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Long-term trends in alkalinity in large rivers of the conterminous US in relation to acidification, agriculture, and hydrologic modification

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HIGHLIGHTS

- We analyzed long-term trends in alkalinity and other solutes in large U.S. rivers.
- Increasing alkalinity concentration and flux were widespread.
- Considering multiple solutes provided insight into controls on alkalinity trends.
- Receding acidification and agricultural lime were linked with alkalinity increases.
- However, a diversity of processes led to alkalinity trends.

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ABSTRACT

Alkalinity increases in large rivers of the conterminous US are well known, but less is understood about the processes leading to these trends as compared with headwater systems more intensively examined in conjunction with acid deposition studies. Nevertheless, large rivers are important conduits of inorganic carbon and other solutes to coastal areas and may have substantial influence on coastal calcium carbonate saturation dynamics. We examined long-term (mid-20th to early 21st century) trends in alkalinity and other weathering products in 23 rivers of the conterminous US. We used a rigorous flow-weighting technique which allowed greater focus on solute trends occurring independently of changes in flow. Increasing alkalinity concentrations and yield were widespread, occurring at 14 and 13 stations, respectively. Analysis of trends in other weathering products suggested that the causes of alkalinity trends were diverse, but at many stations alkalinity increases coincided with decreasing nitrate + sulfate and decreasing cation:alkalinity ratios, which is consistent with recovery from acidification. A positive correlation between the Sen–Thiel slopes of alkalinity increases and agricultural lime usage indicated that agricultural lime contributed to increasing solute concentration in some areas. However, several stations including the Altamaha, Upper Mississippi, and San Joaquin Rivers exhibited solute trends, such as increasing cation:alkalinity ratios and increasing nitrate + sulfate, more consistent with increasing acidity, emphasizing that multiple processes affect alkalinity trends in large rivers. This study was unique in its examination of alkalinity trends in large rivers covering a wide range of climate and land use types, but more detailed analyses will help to better elucidate temporal changes to river solutes and especially the effects they may have on coastal calcium carbonate saturation state.

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1. Introduction

River carbon (C) fluxes are an important link between terrestrial and marine carbon cycles (Aufdenkampe et al., 2011). Globally, rivers deliver 0.3 to 0.6 Pg C yr⁻¹ to oceans (Meybeck, 1993), and >75% of carbon export from the conterminous US occurs as inorganic carbon (IC; Stets

and Striegl, 2012). Alterations of IC delivery can occur due to changes in chemical weathering (Amiotte Suchet et al., 1995). Surface water acidification caused by intensive agricultural production, atmospheric deposition, acid mine drainage, industrial effluents, and municipal wastewater can alter pH and carbonate buffering conditions (Meybeck, 2003) and affect fluvial IC cycling. Positive trends in alkalinity and pH since the early 1990s are common in small headwater systems and indicate a recovery from acidification (Chen and Lin, 2009; Stoddard et al., 1998, 1999). Large rivers also exhibit positive trends in alkalinity concentration and flux, but less is known about the processes driving these trends.

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Large rivers tend to have greater buffering capacity than small headwater catchments and so they are less susceptible to direct ecological effects of acidification (Johnson, 1979). Therefore, studies of acidification have mostly focused on highly susceptible headwater catchments. Nevertheless, acidic inputs interact with the carbonate buffering system and have consequences for IC biogeochemistry of large rivers. Changes in the carbonate buffering characteristics of rivers can affect coastal calcium carbonate equilibria (Duarte et al., 2013), with particularly acute effects on coastal shell-bearing organisms (Salisbury et al., 2008). Therefore, it is important to properly describe and attribute alkalinity trends in large rivers.

Increasing alkalinity flux from the Mississippi River results primarily from increased runoff (Raymond et al., 2008) whereas increasing concentrations in the Eastern U.S. are related to patterns in atmospheric deposition and recovery from acid mine drainage (Kaushal et al., 2013; Raymond and Oh, 2009). In some systems agricultural lime is important to fluvial inorganic carbon cycling (Aquilina et al., 2012; Barnes and Raymond, 2009; Hamilton et al., 2007; Oh and Raymond, 2006) although its overall significance to large rivers is not well quantified.

River alkalinity concentrations respond to a variety of factors which makes discerning the cause of alkalinity trends difficult. Increasing alkalinity can indicate recovery from acidification (Chen and Lin, 2009; Stoddard et al., 1998, 1999) because deposition of N + S acids in poorly buffered systems (alkalinity <200 $\mu\text{eq L}^{-1}$; Stoddard et al., 1999) consumes alkalinity and so a relaxation of this process results in positive alkalinity trends. The underlying theory of soil acidification predicts that in watersheds with ample buffering capacity accelerated weathering rates from additions of N + S acids can increase base cation and alkalinity export (Amiotte Suchet et al., 1995; Van Breemen et al., 1983). According to this theory, acidification would lead to increased alkalinity concentration and flux whereas decreased acidification would result in lower alkalinity in surface waters. However, empirical studies indicate that recovery from acidification can result in increased alkalinity even in highly buffered surface waters (Chen and Lin, 2009; Majer et al., 2005). Urbanization and changing agricultural management practices can also result in changing alkalinity in surface waters.

Urban areas have many possible sources of increased alkalinity. Concrete structures provide additional weatherable material to urban areas; weathering rates increase in disturbed soils; and, elevated CO_2 concentrations in aquifers receiving sewer or septic system effluent may also increase weathering rates (Barnes and Raymond, 2009). Agricultural contribution to increased alkalinity in surface waters can result from similar processes, especially the addition of agricultural lime. Agricultural liming adds carbonate minerals to soils as a means of counteracting the acidifying effects of tilling, fertilizer usage, and nitrogen-fixing plants (Hamilton et al., 2007). Addition of agricultural lime, most commonly as calcium carbonate (CaCO_3) or dolomite ($\text{MgCa}(\text{CO}_3)_2$), counteracts acidification by adding base cations and acid-neutralizing capacity to soils. Reactions between soil acids and agricultural lime are identical to typical carbonate weathering reactions (Table S1) and produce soluble weathering products which can affect solute concentrations in soils and nearby surface waters (Aquilina et al., 2012; Barnes and Raymond, 2009; Hamilton et al., 2007; Oh and Raymond, 2006; Perrin et al., 2008). In silicate-dominated crystalline basins, agricultural lime can be a major component of the overall IC budget (Aquilina et al., 2012).

In this study we examined alkalinity trends in large rivers of the conterminous US between the middle part of the 20th century and the early 21st century. Acidification of rivers has been expressed as a water quality concern since the early part of the 20th century (Cumming, 1916; Leitch, 1926; Purdy, 1930), mostly associated with industrial waste and acid mine drainage (AMD). Atmospheric sources of acidity increased in the middle part of the 20th century and damaged areas that were formerly pristine. Greater regulation of point sources in the U.S. has decreased direct acidic inputs to surface waters and atmospheric sulfur emissions have decreased markedly in recent decades (Smith et al.,

2011). Given this context, we analyzed long-term trends in large US rivers to gain a fuller perspective on how alkalinity and other solutes have responded to the dramatic changes over that time period. We used a rigorous flow-weighting scheme to minimize the effects of changing flow regimes which allowed greater focus on changing river chemical conditions. We analyzed trends in associated ionic weathering products in order to better attribute the observed changes in alkalinity. We also use water quality data from the early 20th century to provide perspective on modern solute concentrations.

2. Methods

2.1. Ionic solute generation by chemical weathering

Chemical weathering results from the interaction of silicate or carbonate minerals with acids. Ionic weathering products are a predominant source of alkalinity and base cations to surface waters. In most soils, carbonic acid (H_2CO_3) produced from root and soil microbial respiration dominates chemical weathering reactions. However, N + S acids, which have both natural and anthropogenically-mediated sources, also contribute to chemical weathering (Lerman et al., 2007; Perrin et al., 2008). Nitric acid arises from nitrification of ammonium, which is a natural process that can be greatly increased by N-fertilizer additions, or from atmospheric deposition. Sulfuric acid arises from atmospheric deposition, and from pyrite oxidation, which occurs naturally but can be greatly increased by mining activity.

Increasing chemical weathering rates will increase the production of weathering products including cations, alkalinity (as HCO_3^-), as well as nitrate (NO_3^-) and sulfate (SO_4^{2-}) if N + S acid weathering is also increasing. Changes in the relative contribution of H_2CO_3 versus N + S acids will also result in trends in cation: HCO_3^- ratios (Aquilina et al., 2012; Hamilton et al., 2007; Perrin et al., 2008). Reactions between H_2CO_3 and carbonate or silicate minerals produce cations and HCO_3^- in 1:1 equivalent ratios (Table S1). When N + S acids weather carbonates in soil with circumneutral pH the reaction produces cation and HCO_3^- equivalents in a 2:1 ratio (Hamilton et al., 2007), whereas the reaction between N + S acids and silicates produces no HCO_3^- (Table S1; Aquilina et al., 2012). The production of NO_3^- and SO_4^{2-} anions instead of HCO_3^- maintains charge balance. Therefore, analyzing trends in a suite of weathering products and their ratios can provide insight into the processes driving alkalinity trends.

We summarize the trend analyses included in this study and their interpretation in Table 1. As mentioned previously, alkalinity responds to a variety of pressures and so attributing a specific process to alkalinity trends is difficult. Coupling alkalinity trends with those of major cations (Ca^{2+} and Mg^{2+}) can help to elucidate how alkalinity trends relate to overall weathering rate within the basin (Table 1). Similarly, trends in the equivalent sum of weathering-related anions, $\text{HCO}_3^- + \text{NO}_3^- + \text{SO}_4^{2-}$ ($\sum A_w$) can help indicate changes to overall weathering rates. Considering the ratio $[\text{Ca}^{2+} + \text{Mg}^{2+}]:\text{HCO}_3^-$ addresses how alkalinity trends relate to acidification processes (understood to mean increased weathering by N + S acids). Increasing $[\text{Ca}^{2+} + \text{Mg}^{2+}]:\text{HCO}_3^-$ indicates increasing prevalence of N + S acid weathering whereas a decreasing ratio indicates the opposite. A related metric, the trend in the equivalent sum of NO_3^- and SO_4^{2-} (N + S) can be indicative of trends acidifying processes.

2.2. Data sources

We assembled long-term water quality and stream discharge datasets for 23 monitoring stations selected for data availability and to represent the range of climate and land use in the conterminous US (Fig. 1, Table 2). We examined trends in alkalinity and other weathering products between the mid-20th and early 21st centuries. A separate publication describes the environmental history, geographic setting, land use changes, and data availability for most of the stations (Stets

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