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

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[1] The partial pressure CO2 (pCO2) in streams and rivers reflects both internal carbon dynamics and external biogeochemical processes in terrestrial ecosystems. CO2 is typically supersaturated in streams because rates of organic matter decomposition exceed photosynthetic uptake, and because of inflow of CO2-saturated 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 pCO2 across the U.S., our analysis revealed that pCO2 significantly declined 78.4 ppmv y−1 from 1973 to 1994. This decline is not attributable to changes in terrestrial weathering or in-stream 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 saturation in rivers across the contiguous United States, Geophys. Res. Lett., 30(10), 1495, doi:10.1029/2003GL017056, 2003.

1. Introduction

[2] The concentration of CO2 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 in-stream 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 terrestrial-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 supersaturated and net sources of CO2 to the atmosphere [Kling et al., 1991; Cole et al., 1994; Jones and Mulholland, 1998a, 1998b].


2. Methods

2.1. Dataset

[4] pCO2 and DIC were calculated using data collected from 1973 through 1994 by the U.S. Geological Survey’s National Stream Water-Quality Monitoring Network (NASQAN) 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 catch-
ments 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] CO$_2$ 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 $p$CO$_2$ 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 $p$CO$_2$ in equilibrium with the atmosphere (360 ppmv) using the Equilibrium Phases module of PHREEQC (eqDIC and eqH$^+$, respectively). The increase of atmospheric $p$CO$_2$ 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 CaCO$_3$ + CO$_2$ + H$_2$O $\rightleftharpoons$ 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 $p$CO$_2$. 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 CO$_2$ is produced, carbonic acid is produced in a reversible reaction through dissociation with water as CO$_2$ (g) + H$_2$O $\rightleftharpoons$ H$_2$CO$_3$ $\rightleftharpoons$ H$^+$ + HCO$_3^-$. The rate of exchange of gases between rivers and the atmosphere is a function of molecular activity ($k$) and a gas exchange coefficient ($k_1$; exchange = $k_1$[DIC]$_{eqH^+}$). Exchange coefficients are a function of molecular activity ($D_1$) of gases and coefficients for two gases are related as $k_1/k_2 = [D_1/D_2]$ to where $n$ is an exponent ranging from 0.5 to 1.0 [Bennett and Rathburn, 1972; Genereux and Hemond, 1992]. Assuming organic matter is decomposed as C$_6$H$_{12}$O$_6$ + 6O$_2$ $\rightarrow$ 6CO$_2$ + 6H$_2$O, then O$_2$ will be consumed and CO$_2$ 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 $[CO_2] = ([O_2]/k_{O_2})[O_2] - [O_2]_{eqH^+} + [CO_2]_{eqDIC}$ where $D_1$ and $D_2$ are set equal to 2.3 $\times$ 10$^{-5}$ cm$^2$ s$^{-1}$ [Wise and Houghton, 1966] and 1.7 $\times$ 10$^{-5}$ cm$^2$ 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, CO$_2$ concentration was calculated with oxygen saturation at sea level and 1000 m (315 μM and 275 μM 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 thieninness 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 CO$_2$ 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.
Physical Parameters Across the Contiguous United States

Dissolved Inorganic Carbon (DIC), and Associated Chemical and Physical Parameters Across the Contiguous United States

Table 1. Long-term Trends in the Partial Pressure of CO₂ (pCO₂), Dissolved Inorganic Carbon (DIC), and Associated Chemical and Physical Parameters Across the Contiguous United States

<table>
<thead>
<tr>
<th>Variable</th>
<th>Mean</th>
<th>Trend (y⁻¹)</th>
<th>Number of stations with significant trend</th>
<th>Number of stations with significant negative trend</th>
</tr>
</thead>
<tbody>
<tr>
<td>pCO₂ (ppmv)</td>
<td>2109</td>
<td>-78.4ᵃ</td>
<td>7.5</td>
<td>194</td>
</tr>
<tr>
<td>DIC (µM)</td>
<td>2660</td>
<td>-3.9ᵃ</td>
<td>1.3</td>
<td>105</td>
</tr>
<tr>
<td>eqDIC (µM)</td>
<td>2480</td>
<td>0.6</td>
<td>1.1</td>
<td>102</td>
</tr>
<tr>
<td>Ca²⁺ (µM)</td>
<td>1553</td>
<td>-12.2ᵃ</td>
<td>3.7</td>
<td>98</td>
</tr>
<tr>
<td>Mg²⁺ (µM)</td>
<td>939</td>
<td>-2.0</td>
<td>1.2</td>
<td>102</td>
</tr>
<tr>
<td>H⁺ (µM)</td>
<td>0.047</td>
<td>-0.0016ᵃ</td>
<td>0.0003</td>
<td>188</td>
</tr>
<tr>
<td>eqH⁺ (µM)</td>
<td>0.008</td>
<td>0.0001</td>
<td>0.00005</td>
<td>87</td>
</tr>
<tr>
<td>H₂CO₃-H⁺</td>
<td>0.039</td>
<td>-0.0017ᵃ</td>
<td>0.0003</td>
<td>188</td>
</tr>
<tr>
<td>Alkalinity (µEq ⁻¹⁻¹)</td>
<td>2622</td>
<td>0.9</td>
<td>1.2</td>
<td>102</td>
</tr>
<tr>
<td>Oxygen (µM)</td>
<td>303.8</td>
<td>0.04</td>
<td>0.12</td>
<td>93</td>
</tr>
<tr>
<td>Oxygen saturation (%)</td>
<td>96.9</td>
<td>0.26ᵃ</td>
<td>0.10</td>
<td>355</td>
</tr>
<tr>
<td>Stream temperature (°C)</td>
<td>14.5</td>
<td>0.008</td>
<td>0.007</td>
<td>63</td>
</tr>
<tr>
<td>pH</td>
<td>7.3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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.

Table 1 shows dramatic reductions, and the vast majority of samples were supersaturated, and only one sampling station in southwestern drainages and in the middle Atlantic revealed 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 µM 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 pCO₂ caused the increase in pH, rather than a change in pH altering pCO₂.

Within the aquatic environment, pCO₂ can decline due to increased primary production or reduced respiration. We found little evidence that changes in aquatic metabolism were responsible for long-term pCO₂ declines. If increased in-river primary production was the primary cause for the reduction in pCO₂, then oxygen concentrations should have increased, and pCO₂ and oxygen saturation would change at similar but opposite rates. Oxygen saturation did increase [Lennonmaier 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 µM, respectively) change in pCO₂, or 2.2 to 5.2 % of the observed decline of −78.4 ppmv y⁻¹.

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 pCO₂. 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 pCO₂ decline of −0.7 ppmv y⁻¹, or 0.9 % of the observed decline of −78.4 ppmv y⁻¹ (Table 1).

4. Conclusions

The decline in pCO₂ 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...
the past century zones, coupled with dramatic losses of these habitats over production and soil respiration of wetlands and riparian ecosystems [Tufekcioğlu 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 pCO2. Regardless of the cause, the trend in pCO2 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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References


