LETTERS
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Sources of and processes controlling CO_2 emissions change with the size of streams and rivers

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Carbon dioxide (CO_2) evasion from streams and rivers to the atmosphere represents a substantial flux in the global carbon cycle[1–3]. The proportions of CO_2 emitted from streams and rivers that come from terrestrially derived CO_2 or from CO_2 produced within freshwater ecosystems through aquatic metabolism are not well quantified. Here we estimated CO_2 emissions from running waters in the contiguous United States, based on freshwater chemical and physical characteristics and modelled gas transfer velocities at 1463 United States Geological Survey monitoring sites. We then assessed CO_2 production from aquatic metabolism, compiled from previously published measurements of net ecosystem production from 187 streams and rivers across the contiguous United States. We find that CO_2 produced by aquatic metabolism contributes about 28% of CO_2 evasion from streams and rivers with flows between 0.0001 and 19,000 $m^3 s^{-1}$. We mathematically modelled CO_2 flux from groundwater into running waters along a stream–river continuum to evaluate the relationship between stream size and CO_2 source. Terrestrially derived CO_2 dominates emissions from small streams, and the percentage of CO_2 emissions from aquatic metabolism increases with stream size. We suggest that the relative role of rivers as conduits for terrestrial CO_2 efflux and as reactors mineralizing terrestrial organic carbon is a function of their size and connectivity with landscapes.

Inland waters play a central role in the global carbon (C) cycle by transforming, outgassing and storing more than half of the C they receive from terrestrial ecosystems before delivery to oceans[1–3]. Terrestrial C inputs to freshwaters are often of similar magnitude to terrestrial net ecosystem production (NEP; refs 1,2,4). Consequently, ignoring inland waters in landscape C budgets may overestimate terrestrial CO_2 uptake and storage[1,5]. In fact, not accounting for terrestrial C exports to and emissions from freshwaters could bias terrestrial NEP and net ecosystem exchange measurements by 4–60% (refs 6–8). Despite small areal coverage, running waters are hotspots for CO_2 emissions[3,9], with high rates of outgassing relative to lake and terrestrial ecosystems on an areal basis[3,10,11]. Given their significant role in landscape C transformations, transport and emissions, there is a fundamental need to understand rates and drivers of C cycling in running waters.

A mechanistic understanding of the processes regulating CO_2 emissions from streams and rivers is necessary for sound predictions of the present and future role of freshwaters in global C cycling and the climate system. Inland waters are often supersaturated with CO_2 due to inputs of terrestrially derived CO_2 and *in situ* aquatic mineralization of terrestrial OC (refs 12–15) (hereafter, 'internal production') as well as abiotic CO_2 production (Supplementary Section 1). CO_2 concentrations and emissions from running waters will thus vary with changes in land cover, climate, terrestrial ecosystem processes, land–water connectivity and internal CO_2 production[15]. Over the past decade, our conceptual model of the role of freshwater ecosystems in larger C budgets has moved beyond defining inland waters as 'passive pipes'[1], but the contribution of internal production to CO_2 emissions from running waters is still poorly constrained. Most freshwater budgets quantify C burial, emissions and export, then back-calculate from these fluxes to estimate terrestrial inputs to inland waters[1,2]. While this approach has been useful for integrating land–water C budgets, these methods limit our understanding of the functional contribution of streams and rivers in C budgets. The extent to which freshwater ecosystems act as direct conduits (that is, 'chimneys') for terrestrially derived CO_2 versus actively metabolize terrestrial OC to CO_2 is not well documented. Are running waters merely acting as chimneys for terrestrially derived CO_2, or are they also biological reactors mineralizing terrestrial OC? Few studies have quantified both external and internal CO_2 sources in streams and rivers, but analyses of C cycling in freshwaters have highlighted the potential significance of aquatic metabolism as a distinct source of internal CO_2 production and emissions[5,11–13,15,16]. Furthermore, site-specific comparisons of ecosystem metabolism and C cycling suggest most CO_2 emissions may be from internal CO_2 production in larger rivers[12,17].

To quantify and differentiate the contributions of terrestrially derived CO_2 and internal production to CO_2 evasion from running waters, we compared rates of aquatic NEP with CO_2 emissions, from small streams to large rivers, in the contiguous United States (US) (Methods and Supplementary Section 2). Aquatic metabolism contributes to net CO_2 emissions when NEP is negative—that is, when ecosystem respiration is greater than gross primary production due to aquatic mineralization of terrestrial OC. Stream and river CO_2 emissions (3.09 $gC\,m^{-2}\,d^{-1}$; 95% CI (high density credible intervals) = 2.95–3.22) exceed rates of internal CO_2 production (0.87 $gC\,m^{-2}\,d^{-1}$; 95% CI = 0.72–1.04) and are of similar magnitude to terrestrial CO_2 fluxes on an areal basis (Supplementary Section 2). Our results show that median internal CO_2 production is 28% of median stream and river CO_2 emissions

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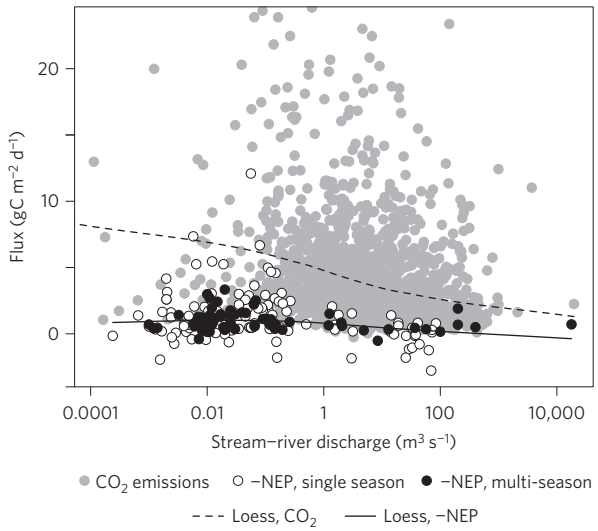

Figure 1 | CO_2 emissions and internal CO_2 production in streams and rivers of the contiguous United States. When negative, aquatic net ecosystem production (NEP) represents internal mineralization of terrestrial organic C and production of CO_2, and thus a distinct net source of CO_2 to the atmosphere. Loess (locally weighted regression) lines for CO_2 and −NEP are for visual interpretation. The upper *y* axis was cut at the 97.5% quantile of CO_2 fluxes to focus on most data.

(credible range = 26–31%; Fig. 1 and Supplementary Table 2-1). By subtraction, 72% of stream–river CO_2 emissions are from other sources (credible range = 69–74%), primarily terrestrially derived CO_2 (but may also derive from internal abiotic CO_2 production; see Supplementary Section 1).

Aquatic CO_2 emissions decline from streams to rivers (Fig. 1 and Supplementary Table 2-1). Further, small streams have highly variable NEP and larger rivers are more metabolically balanced, although there are far fewer metabolism estimates for rivers than streams (Fig. 1 and Supplementary Fig. 2-1). Median internal CO_2 production increases from 14% (credible range = 10–19%) of emissions in the smallest streams (<0.01 m^3 s^{-1}) to 39% (credible range = 25–54%) in the largest rivers (>100 m^3 s^{-1}) (Fig. 2a and Supplementary Table 2-1). The metabolism data available limited our comparison among mid-sized and large rivers: most estimates for mid-sized (10–100 m^3 s^{-1}) rivers are from a single season during productive summer months when net internal production was ~0% of calculated CO_2 emissions (Supplementary Table 2-1). It is difficult to know how much of this low contribution from internal production is a size- or season-specific trend, but we expect contributions of metabolism to CO_2 fluxes vary intra-annually. For example, a comparison of separate analyses of metabolism[18] and CO_2 emissions[19] from the same temperate forest stream suggests that seasonal contributions of metabolism to CO_2 emissions vary from 15–50%, with the most CO_2 sourced from internal production in autumn and least in winter. Accordingly, our results provide preliminary insights of controls on CO_2 emissions across size gradients of running waters, but also highlight the need for direct comparative studies of annual CO_2 dynamics throughout stream–river networks.

Although we did observe increased CO_2 emissions from internal production with stream size (Figs 1 and 2a), internal production was only 39% of estimated emissions in larger rivers (>100 m^3 s^{-1}). If present methods overestimate CO_2 emissions, we may underestimate the contributions of aquatic CO_2 production to net emissions. Of the few studies reporting both CO_2 emissions and metabolism for larger rivers, internal production in the Clark Fork and Hudson Rivers was 85% and 97% of CO_2 emissions, respectively[12,17]. In contrast, annual Mississippi River metabolism[20]

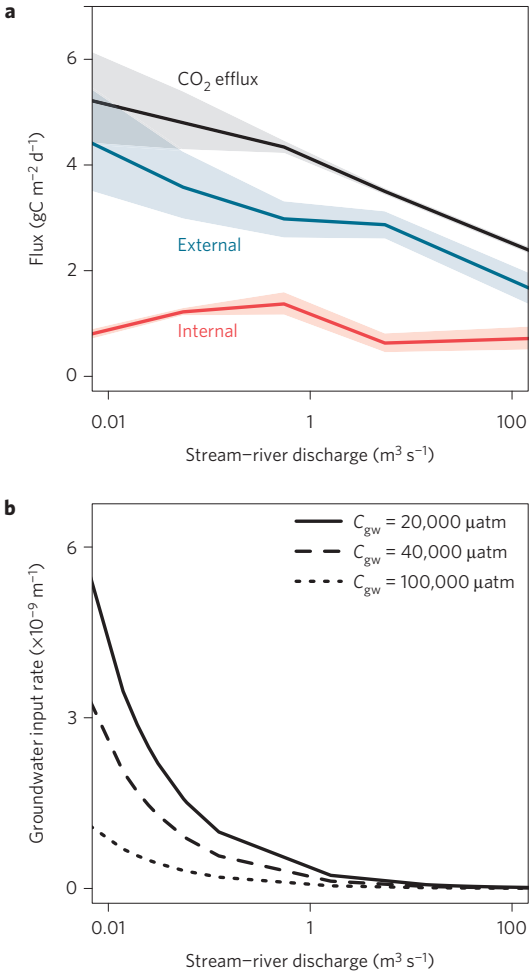

Figure 2 | Modelled CO_2 fluxes and groundwater input rates along a stream–river continuum. a, Binned discharge-specific estimates for CO_2 efflux and internal production and, by subtraction, external CO_2 inputs. Solid lines are median fluxes; shaded regions represent 25–75% credible intervals. These fluxes were used to model the range of groundwater discharge and input rates needed to sustain a steady state balance between internal CO_2 production, external CO_2 inputs and CO_2 efflux (see Methods and Supplementary Section 2). **b**, Modelled stream–river groundwater proportional input rates (k_{gw}) needed to support estimated CO_2 fluxes (**a**) given a range of potential groundwater CO_2 concentrations (C_{gw}).

only accounts for 22% of CO_2 emissions estimated by a separate study[9]. Similarly, Amazon water column respiration contributes only ~20% of river emissions[21] despite rapid rates of terrestrial OC breakdown in rivers[22], probably due to substantial CO_2 inputs from adjacent wetlands[21] as well as internal CO_2 production in river benthic and hyporheic zones. For some rivers, connectivity with floodplains may thus have key implications for rates of CO_2 inputs and emissions, more so than discharge, stream order, or other size-based descriptors. Given that most rivers are managed and no longer interact naturally with their floodplains, this mechanism supporting aquatic CO_2 evasion may be disrupted, but inclusion of floodplains and wetlands will greatly broaden our perspective of aquatic contributions to integrated C budgets.

The amount of groundwater needed to increase CO_2 in rivers is large compared to streams, but low-volume high-CO_2 inputs can still contribute greatly to river CO_2 emissions. Our discharge-specific comparisons of larger-river CO_2 emissions and metabolism suggest that ~60% of CO_2 evasion is from sources other than internal production. To test if external CO_2 inputs could be derived from

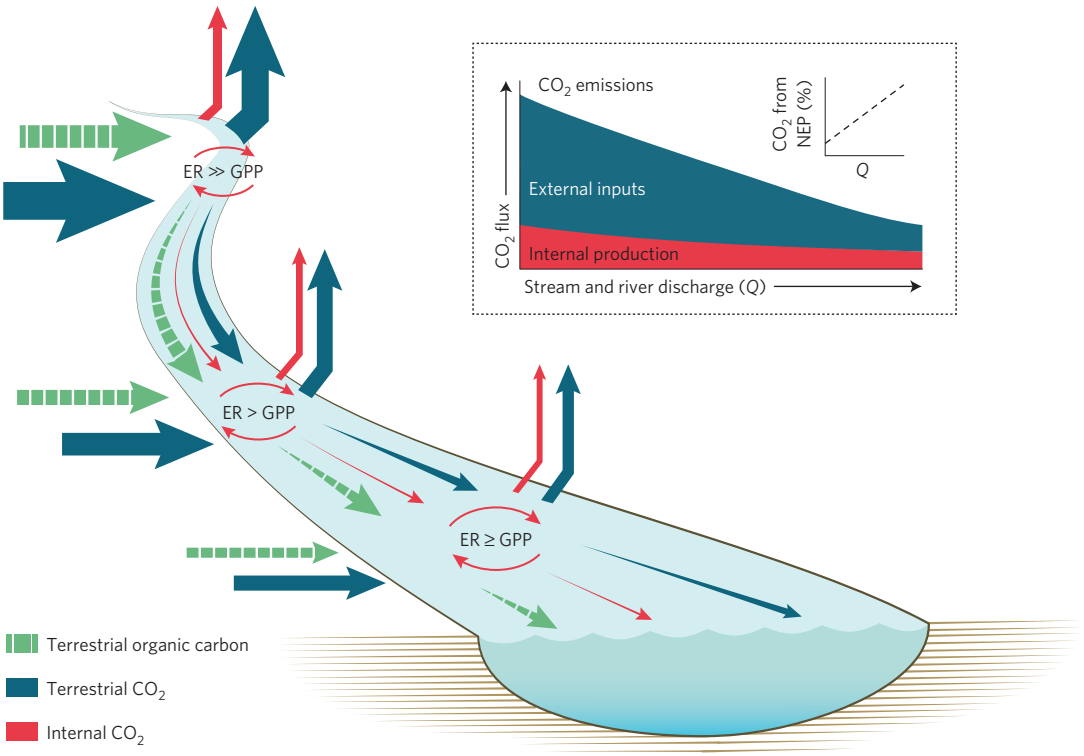

Figure 3 | Sources and magnitude of net CO_2 emissions along a theoretical stream–river continuum. Terrestrially derived CO_2 and organic carbon inputs per unit aquatic area decline downstream, decreasing net CO_2 emission rates in rivers compared to streams. Rapid loss of CO_2 results in a downstream shift in the source contributions to CO_2 emissions, from dominance of external CO_2 in streams to a more balanced supply of internal and external sources in rivers. Thus, aquatic mineralization of terrestrial OC (CO_2 from NEP) should contribute to a higher proportion of annual net CO_2 emissions in large rivers relative to small streams.

groundwater inputs without unreasonable downstream increases in discharge, we modelled lateral groundwater inputs required to sustain flux rates given stream–river trends in CO_2 emissions and internal production (see Methods and Fig. 2a). Groundwater CO_2 inputs needed to sustain estimated CO_2 emissions decrease with stream–river discharge under modelled steady-state conditions (Fig. 2a). Despite higher cumulative groundwater inputs in rivers than streams, our model predicts decreasing proportional input rates along a stream–river continuum (k_{gw}; Fig. 2b). Although there are few data available to put modelled rates in the context of hydrologic predictions, lateral flow velocities (1.5×10^{-8} to 9×10^{-13} m s^{-1}) for modelled groundwater CO_2 and stream–river discharge (Fig. 2b) are realistic as they are within the same range as soil hydraulic conductivity at partial and full saturation[23]. Furthermore, lateral input rates are reasonable in that they do not drastically increase stream–river discharge. For example, the distance to double discharge from modelled groundwater inputs alone ($1/k_{gw}$) is >100,000 km for larger streams and rivers.

On the basis of our findings we propose a framework for considering sources and mechanisms controlling CO_2 emissions along a theoretical stream–river continuum (Fig. 3). Terrestrial CO_2 and OC inputs per unit area should decrease from streams to rivers[24], together leading to lower downstream rates of CO_2 evasion in many river networks. The sources contributing to CO_2 emissions will shift downstream due to varying input, production and loss rates of CO_2 versus OC. We predict that lateral inputs of excess CO_2 to streams from surrounding terrestrial ecosystems are lost more rapidly (mainly controlled by turbulence) compared to the coupled mineralization and loss of OC inputs (controlled by biological and physical processes), implying that a greater fraction of OC will be transported and potentially fuel heterotrophic respiration downstream[24]. Consequently, terrestrially derived CO_2 is the dominant source of stream emissions, despite high terrestrial OC subsidies and internal CO_2 production, while internal production should account for a larger proportion of river CO_2 emissions (Fig. 3). While we found that internal CO_2 production does indeed contribute to a higher proportion of emissions from large rivers than streams, internal production was still <50% of river CO_2 emissions, suggesting a large gap in our present knowledge of river CO_2 dynamics and/or metabolism. To recognize contributions of streams and rivers to CO_2 emissions and large-scale C budgets, we must further explore hypothesized spatial dynamics of terrestrial C inputs and aquatic CO_2 production throughout stream–river networks (Fig. 3). Coupled measurements of lateral C inputs, aquatic metabolism, emissions and export will allow us to test our understanding of the role of running waters in integrated C budgets and advance our knowledge of processes controlling freshwater C dynamics.

Streams and rivers not only relocate and emit terrestrially derived CO_2 to the atmosphere, but also act as active reactors by mineralizing terrestrial OC, which contributes significantly to running water CO_2 emissions. By compiling and comparing large data sets of metabolism and CO_2 emissions, we provide initial evidence that aquatic mineralization of terrestrial OC produces, on average, 28% of CO_2 emissions from running waters. Direct inputs of CO_2 from land and fringing wetlands thus probably support the bulk of stream and river efflux, and our modelling results indicate these inputs can be achieved without invoking unreasonable hydrologic assumptions. Our findings reinforce the notion that running waters must be included in larger-scale C budgets to constrain terrestrial C cycling and fate. Furthermore, we can better identify drivers of inland water C fluxes by considering the mechanisms controlling C inputs from land, aquatic metabolism and CO_2 emissions. Future increases in terrestrial OC exports may fuel aquatic respiration and CO_2 emissions from inland waters[25],

with unknown consequences at catchment and global scales. The effects of future changes in climate and land use for stream and river CO_2 emissions will vary for freshwater ecosystems dominated by inputs of organic versus inorganic C from the landscape. Our effort to partition internal and external sources of stream and river CO_2 emissions represents an essential first step towards understanding these consequences. Without considering the diverse controls on C dynamics in integrated land–water budgets, we cannot anticipate how these dynamics will respond to future environmental change.

Methods

Methods and any associated references are available in the online version of the paper.

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Author contributions

E.R.H. developed the ideas for this analysis and conceptual model in collaboration with J.Karlsson, R.O.H., R.A.S., J.Klaminder, M.R. and H.L. R.O.H. and E.R.H. derived the lateral inputs model and reviewed published metabolism estimates. D.B. provided CO_2 and k_{600} estimates. E.R.H. analysed the data. E.R.H. wrote the paper with assistance from J.Karlsson, R.O.H., R.A.S., D.B., J.Klaminder, H.L. and M.R.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to E.R.H.

Competing financial interests

The authors declare no competing financial interests.

Methods

Internal CO_2 production in running waters. We used aquatic metabolism to budget stream and river internal CO_2 production. NEP reflects the balance between gross primary production (GPP) and ecosystem respiration (ER) where

$$\mathrm{NEP} = \mathrm{GPP} - |\mathrm{ER}|$$

and ER is a negative flux of O_2 consumption. Negative NEP occurs when aquatic ER is subsidized by terrestrial OC, making that ecosystem a net CO_2 source. Conversely, ecosystems with positive NEP (GPP > |ER|) are net CO_2 sinks. We used a compilation of whole-ecosystem stream and river metabolism data updated from a previous study[14] to estimate site-specific NEP (full citation list in Supplementary Section 3). We limited our NEP estimates to streams and rivers in the contiguous US with reported discharge ($n = 187$). We calculated a single site-specific average NEP for streams and rivers with multiple metabolism estimates within or among publications. Median NEP was similar among regions of the US (Supplementary Fig. 2-2). We grouped NEP by measurement period in addition to discharge: metabolism from one day to several months within one season was labelled as 'single season'. Estimates from two or more seasons were grouped as 'multi-season'.

CO_2 emissions from streams and rivers. Stream and river p_{CO_2} was calculated from alkalinity, pH and temperature[9] from United States Geological Survey National Water Quality Information System (USGS NWIS) monitoring sites with pH > 5.4. We modelled normalized air–water gas exchange velocities (k_{600}; m s^{-1}) using the relationship between k_{600}, stream slope (s; m m^{-1}) and velocity (v; m s^{-1}; ref. 26). Stream slopes were derived using NHDPlus and velocity estimates were calculated from hydraulic geometry coefficients using USGS monitoring site data[9,27]. We converted k_{600} to k_{CO_2} using site-specific water temperatures and Schmidt number scaling[26]. Because p_{CO_2} was calculated and k modelled, we removed potential outliers by excluding sites with <50 days of measurements. This left us with 1463 site-specific estimates of p_{CO_2} and k_{CO_2} for a range of streams and rivers in the contiguous US (updated data set from an earlier data compilation[9]; data distributions in Supplementary Fig. 2-3; USGS sites listed in Supplementary Section 4). We converted p_{CO_2} (μatm) to CO_2 concentrations (gC m^{-3}), and calculated site-specific CO_2 emissions (gC m^{-2} d^{-1}) for comparison with other C fluxes:

$$\mathrm{Flux}CO_2 = k_{CO_2}\,(CO_{2,\mathrm{atm}} - CO_{2,\mathrm{stream}})$$

For further information on the data used for $FluxCO_2$ estimates see Data availability below.

Contributions of internal production to stream and river CO_2 emissions. We estimated the percentage of CO_2 emission fluxes from internal production, where

$$\%CO_2 \text{ from internal production} = \frac{-\mathrm{NEP}}{\mathrm{Flux}CO_2}$$

We used −NEP for comparisons with other positive C fluxes because values of NEP < 0 reflect |ER| > GPP, and therefore internal net production of CO_2 (for example, if NEP = −2 gC m^{-2} d^{-1}, we used −NEP = 2 to compare with positive $FluxCO_2$ values, which represent an efflux of CO_2 to the atmosphere). To assess how CO_2 sources change throughout aquatic networks, we binned streams and rivers by discharge: <0.01, 0.01–0.1, 0.1–1.0, 1.0–10, 10–100 and >100 m^3 s^{-1} (Supplementary Table 2-1). We used locally weighted regression (*loess.smooth* in R; ref. 28) to visually interpret discharge-specific trends in $FluxCO_2$ and NEP (Fig. 1).

Simulating external CO_2 inputs along a stream–river continuum. To estimate potential groundwater inputs for streams and rivers (Fig. 2a), we assumed primary sources of CO_2 were aquatic NEP and groundwater inputs (see expanded discussion in Supplementary Section 1) and calculated external fluxes as

$$\mathrm{External}CO_2 = \mathrm{Flux}CO_2 - (-\mathrm{NEP}) \quad (1)$$

We can use the relationship between external CO_2 inputs, emissions, and internal production to solve for unknown parameters of interest in CO_2 budgets. Along a given length of stream (x), downstream changes in CO_2 (C) are a function of groundwater inputs, gas exchange, and internal production, where

$$\frac{dC}{dx} = (k_{gw}\,C_{gw}) + (k_C\,(C_a - C)) + \left(\mathrm{NEP}\,\frac{w}{Q_s}\right) \quad (2)$$

CO_2 gains or losses from the stream are a function of atmospheric and stream CO_2 (C_a and C; gC m^{-3}) and the air–water gas exchange rate for CO_2 (k_C; m^{-1}). NEP is normalized by stream width (w; m) and discharge (Q_s; m^3 s^{-1}). Inputs are a product of groundwater CO_2 (C_{gw}; gC m^{-3}) and a proportional groundwater input rate (k_{gw}; m^{-1}). k_{gw} is derived from estimates of lateral groundwater inflow (Q_L = groundwater discharge (Q_{gw}) per metre downstream; m^3 s^{-1} m^{-1}; refs 29,30), where

$$Q_L = \frac{Q_{gw}}{x}$$

Dividing Q_L by Q_s gives a per metre rate of lateral groundwater inputs relative to Q_s. Thus, calculating k_{gw} simplifies to

$$k_{gw} = \frac{Q_L}{Q_s}$$

Steady-state model simulations ($dC/dx = 0$) were used to show how k_{gw} scales with Q_s (Fig. 2b): we estimated the range of groundwater inputs based on equations (1) and (2), where CO_2 fluxes from groundwater are the product of k_{gw} and CO_2 (C_{gw}). We used a range of possible C_{gw} given the highest stream CO_2 from USGS sites (20,000 μatm) and the high-end of published soilwater CO_2 (40,000–100,000 μatm; refs 19,31). We checked estimates of groundwater input velocities against measured soil hydraulic conductivity values[23] to ensure modelled inputs were realistic. In this simulation, we assumed in-stream production of CO_2 was from −NEP. We did not separate abiotic processes from what we refer to as external CO_2 inputs (Supplementary Section 1), but equation (2) could be expanded to include other distinct sources of CO_2 (further discussion in Supplementary Section 2).

Markov chain Monte Carlo sampling from metabolism and CO_2 emissions data. We used Markov chain Monte Carlo (mcmc) sampling to quantify the certainty of reviewed, binned and simulated CO_2 fluxes. We estimated Bayesian means, medians and credible intervals for CO_2 fluxes from posterior probability distributions derived from mcmc random samples from prior literature data, and used these to propagate uncertainty in model estimates of external inputs (Fig. 2a). The robust medians and credible intervals derived from these simulations allowed us to provide a stronger quantitative case for decreasing contributions of terrestrial CO_2 to stream–river CO_2 emissions with increasing stream size (and, thus, an increasing downstream role for aquatic CO_2 production).

We used mcmc and Gibbs sampling to generate 100,000 random samples from each set of binned data parameters, using a t distribution and acknowledging skewness in our data (Supplementary Fig. 2-3), with code from the BEST package in R for a single parameter[28,32–35]. We selected this method because assuming the data were normally distributed, forcing the data to other distribution forms, or standard bootstrapping with replacement sampling yielded posterior distributions that did not reflect the shape and central tendency of our original data. All 100,000 mcmc simulations were used to generate posterior distributions for each flux parameter, calculate 2.5, 25, 75 and 97.5% credible intervals around median (50%) parameter values (Supplementary Fig. 2-4), and quantify the uncertainty in binned and total CO_2 flux estimates (Supplementary Table 2-1 and Fig. 2a). We used medians and 25–75% credible intervals from CO_2 emissions ($FluxCO_2$) and metabolism (−NEP) posterior distributions to estimate external CO_2 input ($ExternalCO_2$) medians and credible intervals (equation (1) and Fig. 2a), where:

$$\mathrm{External}CO_{2_{\mathrm{median}}} = \mathrm{Flux}CO_{2_{\mathrm{median}}} - (-\mathrm{NEP}_{\mathrm{median}})$$

$$\mathrm{External}CO_{2_{25\%CI}} = \mathrm{Flux}CO_{2_{25\%CI}} - (-\mathrm{NEP}_{75\%CI})$$

$$\mathrm{External}CO_{2_{75\%CI}} = \mathrm{Flux}CO_{2_{75\%CI}} - (-\mathrm{NEP}_{25\%CI})$$

Data availability. Citations for the metabolism data used in these analyses are listed in Supplementary Section 3. Data used to calculate stream and river CO_2 concentrations and velocity are available from USGS NWIS (http://waterdata.usgs.gov/nwis). Data used to estimate stream slope are available from NHDPlus (http://www.horizon-systems.com/nhdplus). USGS water chemistry parameter codes and IDs for the sites included in our analyses are listed in Supplementary Section 4.

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