

aging. We performed EDS analyses with a PGT System IV equipped with Be and thin organic windows. Analyses of the Ir particle were obtained at 25 kV for 2000 s with a Be window. Other EDS analyses with better sensitivity for oxygen were performed at 10 kV for 1000 s with the thin organic window, to determine if the Ir particle was oxide or metal and to evaluate the composition of the silicate coating. Using the same respective instrument conditions, we obtained spectra from polished standard blocks for pure metals of Ru, Re, Os, and Pt and for a Pt-Ir (9:1) alloy, and from a polished fused glass bead from a split of the C1-N10-1 whole rock powder (4, 12). After discovery of the particle, IrO₂ and Ir metal standards were obtained and analyzed. Comparisons of spectra from the particle to those of the above standards, as well as to "composite standards" [J. T. Armstrong, A. El Goresy, G. J. Wasserburg, *Geochim. Cosmochim. Acta* **49**, 1001 (1985)] for Ir₉₉Os₁ and Ir₉₉Pt₁, clearly show that other PGEs are not present in the particle to within EDS detection limits.

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27. El Goresy *et al.* (31) state that ~5% of metal grains within "Fremdlinge" are Ir with subordinate Ru and note that their investigations did not disclose if such grains are indeed homogeneous alloys or aggregates of discrete PGE metals.

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Exchange of Carbon Dioxide by a Deciduous Forest: Response to Interannual Climate Variability

Michael L. Goulden, J. William Munger, Song-Miao Fan, Bruce C. Daube, Steven C. Wofsy*

The annual net uptake of CO₂ by a deciduous forest in New England varied from 1.4 to 2.8 metric tons of carbon per hectare between 1991 and 1995. Carbon sequestration was higher than average in 1991 because of increased photosynthesis and in 1995 because of decreased respiration. Interannual shifts in photosynthesis were associated with the timing of leaf expansion and senescence. Shifts in annual respiration were associated with anomalies in soil temperature, deep snow in winter, and drought in summer. If this ecosystem is typical of northern biomes, interannual climate variations on seasonal time scales may modify annual CO₂ exchange in the Northern Hemisphere by 1 gigaton of carbon or more each year.

Observations of atmospheric CO₂ indicate that the carbon balance [net ecosystem production (NEP)] of the Earth's terrestrial biosphere varies by 1 gigaton of carbon per year (Gt C year⁻¹) (1 Gt = 10⁹ metric tons) or more from year to year (1). Many ecosystem processes are sensitive to weather (2), and the fluctuations in global NEP are probably a consequence of interannual climate variability. However, direct observations of the effects of climate variability on the CO₂ exchange of whole ecosystems are required before the causes of global NEP variation can be assessed reliably.

We used a 5-year record of the turbulent exchange of CO₂ between the atmosphere and a deciduous forest in New England [net ecosystem exchange (NEE)] (3–5) to evaluate the magnitude and causes of interannual variations in net production (NEP), respiration (R) (6), and gross ecosystem exchange (GEE) (7). The eddy-covariance

technique (8, 9) was used to measure hourly NEE from 28 October 1990 to 27 October 1995 (10) at Harvard Forest in central Massachusetts. Ecosystem respiration was measured directly during dark periods and estimated as a function of soil temperature during light periods (8). Hourly GEE was inferred by subtracting R from NEE.

Measurements of NEE were obtained during 27,000 of 44,000 hours, with gaps for calibration, data transfer, maintenance, equipment failure, rain, and stable nocturnal periods. The study included warm (1990–1991, the 2nd warmest year out of

32), cold (1991–1992, the 2nd coldest; 1993–1994, the 4th coldest), and moderate (1992–1993, the 14th coldest; 1994–1995, the 19th coldest) years (10, 11), mild (1991 and 1995, among the four warmest) and cold (1993 and 1994, among the eight coldest) winters, cool (1992, the 3rd coldest) and hot (1993, 1994, and 1995, among the six hottest) summers, and dry (1995, the 6th driest) and wet (1991, 1992, and 1994, among the seven wettest) summers.

The forest gained 30 to 60 kg C ha⁻¹ day⁻¹ in the growing seasons and lost 10 to 20 kg C ha⁻¹ day⁻¹ in the dormant periods (Fig. 1). Annual net CO₂ uptake ranged from 1.4 to 2.8 metric tons C ha⁻¹ (Table 1) (12, 13), with above-average uptake in 1990–1991 and 1994–1995 (14). The rise in sequestration during 1990–1991 was caused by increased annual gross production, and the rise during 1994–1995 was caused by decreased annual R. Annual GEE and R varied as the result of 1- to 2-month-long episodes of anomalous activity (Fig. 2). For example, lower than average annual net production in 1993–1994 (Table 1) was a consequence of both higher than average respiration (Fig. 2) and lower than average gross production (Figs. 2 and 3) in spring.

Large changes in annual GEE were associated with modest changes in the length of the growing season (Figs. 2 and 3). The leaves emerged 6 to 10 days later

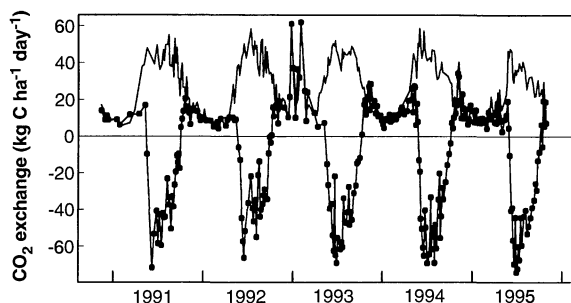


Fig. 1. Daily net CO₂ exchange (NEE) (filled symbols connected by lines) and daily respiration (R) (solid line) during 5 years at Harvard Forest. Observations are means for 4 days (8).

Division of Applied Sciences and Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA 02138, USA.

*To whom correspondence should be addressed.

Table 1. Values of NEE and R summed from day of year (DOY) 301 to DOY 300, and GEE summed from DOY 100 to DOY 300. Exchange from the forest is positive. Numbers in parentheses are 5 and 95 percentile confidence intervals (8, 14). Net exchange in 1994–1995 was significantly more negative than in 1991–1992 and 1993–1994, which in turn were more negative than in 1992–1993. Net exchange in 1990–1991 was significantly more negative than in 1992–1993 and 1993–1994.

Year	Annual exchange (tons C ha ⁻¹ year ⁻¹)		
	NEE	GEE	R
1990–1991	-2.8 (±0.6)	-12.1 (±0.6)	9.6 (±0.3)
1991–1992	-2.2 (±0.3)	-11.1 (±0.4)	9.3 (±0.2)
1992–1993	-1.4 (±0.5)	-12.7 (±0.4)	11.4 (±0.3)
1993–1994	-2.1 (±0.3)	-11.7 (±0.3)	9.7 (±0.4)
1994–1995	-2.7 (±0.3)	-10.7 (±0.4)	8.1 (±0.2)

in 1992, 1994, and 1995 than in 1991 and 1993, with similar delays in the uptake of carbon. Leaf expansion was correlated with air temperature, starting around 300 degree-days (15) and ending around 650 degree-days. Large shifts in annual GEE therefore resulted from brief anomalies in temperature during April and May. Canopy senescence began after the onset of cool nights (below 5° to 10°C). This occurred relatively late in 1992 and 1993, allowing photosynthesis to continue for 5 to 10 days longer than in 1994 and 1995 and increasing gross production by around 500 kg C ha⁻¹.

Prolonged periods of cloudiness during mid-July 1992, mid-August 1992, and August 1994 each reduced gross production by around 400 kg C ha⁻¹ (Fig. 2). The response of forest photosynthesis to the physical environment (light, temperature, and evaporative demand) varied little from summer to summer. We observed small enhancements (5 to 10%) in the instantaneous rates of photosynthesis at a given light level in 1993 and 1994 compared with 1991 and 1992, but these were only slightly

larger than the long-term precision of the measurements (8). A modest (10%) reduction in photosynthesis at a given light level was associated with severe drought in August and September 1995 (Fig. 1).

The most striking period of anomalous respiration occurred in winter 1992–1993, when intermittent increases in efflux released a total of 1.6 to 2.0 tons C ha⁻¹ (Figs. 1 and 2) (16, 17). These episodes coincided with high winds (8), a pattern we attribute to aspiration of CO₂ accumulated in soil pores. The increases were observed only when the flux footprint was northwest of the tower, a poorly drained area that includes a bog. Periods of extreme efflux were not observed from this sector in other years and never from the southwest, an upland area of oaks and maples. The episodes started in December 1992, after a heavy snow on unfrozen soil (Fig. 4). This snowpack and subsequent rains possibly compressed regions of the bog, altering soil aeration and causing increased pore-space CO₂ for several months as a result of accelerated decomposition. The cumulative uptake in 1993 after removal of winter periods with northwest winds was 3.3

tons C ha⁻¹, significantly greater than in 1992, 1994, or 1995, and the cumulative R in 1993 was 9.6 tons C ha⁻¹.

Smaller enhancements in fall, winter, and spring respiration (Fig. 2) were correlated with unusually warm soil temperatures (Fig. 4). An increase in respiration of 200 kg C ha⁻¹ during fall 1993 coincided with a 2°C increase in soil temperature. Respiration rates and soil temperatures were higher than normal in winter 1994, despite colder than normal air temperatures, reflecting thermal insulation by deep snow. The sensitivity of spring and winter respiration to soil temperature was often greater than expected for a direct affect of temperature on metabolism. Soil temperatures averaged 2.7°C from 15 March to 30 April 1992, with freezing periods through most of April, compared with 4.5°C during the other years, when freezing ended in late March or early April. The corresponding decline in respiration during 1992, around 500 kg C ha⁻¹ or 40%, exceeded the 13% reduction expected for a respiration coefficient Q_{10} of 2.0 (8, 18). The rate of microbial decomposition near 0°C may be limited by freezing (19), potentially amplifying the response of ecosystem respiration to weather anomalies that affect soil frost, such as late arrival of spring or deep snow.

Respiration rates in summer were extremely consistent from 1991 to 1994 (Figs. 1 and 2) despite a range of mean air temperatures. A decline in respiration of nearly 1000 kg C ha⁻¹ during late summer 1995 (Figs. 1 and 2) coincided with a severe drought when only 10% of normal precipitation was recorded. Remarkably, this decrease in respiration (30%) more than offset

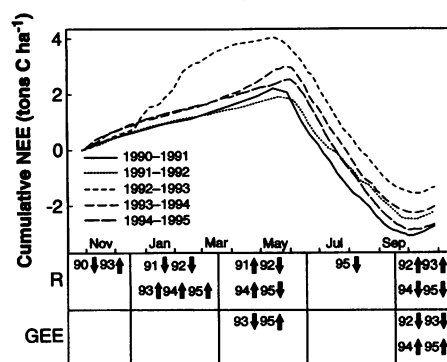


Fig. 2. (Top) Cumulative net carbon exchange during 5 years. (Bottom) Occurrence of anomalous (14) respiration (R) and gross ecosystem exchange (GEE) during 2- or 3-month intervals. Positive exchange is to the atmosphere. Upward arrows indicate greater exchange to the atmosphere (increased respiration or decreased photosynthesis).

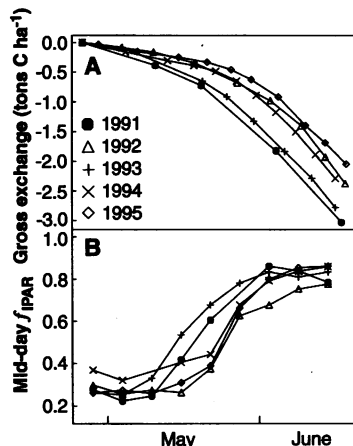


Fig. 3. (A) Cumulative gross carbon exchange during the spring. (B) Fraction of photosynthetically active radiation intercepted by the canopy (f_{IPAR}) as determined with above-canopy (30 m) and below-canopy (8 m) light sensors.

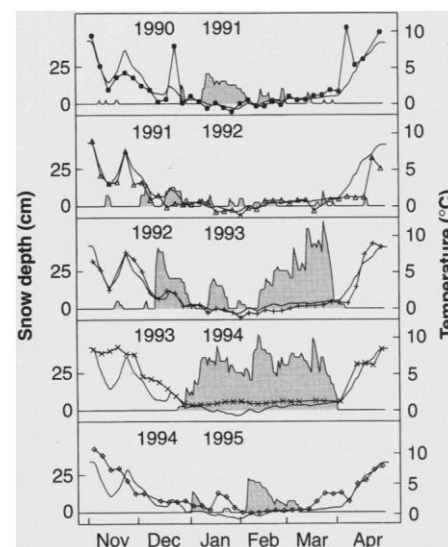


Fig. 4. Snow depth (shaded) and soil temperature (lines separating symbols). The solid line shows the median soil temperature on the given date for the 5 years of observation.

the simultaneous decrease in photosynthesis (10%). The depletion of water near the soil surface apparently reduced soil respiration, while water remaining deep in the soil column supported photosynthesis, resulting in above-average carbon storage during 1994–1995 (Table 1).

Annual CO_2 exchange was particularly sensitive to four aspects of climate: (i) the length of the growing season, regulated by air temperature in spring and early fall, (ii) cloud cover in summer, (iii) snow depth and other factors affecting soil temperature in the dormant season, and (iv) drought in summer. Photosynthesis and respiration were relatively insensitive to other aspects of climate, including growing-season temperature. Shifts in annual CO_2 exchange resulted from weather anomalies during periods when the forest was particularly sensitive, rather than from changes in annual mean conditions. Most predictions of the response of terrestrial ecosystems to climatic warming focus on a shift in annual mean temperature, ignoring the possibility that CO_2 exchange may be especially sensitive to the weather during specific intervals of the year.

A quantitative assessment of the effects of climate variability on global GEE, R , and NEE will require combining long-term flux observations in all of the major biomes (20) with spatially and temporally resolved weather data (21). We can make a rough estimate of the interannual variability in Northern Hemisphere CO_2 exchange by assuming that all northern biomes respond with half the intensity observed at Harvard Forest. Mid-winter snow cover in the Northern Hemisphere has varied over the past 20 years by $7 \times 10^6 \text{ km}^2$ (22), potentially shifting hemispheric R by 0.1 to 0.8 Gt C year^{-1} , depending on whether the phenomenon observed in 1992–1993 occurs elsewhere. Similarly, variations in fall and spring temperatures, inferred from the extent of fall and spring snow cover, could shift hemispheric R by 0.2 to 0.4 Gt C year^{-1} and GEE by 0.2 to 0.4 Gt C year^{-1} . Finally, variation in cloud cover over continents in summer could shift global GEE by at least 1 Gt C year^{-1} (23, 24). These fluctuations in hemispheric CO_2 exchange are of the same magnitude as those derived from analyses of atmospheric CO_2 data (1).

The climate over northern continents has tended in recent decades toward warmer springs (25), warmer autumn nights (26), diminished snow pack (22), and increased cloud cover (23). We have shown that the annual CO_2 exchange at Harvard Forest is sensitive to each of these aspects of climate. If the responses observed at Harvard Forest are indeed typical of northern biomes and persistent over decadal time scales, these trends in cli-

mate may have altered the carbon balance of the northern terrestrial biosphere (21). Longer growing seasons and reduced snow cover may therefore account for some of the net uptake of CO_2 attributed to the terrestrial biosphere (1).

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3. Net ecosystem exchange equals the sum of photosynthetic carboxylation and oxygenation, autotrophic dark respiration, and heterotrophic respiration. We assume annual NEE is equivalent to NEP, because the site did not burn and because carbon exchanges in forms other than CO_2 and by processes other than turbulent transport are likely small. Exchange (NEE and GEE) from the atmosphere is considered a negative flux. Ecosystem processes such as carbon storage (NEP) and photosynthesis (gross production) are discussed as positive.
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5. The observations were made above a 55- to 75-year-old oak and maple stand (10 to 20% conifer) at the Harvard Forest near Petersham, MA; 42.54°N, 72.18°W (4, 8). The net exchange of CO_2 was measured by eddy covariance (9) at a height of 30 m, and the storage of CO_2 beneath 30 m was derived from sequential measurements of CO_2 concentration at eight altitudes (4). Hourly eddy flux and storage change were summed to calculate NEE.
6. The sum of autotrophic dark respiration and heterotrophic respiration.
7. The sum of photosynthetic carboxylation and oxygenation.
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10. We calculate annual NEE, R , and climate from day of year (DOY) 301 to DOY 300 (28 October to 27 October) to avoid a break in mid-winter (Fig. 1). Annual GEE was calculated from DOY 100 to 300. The annual net uptake for calendar years was 2.7, 1.7, 1.6, and 2.2 tons C ha^{-1} in 1991, 1992, 1993, and 1994, respectively.
11. NOAA Meteorological Data (Harvard Forest, Petersham, MA). Snow depth, precipitation, and maximum and minimum temperature 1.6 km from the site has been recorded daily since 1964.
12. The present calculation of net carbon storage for 1991 ($2.8 \pm 0.6 \text{ tons C ha}^{-1}$) is 1 ton C ha^{-1} less than reported previously ($3.7 \text{ tons C ha}^{-1} \text{ year}^{-1}$) (4), reflecting recalibration of a CO_2 standard (lowered calculated annual storage by $0.2 \text{ ton C ha}^{-1}$) and a more detailed accounting for the underestimation of nocturnal exchange (lowered storage by $0.8 \text{ ton C ha}^{-1}$) (8).
13. Annual GEE and R were integrated over different intervals (10) and therefore do not sum exactly to NEE.
14. We used a Monte Carlo simulation to determine the probability that differences in flux were a result of sampling uncertainties caused by discontinuous observations (8). Differences in cumulative uptake were considered significant if fewer than 5% of the Monte Carlo simulations overlapped and, to guard against misinterpretations of a shift in measurement gain (8) as a shift in activity, the fluxes differed by at least 10%. Intervals were considered anomalous if they differed from at least two of the other years. We used this approach to determine the significance of both annual (Table 1) and seasonal (Fig. 2, bottom) shifts in NEE, R , and GEE. Patterns similar to those in Fig. 2 were obtained after changing the demarcations between seasons and also when significance was determined by Student's t test.
15. Daily mean above 0°C integrated since DOY 100.
16. We examined these periods in detail for experimental artifacts. Anthropogenic contamination can be ruled out because there are no known dwellings or traveled roads within 2 km northwest of the site and the concentrations of CO and C_2H_2 (tracers for combustion) remained low. Programming error can be excluded because the same code was used throughout the study. Measurement error is unlikely because (i) the enhancement occurred only during northwest winds and not during intervening southwest winds, (ii) the fluxes of latent heat, sensible heat and momentum, the response and gain of the CO_2 analyzer, and the CO_2 ' and w' spectra and $\text{CO}_2 w'$ cospectrum were normal, and (iii) the enhanced efflux resulted from a simultaneous, correlated increase in both σ_w and σ_{CO_2} . Primes and σ denote instantaneous deviations and standard deviations from the 30-min mean quantity, respectively (9).
17. Heterotrophs account for about 50% of ecosystem respiration in summer [(8); R. D. Bowden, K. J. Nadelhoffer, R. D. Boone, J. M. Melillo, J. B. Garrison, *Can. J. For. Res.* **23**, 1402 (1993)] and likely dominate respiration in winter. Interannual changes in respiration outside of the growing season presumably reflect shifts in decomposition.
18. Q_{10} is the fractional change in the rate of respiration for a temperature change of 10°C ; a value near 2.0 is typical of temperate soils [J. W. Raich and W. H. Schlesinger *Tellus B* **44**, 81 (1992)].
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