DO RIPARIAN PLANTS FIX CO$_2$ LOST BY EVASION FROM SURFACE WATERS? AN INVESTIGATION USING CARBON ISOTOPES

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ABSTRACT. Rivers and streams in many parts of the world contain high concentrations of dissolved carbon dioxide, which is lost to the atmosphere by evasion (outgassing). Recent methodological advances now enable the carbon isotopic composition of this evaded CO$_2$ to be measured directly, with early results from peatland streams showing it to be depleted in ^{13}C relative to the atmosphere. The first direct measurements of the radiocarbon age of evaded CO$_2$ for a stream draining a peatland site in the United Kingdom covered a large range, ranging from modern to >1400 yr BP. We investigated whether a proportion of the carbon fixed by plants growing adjacent to the stream was derived from evasion; this would have implications for the cycling of carbon in such streams, and lead to riparian plants having older, rather than contemporary, ^{14}C ages.

^{13}C analysis of riparian plants at the site suggested that up to 20% of the carbon they fixed was derived from evasion. Although the ^{14}C content of the same samples suggested a similar proportion of plant carbon was derived from evaded CO$_2$, the uncertainty in these estimates was greater. Fixation of evaded CO$_2$ was greatest in plants growing within 1 m of the stream. Although the results for this site suggest a small amount of CO$_2$ lost by evasion from the stream surface is incorporated in plant material, it may be a more important factor at other sites characterized by higher evasion rates, lower wind speeds, and different stream bank morphology.

INTRODUCTION

On a global scale, rivers play an important role in the transfer of carbon from terrestrial to marine environments (Richey et al. 2002). Carbon is present in rivers in a variety of organic and inorganic forms, the relative proportion of each being dependent on a range of catchment biogeochemical processes. Surface waters in wetland or peatland areas also contain high concentrations of dissolved carbon dioxide (CO$_2$), which may form an important vertical flux from the river to the atmosphere (Hope et al. 2001; Richey et al. 2002). Although relatively little is known about the source and age of CO$_2$ lost to the atmosphere from surface waters, a recent isotopic study by Mayorga et al. (2005) suggested that most dissolved CO$_2$ from Amazonian rivers was derived from organic matter that had mainly been fixed less than 5 yr earlier. The authors also reported several much older ages for dissolved CO$_2$ in certain rivers (mainly headwater regions of the Amazon Basin), implying a contribution from the weathering of carbonate minerals.

Using a portable CO$_2$ sampling system connected to a floating chamber, Billett et al. (2006) reported the first direct measurements of the radiocarbon age of evaded CO$_2$ for a stream draining a peatland. The ^{14}C values covered a wide range, extending from modern to >1400 BP. The reported rates of CO$_2$ evasion (per unit water surface area) were greater than other vertical CO$_2$ fluxes reported for peatlands, such as mean nighttime respiration fluxes (e.g. Fowler et al. 1995; Hargreaves et al. 2003).

Previous studies have shown that large sources of CO$_2$ with ^{14}C signatures not in equilibrium with the free atmosphere can influence the isotopic composition of plants growing near the sources of CO$_2$. For example, where volcanic vents emit geologically old (^{14}C-dead) CO$_2$, surrounding plant materials have been shown to have depleted ^{14}C concentrations (e.g. Pasquier-Cardin et al. 1999;

Marzaioli et al. 2005). Similarly, Lichtfouse et al. (2003, 2005) observed depletion in both ^{13}C and ^{14}C in the tissues of urban plants, which they attributed to the fixation of a component of fossil-fuel-derived CO_2. Fontugne et al. (2004) suggested that elevated ^{14}C concentrations in coastal vegetation (furze) surrounding the La Hague nuclear reprocessing plant in France were a result of fixing of $^{14}CO_2$ degassed from seawater.

We investigated whether degassed CO_2 from a stream, which is isotopically distinct from the free atmosphere, could influence the carbon isotopic composition of plants growing near the stream. We considered this study to be important for 2 reasons: First, a fundamental assumption of ^{14}C dating is that the carbon in the material being dated was in ^{14}C equilibrium with the free atmosphere at the time of death; where this assumption cannot be met, ^{14}C dating can be very problematic. The fact that peats and the margins of streams are important areas for the preservation and collection of material for ^{14}C dating emphasizes the need to know more about the isotopic signature of plants growing in this potentially ^{14}C-depleted environment. Second, studies investigating carbon cycling using, for example, the ^{14}C-bomb pulse as a tracer, are usually based on the assumption that carbon being fixed by plants is derived from—and in isotopic equilibrium with—the free atmosphere. Again, if this assumption is not correct, estimates for the rate of carbon cycling and attribution of carbon sources could be problematic.

We performed this investigation of the isotopic signature of plant C and evaded CO_2 on Black Burn, a small peatland stream draining Auchencorth Moss, approximately 17 km southwest of Edinburgh, Scotland. The site has been the focus for a long-term study of land-surface gas exchange (Flechard and Fowler 1998; Fowler et al. 1998), which recently has been linked to streamwater C fluxes (Billett et al. 2004). These include initial measurements of the isotopic signature of evaded CO_2 using a new direct method (Billett et al. 2006).

The 335-ha catchment is relatively flat (249–300 m asl) and dominated by peat soils (histosols) up to 5 m in depth. Parent materials comprise Upper Carboniferous/Lower Devonian sandstones, with occasional bands of limestone, mudstone, coal, and clay, overlain by poorly drained, recent glacial drift deposits. The vegetation is dominated by coarse grasses and rushes with *Calluna vulgaris* occurring in the drier areas. Current land use consists of low-density sheep grazing, with an area of peat extraction in the western part. In the past, attempts have been made to improve soil quality by drainage.

METHODS

Collection of evasion CO_2 samples for isotope analysis and measurement of CO_2 flux rate was achieved by linking a molecular sieve sampling system (Hardie et al. 2005) to a floating chamber as described by Billett et al. (2006). This recently developed method allows direct collection of the evaded CO_2 and is considered preferable to previously used indirect methods (e.g. Mayorga et al. 2005).

The isotopic signature of evaded CO_2 was measured in September 2004 and 2005; full details of the method for collecting evasion CO_2 are provided in Billett et al. (2006). Briefly, the procedure involved the following stages:

1. Measurement of CO_2 evasion rate in the floating chamber;
2. Scrubbing of the atmospheric and evaded CO_2 in the chamber;
3. A period of evasion to allow sufficient CO_2 to build up for isotope analysis;
4. Collection of the evasion CO_2 in a molecular sieve cartridge.

Following sample collection, the molecular sieve cartridges were returned to the NERC Radiocarbon Laboratory and the sample CO_2 recovered by heating and cryogenic trapping (see Hardie et al. 2005 for details about the molecular sieve procedures).

Vegetation was sampled in September 2005 at each of the 3 locations where evaded CO_2 was measured. Samples were obtained from transects on both sides of the stream channel at the following distances from the stream edge: 0–20 cm, ~100 cm, and ~500 cm. Representative vegetation samples were collected at each of these locations, plus an additional site ~0.5 km from the stream ("the control"). Samples were collected by cutting with clean scissors and placing immediately into sealed polythene sample bags. Samples were subsequently stored in the dark at 6 °C prior to isotope analysis.

In the laboratory, samples were identified to species level, and the most recent growth (<1 yr old) removed and retained for further processing. Multiple individuals of a single species from each location were combined to provide a representative sample. All samples were soaked overnight in 1M HCl (room temperature) to remove any potential traces of carbonate in soil fragments. Next, samples were rinsed free of mineral acid with deionized water, dried (at 40 °C), and homogenized. The total carbon in a known weight of the pretreated sample was recovered as CO_2 by heating with CuO in a sealed quartz tube.

Subsamples of both the evaded CO_2 and vegetation sample CO_2 were analyzed for $\delta^{13}C$ by isotope ratio mass spectrometry (IRMS) at the NERC Radiocarbon Laboratory (VG Optima, United Kingdom). ^{13}C results are reported using the delta notation with $^{13}C/^{12}C$ variations relative to the international standard Vienna Pee Dee belemnite (VPDB), as described by the following equation:

$$\delta^{13}C\ (\text{‰}) = \left(\frac{(^{13}C/^{12}C)_{sample} - (^{13}C/^{12}C)_{VPDB}}{(^{13}C/^{12}C)_{VPDB}} \right) \times 1000 \tag{1}$$

For a selection of 6 samples, a further aliquot of CO_2 was converted to graphite by Fe/Zn reduction (Slota et al. 1987) and analyzed for ^{14}C by accelerator mass spectrometry (AMS) using the 5MV tandem accelerator at the Scottish Universities Environmental Research Centre (SUERC), East Kilbride, United Kingdom (Freeman et al. 2004; Xu et al. 2004). ^{14}C data are reported as % Modern and $\Delta^{14}C$ (with results having been normalized to a $\delta^{13}C$ of –25‰; Stuiver and Polach 1977).

Calculation of Percentage Plant Carbon Derived from Evasion

The $\delta^{13}C$ value of plant material is a function of the atmospheric carbon isotope composition and fractionation effects occurring during the assimilation of the CO_2 (Farquhar et al. 1989). $\delta^{13}C$ of plant material fixed by the C3 photosynthetic pathway is related to atmospheric $\delta^{13}C$ using the following equation (Farquhar et al. 1989):

$$\delta_p = \delta_a - a - (b - a)\, p_i/p_a \tag{2}$$

where δ_p and δ_a are the carbon isotopic values of the plant material and atmosphere from which the plant obtained its carbon, respectively. Diffusive fractionation during photosynthesis (4.4‰) is represented in the equation as a, b is the chemical fractionation caused by carboxylation (27‰), and p_i and p_a are the intercellular and ambient partial pressures of CO_2, respectively. Following Lichthouse et al. (2003), we assumed that for all samples in the present study the value of p_i/p_a was constant, and therefore remains the same at increasing concentrations of atmospheric CO_2.

Assuming the $\delta^{13}C$ value for the vegetation collected from the control site was representative for plants that did not obtain any of their carbon from evasion, and assuming an atmospheric ^{13}C value of $-8.5‰$ for δ_a, when no evasion CO_2 was present (Hemming et al. 2005), we determined p_i/p_a by using Equation 2.

Next, we calculated the $\delta^{13}C$ of the air from which plants growing adjacent to the stream obtained their carbon (δ_{a+e}), given that it may contain a proportion of CO_2 derived from evasion (with a ^{13}C signature of δ_e). δ_{a+e} was calculated (Equation 3) for each individual vegetation sample using the $\delta^{13}C$ values of their tissues (for δ_p):

$$\delta_{a+e} = a + (b-a)p_i/p_a + \delta_p \tag{3}$$

The percentage of CO_2 in the plant materials being derived from evaded CO_2 (E_{13}) was calculated from the ^{13}C values for each plant sample using the following equation derived from mass balance:

$$E_{13} = 100 \times (\delta_{a+e} - \delta_a)/(\delta_e - \delta_a) \tag{4}$$

The above equation was slightly modified for calculating the percentage of CO_2 derived from evasion (E_{14}) using the ^{14}C results (note that the ^{14}C results had been normalized to a $\delta^{13}C$ of $-25‰$, which accounts for any mass-dependent fractionation effects):

$$E_{14} = 100 \times (\Delta_{a+e} - \Delta_a)/(\Delta_e - \Delta_a) \tag{5}$$

In Equation 5, Δ_a represents the % Modern of the free atmosphere (determined from plant material considered not to contain any carbon from evasion), Δ_e is the % Modern of the evasion CO_2, and Δ_{a+e} represents the % Modern of the atmosphere from which the plant obtained its carbon (which is equivalent to the measured % Modern of the plant material).

RESULTS

Table 1 shows that, relative to the atmosphere, the evaded CO_2 is depleted in ^{13}C by at least $12‰$; however, the extent of depletion varied between locations, with the lowest evasion ^{13}C concentrations observed for the site nearest the stream source (A2). The ^{14}C content of the evaded CO_2 also showed spatial variation with values of ~900 BP and ~1450 BP associated with sites A5a and A10, respectively, while the result for site A2 was just slightly depleted in ^{14}C compared to the contemporary atmosphere (Levin and Kromer 2004).

Table 1 Characteristics of the evaded CO_2 at each sampling location, including ^{14}C concentration, $\delta^{13}C$, and evasion rate. Evasion rates measured at sites A2, A5a, and A10 are means of 4, 2, and 5 measurements, respectively, made over the period 2004–05.

Location (Figure 1)	CO_2 sampling date	$\delta^{13}C_{VPDB}$ $\pm 0.1‰$	Publication code (SUERC-)	^{14}C enrichment (% Modern $\pm 1\sigma$)	^{14}C enrichment ($\Delta^{14}C \pm 1\sigma$)	Conventional ^{14}C age BP $\pm 1\sigma$	CO_2 evasion rate (g CO_2 m^{-2} s^{-1})
A2	9/1/2005	–26.2	7825	104.58 ± 0.33	38.9 ± 3.3	Modern	328
A5a	9/13/2004	–21.0	5930	83.44 ± 0.30	–171.0 ± 3.0	1454 ± 29	175
A5a	9/13/2004	–21.1	5933	83.56 ± 0.30	–169.8 ± 3.0	1443 ± 29	175
A10	9/13/2004	–21.0	5934	89.94 ± 0.29	–106.5 ± 2.9	852 ± 26	230
A10	9/13/2004	–21.6	5937	88.76 ± 0.29	–118.2 ± 2.9	958 ± 26	230
A10	9/1/2005	–21.5	7826	87.97 ± 0.27	–126.1 ± 2.7	1030 ± 25	230

Species and carbon isotope composition of the vegetation samples from all sites are provided in Table 2. Due to differences in habitat, the same assemblage of species was not represented at each location, and a single species did not exist at every sampling point. The species that occurred at most sites was the grass *Glyceria fluitans*, and therefore most analyses were performed on this species. Where *Glyceria fluitans* was not available, however, another grass, *Deschampsia flexuosa*, was analyzed; to determine whether there were differences between species, we analyzed both species for δ^{13}C when they occurred together.
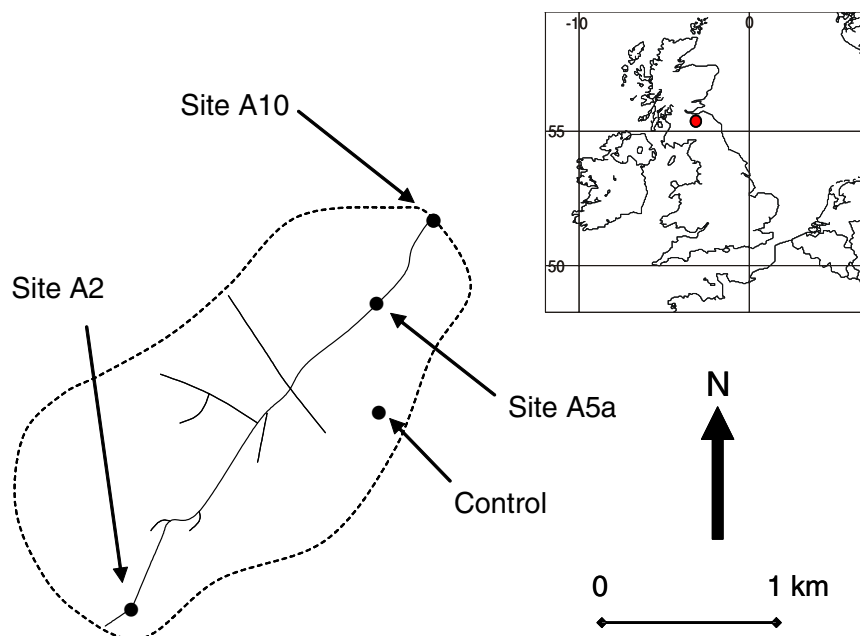

Figure 1 Location of the sampling points along the Black Burn. The dotted line delineates the catchment boundary.

δ^{13}C values for the vegetation ranged from –26.9 to –31.1‰ (Table 2). There was a clear pattern in the values, with results for samples closest to the stream (0–20 cm) having the most depleted ^{13}C values. This pattern was not completely consistent since several δ^{13}C values in the 0–20 cm group were less depleted in ^{13}C than plants located further from the stream. Overall, the means from each group overlapped at 2 σ. There were no consistent differences in plant ^{13}C content where the 2 grass species were collected from the same location.

All plant ^{14}C results (Table 2) covered a narrow range and were very similar to the expected ^{14}C content of the contemporary free atmosphere (~107% Modern; Levin and Kromer 2004). However, the samples from within 20 cm of the stream all had the most depleted ^{14}C concentrations, and the mean of the % Modern values for these samples (106.98 ± 0.13) was significantly (>2 σ) lower than the mean of the samples >20 cm away (107.64 ± 0.17).

The proportion of plant carbon being derived from evasion was calculated for all samples located 0 to 20 cm from the stream (Table 3). Best estimates ranged from 3.2 to 19.2%, based on the δ^{13}C results. For the three 0–20 cm samples available for estimating the percentage of vegetation carbon derived from evasion using ^{14}C content, the range was similar to that derived from the δ^{13}C (3.1 to 16.9%). For 2 of the 3 sites, there was good agreement between both ways of estimating the proportion of evaded CO$_2$ fixed, with values differing by <3%.

Table 2 Characteristics of the vegetation at each sampling location, including ^{14}C concentration and δ^{13}C. All samples were collected on 1 September 2005. Key to species: A = *Glyceria fluitans*; B = *Deschampsia flexuosa.* Results for the 0–20 cm samples are in bold.

Location (Figure 1)	Transect (north or south)	Distance from stream edge (cm)	Species	$\delta^{13}C_{VPDB}$ ±0.1‰	Publication code	[14]C enrichment (% Modern ± 1 σ)	[14]C enrichment ($\Delta^{14}C \pm 1\ \sigma$)
A2	**N**	**0–20**	**A**	**–31.1**	**SUERC-8054**	**107.13 ± 0.33**	**64.2 ± 3.3**
A2	N	500	A	–27.7	—	—	—
A2	**S**	**0–20**	**A**	**–29.9**	—	—	—
A2	S	500	A	–28.5	—	—	—
A5a	**N**	**0–20**	**A**	**–28.2**	—	—	—
A5a	N	100	B	–26.9	—	—	—
A5a	N	500	B	–28.8	—	—	—
A5a	**S**	**0–20**	**A**	**–28.1**	**SUERC-8052**	**106.91 ± 0.33**	**62.0 ± 3.3**
A5a	S	100	B	–27.4	—	—	—
A5a	S	100	A	–27.0	SUERC-8051	107.84 ± 0.36	71.2 ± 3.6
A5a	S	500	B	–27.0	SUERC-8053	107.55 ± 0.32	68.4 ± 3.2
A10	**N**	**0–20**	**A**	**–29.4**	**SUERC-8050**	**106.90 ± 0.32**	**61.9 ± 3.2**
A10	**S**	**0–20**	**A**	**–29.3**	—	—	—
A10	S	500	B	–27.6	—	—	—
A10	S	500	A	–28.4	—	—	—
Tower	S	~0.5 km	B	–27.7	SUERC-8049	107.54 ± 0.29	68.3 ± 2.9

Table 3 Calculated values for the percentage of plant carbon being derived from evaded CO_2 based on the δ^{13}C and ^{14}C results. Values in columns marked * were derived from the mean of multiple samples when available (see Table 1). The 1-σ error ranges for the % plant carbon derived from evasion represent the minimum and maximum values calculated when propagating the 1-σ error range of the evasion and plant isotope results. All samples are *G. fluitans*.

Location (Figure 1)	Transect (north or south)	Distance from stream edge (cm)	Evasion values used in calculations (see Table 1)			% plant carbon derived from evasion (estimated 1-σ error range in parentheses)	
			$\delta^{13}C_{VPDB}$* ‰	[14]C enrichment* (% Modern ± 1 σ)	[14]C enrichment* ($\Delta^{14}C \pm 1\ \sigma$)	Calculated from ^{13}C results	Calculated from ^{14}C results
A2	N	0–20	–26.2 ± 0.1	104.58 ± 0.33	38.9 ± 3.3	19.2 (18.5–19.9)	16.9 (5.6–31.0)
A2	S	0–20	–26.2 ± 0.1	104.58 ± 0.33	38.9 ± 3.3	12.4 (11.8–13.1)	—
A5a	N	0–20	–21.1 ± 0.1	83.50 ± 0.08	–170.4 ± 0.8	4.0 (3.1–4.8)	—
A5a	S	0–20	–21.1 ± 0.1	83.50 ± 0.08	–170.4 ± 0.8	3.2 (2.4–4.0)	3.1 (1.7–4.4)
A10	N	0–20	–21.4 ± 0.3	88.89 ± 0.99	–116.9 ± 9.9	13.2 (12.1–14.3)	4.0 (2.1–6.1)
A10	S	0–20	–21.4 ± 0.3	88.89 ± 0.99	–116.9 ± 9.9	12.4 (11.4–13.5)	—

DISCUSSION

Recent observations that rivers can degas CO_2 at high rates and that this CO_2 can be isotopically old (Billett et al. 2006) led us to consider whether plants growing adjacent to such rivers could obtain a proportion of their carbon from this CO_2. Based on the evidence presented here, we believe that riparian plants can obtain a proportion of their carbon from evasion, and that this is reflected in the carbon isotope composition of their tissues.

We found that plants growing nearest the stream were generally more depleted in ^{13}C, suggesting that the local atmosphere from where they obtained their carbon was relatively ^{13}C-depleted. We

consider the ^{13}C-depleted atmosphere nearest the stream to be due to surface water degassing of CO$_2$ since direct measurements of evasion show it to be ^{13}C-depleted and to be a more significant flux (per unit surface area) than other ^{13}C-depleted CO$_2$ sources, such as peatland respiration.

Although plants growing nearest the stream were most ^{13}C-depleted, there was not a consistent pattern of increasing ^{13}C concentration with distance from the stream. This could be a result of several factors. For example, we assumed that the ^{13}C concentration in the plant materials only varied as a result of variation in the ^{13}C composition of the atmosphere from where the plant obtained its carbon. Although other factors are known to affect plant tissue ^{13}C composition (Farquhar et al. 1989; Arens et al. 2000), Arens et al. (2000) concluded that the dominant factor was the ^{13}C content of the atmosphere from where carbon was obtained. Other references supporting the assumption that the term p_i/p_a is constant are provided by Lichtfouse et al. (2003).

The ^{14}C results are also consistent with riparian plants obtaining a proportion of their carbon from evasion, since plants nearest the stream were ^{14}C-depleted relative to plants growing further away, and since direct measurements of evasion show it to be ^{14}C-depleted. We know of no other sources of "old" CO$_2$ at the sampling sites, and although it could be suggested that part of the ^{13}C depletion in the riparian plants could be from fixing of CO$_2$ derived from soil respiration, this cannot explain the depleted ^{14}C results, since soil respiration is likely to contain elevated ^{14}C concentrations (e.g. Trumbore 2000). Therefore, our only explanation for the ^{14}C-depleted values observed in plants nearest the stream is that they obtained a proportion of their carbon from evasion.

Using the ^{13}C content of the plant material, we calculated that up to ~20% of plant carbon was derived from evasion, and obtained a similar value from the ^{14}C content of the plants. For 2 of the 3 sites where both ^{13}C and ^{14}C results were available, there was good agreement in the estimates; however, the conclusion that riparian plants can fix a proportion of their carbon from evasion is much stronger due to the use of both ^{13}C and ^{14}C isotopes. For example, due to the greater distinction between atmospheric and evasion [13]CO$_2$ (compared to [14]CO$_2$), the 1-σ ranges in the estimates of plant carbon derived from evasion were narrower using the ^{13}C results. However, as discussed above, interpretation of the ^{13}C results requires certain assumptions concerning isotopic fractionation during plant fixation of CO$_2$. The ^{14}C evidence contributes additional information about the source of the CO$_2$, and does not require assumptions regarding mass-dependent fractionation during fixation.

The observation that riparian plants may obtain a significant proportion of their carbon from stream evasion, and that this evaded CO$_2$ may be considerably ^{14}C-depleted relative to the contemporary atmosphere, has several implications for the study of carbon cycling in aquatic systems using isotopes. For example, investigations of the source of DOC or POC in streams may interpret depleted ^{14}C concentrations in these materials as suggesting a component of aged (e.g. pre-bomb) organic matter, whereas this material could have been fixed very recently and acquired a ^{14}C signature slightly depleted relative to the contemporary free atmosphere if it contained carbon from evasion.

These results also have implications for ^{14}C dating of riparian plant remains, since the assumption that the dating material was in ^{14}C equilibrium with the contemporary free atmosphere when living may be invalid if the plant utilized CO$_2$ released by evasion from the water surface. The effect would be quite small at our sampling sites, with living plants being aged the equivalent of ~60 yr. However, it could be more significant at other sites where the CO$_2$ degassed from the stream surface is more ^{14}C-depleted. For example, Mayorga et al. (2005) observed [14]CO$_2$ concentrations in Amazonian rivers as low as ~25% Modern. In addition, at some sites the proportion of plant carbon being derived from evasion might be greater due to higher evasion rates, lower wind speeds, and different stream

bank morphology. Our site A2 had the highest evasion rate but the least ^{14}C-depleted CO_2; if evaded CO_2 at site A2 had the same ^{14}C content as the other sites (and similar atmospheric mixing conditions), fixing of evaded CO_2 would have led to living plants being aged ~300 yr. Fixing of old carbon from evasion may therefore have been a contributor to problems of "old" ^{14}C ages that have been reported when dating some lake sediments.

CONCLUSIONS

The ^{13}C and ^{14}C content of plants growing in close proximity to a peatland stream suggested that up to ~20% of the carbon they fixed was derived from evasion of CO_2 from the water surface. Fixing of evaded CO_2 was greatest in plants growing within 1 m of the stream. Incorporation of evaded CO_2 from water surfaces in plant material could have a more significant impact on the isotopic composition of plants growing close to lakes, streams, or rivers, associated with a more enclosed micro-environment and/or higher rates of degassing.

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