# 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 networks[6]. 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 CO_2 originates largely from terrestrial ecosystem respiration entering the hydrosphere as dissolved soil CO_2, 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 CO_2 from riparian vegetation. The relative importance of these sources coupled with their response to anthropogenic disturbance impacts how we include stream and river CO_2 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 Mississippi[8] (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 CO_2 (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 CO_2 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 CO_2 (refs 9,10) and this overall decreasing trend in p_{CO_2} is consistent with the rapid degassing of CO_2 transported to small streams from terrestrial soil water.
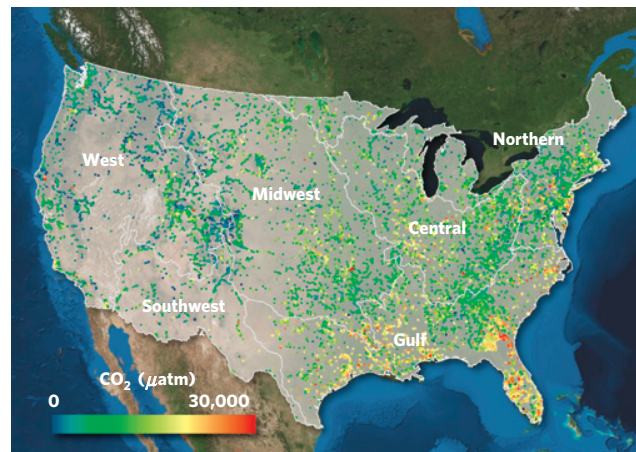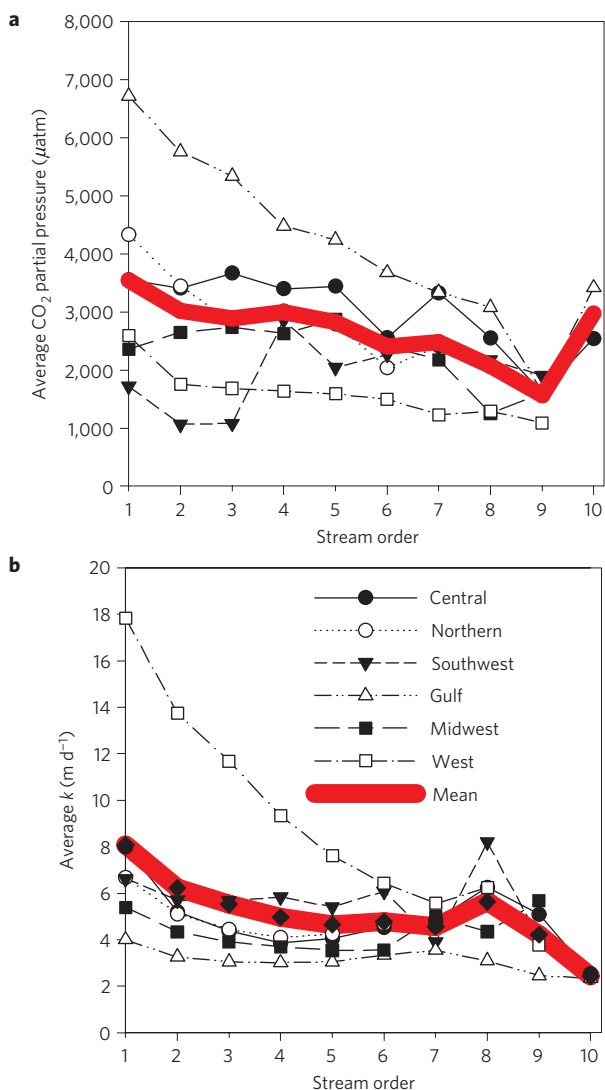

Figure 1 | Spatial distribution of USGS sampling locations and CO$_2$ concentrations across the US. Average concentration at and distribution of USGS gauging stations used to calculated CO_2 efflux from US streams and rivers. The names correspond to the subregions discussed in the text.

We calculated a total conterminous US stream/river surface area of 40,600 km^2 (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 CO_2 within small streams, including the smallest streams not modelled in our analysis could result in an upward refinement of CO_2 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 interface[12]. 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 expected[13].

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

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Figure 2 | Distribution of CO_2 flux model parameters across stream orders in the US. a,b, Average CO_2 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 CO_2 concentration by stream order across regions ranged from −447 μatm per stream order in the Gulf to 102 μatm per stream order for the Southwest (Supplementary Table S.5).

proportion of the total efflux of CO_2 from these systems (Supplementary Fig. S.7). Although CO_2 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 CO_2 across all stream orders[11]. The conterminous US has an average discharge of between 1,380 km³ and 1,780 km³ (Supplementary Information). If we assume soil CO_2 concentrations between 20,000 μatm and 30,000 μatm for soil water[14], 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 CO_2 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 CO_2 is the respiration of allochthonous organic matter[8]. In the Amazon, both floodplain and upland organic matter contribute to the dissolved CO_2 pool[15]. 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 CO_2 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 transport[16], it would generate ∼3.56 Tg of C, or only ∼3.6% of the calculated CO_2 evasion flux.

We found a strong statistical relationship between annual precipitation and regional CO_2 evasion (Fig. 3a). Interestingly the correlation between precipitation and CO_2 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 CO_2 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 CO_2 evasion on both short (CO_2 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 CO_2 efflux. First, forested areas tend to be found in areas of high precipitation. Second, CO_2 partial pressures in soil pore water in forested systems can be greater than 25,000 μatm (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 alkalinity[19]. 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 CO_2 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 CO_2 evasion estimates is presented in Table 1. On average, the US streams and rivers emit 2,370 ± 800 g C m⁻² yr⁻¹ (Table 1). The two highest stream orders that represent the Mississippi had an average flux of 990 ± 320 g C m⁻² yr⁻¹. This is very close to the 1,182 ± 390 g C m⁻² yr⁻¹ projected from an isotopic approach on the same system[8]. The main stem of the Xinjiang River, a large subtropical river in China, ranged from 830 to 1,560 g C m⁻² yr⁻¹ (ref. 20). These Northern Hemisphere rivers show high carbon flux rates when compared with the combined estimate of 830 ± 240 g C m⁻² yr⁻¹ found previously for the large rivers and floodplains of the Amazon[21]. The third–fifth order rivers in the Ji-Parana basin in the southwestern Amazon have a flux of between 226 and 4,780 g C m⁻² yr⁻¹, with an average of ∼1,518 g C m⁻² yr⁻¹, which is similar to the 1,950 g C m⁻² 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 basin[11]. 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 g C m⁻² yr⁻¹ across all streams and rivers[23]. This is close to the 2,370 ± 800 g C m⁻² yr⁻¹ found across the US.
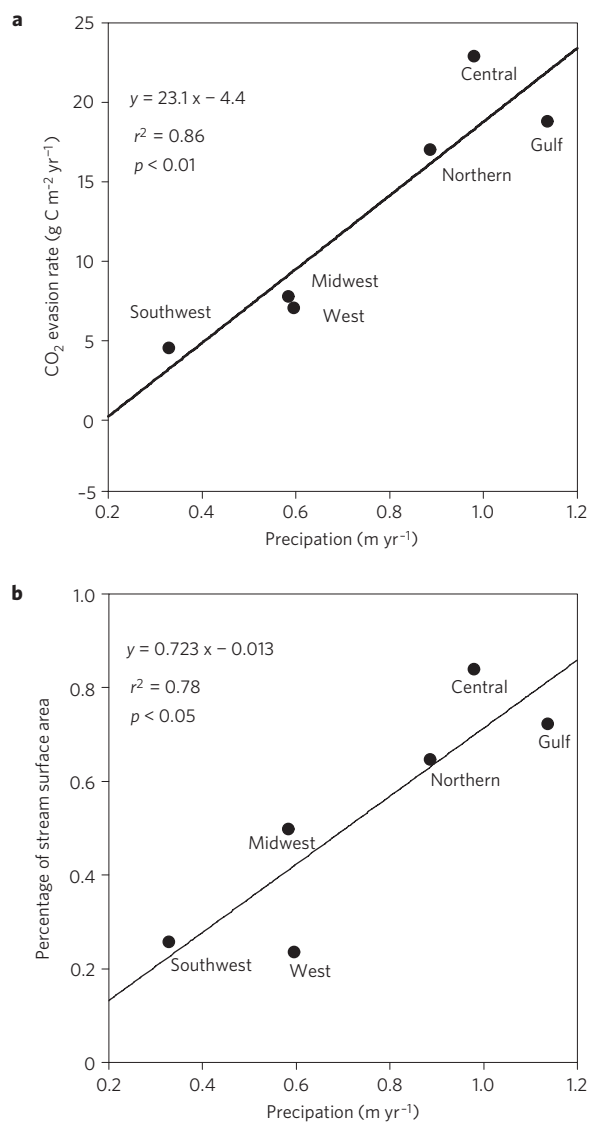
Figure 3 | Precipitation, stream surface area and carbon flux relationships across regions in the US. a,b, Relationship between average annual precipitation and the evasion rate of CO_2 in grams of carbon per square meter per year (**a**) and the percentage of surface area of streams and rivers (**b**) 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 km^2. Using an average flux of 2,370 g C m^2 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 CO_2 flux are underestimating the connection between these systems and the atmosphere[5]. Our research shows a fivefold increase beyond present estimates for the evasion of CO_2 from temperate streams and rivers. Our estimate added to the 0.5 Pg C yr^{-1} presented previously for rivers and floodplains in the Amazon[21] gives a ~1.0 Pg C yr^{-1} flux from the northern temperate

Table 1 | Drainage network CO_2 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 flux[24] (Supplementary Information).

Outgassing of CO_2 from inland waters is now gaining acceptance into the present paradigm of the global carbon cycle. As demonstrated here the amount of CO_2 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 CO_2 source into global carbon budgets (Supplementary Information). One possibility is that it may alter the carbon balance of terrestrial systems[1]. 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 component[26]. Thus, further research is needed to determine the amount of inland waters CO_2 evasion derived from recently fixed atmospheric CO_2 (ref. 15) and allochthonous production and respiration[8] versus ancient sources of soil organic carbon or carbonate weathering[27,28]. Finally, there is a dearth of direct measurements of both CO_2 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 CO_2 flux (fCO_2–C(g)) by stream order within each of our six regions according to:

$$f CO_2\text{–}C(g) = \sum_{\text{Region}} \left[\sum_{\text{SO}} [([CO_2]_{\text{water}} - [CO_2]_{\text{air}}) \times kCO_2 \times SA] \right] \quad (1)$$

where $[CO_2]_{\text{water}}$ and $[CO_2]_{\text{air}}$ are the molar concentrations of CO_2 dissolved in the water and water in equilibrium with the atmosphere, kCO_2 is the gas transfer velocity for CO_2 (m d^{-1}), SA is the surface area of streams and rivers (m^2) and SO is the stream order within a region. The calculation of dissolved CO_2 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 region[29]. We used scaling laws to then calculate width from discharge for each stream order[30] (Supplementary Information). We assigned each stream order a value for kCO_2 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 CO_2 we binned annual average CO_2 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 CO_2 of 390 µatm, to calculate a total evasion for each region. A discussion of both model uncertainty and parameter uncertainty, including the calculation of CO_2 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 CO_2 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.