Tree-ring ^{13}C tracks flux tower ecosystem productivity estimates in a NE temperate forest

2014 Environ. Res. Lett. 9 074011

(http://iopscience.iop.org/1748-9326/9/7/074011)

OPEN ACCESS
IOP Publishing

Environmental Research Letters

Environ. Res. Lett. **9** (2014) 074011 (9pp)

doi:10.1088/1748-9326/9/7/074011

Tree-ring δ^{13}C tracks flux tower ecosystem productivity estimates in a NE temperate forest

Soumaya Belmecheri[1], **R Stockton Maxwell**[2], **Alan H Taylor**[3],
Kenneth J Davis[4], **Katherine H Freeman**[1] **and William J Munger**[5]

[1] Department of Geosciences, Pennsylvania State University, University Park, PA 16802, USA
[2] Department of Geospatial Science, Radford University, Radford, VA 24142, USA
[3] Department of Geography, Pennsylvania State University, University Park, PA 16802, USA
[4] Department of Meteorology, Pennsylvania State University, University Park, PA 16802, USA
[5] School of Engineering and Applied Sciences and Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA 02138, USA

E-mail: sub30@psu.edu

Received 26 December 2013, revised 6 June 2014
Accepted for publication 17 June 2014
Published 22 July 2014

Abstract

We investigated relationships between tree-ring δ^{13}C and growth, and flux tower estimates of gross primary productivity (GPP) at Harvard Forest from 1992 to 2010. Seasonal variations of derived photosynthetic isotope discrimination (Δ^{13}C) and leaf intercellular CO$_2$ concentration (c_i) showed significant increasing trends for the dominant deciduous and coniferous species. Δ^{13}C was positively correlated to growing-season GPP and is primarily controlled by precipitation and soil moisture indicating that site conditions maintained high stomatal conductance under increasing atmospheric CO$_2$ levels. Increasing Δ^{13}C over the 1992–2010 period is attributed to increasing annual and summer water availability identified at Harvard Forest and across the region. Higher Δ^{13}C is coincident with an enhancement in growth and ecosystem-level net carbon uptake. This work suggests that tree-ring δ^{13}C could serve as a measure of forest GPP and be used to improve the calibration and predictive skill of ecosystem and carbon cycle models.

S Online supplementary data available from stacks.iop.org/ERL/9/074011/mmedia

Keywords: tree rings, photosynthetic discrimination, carbon cycle, productivity, soil moisture

1. Introduction

Our ability to project the future carbon cycle is limited by our lack of understanding of terrestrial carbon (C) cycle dynamics and the feedbacks that constrain C budgets. Projections of C-flux and C-sequestration from current coupled terrestrial carbon cycle models give widely divergent results (Friedlingstein *et al* 2006). The lack of agreement among projections is, in part, related to poorly constrained model parameters. Constraining carbon budget projections is an important issue given the current mitigation of anthropogenic emissions by terrestrial ecosystems sequestering C (Le Quéré *et al* 2009). Terrestrial ecosystems sequestered approximately 30% of anthropogenic emissions from 2000 to 2006, and there is interest in the potential to manage forest ecosystems to increase the strength of the carbon sink (Hurtt *et al* 2002, Canadell *et al* 2007, Woodbury *et al* 2007). Longer periods of observational data on C-cycle variability, in particular, would help constrain model parameters and improve model performance. CO$_2$ flux measurements between ecosystems and the atmosphere from eddy covariance flux towers (Baldocchi 2003) are valuable for model evaluation (Suzuki and Ichii 2010, Richardson *et al* 2012, Schaefer *et al* 2012, Keenan *et al* 2012a, Raczka *et al* 2013), but they only measure CO_2 flux conditions over short periods (maximum 20 years, most $\leqslant$10 years) in a small footprint (1 km^2) and the regional tower density is low (e.g., five sites in northeastern US forests with >10 years of data). Consequently, a variety of other types of measurements are needed to constrain C-cycle model parameters and to improve projections of interannual variability in C-cycle dynamics in terrestrial ecosystems (Pan *et al* 2006, Sims *et al* 2006, Randerson *et al* 2009, Babst *et al* 2013).

Annual measurements of forest carbon production can be obtained from tree rings that integrate the influence of climate and site factors on forest growth (Babst *et al* 2013). Attempts to associate tree-ring width with net ecosystem exchange (NEE) and gross primary productivity (GPP) measurements from flux towers have proven inconclusive (Rocha *et al* 2006). Integrals of annual growth over a few to several years have yielded similar net carbon fluxes as continuous flux tower measurements, but annual increment and flux tower measurements do not show strong inter-annual correlations (Barford *et al* 2001).

The composition of carbon isotopes ($\delta^{13}C$) of an annual tree ring records the proportions of assimilated carbon and is closely linked to photosynthetic capacity and stomatal regulation during tree growth (Farquhar *et al* 1989, Ogée *et al* 2009). Therefore, the distribution of stable carbon isotopes within a tree ring reflects the carbon assimilation and environmental conditions experienced by a tree through the growing season. The $\delta^{13}C$ is widely used to study the linkage between environmental conditions and the physiological processes that control tree growth at inter- and intra-annual time resolutions (Loader *et al* 1995). Tree rings, particularly wood cellulose $\delta^{13}C$, contain valuable records of past climate, leaf-gas exchange, and carbon allocation within trees (e.g. Barbour *et al* 2002). Several studies used tree-ring $\delta^{13}C$ to reconstruct the intrinsic water use efficiency (iWUE) of trees (e.g. Duquesnay *et al* 1998), and $\delta^{13}C$ within a tree ring has been shown to track the physiological changes at the canopy level as recorded by the flux towers (Walcroft *et al* 1997, Michelot *et al* 2011). This approach has shown the potential to better understand the link between canopy-level physiology, tree-ring isotopic signature and climate drivers (Offermann *et al* 2011).

In this paper, we identify the relationships between interannual variability in tree-ring $\delta^{13}C$, tree-ring increment, flux tower measurements of CO_2, and climate for a temperate forest in the northeastern United States. The period of analysis spans 18 years (1992–2010) and is from the longest available record of continuous flux tower measurements (Harvard Forest, Petersham, Massachusetts; Urbanski *et al* 2007). We analyzed the $\delta^{13}C$ (of α-cellulose) from tree-ring latewood (LW) because it is less dependent on carbon stored during the previous growth year and therefore corresponds to the isotopic signal of recently assimilated C during the growing season. We conducted this analysis for one broad-leaf deciduous and one evergreen needle-leaf co-dominant species in the flux-tower footprint to contrast species response. Specifically, we: (1) identified the relationship between tree-ring $\delta^{13}C$, GPP, and tree growth, and, (2) assessed the responses of tree physiology and growth to rising atmospheric CO_2 mole fraction and climate variation. We also discuss how changes in climate conditions and atmospheric CO_2 concentration over the period of record may have modulated growth and forest productivity over the last 18 years.

Table 1. Sample characteristics for *Quercus rubra* and *Tsuga canadensis* from the Harvard Forest site.

Species	*Quercus rubra*	*Tsuga canadensis*
No. of dated cores	42 (16 trees)	55 (22 trees)
No. of isotopic cores	5 (5 trees)	4 (4 trees)
Mean intercorrelation RW	0.67	0.61
Mean intercorrelation $\delta^{13}C$	0.71	0.67
EPS RW (1992–2010)	0.95	0.96
EPS $\delta^{13}C$ (1992–2010)	0.85	0.86

Numbers of dated cores and trees for chronology and isotopic analyses. Mean intercorrelation for isotopic cores. Note that only one core per tree was sampled for isotopic analyses as the intra-tree variability is small in comparison with the inter-tree variability (Daux *et al* 2011).

2. Materials and methods

2.1. Study site and tree-ring chronologies

The forest within the flux-tower footprint (1 km^2; Harvard Forest-EMS tower) is mainly deciduous and is dominated by *Quercus. rubra* (L.) (northern red oak; 52% of basal area), *Acer rubrum* L. (red maple; 22% of basal area) and *Tsuga canadensis* (L.) (eastern hemlock; 17% of basal area). Increment core sampling focused on canopy dominant trees. To identify interannual variability in tree growth and tree-ring $\delta^{13}C$, we cored *Q. rubra* and *T. canadensis* with a 5 mm increment borer at 1.37 m stem height (table 1). Two cores were taken from each tree to build ring-width chronologies. Additionally, we cored five and four trees respectively of each species at the same height with a 12 mm increment borer. The large cores were used to analyze the $\delta^{13}C$ in the LW of the tree rings. A sample of four trees is sufficient to achieve good precision of the $\delta^{13}C$ sample mean (McCarroll and Loader 2004, Leavitt 2008).

Ring-width chronologies were developed for each species using standard dendrochronological techniques (Speer 2010). For the site, *Q. rubra* mean age was 97 years (range 71–115 years) and *T. canadensis* mean age was 145 years (range 89–221 years). For isotope cores, *Q. rubra* mean age was 103 years (range 87–113 years) and *T. canadensis* mean age was 142 years (range 93–188 years). All ages were estimated from inner ring dates.

Basal area increment (BAI) was calculated for each tree and species using the dplR package in R (Bunn 2008). We used the 'outside in' function to convert raw ring-width measurements to BAI based on the diameter of the tree and the width of each ring moving towards the pith of the tree. The method assumes a circular growth pattern. BAI was used instead of ring width as a surrogate of radial growth and carbon gain because it represents more accurately tree annual biomass increment without the need for standardization

(Biondi and Qeadan 2008). A mean BAI value was computed for each species at an annual resolution, averaged over all the trees cored for both carbon isotope analyses and ring-width chronologies (i.e., 16 trees/42 cores for *Q. rubra* and 22 trees/ 55 cores for *T. canadensis*).

2.2. Stable istope analyses

We analyzed the LW portion of each tree ring from individual trees over the 1992–2010 period (table 1). The samples were milled using an ultra-centrifugation mill (Qiagen TissueLyserII) and α-cellulose was extracted from each wood sample following the Soxhlet method elaborated by Green (1963) and modified by Leavitt and Danzer (1993). δ^{13}C ratios were measured on the CO_2 produced by α-cellulose combustion in a Costech elemental analyzer coupled with a Thermo Delta V-IRMS. The sample accuracy was determined to be ±0.08‰ (1 σ standard deviation calculated from the average difference between measured and true internal standard, $n = 13$). The isotopic value is expressed in the delta (δ) notation relative to the VPDB (‰ VPDB).

2.3. Calculation of Δ, c_i and iWUE

We used δ^{13}C to determine carbon isotope discrimination (Δ) by the plant against atmospheric δ^{13}C, and variation in plant iWUE. The Δ describes the isotopic difference between the δ^{13}C of air ($\delta^{13}C_{\mathrm{air}}$) and the plant ($\delta^{13}C_{\mathrm{plant}}$) and results from the preferential use of ^{12}C over ^{13}C during photosynthesis. Δ is calculated using:

$$\Delta‰ = \left(d^{13}C_{\mathrm{air}} - \delta^{13}C_{\mathrm{plant}}\right) \Big/ \left(1 + \delta^{13}C_{\mathrm{plant}} \big/ 1000\right). \qquad (1)$$

Records of $\delta^{13}C_{\mathrm{air}}$ were obtained from Mauna Loa from 1992 to 2002, and from aircraft measurements collected in Worcester, Massachusetts at 500 m above ground and available from 2003 to 2010 (White and Vaughn 2011). The model of Farquhar *et al* (1982) describes isotopic Δ for C_3 plants via:

$$\Delta‰ = a + (b - a)\, c_i/c_a, \qquad (2)$$

where a is the fractionation during CO_2 diffusion through the stomata (4.4‰: O'Leary 1981); b is the fractionation by RuBP carboxylase (27‰: Farquhar and Richards 1984); and c_{i} and c_a, are the leaf intercellular space and ambient CO_2 concentrations (μmol Mol^{-1}), respectively. We used the data of atmospheric CO_2 concentration (c_{a}) measured at 29 m height on the eddy-covariance tower to calculate c_{i} from equation (2). The fractionations due to diffusion and carboxylation are constant but additive; therefore, the δ^{13}C records variations in c_{i} as regulated by two main processes: stomatal conductance ($c_{\mathrm{a}}/c_{\mathrm{i}}$) and photosynthetic assimilation rate (A). The iWUE is the ratio of the net photosynthetic assimilation rate (A) and water vapor conductance (g_{H2O}) and is described by Ehleringer and Cerling (1995) as:

$$iWUE = A/g_{H2O} = c_a - c_i\,(1/1.6). \qquad (3)$$

The iWUE derived from plant isotope data is used to compare photosynthetic properties independent from evaporative demand (Osmond *et al* 1980), and is therefore, often applied as an indicator of long-term trends in the internal regulation of carbon uptake and water loss of plants (Seibt *et al* 2008). We used summer (June, July and August) values of $\delta^{13}C_{\mathrm{air}}$ and c_{a} to calculate Δ, and to reconstruct c_{i} and iWUE for the period corresponding to LW formation.

2.4. Meteorological and CO_2 flux data and data analyses

We used hourly gap-filled meteorological data from the eddy-covariance tower measured by sensors above the canopy at 29 m height (Urbanski *et al* 2007, Harvard Forest Data Archive HF004) to compute monthly mean temperature, vapor pressure deficit (VPD), incident photosynthetically active radiation, relative humidity as well as monthly total precipitation from 1992 to 2010. Hourly gap-filled GPP was used to provide monthly cumulative GPP. We used the Palmer Drought Severity Index (PDSI) for the central Massachusetts climate region from the National Climatic Data Center.

The association between climate variables and tree-ring Δ chronologies were assessed using correlation analyses. The GPP time series during the growing season (from May to October) were compared to tree-ring Δ chronologies for each species. Correlations were calculated between monthly GPP and LW-Δ using the Pearson (pairwise) product-moment correlation. Trends over the 1992–2010 period were estimated using linear regression.

3. Results

We assessed the number of trees required to extract a common reliable climate signal (thus, the degree to which isotopic composition series vary in parallel) using the expressed population signal (EPS, Robertson *et al* 1997, McCarroll and Pawellek 1998). The EPS values calculated using the 1992–2010 isotopic compositions are ⩾0.85 for two trees from each species. An EPS value of ⩾0.85 suggests that the sample size is adequate (Wigley *et al* 1984). At the high frequency investigated in this study (year to year), the δ^{13}C series display a high common variance within each species (table 1). We assessed the confidence interval (CI) around annual mean values to account for the differences in the absolute isotopic values (McCarroll and Loader 2004). The sample size of 4 *T. canadensis* and 5 *Q. rubra* provided a $CI_{95\%} = 0.3‰$ and 0.18‰ respectively. The mean values of 1992–2010 individual series were calculated for all tree cores to produce one main series for each species (Shi *et al* 2011) hereafter called $\delta^{13}C_{\mathrm{TSCA}}$ for *T. canadensis* and $\delta^{13}C_{\mathrm{QURU}}$ for *Q. rubra*.

δ^{13}C measurements were significantly different between species ($t = 2.02$, $P < 0.05$). The mean $\delta^{13}C_{\mathrm{TSCA}}$ display higher ratios than $\delta^{13}C_{\mathrm{QURU}}$, this difference is probably linked to hydraulic conductivity in conifers which is less efficient than in ring-porous deciduous species (Stuiver and Braziunas 1987, McCulloh *et al* 2010) or other factors such as differences in the maximum photosynthetic capacity or leaf morphology (Barbour *et al* 2002). The species specific time series of annual δ^{13}C variations are positively correlated with each other ($r = 0.61$ $P < 0.001$). The derived Δ and c_{i} series for

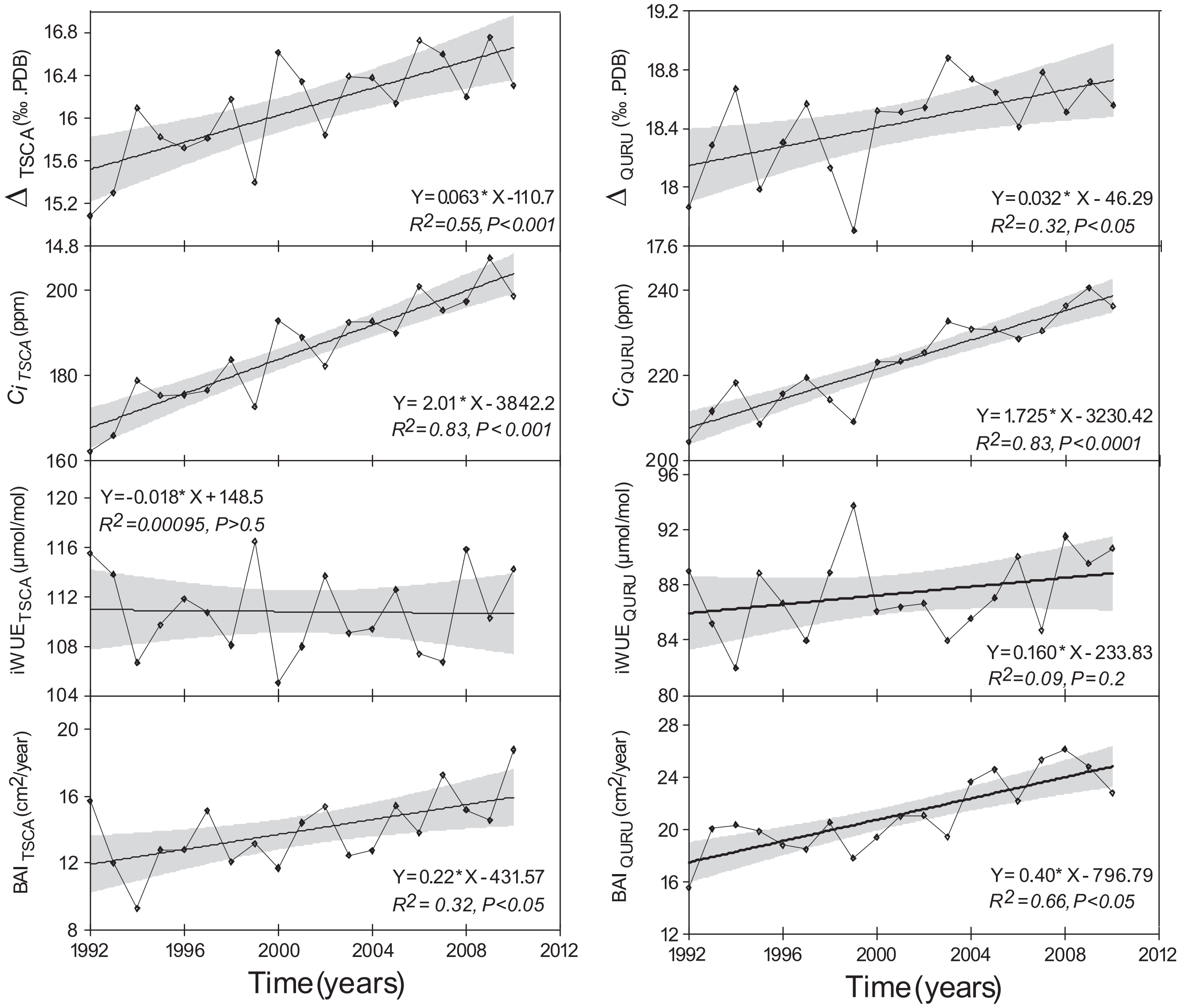

Figure 1. *From top to bottom*: trends in the δ^{13}C discrimination Δ (‰), the leaf intercellular CO$_2$ concentration (c_{i}, *ppm*), intrinsic water use efficiency (iWUE) and basal area increment (BAI) for *T. canadensis* (Left) and *Q. rubra* (Right) throughout time. The slopes of the linear regressions fitted to the data, the coefficients of determination and the *P*-values are reported for each parameter (see also table 2). The upper and lower levels of the 95% confidence interval for each linear trend are shaded in gray.

each species reveal similar and significant increasing trends over time, although the increase was more pronounced for *T. canadensis* (figure 1). The iWUE over the period of record remained stable which translates into a constant $c_{\mathrm{a}} - c_{\mathrm{i}}$ or an increasing c_i/c_a. A few years did display a higher iWUE in comparison to most years; in particular, iWUE spikes in 1999 in both species records.

The mean BAI also showed a significant increasing trend over the period of record for *Q. rubra* ($R^2 = 0.64$, $P = 0.0001$) but the trend was less pronounced for *T. canadensis* ($R^2 = 0.32$, $P < 0.05$). Overall, the trends analysis using linear regression shows that Δ, c_i and BAI have increased for each species. The changes were significant ($p < 0.05$) and the slopes were positive (table 2).

The Δ was strongly correlated with July (0.55, $P < 0.05$) and October (0.53, $P < 0.05$) GPP for *T. canadensis*, and with July (0.49, $P < 0.05$), August (0.58, $P < 0.01$), and October (0.55, $P < 0.05$) GPP for *Q. rubra*. Online supplementary table S1 (available at stacks.iop.org/ERL/9/074011/mmedia) summarizes the Pearson correlation obtained between monthly climate variables and Δ_{QURU} and Δ_{TSCA}. Overall, the strongest positive correlations were found with PDSI from May to August for *T. canadensis* and for May for *Q. rubra*. A positive correlation was found between Δ of both species and early-growing season precipitation (April and May).

4. Discussion

4.1. Relationship between Δ, growth, and flux tower estimates of GPP

The carbon contribution to stem growth during LW formation should primarily originate from the immediate product of

Table 2. Trend statistic, per species, for isotopic discrimination (Δ), intercellular CO$_2$ concentration (c_i), intrinsic water use efficiency (iWUE) and basal area increment (BAI). All units are given per year (*yr*). The slopes are estimated using linear regression.

	Slope	Sig
Δ $_{\mathrm{TSCA}}$ (‰ yr^{-1})	0.06	<0.0001*
Δ $_{\mathrm{QURU}}$ (‰ yr^{-1})	0.03	0.01**
c$_{\mathrm{i}}$ $_{\mathrm{TSCA}}$ (ppm yr^{-1})	2.01	<0.0001*
c$_{\mathrm{i}}$ $_{\mathrm{QURU}}$ (ppm yr^{-1})	1.72	<0.0001*
iWUE$_{\mathrm{TSCA}}$ (μmol mol yr^{-1})	−0.018	0.9***
iWUE$_{\mathrm{QURU}}$ (μmol mol yr^{-1})	0.16	0.2***
BAI$_{\mathrm{TSCA}}$ (cm^2 yr^{-1})	0.22	0.01**
BAI$_{\mathrm{QURU}}$ (cm^2 yr^{-1})	0.40	<0.001*

The significance of each variable slope is given * $p < 0.01$, ** $p < 0.05$ and *** Positive or negative but non-significant.

carboxylation thus reflecting the δ^{13}C signature of recent assimilates (Helle and Schleser 2004). The interannual variability of Δ was compared with monthly GPP to identify the seasonality of carbon uptake and allocation to aboveground woody biomass. The correlations shown in figure 2 indicate that recent photosynthates provided the substrates for stem radial growth occurring in the second part of the growing season (Gessler *et al* 2009, Offermann *et al* 2011). The Δ-GPP correlations are logical based on the timing of LW formation for both *T. canadensis* and *Q. rubra*. LW tracheid formation and cell wall thickening in *T. canadensis* begins later in the growing season (late July–October, Skene 1972) coincident with the significant correlations. In contrast, LW formation in *Quercus* species begins approximately five weeks after the unfolding of first leaves and continues until radial growth cessation in late summer or early fall (Zasada and Zahner 1969, Voelker *et al* 2012).

The Δ-GPP correlations are consistent with the seasonality of carbon uptake from eddy flux measurements and C storage estimates at the deciduous forest-EMS tower site and the Hemlock Forest tower site located 0.5 km from the EMS tower (Hadley and Schedlbauer 2002, Hadley *et al* 2009). Net C uptake at the deciduous forest site occurs between the end of May and mid-October. At the hemlock site, the peak in net C uptake and storage occurs in April and May. This period is not influencing the δ^{13}C in the LW, although it shows the effect of conifers on the annual pattern of the C exchange. Conifers currently represent 17% of the total basal area at the deciduous forest site. After C uptake declines in June, it increases in July, and falls in August before a second uptake peak in October, consistent with the Δ-GPP correlations for *T. canadensis*.

The species seasonality of carbon allocation is further reflected in the relationship between LW-Δ and growth. The correlation for *Q. rubra* LW-Δ and mean BAI was significant ($r = 0.72$, $P < 0.001$), and was slightly higher with the mean *Q. rubra* BAI of all sampled trees ($r = 0.75$, $P < 0.001$). To illustrate the relationship between aboveground carbon gain and photosynthetic discrimination we regressed BAI against Δ, and a strong positive trend was obtained for *Q. rubra* ($R^2 = 0.39$ $P < 0.01$). The growth increase of *Q. rubra* could be interpreted as the result of a greater photosynthetic rate induced by increased c_i concentrations (von Caemmerer and Farquhar 1981, Schubert and Jahren 2012), and a substantial allocation of carbohydrates to LW formation and radial growth (Keel *et al* 2006, Palacio *et al* 2011). However stage of stand development may also be contributing to this increase in BAI (e.g. Foster *et al* 2014, figure S1). A relationship between Δ and BAI was not found for *T. canadensis,* probably because carbon sequestered after June contributes little to the current year radial growth or that carbon allocation differs by species (Richardson *et al* 2013). The trend in the BAI growth enhancement for *Q. rubra* is consistent with changes in the measured annual increment of aboveground biomass in the flux-tower footprint from 1993–2010 (~20% increase, Data Archive: HF069), and provides a quantification of carbon stored in aboveground woody biomass. Interestingly, the aboveground biomass over the last decade accounted for ~50% of the total carbon sequestered (Keenan *et al* 2012a) confirming the relationship we found between *Q. rubra* BAI and Δ, and growing season GPP (figure 2). The remaining carbon uptake could be attributed to litter or soil pools; however, these carbon proportions and stocks are not accounted for in the tree-rings δ^{13}C.

The inter-annual variability and fraction of carbon uptake and sequestration explained by the tree-ring derived Δ (figures 2(c), (d)) provides a quantitative proxy that can be used to constrain models that estimate forest productivity. Process-based models fail to accurately reproduce the observed inter-annual variability of C-fluxes (Keenan *et al* 2012b) mainly because of inaccurate model allocation structure and lagged effects of climate variability on tree growth and physiology (Gough *et al* 2009). In contrast, the Δ integrates biotic factors which modulate the δ^{13}C fractionation and the isotopic composition of the total pool of carbon fixed during photosynthesis at seasonal and annual cycles (Leavitt 1993).

4.2. Climate drivers and physiological implication of the Δ trend

We examined the climatic drivers of Δ using meteorological data from the eddy-covariance tower and PDSI. The climate signal within both species Δ series is dominated by monthly precipitation and PDSI during the growing season (table S1), although they have a stronger influence on *T. canadensis* due to its particularly drought-sensitive nature caused by a relatively shallow rooting-depth (Cook and Cole 1991).

The carbon isotope discrimination properties can be used to assess how trees are responding to increasing atmospheric concentration c_{a} and changes in climate. Three physiological response scenarios described by Saurer *et al* (2004) identify possible changes in iWUE and c_{i} following c_{a} increase: (1) c_{i} remains constant such that $c_{\mathrm{i}}/c_{\mathrm{a}}$ decreases and iWUE increases; (2) c_{i} increases proportional to c_{a} such that $c_{\mathrm{i}}/c_{\mathrm{a}}$ remains constant and iWUE increases; (3) c_{i} increases at the same rate as c_{a}, $c_{\mathrm{i}}/c_{\mathrm{a}}$ increases and iWUE remains constant. In this study, Δ and c_{i} increased and there was no increase in iWUE for both species (figure 2, table 2). The $c_{\mathrm{i}}/c_{\mathrm{a}}$ calculated for

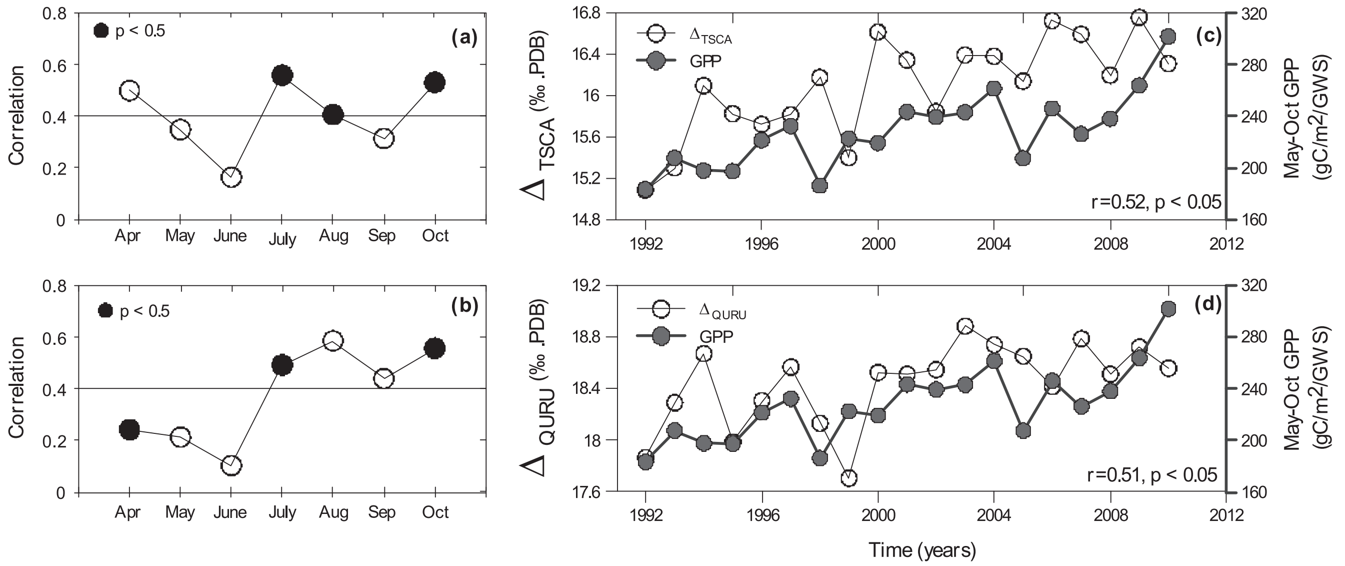

Figure 2. Tree-ring *Δ* chronologies and monthly GPP data from April to October. Pearson correlations from 1992 to 2010 between *Δ* and mean monthly GPP data for *T. canadensis* (a) and *Q. rubra* (b). May–October GPP and the *Δ* chronologies for *T. canadensis* (c) and *Q. rubra* (d) versus time.

both species increases indicating c_i follows the increase in c_a at a rate of 2 ± 0.21 ppm yr^{-1} for *T. canadensis*, and 1.7 ± 0.17 ppm yr^{-1} for *Q. rubra.* The c_i/c_a increase and no change in iWUE suggest a weak stomatal response to c_a increase and is described as a passive response to changes in c_a (McCarroll *et al* 2009) where neither stomatal conductance nor photosynthetic rate change. The most common response documented in trees is an active response as stomatal conductance is reduced (Bert *et al* 1997, Saurer *et al* 2004, Peñuelas *et al* 2011). The iWUE trends derived from the tree-rings δ^{13}C in our study show a divergence from the instantaneous WUE (the ratio of carbon assimilation to transpiration, Farquhar and Richards 1984) trend documented at the ecosystem level using continuous measurements of CO_2 and water vapor fluxes at HF (Keenan *et al* 2013). The canopy-integrated water use efficiency calculated as the ratio between gross ecosystem photosynthesis (GEP) and Ecosystem evapotranspiration (E) shows a significant increase over the measurements period (3.5% change yr^{-1}, $P = 0.01$). The latter was calculated taking into account the atmospheric evaporative demand and therefore is referred to as ‘inherent’ water use efficiency (W_{ei}). The ‘intrinsic’ water use efficiency as derived from tree-rings δ^{13}C is often used as an indicator of long-term trends in the internal regulation of carbon uptake and water loss independently from evaporative demand (Osmond *et al* 1980). Therefore iWUE inferred from δ^{13}C may not be representative of instantaneous or inherent WUE. Although both are affected by similar processes (i.e. stomatal conductance), they can vary independently because they are influenced by additional factors like mesophyll conductance, leaf N-content and C-respiratory losses (Griffiths *et al* 1999, Seibt *et al* 2008). We note that when iWUE is calculated from the flux tower measurements (as the ratio between GEP and canopy water conductance), the magnitude of the trend is lower and the statistical strength is no longer significant compared to those calculated for W_{ei} (1% change yr^{-1}, $P = 0.2$, Keenan *et al* 2013).

The *Δ* trend found in this study during the last 18 years is unusual but not unique. Results from literature often reported a decrease in *Δ* inferred from tree-ring records, and thus a strong improvement of iWUE during the last 100 years under increased atmospheric CO_2 (Arneth *et al* 2002). However, Marshall and Monserud (1996) showed that iWUE has remained static in sites from western US and a switch in iWUE from an active to a passive response around AD 1970 has been noted in several European sites (Gagen *et al* 2011). The spatial variability of stomatal regulation and iWUE response to increasing c_a is explained by the strong dependence of water and carbon usage on moisture stress experienced at a specific site and species sensitivity to moisture availability (Warren *et al* 2001). The increased discrimination is a reflection of the availability of CO_2. When the level of CO_2 (c_i) is high, large discrimination is observed reflecting the RuBisCO enzymatic preference for $^{12}CO_2$ (Stewart *et al* 1995). Clearly, the *Δ* chronologies at HF indicate that despite higher c_a concentrations, factors like physiology and site condition contributed to stomatal openness and conductance.

The strong correlation between *Δ* and growing season PDSI and precipitation for both species suggest a link between water availability and stomatal conductance (Dupouey *et al* 1993). The climatic data for central Massachusetts indicates that precipitation and moisture (PDSI) are high at HF and are rarely limiting tree growth (Voelker 2011). In fact, the region became wetter over the period of analysis. The mean annual precipitation from 1898 to 2010 was 107.45 cm and increased 0.28 ± 0.06 cm yr^{-1} ($p < 0.0001$). The trend in precipitation is also reflected in a trend of increasing PDSI of 0.03 ± 0.005 units yr^{-1} ($P < 0.0001$) over the same period. Since 1992, precipitation and PDSI have increased at rates of $1.30 \pm 0.67\,\mathrm{cm\,yr^{-1}}$ ($P < 0.07$) and 0.15 ± 0.05 units $\mathrm{yr^{-1}}$ ($P < 0.006$), respectively. The increase in regional scale water availability (Wang *et al* 2013) is also evident at the HF site. Annual precipitation and growing season precipitation have increased by 10% and 15% over the last 18 years, respectively (Keenan *et al* 2013).

We conclude on the basis of the photosynthetic discrimination sensitivity to water availability that the long-term increase in moisture which controls Δ drove the increase in stomatal conductance and carbon photosynthetic discrimination. A positive correlation between Δ and mean annual and summer precipitation has been confirmed for modern leaf tissues from multiple biomes in North America (Diefendorf *et al* 2010). This correlation is explained by the effect of the mean annual and summer precipitation levels on both soil water status and VPD (Hartman and Danin 2010). It is noteworthy that despite the mesic conditions of the HF site, precipitation and soil moisture levels remain very strong predictors of CO_2 discrimination. Similar to our findings, drought sensitivity has been demonstrated for radial growth of *T. canadensis* and *Q. rubra* growing in mesic sites located in the New York City watershed (Pederson *et al* 2013).

The sensitivity to water availability is further illustrated by iWUE data for the year 1999. Both species exhibited a higher iWUE reflecting lower Δ values (figure 1). The summer of 1999 was very dry with decreased soil moisture levels resulting in the restriction of the CO_2 supply to the leaf (Brugnoli *et al* 1988) because of stomatal closure, and in a weaker carbon uptake observed in the summertime NEE record (Urbanski *et al* 2007).

5. Conclusion

An enhancement in photosynthetic isotopic ^{13}C discrimination and c_i was observed over the last 18 years for two co-dominant species at the Harvard Forest. The combined effect of increased water availability and higher atmospheric CO_2 concentration lead to increased plant CO_2 assimilation. The higher net photosynthesis can in part explain the growth enhancement of *Q. rubra* and above-ground GPP (e.g. Linares and Camarero 2012) and is consistent with the observed higher CO_2 uptake and C storage documented in the flux-tower measurements over the same period. The tree-ring Δ-GPP relationship identified in this study can be used as a quantitative proxy to reconstruct and interpret past forest productivity, as driven by climate variability and in response to long-term atmospheric CO_2 increase.

The photosynthetic carbon isotopic discrimination model is embedded in most of the models of forest carbon cycling (Richardson *et al* 2012) that are coupled with earth-system models to project terrestrial carbon cycle and feedbacks to climate change (Sitch *et al* 2008). We show that the data provided by tree-ring $\delta^{13}C$, recording the seasonal and interannual patterns of plant carbon assimilation, can be used to inform forest ecosystem model parameterization (Bodin *et al* 2013), to improve simulations of monthly scale ecosystem-function (e.g. Medvigy *et al* 2013), and to constrain longer term terrestrial carbon dynamics in response to climate fluctuations and forest management (e.g. Brooks and Mitchell 2011).

Whether the documented isotopic trends in the present study are merely temporary or a site specific phenomenon remains to be seen. Further investigations of tree-ring $\delta^{13}C$ and ecosystem physiology measurements from other flux-tower sites in northeastern US forests need to be explored to assess physiological responses at the regional scale.

Acknowledgements

This study was supported by the US Department of Energy through the Northeast Regional Center of the National Institutes for Climatic Change Research, the College of Earth and Mineral Science's Earth and Environmental Sciences Institute at The Pennsylvania State University, Penn State's Institutes of Energy and the Environment and the National Science Foundation grant NSF-BCS- ♯ 1229887. The Harvard Forest EMS tower is a component of the Harvard Forest LTER, supported by National Science Foundation, and is additionally supported by the Office of Science (BER), US Department of Energy. We thank the three anonymous reviewers for their helpful comments and suggestions to improve this manuscript.

References

Arneth A, Lloyd J, Šantrůčková H, Bird M, Grigoryev S, Kalaschikov Y N, Gleixner G and Schulze E-D 2002 Response of central Siberian Scots pine to soil water deficit and long-term trends in atmospheric CO_2 concentration *Glob. Biogeochem. Cycles* **16** 5-1–5-13

Babst F *et al* 2013 Above-ground woody carbon sequestration measured from tree rings is coherent with net ecosystem productivity at five eddy-covariance sites *New Phytologist* doi:10.1111/nph.12589

Baldocchi D D 2003 Assessing the eddy covariance technique for evaluating carbon dioxide exchange rates of ecosystems: past, present and future *Glob. Change Biol.* **9** 479–92

Barbour M M, Walcroft A S and Farquhar G D 2002 Seasonal variation in $\delta^{13}C$ and δ18O of cellulose from growth rings of Pinus radiata *Plant Cell Environ.* **25** 1483–99

Barford C C, Wofsy S C, Goulden M L *et al* 2001 Factors controlling long- and short-term sequestration of atmospheric CO_2 in a mid-latitude forest *Science* **294** 1688–91

Bert D, Leavitt S W and Dupouey J-L 1997 Variations of wood $\delta^{13}C$ and water-use efficiency of abies alba during the last century *Ecology* **78** 1588–96

Biondi F and Qeadan F 2008 A Theory-driven approach to tree-ring standardization: defining the biological trend from expected basal area increment *Tree-Ring Research* **64** 81–96

Bodin P E *et al* 2013 Comparing the performance of different stomatal conductance models using modelled and measured plant carbon isotope ratios ($\delta^{13}C$): implications for assessing physiological forcing *Glob. Change Biol.* **19** 1709–19

Brooks J R and Mitchell A K 2011 Interpreting tree responses to thinning and fertilization using tree-ring stable isotopes *New Phytol.* **190** 770–82

Brugnoli E *et al* 1988 Correlation between the carbon isotope discrimination in leaf starch and sugars of C_3 plants and the ratio of intercellular and atmospheric partial pressures of carbon dioxide *Plant Physiol.* **88** 1418–24

Bunn A G 2008 A dendrochronology program library in R (dplR) *Dendrochronologia* **26** 115–24

Canadell J G, Quéré C L, Raupach M R, Field C B, Buitenhuis E T, Ciais P, Conway T J, Gillett N P, Houghton R A and Marland G 2007 Contributions to accelerating atmospheric CO_2 growth from economic activity, carbon intensity, and efficiency of natural sinks *Proc. Natl. Acad. Sci.* **104** 18866–70

Cook E R and Cole J 1991 On predicting the response of forests in eastern North America to future climatic change *Clim. Change* **19** 271–82

Daux V, Edouard J L, Masson-Delmotte V, Stievenard M, Hoffmann G, Pierre M, Mestre O, Danis P A and Guibal F 2011 Can climate variations be inferred from tree-ring parameters and stable isotopes from larix decidua? juvenile effects, budmoth outbreaks, and divergence issue *Earth Planet. Sci. Lett.* **309** 221–33

Diefendorf A F, Mueller K E, Wing S L, Koch P L and Freeman K H 2010 Global patterns in leaf 13C discrimination and implications for studies of past and future climate *Proc. Natl. Acad. Sci* **107** 5738–43

Dupouey J-L, Leavitt S, Choisnel E and Jourdain S 1993 Modelling carbon isotope fractionation in tree rings based on effective evapotranspiration and soil water status *Plant Cell Environ.* **16** 939–47

Duquesnay A, Bréda N, Stievenard M and Dupouey J L 1998 Changes of tree-ring $\delta^{13}C$ and water-use efficiency of beech (Fagus sylvatica L.) in north-eastern France during the past century *Plant Cell Environ.* **21** 565–72

Ehleringer J R and Cerling T E 1995 Atmospheric CO_2 and the ratio of intercellular to ambient CO_2 concentrations in plants *Tree Physiol.* **15** 105–11

Farquhar G D, O'Leary M H and Berry J A 1982 On the relationship between carbon isotope discrimination and the intercellular carbon dioxide concentration in leaves *Aust. J. Plant Physiol.* **9** 121–37

Farquhar G and Richards R 1984 Isotopic composition of plant carbon correlates with water-use efficiency of wheat genotypes *Funct. Plant Biol.* **11** 539–52

Farquhar G D, Ehleringer J R and Hubick K T 1989 Carbon isotope discrimination and photosynthesis *Annu. Rev. Plant Physiol. Plant Mol. Biol.* **40** 503–37

Foster J R, D'Amato A W and Bradford J B 2014 Looking for age-related growth decline in natural forests: unexpected biomass patterns from tree rings and simulated mortality *Oecologia* **175** 363–74

Friedlingstein P *et al* 2006 Climate–carbon cycle feedback analysis: results from the C^4MIP model intercomparison *J. Clim.* **19** 3337–53

Gagen M *et al* 2011 Evidence of changing intrinsic water-use efficiency under rising atmospheric CO_2 concentrations in Boreal Fennoscandia from subfossil leaves and tree ring $\delta^{13}C$ ratios *Glob. Change Biol.* **17** 1064–72

Gessler A, Brandes E, Buchmann N, Helle G, Rennenberg H and Barnard R L 2009 Tracing carbon and oxygen isotope signals from newly assimilated sugars in the leaves to the tree-ring archive *Plant Cell Environ.* **32** 780–95

Gough C M, Flower C E, Vogel C S, Dragoni D and Curtis P S 2009 Whole-ecosystem labile carbon production in a north temperate deciduous forest *Agric. Forest Meteorol.* **149** 1531–40

Green J W 1963 Wood cellulose *Methods in Carbohydrate Chemistry* vol 3 (New York: Academic Press) pp 9–21

Griffiths H, Borland A M, Gillon J S, Harwood K G, Maxwell K and Wilson J M 1999 Stable isotopes reveal exchanges between soil, plants and the atmosphere *Advances in Physiological Plant Ecology* ed M C Press, J D Scholes and M G Barker (Oxford: Blackwell Science) pp 415–41

Hadley J L and Schedlbauer J L 2002 Carbon exchange of an old-growth eastern hemlock (Tsuga canadensis) forest in central New England *Tree Physiol.* **22** 1079–92

Hadley J L, O'Keefe J, Munger J W, Hollinger D Y and Richardson A D 2009 Phenology of forest-atmosphere carbon exchange for deciduous and coniferous forests in Southern and Northern New England *Phenology of Ecosystem Processes* ed A Noormets (New York: Springer) pp 119–41

Hartman G and Danin A 2010 Isotopic values of plants in relation to water availability in the Eastern Mediterranean region *Oecologia* **162** 837–52

Helle G and Schleser G H 2004 Beyond CO_2-fixation by Rubisco—an interpretation of 13C/12C variations in tree rings from novel intra-seasonal studies on broad-leaf trees *Plant Cell Environ.* **27** 367–80

Hurtt G C, Pacala S W, Moorcroft P R, Caspersen J, Shevliakova E, Houghton R A and Moore B 2002 Projecting the future of the US carbon sink *Proc. Natl. Acad. Sci* **99** 1389–94

Keel S G, Siegwolf R T W and Körner C 2006 Canopy CO_2 enrichment permits tracing the fate of recently assimilated carbon in a mature deciduous forest *New Phytol.* **172** 319–29

Keenan T F, Davidson E, Moffat A M, Munger W and Richardson A D 2012a Using model-data fusion to interpret past trends, and quantify uncertainties in future projections, of terrestrial ecosystem carbon cycling *Glob. Change Biol.* **18** 2555–69

Keenan T F *et al* 2012b Terrestrial biosphere model performance for inter-annual variability of land-atmosphere CO_2 exchange *Glob. Change Biol.* **18** 1971–87

Keenan T F *et al* 2013 Increase in forest water-use efficiency as atmospheric carbon dioxide concentrations rise *Nature* doi:10.1038/nature12291

Le Quéré C *et al* 2009 Trends in the sources and sinks of carbon dioxide *Nat. Geosci.* **2** 831–6

Leavitt S W and Danzer S R 1993 Method for batch processing small wood samples to holocellulose for stable-carbon isotope analysis *Anal. Chem.* **65** 87–9

Leavitt S W 1993 Seasonal 13C/12C changes in tree rings: species and site coherence, and a possible drought influence *Can. J. For. Res.* **23** 210–8

Leavitt S W 2008 Tree-ring isotopic pooling without regard to mass: No difference from averaging $\delta^{13}C$ values of each tree *Chem. Geol.* **252** 52–5

Linares J C and Camarero J J 2012 From pattern to process: linking intrinsic water-use efficiency to drought-induced forest decline *Glob. Change Biol.* **18** 1000–15

Loader N J, Switsur V R and Field E M 1995 High-resolution stable isotope analysis of tree rings: implications of 'microdendroclimatology' for palaeoenvironmental research *The Holocene* **5** 457–60

Marshall J D and Monserud R A 1996 Homeostatic gas-exchange parameters inferred from 13C/12C in tree rings of conifers *Oecologia* **105** 13–21

McCarroll D and Pawellek F 1998 Stable carbon isotope ratios of latewood cellulose in Pinus sylvestris from northern Finland: variability and signal-strength *The Holocene* **8** 675–84

McCarroll D *et al* 2009 Correction of tree ring stable carbon isotope chronologies for changes in the carbon dioxide content of the atmosphere *Geochim. Cosmochim. Acta* **73** 1539–47

McCarroll D and Loader N J 2004 Stable isotopes in tree rings *Quat. Sci. Rev.* **23** 771–801

McCulloh K, Sperry J S, Lachenbruch B, Meinzer F C, Reich P B and Voelker S 2010 Moving water well: comparing hydraulic efficiency in twigs and trunks of coniferous, ring-porous, and diffuse porous saplings from temperate and tropical forests *New Phytol.* **186** 439–50

Medvigy D, Jeong S-J, Clark K L, Skowronski N S and Schäfer K V R 2013 Effects of seasonal variation of photosynthetic capacity on the carbon fluxes of a temperate deciduous forest *J. Geophys. Res.: Biogeosci.* doi:10.1002/2013JG002421

Michelot A, Eglin T, Dufrêne E, Lelarge-Trouverie C and Damesin C 2011 Comparison of seasonal variations in water-use efficiency calculated from the carbon isotope composition of tree rings and flux data in a temperate forest *Plant Cell Environ.* **34** 230–44

O'Leary M H 1981 Carbon isotope fractionation in plants *Phytochemistry* **20** 553–67

Offermann C, Ferrio J P, Holst J, Grote R, Siegwolf R, Kayler Z and Gessler A 2011 The long way down—are carbon and oxygen isotope signals in the tree ring uncoupled from canopy physiological processes? *Tree Physiol.* **31** 1088–102

Ogée J *et al* 2009 A single-substrate model to interpret intra-annual stable isotope signals in tree-ring cellulose *Plant Cell Environ.* **32** 1071–90

Osmond C B, Björkman O and Anderson D J 1980 *Physiol. Process. in Plant Ecology: Toward A Synthesis with Atriplex* (Berlin: Springer)

Palacio S, Paterson E, Sim A, Hester A J and Millard P 2011 Browsing affects intra-ring carbon allocation in species with contrasting wood anatomy *Tree Physiol.* **31** 150–9

Pan Y, Birdsey R, Hom J, McCullough K and Clark K 2006 Improved estimates of net primary productivity from MODIS satellite data at regional and local scales *Ecol. Appl.* **16** 125–32

Pederson N *et al* 2013 Is an Epic Pluvial masking the water insecurity of the greater New York city region? *J. Clim.* **26** 1339–54

White J W C and Vaughn B H 2011 Stable Isotopic Composition of Atmospheric Carbon Dioxide (13C and 18O) from the NOAA ESRL Carbon Cycle Cooperative Global Air Sampling Network, (Co USA: University of Colorado, Institute of Arctic and Alpine Research (INSTAAR)) 1990-2010, Version: 2011-11-08, Path: ftp://ftp.cmdl.noaa.gov/ccg/co2c13/flask/event/

Peñuelas J, Canadell J G and Ogaya R 2011 Increased water-use efficiency during the 20th century did not translate into enhanced tree growth *Glob. Ecol. Biogeogr.* **20** 597–608

Raczka B M *et al* 2013 Evaluation of continental carbon cycle simulations with North American flux tower observations *Ecol. Monogr.* doi:10.1890/12-0893.1

Randerson J T *et al* 2009 Systematic assessment of terrestrial biogeochemistry in coupled climate–carbon models *Glob. Change Biol.* **15** 2462–84

Richardson A D *et al* 2012 Terrestrial biosphere models need better representation of vegetation phenology: results from the North American carbon program site synthesis *Glob. Change Biol.* **18** 566–84

Richardson A D, Carbone M S, Keenan T F, Czimczik C I, Hollinger D Y, Murakami P, Schaberg P G and Xu X 2013 Seasonal dynamics and age of stemwood nonstructural carbohydrates in temperate forest trees *New Phytol.* **197** 850–61

Robertson I, Rolfe J, Switsur V R, Carter A H C, Hall M A, Barker A C and Waterhouse J S 1997 Signal strength and climate relationships in 13C/12C ratios of tree ring cellulose from oak in southwest Finland *Geophys. Res. Lett.* **24** 1487–90

Rocha A V, Goulden M L, Dunn A L and Wofsy S C 2006 On linking interannual tree ring variability with observations of whole-forest CO_2 flux *Glob. Change Biol.* **12** 1378–89

Saurer M, Siegwolf R T W and Schweingruber F H 2004 Carbon isotope discrimination indicates improving water-use efficiency of trees in northern Eurasia over the last 100 years *Glob. Change Biol.* **10** 2109–20

Schaefer K *et al* 2012 A model-data comparison of gross primary productivity: Results from the North American Carbon Program site synthesis *J. Geophys. Res.: Biogeosci.* **117**

Shi C *et al* 2011 Sampling strategy and climatic implications of tree-ring stable isotopes on the southeast Tibetan Plateau *Earth Planet. Sci. Lett.* **301** 307–16

Schubert B A and Jahren A H 2012 The effect of atmospheric CO_2 concentration on carbon isotope fractionation in C3 land plants *Geochim. Cosmochim. Acta* **96** 29–43

Seibt U, Rajabi A, Griffiths H and Berry J A 2008 Carbon isotopes and water use efficiency: sense and sensitivity *Oecologia* **155** 441–54

Sims D A *et al* 2006 On the use of MODIS EVI to assess gross primary productivity of North American ecosystems *J. Geophys. Res.: Biogeosci.* **111** G04015

Skene D S 1972 The kinetics of tracheid development in Tsuga canadensis Carr. And its relation to tree vigour *Ann. Bot.* **36** 179–87

Sitch S *et al* 2008 Evaluation of the terrestrial carbon cycle, future plant geography and climate-carbon cycle feedbacks using five dynamic global vegetation models (DGVMs) *Glob. Change Biol.* **14** 2015–39

Speer J H 2010 *Fundamentals of Tree-Ring Research* (Tucson: University of Arizona Press)

Stewart G, Turnbull M, Schmidt S and Erskine P 1995 13C natural abundance in plant communities along a rainfall gradient: a biological integrator of water availability *Funct. Plant Biol.* **22** 51–5

Stuiver M and Braziunas T F 1987 Tree cellulose 13C/12C isotope ratios and climatic change *Nature* **328** 58–60

Suzuki T and Ichii K 2010 Evaluation of a terrestrial carbon cycle submodel in an Earth system model using networks of eddy covariance observations *Tellus* B **62** 729–42

Urbanski S *et al* 2007 Factors controlling CO_2 exchange on timescales from hourly to decadal at Harvard Forest *J. Geophys. Res.: Biogeosci.* **112** 1–25

Voelker S L 2011 Age-dependent changes in environmental influences on tree growth and their implications for forest responses to climate change *Size and Related Changes in Tree Structure and Function* ed F C Meinzer, T Dawson and B Lachenbruch (Berlin: Springer) pp 455–79

Voelker S L, Noirot-Cosson P, Stambaugh M C, McMurry E R, Meinzer F C, Lachenbruch B and Guyette R P 2012 Spring temperature responses of oaks are synchronous with North Atlantic conditions during the last deglaciation *Ecol. Monogr.* **82** 169–87

von Caemmerer C and Farquhar G D 1981 Some relationships between the biochemistry of photosynthesis and the gas exchange of leaves *Planta* **153** 376–87

Walcroft A S, Silvester W B, Whitehead D and Kelliher F M 1997 Seasonal changes in stable carbon isotope ratios within annual rings of pinus radiata reflect environmental regulation of growth processes *Funct. Plant Biol.* **24** 57–68

Wang H *et al* 2013 Increased water storage in North America and scandinavia from GRACE gravity data *Nat. Geosci* **6** 38–42

Warren C R, McGrath J F and Adams M A 2001 Water availability and carbon isotope discrimination in conifers *Oecologia* **127** 476–86

Wigley T M L, Briffa K R and Jones P D 1984 On the average value of correlated time series, with applications in dendroclimatology and hydrometeorology *J. Clim. Appl. Meteorol.* **23** 201–13

Woodbury P B, Smith J E and Heath L S 2007 Carbon sequestration in the US forest sector from 1990 to 2010 *Forest Ecol. Manage.* **241** 14–27

Zasada J C and Zahner R 1969 Vessel element development in the earlywood of red oak (*Quercus rubra*) *Can. J. Bot.* **47** 1965–71