

Significant efflux of carbon dioxide from streams and rivers in the United States

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The evasion of carbon dioxide from inland waters was only recently included in assessments of the global carbon budget^{1–3}. Present estimates of carbon dioxide release from global freshwater systems, including lakes and wetlands, range from 0.7 to 3.3 Pg C yr⁻¹ (refs 1,4–7). However, these estimates are based on incomplete spatial coverage of carbon dioxide evasion, and an inadequate understanding of the factors controlling the efflux of carbon dioxide across large drainage networks⁶. Here, we estimate the amount of carbon degassed from streams and rivers in the United States using measurements of temperature, alkalinity and pH, together with high-resolution data on the morphology and surface area of these waterways. We show that streams and rivers in the US are supersaturated with carbon dioxide when compared with the atmosphere, emitting 97 ± 32 Tg carbon each year. We further show that regionally, carbon dioxide evasion from streams and rivers is positively correlated with annual precipitation, which we attribute to climatic regulation of stream surface area, and the flushing of carbon dioxide from soils. Scaling our analysis from the US to temperate rivers between 25° N and 50° N, we estimate a release of around 0.5 Pg carbon to the atmosphere each year.

Stream and river dissolved CO₂ originates largely from terrestrial ecosystem respiration entering the hydrosphere as dissolved soil CO₂, the oxidation of allochthonous and emergent autochthonous organic carbon, the acidification of buffered waters, the precipitation of carbonate minerals, and the direct pumping of root respiration CO₂ from riparian vegetation. The relative importance of these sources coupled with their response to anthropogenic disturbance impacts how we include stream and river CO₂ evasion in global and regional budgets. The source can change spatially in a large basin such as the Mississippi from terrestrial soil respiration and the influence of agricultural liming in the Ohio and upper Mississippi to *in situ* respiration of allochthonous organic matter in the lower Mississippi⁸ (further discussion in Supplementary Information). Regardless of the source, inland streams and rivers tend to be supersaturated when compared with the atmosphere, and are a source of atmospheric CO₂ (ref. 6).

Streams and rivers of the US show a clear dominance of supersaturation with respect to the atmosphere (Fig. 1). The partial pressure of CO₂ was found to decrease as a function of stream order, showing an average decrease of 128 μatm with increasing stream order for the entire US data set (Fig. 2a). This relationship varied from a decrease of 447 μatm by stream order in the Gulf region to slightly positive in the Southwest (Supplementary Table S.5). Small streams have been shown through field analysis to contain very high concentrations of dissolved CO₂ (refs 9,10) and this overall decreasing trend in p_{CO_2} is consistent with the rapid degassing of CO₂ transported to small streams from terrestrial soil water.

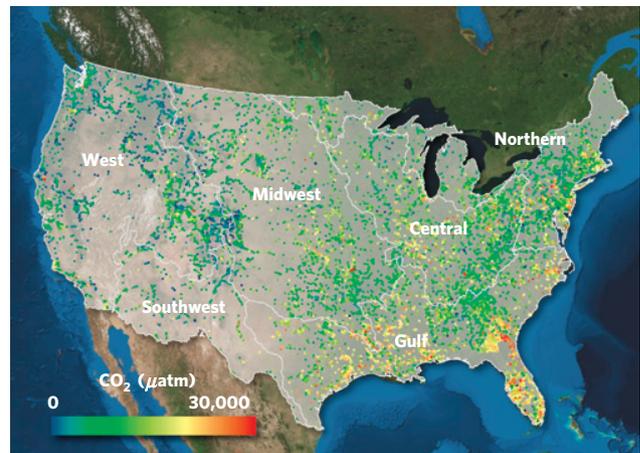


Figure 1 | Spatial distribution of USGS sampling locations and CO₂ concentrations across the US. Average concentration at and distribution of USGS gauging stations used to calculate CO₂ efflux from US streams and rivers. The names correspond to the subregions discussed in the text.

We calculated a total conterminous US stream/river surface area of 40,600 km² (Supplementary Information). This represents 0.52% of the total land area of the conterminous US. Estimates of stream surface area vary between 0.2% and 1.5% of the total watershed area and our estimates fall within this range^{5,11} (Fig. 2b, Supplementary Table S.2.2, Supplementary Information). According to our analysis, first-order streams represent the highest proportion of the total stream surface area at 20% (Supplementary Table S.4.2 and Fig. S.7). Owing to the high concentration of CO₂ within small streams, including the smallest streams not modelled in our analysis could result in an upward refinement of CO₂ evasion.

The variability in the gas transfer velocity (k ; Supplementary Information) across different systems has been shown to be a function of turbulence at the air–water interface¹². Our model predicts that gas transfer velocities decreased with increasing stream order (Fig. 2b). In smaller systems below stream order 4, values for k are similar across regions at ~ 4.5 m d⁻¹ whereas the largest reaches of the Mississippi at stream order 10 were less than 2.5 m d⁻¹. The highest average (k) of 18 m d⁻¹ was found in the steep headwaters of the West region that includes the Rocky Mountains. Headwater streams tend to originate in areas of steep topography increasing the turbulent energy within the system that directly affects the gas transfer velocity. Across wider rivers with lower slopes, the controls on gas transfer can shift from physical characteristics of the river bed to other mixing mechanisms, and under this condition lower gas transfer velocities are expected¹³.

The higher concentrations, gas transfer velocities and surface area of first-order streams translated to the largest (36%)

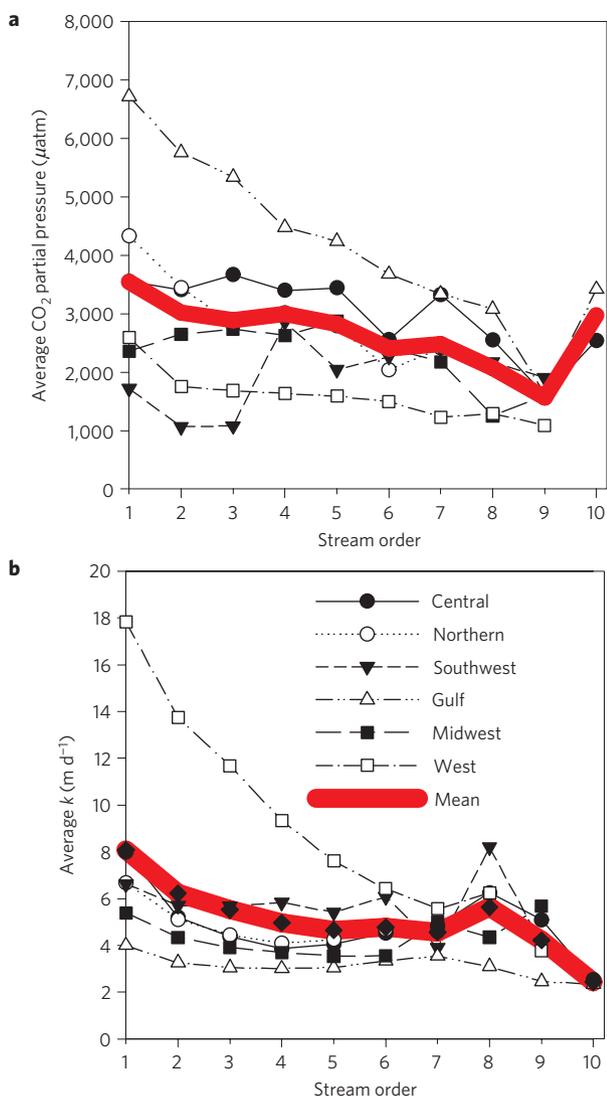


Figure 2 | Distribution of CO₂ flux model parameters across stream orders in the US. **a, b**, Average CO₂ partial pressure (**a**) and the average gas transfer velocity (k ; **b**) across stream orders for the conterminous US. Red lines represent the average values for the US. Changes in CO₂ concentration by stream order across regions ranged from $-447 \mu\text{atm}$ per stream order in the Gulf to $102 \mu\text{atm}$ per stream order for the Southwest (Supplementary Table S.5).

proportion of the total efflux of CO₂ from these systems (Supplementary Fig. S.7). Although CO₂ dissolved in soil water derived from root respiration can be highly concentrated, its concentration is unlikely to be high enough to balance the total evasion of CO₂ across all stream orders¹¹. The conterminous US has an average discharge of between $1,380 \text{ km}^3$ and $1,780 \text{ km}^3$ (Supplementary Information). If we assume soil CO₂ concentrations between $20,000 \mu\text{atm}$ and $30,000 \mu\text{atm}$ for soil water¹⁴, lateral export is between 21 Tg C yr^{-1} and 30 Tg C yr^{-1} and can account for only 21–32% of the total stream/river CO₂ evasion to the atmosphere (Supplementary Information). However, this could explain upwards of 90% of first-order stream evasion.

In the lower Mississippi, stable isotopes indicate that the dominant source of CO₂ is the respiration of allochthonous organic matter⁸. In the Amazon, both floodplain and upland organic matter contribute to the dissolved CO₂ pool¹⁵. Across the US, the average concentrations of organic matter as dissolved organic carbon ranged from 14 mg l^{-1} in first-order streams to 8 mg l^{-1} for

the highest-order rivers within the US Geological Survey (USGS) data set. In general this material is not considered to be highly labile and therefore only a fraction will contribute to the dissolved CO₂ pool. If we assume a loading of 10 mg l^{-1} of dissolved organic carbon across the conterminous US, and 20% of this is used during transport¹⁶, it would generate $\sim 3.56 \text{ Tg of C}$, or only $\sim 3.6\%$ of the calculated CO₂ evasion flux.

We found a strong statistical relationship between annual precipitation and regional CO₂ evasion (Fig. 3a). Interestingly the correlation between precipitation and CO₂ evasion is stronger than discharge and evasion (Supplementary Fig. S.5.1 and Supplementary Information). We reason that there are three factors responsible for the strong correlation between precipitation and carbon flux. First, there is a correlation between stream surface area and precipitation (Fig. 3b) demonstrating that the delivery of water (for example, precipitation) to watersheds is impacting the prevalence and therefore surface area of streams. Furthermore, we suggest that higher annual precipitation leads to higher flushing and delivery of soil and riparian/wetland CO₂ that would otherwise be shunted to the atmosphere directly from terrestrial systems. Finally, rates of precipitation correlate with terrestrial ecosystem fluxes such as annual net primary production^{17,18}. We therefore propose that precipitation impacts stream CO₂ evasion on both short (CO₂ production and flushing) and long (geomorphologic) timescales.

Stream surface area, annual precipitation and both the percentage of forest and the percentage of agriculture within a basin correlate with the total carbon flux (Fig. 3 and Supplementary Fig. S.5.2). The correlation with both forest and agriculture area indicates multiple mechanisms influencing CO₂ efflux. First, forested areas tend to be found in areas of high precipitation. Second, CO₂ partial pressures in soil pore water in forested systems can be greater than $25,000 \mu\text{atm}$ (ref. 14). Third, on average, forested areas are found in steeper topography with higher gas transfer velocities than other dominant land covers. Fourth, agriculture practices have been shown to dominate the carbon balance in the Mississippi River basin, increasing the total alkalinity¹⁹. Thus, the biologically active soil environment influenced by soil and root respiration in forested systems, and the impact of anthropogenic activities in agricultural systems coupled with a large volume of water throughput facilitate the efficient routing of soil CO₂ to a drainage network with high stream surface area (Supplementary Fig. S.5.2). We reason that a similar analysis across many small watersheds would continue to show these land cover relationships.

A comparison of other large basin CO₂ evasion estimates is presented in Table 1. On average, the US streams and rivers emit $2,370 \pm 800 \text{ g C m}^{-2} \text{ yr}^{-1}$ (Table 1). The two highest stream orders that represent the Mississippi had an average flux of $990 \pm 320 \text{ g C m}^{-2} \text{ yr}^{-1}$. This is very close to the $1,182 \pm 390 \text{ g C m}^{-2} \text{ yr}^{-1}$ projected from an isotopic approach on the same system⁸. The main stem of the Xinjiang River, a large subtropical river in China, ranged from 830 to $1,560 \text{ g C m}^{-2} \text{ yr}^{-1}$ (ref. 20). These Northern Hemisphere rivers show high carbon flux rates when compared with the combined estimate of $830 \pm 240 \text{ g C m}^{-2} \text{ yr}^{-1}$ found previously for the large rivers and floodplains of the Amazon²¹. The third–fifth order rivers in the Ji-Parana basin in the southwestern Amazon have a flux of between 226 and $4,780 \text{ g C m}^{-2} \text{ yr}^{-1}$, with an average of $\sim 1,518 \text{ g C m}^{-2} \text{ yr}^{-1}$, which is similar to the $1,950 \text{ g C m}^{-2} \text{ yr}^{-1}$ found across those same stream orders within the US (refs 21,22). A complete comparison of modelled versus measured p_{CO_2} within the US is presented in Supplementary Information. Our headwater concentrations are similar to those found within first-order streams in the Amazon basin¹¹. However, gas transfer velocities are not yet available for the Amazon headwaters to fully compare fluxes. A recent estimate for the stream and river efflux in Sweden gives an average of $1,850 \text{ g C m}^{-2} \text{ yr}^{-1}$ across all streams and rivers²³. This is close to the $2,370 \pm 800 \text{ g C m}^{-2} \text{ yr}^{-1}$ found across the US.

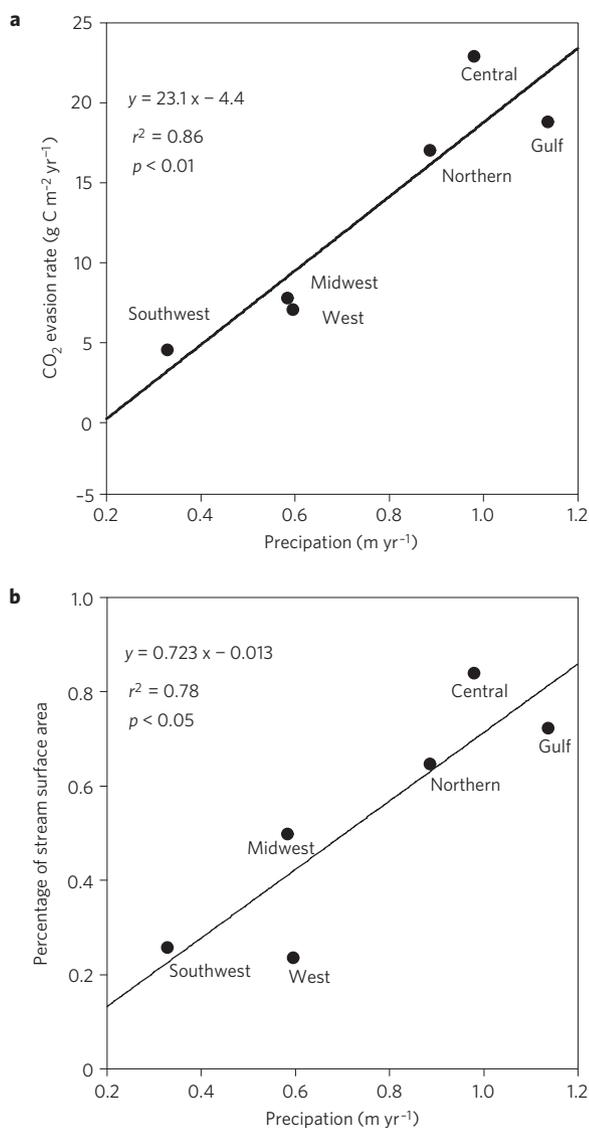


Figure 3 | Precipitation, stream surface area and carbon flux relationships across regions in the US. **a, b**, Relationship between average annual precipitation and the evasion rate of CO₂ in grams of carbon per square meter per year (**a**) and the percentage of surface area of streams and rivers (**b**) within the six subregions defined in the text and illustrated in Fig. 1. Stream surface area is derived from the NHDPlus data set and discharge; methods are discussed in Supplementary Information.

If we assume that on average 0.52% of the total temperate land area between 25° N and 50° N is represented by streams and rivers, this results in a stream surface area of 230,000 km². Using an average flux of 2,370 g C m² yr⁻¹ provides a total flux from northern temperate rivers of 0.54 Pg C yr⁻¹, which alone matches the most recent estimate for all rivers (excluding wetlands) of 0.53 Pg C yr⁻¹ (ref. 5). Alternatively, if we use our relationship between precipitation and flux from Fig. 3a and apply it to a gridded annual precipitation data set for the same temperate region, we obtain an estimate of 0.51 Pg C yr⁻¹ (Supplementary Information). If our extrapolation is accurate, present estimates of temperate stream and river CO₂ flux are underestimating the connection between these systems and the atmosphere⁵. Our research shows a fivefold increase beyond present estimates for the evasion of CO₂ from temperate streams and rivers. Our estimate added to the 0.5 Pg C yr⁻¹ presented previously for rivers and floodplains in the Amazon²¹ gives a ~1.0 Pg C yr⁻¹ flux from the northern temperate

Table 1 | Drainage network CO₂ efflux estimates from other large river systems.

Region	Total C from CO ₂ (Pg yr ⁻¹)	Average efflux (g C m ⁻² yr ⁻¹)	Source
Sweden	8.5 × 10 ⁻⁴	1,850	(ref. 23)
Amazon basin*	0.5	830	(ref. 21)
Mississippi basin†	0.01	1,182	(ref. 8)
Xijiang river‡	2.22 × 10 ⁻⁴	830–1,560	(ref. 20)
Globe	0.56	NA	(ref. 5)
Globe§	0.23	NA	(ref. 6)
Humid tropics	0.9	NA	(ref. 21)
Conterminous US	0.1	882–4,008¶	This study
Temperate zone	0.13	1,675	(ref. 5)
Temperate zone (25° N–50° N)	0.5	2,370#	This Study

Average efflux values are based on the estimated surface areas of streams and rivers. *Calculated for large Amazon rivers and floodplains alone. †Calculated for larger tributaries alone. ‡Calculated for the main stem alone. §This does not include streams. ||This extrapolation includes wetlands and floodplain systems. ¶The range presented here represents the average flux across stream orders 1–10 within the US. # Assumed the area-weighted average of the Conterminous US.

zone and the lowland Amazon basin. Expanding globally to all rivers and streams and including carbon sources such as methane and the degassing from lakes and wetlands will enhance this flux²⁴ (Supplementary Information).

Outgassing of CO₂ from inland waters is now gaining acceptance into the present paradigm of the global carbon cycle. As demonstrated here the amount of CO₂ degassed in streams and rivers seems to be high, up to 10% of net ecosystem exchange in the US (ref. 25). Unfortunately, at present, it is impossible to determine how to partition this CO₂ source into global carbon budgets (Supplementary Information). One possibility is that it may alter the carbon balance of terrestrial systems¹. We feel that, although this may be true, a significant component of stream and river evasion is simply a relocation of terrestrial respiration to downstream evasion. Dissolved inorganic carbon in streams and rivers can also have a significant older component²⁶. Thus, further research is needed to determine the amount of inland waters CO₂ evasion derived from recently fixed atmospheric CO₂ (ref. 15) and allochthonous production and respiration⁸ versus ancient sources of soil organic carbon or carbonate weathering^{27,28}. Finally, there is a dearth of direct measurements of both CO₂ concentrations and fluxes in streams and rivers and future measurements are necessary to help refine regional estimates such as those made here.

Methods

A discussion of how regions were defined across the US is presented in the methods section of the Supplementary Information. For this study we calculated CO₂ flux (f_{CO₂-C(g)}) by stream order within each of our six regions according to:

$$f_{CO_2-C(g)} = \sum_{Region} \left[\sum_{SO} [(CO_2]_{water} - [CO_2]_{air}) \times k_{CO_2} \times SA \right] \quad (1)$$

where [CO₂]_{water} and [CO₂]_{air} are the molar concentrations of CO₂ dissolved in the water and water in equilibrium with the atmosphere, k_{CO₂} is the gas transfer velocity for CO₂ (m d⁻¹), SA is the surface area of streams and rivers (m²) and SO is the stream order within a region. The calculation of dissolved CO₂ is derived from measurements of pH, temperature and alkalinity for 4138 USGS gauging station locations across the US (Fig. 1 and Supplementary Information). We used the National Hydrography Dataset Plus (NHDPlus) data set to determine the total stream length, average slope, average velocity and average discharge for each stream order within a region²⁹. We used scaling laws to then calculate width from discharge for each stream order³⁰ (Supplementary Information). We assigned each stream order a value for k_{CO₂} from a model developed to predict the gas transfer velocity from the slope and velocity of streams (Supplementary

Information). The total surface area of streams for each stream order in each region was calculated as a product of length and width. For CO₂ we binned annual average CO₂ concentrations by stream order within each region and calculated the average. Then for each stream order within a region we use equation (1), assuming a uniform atmospheric concentration of CO₂ of 390 μatm, to calculate a total evasion for each region. A discussion of both model uncertainty and parameter uncertainty, including the calculation of CO₂ from alkalinity and pH, is presented in Supplementary Information. The final results of equation (1) are presented as grams of carbon per year converted from micromoles of CO₂ per year.

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Author contributions

D.B. and P.A.R. conceived and designed the analysis. D.B. carried out all computations and data analysis and wrote most of the manuscript. P.A.R. supervised the research, aided in interpretation of the data and helped write the manuscript.

Additional information

The authors declare no competing financial interests. Supplementary information accompanies this paper on www.nature.com/naturegeoscience. Reprints and permissions information is available online at <http://www.nature.com/reprints>. Correspondence and requests for materials should be addressed to D.B.