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Chemical weathering and the subsequent export of carbonate alkalinity ($\text{HCO}_3^- + \text{CO}_3^{2-}$) from soils to rivers account for significant amounts of terrestrially sequestered atmospheric CO_2 . We show here that during the past half-century, the export of this alkalinity has increased dramatically from North America's largest river, the Mississippi. This increased export is in part the result of increased flow resulting from higher rainfall in the Mississippi basin. Subcatchment data from the Mississippi suggest that the increase in the export of alkalinity is also linked to amount and type of land cover. These observations have important implications for the potential management of carbon sequestration in the United States.

In terrestrial systems, there are two major processes that sequester atmospheric CO_2 : Organic carbon produced during photosynthesis can be stored on land or exported in rivers, or terrestrial alkalinity (carbonate and bicarbonate ions) produced during chemical weathering in soils can be fluvially exported. The fluvial export of terrestrial alkalinity is also the major source of oceanic alkalinity and is a key regulator of the CaCO_3 saturation state of the oceans (1). During chemical weathering, the atmosphere provides the reservoir of CO_2 either directly, or indirectly through the respiration of plant-derived organic matter. The lithosphere converts some of this CO_2 to dissolved bicarbonate or carbonate through the weathering of the parent rock material, and the hydrologic cycle transports this dissolved inorganic carbon, as alkalinity, to rivers and ultimately to the ocean. Regional chemical weathering rates are controlled, in part, by regional rainfall characteristics (2), because during weathering, water operates as both a reactant and a transporting agent (3). Thus, changes in water delivery can alter the export rates of elements with a weathering source (4). It has recently been shown that levels of precipitation (5, 6) and stream flow (6, 7) have been increasing over the Mississippi watershed during the past 80 years and that the seasonality of stream flow has also shifted (6). Here we show that the rate of alkalinity export from the largest river in North America, the Mississippi, has responded positively to the increase in water delivery. We also provide evidence that alkalinity export rates from the Mississippi and

the ability of the watershed to respond to increases in rainfall may be linked to agricultural practices.

The production of alkalinity through chemical weathering in soils sequesters atmospheric CO_2 through reactions of CO_2 with parent rock material during dissolution. During the weathering of silicates, a single mole of atmospheric CO_2 is sequestered for every mole of alkalinity produced. During carbonate weathering, the carbonate minerals donate a second mole of carbon for every mole of CO_2 sequestered; thus, half of the alkalinity exported from streams by this mechanism is of atmospheric origin. It has been argued that the weathering of silicate parent material sequesters CO_2 for millions of years and controls atmospheric CO_2 concentrations over geological time scales (8, 9), whereas the weathering of carbonate parent rock material only sequesters atmospheric CO_2 for hundreds to thousands of years because of "reverse weathering" in the oceans (8, 10, 11). Regardless, in both cases the transport of atmospherically derived CO_2 via weathering from land is part of the terrestrial C sink.

Controls on long-term chemical weathering rates are complex and include temperature (12, 13), precipitation (14), changes in plant communities (15, 16), the rise and fall of sea level and mountains (17, 18), and mechanical weathering (19). Plant processes play a major role in evaluating controls on present-day weathering rates (20–23) by adding weathering agents or protons (CO_2 and organic acids) to soil water (24) and facilitating microbial activity, which can enhance soil disaggregation (25) and the production of CO_2 and other acids (26). Although some small-scale studies have linked alkalinity export to agricultural practices (27), the effect of changes in land cover on rates of alkalinity export is not currently being assessed in the U.S. C budget.

Analysis of contemporary weathering rates is often done through solute export from

river and stream systems (4, 10, 28). We analyzed data from the mouth of North America's largest river, the Mississippi, at the most seaward station [U.S. Geological Survey (USGS) site 07373420, near St. Francisville, LA; $30^\circ45'30''$, $91^\circ23'45''$] for which long-term (>30 years) data were available. For the St. Francisville station, a 48-year record beginning in 1953 with 849 alkalinity values, averaging 17 samples per year or about 1.4 samples per month, was obtained from USGS data sets (29). Sampling was well spaced over the year, providing a robust opportunity for computing average annual fluxes (30). Because alkalinity concentrations in the Mississippi are dominated by bicarbonate (30), all values reported here are converted to milligrams of C (mg C) (29).

The trend of increasing rainfall and stream flow in the Mississippi drainage basin is also

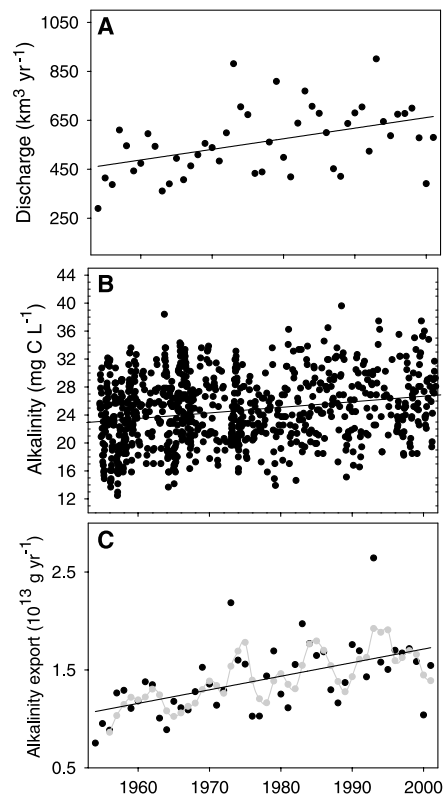


Fig. 1. Water and alkalinity export for the Mississippi River. Panels show time series of (A) annual export of water, (B) the concentration of alkalinity in the river, and (C) the export of alkalinity over time. In (C), we present annual export values (black circles) and 3-year running averages (gray squares connected by lines). Alkalinity concentrations are from the St. Francisville USGS site, whereas discharge data are the cumulative flow from the Tarbert Landing and Old River USGS sites. These two sites make up the total latitudinal flow from the Mississippi drainage basin (natural water plus Mississippi watershed water diverted to the Atchafalaya) and are both proximate to St. Francisville. All linear regression relationships are significant at the $P < 0.0009$ level.

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apparent in the Mississippi River discharge data (Fig. 1A). Although the discharge of water has increased during the past 50 years (Fig. 1A), the concentration of alkalinity has not decreased (Fig. 1B). Rather, the concentration of alkalinity has increased slightly over time and has increased to a greater extent than that of other anions in the database (31). Thus, the proximate cause of the increased alkalinity export (Fig. 1C) is increased water delivery with no concomitant alkalinity dilution effect.

The three main tributaries of the Mississippi—the upper Mississippi [34% of total discharge (Q)], the Missouri (14% of Q), and

the Ohio (52% of Q)—also show increases in the export of both water and alkalinity when analyzed separately (fig. S1). The three main tributaries have markedly different alkalinity concentrations, and the high concentrations in the upper Mississippi result in a large contribution (~49%) to the total alkalinity export flux, with the remaining 32 and 19% originating from the Ohio and Missouri, respectively (fig. S1). Regarding the increase in the export of both water and alkalinity from 1954 to 2000, the upper Mississippi experienced the largest changes and is responsible for 49 and 56% of the additional water and alkalinity export increase for the entire Mis-

issippi, respectively (fig. S1). The upper Mississippi also has the highest percent of land coverage in cropland, 55%, of the three tributaries, with the Missouri and Ohio having 33 and 27%, respectively (data are from USGS Digital Data Series DDS-37 for 1985). In order to further analyze the mechanism of increased alkalinity export from the Mississippi, subcatchment data for the three main tributaries were analyzed using USGS Digital Data Series DDS-37. Within this data set, for the upper Mississippi and Ohio River basins, the subcatchment data indicate a strong negative relationship between land cover consisting of forest and stream alkalinity and a positive relationship between land cover consisting of cropland and stream alkalinity (fig. S2). The export rates, normalized to watershed area, were calculated for the stations that had matching discharge and drainage area data. These areal rates demonstrate a strong relationship between land cover and alkalinity export (Fig. 2). Using linear regressions from the cropland land-class relationships, we estimate that lands that are covered in cropland have riverine alkalinity concentrations that are six and five times higher than those of noncropland land covers for the upper Mississippi and Ohio basins, respectively; whereas alkalinity export per unit area of watershed is four and nine times higher, respectively, for cropland sites.

Finally, rating curve plots of daily Q versus alkalinity concentration from forest and cropland end-member systems indicate that the response of cropland watersheds to increased rainfall and water delivery is different than that of watersheds with a larger forest component (Fig. 3). Watersheds with a high forest cover component show a significant dilution effect, with alkalinity concentrations decreasing exponentially with discharge, whereas cropland systems exhibit a less pronounced dilution effect (Fig. 3).

Collectively, Figs. 2 and 3 indicate that land cover change plays a critical, yet not currently well constrained, role in rates of contemporary alkalinity export, and cropland weathering rates may respond differently than those of forests to variations in rainfall. Future research needs to evaluate the relative contributions of direct and indirect effects of agricultural practices on weathering rates. Direct effects would include tilling practices, which may increase the surface area of soil minerals and alter the hydrology of surficial soils, both of which may increase the contact rate between water and minerals. Agricultural fields are also engineered to have high rates of plant productivity, which may increase the production of CO_2 and organic acids in soil waters. Indirect effects include potential contributions from landscape attributes that may co-vary with agricultural land placement (such as mean soil depth and soil type). De-

Fig. 2. Relationships between land cover class and annual riverine alkalinity flux for the upper Mississippi (top panels) and Ohio (bottom panels) Rivers. Percent catchment in cropland versus alkalinity flux is shown on the left; percent catchment in forest versus alkalinity flux is shown on the right. All data, including land class and basin size, are from USGS Digital Data Series DDS-37. Because the data series reports land-class information for 1985, we used average annual alkalinity concentrations and annual discharge data from 1985 to calculate annual fluxes. For a few systems where 1985 data was not available, we used proximate-years data. Data from the Missouri River catchment showed no cropland or forest relationship, which is due to the large occurrence of rangelands and low forest cover in the Missouri watershed.

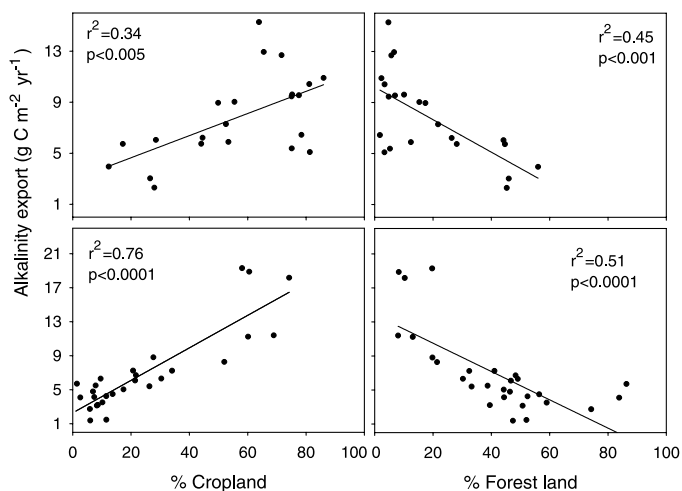
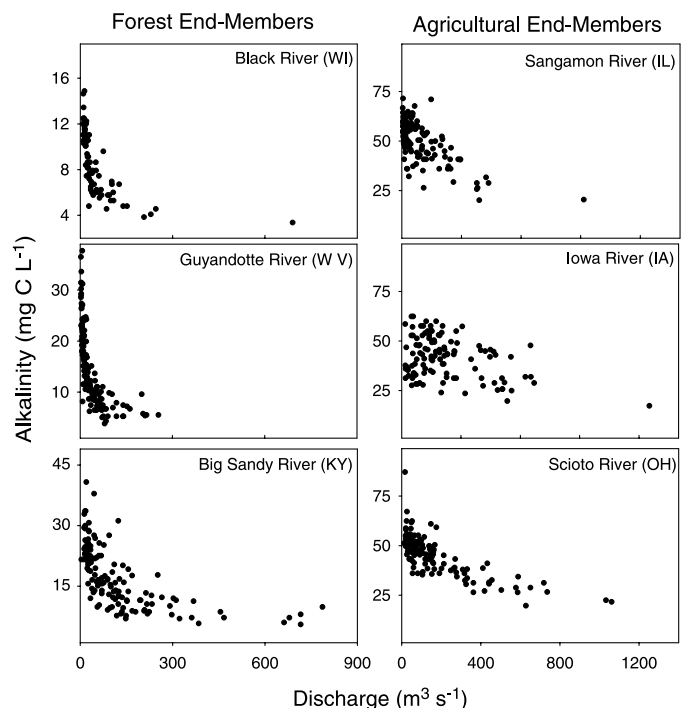


Fig. 3. Instantaneous flow versus alkalinity concentration for catchment land-class end-members. Graphs on the left are from three forest end-members; graphs on the right are three cropland end-members. Data are from USGS Digital Data Series DDS-3.



REPORTS

termining the relative roles of direct and indirect effects is of paramount importance, because a large portion of the Mississippi watershed is currently in agricultural usage, and if land use change to agriculture results in the export of four to nine times more alkalinity (Fig. 2), preagricultural rates of alkalinity export from the Mississippi drainage basin may have been approximately one-half to one-third of what they are today.

Regardless of the mechanism, the rate of bicarbonate export from the Mississippi drainage basin has increased from 1.10×10^{13} to 1.75×10^{13} g of C per year (g C year⁻¹) from 1954 to 2001 (Fig. 1C). Gaillardet *et al.* (10) reported export rates of $\sim 1.2 \times 10^{13}$ g C year⁻¹ for the Mississippi. Although that study did not investigate temporal trends, through dissolved ion ratios and inverse modeling they concluded that $\sim 60\%$ of the Mississippi bicarbonate flux originates from atmospheric CO₂ (10). Assuming that this percentage has remained constant, we estimate a potential net annual increase in atmospheric CO₂ sequestration of 0.39×10^{13} g C year⁻¹ from 1954 to 2001, which equates to an areal normalized increase of ~ 1.2 g C m⁻² year⁻¹ over the 47 years of record. Normalizing this rate globally equates to an additional sink of $\sim 0.18 \times 10^{15}$ g C year⁻¹, which suggests the potential for a doubling of the reported rates of atmospheric CO₂ consumption through weathering (28) in ~ 50 years.

Recently, some authors have argued for the importance of CO₂ evasion from rivers to the atmosphere in regional terrestrial C budgets (32, 33). With respect to a major terrestrial C sink, it has been demonstrated that the conversion of agricultural fields to forests results in the sequestration of atmospheric CO₂ in forest biomass and soils (34, 35). Our land cover data indicate that converting croplands to noncroplands results in a decrease in alkalinity export of ~ 5 to 20 g C m⁻² year⁻¹ (Fig. 3), of which approximately $\sim 60\%$ may originate from the atmosphere. Although we do not have an estimate for the amount of C sequestration by other mechanisms for the Mississippi basin alone, normalizing the conterminous United States sink of 0.06 to 0.15 Pg C year⁻¹ accumulating in forest trees (34, 35) over the land area of the conterminous United States provides a sink of ~ 8 to 13 g C m⁻² year⁻¹ (or ~ 40 g C m⁻² year⁻¹ when normalized to the land area of forests). Others have also recently argued that the fate of terrestrial soil organic C eroded from the landscape is storage in fluvial impoundments and not oxidation to CO₂, representing a terrestrial sink for atmospheric CO₂ of ~ 0.04 Pg C year⁻¹ for the conterminous United States (36). The fluvial export of soil organic carbon is also strongly accelerated by agricultural practices

(37) and represents a second important fluvial sequestration pathway that has higher rates in agricultural than in forested land covers. Collectively, these studies question the conversion of croplands to forests as a potential C sequestration policy and stress the need to account for changes in stream export rates in terrestrial C budgets.

Finally, these data demonstrate an increase in the export of alkalinity from the Mississippi watershed over the past five decades, which demands an increase in the supply of protons to mineral surfaces or an increase in the rate of chemical weathering due to warming. The acidity of rain has not increased in recent decades (38), and therefore the increase in proton delivery does not appear to be linked to acid rain. Potential mechanisms for an increase in proton delivery include an increase in atmospheric CO₂, an increase rainwater throughput, or an increase in plant and microbial production of CO₂ and organic acids in soils due to biological responses to increased rainfall and temperature. Plant productivity responses to increased temperature and rainfall are already documented for the United States (39, 40). Determining the relative contribution of these mechanisms, which will vary in importance regionally, is a critical component of future research. In particular, because nitrogen loading has also increased in the Mississippi watershed over the study period and is linked to agricultural practices (41, 42), studies must also determine the relationship between nitrogen loading and alkalinity export. Nitrogen loading could stimulate both soil respiration (43) and nitrification (44), the latter of which represents a source of acid to weather minerals that does not consume atmospheric CO₂ and was found to be responsible for $\sim 6\%$ of the bicarbonate generation in a carbonate-rich, extensively farmed watershed (45).

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- Alkalinity titrations began in 1973, using a fixed end-point titration on unfiltered samples. Starting in 1984, the USGS switched to a fixed end-point titration on filtered samples. This resulting switch would result in an underestimate of any potential increase in alkalinity and therefore doesn't affect our interpretations. Furthermore, in 2001 the USGS began measuring particulate inorganic carbon (PIC; the difference between unfiltered and filtered titrations) and found that levels are generally at detection limits, or < 0.1 mg of PIC liter⁻¹. In order to extend our database to 1954, we used values of total and non-carbonate hardness (a similar titration) measured by the USGS from 1954 to 1983. The methods of hardness and alkalinity overlapped for 10 years and 178 measurements, allowing for the determination of the appropriateness of using the two different methods. Over the 10 years, carbonate hardness (total hardness - noncarbonate hardness) averaged $99.8 \pm 0.8\%$ of alkalinity estimates. Finally, for the St. Francisville site, the USGS reports bicarbonate concentrations from 1997 to 2001 for a total of 67 samples. During these sampling events, the equivalent neutralizing capacity due to bicarbonate was $97.3 \pm 5.8\%$ of total acid-neutralizing capacity and $99.9 \pm 0.5\%$ of total dissolved alkalinity. Therefore, at Mississippi pH values, alkalinity and carbonate hardness are dominated by bicarbonate, and we report alkalinity concentrations as mg C liter⁻¹, remembering that 1 mg of CaCO₃ (as reported by the USGS) is 2 mg of dissolved bicarbonate because of the charge difference between carbonate and bicarbonate.
- Alkalinity export was calculated by multiplying annual average alkalinity concentrations by annual average discharge. We also estimated annual export according to the conventions of Goolsby and Battaglin (41). Using their conventions, we calculated fluxes that were slightly higher than our method ($\sim 10\%$). The slopes of the increase in alkalinity export over the 47-year study period, and the predicted increase in alkalinity export, were virtually indistinguishable, with the Goolsby and Battaglin method being 0.2% smaller than our method. Thus, our method compares well with previous methods.
- USGS data from St. Francisville indicate that the concentrations of sulfate and chloride decreased over the same time period (according to linear regressions of all data points, $P = 0.046$ for sulfate and $P < 0.0001$ for chloride). Over the 47-year study period, the increase in anions is dominated by HCO₃⁻, which is responsible for $\sim 69\%$ of the anion increase. The anion increase is well balanced by a reciprocal increase in cation flux, with the cation flux being 8% higher than the anion flux and well within the error for the combined estimates. The increase in cation flux is dominated by calcium and magnesium, which are responsible for 45 and 36% of the cation flux increase, respectively.
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Supporting Online Material

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Figs. S1 and S2

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