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What controls the spatial patterns of the riverine carbonate system? — A case study for North America

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ABSTRACT

In this study we analyzed the large scale spatial patterns of river pH, alkalinity, and CO_2 partial pressure (PCO_2) in North America and their relation to river catchment properties. The goal was to set up empirical equations which can predict these hydrochemical properties for non-monitored river stretches from geodata of e.g. terrain attributes, lithology, soils, land cover and climate.

For an extensive dataset of 1120 river water sampling locations average values of river water pH, alkalinity and PCO_2 were calculated. The catchment boundaries and catchment properties were calculated using GIS and different sets of geodata. The correlations between the hydrochemical properties and the catchment properties were explored using simple and multiple linear regression analysis.

For each of the considered hydrochemical parameters, a multiple regression equation was fitted: for pH with the predictor's mean annual precipitation and areal proportions of carbonate rocks ($r^2 = 0.60$); for alkalinity, in addition to these two predictors, with subsoil pH and areal proportions agricultural lands ($r^2 = 0.66$); and for $pPCO_2$ (i.e. the negative logarithm of PCO_2) with mean air temperature, mean catchment slope gradient, and mean annual precipitation ($r^2 = 0.43$). Based on these results, we argue that spatial patterns in river water pH and alkalinity are governed by catchment processes related to chemical rock weathering. For the PCO_2, on the other hand, the spatial patterns are governed by in-river processes on which catchment properties can have an indirect effect. We conclude that our approach can be used to predict averages of these parameters for non-monitored river stretches, which in-turn allows for a better spatially explicit representation of the rivers' carbonate system at the regional to global scale, which will be needed for a refined analysis of rivers in the global carbon cycle.

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1. Introduction

The land–ocean transfer of dissolved inorganic carbon (DIC) through rivers is an important part of the global carbon cycle and has been assessed at the global scale by various studies (Livingstone, 1963; Garrels and Mackenzie, 1971; Kempe, 1979; Meybeck, 1979; Ludwig et al., 1996a). The estimated total fluvial exports range from 320 Mt a^{-1} (Ludwig et al., 1996a) to 450 Mt a^{-1} (Kempe, 1979). DIC contributes to about 45% of fluvial carbon exports to the coastal zones (Ludwig et al., 1996a).

Most of the previous studies at continental to global scale focused on the lateral fluxes of carbon only, and thus regarded rivers as "pipes" in the carbon cycle (cf. Cole et al., 2007), although it has long been recognized that rivers are mostly supersaturated with CO_2 relative to the ambient air and are thus a net source of CO_2 to the atmosphere (e.g. Park et al., 1969; Garrels and Mackenzie, 1971; Kempe, 1982). More recent studies focused on rivers as biogeochemical reactors with substantial net-fluxes of CO_2 to the atmosphere (Cole et al., 2007; Battin et al., 2008; Battin et al., 2009; Humborg et al., 2010; Aufdenkampe et al., 2011; Butman and Raymond, 2011). At the global scale, the freshwater-atmosphere flux of CO_2 was estimated to amount to 750 to 1400 Mt Ca^{-1} (Aufdenkampe et al., 2011), to which streams and rivers contribute about 560 Mt Ca^{-1} (Aufdenkampe et al., 2011).

Fluvial carbon fluxes observed at the river mouths are not sufficient to assess the exports of carbon from the catchments to the fluvial system (Worrall et al., 2007; Battin et al., 2009). Reasonable estimates of CO_2 evasion from lakes and rivers, which also account for its spatial variability, would help refine carbon budgets of terrestrial ecosystems (cf. Jones and Mulholland, 1998a; Cole and Caraco, 2001; Billett et al., 2004; Jenerette and Lal, 2005; Jonsson et al., 2007).

Knowledge about the controls of the rivers' carbonate system is essential for the spatially explicit prediction and modeling of the river–atmosphere CO_2-flux. While latitudinal gradients in CO_2 partial pressures (PCO_2) were stated at global scale (Aufdenkampe et al., 2011) and the spatial variability of river water PCO_2 and CO_2 flux was already described for the conterminous USA (Jones et al., 2003; Butman and Raymond, 2011), the controlling factors of the spatial

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variability in the carbonate system of rivers are still an active area of research. For the United States, studies to date have demonstrated that climate (Raymond and Oh, 2007; Raymond et al., 2008) and land-use (Oh and Raymond, 2006; Barnes and Raymond, 2009; Raymond and Oh, 2009) can alter the concentration and flux of DIC from a watershed. Other studies showed that lithology or soil pH has a pronounced impact on fluvial alkalinity fluxes (Hartmann, 2009; Moosdorf et al., 2011a).

The objective of this study was to reveal the spatial patterns in the carbonate system of North America's rivers and to identify the controlling factors. Throughout the study area, hydrochemical data from 1120 sampling locations were considered. For these sampling locations, the mean values of the main parameters of the carbonate system, i.e. PCO_2, alkalinity, and pH, were analyzed with regard to functional relationships to the related river catchments. The aim was to set up empirical equations explaining the spatial variability in these parameters based on predictors derived from available geodata on climate, lithology, land cover, and relief.

Note that contrary to existing regional to global scale studies (e.g. Bluth and Kump, 1994; Hartmann, 2009; Moosdorf et al., 2011a), this study focuses on the mean alkalinity of the river water instead of the fluvial alkalinity fluxes. In-river biogeochemical processes and gas-exchange with the atmosphere have a substantial effect on river water PCO_2 and pH. Therefore, the catchment–river coupling with regard to these parameters, and thus the spatial predictability of these parameters, may be weaker. Further, the catchment–river coupling might decrease with increasing catchment size, i.e. with increasing transport time during which in-river processes take place. Both hypotheses were tested in this study.

2. Methods

2.1. Processing of hydrochemical data

Hydrochemical data were taken from various sources. For the USA, two extensive databases from the US Geological Survey were used: the Water Quality Network (WQN) (Alexander et al., 1998) and the National Water Information System (NWIS) (USGS). For Canada, different databases from the national and provincial surveys were used (Government of Alberta — Environment; Ontario — Ministry of the Environment; Environment Canada, 2009; Environment Canada, 2010). From these databases, all samples with measurements of water temperature, pH, and alkalinity were selected. If available, additional information on the concentrations of major ions, dissolved silica, dissolved organic carbon (DOC), or suspended matter (SPM) concentrations was taken as well. The combined dataset covers a sampling period from 1962 to 2008. Temporal trends and their effects on the analysis of spatial patterns and their controls are discussed later in the text (Section 3.4).

For each sample, the partial pressure of CO_2 (PCO_2) was calculated from water temperature, pH, and alkalinity using the software PhreeqC v2 (Parkhurst and Appelo, 1999). As far as available, concentrations of other major solutes and their effects on the hydrochemical equilibrium were taken into account. If Ca^{2+} concentrations were available, the saturation index for calcite $SI_{calcite}$ was calculated.

The following procedure was applied to calculate representative mean values of all hydrochemical parameters for each sampling location.

1) For the aggregation of hydrochemical parameters, it was necessary to avoid logarithmic values. Thus, pH values were transformed to H^+-concentration values. Similarly, $SI_{calcite}$, which is considered in its logarithmic form (Eq. (1)), was recalculated to the saturation $\Omega_{calcite}$ (Eq. (2)) before the aggregation procedure

$$SI_{calcite} = \log_{10}(IAP/K_{calcite}) \quad (1)$$

$$\Omega_{calcite} = IAP/K_{calcite} \quad (2)$$

with:

IAP ion activity product

$K_{calcite}$ solubility constant for calcite.

2) The calculation of PCO_2 is very sensitive to uncertainties in the source data, particularly with regard to pH (cf. Kempe, 1982). This circumstance partly led to unreasonably extreme PCO_2 values. As an objective and reproducible strategy to cope with this problem, for each sampling location only samples with calculated PCO_2 values between the 10th and 90th percentiles of the respective time series were selected for the following procedure steps and analyses.
3) With the remaining data, for each sampling location long-term monthly arithmetic means of each hydrochemical parameter were calculated.
4) For 814 catchments, an average PCO_2 could be calculated for each month of the year. For the other sampling locations, gaps of up to three months were filled by linear interpolation between the last reported value before the gap and the first reported value after the gap.
   According to the size of the gaps within the 'annual cycle', one of four quality levels was assigned to each sampling location (Table 1).
5) For the sampling location and parameters for which a complete cycle of twelve monthly values was present after this procedure, a mean parameter value was calculated.

Note that by steps 4) and 5) a seasonal weighting is applied, which accounts for the seasonality in the variability of the hydrochemical parameters. For $\Omega_{calcite}$, geometric means have been used for aggregation, being the appropriate averaging technique for ratios. Five of the 1125 sampling locations had to be discarded from the following analyses, because of unrealistic average PCO_2 values (>15,000 ppmv) that were still present after the procedure described above, leaving a total of 1120 sampling locations considered.

2.2. Calculation of catchment properties

For deriving the catchments' boundaries, the position of each sampling location was adjusted to fit the stream network of the applied digital elevation model (DEM), i.e. the Hydrosheds DEM in a resolution of 15″ (Lehner et al., 2008; 'Flow direction' in Table 2). Note that this DEM only covers areas south of 60° N, which restricts the study area accordingly.

The catchment properties were derived as mean values of the geodata (Table 2) overlain by each catchment. Slope gradient was calculated from the SRTM digital elevation model from Jarvis et al. (2006). We preferred this DEM over the Hydrosheds 15″ DEM because of its higher resolution and the sensitiveness of the parameter slope gradient to the resolution of the DEM used (cf. Wolock and McCabe, 2000). The Hydrosheds DEM on the other hand is a hydrologically sound DEM, i.e. it was optimized for representing the stream network, and was thus used for deriving the catchment boundaries (Lehner et al., 2008).

The UNH/GRDC runoff dataset represents long-term averages (1960–1990) of monthly and annual runoff at 30′ resolution. It is a

Table 1
Quality levels for stations concerning the coverage of the annual cycle by available parameter values.

Quality code	Description	Number of sampling locations
1	All twelve months	814
2	No gaps larger than 1 month	226
3	No gaps larger than 2 months	53
4	No gaps larger than 3 months	32

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