An empirical study of climatic controls on riverine C export from three major U.S. watersheds

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The correlations between annual precipitation, evaporation, temperature, and annual carbon export (bicarbonate, dissolved organic carbon, and particulate organic carbon) are established for the Ohio, upper Mississippi, and Missouri watersheds and coefficients that predict C export on the basis of precipitation, evapotranspiration, and seasonal temperature are provided. Interannual variation in carbon export is controlled by the level of precipitation and evapotranspiration, the discharge to precipitation ratio (D:P), the concentration of the major carbon pool, the rating curve (discharge versus carbon concentration plots), and seasonal temperature. Within a watershed, precipitation has the strongest correlation with annual carbon export for all carbon pools. In the upper Mississippi and Ohio, levels of evapotranspiration can predict the majority of the residuals of precipitation versus carbon export. Bicarbonate demonstrates the largest response in yield to annual precipitation variation for each watershed. Rating curves, however, indicate that dissolved organic carbon and particulate organic carbon generally increase with increasing discharge, while bicarbonate decreases, causing a larger percentage response to precipitation for the organic carbon pools. Across watersheds the discharge to precipitation (D:P) ratio is the dominant determinant of how carbon yields respond to changes in precipitation, and watersheds with a high D:P ratio should demonstrate large changes in carbon yields with forecasted changes to precipitation.


1. Introduction

The export of carbon from watersheds has important implications to both terrestrial and oceanic biogeochemical budgets. Organic carbon (OC) fluxes to the coastal zone are important to determining the net metabolism of these systems [Hopkinson and Vallino, 1995] and can cause associated continental shelves to be supersaturated in CO$_2$ and a net source of CO$_2$ to the atmosphere [Cai et al., 2003]. Inorganic nutrients released from terrestrial OC during remineralization in coastal waters can be a source of inorganic nutrients for primary production [Raymond and Bauer, 2000]. Bicarbonate (HCO$_3^-$) exported from rivers represents a terrestrial CO$_2$ sink [Raymond and Cole, 2003] and once exported to the ocean is important to the net carbon budget, buffering capacity, and pH of the receiving coastal waters [Green et al., 2006]. With respect to terrestrial systems, C fluxes from rivers also represent an important net flux and are often as large as terrestrial net ecosystem productivity [Cole et al., 2007]. Various factors, including land cover [Howarth et al., 1991; Humborg et al., 2004; Mattsson et al., 2005], precipitation [Clair et al., 1999, 1994; Correll et al., 2001], temperature [Correll et al., 2001], alteration of watershed flow paths [Smith et al., 2005; Worrall and Burt, 2004], soil C stocks [Aitkenhead and McDowell, 2000; Gaillardet et al., 1999; Hope et al., 1997], terrestrial primary and secondary productivity [Kardjilov et al., 2006; Striegl et al., 2005], winter snowpack [Clair and Ehrman, 1998], watershed relief [Canfield, 1997; Ludwig et al., 1996; Milliman and Syvitski, 1992], discharge [Harrison et al., 2005], increasing atmospheric CO$_2$ [Freeman et al., 2004; Gedney et al., 2006; Hejzlar et al., 2003] and others are all integral to riverine carbon export. Many of these factors interact and operate on different timescales.

It has long been recognized that across system variation in the flux of carbon from watersheds is strongly correlated with precipitation [Meybeck and Carbonnel, 1975]. Within a watershed, annual variation in precipitation is also a driver of the annual export of carbon [Clair et al., 1994; Correll et al., 2001]. This is not surprising, since precipitation is a strong determinant of discharge both across and within watersheds, and the flux of a constituent is discharge multiplied by concentration. One major change forecasted with global warming is an accelerated hydrologic cycle [Douville et al., 2002; Labat et al., 2004], although regional areas of decreased precipitation are also possible. Large-scale changes to the United States hydrologic cycle are already being reported [Groisman et al., 2004; Lins and...
Table 1. USGS Gauging Stations and Data Availability

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<td>POC</td>
<td>11/08/95</td>
<td>09/21/04</td>
<td>131</td>
</tr>
</tbody>
</table>

\*Dates given as mm/dd/yy.
\*Ohio River at Dam 53 near Grand Chain, Illinois.
\*Mississippi River below Grafton, Illinois.
\*Missouri River at Hermann, Missouri.

Slack, 1999), as are associated changes in riverine carbon export [Raymond and Cole, 2003]. What is lacking is a thorough mechanistic understanding of how watersheds of varying hydrology, surficial geology, and land use will respond to future alterations in climate. Are precipitation changes more important than temperature? Do we expect a 10% increase in carbon export with a 10% increase in precipitation? How is this ratio different for the three major carbon species and how will this ratio be altered by landscape characteristics and watershed hydrology?

[4] Data sets are now available to approach these questions possible at exciting new spatial and temporal scales with a historical unprecedented accuracy. The goal of this work was to investigate how the annual export of riverine carbon responds to contemporary variation in climate. This was done by investigating the empirical relationship between climate and dissolved organic, particulate organic and bicarbonate C export (DOC, POC, HCO\textsuperscript{3-}, respectively) from three large U.S. watersheds over a relatively short time period when land use change was minimal. The Ohio, upper Mississippi and Missouri watersheds were chosen because they are regionally important watersheds and vary greatly in annual average precipitation and temperature. Our conclusion is that the ratio of discharge to precipitation is a primary determinant of how carbon export from specific watersheds of the United States will respond to climate change in coming decades to centuries.

2. Methods

[5] Three USGS gauging stations were selected, the Ohio + Tennessee (USGS number 03612500; called the Ohio in this manuscript), upper Mississippi (05587455), and Missouri River basins (06934500; Table 1). Although basin boundaries of the gauging stations were similar to the two-digit USGS hydrologic units (http://water.usgs.gov/GIS/huc.html), the delineated area of 05587455 was ~90% of the USGS hydrologic unit 07 because the upper Mississippi river merges with the Missouri river above the mouth of the USGS hydrologic unit 07.

[6] Since concentration and discharge data are needed to calculate riverine export of bicarbonate, DOC, and POC flux, both the concentration and daily discharge data were downloaded from the USGS water data website (http://waterdata.usgs.gov/nwis). There were 7–12 years of data depending on the watershed and parameter, and a minimum of 87 values for any single parameter (Table 1). For this study we extracted bicarbonate from USGS water quality reports. At the average pH of these river bicarbonate is 95, 97, and 97% of total dissolved inorganic carbon (DIC) for the Ohio, upper Mississippi and Missouri, respectively. When daily discharge data were not monitored at the water quality monitoring stations, daily discharge data were obtained from nearby stations and used to estimate C fluxes (e.g., daily discharge data of 03611500 and 05587450 were used for 03612500 and 05587455, respectively). The nearby stations had watershed areas that were <0.1% different.

[7] Carbon export from the three stations were estimated using USGS LOADEST (Load Estimator) program [Runkel et al., 2004]. LOADEST uses daily element concentration (the daily mean values in Table 1) and flow data to establish relationships between discharge and carbon export and extrapolates these relationships to the daily discharge record. There were at least 87 daily mean concentration values of each carbon species to calibrate LOADEST (Table 1). Although LOADEST can select the best fit model for daily load automatically from 9 available models [Runkel et al., 2004], we used a conservative model without a time trend (Loadest Model 06 [Runkel et al., 2004]) owing to a lack of calibration period in DOC and POC for 1992–1996.

\[
\ln(\text{load}) = a_0 + a_1 \ln Q + a_2 \ln Q^2 + a_3 \sin(2\pi \text{dtime}) + a_4 \cos(2\pi \text{dtime}),
\]

where Q and dtime are the centered values of discharge and time [Runkel et al., 2004]. The sine and cosine terms are added to consider seasonality. a0 through a4 are the model coefficients with a0 being the intercept. The same model was applied to each C species of the three basins to estimate daily flux, which were summed later to calculate monthly and yearly fluxes.

[8] Monthly and yearly precipitation maps from 1992 to 2004 were downloaded from the Spatial Climate Analysis Service website (http://www.ncdc.noaa.gov/oa/nci/cgi-bin/prism/) and ArcGIS zonal analysis was conducted to estimate the
precipitation amount within the basins. Since the precipitation data were available only within the U.S. boundary, the precipitation of Missouri River basin was slightly underestimated. However, considering that the Canadian portion of the basin is only ~2% of the total basin area and that precipitation decreases significantly from southeastern to northwestern part of the basin, the error associated with the missing Canadian portion should be minimal. The 1993 data was excluded from the upper Mississippi because of the massive floods that occurred in the basin in this year.

3. Results

The three major basins have very different hydrology. Of the three major basins, the Missouri receives the highest volume of precipitation at ~724 km$^3$ yr$^{-1}$, with the Ohio and the upper Mississippi receiving 642 and 377 km$^3$ yr$^{-1}$, respectively (Table 2). When normalized to the large basin area, however, the amount of precipitation for the Missouri is only 0.53 m yr$^{-1}$, compared to 1.22 and 0.85 m yr$^{-1}$ for the Ohio and upper Mississippi, respectively. Furthermore, in the Missouri, the majority (88%) of the rainfall entering the basin is lost to evapotranspiration and storage (simplified to evapotranspiration for this paper, although it should be noted that storage could be important in the Missouri), and therefore the Missouri has the lowest discharge contribution of the three major basins (Table 2). The Ohio only loses 58% of its precipitation to evapotranspiration, leading to the largest discharge of the three major basins (Table 2).

In all basins the interannual variation in precipitation is strongly related to interannual variation in discharge (Figure 1). Annual precipitation can predict 76, 51, and 81% of the variation in annual discharge for the Ohio, upper Mississippi, and Missouri, respectively (Figure 1; $r^2$ of P:D in Table 3). It is not clear why the upper Mississippi has a weaker correlation for this data set (Table 3), but the strength of the correlation increases if one uses a longer data set (a 20 year data set from 1984–2004 has an $r^2$ of 0.72 with a slope of 0.54). More importantly, the slope of the line for the upper Mississippi, a focus of this study, does not significantly change when the longer data set is used. The slope of the precipitation versus discharge curves are 0.90, 0.50, and 0.32, for the Ohio, upper Mississippi, and Missouri, respectively (Figure 1 and Table 3). This indicates that a 10-cm interannual change in precipitation in the Ohio, leads to a 9.0-cm increase in discharge (D:P; slope in Table 3), while for the Missouri a 10-cm increase in precipitation only results in a 3.2-cm increase in discharge. It is important to note, however, that because of the Missouri’s low discharge the smaller increase in discharge (just 32% of additional precipitation) can translate to a large percentage change in its annual discharge (Figure 1).
Table 3. Statistics for Annual Precipitation Versus Annual Discharge, Annual Evapotranspiration, and Annual Carbon Export; Annual Evapotranspiration Versus the Residuals of Annual Carbon Export Versus Precipitation; and Seasonal Temperature and Carbon Export Relationships for the Three Major Basins*

<table>
<thead>
<tr>
<th></th>
<th>Slope</th>
<th>Y Intercept</th>
<th>r²</th>
<th>P Value</th>
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<tbody>
<tr>
<td>Ohio</td>
<td></td>
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<tr>
<td>P versus D</td>
<td>0.90</td>
<td>-0.59</td>
<td>0.76</td>
<td>0.0001</td>
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<tr>
<td>P versus E</td>
<td>0.10</td>
<td>+0.59</td>
<td>0.04</td>
<td>0.52</td>
</tr>
<tr>
<td>P versus HCO₃</td>
<td>16.2</td>
<td>-10.2</td>
<td>0.81</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>P versus DOC</td>
<td>2.90</td>
<td>-2.0</td>
<td>0.75</td>
<td>0.0001</td>
</tr>
<tr>
<td>P versus ROC</td>
<td>2.97</td>
<td>-2.5</td>
<td>0.71</td>
<td>0.0003</td>
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<tr>
<td>E versus HCO₃r</td>
<td>-14.8</td>
<td>10.5</td>
<td>0.93</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>E versus DOCr</td>
<td>-3.2</td>
<td>2.3</td>
<td>0.96</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>E versus ROCr</td>
<td>-3.5</td>
<td>2.5</td>
<td>0.92</td>
<td>&lt;0.0001</td>
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<tr>
<td>Spring T versus HCO₃r</td>
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<td>2.56</td>
<td>0.41</td>
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<tr>
<td>Spring T versus DOCr</td>
<td>0.04</td>
<td>0.47</td>
<td>0.36</td>
<td>0.03</td>
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Upper Mississippi

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<tr>
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<td>0.51</td>
<td>0.009</td>
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<td>0.01</td>
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<td>0.57</td>
<td>0.004</td>
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<td>E versus HCO₃</td>
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<td>E versus ROC</td>
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Missouri

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<th>Slope</th>
<th>Y Intercept</th>
<th>r²</th>
<th>P Value</th>
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<tbody>
<tr>
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<td>P versus E</td>
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<tr>
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<td>0.69</td>
<td>0.0004</td>
</tr>
<tr>
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<td>0.26</td>
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<td>Summer T versus DOC</td>
<td>0.06</td>
<td>1.53</td>
<td>0.24</td>
<td>0.09</td>
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</table>

*Units of measure: annual precipitation, P in m yr⁻¹; annual discharge, D in m yr⁻¹; annual evapotranspiration, E in m yr⁻¹; annual carbon export, g C m⁻² yr⁻¹; and temperature, T, °C. Precipitation denotes DOCr, etc. The statistics of the upper Mississippi are calculated without 1993 owing to the flood event. The annual sum of P, D, and E were used to calculate the statistics, and the seasonal and annual sum of C export were estimated by LOADEST run for 1992–2004. HCO₃⁻ is in grams of carbon (HCO₃-C).

ally strongest for the dissolved species, and weakest for POC (Table 3), presumably owing to the connection between POC export and storm intensity, with more energetic precipitation events leading to high POC export. The increase in carbon export with changes in precipitation (i.e., the slope of P versus C export) is similar for the Ohio and upper Mississippi and smaller for the Missouri (Table 3). The largest slope is for bicarbonate (Table 3).

[12] In the Ohio and upper Mississippi the residuals of precipitation versus carbon export for all carbon species can be explained by annual levels of evapotranspiration. In the Ohio, annual evapotranspiration predicts 93, 96 and 92% of the residuals for HCO₃⁻, DOC, and POC, respectively, while in the upper Mississippi 98, 99, and 89% of the residuals are explained by evapotranspiration (Figure 4 and Table 3). In the Missouri, the residuals are not related to evapotranspiration. Therefore, in these watersheds, the cumulative predictive power of annual precipitation and evapotranspiration can explain ~98, 97, 76% of the variation in annual carbon export for the Ohio, upper Mississippi and Missouri, respectively. The lack of a relationship in the Missouri could be from confounding factors due to water storage or snowmelt.

[14] Seasonal relationships between temperature and carbon export were also investigated using multiple regressions. Summer temperature (June–August) was found to be important to dissolved carbon export for the Missouri (r² > 0.24, p < 0.1; Table 3; graphs not shown). Average summer temperatures could predict 26 and 24% of the annual variation in carbon export for HCO₃⁻ and DOC, respectively (Table 3; graphs not shown). The slopes of the these relationships indicate that with a one degree warming of average summer temperatures, annual carbon export would decrease by 0.3 and 0.06 g C m⁻² yr⁻¹ for HCO₃⁻ and DOC, respectively (Table 3). In the Ohio watershed, the average spring temperature (March–May) could predict 41, and 36% of the variation in the residuals of carbon export for HCO₃⁻, DOC, respectively. According to these relationships, a 1 degree warming of spring Ohio temperatures would decrease carbon export by 0.2 and 0.04 g C m⁻² yr⁻¹ for HCO₃⁻ and DOC, respectively.

4. Discussion

[15] As the rate of water export increases in these three watersheds, the concentration of POC and DOC also increases (Figure 2). Although concentrations of HCO₃⁻ decrease with increasing water export, dilution is small relative to the increase in water export. For instance, if precipitation in a given year in the Ohio was 10 cm above average, this would lead to an increase in discharge of 9 cm raising discharge from 0.51 to 0.62, a 21% increase in discharge. Using the relationship established with the bicarbonate rating curve (Figure 2), and assuming this increase in precipitation is distributed equally over the entire year, it would result in a dilution of HCO₃⁻ of ~0.3 mg C L⁻¹, (from ~11.3 to ~11 mg C L⁻¹) or ~2%. Remembering that flux is discharge multiplied by concentration, the above example would lead to a ~16% increase if bicarbonate is allowed to dilute and only a 18% change in export if there is no dilution. Similar results are obtained in the other two basins for the same exercise, and therefore in these large watersheds, the response of riverine carbon export to changes in precipitation is strongly controlled by how much of the additional precipitation is routed to discharge, as opposed to changes in carbon concentrations. Consequently on annual timescales, factors that can increase the amount of water exported from large watersheds will generally enhance the export of all three carbon pools. For POC and DOC, the increase in concentration with discharge leads to a slight additive effect to precipitation increases compared to bicarbonate (Figure 2).

[16] The largest response in carbon yield to precipitation for each watershed is for bicarbonate (Table 3). This is because bicarbonate concentrations are 3–8 times greater than other carbon species in these watersheds and the dilution effect is minimal (Figure 2). Even though bicarbonate concentrations dilute with increased discharge, and therefore dilute with increased precipitation, the dilution is
not great enough to offset an overall greater increase in bicarbonate fluxes at higher water through-put. Bicarbonate concentrations can be much lower in other regions of the United States that have different soils and land cover, and therefore the large responses for bicarbonate found in this study is not representative of all United States watersheds.

[17] In the Ohio and upper Mississippi, the residuals of the empirical relationship between annual precipitation and annual carbon export can be explained by evapotranspiration (Figure 4). Thus, for carbon species in the Ohio and upper Mississippi, secondary factors which can alter the ratio of discharge to precipitation for a given year are also important to carbon export. Factors that might be important to this ratio at the large basin scale include seasonal temperature (see below), monthly variation in precipitation [Kim et al., 2006; Twine et al., 2005], severe precipitation events [Christensen and Christensen, 2004], irrigation [Haddeland et al., 2006], snowpack [Barnett et al., 2005], soil conditions [Cherkauer and Lettenmaier, 1999; Stieglitz et al., 1997] and the previous years net hydrology.

[18] The empirical evidence gathered here argues that variation in annual precipitation is a dominant control on annual carbon export variation and that annual or seasonal change in temperature plays a weaker secondary role. However, even though the $r^2$ are weaker for temperature than the corresponding precipitation relationships (Table 3), it is important to remember the wider range in annual precipitation as compared to temperature. In the Missouri, summer temperature is correlated with annual carbon export (Table 3). A large amount of the annual precipitation falls in the summer period (~40% of the rainfall falls from June to August, compared to ~30% for the Ohio) when evapotranspiration potential is the highest. Similarly, in the Ohio, spring temperature is negatively correlated with the residuals of precipitation versus carbon export (Table 3). Therefore the negative relationship between temperature and annual carbon export is likely due to higher rates of

Figure 2. Relationship between instantaneous discharge and concentrations of bicarbonate, DOC, and POC.
evapotranspiration and therefore lower water throughput during warmer years. The slopes of the relationships between temperature and carbon export, however, predict only small changes in carbon export with a two degree warming (Table 3).

All of these relationships argue that water throughput is a dominant determinant of annual variation in carbon export from all three watersheds investigated. Over the 12 years of this study, the Missouri and Ohio have a similar range in annual precipitation of ~0.3 m yr⁻¹ (Figure 3). In the Missouri, however, the majority (70%) of any excess precipitation in higher precipitation years is lost to evapotranspiration and storage. In the Ohio most (90%) of the additional precipitation in wet years is realized as discharge and this additional water carries terrestrial carbon at concentrations similar to lower discharge years. Although there is some evaporative concentration effects [White and Blum, 1995] in the Missouri that somewhat offsets the lower water yields, the net effect is much lower responses in carbon export despite of the similar range in annual precipitation.

For all three watersheds there is a general relationship between the discharge to precipitation ratio, a measurement of water throughput, and the response in carbon yields expected with a 10% acceleration of the precipitation cycle (Figure 5). For the Ohio River watershed, a 10% increase in precipitation would result in an increase of ~2.7 g C m⁻² yr⁻¹, a 25% increase. The upper Mississippi would witness a 1.9 g C m⁻² yr⁻¹, or 17% increase and the Missouri would realize a 0.8 g m⁻² yr⁻¹ or 23% increase. In all three basins about 70% of this additional carbon is inorganic and 30% organic (Figure 5). Thus, as the hydrologic cycle accelerates in temperate watersheds, the acceleration of the carbon export term in terrestrial budgets will be the highly sensitive to the discharge to precipitation ratio owing to a larger percentage of the additional rainfall making it to the receiving river in systems with a high D:P ratio.

It is important to note that this empirical study is at the large basin scale. Studies have noted the potential for abiotic and biotic processing/storage of carbon pools during transport in smaller streams [McDowell, 1985; Newbold et al., 1982; Qualls and Haines, 1992]. Therefore the export numbers utilized in this study do not represent the true lateral transport of carbon from terrestrial systems. POC, for instance has been demonstrated to be trapped in reservoirs and dams [Smith et al., 2005; Stallard, 1998] that exist upstream of the gauging stations utilized by this study, and

Figure 3. Annual carbon export versus annual precipitation. Statistics are provided in Table 2.
therefore the POC export quantified here is an underestimate of the amount of POC laterally transported from terrestrial soils. The climate effects on carbon export reported here, however, are a reasonable estimate of how the export of carbon species to the coastal zone will be altered for large watersheds of similar landcover, climate and soil.

[22] The potential also exists in each of these watersheds for the existence of thresholds and feedbacks in the relationship between carbon export and precipitation that operate on timescales that are longer than the 12 year time period utilized here. Feedbacks within the watershed, for instance, could create shifts in the rating curves that would propagate into a shifting response of carbon export to precipitation. Raymond and Cole [2003] have demonstrated a long-term increase in bicarbonate concentration for the Mississippi, and thus it is likely that the current precipitation to carbon export slope is slightly greater than it was in the 1950’s. Authors are also noting changes in the concentration of DOC for a number of watersheds [Evans et al., 2005; Findlay, 2005; Striegl et al., 2005]. These long-term shifts might not simply be a direct response to climate change itself but produced by complex interactions between climate, rising atmospheric CO$_2$, atmospheric nitrogen deposition, biotic responses and/or a change in land cover or land use. For instance, regional increases in NPP in response to

Figure 4. Evapotranspiration versus the residuals of precipitation/annual carbon export graphs (Figure 2, y axis). Statistics are provided in Table 2.

Figure 5. Discharge to precipitation ratio (D:P) graphed against the increase in carbon export (HCO$_3$ + DOC + POC) predicted with a 10% increase in average annual precipitation using coefficients from Table 2. For the Ohio, 73, 13, and 14% of these changes were for HCO$_3$, DOC, and POC, respectively. These same percentages are 78, 13, and 9% and 62, 12, and 26% for the upper Mississippi and Missouri, respectively.
increased precipitation, have also been modeled for much of the United States [Nemani et al., 2002]. These changes could slowly change watershed properties such as soil C:N ratios, which have been demonstrated to correlate with DOC export on broader scales and postulated to be ultimately linked to climate [Aitkenhead-Peterson et al., 2005].

It is also highly likely that land use change alters the relationship between precipitation and carbon export. Wetland loss has decreased the export of DOC from areas of the United States by as much as 20–30% [Raymond et al., 2004]. Agricultural practices have augmented the amount of bicarbonate and POC available for export to streams [Howarth et al., 1991; Oh and Raymond, 2006], while cities and suburbs have greatly altered stream hydrology and presumably carbon export [Paul and Meyer, 2001]. Understanding how past and future land use change and climate change has altered the slope of precipitation to carbon export should therefore be an integral part of future research.

5. Conclusions

The empirical results indicate that for temperate watersheds interannual variation in precipitation is a strong determinant of the interannual variability in carbon export. Precipitation amounts are most strongly linked to dissolved species. These results at the large basin scale are consistent with earlier studies at the small watersheds scale that stressed the importance of water throughput to carbon export [Hornberger et al., 1994]. The hydrologic balance of a watershed is an important characteristic for shaping how watershed C export will respond to short-term (i.e., decadal) changes in climate, and carbon export in watersheds that have a higher discharge to precipitation ratio will respond with greater changes in carbon yield. Remembering that the net ecosystem productivity of the Mississippi watershed is currently close to balanced [Lee and Veizer, 2003], these fluxes and responses to future climate change should be included in terrestrial carbon budgets.

If a 10% increase in precipitation occurs the empirical relationships predict ~20% increase in bicarbonate export or an additional 1.3 g of C m⁻² yr⁻¹ export averaged over the three basins. This number is largest for the Ohio (an additional 2.0 g of HCO₃⁻ C m⁻² yr⁻¹) and smallest for the Missouri (an additional 0.5 g of HCO₃⁻ C m⁻² yr⁻¹). Assuming that ~60% of this carbon originates from the atmosphere [Raymond and Cole, 2003] this represents an increase in CO₂ sequestration by chemical weathering of ~1.0 g C m⁻² yr⁻¹ and can influence abiotic carbon fluxes in the Mississippi plume [Green et al., 2006]. This same 10% increase would lead to a 21% and 32% increase in DOC and POC export, respectively. Since all organic matter ultimately originates from the atmosphere this equates to an additional 0.45 g of C m⁻² yr⁻¹ of atmospheric CO₂ laterally transported to coastal systems. The fate of a percentage of this material will be oxidation in the associated coastal waters [Benner and Opalski, 2001], releasing inorganic nutrients and CO₂ into coastal waters, with the remaining material being buried in coastal sediments or exported to the open ocean.

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