ leaves the forest in draining cool air that subsequently mixes upwards away from the tower. Alternatively, CO₂ may leave the forest in fluctuations that are too small or too short to be resolved with the available instrumentation. A third possibility is that the flux calculation is inadequate for calm nocturnal periods, and a longer averaging time or a different detrending algorithm is required due to the dominance of sporadic mixing events.

The efflux of CO₂ during summer nights becomes insensitive to atmospheric turbulence at u* > 0.17 m s⁻¹ (Fig. 11a). A critical question is whether eddy covariance provides an accurate measure of ecosystem respiration during these periods. The flux of CO₂ during windy nights is insensitive to net radiation (Fig. 12a), to the temperature gradient beneath the canopy (Fig. 12b), and to the temperature gradient above the canopy (Fig. 12c), establishing that there is no apparent difference between periods that are thermally stratified to those that are unstratified. Since there is no apparent selective error between daytime periods that are neutral and those that are unstable, we conclude that night-time observations at u* > 0.17 m s⁻¹ are reliable. The contention that flux measurements in windy dark periods are not systematically different from those in light periods is supported by the observation that the relationship between u* and CO₂ flux does not vary from day to night during the winter (Fig. 8).

We correct for the selective underestimation of respiration at u* < 0.17 m s⁻¹ by substituting the respiration predicted from soil temperature (Fig. 5) for the observed flux. The buildup of carbon dioxide beneath 30 m during calm periods is relatively small (Fig. 11b), minimizing problems with double counting. The replacement of data during calm periods increases the calculated annual respiration by 0.5–1.0 t C ha⁻¹. This correction is largely responsible for a revision of our estimate of 1991 carbon sequestration from 3.7 t C ha⁻¹ to 2.8 t C ha⁻¹ (Goulden et al. 1996), a somewhat larger effect than the 0.5 t C ha⁻¹ anticipated by Wofsy et al. (1993).
Fig. 12 Nocturnal net ecosystem exchange during well-mixed periods (\( \mu^* > 0.17 \) m s\(^{-1}\)) as a function of (a) net radiation (b) the temperature gradient beneath the canopy (\( T \) at 15 m minus \( T \) at 2 m), and (c) the temperature gradient above the canopy (\( T \) at 28 m minus \( T \) at 15 m). Points are means ±1 standard deviation of (a) 42 hourly observations (b) 26 hourly observations, and (c) 26 hourly observations, recorded from 10 June 1992 to 16 Sept. 1992.

Table 1. Average nocturnal net ecosystem exchange during well-mixed periods between 10 June 1992 and 16 Sept. 1992 (\( n = 660 \), mean soil and air temperature = 17.5 °C) compared to component diamber fluxes at 17 °C. Soil respiration was calculated as Flux (\( \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \)) = \( \exp (0.14 + 0.079 \cdot T) \), \( n = 2450 \). Stem respiration was calculated as Flux (\( \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \)) = \( \exp (-2.24 + 0.062 \cdot T) \), \( n = 965 \). Leaf respiration was based on nocturnal observations on 10 leafy branches during August 1992.

| Nocturnal NEP well-mixed periods | Aggregated open chamber |
|----------------------------------|-------------------------|
| Leaf                             | 1.6 \( \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \) | 6.5 \( \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \) |
| Stem                             | 0.3 \( \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \) | 4.4 \( \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \) |
| Soil                             | 4.2 \( \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \) | 6.5 \( \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \) |

Sampling uncertainty

One of our goals is to determine the annual rate of carbon sequestration (annual net ecosystem production, NEP). We assume that NEP is equal to the annual net exchange of \( \text{CO}_2 \) with the atmosphere (integrated NEE) since the site has not burned during the study, and carbon exchanges in forms other than \( \text{CO}_2 \) and by processes other than turbulent transport, are likely small.
Our current approach for calculating long-term carbon sequestration involves: (i) Estimating CO₂ exchange as a function of soil temperature (Fig. 5) for dark periods when $u^* < 0.17 \text{ m s}^{-1}$ or when flux measurements are unavailable. Estimating CO₂ exchange as a function of PPFD (Fig. 7) and soil temperature (Fig. 5) for summer light periods when flux measurements are unavailable, (ii) Dividing the record of hourly CO₂ exchange into intervals that encompass four days with complete observations. (Most of the intervals are 4 days, but longer periods may be required due to equipment malfunction.) (iii) Averaging by hour within each interval, (iv) Summing to calculate the carbon balance of each interval, (v) Summing through the year assuming for each interval that the carbon balance calculated from the 4-days of observations is representative of the complete interval (Fig. 13a). Sampling uncertainty arises in step 1 when an empirical relationship is used to fill missing periods, and in step 5 when the carbon balance determined from 4 days of observations is assumed representative of a longer interval.

We estimated this uncertainty using a Monte Carlo method to simulate the sampling process. We assembled a total of eight populations of daily carbon balances that were intended to represent the typical patterns of day-to-day variation. Each population consisted of the daily carbon balances of 30 nearly consecutive days drawn from observations during 1994, with a pair of populations representing each season. One population within each season was composed of the actual measurements of daily carbon balance, and the other of the simultaneous carbon balances calculated from the empirical relationships (Figs 5, 7). For each interval we sampled from the appropriate population one hundred randomly selected sequences of the interval length. The average of 4 randomly selected days within each sequence was compared with the true sequence average to simulate the sampling error for each of the 100 cases. The sampling error for each of the 100 cases was accumulated through the year and sorted to determine the 5th and 95th percentiles.

The integrated carbon sequestration from Day 301, 1993 through Day 300, 1994 was $-2.1 \text{ t C ha}^{-1}$, with an accumulated sampling uncertainty of ±0.3 t C ha⁻¹.

Fig. 13 (a) Cumulative net carbon exchange (points) and 90% confidence interval (shading) from Day 301, 1993 to Day 300, 1994. Points are at intervals with 4 complete days of observations. (b) Increase through the year in 90% confidence interval due to sampling uncertainty. The annual net exchange during 1994 was $-2.1 \text{ t C ha}^{-1}$, with an accumulated sampling uncertainty of ±0.3 t C ha⁻¹.

Two strategies are important for reducing sampling uncertainty. First, a continuous set of climate data may be collected and used to fill periods when flux observations are unavailable. The uncertainty caused by filling missing periods as a function of the physical environment is smaller than that caused by assuming that the days with observations are representative. Second, the sampling strategy should minimize the length of intervals without flux data. The correlation at Harvard Forest between the carbon balance on days that are separated by less than a week is high (i.e. the lag correlation, $r^2 = 0.6-0.7$), whereas the correlation between days that are separated by longer than two weeks is low ($r^2 = 0.2-0.3$). The correlation between days separated by more than a week is especially low in spring and fall when the carbon balance is changing rapidly. Long gaps create disproportionately large uncertainty, whereas short gaps (a few days) spread throughout the year are acceptable. This pattern supports the deployment of unattended monitoring systems, provided that malfunctions can be repaired quickly. Periodic breakdowns of unattended systems are inevitable, but the uncertainty caused by these gaps is offset by the advantage of year-round monitoring.

Conclusions
1 Long-term eddy covariance provides an effective technique for measuring the hourly, daily, monthly, and annual rates of carbon exchange by terrestrial ecosystems. The long term precision of the approach is very good.
(±5%). Long-term eddy covariance is particularly well suited for quantifying the effects of stress, climate, and phenology on carbon exchange, and for developing and testing mechanistic models and remote-sensing algorithms.

2 We observe a selective systematic underestimation of flux during calm (u* < 0.17 m s⁻¹) nocturnal periods at Harvard Forest, for which we compensate using an estimation of ecosystem respiration based on temperature. Additional work is needed to fully establish the reliability of eddy covariance during nocturnal periods. In particular, we are unable to fully account for a discrepancy between the ecosystem respiration at Harvard Forest measured as NEE during mixed nocturnal periods, and that measured using chambers.

3 The uncertainty in the measurement of carbon exchange at Harvard Forest due to uniform systematic errors is ±20 to 0%. The annual carbon sequestration in 1994 was 2.1 t C ha⁻¹ y⁻¹ with a 90% confidence interval due to sampling uncertainty of ±0.3 t C ha⁻¹ y⁻¹. Sampling uncertainty is reduced by estimating the flux as a function of the physical environment during periods when direct observations are unavailable, and by minimizing the length of intervals without flux data, especially during spring and fall. The combined effects of uniform systematic errors, sampling uncertainty, and the estimation of respiration during calm nocturnal periods leads to an overall confidence interval for carbon sequestration in 1994 of 0.3 to 0.8 t C ha⁻¹ y⁻¹.

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