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Water fluxes and their control on the terrestrial carbon balance: Results from a stable isotope study on the Clyde Watershed (Scotland)

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Abstract

The gradients between precipitation and runoff quantities as well as their water isotopes were used to establish a water balance in the Clyde River Basin (Scotland). This study serves as an example for a European extreme with poorly vegetated land cover and high annual rainfall and presents novel water stable isotope techniques to separate evaporation, interception and transpiration with annual averages of 0.029 $km^3\ a^{-1}$, 0.220 $km^3\ a^{-1}$ and 0.489 $km^3\ a^{-1}$, respectively. Transpiration was further used to determine CO_2 uptake of the entire basin and yielded an annual net primary production (NPP) of 352×10^9 g C (Giga gram) or 185.2 g C m^{-2}. Compared to other temperate areas in the world, the Clyde Basin has only half the expected NPP. This lower value likely results from the type of vegetation cover, which consists mostly of grasslands. Subtracting the annual heterotrophic soil respiration flux (R_h) of 392 Gg (206.1 g C $m^{-2}\ a^{-1}$) from the NPP yielded an annual Net Ecosystem Productivity (NEP) of −40 Gg C, thus showing the Clyde Watershed as a source of CO_2 to the atmosphere. Despite the unusual character of the Clyde Watershed, the study shows that areas with predominant grass and scrub vegetation still have transpirational water losses that by far exceed those of pure evaporation and interception. This infers that vegetation can influence the continental water balances on time scales of years to decades.

1. Introduction

Currently, about one quarter of anthropogenic CO_2 emissions remains unaccounted for (Houghton et al., 1998; Prentice et al., 2001) and the sink for this C is suspected to be in terrestrial ecosystems (Brown and Lugo, 1982; Ciais et al., 1995; Rayner et al., 1999; Thompson et al., 1996; Sarmiento and Wofsy, 1999; Prentice et al., 2001). It is known that CO_2 exchanges between plants, soils, water and the atmosphere is dependent on photosynthesis and respiration that in turn rely on water availability, vegetation type, temperature and solar radiation

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(Buchmann and Schulz, 1999; Kirschbaum, 1995, 2000; Valentini et al., 2000; Hanson et al., 2000; Schlesinger and Andrews, 2000; Nemani et al., 2002, 2003). Model estimates suggest that boreal and temperate ecosystems are a ‘‘slight’’ net sink of CO_2. However, these estimates have large uncertainties that often exceed net fluxes (Ciais et al., 1995; Rayner et al., 1999; Sarmiento and Wofsy, 1999; Prentice et al., 2001).

While photosynthesis is controlled by sunlight (solar energy), water availability and temperature (Nobel, 1999; Nemani et al., 2002, 2003), any of these factors could be limiting and thus control the net flux of CO_2 to ecosystems. Plants sequester CO_2 from the atmosphere and simultaneously recycle precipitation into the atmosphere through transpiration thus showing the strong coupling between water and C cycles (Ehleringer et al., 1991, 1997; Hopkins, 1995; Jarvis et al., 1997; Orsenigo and Patrignani, 1997; Pessarakli, 1997; Gillon et al., 1998; Nobel, 1999; Saga and Monson, 1999; Ehleringer and Cerling, 2002). Moreover, water and C cycling occur at a specific $H_2O:CO_2$ ratio, known as the ‘‘Water Use Efficiency’’ (WUE). It describes the moles of H_2O that are transpired to enable the uptake of one mol CO_2. Telmer and Veizer (2000, 2001) utilized the WUE to estimate CO_2 sequestration for the Ottawa River watershed. This technique relies on the isolation of the transpirational water flux of a river basin. Lee and Veizer (2003) tested this concept on the Mississippi Watershed and obtained Net Primary Productivity (NPP) fluxes that were in good agreement with empirical model estimates of heterotrophic soil respiration (R_h). They also proposed that it is likely that the overall terrestrial ecosystem is water limited, due to the global deficiency of soil water. This hypothesis has been further tested on the Saskatchewan, Great Lakes-St. Lawrence, Ottawa River and Volta Basin watersheds (Telmer and Veizer, 2000, 2001; Karim et al., 2007; Freitag et al., 2007) and yielded comparable results.

The above approach enables determination of photosynthetic CO_2 fluxes in selected watersheds and can also provide estimates for entire river basins at a fraction of the cost associated with the standard approaches that include eddy covariance and lysimeter measurements. Here the technique is tested on the Clyde Watershed in Scotland (Fig. 1) with the objectives:

1. to quantify transpirational water fluxes using water stable isotope ratios ($\delta^{18}O$ and δD);
2. to determine whether the Clyde Watershed is a source or sink of CO_2.

With transpiration usually playing a significant role in the water balance, its improved understand-

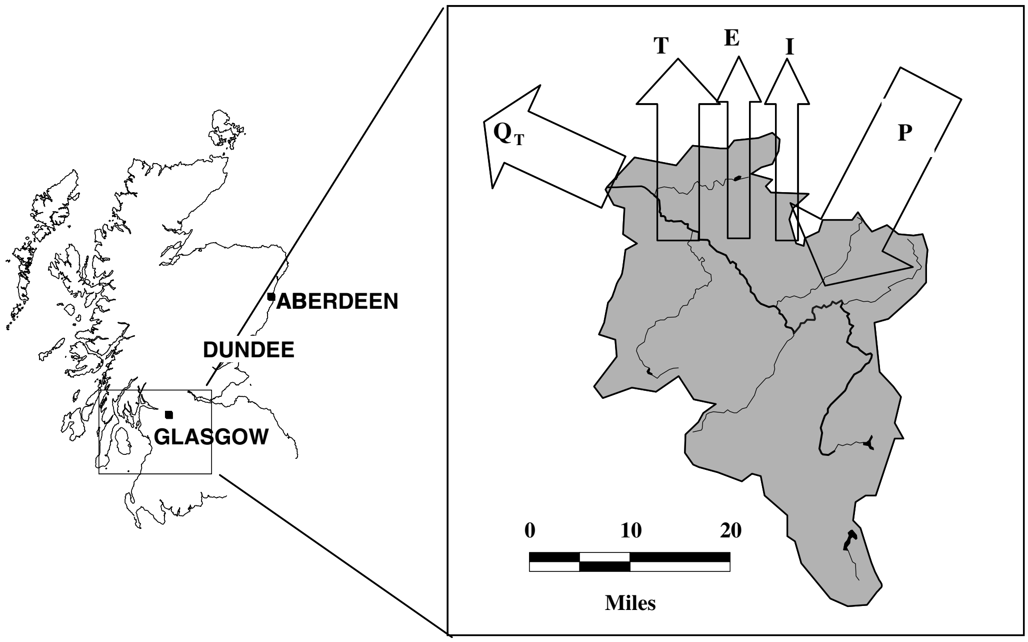

Fig. 1. Location of the Clyde River Basin in the UK.

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ing may help in the planning of agricultural and vegetation schemes to prevent against catastrophic events such as flooding or droughts. The Clyde area is unlikely to be limited by water availability and represents a European extreme in terms of high precipitation and predominant grass vegetation with sparse forest vegetation. This offers an excellent opportunity to compare this watershed to well-forested areas. The work presented here is the first European catchment study that applies the above-mentioned stable isotope approach for determination of transpiration and CO_2 uptake. Results therefore offer new end member values for other water balance and C sequestration studies in Europe and elsewhere.

2. Materials and methods

2.1. Concept

A detailed description of terrestrial water balances and the coupling between the C and water cycles is given in Telmer and Veizer (2000, 2001) and Lee and Veizer (2003). The general hydrologic balance of a watershed is:

$$ET = P - (Q_{DS} + Q_{BF}) - \Delta S = P - Q_T - \Delta S \qquad (1)$$

(Chow, 1964; Linsley et al., 1975; Braud et al., 1995; Leopoldo et al., 1995)

where ET = water lost to evapotranspiration; P = precipitation; Q_{DS} = surface runoff; Q_{BF} = base flow; Q_T = total runoff; ΔS = change in groundwater storage.

Over sufficiently long time periods ΔS becomes negligible under the assumption that groundwater table rises and falls cancel each other out and the equation simplifies to

$$ET = P - Q_T \qquad (2)$$

The water in- and output parameters, P and Q_T, are directly measurable. The evapotranspiration term (ET) includes evaporation (E), transpiration (T) and interception (I):

$$ET = E + T + I \qquad (3)$$

In order to separate this flux into its sub-components, determination of the pure evaporation flux (E) is required in a first instance. It can be calculated with an isotope balance equation developed by Gonfiantini (1986) that writes

$$X = E/I = (\delta_S - \delta_I)(1 - h + \Delta\varepsilon)/(\delta_S + 1)(\Delta\varepsilon + \varepsilon/\alpha) + h(\delta_a - \delta_S) \qquad (4)$$

where X = proportion of precipitation that is lost to evaporation (expressed in % if multiplied by 100); δ_S = mean value of $\delta^{18}O$ (or δD) of the river at the outflow (in this case the isotopic composition of the Clyde River at the Tidal Weir); δ_I = average isotopic composition of incoming precipitation; δ_a = mean $\delta^{18}O$ (or δD) value of the water vapour; α = equilibration fractionation factor for O ($\ln \alpha = 1137T^{-2} - 0.4156T^{-1} - 0.00207$) or H isotopes ($\ln \alpha = 24{,}844T^{-2} - 76.248\ T^{-1} + 0.05261$) (Majoube, 1971) with T being the temperature in Kelvin; $\varepsilon = \alpha - 1$; $\Delta\varepsilon$ = kinetic enrichment factor for O ($14.2\ (1 - h)$) and for H isotopes ($12.5\ (1 - h)$); h = the relative average humidity that can be calculated by average δD and $\delta^{18}O$ values ($0.015 \times (\delta D_p - (8 \times \delta^{18}O_p)) + 1$) with the subscripts "p" meaning the average values for precipitation (Clark and Fritz, 1997).

Note that this equation only calculates the amount of partial evaporation that affords isotope shifts. Therefore, neither light rain that evaporates to dryness nor interception cause any isotope fractionation because they completely evaporate the deposited water. The amount of light rain that completely evaporates is assumed to be negligible here since the Clyde Basin belongs to a humid region, and the amount of interception is being considered separately below.

The isotope numbers enter Eq. (4) as per mille (‰) values that are again divided by 1000. Similar approaches can be found in Gat and Bowser (1991), Gat and Matusi (1991) and Gibson et al. (1999).

Interception (I) is calculated via the leaf area index for different vegetation types and their proportions in a given watershed (Reichle, 1981; Lange et al., 1982; Heatherington, 1987; Brooks et al., 1991; Leopoldo et al., 1995; Gash et al., 1995; Telmer and Veizer, 2000, 2001; Lee and Veizer, 2003). These data stem from the global continuous field of vegetation cover at 0.5° (DeFries and Townshed, 1999; DeFries et al., 2000).

Transpiration (T) by plants involves CO_2 diffusion inward and O_2 and H_2O diffusion outward via leaf stomata. This loss of water is a major mechanism by which soil moisture is returned to the atmosphere (Schlesinger, 1997; Nobel, 1999;

Schantz and Piemeisel, 1927; Jarvis et al., 1997; Taiz and Zeiger, 1991). The transpiration (T) values can be calculated by re-arranging Eq. (3) and substituting into Eq. (2) so that

$$T = P - Q_T - E - I.$$

Subsequently, the net primary productivity (NPP) can then be estimated for a given basin with

$$\text{NPP (moles C a}^{-1}) = T \text{ (moles H}_2\text{O a}^{-1}) \text{ /WUE (moles H}_2\text{O/moles CO}_2) \quad (5)$$

The NPP can also be expressed in moles C a^{-1} m^{-2} when divided by the area of the watershed. The WUE, in turn, depends on the proportion of C3 and C4 plants in the basin. This can be estimated with data from Still et al. (2003).

Finally, in order to estimate whether a watershed is a source or sink of CO_2, an estimate of the heterotrophic soil respiration (R_h) is required and the net ecosystem productivity (NEP) of a watershed is expressed as

$$\text{NEP (g C a}^{-1}) = \text{NPP (g C a}^{-1}) - R_h \text{ (g C a}^{-1}) \quad (6)$$

2.2. Sampling and analytical techniques

Precipitation samples for $\delta^{18}O$ and δD measurements were collected monthly from 2003 to 2004 at East Kilbride in the Clyde River Basin. Through its central position this series reflects the currently best average of isotopes in precipitation for the Clyde Watershed. According to standardised sampling methods from the International Atomic Energy Agency (IAEA) monthly precipitation samples were collected through a funnel into a 10-L water tank that contained a 0.5 cm liquid paraffin film to avoid secondary evaporation effects. River samples for $\delta^{18}O$ and δD measurements were collected every two months about 1 km upstream of the Clyde River Tidal Weir, the transition to the estuary. Samples were collected at 1 m depth in the middle of the river and into 12 mL glass vials. These were rinsed three times with river water before being filled.

The $\delta^{18}O$ was determined after transposing the water O-isotopic fingerprint to CO_2 following the method of Epstein and Mayeda (1953). The CO_2 was then measured on an Analytical Precision (Model 2003) mass spectrometer. The δD compositions were measured, after separation of H_2 from Water on hot chromium, on a VG-Optima dual inlet isotope mass spectrometer (Donnelly et al., 2001). Isotope ratios were expressed in the per mille notation

$$\delta = [(\text{H/L}_{\text{sample}} - \text{H/L}_{\text{standard}})/(\text{H/L}_{\text{standard}})] \times 1000 \quad (‰) \quad (7)$$

with 'H' being the heavy isotope (^{18}O or D) and 'L' the light isotope (^{16}O or H). The standard for both isotopes is the Vienna Standard Mean Ocean Water (VSMOW) and has a mole fraction of 0.00200045 and 0.000155745 for $^{18}O/^{16}O$ and D/H, respectively (Coplen et al., 2003). Standard deviations of $\delta^{18}O$ and δD repeat measurements were ±0.2 and ±1‰.

3. Background data and results

The Clyde River is about 121 km long and drains an area of 1903.1 km^2 (Fig. 1). As indicated by the Scottish Environmental Protection agency (SEPA), the mean precipitation input to the Clyde River watershed is 1170 mm a^{-1} ($P = 2.227$ km^3 a^{-1}). These values correspond well with averages supplied by the British Atmospheric Data Centre. The mean annual discharge from 1963 to 2004 near the Tidal Weir at the entrance to the estuary is 47.2 m^3 s^{-1} ($Q_T = 1.489$ km^3 a^{-1}). This yields a mean annual amount for evapotranspiration (ET) and interception of 0.738 km^3 a^{-1}. In other words, ~66.8% of the water entering the basin via precipitation leaves via runoff and ~33.2% is lost by ET and interception. These numbers assume no other transport of water to or from the basin. As long as the water is being used and recycled within the basin (which is usually the case) the long-term water balance should not be affected. In order to isolate the pure evaporation term (E), stable isotope values of river runoff and precipitation (Tables 1 and 2) were used in Eq. (4).

3.1. Evaporation

To calculate the mean isotopic inputs and outflows of the basin precipitation values at the Strathclyde Country Park were used, as it is only a few km away from the isotope precipitation sampling station in East Kilbride. This yielded weighted average input values of −8.4 and −55‰ for $\delta^{18}O$ and δD (Table 1). The mean isotopic output was determined by the weighted average of runoff and isotope measurements at the Tidal Weir. This yielded weighted averages for the output of −8.1 and

Table 1
Monthly isotope values from East Kilbride and precipitation heights from the nearby Strathclyde Country Park, both located in the Clyde Watershed

	$\delta^{18}O$	δD	mm Precip. Strathclyde Park
January 2003	−6.4	−40	82.2
February 2003	−8.4	−55	32.7
March 2003	−6.6	−44	44.2
April 2003	−8.7	−58	45.1
May 2003	−8.2	−55	101.1
June 2003	−5.1	−28	65.7
July 2003	−5.7	−38	47.3
August 2003	−3.6	−22	13.4
September 2003	−5.5	−33	81.4
October 2003	−9.4	−60	14.8
November 2003	−11.4	−76	83.9
December 2003	−10.4	−69	59.1
January 2004	−11.2	−74	134.0
March 2004	−8.8	−59	46.6
April 2004	−10.6	−71	59.9
May 2004	−9.0	−61	53.9
June 2004	−7.9	−54	65.8
Weighted average	−8.4	−55	

Table 2
River isotope data and associated long-term runoff measurements at the Clyde Tidal Weir shortly before it enters the estuary

Clyde Tidal Weir	$\delta^{18}O$	δD	Runoff, $m^3 s^{-1}$
July 2003	−7.2		19.2
September 2003	−6.9	−44	36.3
November 2003	−8.5	−54	70.6
January 2004	−8.5	−57	72.6
March 2004	−8.1	−50	55.3
May 2004	−8.6	−55	24.6
July 2004	−7.8	−53	19.2
Weighted average	−8.1	−53	

−53‰, respectively when considering monthly runoff data (Table 2). The close proximity of the input and output isotope values already indicates that only small amounts of water were lost to evaporation in the Clyde River Watershed. This was also confirmed by plotting δD and $\delta^{18}O$ values of all precipitation samples together with all river samples from this study (Fig. 2). The δD and $\delta^{18}O$ values of precipitation form a linear regression that is known as the local meteoric water line (LWML). In the present study, all river water samples collected over the entire length of the river plot close to this regression. This shows that evaporation cannot have significantly influenced the isotopic composition of surface water of the Clyde. Otherwise the surface water samples would plot below the meteoric water line and form a separate evaporation

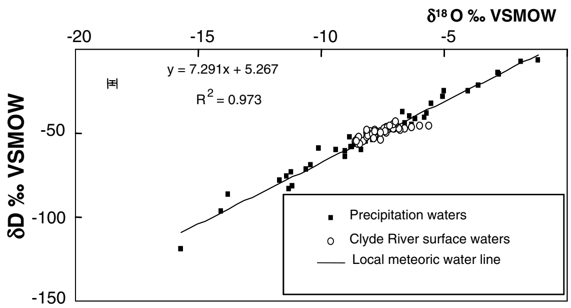

Fig. 2. Cross plot between δD and $\delta^{18}O$ values of precipitation from East Kilbride and Strathclyde Park (dark points) forming the local meteoric water line as a linear regression. The river water samples (white circles) are closely scattered around this meteoric water line, thus showing no clear evaporation trends of the surface water. The error bars of repeat measurements are shown in the top-left of the figure.

line due to more rapid enrichment of the remaining water in ^{18}O (Clark and Fritz, 1997). This is only true for a few surface water samples from summer, which plotted too close to each other to construct a reasonable regression line. Due to this unsatisfactory surface water evaporation trend line, the average isotope values of precipitation had to be determined by weighted averages from precipitation amounts as shown in Table 1, rather than from the cross-over point between the LMWL and the evaporation trend line as practised by Telmer and Veizer (2000).

The mean long-term annual temperature of the entire watershed is 8.5 °C and the mean annual humidity of the catchment was determined to be 0.82%. Feeding all these conditions into Eq. (4) yielded the proportion of water entering the basin that is lost to evaporation as 0.0129. In other words, annually 1.3%, or 0.029 $km^3 a^{-1}$, of the incoming precipitation is lost to evaporation.

3.2. Interception

Interception (*I*), the proportion of precipitation that is mostly evaporated from plant surfaces, constitutes a significant portion of the water lost other than runoff (Brooks et al., 1991; Lange et al., 1982; Reichle, 1981; Leopoldo et al., 1995). It depends on climatic and physical factors and to a large extent on the type of vegetation cover (Sellers and Lockwood, 1981; Heatherington, 1987). Here vegetation types and interception values from the Global Continuous Fields of Vegetation Cover at

0.5° were used (DeFries and Townshed, 1999; DeFries et al., 2000).

The datasets were subdivided into broadleaf, needle leaf and grassland. Heatherington (1987 and references therein) proposed average values of 14.5% for broad leaf, 35.5% for needle leaf and 9.5% for grassland for the subsequent calculations. According to DeFries and Townshed (1999) and DeFries et al. (2000) the vegetation cover in the Clyde River Basin can be divided into 6.8% broad leaf, 2.5% needle leaf and 84.5% grassland. The remainder is non-vegetated land such as sealed surfaces in cities (Table 3). Multiplying these percentages by the appropriate interception value of each leaf type results in 9.9% of the incoming precipitation leaving the watershed via interception. This amounts to a volume of 0.220 $km^3\ a^{-1}$. The averages for interception loss by Heatherington (1987) are based on empirical data and the calculated 9.9% water loss by interception is only an approximation. For instance Lee and Veizer (2003) noted a 50% variability between accepted mean values of interception in the literature, which would impart an error of ±15% on the transpiration flux. In addition to this, any larger areal coverage by trees would render the amount of water lost to interception larger. Nevertheless the amount of grassland coverage remains by far the largest proportion in the Clyde Basin so that the 0.220 $km^3\ a^{-1}$ is the best available evaluation for the interception.

3.3. Transpiration

The transpiration flux (T) can now be calculated from Eq. (3) and accounts for 22.0% (0.489 $km^3\ a^{-1}$) of the annual precipitation input to the Clyde River Basin. This biological water flux therefore accounts for the second biggest loss of water from the basin after runoff. With this isolated transpiration quantity, the coupling of water and C cycles in the Clyde Watershed can also be considered. For this procedure the different water use efficiencies by C3 and C4 plants needs to be considered.

Table 3
Interception data determined for the Clyde Watershed

Vegetation type	Area of vegetation cover, %	Intercepted precipitation, %
Broadleaf	6.8	0.98
Needle leaf	2.5	0.87
Grassland	84.5	8.03
Water/Town	6.2	0.00
Total	100.0	9.88

3.4. Distribution of C3 and C4 plants and their water use efficiencies (WUE)

The WUE describes the ability of terrestrial plants to photosynthesise C while simultaneously losing water to the atmosphere through the stomata of leafs (Schlesinger, 1997; Nobel, 1999; Schantz and Piemeisel, 1927; Jarvis et al., 1997; Taiz and Zeiger, 1991). It depends on the photosynthetic pathway (C3, C4 or CAM) and on environmental parameters such as light intensity, humidity, temperature, precipitation and CO_2 concentration (O'Leary, 1988; Ehleringer et al., 1991, 1997; Orsenigo and Patrignani, 1997; Pessarakli, 1997; Gillon et al., 1998; Saga and Monson, 1999). From a global perspective, the photosynthetic pathway is the most important variable for the ability of an ecosystem to fix C (Ehleringer and Cerling, 2002).

Values for the long-term WUE by Jones (1992) list averages of 1 mol CO_2 per 1000 mol H_2O for C3 plants and are similar to those from Molles (2002) with 1 mol CO_2 per 850 mol. C4 plants are known to have a lower WUE, but were not considered here because the study area is completely dominated by C3 plants. This was also confirmed by the plant-type distribution maps of Still et al. (2003), Collatz et al. (1998) and DeFries and Townshed, 1999). The input WUE for the following calculations thus was assumed with a value of 925 moles H_2O:mole CO_2.

3.5. Net primary productivity (NPP) and net ecosystem productivity (NEP)

The net primary productivity (NPP) is the amount of new plant volume for a specified area over a defined time period, or in other words the total photosynthetic amount minus the respiratory losses of plants per defined surface area (Thompson et al., 1996). In the present approach the NPP can be calculated from Eq. (5). This calculation yields an annual NPP for the Clyde River watershed of 352×10^9 g C (Giga gram = Gg), or an average of 185.2 g C m^{-2} (Table 4).

In order to calculate the net C budget for the Clyde Watershed, the NPP has to be compared with the heterotrophic soil respiration R_h. Subtracting R_h from the NPP yields the Net Ecosystem Productivity (NEP) that defines whether an ecosystem is a

Table 4
Summary of annual transpiration, net primary production and annual net ecosystem production

	Annual transpiration	Annual NPP		Annual heterotrophic soil respiration (R_h)	Annual NEP
Unit:	km^3 H_2O	Giga g C	g m^{-2}	Giga g C	Giga g C
Clyde River Watershed	0.489	352	185.2	392	−40

C sink or source (Thompson et al., 1996; Kirschbaum, 1995, 2000; Valentini et al., 2000; Buchmann and Schulz, 1999; Potter et al., 2003a,b). Soil respiration is one of the main pathways by which ecosystems can return CO_2 to the atmosphere (Brown and Lugo, 1982; Schlesinger and Andrews, 2000). It is composed of two parts:

(A) The heterotrophic part that includes microbes and decaying organic matter (R_h).
(B) The autotrophic part that includes the activity of the plant root system (R_a).

The latter is already incorporated into the NPP because the long-term WUE defines C sequestration of entire plants above and below ground. Hanson et al. (2000) reviewed several methods to determine soil CO_2 emissions and estimated R_a to be 60.4% of the total C flux in predominantly non-forested regions such as the Clyde Watershed. Therefore, R_h was determined to be 39.6% by subtracting R_a from the total C flux from the soil. With the latter being 520.5 g C m^{-2} a^{-1} (Raich and Potter, 1995), R_h assumes a value of 206.1 g C m^{-2} a^{-1} or 392 Gg for the Clyde Watershed (Table 4). Subtracting this value from the above-determined NPP, the Clyde River watershed appears to be a CO_2 source to the atmosphere with an annual NEP of −40 Gg C (Eq. (6), Table 4). This value could be closer to zero if the estimate for root respiration (R_a) assumes a bigger portion due to longer growing seasons thus lowering the contribution of decaying litter and microbes (R_h).

Other studies on grassland and temperate ecosystems have often characterised these ecosystems as either slight CO_2 sinks or in photosynthesis/respiration balance (Malhi and Grace, 2000; Grace and Rayment, 2000; Meir and Grace, 2002). Nevertheless, error bars for all these studies, including the present one, can significantly exceed the claimed magnitudes of the proposed sources, thus underlining the uncertainty in whether the Clyde Watershed is indeed a C source to the atmosphere.

4. Discussion

The uncertainty of the determined evaporation term is controlled by the repeatability of the isotope measurements, but also by terms such as the estimated humidity and the estimated isotopic composition of the atmospheric water vapour. These, particularly the latter two terms, are difficult to determine and it therefore remains a challenge to place an overall uncertainty estimate on the water balance by propagation of error analyses. Yet this method yields a reasonable estimate of the evaporation component (without interception and complete evaporation) as confirmed by the closeness of the surface water samples to the meteoric water line. On the other hand the interception term depends on the detail of the data and has to be regarded as a rough approximation. Nevertheless, it lies within the ranges of interception values observed in the region. As a result the uncertainty of the transpiration term, depends strongly on the variability of the calculated values for interception and evaporation but is also controlled by the input data for precipitation and runoff. In any case, regardless of the uncertainties involved in the determination of each single parameter of this water balance transpiration plays a major role in the water balance presented above. With the estimation of the NPP and GPP the uncertainties are mainly controlled by correct estimates of the water use efficiency applied. Although the Clyde basin was found to represent a slight C source to the atmosphere it remains close to being in photosynthesis/respiration balance.

With an average precipitation of 1170 mm a^{-1}, the Clyde River basin counts among the areas in Europe with the highest rainfall. Plotting precipitation heights for global vegetation zones against temperature results in a boomerang-shaped plot with one regime for the cold to temperate zones and another for the tropical zones (Fig. 3). As expected, the Clyde Basin plots towards the outer boundaries of the temperate zone. This confirms that, in terms

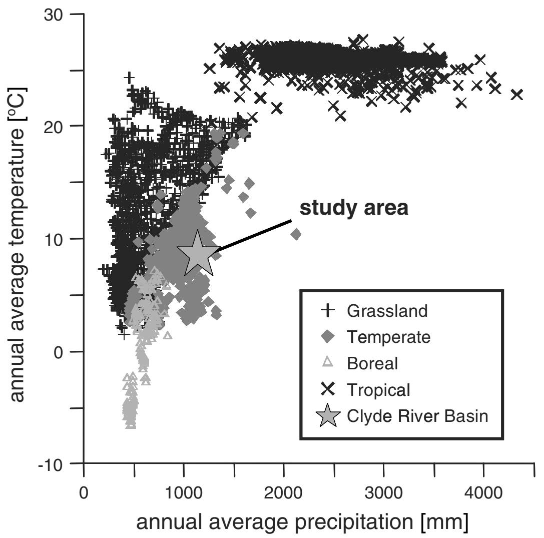

Fig. 3. Annual average values of temperature plotted versus precipitation for various ecosystems, with the Clyde Watershed plotting to the outer area or temperate regions.

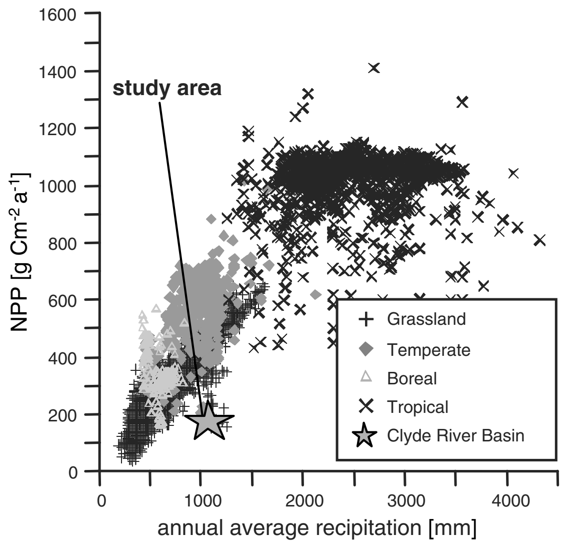

Fig. 5. Annual average precipitation versus NPP, with the value determined for the Clyde Watershed plotting below the general trend for grassland boreal and temperate areas.

of precipitation, this area is a European extreme and could be a global end member.

When plotting NPP versus temperature, the Clyde Basin falls into the zone of grassland vegetation, which nicely reflects the predominant vegetation cover by grasses in the Clyde Basin (Fig. 4). The lack of correlation in Fig. 4 also shows that, in a global context, temperature is not a controlling factor for Transpiration and NPP. Such correlation can only be found when plotting NPP versus precipitation (Fig. 5). It is therefore more likely that water availability can be limiting for NPP also in cold to temperate ecosystems. However, in this study area the high precipitation amounts make water availability an unlikely limiting factor for NPP and another limiting factor may be the amount of available sunlight (Nemani et al., 2002, 2003).

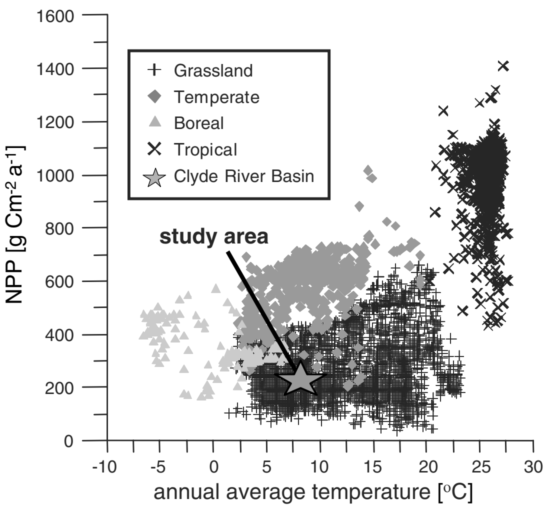

Fig. 4. Annual average temperature versus NPP, with the value determined for the Clyde Watershed plotting in the grassland and temperate areas.

Typically, transpiration by ecosystems in cold to temperate regions recycles about 50–66% of the incoming precipitation to the atmosphere (Ciais et al., 1995; Rayner et al., 1999; Sarmiento and Wofsy, 1999; Prentice et al., 2001). Comparison to other studies of this type apportion the following proportions of transpiration as a percentage of the incoming precipitation: 50% for the Volta Basin (Freitag et al., 2007), 47% for the Great Lakes Basin (Karim et al., 2007), 45% for the Ottawa Basin (Telmer and Veizer, 2000) and 59% for the Mississippi Basin (Lee and Veizer, 2003). For the Clyde it was determined that only about 22% of the incoming water is being lost to transpiration and if light is the limiting factor it can only be the case during the cold season because during summer daylight is present for about 20 h per day in Scotland. Assuming that most photosynthetic activity happens during this time of year, the availability of light is unlikely to be a limiting factor for the comparatively reduced transpiration rates found and its associated lower NPP in the Clyde Watershed. The most plausible explanation for limited transpiration and NPP is therefore the type of vegetation. It is known that trees, and particularly evergreens, are much more efficient than grasses in transpiring water as they are active for the whole year and have deeper root systems. It is therefore plausible that the Clyde represents a slight source of CO_2 to the atmosphere. For comparison, using similar techniques, Karim et al. (2007), Telmer and Veizer (2000) and Lee and Veizer (2003) found slight sinks for CO_2 for the Great Lakes, Ottawa and Mississipi Basins, respectively, while Freitag et al. (2007) found a slight source of CO_2 in a savanna and grassland dominated Watershed of the Volta Basin.

5. Summary and conclusions

The Clyde Watershed receives 2.227 km^3 of precipitation per year. Setting this input to be 100%, the total evapotranspiration flux (ET) and interception accounts for 33.14% or 0.738 $km^3\ a^{-1}$ as determined from long-term runoff data. Using stable isotope methods and additional background information about the area, it was possible to separate the ET components into

- evaporation (E) of 1.3% or 0.029 $km^3\ a^{-1}$;
- interception (I) of 9.88% or 0.220 $km^3\ a^{-1}$;
- transpiration (T) of 21.96% or 0.489 $km^3\ a^{-1}$

with respect to the incoming precipitation. The latter term was used to calculate CO_2 uptake of the basin by considering how many moles of water have to be transpired before one mole of CO_2 is sequestered by the vegetation, the so called water use efficiency (WUE). With predominant C3 plant coverage and an average long-term WUE of 925 moles H_2O per mol CO_2 the net primary production (NPP) was determined to be 352×10^9 g C (Giga gram) per year. For the entire basin size of 1903.1 km^2 this translates to an amount of 185.2 g C $m^{-2}\ a^{-1}$. Comparing this to the heterotrophic soil respiration flux (R_h), the Clyde Watershed represents a slight net source of CO_2 to the atmosphere with an annual net ecosystem productivity (NEP) of −40 Gg C.

Compared to other temperate areas the Clyde Basin has about half the NPP. As Western Scotland is an area with one of the highest precipitation amounts within Europe, it seems unlikely that the NPP is limited by water availability. Furthermore, with most NPP occurring through photosynthesis during the warm season with long daylight hours, availability of light does not seem to be a limiting factor either. The most plausible interpretation for reduced NPP is therefore the type of vegetation cover, which consists mostly of grassland. It remains an intriguing question whether the catchment has once acted as a sink for CO_2 when it was still covered to a much larger degree with forests.

The study shows that transpiration from watersheds plays an important role in the continental water balance. Even in an area like the Clyde Watershed, with predominantly grass and scrub vegetation, this flux accounts for the biggest loss of water next to runoff. Together with interception it accounts for significant biological water fluxes (i.e., 31.9% of the incoming water). Through agricultural and forest vegetation schemes this biological water flux could be influenced on time scales of years to decades. In a more global context on continental water balances transpiration is relatively easy to influence on timescales of decades. Compared to precipitation and evaporation that are difficult to control, this may represent an avenue to devise schemes against flooding or droughts and to influence C sequestration.

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References

Braud, I., Dantas-Antonio, A.C., Vauclin, M., Thont, J.L., Ruelle, P., 1995. A simple soil–plant–atmosphere transfer model (SiSPAT) development and field verification. J. Hydrol. 166, 213–250.

Brooks, K.N., Folliott, P.F., Gregersen, H.M., DeBano, L.F., 1991. Hydrology and the Management of Watersheds. Iowa State University Press, Ames, IA.

Brown, S., Lugo, A.E., 1982. The storage and production of organic matter in tropical forests and their role in the global carbon cycle. Biotropica 14, 161–187.

Buchmann, N., Schulz, E.D., 1999. Net CO_2 and H_2O fluxes of terrestrial ecosystems. Global Biogeochem. Cycles 13, 751–760.

Chow, V.T., 1964. Handbook of Applied Hydrology. McGraw Hill, New York.

Ciais, P., Tans, P.P., Troiler, M., White, J.W.C., Francey, R.J., 1995. A large northern hemisphere terrestrial CO_2 sink indicated by the C^{13}/C^{12} ratio of atmospheric CO_2. Science 269, 1098–1101.

Clark, I., Fritz, P., 1997. Environmental Isotopes in Hydrology. CRC Press/Lewis Publishers, Boca Raton.

Collatz, G.J., Berry, J.A., Clark, J.S., 1998. Effects of climate and atmospheric CO_2 partial pressure on the global distribution of C4 grasses: present, past, and future. Oecologia 114, 441–454.

Coplen, T.B., Hopple, J.A., Böhlke, J.K., Peiser, H.S., Rieder, S.E., Krouse, H.R., Rosman, K.J.R., Ding, T., Vocke Jr., R.D., Révész, K.M., Lamberty, A., Taylor, P., De Bièvre, P., 2003. Compilation of minimum and maximum isotope ratios of selected elements in naturally occurring terrestrial materials and reagents. US Geological Survey, Water Resour. Invest. Rep. 01-4222, Reston, VA.

DeFries, R.S., Townshed, J.R.G., 1999. Global land cover characterization from satellite data: from research to operational implementation?. Global Ecol. Biogeog. 8 367–379.

DeFries, R.S., Hansen, M.C., Townshed, J.R.G., Janetons, A.C., Loveland, T.R., 2000. A new global 1-km dataset of percentage tree cover derived from remote sensing. Global Change Biol. 6, 247–254.

Donnelly, T., Waldron, S., Tait, A., Dougans, J., Bearhop, S., 2001. Hydrogen isotope analysis of natural abundance and deuterium-enriched waters by reduction over chromium online to a dynamic dual inlet isotope-ratio mass spectrometer. Rapid Comm. Mass Spectrom. 15, 1297–1303.

Ehleringer, J.R., Cerling, T.E., 2002. C_3 and C_4 photosynthesis. In: Mooney, H.A., Canadell, J.G. (Eds.), Encyclopaedia of Global Environmental Change, vol. 2. John Wiley, Chichester, pp. 186–190.

Ehleringer, J.R., Cerling, T.E., Helliker, B.R., 1997. C4 photosynthesis, atmospheric CO_2 and climate. Oecologia 112, 285–299.

Ehleringer, J.R., Saga, R.F., Flanagan, L.B., Pearcy, R.W., 1991. Climate change and the evolution of C4 photosynthesis. Trends Ecol. Evol. 6, 95–99.

Epstein, S., Mayeda, T., 1953. Variation of ^{18}O content from natural sources. Geochim. Cosmochim. Acta 4, 213–224.

Freitag, H., Ferguson, P.R., Dubois, K., Hayford, E.K., von Vordzogbe, V., Veizer, J., 2007. Water and carbon fluxes from savanna ecosystems of the Volta River watershed, West Africa. Global Planet. Change., in press (special issue)

Gash, J.H.C., Lioyd, C.R., Lachaud, G., 1995. Estimating sparse forest rainfall interception with an analytical model. J. Hydrol. 170, 79–86.

Gat, J.R., Bowser, C., 1991. The heavy isotope enrichment of water in coupled evaporative systems. In: Taylor, H.P., O'Neil, J.R., Kaplan, I.R. (Eds.), Stable Isotope Geochemistry, A Tribute to Samuel Epstein, Geochemical Society Special Publication, vol. 3, pp. 159–168.

Gat, J.R., Matusi, E., 1991. Atmospheric water balance in the Amazon basin: an isotopic evapotranspiration model. J. Geophys. Res. 96 (D7), 13179–13188.

Gibson, J.J., Edwards, T.W.D., Prowse, T.D., 1999. Pan-derived isotopic composition of atmospheric water vapour and its variability in northern Canada. J. Hydrol. 217, 55–74.

Gillon, J.S., Borland, A.M., Harwood, K.G., Roberts, A., Broadmeadow, M.S.J., Griffiths, H., 1998. Carbon isotopes discrimination in terrestrial plants: carboxylations and decarboxylations. In: Griffiths, H. (Ed.), Stable Isotopes: Integration of Biological, Ecological and Geochemical Processes. BIOS Scientific Publishers Ltd., Herdon, VA, pp. 111–132.

Gonfiantini, R., 1986. Environmental isotopes in lake studies. In: Fritz, P., Fontes, J.C. (Eds.), Handbook of Environmental Isotope Geochemistry. Elsevier Scientific Publishing Company, New York, pp. 113–168.

Grace, J., Rayment, M., 2000. Respiration in the balance. Nature 404, 819–820.

Hanson, P.J., Edwards, N.T., Garten, C.T., Andrews, J.A., 2000. Separating root and soil microbial contributions to soil respiration: a review of methods and observations. Biogeochemistry 48, 115–146.

Heatherington, E.D., 1987. The importance forests in the hydrological regime. In: Healy, M.C., Wallace, R.R. (Eds.), Canadian Aquatic Resources. Department of Fisheries and Oceans, Ottawa, pp. 179–213.

Hopkins, W.G., 1995. Introduction to Plant Physiology. John Wiley, Chicester.

Houghton, . R.A., Davidson, E.A., Woodwell, G.M., 1998. Missing sink, feedbacks and understanding the role of terrestrial ecosystems in the global carbon balance. Global Biogeochem. Cycles 12, 25–34.

Jarvis, P.G., Massheder, J.M., Hale, S.E., Moncrieff, J.B., Rayment, M., Scott, S.L., 1997. Seasonal variation of carbon dioxide, water vapor, and energy exchange of a boreal black spruce forest. J. Geophys. Res. 102, 28953–28966.

Jones, H.G., 1992. Plants and Microclimate: A Quantitative Approach to Environmental Plant Physiology. Cambridge University Press, Cambridge.

Karim, A., Veizer, J., Barth, J.A.C., 2007. Net ecosystem production in the Great Lakes basin and its implications for the North American missing carbon sink: a hydrologic and stable isotope approach, Global Planet. Change., in press (special issue).

Kirschbaum, M.U.F., 1995. The temperature dependence of soil organic matter decomposition, and the effect of global warming on soil organic C storage. Soil Biol. Biochem. 27, 753–760.

Kirschbaum, M.U.F., 2000. Will changes in soil organic carbon act as a positive or negative feedback on global warming. Biogeochemistry 48, 21–51.

Lange, O.L., Nobel, P.S., Osmond, C.B., Ziegler, H., 1982. Encyclopedia of Plant Physiology (New Series). Springer-Verlag, Berlin.

Lee, D., Veizer, J., 2003. Water and carbon cycles in the Mississippi River Basin: potential implications for the northern hemisphere – residual terrestrial sink. Global Biogeochem. Cycles 17, doi: 10.1029/2002GB001984.

Leopoldo, P.R., Franken, W.K., Villa-Nova, N.A., 1995. Real evapotranspiration and transpiration through a tropical rain forest in central Amazonia as estimated by the water balance method. Forest Ecol. Manag. 73, 185–195.

Linsley, R.K., Kohler, M.A., Paulhus, J.L.H., 1975. Applied Hydrology, third ed. McGraw Hill, New York.

Majoube, M., 1971. Fractionnement en oxygène-18 et en deutérium entre l'eau et sa vapeur. J. Chem. Phys. 197, 1423–1426.

Malhi, Y., Grace, J., 2000. Tropical forests and atmospheric carbon dioxide. Trends Ecol. Evol. 15, 332–337.

Meir, P., Grace, J., 2002. Scaling relationship for woody tissue respiration in two tropical rain forests. Plant, Cell Environ. 25, 963–973.

Molles, M., 2002. Ecology: Concepts and Applications. WCB/McGraw-Hill, Boston.

Nemani, R., Kelling, C.D., Hashimoto, H., Jolly, W.M., Piper, S.C., Tucker, C.J., Myneni, R.B., Running, S.W., 2003. Climate-driven increases in global terrestrial net primary production from 1982 to 1999. Science 300, 1560–1563.

Nemani, R., White, M., Thornton, P., Nishida, K., Reddy, S., Jenkins, J., Running, S., 2002. Recent trends in hydrologic balance have enhance the terrestrial carbon sink in the United States. Geophys. Res. Lett. 29, 1468. doi:10.1029/2002GL014867.

Nobel, P.S., 1999. Physiochemical and Environmental Plant Physiology, second ed. Academic Press, San Diego.

O'Leary, M.H., 1988. Carbon isotopes in photosynthesis. Biol. Sci. 38, 328–336.

Orsenigo, M., Patrignani, G., 1997. Ecophysiology of C3, C4 and CAM plants. In: Pessarakli, M. (Ed.), Handbook of Photosynthesis. Marcel Dekker, New York, pp. 1–29.

Pessarakli, M. (Ed.), 1997. Handbook of Photosynthesis. Marcel Dekker, New York.

Potter, C., Klooster, S., Myneni, R., Genovese, V., Tan, P.N., Kumar, V., 2003a. Continental-scale comparison of terrestrial carbon sink estimated from satellite data and ecosystem modelling 1982–1998. Global Planet. Change 39, 201–213.

Potter, C., Klooster, S., Steinbach, M., Tan, P., Kumar, V., Shekhar, S., Nemani, R., Myneni, R., 2003b. Global teleconnections of climate to terrestrial carbon flux. J Geophys. Res. 108, D17, JD00297.

Prentice, I.C., Farquhar, G.D., Fasham, M.J.R., Goulden, M.L., Heimann, M., Jaramillo, V.J., Kheshgi, H.S., LeQuere, C., Scholes, R.J., Wallace, D.W.R., 2001. The carbon cycle and atmospheric carbon dioxide. Climate Change 2001: The Scientific Basis. Cambridge University Press, Cambridge, pp. 99–181.

Raich, J.W., Potter, C.S., 1995. Global patterns of carbon dioxide emissions from soils. Global Biogeochem. Cycles 9, 23–36.

Rayner, P.J., Enting, I.G., Francey, R.J., Langenfeld, R., 1999. Reconstructing the recent carbon cycle from atmospheric CO_2, $d^{13}C$ and O_2/N_2 observations. Tellus B 51, 213–232.

Reichle, D.E., 1981. Dynamic Properties of Forest Ecosystems. Cambridge University Press, Cambridge.

Saga, R.F., Monson, R.K., 1999. C_4 Plant Biology. Academic Press, San Diego.

Sarmiento, J.L., Wofsy, S.C., 1999. A US carbon cycle science plan. A Report of the Carbon and Climatic Working Group. US Global Change Research Program, Washington, DC.

Schantz, H.L., Piemeisel, L.N., 1927. The water requirement of plants at Akron, Colorado. J. Agric. Res. 34, 1093–1189.

Schlesinger, W.H., 1997. Biogeochemistry: An Analysis of Global Change, second ed. Academic Press, Toronto.

Schlesinger, W.H., Andrews, J.A., 2000. Soil respiration and the global carbon cycle. Biogeochemistry 48, 7–20.

Sellers, P.J., Lockwood, A., 1981. A numerical simulation of the effects of changing vegetation type on surface hydroclimatology. Climate Change 3, 121–136.

Still, C.J., Berry, J.A., Collatz, G.J., DeFries, R.S., 2003. Global distribution of C3 and C4 vegetation: carbon cycle implications. Global Biochem. Cycles 17. doi:10.1029/2001GB001807.

Taiz, L., Zeiger, E., 1991. Plant Physiology. The Benjamin/Cummings Publishing Company Inc., Redwood City, CA.

Telmer, K., Veizer, J., 2000. Isotopic constrains on the transpiration, evaporation, energy, and gross primary production budgets of a large boreal watershed: Ottawa River basin, Canada. Global Biogeochem. Cycles 14, 149–165.

Telmer, K., Veizer, J., 2001. Correction to isotopic constrains on the transpiration, evaporation, energy, and gross primary production budgets of a large boreal watershed: Ottawa River basin, Canada. Global Biogeochem. Cycles 15, 1035.

Thompson, M.V., Randerson, J.T., Malmstroem, C.M., Field, C.B., 1996. Change in net primary production and heterotrophic respiration: How much is necessary to sustain the terrestrial carbon sink? Global Biogeochem. Cycles 10, 711–726.

Valentini, R., Matteucci, G., Dolamn, A.J., Schulze, E.-D., Rebmann, C., Moors, E.J., Granier, A., Gross, P., Jensen, N.O., Pilegaard, K., Lindroth, A., Grelle, A., Bernhofer, C., Grünwald, T., Aubinet, M., Ceulemans, R., Kowalski, A.S., Vesala, T., Rannik, Ü., Berbigier, P., Loustau, D., Guåmundsson, J., Thorgeirsson, H., Ibrom, A., Morgenstern, K., Clement, R., Moncrieff, J., Montagnani, L., Minerbi, S., Jarvis, P.G., 2000. Respiration as the main determinant of carbon balance in European forests. Nature 404, 861–865.