Long-term decline in carbon dioxide supersaturation in rivers across the contiguous United States

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[1] The partial pressure CO_2 (pCO_2) in streams and rivers reflects both internal carbon dynamics and external biogeochemical processes in terrestrial ecosystems. CO_2 is typically supersaturated in streams because rates of organic matter decomposition exceed photosynthetic uptake, and because of inflow of CO₂ supersaturated ground waters. Using the U.S. Geological Survey's NASQAN database, we calculated pCO₂ and dissolved inorganic carbon (DIC) concentration in 417 streams and rivers distributed across the contiguous United States over a 22-year period. In addition to demonstrating widespread supersaturation and distinct regional variation in pCO_2 across the U.S., our analysis revealed that pCO_2 significantly declined 78.4 ppmv y⁻¹ from 1973 to 1994. This decline is not attributable to changes in terrestrial weathering or instream processes, but instead suggests large-scale declines in terrestrial CO₂ production and import into aquatic ecosystems during this 22-year period. INDEX TERMS: 1615 Global Change: Biogeochemical processes (4805); 1806 Hydrology: Chemistry of fresh water; 1886 Hydrology: Weathering (1625); 1803 Hydrology: Anthropogenic effects. Citation: Jones, J. B., Jr., E. H. Stanley, and P. J. Mulholland, Long-term decline in carbon dioxide supersaturation in rivers across the contiguous United States, Geophys. Res. Lett., 30(10), 1495, doi:10.1029/2003GL017056, 2003.

1. Introduction

[2] The concentration of CO_2 is an important property of aquatic ecosystems, reflecting both internal carbon dynamics and external biogeochemical processes in the terrestrial ecosystem [*Cole et al.*, 1994; *Jones and Mulholland*, 1998a; *Richey et al.*, 2002]. CO₂ and dissolved inorganic carbon (DIC) concentrations in rivers and streams result from an interplay between inorganic carbon fixation via aquatic primary production, organic matter decomposition, import via ground waters, and exchange with the atmosphere [*Hope et al.*, 2001; *Palmer et al.*, 2001]. CO₂ is typically supersaturated in stream and river ecosystems due to instream rate of organic matter decomposition routinely exceeding photosynthetic uptake and because ground water flowing to the channel is often CO₂-rich [*Kling et al.*, 1991,

1992; Jones and Mulholland, 1998b; Cole and Caraco, 2001]. Free CO₂ in ground waters is principally derived from respiration in soil environments, but can also be influenced by weathering production of DIC and alkalinity, and the resulting changes in pH. The flux of ground water enriched with terrestrially-derived (largely soil-respired) CO₂, supplemented by the decomposition of terrestrial organic matter within streams, dominate the aquatic carbon cycle in most rivers, and makes these systems CO₂ super-saturated and net sources of CO₂ to the atmosphere [*Kling et al.*, 1991; Cole et al., 1994; Jones and Mulholland, 1998a, 1998b].

[3] We examined longer-term (22-years) trends in pCO_2 and DIC across the contiguous United States addressing two questions. First, how do pCO_2 and DIC concentration vary over longer-time scales? Second, what regulates longer-term pCO_2 dynamics? Factors potentially affecting pCO_2 that we addressed included changes of in-stream primary production and respiration, rates of weathering and production of DIC and alkalinity, and changes in stream pH.

2. Methods

2.1. Dataset

[4] pCO_2 and DIC were calculated using data collected from 1973 through 1994 by the U.S. Geological Survey's National Stream Water-Quality Monitoring Network (NAS-QAN) program. Stations for NASQAN program were selected to monitor water quality conditions in the major U.S. rivers and streams. Station locations were selected based upon major hydrologic units to satisfy one of the network's primary goals of accounting for chemical mass from the U.S. watersheds. The NASQAN program consisted of 679 stations with watersheds ranging in size from 2.6 km² to 2,900,000 km² of which 50 % were smaller than 11,370 km². Stations were sampled at regular intervals that ranged from monthly to quarterly among stations.

[5] The largest rivers (>50,000 km² catchment) were omitted from the analysis for two reasons. First, we were interested in evaluating watershed scale inorganic carbon export. In larger rivers, in-stream processes are more likely to dominate river chemistry [*Cole and Caraco*, 2001], whereas in smaller rivers and streams chemistry is more strongly influenced by aquatic-terrestrial connections [*Jones and Mulholland*, 1998b]. Second, because the largest catchments consisted of stations aligned along major rivers, the largest rivers were omitted to prevent the same rivers from being repeatedly sampled in the analysis.

2.2. Chemical Analyses

[6] CO₂ and DIC concentrations were calculated with correction for ionic strength of solution using PHREEQC version 2.2 [*Parkhurst and Appelo*, 1999]. We corrected for ionic strength of solution using the concentrations of calcium, magnesium, potassium, sodium, aluminum, chloride, sulfate, iron, selenium, silica, ammonium, nitrate, and phosphate. The calculation of pCO_2 from pH and alkalinity is sensitive to error in pH measurements, particularly at lower pH values. Consequently, stations with a mean pH below 6 (typically those closest to headwaters and draining areas with high soil organic matter pools) were omitted from the analysis.

[7] The concentrations of DIC and H⁺ produced from CO_2 supersaturation and the resulting carbonic acid were calculated as the differences between the total DIC and H⁺ concentrations and the concentrations of DIC and H⁺ with pCO_2 in equilibrium with the atmosphere (360 ppmv) using the Equilibrium Phases module of PHREEQC (eqDIC and eqH^+ , respectively). The increase of atmospheric pCO_2 from 1973 to 1994 from ca. 327 to 360 ppmv would result in a change in eqDIC of only 0.3 % on average. eqDIC and eqH⁺ are derived from weathering of carbonate geologies, such as limestone, which commonly weather as CaCO₃ + $CO_2 + H_2O \rightleftharpoons CaCO_3 + H^+ + HCO_3^- \rightleftharpoons Ca^{2+} + 2HCO_3^-$. As carbonate weathers, alkalinity is generated leading to an increase in pH and a reduction in pCO_2 . Assuming the reaction is reversible, then bicarbonate-carbon originally derived from CO_2 will fully degas as a solution comes into equilibrium with the atmosphere. As organic matter is decomposed and CO₂ is produced, carbonic acid is produced in a reversible reaction through dissociation with water as $CO_2(g) + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons H^+ +$ CO_3^{2-} , which reduces pH and increases the proportion of CO_2 in the total DIC pool (DIC = $CO_2 + HCO_3^- + CO_3^{2-}$).

[8] To test if in-stream processes (i.e., primary production, respiration, and evasion to the atmosphere) solely regulated stream water CO₂, a simple stream metabolism model was used that calculates the pCO_2 from oxygen saturation. The rate of exchange of gases between rivers and the atmosphere is a function of gas concentration ([C]_i) relative to the atmosphere equilibrium concentration ([C]_{atm eq}) and a gas exchange coefficient (k_i ; exchange = $k_i([C]_i - [C]_{atm eq})$. Exchange coefficients are a function of molecular activity (D_i) of gases and coefficients for two gases are related as k₁/ $k_2 = [D_1/D_2]^n$ where n is a exponent ranging from 0.5 to 1.0 [Bennett and Rathbun, 1972; Genereux and Hemond, 1992]. Assuming organic matter is decomposed as $C_6H_{12}O_6 + 6O_2$ \rightarrow 6CO₂ + 6H₂O, then O₂ will be consumed and CO₂ produced at equal molar rates. If gases are regulated solely by in-stream processes then the concentration of CO_2 can be calculated from oxygen as $[CO_2] = - (k_{O2}/k_{CO2})([O_2] - k_{CO2})([O_2])$ $[O_2]_{atm eq}$ + $[CO2]_{atm eq}$. D_{O2} and D_{CO2} were set equal to 2.3 × 10⁻⁵ cm² s⁻¹ [*Wise and Houghton*, 1966] and 1.7 × 10⁻⁵ cm² s⁻¹ [*Jähne et al.*, 1987], respectively, and n as 0.7 [Genereux and Hemond, 1992]. To account for variation in oxygen saturation due to elevation and atmosphere pressure effects, CO₂ concentration was calculated with oxygen



Figure 1. The mean partial pressure of CO_2 (pCO_2 ; panel a), and the annual absolute (panel b) and relative (panel c) rate of change of pCO_2 in stream and river water across the contiguous United States from 1973 through 1994. Lines within maps outline the major watersheds.

saturation at sea level and 1000 m (315 μ M and 275 μ M at 15 °C, respectively).

2.3. Statistical Analysis

[9] Trends were calculated using simple linear regression for each of the sampling stations using the annual means. Annual means for each station were calculated from seasonal means. From the station trends, mean trends for the contiguous U.S. were calculated as spatially-weighted means to account for the spatial distribution of sampling stations. Spatial weightings were generated from thiessen polygons calculated using ArcView. Mean trends were tested for significant differences from zero using weighted t-tests. For all variables, an outlier analysis was performed to remove erroneous data points [*Neter et al.*, 1990] and only stations with at least 10 years of data were included (N = 417 stations and 62,011 samples).

3. Results and Discussion

[10] Riverine pCO_2 was consistently high and showed pronounced spatial variability across the U.S. with greatest values in the southeastern U.S. and lowest in the western U.S. (Figure 1). Riverine pCO_2 across the contiguous U.S. is similar to the patterns of evapotranspiration rate, terrestrial leaf litter production [*Bray and Gorham*, 1964], soil organic matter decomposition [*Meentemeyer*, 1978; *Meentemeyer et al.*, 1982], and evasion of CO₂ from soils to the atmosphere [*Raich and Potter*, 1995], underscoring the strong relationship between aquatic and terrestrial ecosystems. The mean pCO_2 (2109 ppmv) was six-fold greater

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Table 1. Long-term Trends in the Partial Pressure of CO_2 (pCO_2), Dissolved Inorganic Carbon (DIC), and Associated Chemical and Physical Parameters Across the Contiguous United States

Variable	Mean	Trend (y^{-1})	Trend standard error	Number of stations with significant trend	Number of stations with significant negative trend
pCO_2 (ppmv)	2109	-78.4^{a}	7.5	194	185
DIC (µM)	2660	-3.9^{a}	1.3	105	65
eqDIC (µM)	2480	0.6	1.1	102	39
Ca^{2+} (µM)	1553	-12.2^{a}	3.7	98	62
Mg^{2+} (μM)	939	-2.0	1.2	102	44
$H^{+}(\mu M)$	0.047	-0.0016^{a}	0.0003	188	183
eqH^{+} (μM)	0.008	0.0001	0.00005	87	59
$H_2CO_3-H^+$ (μM)	0.039	-0.0017^{a}	0.0003	188	183
Alkalinity $(\mu Eq l^{-1})$	2622	0.9	1.2	102	33
Oxygen (µM)	303.8	0.04	0.12	93	48
Oxygen saturation (%)	96.9	0.26 ^a	0.10	355	0
Stream temperature (°C)	14.5	0.008	0.007	63	20
pН	7.3				

Overall trends were calculated as weighted means of trends calculated for each station using linear regression (N = 417 stations).

^aSignificantly different than zero at p < 0.05 significance level.

than atmospheric concentration (360 ppmv), 88 % of all samples were supersaturated, and only one sampling station had an overall mean pCO_2 below atmospheric equilibrium. Of the DIC in solution, carbon derived from weathering (eqDIC) accounted for 93.2 % of the total pool on average (Table 1).

[11] Over the 22-years of data, pCO_2 significantly declined -78.4 ppmv y⁻¹ (Table 1). Considering each of the 417 NASQAN stations used in our analysis, pCO_2 changed significantly over this period in over one-third (194) of the NASQAN streams, 184 of which had significant declines in pCO_2 . Greatest declines occurred in the southeastern U.S., whereas little or no change was detected in southwestern drainages and in the middle Atlantic (Figure 1).

[12] The decline in pCO_2 over time cannot be explained by changes in weathering. DIC is composed of carbon derived from weathering and gaseous CO₂ and the resulting dissociation with water. As with pCO_2 , mean DIC concentration decreased significantly from 1973 to 1994 (Table 1). The proportion of DIC derived from weathering sources, however, did not change. DIC concentration calculated with CO₂ in equilibrium with the atmosphere (eqDIC) and alkalinity did not change over this period (Table 1) indicating that weathering rate of carbonate geologies did not change. The concentration of Ca²⁺ declined over the 22 years of record (Table 1), suggesting a reduction in carbonate weathering, which would lead to lower pH and increased pCO_2 . Unlike pCO_2 , the decline in Ca²⁺¹ concentration, however, was highly skewed with a few stations showing dramatic reductions, and the vast majority of stations showing little change.

[13] Change in stream pH, as might result from acid deposition, was also apparently not responsible for the change in pCO_2 . The pH of NASQAN streams increased

significantly during the 22 years with the mean H⁺ concentration changing $-0.0016 \ \mu M \ y^{-1}$ (Table 1). The pH calculated with pCO_2 in equilibrium with the atmosphere (eqH⁺), however, did not significantly vary (Table 1), revealing that pH was not altered by changes in atmospheric and watershed inputs of H⁺. The H⁺ in solution due to CO₂ supersaturation (H₂CO₃-H⁺) also significantly declined $-0.0017 \ \mu M \ y^{-1}$ indicating that the decline in H⁺ concentration and increase in pH was due to reduction of carbonic acid. These pH changes, along with a lack of change in stream alkalinity (Table 1), suggest that the decline in pCO_2 caused the increase in pH, rather than a change in pH altering pCO_2 .

[14] Within the aquatic environment, pCO_2 can decline due to increased primary production or reduced respiration. We found little evidence that changes in aquatic metabolism were responsible for long-term pCO_2 declines. If increased in-river primary production was the primary cause for the reduction in pCO_2 , then oxygen concentrations should have increased, and pCO_2 and oxygen saturation would change at similar but opposite rates. Oxygen saturation did increase [*Lettenmaier et al.*, 1991] (0.26 % y⁻¹; Table 1). However, the increase in dissolved oxygen concentration can only account for -1.7 to -4.1 ppmv y⁻¹ (assuming oxygen saturations of 315 and 275 μ M, respectively) change in pCO_2 , or 2.2 to 5.2 % of the observed decline of -78.4ppmv y⁻¹.

[15] The potential for spurious results due to changes in analytical methods was analyzed by sensitivity analysis. Improvement of pH probes in particular could affect calculated values of pCO_2 . The accuracy of pH probes improved from ± 0.05 to ± 0.01 pH units from 1973 to 1994, but there is no evidence to indicate a directionality of change associated with increased probe accuracy [*American Public Health Association*, 1975, 1995]. This reduction in error would generate an apparent pCO_2 decline of -0.7 ppmv y⁻¹, or 0.9 % of the observed decline of -78.4 ppmv y⁻¹ (Table 1).

4. Conclusions

[16] The decline in pCO_2 , given the lack of change in alkalinity, eqDIC, or eqH⁺, points to a reduction or alteration in the quantity and/or quality of carbon import from terrestrial ecosystems. These changes could be caused by a myriad of factors but we suggest that either a decline in soil respiration or alteration in the nature of the hydrologic connections between terrestrial and aquatic ecosystems are the likely explanations. Baseflows (i.e., groundwater fluxes to streams) have declined in the southeastern U.S. over the past 30 years [Lins and Slack, 1999], which could reduce the import of terrestrial carbon to streams [Jones and Mulholland, 1998b]. However, baseflow increased in other parts of the country where we also observed CO₂ declines. Terrestrial production appears to have increased given trends in North America of increased plant growth [Myneni et al., 1997], afforestation [Delcourt and Harris, 1980; Dixon et al., 1994], and nitrogen deposition [Townsend et al., 1996], which may lead to increased soil respiration and CO₂. More recent evidence, however, suggests that increased nitrogen deposition may lead to reduced soil CO₂; results from experimental additions of nitrogen to

forest soils have demonstrated a reduction in the rate of organic matter decomposition [Berg and Matzner, 1997; Berg and Meentemeyer, 2002]. The reduction in riverine pCO_2 may have also been caused by a decline in riparian and wetland habitat. Wetlands and near-stream environments can affect in-river metabolism and pCO_2 by releasing organic matter and contributing water supersaturated in CO₂ from soil respiration. Indeed, respiration rates in riparian soils can exceed those in adjacent forest and cropland ecosystems [Tufekcioglu et al., 2001]. High rates of primary production and soil respiration of wetlands and riparian zones, coupled with dramatic losses of these habitats over the past century [Mitsch and Gosselink, 1993] should have a strong and direct effect on stream pCO_2 . Regardless of the cause, the trend in pCO_2 indicates that gaseous carbon losses from terrestrial ecosystems via aquatic pathways have likely declined across much of the contiguous U.S. and that ecosystem functioning significantly shifted during the latter part of the 20th century.

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