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Measurement of Inorganic Carbon Fluxes from Large River Basins in South Central Kentucky Karst

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Introduction

Atmospheric CO_2 concentrations are an important factor impacting current global climate change. As such, a greater understanding of the processes that govern atmospheric CO_2 fluxes is required in order to predict and potentially mitigate future climate change (Cox et al. 2000; Falkowski et al. 2000). Current carbon budgets do not sufficiently account for a substantial terrestrial sink of atmospheric CO_2 and therefore these budgets are unacceptably imprecise (Tans et al. 1990; Sundquist 1993; Fan et al. 1998). One of the processes that act as a sink of atmospheric CO_2 on the continents is weathering of carbonate rock minerals. While this sink is to some degree or perhaps wholly offset by carbonate mineral precipitation in the oceans, only a more precise accounting of the magnitudes of these fluxes will quantify the net effect.

Measurement of the CO_2 sink on the continents from carbonate mineral weathering involves two parts: 1) measurement of the inorganic carbon flux leaving a river basin over a given period of time and 2) partitioning that carbon between that having been removed from the atmosphere and that coming from the carbonate bedrock. While previous investigations have attempted to account for a terrestrial sink of atmospheric CO_2 by weathering of carbonate rocks (Figure 1) (e.g. Liu and Zhao 2000; He et al. 2012), this sink is still poorly characterized.

The purpose of this research is to improve methods for measuring the inorganic carbon flux from carbonate rock weathering at the river basin scale, so this carbon sink effect can potentially be more accurately characterized on a global scale.

This study made use of one year of existing, publically available water chemistry data and discharge data for two river basins along with geologic and hydrologic GIS data, and local precipitation and temperature data. The total dissolved inorganic carbon (DIC) flux over a year for the Barren River upstream from Bowling Green (October 1, 2012-September 30, 2013), and the Green River upstream from Greensburg (February 1, 2013-January 31, 2014) were measured, and then normalized by time, water available for carbonate rock weathering (precipitation minus evapotranspiration (P-ET)), and the area of carbonate rock outcrop over each area.

We can simplify this by expressing the normalized fluxes as g C $(km^3\ H_20)^{-1}day^{-1}$ (grams of carbon per cubic kilometer of water, per day) by multiplying the average depth of the available water (P - ET) by the area of carbonate rock outcrop. These normalized values have shown favorable comparison, and a positive linear relationship between total DIC and $(km^3\ H_20)^{-1}\ day^{-1}$ over the area of carbonate rock has been observed.

This linear relationship suggests, if it holds over a larger range of basin sizes and climates, that this flux could perhaps be estimated over much larger areas without the direct use of water chemistry, or discharge data, and may be reduced to a Geographic Information Systems (GIS) technique involving only climatic and geologic data.

Methods and Results

Calculation of the DIC flux and normalization by depth of precipitation minus evapotranspiration over the carbonate rock area involved the use of water chemistry, discharge, geologic and hydrologic map data, and local precipitation and temperature data, all publically available and freely obtained. Calculation and normalization of this flux involved delineation of the drainage basin upstream from the sampling locations, determination of the area of geologic rock, estimation of average precipitation minus evapotranspiration over the basin, as well as the use of water chemistry and discharge data to measure the flux.

Data utilized to delineate the drainage area of the Barren River upstream from Bowling Green included US Geological Survey (USGS) Watershed Boundary Database (USGS WBD) data, Kentucky Geological Survey (KGS) Karst Atlas groundwater flow maps, and topographic maps. Accurate delineation of the drainage area is crucial to the final calculation of area of carbonate rock, and in carbonate rock dominated areas, subsurface flow can often strongly influence drainage and sometimes the locations of drainage divides.

The original USGS WDB drainage boundary for the Barren River was used as the starting point for delineation, but then karst flow that affected the locations of basin divides was taken into account using the KGS Karst Atlas maps. Groundwater sub basins identified as discharging downstream from Bowling Green, or into a bordering drainage basin, were accounted for and removed (Figure 1) and the new drainage area was carefully delineated using topographic base maps. The drainage area upstream from Bowling Green with these corrections for karst influenced drainage divides was found to be 4247.7 km^2.

The area of carbonate rock was measured using the newly-delineated drainage basin. Geologic map data were obtained from the KGS Geospatial Data Gateway, and the USGS Mineral Resources Online Data Gateway. Using these map data, all formations classified as a limestone or dolostone according the Kentucky Geological Survey classification (as the majority of the drainage basin is in Kentucky, with a small amount in Tennessee) were selected. These formations were then combined into a single map layer using geoprocessing tools.

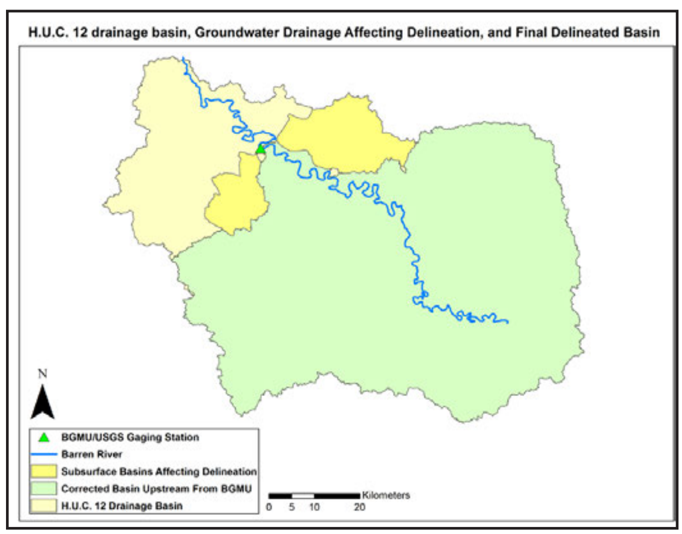

Figure 1: Barren River H.U.C 12 drainage basin, groundwater sub-basins affecting delineation, and delineated basin upstream from Bowling Green. Data sources: USGS WDB (2014); KGS (2014); USDA NRCS (2014).

The area of this final map layer was calculated, resulting in the area of carbonate rock within the drainage basin (Figure 2). The total area of carbonate rock within the basin was found to be 3995.5 km^2 or 94.1% of the drainage area. The area of carbonate rock for the Green River drainage basin upstream from Greensburg was obtained from Osterhoudt, (2014).

Precipitation and temperature data were obtained from the Kentucky Mesonet and the Midwest Regional Climate Center Cli-MATE Online Data Portal. Point precipitation data were obtained for stations in and surrounding the drainage basins. Potential Evapotranspiration (PET) was calculated using the Thornwaithe equation (Thornthwaite, 1948), and used to represent actual evapotranspiration (ET) during the study period. These monthly evapotranspiration values were subtracted from precipitation.

Final precipitation minus evapotranspiration (P – ET) values were interpolated in ArcGIS 10.1 using Inverse Distance Weighted (IDW) interpolation (Figure 3). Results from the IDW interpolation were compared to an identical data set but using Kriging methods, and the resulting total values agreed to within 0.52%. Average basin wide precipitation minus evapotranspiration over the drainage basins for each hydrologic year was 78.7 cm for the Barren River, and 66.7 cm for the Green River upstream from Greensburg.

Water chemistry data were provided by Bowling Green Municipal Utilities, for the Barren River at Bowling Green and by the Greensburg Water Works for the Green River at Greensburg. River stage data were provided by the US Geological Survey for both locations, and discharge was also available from USGS for Bowling Green. River stage from Greensburg was used to develop a rating curve from existing National Oceanic and Atmospheric Administration (NOAA) data (Osterhoudt, 2014) to obtain discharge. Alkalinity,

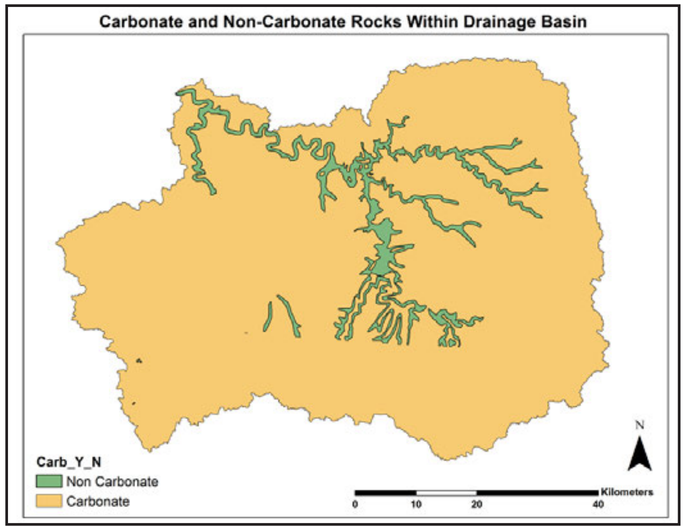

Figure 2: Carbonate and non-carbonate rocks within the drainage basin. Data Sources: KGS (2014); USDA NRCS (2014).

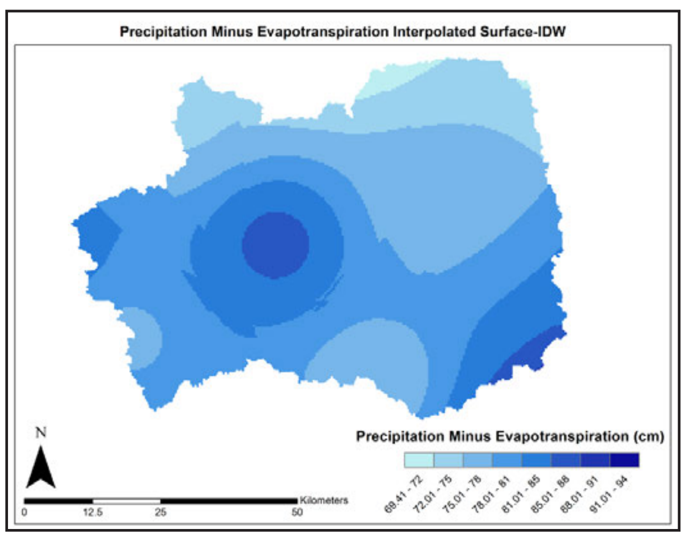

Figure 3: Annual precipitation minus evapotranspiration interpolated surface for the Barren River Drainage Basin using IDW. (Data Source: MWRCC, 2015).

pH, and temperature data had eight-hour resolution for Bowling Green, and daily resolution for Greensburg, while discharge data were of 15-minute resolution.

From the water chemistry data, DIC concentrations were calculated for each period of measurement, this value was multiplied by total volume of water discharged in each period, resulting in the total DIC flux. These flux values for each period of measurement were summed to find the total DIC flux for the year of study at both locations.

The total DIC flux was then normalized by time, in days, and volume of water available for carbonate rock dissolution, which is the product of the area of carbonate rock area and depth of P - ET. Resultant normalized values were of 5.61x107g C $(km^3\ H_20)^{-1}\ day^{-1}$ (grams of carbon per cubic kilometer of water, per day) for the Barren, and 7.43x107g C $(km^3\ H_20)^{-1}\ day^{-1}$ for the Green River.

Conclusions

Time and volume of water (carbonate rock area * (P – ET)) normalized DIC flux values for a year long of study for two separate basins were found to agree within 25%. Additionally, individual monthly normalized flux values were calculated for the year-long study period for the Barren River drainage basin.

When these twelve values are graphed along with the two for the Barren, and Green River hydrologic year values (Figure 4), the resultant r^2 value is 0.9495 which indicates a strong positive relationship between DIC flux and time-volume of water over carbonate rock. This positive relationship indicates that the primary variables affecting DIC flux for theses drainage basins, are time, and volume of water available for dissolution, and that other potential variables may constitute much weaker inputs into the system.

These results show promise in the potential for estimation of DIC flux values over large areas using only climatic and geologic data. Future work in this area should include analysis of larger basins, and likewise normalization, to see if this trend continues with larger basins having varying area of carbonate rock and varying climate.

If this statistical relationship can be demonstrated over a larger range of basin sizes and climates, this will potentially allow for a much more accurate estimation of this carbon flux on a continental, or global scale. The ability to accurately estimate the magnitude of this sink effect over large areas without the direct use of water chemistry data could considerably contribute to the current understanding of this carbon sink

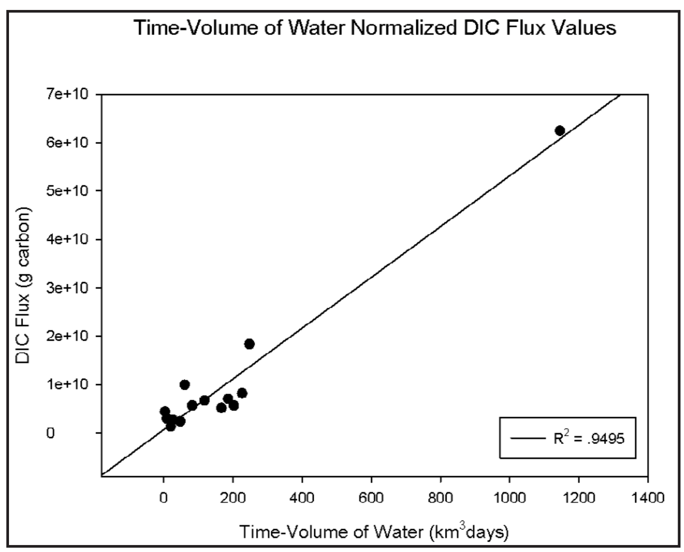

Figure 4: DIC flux versus time-volume of water available for carbonate rock dissolution, for the Barren, and Greensburg hydrologic years, and twelve months of the Barren hydrologic year. (Data sources: BGMU, GBWW, USGS)

effect and its magnitude on a global scale. This would result in more accurate carbon budgeting, potentially leading to a better understanding of the carbon sink currently un-accounted for by global carbon budgets (Liu & Zhao, 2000; Liu et al., 2011; White, 2013).

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