Current forest carbon fixation fuels stream CO₂ emissions

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Stream CO₂ emissions contribute significantly to atmospheric climate forcing. While there are strong indications that groundwater inputs sustain these emissions, the specific bio-geochemical pathways and timescales involved in this lateral CO₂ export are still obscure. Here, via an extensive radiocarbon (14C) characterisation of CO₂ and DOC in stream water and its groundwater sources in an old-growth boreal forest, we demonstrate that the 14C-CO₂ is consistently in tune with the current atmospheric 14C-CO₂ level and shows little association with the 14C-DOC in the same waters. Our findings thus indicate that stream CO₂ emissions act as a shortcut that returns CO₂ recently fixed by the forest vegetation to the atmosphere. Our results expose a positive feedback mechanism within the C budget of forested catchments, where stream CO₂ emissions will be highly sensitive to changes in forest C allocation patterns associated with climate and land-use changes.

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he flushing of terrestrially-derived C through runoff can represent up to 30% of the annual C balance of forested ecosystems, of which greenhouse gases such as CO₂ hold a major contribution1–3. Once released from soils to surface waters, this CO₂ is rapidly evaded to the atmosphere as a result of physical gas exchange4. This lateral CO₂ flux is particularly relevant to headwater streams, which account for the bulk of surface water CO₂ emissions5,6. Streams thus contribute actively to atmospheric climate forcing by returning terrestrially seques-
tered CO₂ to the atmosphere. To date, the evidence supporting the terrestrial origin of stream CO₂ has relied solely on mass balance exercises; demonstrating that the pool of groundwater CO₂ is often sufficiently large to sustain stream CO₂ fluxes7–9. Explicit demonstrations of this link are still absent. Most of all, the specific biogeochemical pathways giving rise to stream CO₂, along with their associated timescales, have yet to be resolved. Without a clear assessment of the sources of lateral CO₂ fluxes, the terrestrial and aquatic components of catchment C budgets cannot be reconciled.

Soil and groundwater CO₂ can arise from several different biological sources, each confined across a spectrum between two main timescales10,11. Operating in the short timescales, is the current forest fixation of atmospheric CO₂, which fuels autotrophic root respiration12 and heterotrophic mineralisation of recent photosynthates, transported to soils via throughfall, stemflow,13 and root leachates14. Alternatively, over longer times-
scales, saprotrophic decomposition embodies all forms of het-
erotrophic decomposition of older plant detritus and soil organic matter15. In groundwater, saprotrophic decomposition is sup-
ported mainly by dissolved organic C (DOC), which incorporates an assemblage of chemical properties and ages from the vegeta-
tion and soils traversed by the groundwater during its journey through the catchment16,17. Boreal forest catchments often comprise a peat-rich riparian zone, which serves as a repository of ancient soil organic matter that can support saprotrophic meta-
bolism and may be remobilized through decomposition and runoff18–20. The source determination of lateral C fluxes may enable assessment of the vulnerability of these ancient C stocks19,21,22. Boreal forests also drive a considerable share of the global continental CO₂ sink23, a process that is considered sen-
titive to a variety of anticipated disturbances24,25. The separation of timescales in the biological pathways governing lateral CO₂ fluxes in boreal forested catchments is thus critical information, since different CO₂ sources will likely follow distinct trajectories in response to environmental changes.

Here, we identify and apportion the sources of stream CO₂ with particular emphasis on the separation of timescales and biogeochemical pathways involved in the lateral CO₂ fluxes from an old-growth boreal forest catchment. We characterize the terrestrial and aquatic CO₂ sources via repeated measure-
ments of the groundwater and stream water radiocarbon (¹⁴C) content of CO₂ and DOC (¹⁴C-CO₂, ¹⁴C-DOC). Our sampling was designed following a three-level Upslope-Riparian-Stream transect, repeated over three different occasions during the growing season, thus allowing to associate spatio-temporal ¹⁴C patterns to different CO₂ sources. The transect sampling was complemented with a year-round characterisation of the stream water ¹⁴C-CO₂ and ¹⁴C-DOC, to further explore potential shifts in CO₂ sources over time. Automated sensors recording hourly CO₂ concentrations at each location along the transect and further downstream, allowed us to derive a complete annual C budget for this forested catchment using the age component of the lateral C fluxes to reveal links between the terrestrial and aquatic components. This study reveals that soil respiration, derived from the current forest C fixation, is the main source of stream CO₂ fluxes.

Results

Interpretation of ¹⁴C-contents. Radiocarbon analysis can be used to determine the average age of CO₂ and DOC based on conventional ¹⁴C dating techniques and represents one of the most robust approaches for the separation of respiratory processes in soils16,11,26. However, the ¹⁴C content of gases or solute samples potentially originates from multiple combinations of sources, each with a different ¹⁴C-age, thus complicating the interpretation of the single average ¹⁴C-content. While the incorporation of post-bomb ¹⁴C in the C cycle, resulting from the atmospheric testing in the 1950–60s, precludes a linear interpretation of ¹⁴C-content, it can provide clear evidence of carbon fixed from the atmosphere post ~AD1955 (i.e., when ¹⁴C concentration >100%). Here, we specifically avoided referring to the measured ¹⁴C contents in terms of age from conventional ¹⁴C dating and instead focused our analysis on the relative differences in ¹⁴C contents between C species, in our case CO₂ and DOC, as well as their changes over time and space to help define the stream C sources in connection to terrestrial processes.

Stream water ¹⁴C-CO₂ and ¹⁴C-DOC. Stream water ¹⁴C-CO₂ was surprisingly constant throughout the year, ranging from 102.5 to 105.3 %modern (n = 11) (Fig. 1a, Supplementary Table 1). In comparison, the stream water ¹⁴C-DOC was more variable and more ¹⁴C-enriched, ranging from 103.5 to 112.2 % modern (n = 8) (Fig. 1a, Supplementary Table 2). Stream water ¹⁴C-DOC was negatively related to the riparian water table position, indicating that more superficial water tables corre-
sponded to more ¹⁴C-enriched DOC in the stream waters (Fig. 1b). There was no significant relationship between stream water ¹⁴C-CO₂ and any of the measured variables included in the study, for example: temperature, discharge, water table position, C concentrations, net ecosystem exchange (NEE) or photo-
synthetic photon flux density (PPFD) (all p > 0.05, Fig. 1).

Groundwater ¹⁴C-CO₂ and ¹⁴C-DOC. The patterns in ¹⁴C-CO₂ and ¹⁴C-DOC in the connecting groundwater were generally similar to those of the stream waters. As such, groundwater ¹⁴C-
CO₂ was also remarkably homogenous across locations, depths and sampling dates. All samples were enriched in post-bomb ¹⁴C, together ranging from 101.1 to 106.6 %modern (n = 7), with the exception of one sample collected in the riparian deep soil water in August, where ¹⁴C-CO₂ was 99.0 %modern (Fig. 2, Supple-
mentary Table 2). Differences in ¹⁴C-CO₂ between upslope and riparian groundwater were not significant (p = 0.6), despite a near doubling of the CO₂ concentrations between the two locations. In contrast, the range in groundwater ¹⁴C-DOC was much larger than for ¹⁴C-CO₂. Most of the groundwater ¹⁴C-DOC were enriched in post-bomb ¹⁴C, ranging from 100.8 to 116.8 % modern (n = 9), but there were two groundwater samples for which ¹⁴C-DOC was remarkably depleted (49.7 and 67.8 % modern, respectively) (Fig. 2, Supplementary Table 2). Both were collected in the upslope deep location, in August and October. Excluding these two groundwater samples, the ¹⁴C-DOC was significantly negatively correlated with the DOC concentration across the groundwater and stream waters (Fig. 3). There was no similar relationship between ¹⁴C-CO₂ and CO₂ concentrations in either the groundwater or stream water (Fig. 3).

The ¹⁴C-CO₂ and ¹⁴C-DOC showed little correspondence in both groundwater and stream waters, with the DOC being on average 6 %modern more ¹⁴C-enriched than the CO₂ across all discrete samples (n = 9), with the exception of the upslope deep groundwater in August and October (Figs. 1a, 2). In these groundwater, the difference in ¹⁴C content between CO₂ and DOC was even larger, corresponding to 55 and 33 %modern for
August and October, respectively, where DOC was suddenly much older than CO₂ (Fig. 2). In the riparian deep groundwater, the 14C-CO₂ and 14C-DOC matched most closely and also showed the least temporal variability (only ~2% modern across the three-sampling occasions despite a near doubling of the DOC concentrations between sampling occasions) (Fig. 2). In the stream waters, the differences in 14C content between CO₂ and DOC, was largest during the spring freshet, but decreased during winter base flow conditions (Fig. 1a).

**CO₂ and DOC concentrations.** The average CO₂ concentrations doubled between the up slope mineral soils and the riparian organic-rich soils (d = 0.45) (Fig. 4e, f). In the riparian soils, the CO₂ concentrations were similar between the shallow and deep layers (17.7 ± 3.5 and 14.9 ± 3.3 mg C L⁻¹, respectively n = 8028 (d = 0.2)), while in the up slope soils, the CO₂ concentrations were significantly lower in the shallow compared with the deep layers (4.6 ± 2.0 mg C L⁻¹ n = 707, and 11.7 ± 3.3 mg C L⁻¹ n = 8027 (d = 1.2), respectively) (Fig. 4e, f). Stream water CO₂ concentrations during the open water season were significantly higher in the location adjacent to the transect (3.4 ± 1.1 n = 3496), compared with the stream gauging station, located 250 m downstream (2.8 ± 0.9 n = 3235), (d = 1.3) (Fig. 4d). Year-round hourly stream water CO₂ concentrations were recorded at the downstream location, but showed no significant difference between the ice-covered and open-water period (d = 0.48, annual mean 2.8 ± 1.4 n = 8311) (Fig. 4d). The stream water CO₂ concentrations never exceeded the groundwater CO₂ concentrations in the riparian or up slope location (Fig. 4d–f).

Groundwater DOC concentrations were on average five times higher in the riparian compared with the up slope groundwater (39.2 ± 10.4 mg C L⁻¹ n = 11, and 7.4 ± 6.7 mg C L⁻¹ n = 8, respectively, p < 0.0001) (Fig. 4e, f). DOC concentrations were similar across the two groundwater depths, in both the riparian and up slope soils (p = 0.06, p = 0.5, respectively). The riparian DOC concentrations increased steadily between May and October, by 87 and 33% in the shallow and deep layers, respectively (Fig. 4e). This increase was not as clear in the up slope soils. The stream water DOC concentrations (19.8 ± 4.8 mg C L⁻¹ n = 8) were significantly lower and never exceeded the riparian groundwater DOC concentrations (p < 0.0001) (Fig. 4d, e). Together, the trends in DOC and CO₂ concentrations along the up slope-riparian-stream transect resulted in a progressive shift, from a slight dominance of CO₂ over DOC in the up slope groundwater (average CO₂-C:DOC = 1.5), to a clear dominance of DOC over CO₂ in the riparian groundwater (average CO₂-C:DOC = 0.4), which was more pronounced in the stream waters (average CO₂-C:DOC = 0.1).

**Hydro-climatic conditions and catchment C budget.** The NEE (determined by Eddy Covariance) of the forest ecosystem in the catchment for the study year was −205 g m⁻² yr⁻¹ (Fig. 5). The annual runoff for the catchment during the study year was 257 mm, representing about half of the annual precipitation
The annual CO₂ export from the riparian location was more than double that of the upslope location (Fig. 5). The contribution of the riparian soils was even more substantial for the annual DOC export, which was more than five times larger compared with the upslope site (Fig. 5). Downstream CO₂ export represented only 13% of the initial riparian groundwater CO₂ export, which can be attributed to rapid CO₂ evasion to the atmosphere. The downstream DOC export was more comparable to the riparian groundwater DOC export, representing about 70% of the initial flux. The cumulative age of the lateral C fluxes was 104 and 110 %modern for CO₂ and DOC, respectively. The difference in ¹⁴C content between the annual CO₂ and DOC exported from the catchment could be explained by a 75% contribution from currently fixed CO₂ from the atmosphere (i.e., during the last growing season 2015–2016), with the remaining fraction originating from the bulk DOC mineralization.

Discussion
This study provides, to our knowledge, the first explicit evidence that stream CO₂ fluxes are sustained by currently fixed CO₂ from atmosphere via the forest vegetation’s photosynthetic activity (i.e., during the last growing season 2015–2016). The first piece of evidence supporting our interpretation was the persistent gaps between ¹⁴C-CO₂ and ¹⁴C-DOC in groundwater and stream water, highlighting a major disconnect in the cycling of the two C species. Secondly, the homogeneity of the ¹⁴C-CO₂ in groundwater and stream water, which remained systematically close to the current atmospheric ¹⁴C level, indicated that CO₂ was sustained by a large and steady source, likely associated with current photosynthesis. Previous studies have provided indications that groundwater inflow of soil-derived CO₂ is sufficient to support stream CO₂ sources[7-9]. However, explicit demonstrations of the
link between soil and stream CO$_2$ along with determination of the biogeochemical pathways involved, were still lacking. Our results imply that stream CO$_2$ fluxes are cycled rapidly, and likely provide a fast pathway for returning CO$_2$ fixed from the atmosphere by the forest vegetation during this year’s growing season. The main implication of this work is that anticipated alterations in boreal forest growth and ecosystem level C allocation patterns, driven by climate change and other disturbances, will produce a rapid response in the stream CO$_2$ fluxes, since both processes are tightly linked by the current forest activity.

The systematic offset between the 14C-DOC and 14C-CO$_2$ in groundwater and stream water is key evidence of the limited overlap in their respective sources and controls (Figs. 1a, 2). The substantial variability in groundwater and stream water 14C-DOC, which contained both severely 14C-depleted and 14C-enriched post-bomb values (Figs. 1, 2), indicated that DOC arises from more diverse sources than CO$_2$ and is cycled more slowly, up to millennia. There was a clear connection between the 14C-DOC and hydrological retention and flowpaths (Figs. 1b, 3), as suggested by previous studies in this catchment using independent methods$^{19,27,28}$. Activation of fast flowing superficial flowpaths$^{29}$ was associated with the transport of modern 14C-DOC, with rising water tables leading to an increase proportion of post-bomb 14C and dilution of the DOC, for example during spring freshet (Figs. 1b, 3). These dynamic superficial flowpaths are supplemented by intermittent activations of deeper flowpaths associated with longer water retention times$^{30}$ and the transport of aged-DOC, for example, the upslope groundwater later in the growing season (Figs. 2, 3). Despite these profound changes in hydrological flowpaths across locations and seasons, the groundwater and stream water 14C-CO$_2$ remained relatively unchanged (Figs. 1, 2). In fact, the groundwater 14C-CO$_2$ was similar between the upslope mineral soils and the riparian organic soils, despite major contrasts in soil properties and contributing flowpaths (e.g., a near doubling of the CO$_2$ concentrations and a five times increase in DOC concentrations (Fig. 4e, f), and a shift from severely 14C-depleted to post-bomb enriched DOC between the two locations later in the growing seasons (Fig. 3). This suggest that the sources governing groundwater CO$_2$ can override these dynamics in hydrological flowpaths and soil chemistry.

Inconsistencies between the 14C content of DOC and CO$_2$ have been reported in other catchments including the Amazon river network$^{31}$ and various peatland dominated catchments$^{32-34}$ (Supplementary Fig. 2). Other studies comparing the 14C content of DIC and DOC in surface waters also concur with these observations$^{35}$. Although the form of these isotopic inconsistencies may vary across catchments, the 14C-DOC often reveals greater levels of post-bomb C than the CO$_2$, suggesting more association with moderately old organic C reservoirs$^{31,35}$. Severely 14C-depleted CO$_2$ and DIC in surface waters are also more frequently reported than DOC, but these are typically connected to weathering of carbonate-containing minerals$^{36,37}$. Such geological sources of CO$_2$ are absent in this catchment, as indicated by the δ$^{13}$C-CO$_2$ values that were consistent with the C3 plant metabolic pathway (Supplementary Fig. 2$^{38}$). A considerable number of observations in the literature demonstrate a close agreement between the surface water 14C-CO$_2$ and the current atmospheric 14C level, together with a clear photosynthetic δ$^{13}$C value$^{31,35}$. These observations, comply with ours, and suggests that surface water CO$_2$ sources may often arise from rapid C cycling processes within catchment soils.

The uniformity of 14C-CO$_2$ and its similarity with the current atmospheric 14C level, underlined that groundwater and stream water CO$_2$ was sustained by a large and steady source, with rapid turnover times and omnipresent across this catchment (Figs. 1a, 2). Forest C fixation can fuel groundwater CO$_2$ via autotrophic root respiration$^{12}$ or the transport of recent photosynthates to soils by root exudates$^{14}$, throughfall and stemflow$^{13}$, thereafter mineralized by the soil microbial communities. Invasion of atmospheric CO$_2$ in groundwater and stream water could not explain this close agreement between the 14C-CO$_2$ content of the current atmospheric 14C level, as indicated by high CO$_2$ concentrations in soil and stream waters, consistently above atmospheric saturations (Fig. 4d–f) and the low δ$^{13}$C-CO$_2$ values,
conformed with C3 derived organic matter (Supplementary Fig. 2). The stability of the $^{14}$C-CO$_2$ content was remarkable, considering the dramatic seasonal changes in groundwater and stream water C concentrations, forest productivity, precipitation, runoff and temperature over the year. In fact, the $^{14}$C-CO$_2$ was independent of all measured environmental variables monitored in this study and showed no connection to seasonal patterns, further supporting a steady source (Figs. 1–3). Seasonal changes in hydro-climatic conditions are major controls on forest C fixation, soil respiratory processes, and hydrological connectivity between soils and streams, but the large amount of CO$_2$ fixed by the forest vegetation during the growing season is likely sufficient to support the lateral CO$_2$ export throughout the year (Fig. 5).

Based on the cumulative $^{14}$C content of stream CO$_2$, an estimated 75% of the lateral CO$_2$ export from the catchment possibly originated from the forest C fixation during the last growing season, with the remaining fraction arising from saprotrophic respiration, subsidized by the cumulative bulk $^{14}$C-DOC export (Fig. 5). This rough estimate agrees well with studies partitioning the vertical soil CO$_2$ fluxes, where autotrophic root respiration contributes 50–64% of the total soil respiration in various forested catchments, as well as in a nearby boreal forest catchment. This flux is likely supplemented by heterotrophic mineralization of recent photosyntheses, but the relative importance of these processes cannot be separated here. While there is general consensus that autotrophic root activity makes up a major fraction of vertical soil CO$_2$ efflux, there is also awareness that mineralization of root exudates and DOC transported via throughfall and stemflow may not be adequately quantifiable due to rapid turnover rates. The specific contribution of these different biological pathways to lateral CO$_2$ export remains to be further investigated, but our results support a steady and widespread connection to rapidly cycling CO$_2$ sources fuelling lateral CO$_2$ export. Only a small fraction (ca. 2%) of the net CO$_2$ fixed from the atmosphere by the vegetation that year (NEE: $-$205 g C m$^{-2}$ yr$^{-1}$) was lost through the lateral CO$_2$ export (Fig. 5). This is consistent with mass balance estimates from the same catchment reported by Öquist, Bishop during years with similar precipitation. Considering that precipitation and runoff were low during our study year, the fraction of currently fixed CO$_2$ lost through lateral CO$_2$ export in this forested catchment is likely higher in other years (up to 9%)

Since the bulk DOC pool contains a mixture of C ages, the $^{14}$C-DOC in this catchment could reflect refractory DOC compounds, not mineralized during transit, masking an underlying connection between $^{14}$C-CO$_2$ and $^{14}$C-DOC. Further studies are needed to assess the age-composition of DOC, but this does not invalidate that the current atmospheric $^{14}$C-CO$_2$ was reflected in the stream and groundwater of this boreal forest catchment. Saprotrophic respiration may be limited in these CO$_2$-rich groundwater, owing to lack of oxygen and short water transit time in the transiently saturated zone. The best agreement between $^{14}$C-CO$_2$ and $^{14}$C-DOC was observed in the deep riparian groundwater, which is found below the dominant source layer. The latter is responsible for the majority of DOC, DIC and water export to the stream. Longer residence time in the deeper groundwater may promote DOC mineralization, likely through fermentative processes, hence a closer overlap between $^{14}$C-CO$_2$ and $^{14}$C-DOC.

Closer agreements between the $^{14}$C-DIC and $^{14}$C-DOC than those observed in this study have sometimes been reported in larger river catchments and lakes. This highlights that the terrestrial DOC export may remerge as an important source sustaining CO$_2$ emissions further downstream; when connectivity with the catchment soils decreases and longer water residence time allows for in-situ mineralisation to occur. Both aged and modern DOC were exported from this catchment during the study year, but our results do not indicate any significant incorporation of severely $^{14}$C-depleted or highly $^{14}$C-enriched post-bomb DOC in the lateral CO$_2$ export. Emerging new research is now demonstrating that aged-DOC may be bioavailable for freshwater microbial communities leading to the production of aged-CO$_2$. The remobilization of ancient DOC in the upwelled soils of this catchment is a concern, and more studies are needed to assess its sources and fate. While previous studies have shown that aquatic DOC mineralization remains low across the Krycklan catchment, there is also mounting evidence of deeper groundwater contribution increasing further downstream and potentially transporting aged-DOC.

This study reveals that stream CO$_2$ fluxes are fuelled by the current forest C fixation and its associated soil respiration processes in a boreal forest catchment. The close connection between the forest C sink and lateral CO$_2$ fluxes had already been put forward based on inter-annual coupling in flux measurements. Our study provides further description of the mechanistic underpinning of this connection between terrestrial and aquatic C fluxes. The lateral CO$_2$ export rapidly mobilises a significant fraction of the C currently fixed from the atmosphere by the forest vegetation. Groundwater CO$_2$ inputs support surface waters CO$_2$ emissions across multiple types of aquatic ecosystems, thus suggesting that rapidly cycling CO$_2$ sources may have a widespread contribution to aquatic CO$_2$ emissions. Owing to the prevalence of root respiration and mineralization of recent photosyntheses in forested soils, our results may also be generalized across a large number of forested ecosystems and biomes. Forest C balance and ecosystem level C allocation patterns in the northern high latitudes are vulnerable to a large number of disturbances including global warming, increased forest fire frequency, insect outbreaks and commercial exploitation. Stream CO$_2$ emissions will quickly feedback on these disturbances, because of the speed of stream CO$_2$ cycling and its close connection to the current forest activity.

**Methods**

**Catchment characteristics.** The study was conducted in a 0.13 km$^2$ catchment located in northern Sweden within the Krycklan Catchment Study (64°14′ N, 19°46′ E). The catchment has been heavily studied for more than two decades and is occasionally referred to as “Vastrabäcken” or “C2” across the literature. The catchment is almost completely forested (99%), with Scots pine (Pinus sylvestris) (64%) and Norway spruce (Picea abies) (36%). The active root depth is mostly distributed above the average groundwater table position. The average tree stand age is 103 years old. Man-made ditching of the stream to improve forest productivity occurred about a century ago. The stream is a peat-rich riparian zone, with the soil profile consisting of ~70 cm thick peat transitioning to the underlying till at ~90 cm depth. The age of the accumulated soil materials from modern near the surface to 2810 years BP at 70 cm depth (Bishop, unpublished data). The organic soil content is >80% in the riparian zone, which is considerably higher than the upslope podzols (<5%) . The latter is composed of well-developed iron podzols on sandy till, comprising a 5 cm humus layer at the surface, overlying a 12 cm thick sandy bleached E-horizon and a 60 cm thick B-horizon. The underlying bedrock is composed predominantly of base-poor Sveco-fennian metasediments-metagraywacke and holds no known carbonate containing minerals. Carbonate alkalinity is rather produced by weathering of silicate minerals.

The climate is cold temperate humid and bears a persistent snow cover from November to April. The 30 year mean annual precipitation is 640 mm (1981-2010), of which 35% falls as snow. The annual precipitation during our study year (507 mm) corresponds to the bottom 6% of the previous 30 years observations (1981-2012). The 30 years mean annual, July and January temperatures are +1.8, +14.7 and ~9.5°C, respectively. The annual peak stream discharge in the region typically occurs during spring in connection to snow melt, but storm events during summer and autumn can also generate peak flows in some years. The winter is typically dominated by low flow conditions.
Soil and stream instrumentation. Groundwater and stream water sampling was carried out following an upslope-riparian-stream transect, as described in ref. 38,41. Groundwater wells were installed along the assumed hydrological flowpaths, with a first set located at 1–2 m (riparian) and the second at 10–12 m (upstream) distance from the stream. The 10-year mean water travel time for the entire catchment is estimated at 690, ranging between 470 and 2064 days42. The water turnover time, from the water divide to the stream and with depths ranging between 0.5 and 3 m, is estimated to 4.6 years43. The area represented by the groundwater transect was estimated at 2540 m² with an average width of 17.7 m, occupying 2% of the total catchment area41. The estimated time for water to exit this transect is in the scale of a month (near the upslope mineral soils) to hours (near the stream).48

The groundwater characterisation at both locations was focused to the upper one metre of the soil profile, where most of the runoff generation is confined41. The groundwater installation comprised a set of wells with screening of the upper 0.5 m (shallow) and lower 0.5–1 m (deep), respectively. For each of the two locations and depths, two identical sets of groundwater wells were installed, with one allowing manual sampling of the groundwater and the other containing sensors for continuous reading of groundwater temperature and CO₂ concentration. Alongside, a fifth well was installed at each of the upslope and riparian locations where water table position was recorded.

Continuous reading of dissolved CO₂ concentration at each location and depth was enabled using Vaisala CARBOCAP GMP221 nondispersive infrared (NDIR) CO₂ sensors (range 0–3%, 0–5%, in the stream, and groundwater, respectively, except for the upslope shallow groundwater where the range was 0–1%). The sensors were enclosed inside a water-tight, gas-permeable Teflon membrane (PTFE) and sealed with Plasti Dip (Plasti Dip International, Saine, MN, USA) to ensure that the sensors were protected from water retained in the dissolved gas. The groundwater CO₂ concentration in the riparian and upslope location at the deep and shallow depth was recorded during the full year. The upslope shallow groundwater well was completely dry for 245 days out of the studied year, but all other sensors remained below the groundwater table at all times. The measurements in the stream adjacent to the groundwater wells were restricted to the open-water season. However, year-round measurements of stream water CO₂ concentration was undertaken in a heated dam house (C2), located 250 m downstream from the soil transect location. The continuous reading of groundwater and stream water CO₂ concentrations were validated against manual samples collected monthly for DOC at each location and depth during the ice-free season (May–November 2015). The DOC concentration was analysed from 10 ml of ground and stream water, filtered through glass-fiber Whatman GF/F filters (0.7 μm) in the field and stored in high-density polyethylene bottles. Prior to analysis, samples were acidified and sparged to remove inorganic carbon. The samples were analysed using a Shimadzu Total Organic Carbon Analyzer TOC-VCPH, following storage at 4 °C for 2–3 days44.

Radiocarbon analysis. The radiocarbon sampling was carried out in two phases, first a repeated catchment scale characterisation of groundwater and stream water in May (spring), August (summer) and October (autumn), and consecutive, a component characterisation in stream waters. 21 samples were collected and analysed for 14C-CO₂ and 16 for 14C-DOC in groundwater and stream water between May 2015 and June 2016. The stream water samples were collected directly adjacent to the groundwater transect during the open water periods and downstream in the heated dam house (C2) during the ice-covered periods for accessibility. Simultaneous measurement of 14C-CO₂ at both stations in July 2015 showed close correspondence, with only a <0.1‰ modern difference, which was within the range of measurement precision. The hillslope transect sampling included all four groundwater locations and depths; riparian/upslope and deep/shallow. However, the available water volume in the shallow riparian and upslope locations was insufficient for radiocarbon analysis in August and October.

Sample collection for 14C-CO₂ included two different methods, one using manual spot measurements applied to groundwater and stream water (n = 11) and the other allowing for time-integrated sampling in the stream water (n = 10). Manual spot measurements of 14C-CO₂ were carried out with the super headspace method whereby manually equilibrated CO₂ samples were trapped onto molecular sieves, dried41 and sealed with Plasti Dip (Plasti Dip International, USA) to ensure that the samples were protected from water retained in the dissolved gas (Accurrel PP V8/2 HF tubing; Membrana GmbH, Germany67). These passive samplers were deployed for periods ranging from 26 to 72 days; collectively they cover more than a full year (May 2015–June 2016). The trapping capacity of the MSC was never exceeded (< 100 ml CO₂). Unfortunately, two time integrated 14C-CO₂ samples were discarded due to contamination that resulted from cracks in the MSC glass casing during deployment or transportation that caused stream water or air contamination of the sample. At the NERC Radiocarbon Facility (East Kilbride, UK), CO₂ samples were recovered from the MSCs by heating and cryogenically purified. The 14C-DOC analysis was performed on 1 L samples of groundwater and stream water collected in acid-washed glass bottles. The samples were filtered in the laboratory through 0.7 μm glass fibre filters, rotary evaporated and freeze-dried. Acid-fumigation of samples was undertaken to guard against carbonate contamination, and the dried DOC was combusted to CO₂ in an elemental analyser (Costech ECS 4010, Italy) and cryogenically recovered. Manual spot measurements of stream water 14C-DOC were taken at each change of the passive 14C-CO₂ samplers in order to characterize cumulative 14C-DOC under a large range of hydrological conditions.

All radiocarbon samples were converted to graphite using Fe-Zn reduction and measured by accelerator mass spectrometry at the Scottish Universities Environmental Research Centre (East Kilbride, UK). Stable carbon isotope measurement (δ13C) was performed on an aliquot of the recovered CO₂ using isotope ratio mass spectrometry (IRMS; Thermo-Fisher Delta V, Germany) and reported relative to the Vienna PDB standard. All radiocarbon results were normalised to a δ13C of –25 % using the measured δ13C values, and expressed as %modern or conventional radiocarbon age (years before present (BP), where 0 BP = AD 1950), with ± 1‰ analytical precision. The passively collected 14C-CO₂ samples were additionally corrected for the +4.2‰ isotopic fractionation effect caused by the gas trapping into the molecular sieves66. The northern hemisphere atmospheric 14C-CO₂ content during the study period ranged from 101.4 to 100.8 according to ref. 68.

Catchment C budget and statistical analysis. The contribution of fixed CO₂ from the atmosphere by the forest vegetation during the growing season of the studied year (2015–2016; Atm14C (%)) was estimated using a simple two-endmember mixing model, solving for the mass of current atmospheric 14C-CO₂ (Atm14C) required to explain the observed gap between the cumulative lateral 14C-CO₂ and 14C-DOC export as follows: 

\[
\text{Atm14C} = \left( \frac{\text{L}_{14C} - \text{DOC}_{14C}}{\text{L}_{14C}} \right) \times 100
\]

The forest NEE and PPFD were obtained from the ICOS data from the Swedish target site (http://www.icos-cp.net/sv). The groundwater C export for each soil depth and location was estimated by combining the modelled specific discharge according to Amvrosiadis, Seibert41, along with the measured hourly DOC concentrations and the interpolated monthly point measurements of DOC concentrations. The total 14C content export at the upslope, riparian and stream locations was estimated by calculating the weighted average 14C content of both CO₂ and DOC export over the full year. Significant differences in soil or stream water chemistry were tested using the non-parametric Wilcoxon test, with p-values reported in brackets in the result sections. For large sample sizes, such as hourly measurements of DOC concentrations, statistical differences between means were tested using Cohen’s d test for effect size. Differences were considered statistically significant when p-value < 0.01. Means values followed with the standard deviation and the number of observations are presented in brackets in the text.

All analyses were performed using R Core Team (2013). R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. URL http://www.R-project.org/.

Data availability

All radiocarbon data are presented in Supplementary Tables 1 and 2. The accompanying datasets and codes generated analysed during the current study are available from the corresponding author on reasonable request.

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Author contributions

A.C., M.B.W., M.F.B. and K.B. designed the study. M.B.W., K.B. and M.F.B. contributed materials and funding, and H.L. provided infrastructure for the data collection. A.C. and M.B.W. wrote the paper. A.C., M.F.B., M.B.W. and K.B. carried out the fieldwork. M.H.G. helped coordinate the radiocarbon sampling and laboratory analysis. A.C. processed and analysed the data. N.A. modelled the hillslope hydrological export. H.L., M.O., M.H.G. and M.F.B. provided scientific insight to the analysis and interpretation of the data. All authors commented on earlier versions of this paper.

Additional information

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