Biogeochemistry (2005) 75: 109–176
DOI 10.1007/s10533-004-6321-y

The biogeochemistry of carbon at Hubbard Brook

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Received 9 April 2004; accepted in revised form 8 November 2004

Key words: Forest ecosystem, Net ecosystem exchange, Primary productivity, Heterotrophic respiration

Abstract. The biogeochemical behavior of carbon in the forested watersheds of the Hubbard Brook Experimental Forest (HBEF) was analyzed in long-term studies. The largest pools of C in the reference watershed (W6) reside in mineral soil organic matter (43% of total ecosystem C) and living biomass (40.5%), with the remainder in surface detritus (14.5%). Repeated sampling indicated that none of these pools was changing significantly in the late-1990s, although high spatial variability precluded the detection of small changes in the soil organic matter pools, which are large; hence, net ecosystem productivity (NEP) in this 2nd growth forest was near zero (± about 20 g C/m^2-yr) and probably similar in magnitude to fluvial export of organic C. Aboveground net primary productivity (ANPP) of the forest declined by 24% between the late-1950s (462 g C/m^2-yr) and the late-1990s (354 g C/m^2-yr), illustrating age-related decline in forest NPP, effects of multiple stresses and unusual tree mortality, or both. Application of the simulation model PnET-II predicted 14% higher ANPP than was observed for 1996–1997, probably reflecting some unknown stresses. Fine litterfall flux (171 g C/m^2-yr) has not changed much since the late-1960s. Because of high annual variation, C flux in woody litterfall (including tree mortality) was not tightly constrained but averaged about 90 g C/m^2-yr. Carbon flux to soil organic matter in root turnover (128 g C/m^2-yr) was only about half as large as aboveground detritus. Balancing the soil C budget requires that large amounts of C (80 g C/m^2-yr) were transported from roots to rhizosphere carbon flux. Total soil respiration (TSR) ranged from 540 to 800 g C/m^2-yr across eight stands and decreased with increasing elevation within the northern hardwood forest near W6. The watershed-wide TSR was estimated as 660 g C/m^2-yr. Empirical measurements indicated that 58% of TSR occurred in the surface organic horizons and that root respiration comprised about 40% of TSR, most of the rest being microbial. Carbon flux directly associated with other heterotrophs in the HBEF was minor; for example, we estimated respiration of soil microarthropods, rodents, birds and moose at about 3, 5, 1 and 0.8 g C/m^2-yr, respectively, or in total less than 2% of NPP. Hence, the effects of other heterotrophs on C flux were primarily indirect, with the exception of occasional

irruptions of folivorous insects. Hydrologic fluxes of C were significant in the watershed C budget, especially in comparison with NEP. Although atmospheric inputs (1.7 g C/m^2-yr) and streamflow outputs (2.7 g C/m^2-yr) were small, larger quantities of C were transported within the ecosystem and a more substantial fraction of dissolved C was transported from the soil as inorganic C and evaded from the stream as CO_2 (4.0 g C/m^2-yr). Carbon pools and fluxes change rapidly in response to catastrophic disturbances such as forest harvest or major windthrow events. These changes are dominated by living vegetation and dead wood pools, including roots. If biomass removal does not accompany large-scale disturbance, the ecosystem is a large net source of C to the atmosphere (500–1200 g C/m^2-yr) for about a decade following disturbance and becomes a net sink about 15–20 years after disturbance; it remains a net sink of about 200–300 g C/m^2-yr for about 40 years before rapidly approaching steady state. Shifts in NPP and NEP associated with common small-scale or diffuse forest disturbances (e.g., forest declines, pathogen irruptions, ice storms) are brief and much less dramatic. Spatial and temporal patterns in C pools and fluxes in the mature forest at the HBEF reflect variation in environmental factors. Temperature and growing-season length undoubtedly constrain C fluxes at the HBEF; however, temperature effects on leaf respiration may largely offset the effects of growing season length on photosynthesis. Occasional severe droughts also affect C flux by reducing both photosynthesis and soil respiration. In younger stands nutrient availability strongly limits NPP, but the role of soil nutrient availability in limiting C flux in the mature forest is not known. A portion of the elevational variation of ANPP within the HBEF probably is associated with soil resource limitation; moreover, sites on more fertile soils exhibit 20–25% higher biomass and ANPP than the forest-wide average. Several prominent biotic influences on C pools and fluxes also are clear. Biomass and NPP of both the young and mature forest depend upon tree species composition as well as environment. Similarly, litter decay differs among tree species and forest types, and forest floor C accumulation is twice as great in the spruce–fir–birch forests at higher elevations than in the northern hardwood forests, partly because of inherently slow litter decay and partly because of cold temperatures. This contributes to spatial patterns in soil solution and streamwater dissolved organic carbon across the Hubbard Brook Valley. Wood decay varies markedly both among species and within species because of biochemical differences and probably differences in the decay fungi colonizing wood. Although C biogeochemistry at the HBEF is representative of mountainous terrain in the region, other sites will depart from the patterns described at the HBEF, due to differences in site history, especially agricultural use and fires during earlier logging periods. Our understanding of the C cycle in northern hardwood forests is most limited in the area of soil pool size changes, woody litter deposition and rhizosphere C flux processes.

Introduction

The Group IV element carbon (C_i A.W. = 12.011) plays a pivotal role in biogeochemistry because it is the molecular structural skeleton of all organisms on Earth. For this reason, energetic and mineral nutrient constraints on biological activity often are conceived in terms of the flows and storage of C; hence, understanding the biogeochemical behavior of C in ecosystems is essential for understanding all ecological interactions. The importance of this understanding is heightened by the effects of human activity on the atmospheric concentration of CO_2 and consequences for Earth's energy balance (Keeling 1973). The overall goal of this monograph is to provide a comprehensive account of the biogeochemistry of C in the Hubbard Brook Experimental Forest (HBEF), New Hampshire, and thereby to continue the

development of the framework for future syntheses of biogeochemical cycle interactions at this site (Likens et al. 1994, 1998, 2002; Lovett et al. in press). Our specific objectives were to evaluate (1) the ecosystem C balance in the second-growth forest at the HBEF and the uncertainties in this evaluation, (2) the relationships between ecosystem C pools and fluxes, (3) temporal changes in pools and fluxes following forest disturbances, (4) constraints on C biogeochemistry in the Hubbard Brook ecosystem, (5) patterns of spatial variation in C pools and fluxes at a range of scales with the HBEF, and (6) the role of carbon in soil formation and mineral weathering. On the basis of these evaluations for the HBEF, we also speculate on regional patterns of C biogeochemistry and prospects for future trends.

The basic scale of study in the Hubbard Brook Ecosystem Study has been the small watershed ecosystem, represented by a suite of similar catchments on the south-facing slope of the Hubbard Brook Valley. In the present monograph we focus on C biogeochemistry at this scale in order to optimize integration with other element cycles that have been described at this scale (Likens et al. 1994, 1998, 2002; Lovett et al. in press) and to address linkages between terrestrial and aquatic systems. However, we also consider C storage and flux at larger and smaller scales to inform our interpretations of pattern and process. We include some new data and update summaries on many storage pools, processes and flux pathways from earlier treatments (Gosz et al. 1978; Bormann and Likens 1979; McDowell and Likens 1988).

The extraordinary biochemical properties of carbon are explained largely by the great variety of chemical bonds that C forms with other elements and by the ability of C to catenate, or bond with itself, as illustrated especially by the compounds formed with hydrogen. Although its crustal abundance is relatively low (average = 0.018%; 17th among the elements in abundance; Greenwood and Earnshaw 1984), carbon is effectively supplied to most biological systems because it is rapidly dispersed through the atmosphere and the hydrosphere. Following the dissolution of CO_2 in water, carbon may be sequestered in sediments after reacting with the electropositive elements to form stable and less water-soluble carbonate compounds especially the secretion of skeletal hard parts by marine biota. Together with the complex cycles associated with organic forms of C, these chemical properties govern the global cycle of C and its role in biogeochemistry (Morse and Mackenzie 1991).

Although it was developed principally to study the local cycles of water and mineral nutrients, the small watershed-ecosystem approach has proven valuable also for improving understanding of carbon biogeochemistry of terrestrial landscapes (e.g., Whittaker et al. 1974; Gosz et al. 1978). It has become clear that the net annual sequestration of C in the mineral soil is relatively small in temperate forest ecosystems (Schlesinger 1990; Goulden et al. 1996) and that the aqueous cycle of C is nearly in balance; by comparison, C transformations within the ecosystem 'black box' are very large (Grace and Rayment 2000). Similarly, whereas long-term rates of C accumulation in major ecosystem storage pools have been very low (on the order of 1 g C/m^2-yr over post-glacial

time), dynamic changes occurring at shorter time scales can be relatively large (Valentini et al. 2000). Because the biogeochemical behavior of carbon influences nearly all ecological interactions, a complete accounting of this behavior at various temporal and spatial scales is needed. The scale of the small watershed-ecosystem provides a suitable reference framework because precise quantification of aqueous budgets of carbon and other elements can only be derived at this scale (Likens and Bormann 1995).

Methodological overview

Study site

Mean annual precipitation at the HBEF is approximately 1395 mm (SD = 189), with 25–33% of the total occurring as snow (Bailey et al. 2003). Over the period of record (since 1955) mean annual precipitation has varied from 975 mm in 1964–1965 to 1888 mm in 1973–1974. Mean annual streamflow is 869 mm (SD = 175), and has varied from 496 mm in 1964–1965 to 1401 mm in 1973–1974. About 50% of annual streamflow occurs during March, April, and May of each year (Bailey et al. 2003). The northern hardwood forest at the HBEF is dominated by American beech (*Fagus grandifolia* Ehrh.), sugar maple (*Acer saccharum* Marsh.) and yellow birch (*Betula alleghaniensis* Britt.). At higher elevations, white birch (*B. papyrifera* Marsh.), red spruce (*Picea rubens* Sarg.) and balsam fir (*Abies balsamea* L.) increase in abundance. The leaf area index of mature northern hardwood forests at the HBEF averages 6.3.

The HBEF encompasses 3037 ha, ranging in elevation from 222 to 1015 m. Most of the research reported here has been conducted on a series of gauged headwater catchments on the south-facing slope of the HBEF (Figure 1). These numbered catchments, watersheds 1 through 6, will be repeatedly referred to as W1, W2, etc. in this monograph. The areas encompassing these small catchments is further sub-divided into three elevation zones for many of our measurements.

The highest elevation zone is dominated by red spruce, balsam fir and white birch (Figure 1). In the deciduous forest below two zones are distinguished (high and low elevation hardwoods). These zones exhibit contrasting biogeochemical behavior as summarized by Johnson et al. (2000). Our calculations of C pools and fluxes in the mature forest ecosystem are based upon the biogeochemical reference watershed, W6, where most measurements have been made. For measurements and studies conducted in other parts of the HBEF, we detail the locations with reference to Figure 1.

Detailed descriptions of the Hubbard Brook Experimental Forest (HBEF), and of many of the procedures used to study its biogeochemistry, can be found in previous reports (Likens et al. 1994, 1998; Likens and Bormann 1995; Buso et al. 2000). Only those procedures most relevant to this paper are provided here.

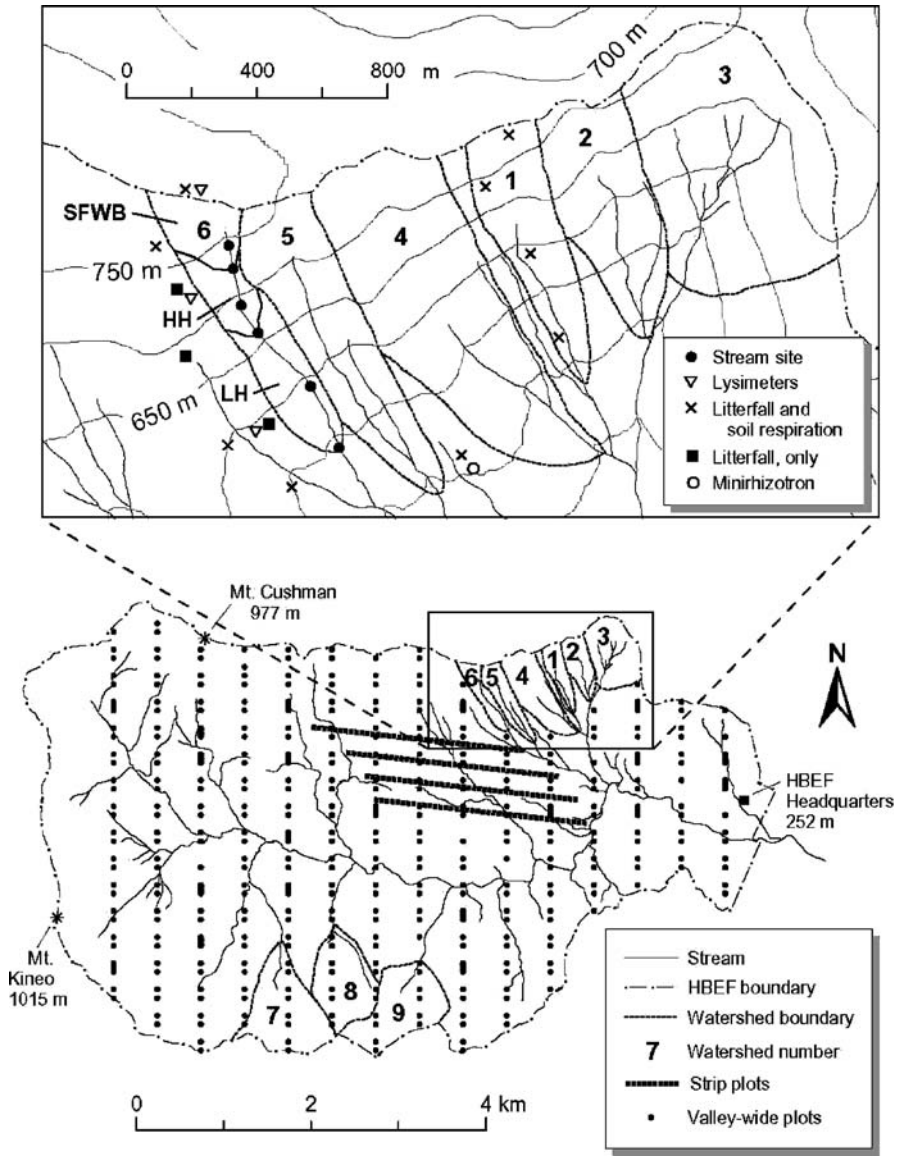

Figure 1. Map of the principal study areas in the Hubbard Brook Experimental Forest, NH.

Biomass and productivity

Biomass of the forest in the reference watershed, W6, was calculated on the basis of diameter measurements in 1965, 1977, and at 5-yr intervals thereafter (Likens et al. 1994). Except for 1965, the sampling included all trees ≥2 cm

DBH and both live and standing dead stems. Site-specific allometric relationships for the dominant species were developed from the harvest of a total of 93 trees and subsequently improved for the purpose of estimating biomass and production (Whittaker et al. 1974; Siccama et al. 1994). Carbon concentrations have been measured for some of the plant tissues in the forest at the HBEF, and they range from about 48 to 53% oven-dry weight (ODW). For simplicity and to facilitate comparisons, we assume for all the calculations herein a C concentration of 50% ODW for all plant, animal and detrital tissues. In contrast, C concentrations in soil organic matter differ substantially from 50% of ash-free ODW; therefore, measured values (Johnson et al. 1995) are used for calculations of soil organic matter. Other biomass and C pool estimates are available periodically for adjacent watersheds that were experimentally harvested. In W2, which was deforested in 1966 and allowed to begin regrowing in 1969, 70 plots (10×10 m) were measured in years 1, 2, 3, 5, 11 and 20 of regrowth (Reiners 1992). In W5, which underwent whole-tree harvest in 1984–1985, 100 plots (1 m^2) were measured in years 1, 2, 3, 5, 7, 11 and 16 of regrowth for herbs and small plants, and in years 7, 11, and 16 an additional 100 plots were measured for larger stems. These C pool estimates are placed in a wider context by comparison with biomass estimates from a set of 430 permanent plots (0.05 ha each) covering the entire Hubbard Brook Valley (Schwarz et al. 2003, Figure 1).

Belowground biomass was estimated for the HBEF by harvesting individual trees and developing allometric equations for the dominant species (Whittaker et al. 1974). Coarse roots also were excavated from quantitative soil pits in the mature forest on W5 prior to its harvest in 1983 and values were observed to agree within 8% of allometric estimates (Fahey et al. 1988). Fine root biomass was measured in a mature forest plot adjacent to W6 (minirhizotron plot; Figure 1) each June from 1993 to 1997 by hand sorting from soil cores (Fahey and Hughes 1994; Tierney and Fahey 2001). In 1998, fine root biomass was measured with 12 soil cores (20 cm^2, each) in eight plots distributed along the elevation gradient near W6 and W1 (litterfall plots – see below; Figure 1).

Net primary productivity in the HBEF was estimated for various time intervals on the basis of allometric and radial increment measurements (Whittaker et al. 1974). In 1991, living and standing dead trees were tagged in a set of four strip plots (2.5 km long and 10 m wide) located in the mature forest west of W6 (Figure 1), and these trees were resurveyed at 2-year intervals through 2001. These measurements provide detailed information on growth and mortality for estimating aboveground net primary productivity (ANPP). We calculated ANPP for W6 in 1996–2000 as the sum of woody biomass increment estimated for all the trees ($\leq$ cm diameter) plus average annual fine litterfall (leaves, twigs, fruits). Fine litterfall was collected from a network of 91 litter traps (0.10 m^2 each) placed in twelve plots distributed in a stratified (by elevation zone) random design in the mature forest to the west of W6 and in W1 (Figure 1). Approaches for extrapolating these values are detailed later. We also measured coarse woody litterfall annually from 1995 to 2002 using 20

4.0-m^2 plots positioned randomly within four of the litter trap plots. These values can be compared with litterfall sampling in 1968–1969 (Gosz et al. 1972). Carbon retranslocation prior to leaf fall was estimated from the difference in specific leaf area (area/mass ratio) between freshly-fallen leaf litter and live foliage of each of the dominant species (Fahey et al. 1998).

Soil respiration and belowground carbon allocation

We measured total soil respiration (TSR) at 12 random locations in eight of the litterfall plots described above (Figure 1) using a cuvette method and a LiCor 6200 infra-red gas analyzer (Norman et al. 1992). Permanent collars were installed to avoid disrupting the forest floor and the soil CO_2 gradient at the air–soil interface. We measured TSR in these plots on a total of 23 dates during the snow-free season from 1998 to 2002 (Fahey et al. in press). Although TSR beneath winter snowpack was not measured, field measurements in late November and December 1998 were similar to those predicted by a linear regression model based on soil temperature (see below). Soil respiration measurements also were made by the same methods on a network of 20 collars for 16 dates in 1997–1999 in the minirhizotron plot (Figure 1) and on a parallel transect in the adjacent watershed (W5) that was clearcut in 1984. We quantified processes contributing to belowground C allocation by (1) allometric estimates of changes in living woody root biomass, described above; (2) minirhizotron measurements of fine root turnover; and (3) cuvette measurements of respiration by detached fine roots. Root longevity was measured using the minirhizotron (MR) approach. Five MR tubes were installed in the minirhizotron plot (Figure 1) in 1995 and MR images were collected monthly during the snow-free period from these tubes from 1996 to 2000. Fine root longevity was estimated on the basis of individual root disappearance from images for about 2000 roots. The accuracy of our estimates of root longevity and root turnover have been partially confirmed by comparison with a radiocarbon method (Tierney and Fahey 2002). Respiration of detached fine roots (< 1 mm diameter) was measured by a cuvette method using a LiCor respiration chamber and LI-6200 system, for both mineral soil and forest floor roots during the snow-free season (May–November, Fahey et al. in press) at a site in the lower valley of the HBEF at 250 m elevation. Roots were collected from a mixed stand of northern hardwoods, gently cleaned under stream flow and sealed in the chamber. Air temperature was maintained within 3 °C of ambient soil temperature by adjusting the time of day measurements were made. Our approaches for scaling measurements of TSR and root respiration to the watershed level are detailed later.

We used an empirical approach to distinguish forest floor and mineral soil CO_2 fluxes (Fahey et al. in press). Total respiration for the forest floor was measured by inserting a sheet metal barrier (30×30 cm) at the mineral soil–forest floor interface. After allowing 60 min to reach a new steady-state flux,

CO_2 emission was measured using the LiCor soil respiration cuvette. A total of 19 such measurements were made on three dates in the minirhizotron plot (Figure 1).

Dissolved carbon

Water samples from the HBEF are routinely analyzed for pH, alkalinity, dissolved inorganic C (DIC) and dissolved organic C (DOC). Bulk precipitation has been collected weekly since 1963 in several large forest openings distributed throughout the study area (Likens and Bormann 1995). The organic C chemistry in precipitation at the HBEF was measured during June 1976–May 1977 using wet-only precipitation collectors (Likens et al. 1983). Weekly bulk precipitation samples have been routinely analyzed for TOC at a collector adjacent to W6. Unless noted otherwise, the precipitation organic C values reported are based on these more recent samples collected during water years (WY) 1995–1996 through 1998–1999 (WY runs from June 1 through May 31). Throughfall was collected beneath the forest canopy during the growing season (June–September) for 4 years (1989–1992) at four sites distributed along the elevation gradient in the mature forest west of W6 (Lovett et al. 1996). In addition, earlier work by McDowell and Likens (1988) examined fractions of organic C in throughfall.

Soil solutions have been collected on a monthly basis since 1982 using zero-tension lysimeters at three depths in the soil profile (O_a, B_h and B_s horizons) in three sites (Figure 1) along the elevation gradient in the mature forest west of W6 (Driscoll et al. 1988). In 1996 the dissolved organic C (DOC) in these solutions was fractionated into six standard fractions using the procedure of Leenheer (1981). Streamwater samples have been collected weekly since 1963 on a series of small watersheds in the HBEF (Likens et al. 1994, 1998; Likens and Bormann 1995) and inorganic and organic C have been quantified on a subset of these samples during various time periods. Routine TOC analysis of weekly stream samples began in 1995 at Watersheds 6, 7, 8, and 9, coincident with weekly precipitation sampling. Longitudinal sampling of first-order streams has also been periodically conducted in several small watersheds (Likens et al. 1994). In soil solutions and streamwater, concentrations of naturally occurring organic anions were estimated using a charge balance approach (Driscoll et al. 1994). The partial pressure of CO_2 (P_{CO_2}) in soil solutions and stream water was calculated for all samples using measured values of DIC, pH and temperature with appropriate mass law expressions (Stumm and Morgan 1981). During 1992 and 1993 direct measurements of P_{CO_2} were made at weekly intervals in W6 using the headspace equilibration method (Cole et al. 1994). To estimate the gas piston velocity for the streams, an inert tracer (sulfur hexafluoride), along with a hydrologic tracer (NaCl), was added to a stream adjacent to W6 (Bear Brook) on several occasions. The CO_2 outgassing from the stream is the product of the difference in P_{CO_2} between the

water and the air, and the gas piston velocity, corrected for temperature (Cole and Caraco 1998).

Detritus and soil carbon pools

The organic matter content of the forest floor organic horizons (O_{ie} + O_a) in the reference watershed, W6, have been measured periodically since 1976 using an excavation method, with correction for ash content by dry combustion. Coarse woody debris on W6 was measured in 1978 and 1995 using a line intercept method, stratified by elevation zone (Tritton 1980; Fahey et al. in press). Pools of soil C have been measured in the mature forest and in a cutover watershed (W5) using a quantitative pit method (Johnson et al. 1995). The total C concentration of the <2-mm fraction was determined by combustion-gas chromatography using the modified Dumas method. Total C is a reliable measure of organic C in these granitic soils (Huntington et al. 1988).

The content of humic substances (fulvic and humic acids) was determined on selected soil samples using standard procedures (Stevenson 1994), with one modification: a polysaccharide fraction was isolated from the fulvic acid fraction as described in Ussiri and Johnson (2003). Selected soil extracts were fractionated into hydrophobic and hydrophilic acids, bases, and neutrals according to the procedure of Leenheer (1981), as modified by Vance and David (1991). Some whole soils, freeze-dried isolates of humic substances, and freeze-dried dissolved organic matter from soil solution and stream water samples were characterized using nuclear magnetic resonance (NMR) spectroscopy (Wilson 1987). All spectra were acquired with ^{13}C as the target nucleus, using the cross-polarization with the magic-angle spinning (CPMAS) technique. This method is only semi-quantitative, but generally reliable when comparing spectra derived from similar source materials (Kinchesh et al. 1995). Details of NMR analytical conditions can be found elsewhere (Dai et al. 2001; Ussiri and Johnson 2003).

Additional details on the dynamics of the forest floor horizons have been obtained by periodic quantitative collections following the clearcut harvest of W5 (Johnson et al. 1995; Yanai et al. 1999). We directly measured net C loss from undisturbed locations in W5 in 1996, 13 years after harvest. Sixty undisturbed locations were chosen randomly from a set of transects distributed across the watershed that were mapped immediately after harvest of W5. Forest floor blocks were collected by our standard methods and organic matter content measured as the ash-free dry mass. These values were compared with pre-harvest data for 235 forest floor blocks collected in 1982 from W5 (Johnson et al. 1995).

Detailed studies of the decomposition of aboveground litter have been conducted at the HBEF over both short (Gosz et al. 1972) and long time scales (Kratz et al. 2003). Decomposition of fine roots and woody roots also has been measured (Fahey et al. 1988; Fahey and Arthur 1994). A time series of

measurements of the biomass of coarse woody debris following the deforestation of W2 provides information on wood decay rates (Arthur et al. 1993). Direct measurements of bole decay rates also have been conducted in the mature forest (T. Siccama and D. Vogt, unpublished).

Heterotrophic activity

Gosz et al. (1978) summarized the energetics of heterotrophs at the HBEF based upon detailed research done during the first decade of the Hubbard Brook Ecosystem Study. Since that time, continuing studies of populations of birds and lepidopteran insects provide a longer-term perspective on the grazing food chain (Holmes and Sherry 2001). Also, our observations of the recent expansion of moose (*Alces alces*) populations and their obvious effect in browsing understory vegetation led us to estimate their likely role in C flux. The consumption of ANPP by moose was calculated on the basis of regional estimates of moose density in the White Mountains, the size-class distribution in these populations (K. Bontaite, personal communication) and literature values for food ingestion rates for moose in summer and winter (Schwarz and Renecker 1997).

Seasonal measurements of several groups of soil heterotrophs have been conducted at four plots distributed along the elevation gradient in the mature forest west of W6 in the same plots used for litterfall collections (Figure 1). Microbial biomass was measured using a chloroform fumigation and incubation procedure (Bohlen et al. 2001). The production, emission and consumption of methane have been quantified on a landscape scale using static chamber measurements coordinated with laboratory incubations (Yavitt and Fahey 1993). Soil microinvertebrates have been enumerated microscopically for soil cores following a modified Tullgren extraction procedure (Crossley and Blair 1991).

Energy flow and biogeochemical studies in stream ecosystems of the HBEF have a long history (Fisher and Likens 1973; Hedin 1990; Findlay et al. 1997; Hall et al. 2002; Stelzer et al. 2003). Organic debris dams are a prominent and important feature of the headwater streams at the HBEF, and numerous studies have revealed their importance for stream metabolism and particulate C transport (Bilby and Likens 1980; Bilby 1981; Likens and Bilby 1982; Hedin 1990; Steinhart et al. 2000).

Extrapolations, error estimates and modeling

In general, our pool and flux estimates are expressed at the scale of the small headwater catchments (reference watershed, W6) where our measurements are concentrated and hydrologic fluxes can be calculated. Biomass, detritus and soil C pools have been estimated at this scale based on averages derived from stratified random sampling in three elevation zones (as described in section

'Study sites') and the area of each zone. For a variety of other pools and fluxes sampling was conducted at the 0.5 ha scale in eight plots distributed in and around W1 and W6 (Figure 1). These measurements include fine root biomass, soil microbial and microarthropod biomass, fine and coarse litterfall, and throughfall. For these pools and fluxes extrapolation from the plot to watershed scale used the arithmetic mean values across plots. We also measured TSR at this plot scale, but extrapolations were conducted using the best-fit relationship between TSR and soil temperature. Long-term (1959–1997) mean daily soil temperature values from an intensive plot near the bottom of W1 (Bailey et al. 2003, Figure 1) were applied to the regression equation to obtain annual flux estimates. A similar approach was taken to estimate fine root respiration: empirical measurements were used to develop separate regression models on soil temperature for forest floor and mineral soil fine roots. These equations were applied with daily soil temperature data, and fine root respiration flux was calculated as the product of long-term average fine root biomass and fine root respiration rate (Fahey et al. in press). Estimates of uncertainty for TSR were obtained on the basis of confidence intervals around the Q_{10} values for the regression model based on soil temperature. In the case of fine root respiration, propagation of error was derived using Monte Carlo simulations based on the statistical distributions for fine root biomass and for the root respiration regressions (Fahey et al. in press).

Hydrologic fluxes of C were calculated at the watershed and sub-watershed scale as the product of water flux and C concentration. For streamflow these estimates were based on weekly stream chemistry applied to discharge values from instantaneous streamflow measurement. Soil water fluxes of C were estimated as the product of monthly average soil solution concentrations collected by lysimeters in the three elevation strata and soil water fluxes simulated using a forest hydrology model (BROOK 90, Federer 1995) which was developed and validated at this study site.

We used Monte Carlo randomizations to propagate and combine the errors that contribute to the uncertainty associated with our measurements of tree biomass (Taylor 1982; Chave et al. 2004; Harmon et al. 2004). The primary sources of error include: (1) variation in the non-linear equations predicting tree height from tree diameter; (2) variation in the non-linear equations predicting tree biomass from parabolic volume; and (3) spatial variation among sample plots. It is important to note that at Hubbard Brook some pools have been completely inventoried at the watershed scale (e.g., trees in Watershed 6). In these instances, there is no spatial variation even though we still use plots as a convenient accounting tool.

We took advantage of an experimental whole-tree harvest to assess the uncertainty associated with allometric scaling (Whittaker et al. 1974; Siccama et al. 1994). On average, there was less than a 3% difference between harvest-based and allometric-based biomass estimates (Siccama et al. 1994). On an individual plot level, the relative root mean square error (rRMSE) from 1000 Monte Carlo realizations of biomass was $\pm 34\%$. We used this plot-level error

rate in all error propagation routines and report the standard deviation of 1000 estimates of the mean (i.e., the standard error, Table 1).

Carbon fluxes in photosynthesis and respiration were estimated using the simulation model, PnET-II (Aber et al. 1995) because direct measurements were not available. PnET-II is a generalized monthly time step model of forest water and C balances that has been validated successfully against water balances for the HBEF and C balances for the Harvard Forest. In the model, photosynthesis is regulated by climatic factors and foliage nitrogen concentration as synthesized from literature sources (Aber et al. 1996). Foliage and wood production are driven by the accumulation of growing degree-days and water stress reduces potential photosynthesis. The model was run over the long term (50 years) using site-specific parameters (e.g., vegetation characteristics) and driving variables (e.g., climatic data) that were available for W6 at the HBEF.

Table 1. Major pools of carbon in the reference forest watershed-ecosystem (W6) at the Hubbard Brook Experimental Forest, New Hampshire in 1997.

Component	Carbon pool (g/m^2)
Living plant biomass	
Foliage	201
Branch/twig	2718
Bark	610
Bole wood	5966
Aboveground biomass	9495 (124)
Root crown	790 (11)
Lateral woody roots	1460 (294)[a]
Fine roots	261 (14)[a]
Belowground biomass	2511 (319)
Total plant biomass	12,006
Heterotroph biomass	
Soil microbes[a]	66 (9)
Other heterotrophs	3
Total biomass	12,075
Woody detritus	
Standing dead	657 (72)
Coarse woody debris (on the ground)	468 (37)
Dead roots	188
Total woody detritus	1313
Soil organic matter[b]	
Organic horizons	2970 (340)
0–10 cm	3170 (120)
10–20 cm	2600 (140)
20+	7000 (660)
Total SOM	15,740 (914)
Stream channel	550
Total ecosystem	29,612

Standard errors are given in parentheses. See text for explanation of error estimates.
[a]Standard errors for roots based on spatial variation for soil pits and cores.
[b]Soil heterotroph biomass is measured as part of soil organic matter.

Ecosystem carbon pools

The pools of C in living biomass, detritus and soils in the mature forest of the biogeochemical reference watershed (W6) at the HBEF are summarized in Table 1. The largest C pool in this forest is organic C in the mineral soil horizons, which comprises 43% of the total ecosystem C. The living biomass pool is only slightly smaller (40.5% of ecosystem C) and detrital pools (forest floor and coarse woody debris) constitute most of the remaining C (14.5%). A relatively small proportion of C ($< 2\%$) is stored in the stream channel. Vogt et al. (1995) summarized literature values for ecosystem organic matter distribution across global forest types; in their cold-temperate broadleaf deciduous type, 41% of organic matter was in mineral soil, 45% in living biomass and 14% in aboveground detritus.

These C pools appear to be near steady state in the mature forest at the HBEF. Repeated measurements of forest biomass on W6 indicate that living biomass has remained nearly constant from 1982 to 1997 (Figure 2); hence, C accumulation in living trees is now approximately balanced by mortality. These direct observations contradict earlier projections based upon the assumption that canopy trees would maintain growth rates observed in the 1960s (Whittaker et al. 1974) and as represented in the forest growth simulator (JABOWA; Bormann and Likens 1979); these projections suggested that the mature forest at the HBEF might attain a maximum biomass considerably higher than that observed on W6 in the 1990s. However, the biomass of an old-growth northern hardwood forest at the Bowl Research Natural Area is similar to that in W6 of the HBEF (Martin and Bailey 1999). It is notable that the C density of biomass

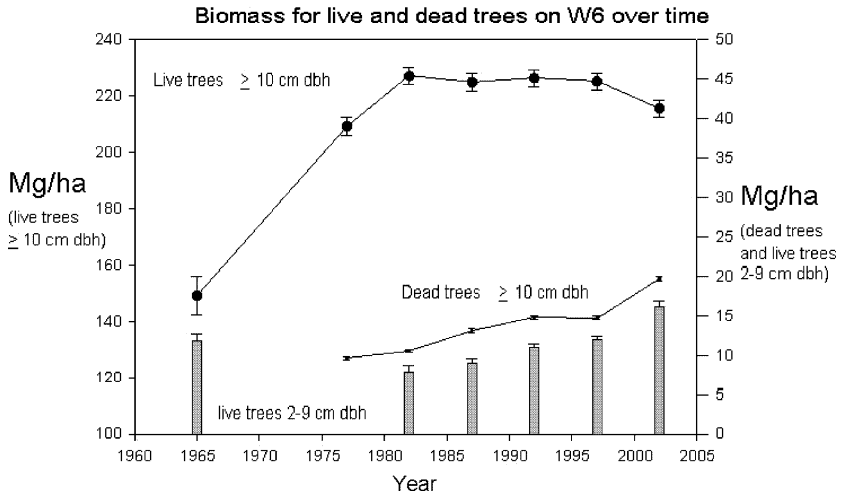

Figure 2. Total tree biomass of the reference watershed (W6) at the Hubbard Brook Experimental Forest from 1965 to 2002. Error bars indicate standard errors.

in these mature forests is about twice as high as the average for the northern hardwoods forest type in the northeastern United States (Birdsey 1992).

Repeated remeasurements indicate that C storage in forest floor organic horizons is also at or near steady state (Figure 3). Over a total of eight sampling dates between 1976 and 2002 the mass of organic matter in the forest floor did not change significantly in a univariate regression. However, given the high sampling variation observed, a change of 23% over this time period would have been required to detect the change at $\alpha = 0.05$ (Yanai et al. 1999); hence, changes in organic C content of the forest floor as large as 24 g C/m^2-yr cannot be ruled out. The uncertainty in these observations arises from high spatial variation (CVs ranged from 62 to 100% across sampling dates) as well as subjectivity in separating forest floor and mineral soil (Federer 1982; Yanai et al. 1999).

Direct observations of coarse woody debris (CWD) on the ground on W6 in 1978 (Tritton 1980) and 1995 (Fahey et al. in press) indicate that this C pool also has not changed significantly in recent years (543 $\pm$ 112 g C/m^2 in 1978 and 468 $\pm$ 46 g C/m^2 in 1995). This result is somewhat surprising because the forest on W6 was heavily cut over in the decade 1910–1920 and parts of the watershed received additional damage to overstory biomass in the 1938 hurricane and subsequent salvage cutting operations (Cogbill, unpublished manuscript; Merrens and Peart 1992); hence, we might expect CWD pools to be

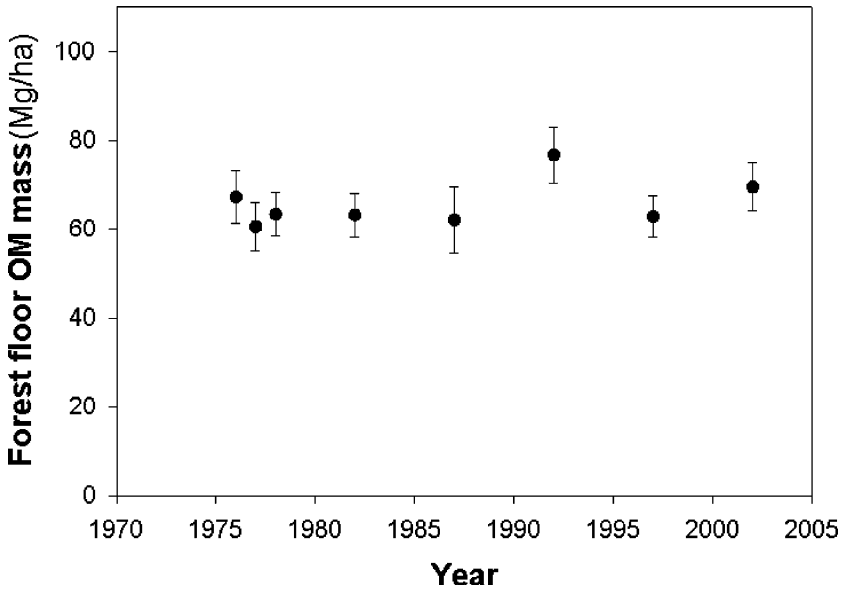

Figure 3. Organic matter content of the surface organic horizons (O_{ie} + O_a) on the reference watershed (W6) at the Hubbard Brook Experimental Forest for eight years of measurement. Error bars indicate standard errors.

accumulating. A relatively steady increase in standing dead tree biomass has been observed on W6 (Figure 2) since 1982, most recently coinciding with a decline in live biomass associated with high mortality of sugar maple in the high hardwood zone. In contrast, detailed measurements between 1981 and 2001 indicate that the biomass of standing dead and snag trees in the forest to the west of W6 (Figure 1) remained nearly constant (600 $\pm$ 5 g C/m^2) over two decades (T.G. Siccama, unpublished data). The CWD pool at W6 in the HBEF is smaller than most regional values, compiled by McGee et al. (1999). They reported a range of 750–2250 g C/m^2 for downed CWD in old-growth northern hardwood forests and 300–2700 g C/m^2 for second-growth stands. Hence, we would anticipate some long-term accumulation of C in the woody detrital pool in future stages of stand development.

Direct measurement of changes in the largest ecosystem C pool, mineral soil organic matter, is difficult because of high spatial variability (CV of 46%; Johnson et al. 1990). Even using quantitative soil pits, 32 samples would be required to detect a 30% change in the mineral soil C pool at $\alpha = 0.05$. For purposes of ecosystem C budgeting in the mature forest, we will assume that the mineral soil and forest floor C pools are currently at steady state; however, we will explore possible consequences to budget calculations of undetectable changes that may be occurring in these C pools.

Our observation that the ca. 80-year-old forest (in 1995) at the HBEF is nearly neutral with respect to net ecosystem exchange of C contrasts with broad-scale observations for second-growth forests in the north temperate zone (Pacala et al. 2001). Our measurements since about 1980 of stable pools in live biomass, standing dead and CWD, and surface organic horizons suggest that beyond the age of ca. 70 years, northern hardwood forests recovering from intensive harvest do not continue to accumulate carbon, at least under the current suite of environmental drivers (e.g., climate, CO_2, acid deposition) and biotic composition (sugar maple, beech, yellow birch, red spruce and attendant symbionts, pests and pathogens) at the HBEF. A relatively small amount of C might be expected to accumulate in CWD over the next century, based upon regional observations of old-growth forests (McGee et al. 1999). Our study site appears to be representative of widely-distributed second-growth northern hardwoods on base-poor soils in the Northeast (Likens and Bormann 1995). Evaluating how widely these conclusions apply beyond this situation is a pressing need for global C balance research.

Ecosystem carbon fluxes

The largest annual C fluxes to and from the forest ecosystem are in gaseous form: the photosynthetic fixation of CO_2 by the vegetation and the CO_2 emission associated with autotrophic and heterotrophic respiration. An additional mineral soil process contributing to the C budget is abiotic fixation of CO_2 through the release of basic cations and the formation of bicarbonate

during mineral weathering (Berner 1992). The geology of the HBEF is dominated by minerals that supply basic cations at slow rates (sillimanite-grade politic schists and quartz monzonite); hence, the fixation of CO_2 by weathering occurs only to a limited degree. This process has been estimated at 0.12 g C/m^2-yr in W6 (van Breemen et al. 1983, 1984), about two orders of magnitude lower than for calcareous sites.

Although aerodynamic estimates of the balance between C fixation and all respiratory losses (i.e., NEP or NEE) have been obtained in some forests (e.g., Harvard Forest; Wofsy et al. 1993), the rugged terrain of the HBEF presents serious problems for such an approach. Our approach to apportioning C fluxes in the northern hardwood forest ecosystem includes the following elements: (1) direct, watershed-wide measurements of several fluxes that can be reliably quantified (litterfall, tree growth, total soil respiration, root turnover, hydrologic fluxes); (2) indirect estimates of some belowground fluxes based on mass balance calculations under the steady-state assumption described above; and (3) simulation of gross and net photosynthetic C flux and autotrophic respiration using PnET-II (Aber et al. 1995), which has been validated for C balance at Harvard Forest, Massachusetts, where aerodynamic measurements were available, and where forest physiognomy and climate are similar to the HBEF.

Detrital carbon fluxes

A major C flux that can be measured with accuracy and precision is aboveground litterfall. The long-term average C flux in fine litterfall (i.e. leaves, twigs <2 cm diameter, fruits, and bark) measured with a network of 91 litter traps (0.10 m^2 each) in the forest adjacent to W6 was 170.7 g C/m^2-yr (Table 2). Across eight study plots the range was from 146 to 199 g C/m^2-yr, with the lowest value observed in the spruce–fir–birch forest at the highest elevations of the experimental watersheds (Figure 1). As noted previously by Knapp and Smith (2001), annual variability in fine litterfall flux at the HBEF is low, with annual flux averaged across the eight plots ranging from 166 to 172 g C/m^2 among years. Spatial and annual variation of C flux in coarse litterfall (mostly branches) was much higher, but the average annual flux (15.5 g C/m^2-yr) was much lower than for fine litterfall. Across 6 years of collection (not including the ice storm event of January 1998), annual coarse litterfall C flux varied by over 2-fold. Coarse litterfall is highly episodic: two major episodes of high flux have been observed over the measurement period at the HBEF, both associated with severe weather events, and the long-term average coarse woody litterfall remains somewhat uncertain for this reason. In particular, coarse litterfall in 1968–1969 for the same study area (i.e., west of W 6) was 63.4 g C/m^2-yr, about four times higher than the 6-year mean reported above. That high flux was associated with severe wind storms and an unusual late-summer hail storm (Gosz et al. 1972). A severe ice storm in January 1998 resulted in very

high coarse litterfall in a band of high damage between 600 and 800 m elevation in W1–W6 (Rhoads et al. 2002); based upon eleven random plots (100 m^2 each) in this zone, average C flux from this event was 434 ± 93 g C/m^2. Hence, infrequent extreme events can result in coarse litterfall fluxes as large as the total for 10 years or more of chronic litterfall. Assuming that the high coarse litterfall of 1968–1969 was a 25-yr event and that the 1998 ice storm was a 100-yr event, the long-term average coarse litterfall flux would increase to about 20g C/m^2-yr; this value is assumed in later budget calculations.

Carbon flux associated with larger, coarse woody debris was estimated in the forest west of W-6 (Figure 1) using a biennial inventory of mortality for

Table 2. Carbon fluxes for a mature northern hardwood forest on watershed (W6) at the Hubbard Brook Experimental Forest in the late-1990s.

Gross photosynthesis	[1230]
Autotrophic respiration	[645]
Foliage	[324]
Other aboveground (incl. root crowns)	[62]
Total root	[259]
Total forest NPP (model)	[585]
Aboveground NPP (model)	[404]
Aboveground NPP (measured)	354
Annual tissues	171 (16.2)
Perennial tissues	183 (45.6)
Belowground NPP (model)	[181]
Fine root (< 1 mm)	91
Coarse root	38
Rhizosphere carbon flux	80[a]
Total root respiration	660 (54)[b]
Total root allocation	468[a]
Heterotrophic respiration	
Soil heterotrophs	460[c]
Other terrestrial heterotrophs	10
Hydrologic fluxes	
Atmospheric deposition	1.7 (1.3)
Net throughfall (canopy leaching)	3.1 (1.3)
Forest floor leaching	25 (8.6)
Subsoil leaching	8 (2.4)
Stream flow	
Dissolved organic	1.72 (0.65)
Dissolved inorganic	0.39 (0.17)
Particulate	0.56
Stream degassing	4.0

Values in brackets estimated by the model PnET-II (Aber et al. 1995); other values estimated by field measurements as detailed in text. Standard deviations are given in parentheses, except where noted.

[a]Estimated by difference, see text.

[b]95% confidence interval (Fahey et al. in press).

[c]Includes coarse woody debris.

4672 tagged trees (>10 cm DBH) from 1991 to 2001. Over this 10-year interval the total C flux into the coarse woody debris pool (including standing dead) averaged 120 g C/m^2-yr, intermediate between the fine and coarse litterfall C flux values. The C flux to this pool differed substantially from year to year during this interval; for example, it was almost twice as high for 1995–1997 as for 1991–1993. Hence, annual variation in deposition of CWD is an important source of uncertainty in the ecosystem C budget at the HBEF.

Carbon flux associated with belowground plant detritus (root turnover) is more difficult to measure. We have estimated fine root production and detrital C flux on the basis of soil core measurements of fine root biomass and minirhizotron estimates of fine root longevity (Fahey et al. 1999; Tierney and Fahey 2001, 2002). In the forest adjacent to W6 where root turnover has been measured, C content of fine roots (<1 mm diameter) averaged 274 ± 13 g C/m^2 over 5 years of measurement, which is similar to the watershed-wide average value (261 ± 13 g C/m^2) based upon measurements from the eight litterfall plots (Table 1). High spatial variability precluded the detection of any significant differences between years. Minirhizotron (MR) measurements indicate that fine root turnover is about 0.35 $year^{-1}$ (Tierney and Fahey 2002). This value is considerably lower than previous estimates of fine root turnover for northern hardwood forests (Hendrick and Pregitzer 1992; Tierney and Fahey 2001), but it is higher than estimates based upon bomb ^{14}C (Gaudinski et al. 2001). In previous MR studies based on only 2 years of observations, mean root longevity was estimated from the median value, but further study revealed that a substantial portion of the fine roots lives 5 years or longer (Tierney and Fahey 2002); hence, the usual assumption that the median longevity accurately characterizes the mean value is false and leads to a substantial overestimation of turnover rate. Similarly, the assumption of normally-distributed root lifetimes in the bomb ^{14}C approach (Gaudinski et al. 2001) would result in underestimates of turnover rate by that method (Tierney and Fahey 2002; Trumbore and Gaudinski 2003). Assuming little or no C retranslocation from dying fine roots (Nambiar 1987), we estimate fine root detrital C flux at 91 g C/m^2-yr, with slightly higher values for mineral soil than forest floor horizons. Thus, C flux associated with fine root turnover is much lower than that of aboveground fine litterfall at the HBEF.

Carbon flux via mortality of coarse roots has not been measured directly at the HBEF (nor to our knowledge in any forest ecosystem). The simplest approach for estimating this flux is to assume that the ratio of aboveground to belowground woody detrital C flux is equal to the ratio of aboveground to belowground woody biomass. The resulting value is 18 g C/m^2-yr. In addition, dead roots associated with tree mortality can be calculated in the analogous way at 20 g C/m^2-yr. This flux can be distributed between the organic and mineral soil horizons under the assumption that woody root mortality rates were proportional to woody root biomass pools in these soil horizons (Fahey et al. 1988).

Tree growth and net primary productivity

Aboveground net primary productivity (ANPP) of the forest on W6 between 1956 and 1965 was estimated as the annual increase in living biomass plus production of ephemeral tissues (e.g., foliage, fruits) (Whittaker et al. 1974) and corrected for dying trees (Binkley and Arthur 1993). Based upon measurements available at that time, Whittaker et al. (1974) estimated average ANPP over this 10-year interval at 420 g C/m^2-yr. Estimated C flux in forest ANPP decreased with increasing elevation in W6, and ANPP was markedly higher for the interval 1956–1960 (462 g C/m^2-yr) than 1961–1965 (380), a difference that the authors attributed to severe drought conditions in the early-1960s (Whittaker et al. 1974).

Aboveground NPP has declined in the forest on W6 since the time of Whittaker's measurements. We employed the same allometric approach for 1996–1998 and estimated ANPP at 354 g C/m^2-yr (Table 2). This decline in productivity seems to be due primarily to reduced growth rates of sugar maple and yellow birch (T.G. Siccama, unpublished data). Sugar maple has suffered high mortality in the high hardwood zone of W6 since the mid-1980s; nearly half of the stems >10 cm DBH died between 1985 and 2000, far exceeding the chronic rate of tree mortality in mature northern hardwoods (Fahey 1998). Fine litterfall flux, however, has not changed significantly during recent decades, as this C flux was similar during the 1969–1970 (176 g C/m^2-yr; Gosz et al. 1972) and 1992–1998 (171 g C/m^2-yr) periods. Hence, decreased production of perennial, woody tissues accounts for most of the decline in ANPP on W6. The elevational pattern of ANPP in W6 reported by Whittaker et al. (1974) persists, associated mostly with lower production in the area dominated by spruce–fir–white birch where recent ANPP averaged 346 g C/m^2-yr compared with 368 g C/m^2-yr for the northern hardwood forest zones.

Calculation of ANPP as the sum of increment in perennial tissues and replacement of annual tissues may slightly overestimate actual production because some organic matter is resorbed from ephemeral tissues prior to senescence (Zimka and Stachurski 1994). We have estimated the maximum extent of C resorption from the differences in leaf area to weight ratio between late-season live foliage and fresh litterfall. This value ranged from 16 to 26% across the three dominant hardwood species for 3 years, and the average value is about 40 g C/m^2-yr. This value is undoubtedly an overestimate because of respiratory and leaching losses of C during senescence and leaf fall, but it provides an indication of the likely significance of this flux. Hence, ANPP could be overestimated by several percent by not accounting for C resorption from leaves.

Detailed studies of root production provide a basis for improving belowground production (BNPP) estimates for the HBEF (Fahey and Hughes 1994). As described earlier, fine root turnover (which equals fine root production under an assumption of steady-state fine root biomass) has been estimated at 91 g C/m^2-yr (Tierney and Fahey 2002). This C flux is added to the production

of woody roots (38 g C/m^2-yr) estimated by assuming proportionality with aboveground growth. The sum of these values (129 g C/m^2-yr) is a conservative estimate of C flux associated with belowground production, but it illustrates that ANPP is much higher than BNPP in the HBEF (Table 2). The BNPP estimate above is conservative because additional belowground C flux must be attributed to root exudation, rhizodeposition and allocation to mycorrhizal fungi (rhizosphere carbon flux – RCF). Although RCF is difficult to measure, budgetary calculations for the HBEF (described later) suggest that BNPP is considerably higher than the 129 g C/m^2-yr attributed to root growth, alone.

Total NPP for the forest on W6 at HBEF in 1997 can be estimated as the sum of ANPP and BNPP (ignoring RCF for the moment) at 483 g C/m^2-yr. The ratio of ANPP:NPP for the HBEF (0.73) is thus similar to that in a series of beech-dominated forests in northern Europe (0.71–0.78; Scarascia-Magnozza et al. 2000).

The actual net C flux between the atmosphere and plant foliage is much larger than NPP because plants respire a large fraction of the assimilated C. The simulation model PnET-II (Aber et al. 1995), parameterized for the HBEF, predicted 1230 g C/m^2-yr of gross photosynthesis. However, NPP estimated by the PnET model (585 g C/m^2-yr) was higher than our field measurements (Table 2). Most of the discrepancy between the estimates is associated with wood production; as noted above, wood growth on W6, especially for sugar maple and yellow birch, has declined markedly in the past two decades. The reasons for the recent decline of growth in the HBEF are not clear and deserve further study. Three prominent possibilities are (1) declining site quality associated with soil base cation depletion (Likens et al. 1998); (2) unusual decline and mortality of beech owing to beech bark disease and of sugar maple from undetermined causes; and (3) stand dynamics resulting from disturbance history, especially the 1938 hurricane (Reams and van Deusen 1993), and age-related growth decline (Gower et al. 1996; Ryan et al. 1997); that is, in the 1950s–1970s tree growth in the HBEF may have been responding to the hurricane disturbance.

Respiration by autotrophs and heterotrophs

The largest directly measured C flux in the forest is soil CO_2 evolution, a C flux pathway that typically comprises over 70% of total ecosystem respiration in forests (Epron et al. 1999). Following conventions we designate this flux as total soil respiration (TSR, Raich and Schlesinger 1992), although we emphasize that soil CO_2 efflux does not account for respiratory CO_2 leaving the watershed as DIC and CO_2 evasion from streams. Based upon a total of more than 2500 flux chamber measurements over 4 years at eight plots located in the forest adjacent to W6, we estimate that annual TSR averages 660 g C/m^2-yr (Fahey et al. in press). Variation in TSR among the eight stands in our surveys

was moderately high (range = 540–800 g C/m^2-yr), and this variation was not clearly associated with differences in forest composition among the plots. For example, the highest and lowest values were observed in two different spruce–fir–white birch stands at high elevation (Figure 1); the stand with the lowest TSR had a shallow lithic fibrist soil developed on ledges, whereas the other spruce–fir–white birch stand was on a deep hemist. However, there was a consistent pattern of decreasing TSR with increasing elevation in the northern hardwood forest (low elevation = 700, mid = 665, high = 500 g C/m^2-yr) which corresponds with the elevation pattern in NPP noted earlier by Whittaker et al. (1974). This average TSR for the forest surrounding W6 at the HBEF is similar to the average value for temperate deciduous forest reported by Raich and Schlesinger (1992), but somewhat higher than would be predicted from their global regression based on ANPP. Across a range of forest stands at Harvard Forest in Massachusetts, Davidson et al. (1998) reported a similar range (530–870 g C/m^2-yr) and average (720 g C/m^2-yr) as we observed at the HBEF; Gower (2003) reported a mean TSR of 780 g C/m^2-yr for global temperate deciduous forests. We segmented TSR into forest floor and mineral soil contributions using an empirical approach in one of the plots located in the lower hardwood zone (Figure 1). On the basis of 19 measurements of forest floor-only respiration, the proportion of TSR attributed to forest floor respiration was 58 ± 3% (Fahey et al. in press).

Fine root respiration was measured throughout the snow-free period on detached roots of the dominant hardwood tree species at ambient atmospheric CO_2 concentrations. Most of the variability in root respiration was accounted for by ambient soil temperature, and no significant differences were observed between the three dominant tree species of the northern hardwood forest (Fahey and Hughes 1994). However, root respiration rates differed markedly between forest floor and mineral soil horizons, with much higher values observed for roots from the forest floor at all temperatures (Fahey et al. in press). Since forest floor roots have much higher tissue nutrient concentrations than mineral soil roots at the HBEF (Fahey and Arthur 1994), this result is consistent with the observation that roots with high N concentrations have higher respiration rates (Burton et al. 2002).

We applied the long-term average soil temperature curve for the HBEF (Bailey et al. 2003) to the best-fit relationship between soil temperature and fine root respiration for forest floor and mineral soil roots to estimate total fine root respiration. Annual fine root respiration in the forest floor horizons was estimated to be 118 g C/m^2 yr, based upon a long-term average fine root ($\leq$ 1 mm) biomass of 230 ± 13 g/m^2 (Tierney and Fahey 2001). In the mineral soil, fine root respiration was estimated at 90 g C/m^2-yr, based upon fine root biomass of 290 g/m^2 (Fahey and Hughes 1994). The respiration rate of coarse woody roots has not been measured at Hubbard Brook, but was simulated by PnET-II at 51 g C/m^2-yr. It will be important to improve approaches for the measurement of root respiration to constrain more tightly the C budget of forest ecosystems.

Heterotrophic fluxes

Most of the C assimilated by the forest vegetation at the HBEF is eventually utilized in the detrital food web and leaves the ecosystem as CO_2 efflux from soil (Gosz et al. 1978). We partitioned TSR into root and heterotrophic respiration components on the basis of mass balance calculations (see below, Figure 4). Our results suggest that about 40% of the soil CO_2-C efflux can be attributed directly to root respiration, a value that closely corresponds to the biome-wide average of 41% for temperate deciduous forests (Gower 2003). A

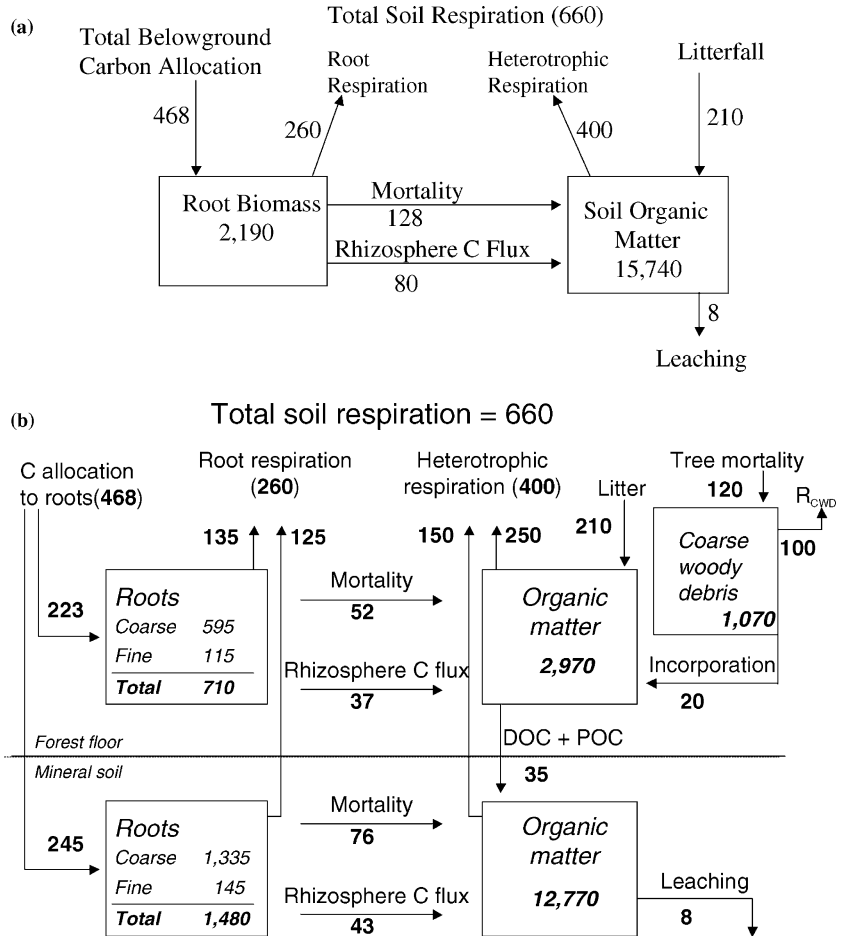

Figure 4. Soil carbon pool (boxes g C/m^2) and annual flux (arrows g C/m^2-yr) estimates for the reference watershed (W6) at the HBEF, NH. Error estimates for most pools and fluxes are provided in Tables 1 and 2. Rhizosphere carbon flux is estimated by mass balance. (a) Summary of soil carbon budget for the whole soil profile and (b) compartmentalized between forest floor (O_{ie} + O_a) and mineral soil horizons. Approaches for compartmentalizing fluxes are detailed in the text.

wide range in this percentage has been reported by different forest studies, due in part to methodological differences, but root respiration probably comprises roughly half of TSR in many forests (Nakane et al. 1996; Hanson et al. 2000). Not surprisingly, the proportion of soil respiration attributed to roots is higher for the mineral soil (45%) than the forest floor (35%) at the HBEF because of the large annual input of labile organic matter to the forest floor in litterfall. Most of the soil heterotrophic respiration probably is associated with soil fungi (Taylor et al. 1999).

The soils at the HBEF are generally well-drained and emissions of CH_4 resulting from anaerobic processing of detrital C are minor. In fact, upland forest soils at the HBEF consume atmospheric CH_4 (Yavitt and Fahey 1993) as has been noted for other forest soils (Keller et al. 1983). However, on a whole watershed basis, the HBEF landscape appears to be a small net source of CH_4 to the atmosphere because poorly-drained, organic soils, which emit methane, cover about 5% of the Hubbard Brook Valley as estimated from a 3-m resolution digital elevation model. The magnitude of this flux, estimated at 0.09 gC/m^2-yr (Yavitt and Fahey 1993), is negligible both from a watershed C budget standpoint and in the global CH_4 budget.

The diverse assemblage of saprotrophs in the detrital food web have received only limited study at the HBEF. Microarthropod densities have been measured for several years in the permanent plots west of W6 and on W1 (Figure 1). Numbers of individuals averaged 177,000/m^2 with a coefficient of variation across sites of 27%. Using biomass conversion from Peterson and Luxton (1982), microarthropod populations average 0.36 g C/m^2. Nematodes have been quantified at HBEF along a riparian zone transect in W1. Nematode densities were converted to estimate biomass at about 0.15 g C/m^2 (Wright and Coleman 2000). Hence, compared to the 66 g C/m^2 estimated for microbial biomass (Bohlen et al. 2001), these higher trophic levels make up a minute fraction of total C storage in organisms of the detrital food web. However, higher trophic levels can stimulate decomposer activity and enhance nutrient remineralization by moderate grazing (Seastedt 1984; Moore et al. 1988).

Gosz et al. (1978) summarized energy flows at the HBEF, with a particular focus on the grazing food web. Their analysis suggested that less than 2% of NPP normally passes directly through the grazing food chain and that the largest grazing C fluxes are associated with rodents. However, during periodic irruptions, defoliating caterpillars (e.g., *Heterocampa guttivita* Walker) consume a large proportion of foliage production (estimated at 44% in 1969–1971 at the HBEF; Gosz et al. 1978). Continued observation of lepidopteran populations at the HBEF have not seen a repetition of the 1969–1971 outbreak, and the long-term average C flux through leaf-eating insects is relatively small (Holmes et al. 1986; R.T. Holmes, unpublished data). The influence of insect-gleaning birds on this C flux has been demonstrated experimentally at the HBEF: birds can significantly reduce caterpillar abundance during midsummer when bird activity is greatest (Holmes et al. 1979; Holmes 1990; Strong et al. 2000). In contrast, the direct role of birds in C flux at the HBEF is minor,

with estimates ranging from about 0.2–0.3% of ANPP based upon bird abundances observed in the mid-1970s (Gosz et al. 1978). Since that time bird abundance at the HBEF has declined to about one-third of the mid-1970s value (Holmes and Sherry 2001), so that the direct role of birds in C flux is even smaller today. By comparison, energy flow through shrews and rodents was estimated at about 1.5% of ANPP (Gosz et al. 1978).

Salamanders are an important component of the heterotrophs at the HBEF. The biomass of salamanders is about twice as large as that of birds during the birds' peak (breeding) season and is about equal to the biomass of small mammals (Burton and Likens 1975a). Salamanders are efficient (60%) at converting ingested C into new tissue and produce more new biomass annually than do bird or mammal populations (Burton and Likens 1975b).

Large mammals play a role in C biogeochemistry in the forest at the HBEF. Gosz et al. (1978) estimated that energy flow through the white-tailed deer (*Odocoileus virginiana*) population was less than 0.1% of NPP in the early 1970s. Since that time, moose (*Alces alces*) populations have recolonized the HBEF, and their impact on understory vegetation is visually obvious, particularly at higher elevations. We estimated the consumption of ANPP by moose based upon regional estimates of moose density in the White Mountains (2.23/km^2), the size-class distributions in this population (K. Bondaites, pers. comm.), and literature values for food ingestion rates for moose in summer and winter (Schwarz and Renecker 1997). The resulting estimate (0.8 g C/m^2-yr) represents only about 0.2% of ANPP. However, moose consume only understory vegetation and the proportion of ANPP consumed in this layer is much higher, about 4.3% based on ANPP measurements of all vegetation $\leq$ 2 cm DBH (Siccama, unpublished data). Hence, the indirect effects of moose browsing in altering the structure and composition of the forest probably have a larger influence on C biogeochemistry than their direct effects. For example, selective moose browsing appears to favor spruce over other tree species (Pastor et al. 1999), a response that could profoundly alter C biogeochemistry through effects on microclimate, NPP and soil organic matter dynamics.

Hydrologic fluxes of carbon

Some organic and inorganic forms of C are soluble in water; hence, C is transported in, through and out of forest ecosystems with hydrologic fluxes. The concentration of inorganic C in solution depends primarily upon the partial pressure of CO_2 (P_{CO_2}) of the gas phase with which it equilibrates. Dissolution of organic C is incompletely understood largely because of the complex suite of organic molecules in the ecosystem (Dai et al. 2001). The input of C in atmospheric deposition is small (1.7 g C/m^2-yr), particularly when compared to net primary production (about 0.3% as large, Table 2). The C deposited in bulk precipitation is about 6% inorganic, the remainder being organic C. The composition of organic C in precipitation and seasonal increase

in concentrations during summer suggest that much of the organic C deposited in precipitation is derived from airborne soil and plant particulate matter (Likens et al. 1983).

As precipitation passes through the forest canopy it becomes enriched in C by about 3.1 g C/m^2-yr, and the throughfall flux is about 2% as large as the C flux in fine litterfall (Table 2). This enrichment is due to organic C, while inorganic C in throughfall is similar to that in bulk precipitation. Precipitation amount is the most important factor influencing event-to-event variation in net throughfall, indicating the importance of canopy exchange in regulating organic C flux (Lovett et al. 1996). The contribution of dry deposition of organic C is relatively minor, even in conifer stands, which are thought to be efficient at scavenging airborne particulates. Stemflow is a relatively minor pathway of C flux to the forest floor because the water flux is minimal (Eaton et al. 1973).

As infiltrating water percolates through the forest floor horizons both inorganic and organic C are dissolved, and net leaching from the forest floor amounts to about 25 g C/m^2-yr (i.e., 22 g C/m^2-yr DOC, 3 g C/m^2-yr DIC; Table 2; Johnson et al. 2000). This value represents the largest dissolved C flux in the system and, as discussed later, probably plays an important role in soil development. DOC decreases with depth in the soil profile (Table 3), with fluxes from the B_h and B_s horizons respectively 54 and 23% of the flux from the O_a horizon (Johnson et al. 2000). This decline in DOC with depth is related to adsorption and coprecipitation of DOC with Fe and Al in mineral soils (McDowell and Wood 1984). Although the immediate fate of this carbon is not known, over longer time-scales most is likely utilized and respired by soil

Table 3. Mean and standard deviation of soil water concentrations of dissolved organic carbon (DOC), organic anions and dissolved inorganic carbon (DIC) collected from zero tension lysimeters west of W6 at the Hubbard Brook Experimental Forest.

Watershed 6	DOC (mg C/l)		Organic anions (μeq/l)		DIC (mg C/l)	
	Mean	(Std. Dev.)	Mean	(Std. Dev.)	Mean	(Std. Dev.)
Spruce–fir–birch						
O_a	24.0	(9.8)	144	(58)	3.10	(2.22)
B_h	14.1	(9.0)	100	(42)	2.75	(1.44)
B_s	8.4	(5.7)	76	(37)	4.03	(2.04)
High elevation hardwood						
O_a	16.8	(7.1)	102	(56)	2.24	(1.26)
B_h	8.2	(5.3)	54	(33)	1.85	(1.24)
B_s	5.5	(2.4)	48	(30)	3.05	(1.64)
Low elevation hardwood						
O_a	16.3	(7.8)	107	(47)	1.91	(1.10)
B_h	11.8	(6.1)	100	(48)	1.75	(0.90)
B_s	3.4	(2.9)	33	(28)	2.04	(2.00)

Values were obtained from monthly collections over the period 1984–1998. Organic anions were calculated as the difference between cations and anions measured in solution.

heterotrophs; if most of the C leached from the forest floor remained stored in the mineral soil, the quantity of soil C storage would greatly exceed that observed (e.g., 10,000 years * 22 g C/m^2 yr^{-2} = 220 kg C/m^2). Alternatively, average erosion of surface soils during the Holocene must have been considerably greater than current rates. The combination of adsorption by mineral soils of all C fractions and microbial decomposition of C, results in fluxes of DOC from deep soil horizons that are similar to those found in streamwater. Like DOC, fluxes of DIC increase markedly in forest floor leachate, relative to values in throughfall, because of microbial and root respiration. However, unlike DOC, concentrations of DIC are relatively uniform through the soil profile (Table 3).

Both DOC and DIC concentrations in soil waters draining the forest floor and mineral soil have decreased over time at all elevational zones at the HBEF (Palmer and Driscoll 2002). Marked temporal decreases in DOC were evident in B_s soil solution draining the spruce–fir–birch zone (–0.22 mg/l-yr; $p = 0.01$). Rates of DOC decrease were much lower in the hardwood zones (−0.02 mg/l-yr; $p = 0.01$). Rates of DIC decrease were more uniform across the landscape, averaging −0.13 mg/l-yr.

The hydrologic output of organic and inorganic C from the forest ecosystem is small relative to gaseous efflux of CO_2 from soil (Table 2) but significant in comparison with NEE. The flux of DIC in streamwater is low relative to the flux from mineral soil horizons, which reflects degassing of CO_2 from soil solutions that are oversaturated with respect to the atmosphere. Evasion of CO_2 from the stream has been estimated at about 4.0 g C/m^2-yr on the basis of long-term data on P_{CO_2} and short-term measurements of gas piston velocity. This evasion of CO_2 is about 10-fold larger than the net advective transport of DIC in stream water as it exits the forested watershed and larger by about 2-fold than the export of DOC. It is similar in magnitude to the DIC flux from the soil profile based on measured concentrations in lysimeters (Table 3).

Most of the C that enters streams is coarse particulate organic matter (>1 mm), whereas the majority of organic C leaving the watershed is in fine particulate organic matter (FPOM; 0.45 μ to 1 mm) and dissolved organic matter (<0.45 μ) (Fisher and Likens 1973). At W6, the concentration of DOC in streamwater is low at the base of the watershed (Table 4) and relatively constant throughout the year, despite great changes in streamflow. This constancy in the concentration of DOC is attributed to the moderating effect of soil discussed previously. In contrast, concentrations of FPOM are strongly dependent on flow, and increase with increasing runoff (Hobbie and Likens 1973). Peak FPOM concentrations occur on the rising limb of the hydrograph and decline prior to maximum discharge (Bilby and Likens 1979). From 1965 to 1973, the average organic particulate matter export (0.56 g C/m^2-yr) comprised some 33% of the total particulate matter transported (Likens and Bormann 1995). Of the organic matter transported, 67% was suspended and bed-load materials collected in the ponding basin, 29% was suspended material

Table 4. Mean and standard deviation of stream water concentrations of dissolved organic carbon (DOC), organic anions and dissolved inorganic carbon (DIC) collected from longitudinal stream sites within W6 at the Hubbard Brook Experimental Forest.

Stream	DOC (mg C/l)		Organic anions (μeq/l)		DIC (mg C/l)	
	Mean	(Std. Dev.)	Mean	(Std. Dev.)	Mean	(Std. Dev.)
751 m	20.6	(8.2)	128	(43)	3.79	(1.79)
732 m	9.3	(2.9)	75	(30)	0.62	(0.38)
701 m	4.6	(1.5)	42	(23)	0.61	(0.34)
663 m	2.9	(1.3)	27	(19)	0.65	(0.55)
602 m	2.4	(3.9)	23	(21)	0.64	(0.70)
544 m	1.8	(0.5)	21	(17)	0.52	(0.71)

Values were obtained from monthly collections over the period 1982–2002. Organic anions were calculated as the difference between cations and anions measured in solution.

sampled in a 1-mm mesh net from water passing through the gauging weir, and 4% was collected on a 0.45-μm pore filter from samples that passed through the net (Likens and Bormann 1995).

As with soil solutions, streamwater shows long-term decreases in concentrations of DOC and DIC. It is not clear why soil water and streamwater DOC and DIC have been decreasing over time at the HBEF. There have been few studies of long-term temporal trends in DOC and DIC. Significant temporal increases in DOC concentrations were reported in 19 of 22 freshwater sites across the UK and attributed to local climatic influences (Monteith et al. 2001), and other freshwater sites in Europe and North America also have exhibited increasing DOC (Freeman et al. 2001; Harriman et al. 2001; Skjelkvale et al. 2001; Driscoll et al. 2003; Stoddard et al. 2003). Hence, the decreases observed at W6 do not represent regional trends and seem likely to reflect decreases in the supply of DOC to drainage waters. As there have been no temporal patterns in above ground litter, it seems that a change in the supply of DOC is due to a change in belowground processes. One possible mechanism is an increase in soil surfaces available for DOC resorption following desorption of sulfate from soil in response to decreases in atmospheric sulfur deposition (Likens et al. 2002). Decreases in DIC in soil and streamwater probably are a response to decreases in the supply of DOC.

Export of organic C, which is dominantly particulate, is partially regulated by the presence of organic debris dams, which slow streamflow and cause particles to sediment to the benthic zone where they are processed into smaller size fractions (Bilby and Likens 1980; Bilby 1981). While organic debris dams are less effective at retaining dissolved than particulate organic matter, abiotic adsorption retains DOC within the stream (McDowell 1985). Exchangeable Al and Fe play a role in this process, which is similar to abiotic adsorption of DOC leachates in soil. The retention of organic matter within streams permits successive C processing and ultimately contributes to CO_2 loss through respiration (Hedin 1990).

Ecosystem carbon budget

General overview

Our analysis of the major C pools and fluxes at the HBEF provides some useful insights into the problem of constructing C budgets for natural landscapes in general and for the northern hardwood forest in particular. Total belowground carbon allocation (TBCA) in a forest where major belowground pools are at or near steady state can be estimated as the difference between C flux in TSR plus soil leaching and total litterfall (plus net throughfall) (Raich and Schlesinger 1992; Giardina and Ryan 2002). For the HBEF, TBCA is thereby estimated at 478 g C/m^2-yr (i.e., 668 minus 200; Figure 4a). As described earlier, root production is estimated at 130 g C/m^2-yr, and the remainder of TBCA must be apportioned between root respiration and heterotrophic respiration of root-derived C (RCF = exudation, rhizodeposition and mycorrhizal fungi). Based upon our best current estimate of root respiration (260 g C/m^2-yr), this would leave about 80 g C/m^2-yr for RCF. Few estimates of RCF in forest trees have been reported despite its clear importance in ecosystem C budgets (Grayston et al. 1996; Kuzyakov and Domanski 2000).

The consistency of these budgetary estimates can be evaluated and the constraints on soil C budgeting illustrated by calculating C allocation to roots separately for the organic and mineral soil horizons (Figure 4b). As noted earlier, we allocated TSR to that associated with organic (58%) and mineral soil (42%) horizons. Hence, about 385 g C/m^2-yr of TSR comes from the forest floor and 275 g C/m^2-yr from mineral soil. Carbon is transported from forest floor to mineral soil both in solution (25 g C/m^2-yr) and as particulate C, which we assume to be about 3% of C input via litterfall and roots in the forest floor (10 g C/m^2-yr). If RCF is apportioned to forest floor and mineral soil in proportion to fine root biomass (Figure 4b), then the C budgets for these horizons appear to be nearly balanced. This balance could be fortuitous, and we emphasize that the budgetary estimates in Figure 4 should be regarded as tentative.

These soil C budget estimates ignore the large C flux to the soil surface associated with tree mortality and the production of CWD (120 g C/m^2-yr; Figure 4b). The justification for omitting this flux in our soil calculations is that in our sampling of both forest floor mass and TSR we selectively avoid most CWD. In essence, the C dynamics of CWD have been defined operationally as separate from the other soil C pools and fluxes, to avoid the unwieldy spatial variation associated with CWD dynamics. This approach represents a source of error in the soil C dynamics calculation because buried CWD is eventually sampled as forest floor mass and its mineralization contributes to TSR. Fahey et al. (in press) assumed that about 20 g C/m^2-yr of highly decayed wood was incorporated into forest floor horizons. The inclusion of this flux in the compartmentalized soil C budget (Figure 4b) results in a small imbalance in the forest floor pools, either implying that this pool is

accumulating or that particulate C flux from forest floor to mineral soil is larger.

Consideration of this tentative soil C budget from the perspective of the overall C budget of the mature forest watershed-ecosystem (Table 2) provides several useful insights. (1) The greatest uncertainties in the C budget result from woody litterfall, all processes involving roots and possible changes in soil pools. (2) Although hydrologic fluxes from the forest and watershed are small compared with primary productivity and ecosystem respiration, they are significant in comparison with NEE. Hence, although dissolved C fluxes from forests may be regarded as negligible in comparison with gaseous fluxes (Raich and Schlesinger 1992), their contribution to the net C exchange, especially in mature forest watersheds, should not be ignored. (3) Estimates of RCF need to be improved. (4) CWD dynamics and stream channel processes must be included in ecosystem C budgets.

Turnover of carbon pools

Our budgetary estimates provide a basis for comparing the mean C residence time in various ecosystem C pools. The rate of turnover of soil C pools in the forest ecosystem reflects a combination of biological activity and access to the organic substrates that fuel this activity. The pool with the slowest turnover is mineral soil organic matter, for which the overall turnover can be estimated as the ratio of pool size to input (or output) fluxes. In the mature forest we estimate the mean residence time of C at 82 years (Table 5), based on C inputs and outputs of about 155 g C/m^2-yr and pool size of 12,770 g C/m^2-yr (Figure 4b). This value is comparable to those for upper mineral soil horizons of beech forests in northern Europe (86–178 years; Persson et al. 2000). The rate of turnover of forest floor C is much more rapid than for mineral soil C, probably largely because of the higher proportion of relatively labile C compounds and because mineral surfaces that afford physical protection are not

Table 5. Estimated carbon residence time in major ecosystem C pools of a northern hardwood forest watershed at the Hubbard Brook Experimental Forest, New Hampshire.

Carbon pool	Residence time (years)
Living plant biomass	21
Woody biomass	52
Fine roots (structural)	2.9
Soil microbial biomass	0.19
Forest floor organic horizons	9.6
Mineral soil organic matter	82
Coarse woody debris	8.9
Stream channel	3
Total ecosystem	50

abundant. We estimate the residence time of forest floor C at 9.6 years (Table 5). For the sites in northern Europe mentioned above, the range of residence times for C in the 'L' layer (O_i) were similar to our value for forest floor (8–10 years), but values for the 'FH' (O_{ea}) layer were much longer (36–57 years) probably because of a more inclusive definition of humus in the European study. By comparison, for CWD the ratio of the current pool size (1070 g C/m^2) to the input to this pool (120 g C/m^2-yr) gives a rough estimate of C turnover of 8.9 years.

The average turnover rate of C in forest biomass depends upon the turnover of ephemeral tissues (especially foliage and fine roots) and the lifespan of the trees, which protect organic matter in their perennial tissues from utilization by heterotrophic organisms. Because the C content of living biomass has remained nearly constant for the past 20 years at the HBEF (Figure 2), the turnover rate of this structural pool can be calculated as the ratio of the biomass C content and NPP. This turnover rate, 21 years, is intermediate between the values for mineral SOM and forest floor; considering only the wood pools, the turnover rate is much longer, 52 years (Table 5). The non-woody, ephemeral plant tissues (foliage and fine roots) turn over rapidly. Obviously, the predominantly deciduous foliage has a lifespan of less than a year, whereas fine roots apparently form a structural C pool with considerably longer residence time (1.9 years, Table 5). However, if we include all the C flux through these tissues in the C residence time calculation, the values are much lower. For example, for fine roots the average pool size is 260 g C/m^2 and annual C inputs and outputs are about 420 g C/m^2-yr, for a C residence time of 0.62 year.

Analogous calculations are possible for the dynamic pool of carbon in microbial biomass. Organic C input in fine detritus (litterfall plus throughfall and fine root turnover plus RCF) averages about 350 g C/m^2-yr in the northern hardwood forest at the HBEF (Figure 4b), and microbial biomass averages 66 g C/m^2 (Bohlen et al. 2001), yielding a residence time of C in this pool of 0.19 year. Microbial growth efficiency has been estimated at 0.23 for young northern hardwoods near the HBEF (Fisk and Fahey 2001) which would result in production of about 80g biomass C/m^2-yr, the remaining 270 g being respired. However, the relatively low microbial turnover rate suggested by these calculations (0.8 year^{-1}) is not consistent with much higher estimates based upon microbial N pools and N uptake (Fisk et al. 2002). Higher microbial turnover would imply proportionally lower microbial growth efficiency.

Forest disturbance and ecosystem carbon dynamics

Conceptual overview

Spatial and temporal patterns in the storage and flux of C in forested landscapes are shaped by environmental factors and by disturbances to the

dominant plants, the overstory trees. Carbon pools and fluxes vary markedly in relation to the time since the trees at a particular location were severely disturbed or died. The natural disturbance regime in most of the eastern forest of North America is dominated by small-scale disturbances (death of individual or small groups of trees) because large-scale disturbances (e.g., crown fires, hurricanes) are rare (Bormann and Likens 1979). Thus, the natural forest landscape has been characterized as a shifting mosaic with small patches of varying size and shape in different stages of recovery following canopy disturbance (Bormann and Likens 1979). The frequency of canopy disturbance varied somewhat systematically across the montane landscape because of differences in susceptibility to various disturbance agents (Warrilow and Mou 1999; Battles and Fahey 2000) and in the lifespan of dominant tree species. Although large-scale disturbances have been comparatively rare, extreme windstorms and fires have occasionally visited the region (Bormann and Likens 1979; Davis et al. 1985); moreover, diffuse disturbances, wherein a moderate percentage of the overstory is damaged over relatively large areas, probably have been associated with agents such as ice storms, windstorms and pathogen irruptions (Bormann and Likens 1979; Krasny and Whitmore 1987; Canham et al. 2001; Rhoads et al. 2002). Hence, the spatial-temporal patterns of C storage and flux in the northern hardwood forest landscape prior to human incursions were very complex. However, at the scale of the small watershed ecosystems at the HBEF, C storage and flux probably remained relatively near long-term, steady-state values except immediately following the most extreme disturbance events. At longer time scales, shifts in climatic conditions probably controlled patterns of C storage and flux (Davis et al. 1985), most dramatically with glacial-interglacial cycles.

Large-scale disturbance and C storage and flux

The activities of industrial society severely disrupted the steady-state C dynamics of the northern hardwood forest though forest harvest. Bormann and Likens (1979) described the sequence of ecosystem recovery following large-scale forest disturbance in four phases: (1) reorganization, (2) recovery, (3) aggradation, and (4) shifting-mosaic steady-state. During the brief reorganization and recovery phases, rapid changes in the sizes of major C pools result from the redevelopment of the forest canopy; a brief interval of negative NEP (positive NEE) is followed by positive NEP (net sink) as production begins to exceed decomposition. The interval of negative NEP and the magnitude of ecosystem C loss probably depend primarily on the amounts of logging debris retained on the site and on the density and composition of the recovering vegetation (Hornbeck et al. 1987; Reiners 1992; Mou et al. 1993). During the prolonged aggradation phase, C accumulates in vegetation and soil until C pools achieve nearly steady-state values in the mature forest, as currently observed on W6.

Studies of detrital C pools in and around the HBEF following overstory removal provide a detailed picture of decay of residual C. Early studies using a chronosequence approach suggested that forest floor C storage declines substantially (up to 50%) during the first two decades after large-scale disturbance (Covington 1981; Federer 1984). This observation inspired a flurry of research into forest floor dynamics, which generally failed to document increased decomposition rates following logging, one of the suggested mechanisms for the decline (Yanai et al. 2003). Subsequent studies following the harvest of W5 at the HBEF indicated that much of the C lost from the forest floor had actually been mixed into the mineral soil during logging operations (Huntington and Ryan 1990; Johnson et al. 1991). Measurements of undisturbed forest floor horizons on W5 13 years after harvest indicated a 17% reduction in C content. Thus, during the first two decades after large-scale disturbance C storage in the forest floor apparently declines by about 20% in areas where soils are not physically disturbed. In areas receiving large inputs of logging residues, forest floor C storage may increase after cutting as decomposition proceeds. Hence, fifteen years after logging on W5, the average forest floor C pool was nearly identical to the pre-harvest value (3.2 kg C/m^2; S.P. Hamburg and C.E. Johnson, unpublished data), suggesting that the incorporation of logging residues into the forest floor, along with inputs from regrowing vegetation, approximately matched the losses from decomposition of the pre-harvest forest floor and mixing into mineral soils.

Large-scale forest disturbance adds large amounts of woody detritus to the ecosystem in the form of boles and branches and the woody root systems of trees. Hence, total detrital pools are much larger in the years immediately after disturbance, the magnitude depending on the biomass killed by the disturbance. Of course, in the case of logging, much of this C is removed from the site. The rates of decay of aboveground and belowground woody detritus are high in the hardwood forest at the HBEF. For example, 13 years after felling all the trees on W2 only 26% of dead wood mass remained and this value decreased to 11% after 23 years (Arthur et al. 1993). Similarly, decaying woody root systems lost about 60% of their mass only 8 years after whole-tree harvest of W5 (Fahey and Arthur 1994). Hence, the interval of increased C storage following large-scale disturbance is brief, and negative NEP accompanies the rapid heterotrophic utilization of this organic C in the first decade.

Organic C pools in mineral soil horizons may decline slightly during the first decade after large-scale disturbance; however, as noted earlier, high spatial variability makes the detection of such changes difficult (Johnson et al. 1991). The C content of soil horizons below 10 cm had declined significantly eight years after whole-tree harvest of W5, but the changes for the mineral soil as a whole were not statistically significant (Johnson et al. 1995). In 1998, 15 years after harvest, the mineral soil C pool was still not distinguishable from the pre-harvest value, though the pool below 20 cm remained significantly lower (S.P. Hamburg and C.E. Johnson, unpublished data). Note, however, that a small

proportional change in this C pool could represent a large flux; for example, 1% loss of mineral soil C pool per year would exceed 100 g C/m^2-yr.

The flux of CO_2 from the soil surface (TSR) provides an integrative measure of soil C loss following large-scale disturbance. TSR was significantly higher (15–20%) in the recovering forest on W5 at age 6–8 years than the adjacent mature forest, a difference that can probably be attributed primarily to decay of residual detritus, especially woody roots, because the treatment on W5 was a whole-tree harvest that removed most of the aboveground biomass. By age 12–13 years this situation was reversed, with significantly higher TSR for the mature forest, presumably because most of the residual woody root biomass had already decayed (Fahey and Arthur 1994). This temporal pattern in TSR following large-scale disturbance is probably generalizable across most forests, although the loss of detrital C would take longer in cases where more of the aboveground biomass was left on site. Toland and Zak (1994) observed no difference in TSR between reference and clear-cut northern hardwood forest soils in the first year after harvest, suggesting that increases in heterotrophic respiration compensated for reductions in root respiration. Three years after harvest, TSR was about 15% higher for a clear-cut site than an adjacent intact northern mixed forest in southern Ontario, Canada (Hendrickson et al. 1989), presumably because the increase in heterotrophic respiration exceeded the decrease in live root respiration. Eventually, exhaustion of the labile C supply from fresh detritus reduces TSR below levels in the mature forest, with the time depending upon the amount of detrital C deposited as a result of disturbance, its decay rate, and the rate of vegetation and root system development. A 9-yr-old recovering slash pine clearcut in Florida had much lower TSR than an adjacent 29-yr-old stand (Ewel et al. 1987). In comparison with the HBEF, the higher decay rate of detritus in the warm Florida climate probably more rapidly exhausted the residual C supply to soil heterotrophs.

Carbon accumulation in living biomass is rapid in the first few decades after large-scale disturbance of northern hardwood forests, with the rate depending on the density and composition of the recovering vegetation (Marks 1974; Hornbeck et al. 1987; Reiners 1992; Mou et al. 1993) and on the quality of the local site (soils, climate) (Fahey et al. 1998). At the HBEF, repeated disturbances associated with logging have resulted in the accumulation of a very large seed bank of the fast-growing pioneer species, *Prunus pennsylvanicum* L. (Marks 1974; Tierney and Fahey 1998), which dominates the vegetation on cut-over sites and results in particularly high rates of C accumulation. For example, over the first five years following whole-tree harvest of W5, regrowing vegetation accumulated almost 470 g C/m^2 aboveground (Figure 5a; Johnson et al. 1995). This rate of C accumulation significantly exceeded that on nearby W2 (376 g C/m^2), where the abundance of pin cherry was reduced by repeated treatment with herbicides (Reiners 1992). Reduction in vegetative sprouting and decline in site fertility due to high nutrient leaching (Likens et al. 1970) probably also contributed to the large difference in C accumulation in the regrowing vegetation between W2 and W5. During the 2nd decade after

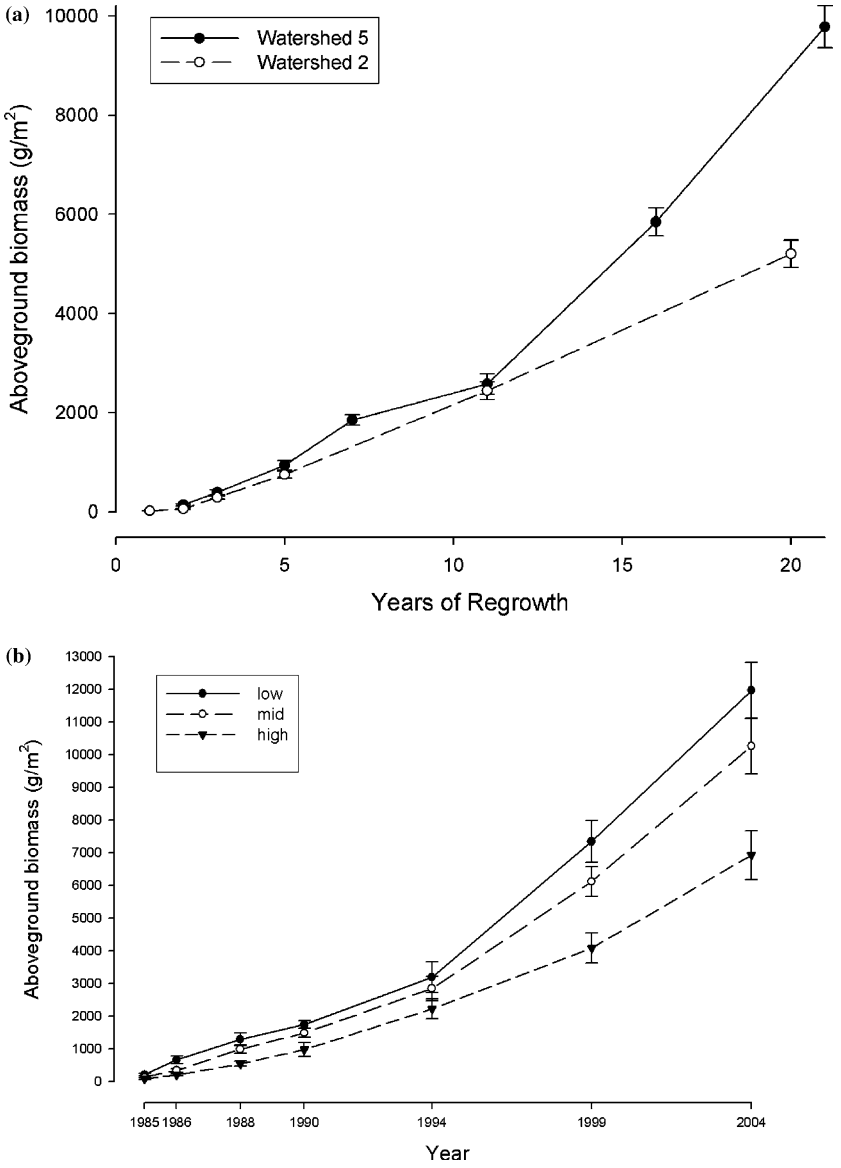

Figure 5. Aboveground biomass through time for (a) two cutover watersheds (W2 and W5) and (b) three elevation zones on a cutover watershed (W5) at the HBEF.

large-scale disturbance, rates of C accumulation in living vegetation accelerated on W5, exceeding 300 g C/m^2-yr, but remained relatively constant on W2, averaging about 150 g C/m^2-yr (Reiners 1992).

The magnitude of net changes in forest floor and soil C pools appear to be much smaller than for vegetation in these early stages of ecosystem recovery

from catastrophic disturbance (Richter et al. 1999). The forest floor C pool probably reaches a minimum well before vegetation dominance shifts from pin cherry to the mature forest species in the 2nd–3rd decade (Fahey et al. 1998). Thereafter, the high mortality of pin cherry adds woody debris to the forest floor (Hughes and Fahey 1994), but changes in this pool remain small compared with the large increment in living biomass (Covington and Aber 1980). Returning after 15 years to the forest floor chronosequence sites measured by Federer (1984), Yanai et al. (2000) observed little pattern in the changes in forest floor organic matter content as a function of stand age (Figure 6). The average change over the 15-year-interval was a statistically insignificant 6% increase; this would correspond to only about 12 g C/m^2-yr (Yanai et al. 2003). The smallest change that could have been detected at $\alpha = 0.05$ was 43 g C/m^2-yr. Together with the evidence of relatively small reductions in forest floor C storage during the first decade of recovery on W5, these results suggest that annual increases in C storage in forest floor during the subsequent aggradation phase are very small compared with C accumulation in vegetation. For example, the average change in forest floor C content over 15 years for seven stands aged 10–45 years (Figure 6) was $+5.5$g C/m^2, not statistically different from zero. Similarly, changes in mineral soil C pools, while difficult to detect because of high spatial variability, probably are minor (Schlesinger 1990; Johnson et al. 1995; Richter et al. 1999). Finally, because most of the coarse woody detritus added during the disturbance would be decayed by year 20

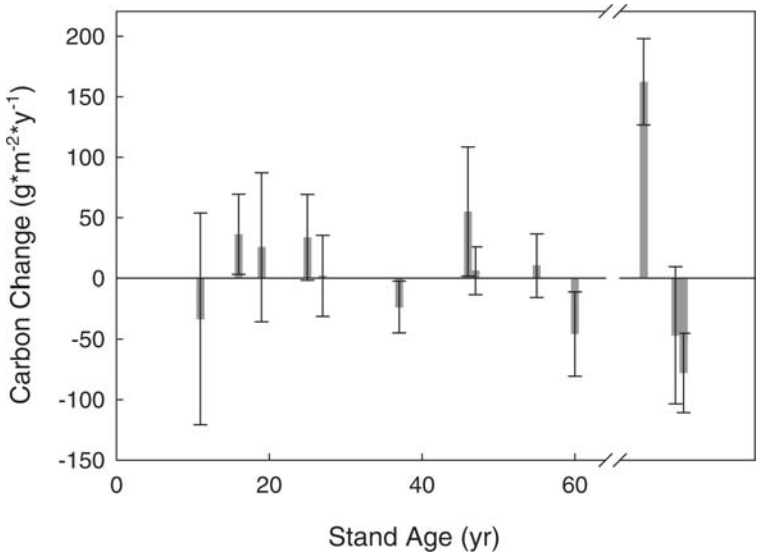

Figure 6. Observed changes in carbon content of the forest floor over 15 years in 13 stands of different ages, measured in 1979–1980 (Federer 1984) and 1994–1995 (Yanai et al. 1999, 2000). Ages of the stands pertain to the second measurement date.

(Arthur et al. 1993), the contribution of this pool to the ecosystem C budget is greatly reduced and NEP becomes positive beginning about 15 years after natural, catastrophic disturbance.

These budgetary calculations and NPP measurements at the HBEF indicate that young northern hardwood forests are a moderate sink for atmospheric C (about 200–300 g C/m^2-yr) for a period of 30–40 years beginning in the 3rd decade following natural, large-scale disturbances like severe blowdowns that leave all detritus on the site (Figure 7). The duration and magnitude of this sink would be considerably greater in the case of logging or recovery from agriculture because of the large losses of C associated with these disturbances. Aerodynamic measurements of NEE in temperate broadleaf forests in Europe (Valentini et al. 2000) and northeastern US (Goulden et al. 1996) recovering from anthropogenic disturbances indicate that many of these forests are net C sinks in this range. Beyond about age 70 years the strength of this C sink declines, according to measurements on W6 at the HBEF indicating that

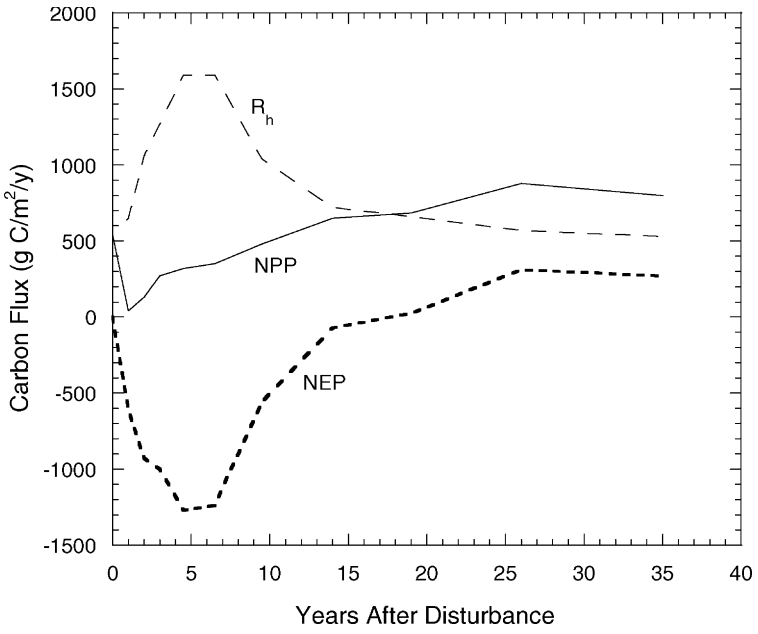

Figure 7. Generalized temporal pattern of C flux in total net primary productivity (NPP), heterotrophic respiration and net ecosystem productivity (NEP) over 30 years of forest recovery following large-scale disturbance (e.g., severe windstorm) for the northern hardwood forest ecosystem at the HBEF, NH. Temporal pattern of NPP is based on observations of forest recovery following harvest of W5 (Figure 5). Heterotrophic respiration is estimated from observation of bole wood decay on W2 (Arthur et al. 1993), woody root decay on W5 (Fahey and Arthur 1994) and dynamics of forest floor carbon as described in the text. NEP calculated as difference between NPP and R_H.

maximum living biomass may be reached relatively early in forest development (Figure 2).

Disturbance and carbon dynamics in the shifting-mosaic, steady-state ecosystem

The disturbance regime in natural forests of the northeastern United States consisted of a range of events in terms of scale and intensity. Disturbance agents such as microburst windstorms, ice storms and pathogen or insect irruptions cause mortality and injury intermediate in magnitude between those caused by catastrophic large-scale disturbances and single tree mortality. Recent examples include the decline of red spruce in the upper elevation zone of the northern hardwood forest (Siccama et al. 1982; Hamburg and Cogbill 1988; Battles and Fahey 1996), the severe ice storm of 1998 (Rhoads et al. 2002), and microburst windstorms that occasionally knock down groups of canopy trees (Canham et al. 2001). Vegetation responses to these disturbances are qualitatively and quantitatively different from large-scale catastrophic disturbances. Crown expansion of neighboring canopy trees and height growth of advance regeneration utilize the locally increased resources; hence, the reduction in NPP following disturbance is less marked than for catastrophic disturbances. Where the biomass reductions are small, the peak rates of biomass accumulation after the disturbance are commensurately modest. Following the severe ice storm of 1998 leaf area index (LAI) was reduced by half in the elevation band from 600 to 800 m at the HBEF, but it returned to near pre-disturbance levels within 3 years (Rhoads et al. 2002). Since additions of detrital C from tree mortality are small, so are increases in heterotrophic dissipation of detrital C. As noted earlier, woody debris (mostly branches) deposited by the ice storm averaged 434 g C/m^2, and this detritus decays more rapidly than tree boles (Harmon et al. 1986). The increased rates of C accumulation in living biomass probably correspond with increased heterotrophic utilization of woody detritus, such that net C fluxes may be little affected, even though gross fluxes increase.

At longer time scales, the pools and fluxes of C in the HBEF landscape have undoubtedly undergone shifts resulting from major changes in climate during the Holocene. Carbon pools probably accumulated gradually following the establishment of woodlands in the valley about 11,500 yr BP and the development of soil humus layer and soil profiles would have accompanied climatic warming to modern temperatures by 10,000 yr BP (Davis et al. 1985). The long-term average rate of soil C accumulation of about 1.5 g C/m^2-yr is in the same range as values summarized by Schlesinger (1990) for post-glacial forested landscapes. Forest development also would be accompanied by the formation of organic debris dams on drainage streams thereby reducing chronic export of particulate organic C. Fire was somewhat more common during the warm, dry period from 10,000 to 7000 yr BP than it has been since, but generally it was still rare. Finally, significant shifts in ecosystem C pools and fluxes probably accompanied the sudden decline of eastern hemlock around 5000 yr

BP (Davis 1981a,b; Bhiry and Filion 1996). Since that time we surmise that C pools and fluxes remained near the steady-state observed in the modern forest.

Environmental and biotic constraints on carbon biogeochemistry

Autotrophic activity

The biogeochemical cycle of C in terrestrial ecosystems is regulated by environmental and biotic constraints on the activity of primary producers and on heterotrophic utilization of plant C. The cold temperate climate and short frost-free season (average = 145 days; Bailey et al. 2003) significantly constrain NPP at the HBEF; NPP of broadleaf deciduous forests in areas with longer growing seasons is considerably higher than at the HBEF. For example, a mature hardwood forest at Coweeta, North Carolina (Monk and Day 1988) had ANPP values about 15% higher than at the HBEF, and average total NPP for broadleaf deciduous forests worldwide (675 gC/m^2-yr; Gower 2003) was considerably higher than for HBEF (Table 1).

Annual variations in temperature appear to play a significant role in regulating NPP of Temperate deciduous forests. At Harvard Forest in central Massachusetts, the timing of spring leaf out and autumn leaf senescence varied by 5–10 days over a 5-yr period and appeared to significantly affect NEE through their influence on seasonal net photosynthesis (Goulden et al. 1996). A large range in leaf phenology is observed at the HBEF: over a 15-year period of record the range in the time interval between leaf out and senescence for *Fagus grandifolia* was 32 days (125–157 days; Bailey et al. 2003). Spring leaf out varied by 24 days and fall senescence by 20 days. According to the PnET model, about 25% of the annual variation in gross photosynthesis can be explained by growing season length. However, annual variation in simulated net photosynthesis is not strongly related to growing season length ($r^2 = 0.06$), because temperature effects on leaf respiration largely offset the effects of growing season length on gross production (Figure 8).

Although precipitation is moderately high and evenly distributed throughout the year at the HBEF, significant soil water deficits and drought stress occasionally occur (Bailey et al. 2003). The dominant trees are drought-avoiders that close their stomates at relatively high soil and leaf water potential, thereby reducing the potential for damage but restricting C fixation (Federer and Gee 1976; Federer 1977). Whittaker et al. (1974) attributed lower ANPP for the interval 1961–1965 than for 1956–1960 on W6 to the effects of severe drought conditions in the later interval. The model PnET confirmed the effects of this drought on photosynthetic C fixation; however, because of the buffering effects of internal C stores in the trees, the effects of the drought on NPP were not indicated in the model until the late-1960s.

The role of nutrients in limiting C fixation and NPP in mature northern hardwood forests has received limited study. Foliar nutrition of canopy trees at

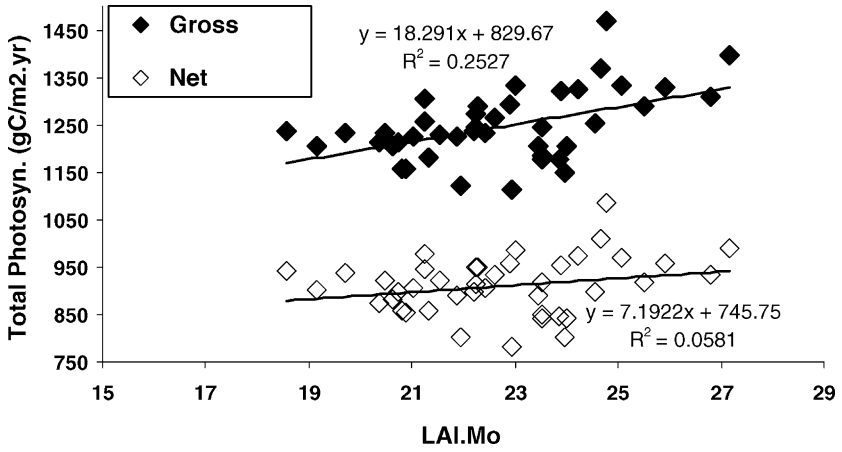

Figure 8. The effect of growing season length on simulated primary productivity using the model PnET-II (Aber et al. 1995) parameterized for a northern hardwood forest at the HBEF. Leaf area duration (LAIMo) represents the product of daily estimated forest LAI and monthly time intervals for each year.

the HBEF generally appears to be within the optimal range for these species, with the possible exception of low foliar Ca concentrations in sugar maple and yellow birch growing on shallow soils at the higher elevations (above 700 m) of the experimental watersheds (Likens et al. 1998). There are some indications that biogeochemical or other stresses are reducing NPP in parts of the HBEF. For example, the production efficiency of the W6 forest, expressed as the ratio of ANPP per unit LAI or leaf biomass, declined by about 23% between the late-1950s and the late-1990s (Table 6). The value observed in the earlier

Table 6. Aboveground net primary productivity and forest production efficiency for selected mature *Acer*-dominated forests.

Location	Ref.[a]	ANPP (g/m^2-yr)	FPE[b] LAI-basis	FPE[c] Mass-basis	Wood PE[d]
HBEF, NH age = 45 years	1	924	147	2.28	na
HBEF, NH age = 85 years	2	708	112	1.76	0.91
Indiana mesic slope	3	678	161	2.19	1.28
Indiana bottomland	3	639	141	2.06	1.04
Wisconsin	4	755	137	2.02	1.02
Wisconsin sandy outwash	5	480	161	na	na
Wisconsin ground moraine	5	920	133	na	na
Himalayas, India	6	990	193	1.80	0.80

[a]References: 1 – Whittaker et al. 1974, 2 – this study, 3 – Jose and Gillespie 1996, 4 – Crow 1978, 5 – Fassnacht and Gower 1997, 6 – Garkoti and Singh 1995.
[b]ANPP/LAI (g/m^2 basis).
[c]ANPP/leaf biomass.
[d]Aboveground wood production/leaf biomass.

interval is comparable to other mature, maple-dominated forests world-wide (Table 6). The recent low production efficiency in the HBEF could be further evidence (together with high mortality) of unusual stresses that have reduced the growth of the canopy trees below their maximum potential.

It is clear that nutrients can limit NPP in young northern hardwood forests (age 6–23 years) (Fahey et al. 1998). Continuous application of complete and balanced fertilizer to plots in a series of nine stands in the White Mountain National Forest from 1989 to 1994 resulted in very high C flux in ANPP (824 g C/m^2-yr) compared with control plots (556 g C/m^2-yr). This response resulted in part from an increase in the dominance of the fast-growing, exploitative species, pin cherry (*Prunus pennsylvanica*), and from a change in its population structure and canopy architecture (Fahey et al. 1998; Cramer et al. 2000). In many of the stands, a reduction in C allocation to roots also contributed to the increased ANPP.

Water and nutrient limitation may contribute to elevational patterns of NPP at the HBEF, along with climatic, soil and biotic (e.g., species composition) factors. For example, observations of biomass accumulation following harvest suggest that the elevational pattern in the biomass C pool may be related primarily to soil resource limitations. On W5 aboveground biomass after 5 years of vegetation recovery (Figure 5b) was not much different between the low and mid elevation zones (1611 g/m^2) and the high elevation zone (1504 g/m^2). In these early years of forest regrowth, plant demand for soil resources is exceeded by supply, resulting in a temporary increase in water and nutrient outflow from the watershed-ecosystem (Bormann and Likens 1979). In contrast, by stand age 15 years, aboveground biomass was much lower in the high elevation zone (4047 g/m^2) than in the mid and low elevation zones (6722 g/m^2). The shallow and infertile soils in the high elevation zone probably constrained resource availability at this stage in forest development when soil resources are most limiting (Fahey et al. 1998). Hence, the role of temperature differences over about 300 m of elevation in causing NPP differences between the base and upper elevations of the experimental watersheds at the HBEF may be smaller than the role of soil differences. This observation is less likely to hold for the entire 700 m elevation range of the HBEF, over which we observe a 35% decline in forest biomass (Figure 9).

Heterotrophic activity

The heterotrophic utilization of C is constrained by a set of environmental and biotic factors analogous to but distinct from those limiting NPP. For example, soil heterotrophic respiration is much less sensitive to temperature fluctuations than root respiration (Boone et al. 1998; Giardina and Ryan 2000). Thus, the effects of annual and spatial variation in temperature on C mineralization probably are smaller than for NPP. Moreover, although cold temperatures undoubtedly limit heterotrophic activity at the HBEF, this effect is not so

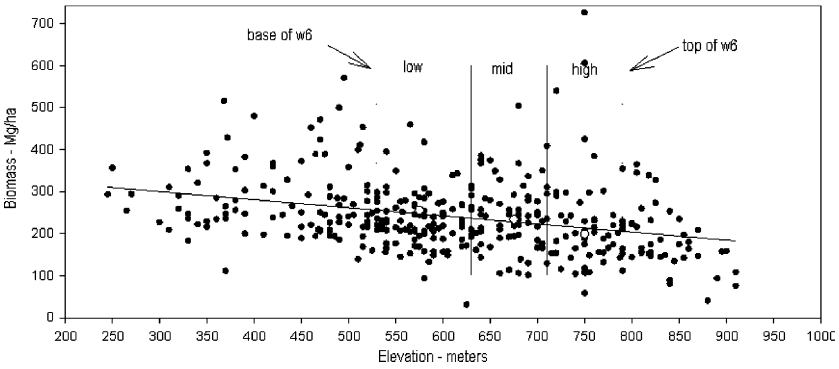

Figure 9. Elevational variation in aboveground biomass for 420 sample plots (0.05 ha) distributed across the Hubbard Brook valley. Open circles represent average values for three elevations in watershed 6, as described in the text.

directly linked with the frost-free season as for the trees because the high thermal mass of the soil buffers soil temperature fluctuations. Hence, whereas NPP occurs almost entirely within the frost-free period, a significant proportion of the heterotrophic processing of plant C occurs outside this interval. Detailed measurements of soil biological activity in winter indicate that about 5–15% of annual C mineralization by soil heterotrophs occurs during the period of snow cover, typically from late November to April (Groffman et al. 2001).

Soil drought may play a significant role as a controller of heterotrophic processing of C at the HBEF. Others have noted reductions of TSR in temperate deciduous forests during severe dry spells (Hanson et al. 1993; Davidson et al. 1998; Epron et al. 1999), likely due to declines in both root and microbial respiration. During five years of measurement at the HBEF (1998–2002), soil drought caused statistically significant reductions in TSR during two intervals in late-summer 2001 and 2002. During these severe droughts measured TSR was only 57% as high as the values predicted by the regressions on soil temperature. However, the levels of volumetric soil moisture content predicted by the hydrologic model, BROOK 90 (Federer 1995), for these drought periods occurred only an average of 4 days per year over 37 years of simulations. Hence, the drought effect on annual TSR is probably minor at the HBEF (Fahey et al. in press). Moreover, short-term reductions owing to environmental factors like soil drought may not affect annual rates of C mineralization in humid temperate forests, because microbes have the capacity to increase greatly their activity when conditions are optimal, such as following wetting of dry soils (Birch 1958; Kieft et al. 1987). Thus, reductions in microbial activity during one season or year might well be compensated for during a subsequent season or year, with average respiration rates controlled by C inputs rather than by environmental factors.

Soil freezing events appear to have complex effects on soil C processing at the HBEF. In unusual years when snowpack is late in developing, soils at the HBEF may freeze to significant depths (Hart 1963); during the period of record (1970–1997) widespread and severe soil freezing occurred several times (Likens and Bormann 1995; Fitzhugh et al. 2003). Snow removal experiments indicate that soil freezing accelerates fine root turnover (Tierney et al. 2001) and probably increases the availability of C substrates (Fitzhugh et al. 2001). Increased leaching of organic C was also stimulated by soil freezing (Fitzhugh et al. 2001). Thus, freezing may provide a short-term stimulus to C utilization and hasten the cycling of C when it occurs on an irregular basis.

The chemistry of organic matter exerts a significant influence on heterotrophic utilization of plant C. For leaf litter at the HBEF, decay rates differ among species in a pattern related to the initial concentrations of nitrogen and lignin (or their ratio) in the tissues: sugar maple > yellow birch > beech (Melillo et al. 1982). Consumption of living foliage of canopy trees by phytophagous insects is usually a minor C flux pathway, probably in part because the foliage is protected biochemically (Mattson 1980; Schowalter 1986). The extent to which fine roots are protected biochemically from consumption by soil fauna remains unclear because the causes of root mortality are poorly understood (Eissenstat and Yanai 1997). Applying fungicide and insecticide to soils significantly reduced the mortality of fine roots of *Prunus persica* (Wells et al. 2002) which suggests that soil invertebrates may consume significant amounts of fine-root C. Although it seems likely that fine-root chemistry would influence the rate of decomposition of dead roots (Bloomfield et al. 1993), the lack of reliable measurements of *in situ* fine root decay rates has precluded the empirical demonstration of such relationships.

Most of the organic matter in mineral soils is much less readily utilized by heterotrophs than fresh plant detritus for several reasons. The biochemical composition of mineral SOM is more resistant to degradation and yields less energy, it may be protected from enzymatic attack by clays or other physical mechanisms, and it may form inaccessible complexes with Al and other metals (Tisdall and Oades 1982). Giardina and Ryan (2000) observed that mineralization of SOM was insensitive to temperature, possibly because SOM quality limits its degradation rate. Besides roots, the principal labile organic substrates in soil are root exudates and microbial biomass. Boone et al. (1998) inferred a strong temperature dependence in the production and utilization of root exudates at the Harvard Forest. Together with the large C flux attributed to RCF at the HBEF (Figure 4), their result emphasizes the importance of improving understanding of environmental and biotic controls on root C dynamics for predicting C flux responses to global environmental change.

Heterotrophic utilization of C in woody biomass is constrained by a complex set of chemical, physical and biotic factors (Harmon et al. 1986). Measurements of bole wood decay on W2 at the HBEF after clearfelling of the forest (Arthur et al. 1993) suggested that decay rates followed the order: beech > sugar maple > yellow birch > white ash > red spruce, and the same

pattern for the three dominant hardwood species has been observed for boles incubated for 10 years in the mature forest (Siccama and Vogt, unpublished). The overall half-life of bole wood in the W2 study was 7.2 years, slightly longer than that measured for a hardwood forest in Tennessee (6.3 years; Onega and Eickmeier 1991). A somewhat longer average half-life (9.7 years) has been observed through 10 years decay in the mature forest (Siccama and Vogt, unpublished). Arthur et al. (1993) suggested that the relatively slow decay of yellow birch bole wood might be explained by the high relative resistance to decay of its bark (probably a biochemically regulated effect) because bark protects the boles from invasion by decay organisms (Harmon et al. 1986). The slower decay of softwood (e.g., spruce) than hardwood boles has been attributed to both substrate and decomposer influences.

Variation in decay rates within species are probably also due to microenvironmental and biotic factors. Boles of the same species and diameter class exhibited over 3-fold differences in decay rate in the W2 experiment at the HBEF. Similarly high variation was observed for the decay of woody roots at the HBEF (Fahey and Arthur 1994). Decay of woody roots was much slower than for aboveground tissues of the same species and size classes, and the order of decreasing decay was similar to that for boles: sugar maple > American beech > yellow birch > red spruce (Fahey and Arthur 1994). Although decay rates were significantly lower in wet, seepage areas, high variation in decay rates among well-drained upland soils were not clearly related to soil properties. The patterns of colonization of woody substrates by fungal species with inherently contrasting capacities for rapid degradation of ligno-cellulose (Rayner and Boddy 1988) might largely explain the high variation in wood decay rates observed at the HBEF and elsewhere.

Spatial variation in carbon pools and fluxes

Aboveground vegetation pools and fluxes

The living biomass of the HBEF varies spatially with environment, disturbance history and species composition. We analyzed the spatial patterns of forest biomass C pools on the basis of 450 plots distributed on a grid throughout the Hubbard Brook Valley and detailed surveys of vegetation on the experimental watersheds on the south-facing slope of the Valley. We used allometric equations developed for the dominant species at the HBEF (Whittaker et al. 1974; Siccama et al. 1994) to estimate biomass in each plot, and we present maps of aboveground C pools at two scales using these estimates (Figure 10). At the valley-wide scale the precision of these estimates is moderately low, as the root mean square error (RMSE) for interpolated vs. measured biomass was 56 Mg/ha compared with a mean of 203.5 Mg/ha; the interpolation correctly predicted the biomass class (Figure 10) of measured plots in slightly less than half the cases. This low precision results both from small-scale spatial variation and

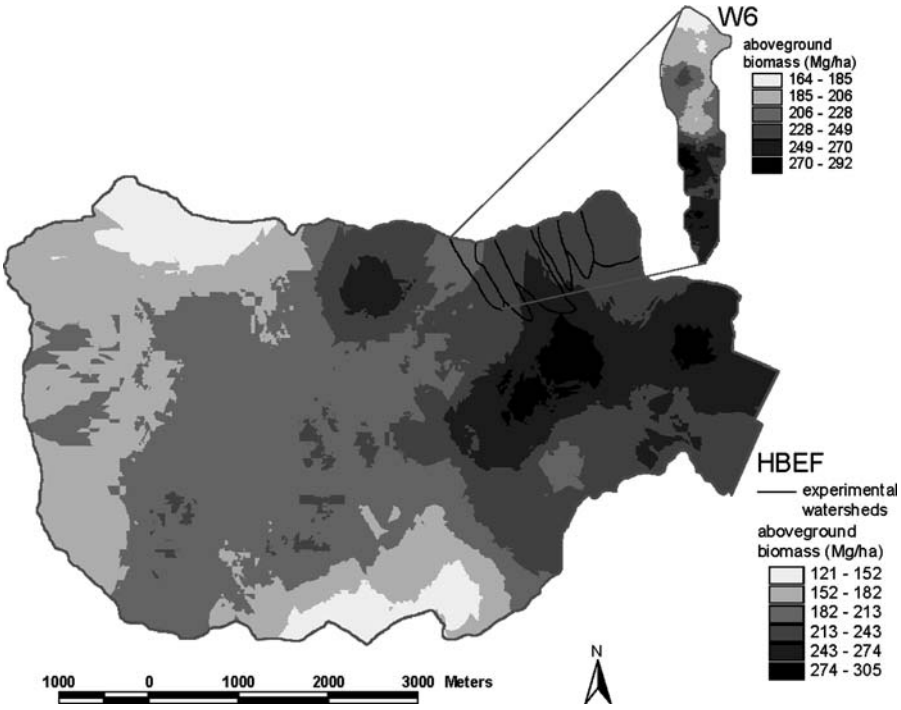

Figure 10. Spatial pattern of estimated aboveground biomass in the reference watershed (W6) and across the Hubbard Brook valley in 1997. The W6 map is based on a 100% survey, grided at 25×25 m spatial scale. The valley-wide interpolations are based on 450 plots (0.05 ha each). Error estimates are given in the text.

from the relatively small size of the measurement plots (0.05 ha) and consequent edge effects.

The principal gradient of spatial variation in biomass C pools is elevation, which explains 16% of the variation in aboveground biomass of forest plots distributed across the HBEF (Figure 9). Our calculations of aboveground biomass take into account the decrease in height of trees of a particular diameter with increasing elevation. For example, across the three elevation zones of W6, a range of 300m, the average height of a 50 cm dbh American beech tree declines by nearly 30% (25.5–18.5 m). For sugar maple and yellow birch the decline in height is about 20%. Hence, environmental stresses associated with increasing elevation clearly influence biomass accumulation. As suggested earlier, these stresses appear to include both soil factors and climatic factors. The effect of elevation on biomass C pools depend in part on distributions of species by elevation. For example, the highest biomass stands in the HBEF are observed at the lowest elevations (Figure 10) in hardwood stands that include a large admixture of white ash (*Fraxinus americana)* or eastern hemlock (*Tsuga canadensis*). Mixed hemlock-hardwood stands support higher

biomass than pure hardwoods, perhaps because of canopy architecture interactions (Kelty 1989). At the highest elevations, forests dominated by dense stands of balsam fir support the lowest biomass C pools in the HBEF (Figure 10). The relative role of climatic and soil factors in regulating these forest composition patterns is unknown, but as noted earlier the soils of the upper slopes and ridges of the HBEF are shallow and probably have limited capacity to store and supply water and essential nutrients.

At the valley-wide scale, notably high biomass is observed at relatively high elevations in the north-central part of the forest (Figure 10) where sugar maple-dominated stands occur on relatively base-rich soils (S. Bailey, unpublished data). At a smaller scale on W6, enriched cove sites (Leak 1978) support high biomass stands at mid-elevation, whereas the shallow soils on the steeper slopes (Johnson et al. 2000) have low biomass (Figure 10).

Not surprisingly, productivity of the forest across the Hubbard Brook Valley (Figure 11) is strongly related to biomass. For 370 permanent plots distributed around the HBEF, 42% of the variation in aboveground woody biomass production was explained by aboveground biomass. Again, the precision of the interpolated map is limited, as the RMSE for interpolated vs. measured ANPP was 156 g/m^2-yr compared with a mean of 649 g/m^2-yr. The ratio of woody biomass production to total biomass varied systematically across the HBEF,

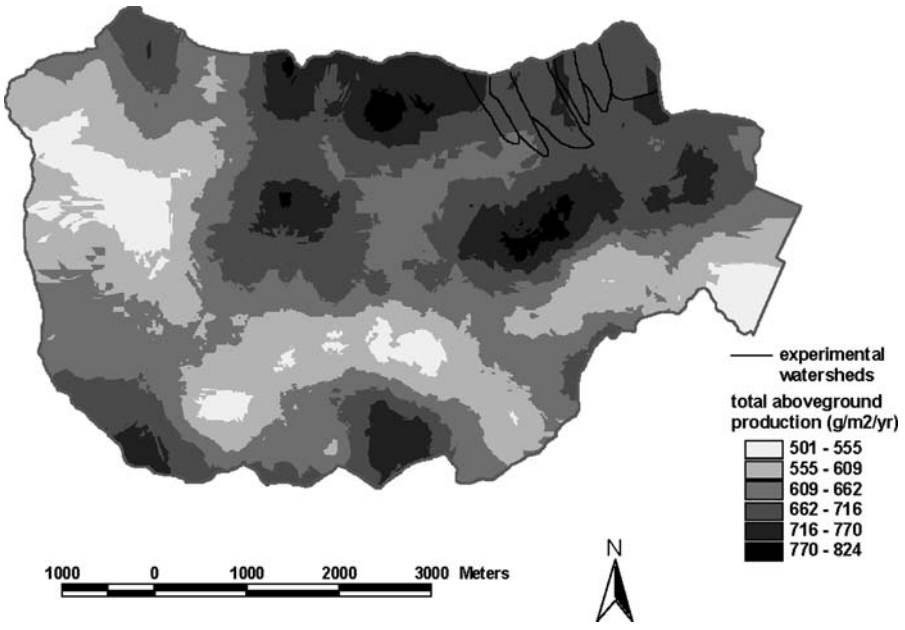

Figure 11. Spatial pattern of estimated aboveground net primary productivity across the Hubbard Brook valley for 1990–1995. The interpolations are based on 370 plots for which diameter growth of all trees (> 10 cm DBH) was measured. Error estimates are given in the text.

with the highest values in the conifer-dominated high elevation stands (Figure 12). In contrast, production efficiency (the ratio of woody biomass production to leaf biomass) was low in the conifer-dominated sites (Figure 13) and declined significantly with increasing elevation in the HBEF ($r^2 = 0.11$, $p < 0.001$). Although the microclimatic effects of aspect would be expected to affect vegetation C pools and fluxes in the cold climate of the HBEF, our valley-wide sampling did not reveal a significant effect of aspect on forest biomass or production. Apparently, the combined effects of disturbance history, species composition and site fertility mask any possible systematic effect of aspect on forest biomass and production in the HBEF.

Spatial variation in soil carbon pools and fluxes

There are striking patterns in the spatial distribution of soil C at the HBEF. Within the soil profile, the C concentration is greatest in the O_i and O_e horizons, approaching 500 g kg^{-1} dry weight (Figure 14). Carbon concentration declines to 25 g kg^{-1} in the highly leached E horizon, then increases to 60–70 g kg^{-1} in the spodic B_h and B_{s1} horizons, where C is precipitated along with Al and Fe during podzolization. In the lower mineral soil, the C concentration declines to 14 g kg^{-1}. Despite lower C concentrations, the pools of C in mineral-soil horizons are greater than in the O horizons because of higher bulk

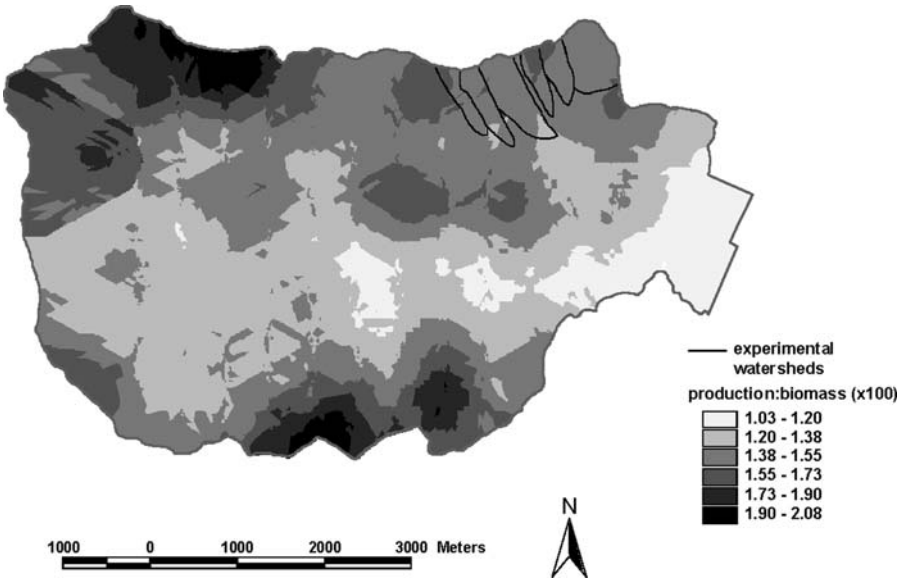

Figure 12. Spatial pattern of the ratio of aboveground wood production to aboveground biomass across the Hubbard Brook valley, based on interpolation from 370 plots.

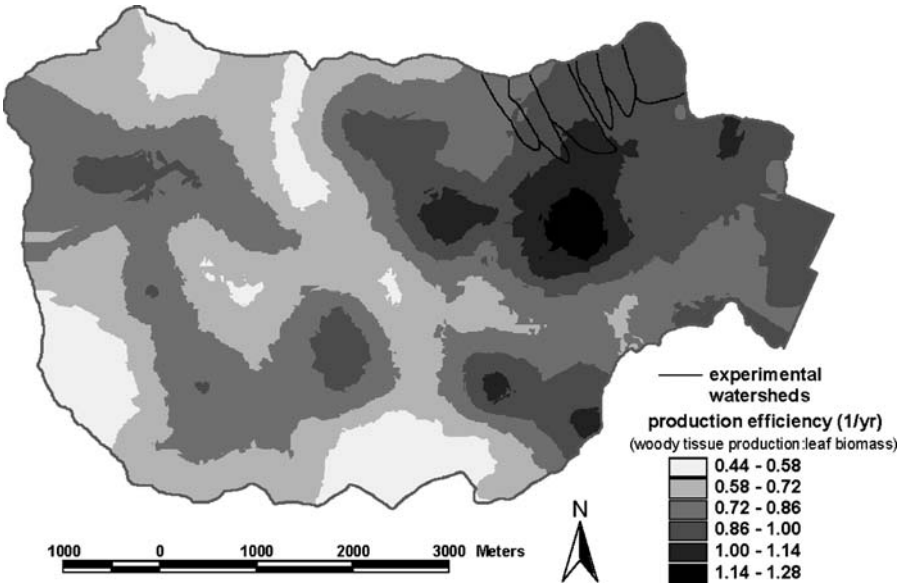

Figure 13. Spatial pattern of the ratio of aboveground woody tissue production to leaf biomass across the Hubbard Brook valley, based on interpolation from 370 plots.

densities and thicknesses (Figure 14). Indeed, approximately half of the soil C at the HBEF is found at depths lower than 20 cm in the mineral soil (Table 1).

The pool of C in HBEF soils is also highly heterogeneous across the landscape (Table 7). Most of this heterogeneity is due to variations in soil mass rather than soil C concentrations. The shallow soils of the spruce–fir–birch zone had significantly lower mineral soil mass (200 kg dry mass/m^2) than high and low hardwood sites (334 and 372 kg/m^2; Johnson et al. 2000), resulting in significantly lower C pools in spruce–fir–birch zone mineral soils (9.2 kg C/m^2) than in hardwood-dominated areas (15.2 and 13.4 g C/m^2) (Johnson et al. 1995). In the forest floor, as in the mineral soil, variations in mass result in spatial variations in C pools. In W5 prior to clear-cutting, the pool of C in the O_a horizon ranged from 20 to 8800 g C/m^2, while the concentration of C in O_a horizons varied only from 109 to 470 g C/kg. In the O horizons, the variations in soil mass are related to species composition and associated litter quality as well as to microtopography. In areas where spruce and fir accounted for greater than 30% of total basal area, the mean forest floor C pool (4860 g C/m^2) was significantly greater than in the hardwood-dominated zones (high hardwood, 2010 g C/m^2 ; low hardwood, 2830 g C/m^2). The higher mass and C content of O horizons in spruce–fir–birch zone can be attributed in part to the slow decomposition of coniferous litter (Johnson et al. 1995).

Total root biomass appears to vary along the elevational gradient roughly in parallel with aboveground biomass. Whittaker et al. (1974) harvested trees,

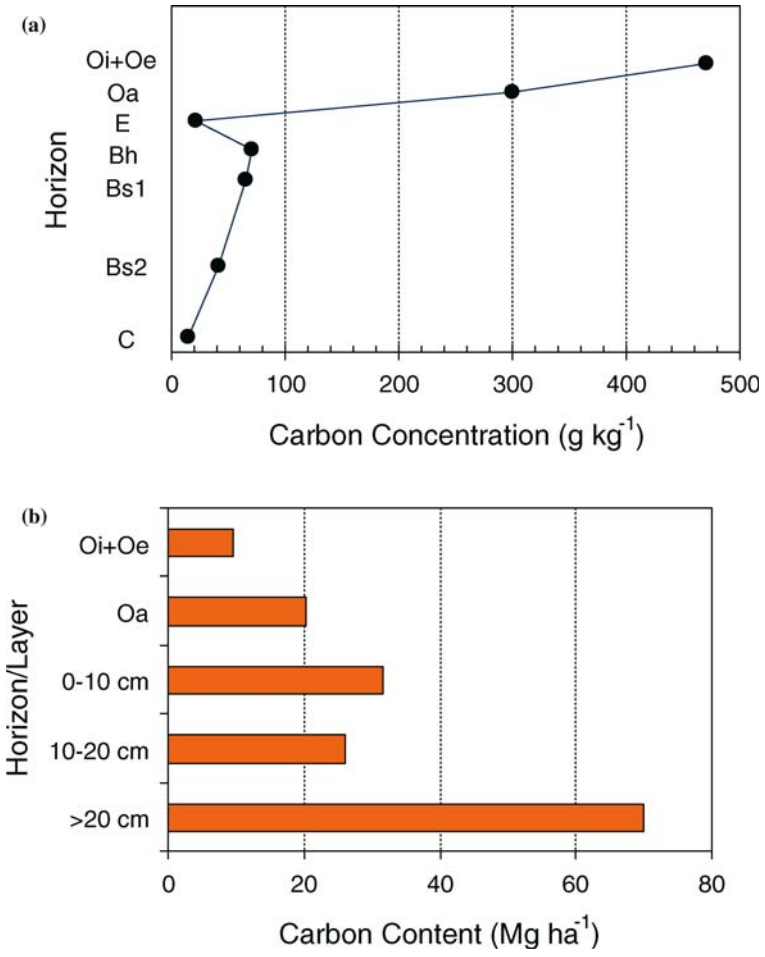

Figure 14. Depth variations in (a) carbon concentration and (b) carbon content in soil of the HBEF.

including coarse root systems, near W6 in the three elevation zones and found no evidence for systematic changes in the ratio of root to shoot biomass. Similarly, although fine root biomass ranged from 401 to 767 g/m^2 among seven northern hardwood plots, the variation was not related to elevation. Overall, the spatial variation in fine root biomass in and around the experimental watersheds was very high. Within-plot CV averaged 54% (based upon 5-cm diameter soil cores) and ranged from 34 to 69% across the nine plots; the between-plot CV averaged 25%. This variation is higher than for any other C pools and fluxes (Table 7), which reflects the functional plasticity of tree rooting in the highly variable, glacially derived soils at the HBEF.

Table 7. Spatial variation in carbon pools and fluxes in the Hubbard Brook Experimental Forest expressed in terms of the coefficient of variation (CV) for small scale and large scale.

Carbon pool or flux	CV%	
	Small-scale[a]	Large-scale[b]
Soil C content	45.5% (n = 60)	na
Fine root (< 1 mm) biomass	54% (n = 12) (34–69%)	25.3% (n = 9)
Microbial biomass C	30% (n = 12) (26–33%)	27.5% (n = 8)
Aboveground fine litterfall	12.4% (n = 12) (11.0–13.4%)	9.5% (n = 12)
Aboveground coarse litterfall	44% (n = 6) (31–56%)	na
Total soil respiration	29% (n = 12) (20–38%)	16% (n = 9)

[a]Within 0.5 ha plots (sample size within plots and range of within-plot CV among plots); sample areas were: soil respiration – 80 cm^2; fine litterfall – 0.10 m^2; coarse litterfall – 4 m^2; fine root biomass – 20 cm^2; soil carbon – 0.5 m^2; microbial biomass – 20 cm^2.
[b]Among 0.5 ha plots.

Carbon input to the soil is dominated by aboveground litterfall. Spatial patterns of litterfall C flux are revealed by long-term collections from eight plots distributed along the elevation gradient in and around the experimental watersheds (Figure 1). At the largest scale, between-plot (0.5 ha) variation in long-term average fine litterfall C flux was relatively small, with the coefficient of variation being only 9.5%. Similarly, small-scale, within plot variation was minimal with CV averaging 12.4% (Table 7). The relatively uniform closed canopy of the forest explains this low variation in fine litterfall flux. Spatial variation in coarse litterfall flux is much higher, particularly at the scale of 4.0 m^2 sample plots (CV = 44%, Table 7). This spatial variation estimate omits the extreme variation associated with episodic events like the 1998 ice storm (Rhoads et al. 2002).

Flux of C from the soil is dominated by the emission of respiratory CO_2 (TSR). Spatial patterns of TSR for the HBEF are available for the same eight plots, with five years of monthly data for 12 permanent collars in each plot. At the largest scale, between-plot variation in annual TSR is moderate with the CV being 16% across the eight stands (Table 7). The range of TSR across the experimental watersheds at the HBEF (560–870 g C/m^2-yr) is similar to that observed in six stands of differing forest composition and soil drainage at the Harvard Forest (530–870 g C/m^2-yr; Davidson et al. 1998). Hanson et al. (1993) measured TSR at four landscape positions in the Walker Branch watershed, Tennessee and concluded that a lack of large between-plot differences resulted from counteracting influences of fine root biomass, soil temperature and soil moisture across the landscape. The large differences in TSR among stands at the HBEF indicate that such counteracting influences are not a general phenomenon, possibly reflecting greater contrasts of soil, climate and vegetation in the HBEF than at Walker Branch. Not surprisingly, small-scale variation in TSR (within 0.5 ha plots) is considerably higher than between plot variations, in contrast with observations for aboveground litterfall (Table 7).

For example, the average, within-plot CV ranged from 20 to 38% across the eight plots. This small-scale variation results both from local differences in respiratory activity of the biota (e.g., fine roots) as well as variation in the soil physical and boundary layer characteristics that strongly influence CO_2 diffusivity. The highest within-plot CVs were observed in two very bouldery sites in the upper elevation zones of W1 (Figure 1).

Spatial variation in hydrologic fluxes of C

While inputs of C in precipitation are thought to be relatively uniform throughout the HBEF Valley, soil water fluxes and, streamwater outputs are highly variable within and among watersheds. There are distinct elevational patterns in dissolved C concentrations in soil water at the HBEF (Table 3). In the relatively flat, shallow soils of the spruce–fir–birch zone, concentrations of soil solution DOC and DIC are higher than in the northern hardwood zones. Additionally, soil water concentrations of DOC and DIC draining the lower mineral soil decrease with decreasing elevation. Although there are elevational patterns in the fluxes of DOC in soil water, the net removal of DOC in the mineral soil (i.e., forest floor DOC flux minus B_s DOC flux) is relatively uniform across the watershed landscape (14.7–17.1 g C/m^2-yr) across elevation zones. As for soil solutions, concentrations of DOC and DIC in streamwater draining W6 decrease markedly with decreases in elevation (Table 4) (Johnson et al. 1981; Lawrence et al. 1986). Lower rates of decomposition, due to relatively cold and acidic conditions, and thin mineral soil allow for elevated concentrations in soil solutions and in streamwater. Downstream, hardwood vegetation, steeper slopes, and deeper mineral soil result in less production of DOC in the forest floor and lower leaching of DOC from the deeper soil layers. Elevational variations in stream DIC reflect patterns of DIC inputs to streamwater from soil solutions and the turbulence of the stream channel due to changes in slope. The P_{CO_2} in high elevation headwater stream reaches draining W6 coincides with high DIC inputs and low stream turbulence. The P_{CO_2} decreases with increasing drainage area eventually approaching atmospheric values.

The net result is that the high-elevation zone exports more organic and inorganic C in stream water than do the mid and lower-elevation zones. These differences may relate to differences in tree species composition, which affect throughfall inputs and soil C pools. The net throughfall flux of organic C in hardwood stands west of W6 was 44–61% of fluxes in the spruce–fir–birch zone (Lovett et al. 1996), so that the throughfall inputs to soil in the upper subcatchment at W6 are higher than inputs in the mid and lower sub-catchments. However, the exports from the high-elevation zone are even higher than can be accounted for by the greater throughfall inputs, suggesting that other factors are also important. In particular, the patterns of streamwater DOC in the subcatchments reflect differences in forest floor organic matter pools (highest at

high elevation) and mineral soil depth. The more shallow mineral soils in the high-elevation zone provide less opportunity for abiotic adsorption, resulting in lower DOC retention within the soils. The high-elevation zone had the greatest DOC fluxes in soil solution as well as in streamwater. Soil solution DIC fluxes were similar to DOC fluxes in all horizons, and they were greatest in the upper sub-catchment and declined downslope.

Many of the factors that contribute to differences in C export within W6 also contribute to differences in C export among study watersheds in the HBEF. Concentrations of organic C in streamwater have been measured weekly at the outlet of W6, which is a south-facing watershed; W7, W8 and W9, which are north-facing watersheds; and in the main channel of Hubbard Brook near the mouth of the Valley (Figure 1). Data collected over four water years (1995–1996 through 1998–1999) provide an opportunity to examine variability in concentrations and fluxes among these watersheds (Likens et al. 2002). Streamwater organic C concentrations in these four watersheds are highly variable (1.9–8.6 mg C/l), even at W7, W8 and W9, which are contiguous. Fluxes of DOC are also highly variable (2.2–9.6 g C/m^2-yr), which is due to the range in concentrations of DOC rather than to the amount of streamwater. One reason for differences in DOC export may be watershed aspect, with slower decomposition rates on the more shaded, and hence cooler, north-facing slopes. The north-facing watersheds are also cooler because they are higher in elevation (610–900 m) compared to W6 (550–790 m). However, the lowest concentrations and exports of DOC occur at W7, suggesting that other factors are more important in regulating C exports in streamwater. Annual volume-weighted concentrations of DOC are similar in the main channel as in W6 and W7 (Likens et al. 2002).

The highest streamwater fluxes of organic C were measured at W9, and were 6–7 g C/m^2-yr higher than the other watersheds investigated. Watershed 9 has the highest proportion of coniferous vegetation (~40%) compared to the other watersheds (~5–15%). Consequently, this watershed is thought to have greater throughfall inputs and a thicker forest floor, consistent with the differences between the spruce–fir–birch and hardwood zones within W6. Watershed 9 is also the only gauged watershed at the HBEF that contains a sizeable wetland area (~2 ha), which provides an additional source of streamwater C.

The role of carbon in soil formation and mineral weathering

Carbon plays a dominant role in the formation of the soils at Hubbard Brook. This role derives from two somewhat distinct biogeochemical functions of carbon: (1) the dissolution of respiratory CO_2 in soil solutions adds acidity through the dissociation of carbonic acid, and (2) the incomplete decomposition of organic substrates, which forms a variety of soluble organic carbon compounds that act both as weak acids and as chelating agents in soil weathering reactions. Although pools and fluxes of DOC and DIC in drainage

waters are small compared to other pools and fluxes in the W6 C budget, these solutes play a critical role in soil development and ecosystem function. Through naturally occurring organic acids, DOC is important in regulating the acid–base chemistry of drainage waters and in the speciation and transport of trace metals. Through sorption reactions, retention of DOC controls the cation exchange capacity (CEC) of mineral soils. Finally both DIC and DOC help mediate weathering processes and soil development at the HBEF.

The nature of organic carbon

During the decomposition of litter, labile components are preferentially utilized by heterotrophs while more refractory components are left to accumulate in the soil. Changes in organic matter composition have been examined using ^{13}C NMR spectroscopy. An example spectrum of an O_a horizon from the HBEF (Figure 15), shows the assignments of regions of ^{13}C resonance to various types of biomolecular bond types. Reading right-to-left, the peaks in the 0–50 ppm range are attributable to alkyl C in aliphatic chains. Peaks in the 50–110 ppm region represent O-substituted alkyl C, with the large peaks at about 72 and 105 ppm attributed to C–O bonds in carbohydrates. Peaks in the 110–160 ppm range represent aromatic C compounds, while the 160–190 ppm region is attributed to carboxyl C and C associated with amide structures (Baldock et al. 1997).

Example spectra for soils, and organic matter isolated from soil solutions and stream waters, are shown in Figure 16. Soil organic matter at the HBEF is largely associated with alkyl and O-alkyl structures, which together account for

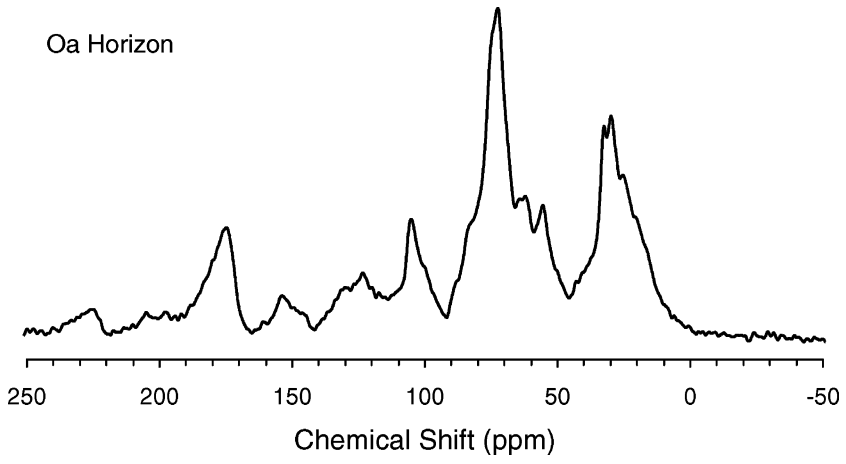

Figure 15. ^{13}C CPMAS NMR spectrum of an O_a horizon soil from the Hubbard Brook Experimental Forest, showing the assignment of the major regions of ^{13}C resonance.

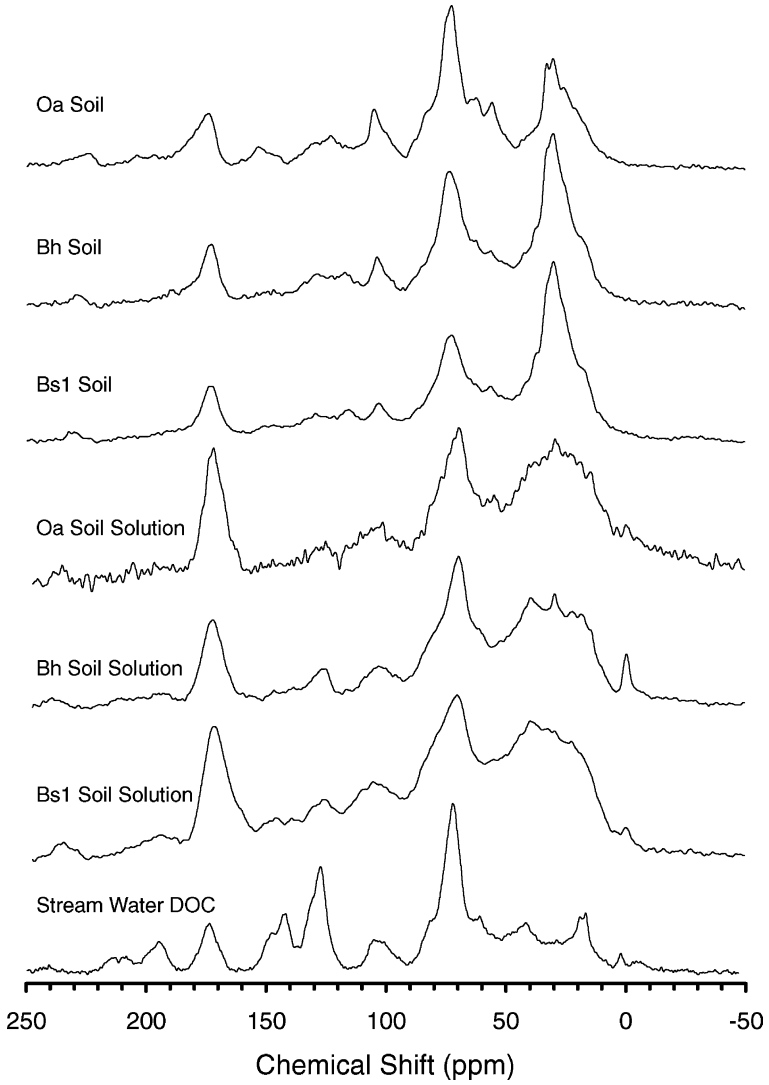

Figure 16. ^{13}C CPMAS NMR spectra of selected soil and drainage water samples from watershed 1 at the Hubbard Brook Experimental Forest, NH. Assignments of resonance peaks are shown in Figure 15.

70–80% of the C (Dai et al. 2001; Ussiri and Johnson 2003). Organic matter in the O_a horizon has a much greater fraction of C in carbohydrate structures, and less in aliphatic structures, than the more highly decomposed organic matter in mineral soil horizons. This pattern indicates that decomposition results in the loss of carbohydrates and the accumulation of alkyl C, probably in recalcitrant fractions such as waxes and resins. Indeed, Baldock and Preston

(1995) suggest that the ratio of O-alkyl-C to alkyl-C is a good indicator of decomposition in forest soils.

The carboxylic functional groups in soil organic matter are an important source of CEC in most soils. This is especially true in the coarse-grained, clay-poor soils found at the HBEF. Johnson (2002) reported highly significant correlations between CEC and organic carbon in organic ($r = 0.61$) and mineral ($r = 0.73$) horizons. Also, the intercept of the soil CEC vs. carbon content relationship is essentially zero, indicating that organic matter contributes virtually all of the CEC to the HBEF soils.

Low molecular weight organic C (< 1000 daltons) comprises 58% of DOC in bulk precipitation (Likens et al. 1983). Carboxylic acids, aldehydes, carbohydrates and tannin/lignin are present in similar amounts, accounting for 6–12% of DOC, whereas amines make up less that 1% (Likens et al. 1983; McDowell and Likens 1988). The composition of organic C in precipitation and the seasonal increase in concentration during summer suggest that much of the organic C deposited in precipitation is derived from airborne soil and plant particulate matter. Although concentrations of all measured DOC fractions also increase, throughfall DOC has a different composition than precipitation DOC, with a higher proportion of carbohydrates, phenolics, and amines, and a lower proportion of carboxylic acids and aldehydes (McDowell and Likens 1988).

In soil solutions from W1, 33–42% of organic C is in aliphatic structures, and C associated with carbohydrates accounts for another 36–39% (Figure 16; Dai et al. 2001). The proportion of C in alkyl structures decreases in deeper soil solutions, while the fraction of aromatic and carboxyl C increase (Dai et al. 2001). These patterns reflect the roles that different structures play in governing organic matter solubility. Compounds rich in alkyl C, such as waxes and resins, tend to be hydrophobic, consistent with the decreasing fraction of alkyl C with depth. Also, higher concentrations of carboxyl groups are associated with greater solubility of organic matter (Tipping and Woof 1990).

Concentrations of naturally occurring organic anions are elevated in soil waters. Concentrations are particularly high in forest floor solutions. Organic anions are the dominant anions in O horizon leachate (Table 3), and are largely responsible for the very low pH values in these soil waters. Concentrations of organic anions decrease with increasing depth in the mineral soil and in streamwater, a pattern that coincides with decreases in DOC concentrations.

Fractionation of soil water DOC using macroreticular resins, indicates that organic acids comprise more than 80% of the DOC (Mo 1997; Dai et al. 2001; Wellington 2002). Hydrophobic acids are the largest DOC fraction in O horizon leachate (averaging 52% of DOC), followed by hydrophilic acids (33%). In B_s horizon solutions there is a shift toward a smaller percentage of hydrophobic acids (39%) and a higher percentage on hydrophilic acids (46%). Ussiri and Johnson (2003) observed preferential sorption of hydrophobic organic matter, compared to hydrophilic organic matter, in sorption experiments using HBEF soils. The distribution of soil water C among hydrophilic

and hydrophobic fractions at the HBEF was similar to observations made in other forest ecosystems (Cronan and Aiken 1985; Yavitt and Fahey 1985; David et al. 1989; Qualls et al. 1991).

The composition of DOC in HBEF streamwater differs from soil solutions in several ways. Streamwater from W1 is more aromatic, contains a larger proportion of carbohydrate-C, and less carboxyl C than soil solutions collected at the same time (Figure 16; Dai et al. 2001). Like soil solutions, most of the DOC in streamwater consists of organic acids (54–83%). However, streamwater contains a greater proportion of hydrophilic neutrals than soil solutions (Dai et al. 2001), consistent with the lower carboxyl content and greater carbohydrate content observed in streamwater. A significant degree of in-stream processing of DOC is known to occur over short distances in HBEF streams (McDowell 1985), which may explain the discrepancies between soil solution and stream DOC composition.

Role of carbon in weathering and metal transport

Soil solution data suggest that DOC is an important weathering agent in soils at the HBEF, especially at higher elevations. In the spruce–fir–birch and high hardwood zones, fluxes of Na and Si from the O horizon were 50–73% as high as the fluxes in the B_s horizon, indicating that the forest floor can be a major zone of mineral weathering in the HBEF (Johnson et al. 2000) although atmospheric inputs and plant cycling also contribute to this pattern. Mineral matter occurs in the O_a horizon due to disruption by soil fauna and windthrow. High DOC concentrations in O_a horizon leachates, coupled with the predominance of acid fractions in soil solution DOC, suggest that organic acids facilitate mineral weathering, as observed by other investigators (Lundstrom and Ohman 1990; Raulund-Rasmussen et al. 1998).

Inorganic carbon also contributes to weathering, particularly in the low-hardwood zone, where only 28% of the Na release occurs from the O horizon. Therefore, 72% of the weathering release occurs in the mineral soil, where DOC concentrations drop by a factor of six (Johnson et al. 2000). This suggests that acidity contributed by inorganic carbon is the principal weathering agent in the deeper mineral soils of this zone.

Regardless of the specific weathering mechanism, naturally occurring organic acids are important in the speciation and transport of trace metals in drainage waters. Of particular interest in the low pH waters at the HBEF is the speciation of aluminum. Elevated concentrations of inorganic species of aluminum may be toxic to forest vegetation (Cronan and Grigal 1995) and aquatic biota (McAvoy and Bulger 1995). High concentrations of naturally occurring organic acids and limited supply of aluminum in the forest floor result in soil solution aluminum that is largely complexed with organic ligands. With increasing depth in the mineral soil, increased mobilization of aluminum coupled with deposition of DOC coincides with a shift in the speciation of

aluminum from largely organic to largely toxic inorganic forms (Lawrence et al. 1986; Driscoll and Postek 1995). Concentrations of lead are strongly correlated with DOC concentrations in soil and stream waters at the HBEF, suggesting that organic ligands also control the speciation and transport of lead (Driscoll et al. 1988; Johnson et al. 1995).

Carbon biogeochemistry: regional perspectives and future prospects

Our analysis of C biogeochemistry has focused on the Hubbard Brook Valley and especially the experimental watersheds during recent decades. In this final section we consider the implications of this analysis from a regional perspective and speculate on the prospects for C biogeochemistry in the future. The HBEF is considered most representative of northern hardwood watersheds of the White Mountains of New Hampshire and nearby mountainous terrain of Maine, Vermont (Green Mts.), New York (Adirondack Mts.) and southern Quebec (Laurentian Mts.). Similar conditions also prevail throughout the larger Laurentian Mixed Forest Province from Maine to Minnesota (Keys et al. 1995). Variation in C biogeochemistry within this region results from differences in physiography and soils, elevation, logging and fire history, agricultural history, and air pollution.

The physiography and soils of the HBEF are dominated by glacial till of relatively low base status and coarse texture, comparable to most of this region. However, for regional sites on glacial outwash or with more base-rich parent materials, C biogeochemistry may depart significantly from the HBEF situation. In particular, areas on coarse outwash are drier, often dominated by conifers and likely to have historic fire influence and hence different soil and vegetation C storage and flux. Sites with base-rich till support forests with somewhat different composition (e.g., more *Acer*, *Tilia*, *Fraxinus)*, higher productivity, and less well-developed surface organic horizons.

The upper elevation limit of the HBEF (ca. 1000 m) lies slightly above the hardwood-conifer transition in the region (Bormann et al. 1970). Watersheds encompassing different elevational ranges would exhibit variation in C biogeochemistry owing to climatic influences on forest composition. Most important in this regard would be differences in the dominance of conifers, especially red spruce and balsam fir at higher elevations. Larger soil C pools, higher hydrologic flux of DOC and lower NPP, as exhibited in the highest elevations of the HBEF, would be expected in such watersheds, although the role of soil and till characteristics influencing these features may be important.

The anthropogenic disturbance history of the northeastern mountains in the U.S. has been broadly similar, with intensive logging occurring from the mid-19th to the early 20th century (Chittenden 1904; Whitney 1994); hence, most of the forests in the region are mature second-growth stands. Additional timber harvest of these stands has a continuing influence on C biogeochemistry. Net ecosystem exchange of C undergoes radical shifts following catastrophic

disturbances, with the temporal pattern depending primarily upon the changes in the vegetation and dead wood pools (Figure 7) and hence on the intensity of the harvest activity. Historical changes in the technology used to transport logs, progressing from horses to motorized devices, also impacted C pools, especially CWD and soil organic horizons. Many areas that were cutover in the late 19th and early 20th century were severely burned, but the HBEF escaped this influence, as the only evidence of fire within the HBEF dates to over 7000 yr BP (Davis et al. 1985).

Regional landscapes with more favorable soils and physiographic conditions were converted for agricultural uses in the 19th century. Agriculture impacted about 60% of Grafton County in which the HBEF is located. The effects of agricultural land use on C biogeochemistry in secondary forests on these sites has been examined in detail near the HBEF. Similar to the patterns of land use seen at Harvard Forest in central Massachusetts (Foster 1992), the forests of the region initially were cleared gradually followed by a period of rapid exploitation. From 1830 to 1850 the amount of cleared land in Grafton County increased from about 5 to 55% (Hamburg 1984a), a deforestation event that was associated with the introduction of sheep to the region. The impact of agricultural activity on C storage in the landscape has been surprisingly small. Soils on plowed sites lost C in the organic layers, but there is no evidence of lower mineral soil C on sites that have been deforested for 150 years than those that remained in forest. In fact the amount of C in the soil of six sites comprising an old-field chronosequence is no different than that measured at the HBEF. The rate of forest floor accumulation during forest regrowth has been, in part, offset by a decline in C storage in the A_p horizon during the first 80 years of regrowth (Hamburg 1984b). Forest floor C in reforested sites is roughly the same as on logged sites after 70 years of forest regrowth.

Reforestation of central New Hampshire began about 1890 and was largely complete by 1950. Rates of biomass accumulation in the old-field forests follow the same curves as for the harvested watersheds at the HBEF (Figure 2), with evidence of a slowing of biomass accumulation between 60 and 80 y (Hamburg 1984a). At this point these old-field forests undergo a shift in species composition resulting from the death of early successional species. It is unclear from the available data if these forests will ultimately accumulate the same amount of aboveground biomass as harvested forests. Overall, the legacies of agriculture disturbance on C pools on the well-drained spodosols of the White Mountains are relatively small and short-lived, persisting about 100 years.

Carbon biogeochemistry at the HBEF and in the White Mountain region is likely to undergo some significant shifts in the future as a result of natural events and especially human-accelerated environmental change. Most prominent among the former would be the recurrence of extreme catastrophic events, like the 1938 hurricane, and among the latter, increases in atmospheric CO_2, changes in climate, continuing deposition of pollutants (especially N), and widespread tree mortality from exotic pests and agents of forest decline. In addition to effects of increasing atmospheric CO_2 on plant production and C

allocation (Norby et al. 2002, 2004), small increases in CO_2 consumption in soil weathering reactions can be anticipated (Andrews and Schlesinger 2001). The effect of climate change on C biogeochemistry of the Earth is a topic of intense debate and mechanistic research and modeling studies at the HBEF are needed. Our current understanding would suggest that the principal mechanisms whereby regional climatic warming would affect the C balance at the HBEF include: (1) slight increases in net photosynthesis and organic matter decomposition resulting from longer growing seasons (Figure 8) and increased summer temperature, (2) probable expansion of hardwood-dominated forests with concomitant responses of NPP and litter decay, (3) possible changes in the frequency and severity of soil drought and soil freezing events with uncertain effects on soil and vegetation C pools and fluxes, and (4) at the extreme, potentially large effects on C biogeochemistry that would be associated with wildfires. Air pollution effects on forest C balance also are highly uncertain. Although the combination of increasing CO_2 and N deposition might be expected to stimulate NPP, evidence to date suggests otherwise, and eventual N saturation might seriously threaten biomass C storage.

In contrast to the uncertainty about atmospheric changes, the effects of catastrophic disturbances are fairly predictable. A severe hurricane would affect C biogeochemistry in approximately the manner depicted in Figure 7. The recovery of NPP and live biomass would be rapid because of the exceptionally high density of long-lived pin cherry seeds that has accumulated in the soil seed bank as a result of repeated forest disturbances at the HBEF (Marks 1974; Tierney and Fahey 1998). In the future high tree mortality due to agents such as hemlock woolly adelgid (Orwig et al. 2002) could have locally significant effects on C pools and fluxes where stands are dominated by a single species. However, most of the HBEF consists of mixed stands in which decline episodes or pest and pathogen irruptions would create diffuse disturbances, with limited influence on watershed-level C biogeochemistry.

Species invasions could influence C pools and fluxes either directly or indirectly. For example, although the return of moose to the HBEF appears to have only a limited direct influence, it is possible that with high moose densities the composition of the forest could change significantly, with red spruce being particularly favored. The difference in C biogeochemistry between conifer and hardwood dominated stands has previously been emphasized. The invasion of European lumbricid earthworms also has the potential to alter C pools; studies of northern hardwood ecosystems in central New York (Bohlen et al. 2004) and elsewhere (Alban and Berry 1994) demonstrated that soil C storage may be greatly reduced by earthworm invasion. Lumbricid earthworms have been observed at very low density in the HBEF in recent years (Fahey, personal observation), but the factors limiting their increase and spread are not well understood.

From a regional standpoint, the most important human factor influencing forest C pools and fluxes is almost certainly forest management. It is beyond the scope of this work to analyze human decision-making processes, but it is

clear that the effects of intensive timber harvest on C biogeochemistry can overwhelm all the other influences considered above. Whether considerations of the potential climatic feedbacks from forest management will become part of the decision framework for northeastern forests, providing a higher level of feedback on regional C cycling, is not yet clear.

Acknowledgements

This research has been supported primarily by grants from the National Science Foundation. The authors thank their many colleagues who have contributed to this work, as well as two anonymous reviewers whose comments greatly improved the manuscript.

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