

SPECIAL ISSUE-CURRENT EVIDENCE

Anthropogenic influences on riverine fluxes of dissolved inorganic carbon to the oceansPeter A. Raymond ¹* Stephen K. Hamilton ²¹Yale School of Forestry and Environmental Studies, Yale University, New Haven, Connecticut; ²W.K. Kellogg Biological Station and Dept. Integrative Biology, Michigan State University, Hickory Corners, Michigan**Scientific Significance Statement**

Fluxes of bicarbonate from land to the oceans via rivers are being altered under the influences of a variety of human activities. The net effect of human activities appears to be to enhance these fluxes, although it is possible that the observed increases are also influenced by the recovery from past acidification caused by activities such as mining, fossil fuel burning, and intensive agriculture.

Abstract

Bicarbonate (HCO_3^-), the predominant form of dissolved inorganic carbon in natural waters, originates mostly from watershed mineral weathering. On time scales of decades to centuries, riverine fluxes of HCO_3^- to the oceans and subsequent reactions affect atmospheric CO_2 , global climate and ocean pH. This review summarizes controls on the production of HCO_3^- from chemical weathering and its transport into river systems. The availability of minerals and weathering agents (carbonic, sulfuric, and nitric acids) in the weathering zone interact to control HCO_3^- production, and water throughput controls HCO_3^- transport into rivers. Human influences on HCO_3^- fluxes include climate warming, acid precipitation, mining, concrete use, and agricultural fertilization and liming. We currently cannot evaluate the net result of human influences on a global scale but HCO_3^- fluxes are clearly increasing in some major rivers as shown here for much of the United States. This increase could be partly a return to pre-industrial HCO_3^- fluxes as anthropogenic acidification has been mitigated in the United States, but elsewhere around the world anthropogenic acidification could be leading to decreased concentrations and fluxes.

Dissolved inorganic carbon (DIC) is a biogeochemically and ecologically important variable in freshwaters that buffers pH, sustains aquatic photosynthesis and biogenic calcification, and interacts with other elemental cycles such as phosphorus and calcium. DIC includes multiple forms (Box 1)

but the bicarbonate ion (HCO_3^-) predominates at the circum-neutral pH of most natural waters (6–8.5), including the major rivers draining to the oceans as well as seawater. In addition to its importance in natural waters, DIC concentrations affect the cost of water treatment for human uses,

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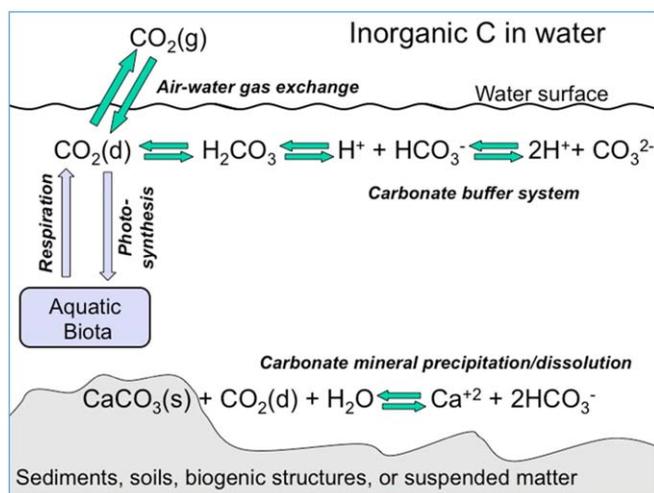
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Data Availability Statement: To access the data for Fig. 2 go to https://figshare.com/articles/Figure_2_csv/5753049/3.

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Box 1. Inorganic carbon cycle in aquatic ecosystems.

Inorganic carbon in surface waters of circumneutral pH exists in multiple forms, as depicted here in simplified reactions (sizes of arrows do not reflect fluxes). The gas carbon dioxide (CO_2) is exchanged across the air-water interface, and dissolved CO_2 is in chemical equilibrium with carbonic acid (H_2CO_3), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions accompanied by protons (H^+); all of these carbon species are referred to collectively as dissolved inorganic carbon (DIC). When dissolved CO_2 is added or removed, as for example by air-water equilibration or metabolism of the aquatic biota, the carbonate buffer system responds and reduces variability in pH.

Alkalinity, or acid-neutralizing capacity, in natural waters is largely due to the excess of HCO_3^- and CO_3^{2-} over H^+ in ionic charge equivalents, and this "carbonate alkalinity" arises mainly from the chemical weathering (dissolution) of minerals in watersheds including silicates as well as limestone (CaCO_3) and dolomite [$\text{CaMg}(\text{CO}_3)_2$]. Dissolved CO_2 and the corresponding acidity increase dissolution rates, whether in soils or sediments. The reaction is reversible, however, and CaCO_3 precipitation can occur due to supersaturation induced by warming or loss of dissolved CO_2 , or via biogenic calcification to produce shells or other structures.

particularly when the water is prone to calcium carbonate precipitation. Information on the sources and cycling of DIC is therefore key to understanding aquatic biogeochemistry and water quality.

In addition to the importance of inorganic carbon cycling to aquatic ecosystems, its role in the global carbon cycle is increasingly recognized as fundamental for understanding the future response of the Earth system to anthropogenic climate change (Martin 2017). The implications of changes in the balances between organic carbon synthesis and degradation on land and in the oceans for atmospheric carbon dioxide (CO_2) and therefore climate have been studied in detail (Berner 1982). Yet the picture is incomplete without also considering inorganic carbon cycling (Berner et al. 1983), both on land and in water, and fewer studies have addressed inorganic carbon in the context of global environmental change. In particular, the partial pressure of atmospheric CO_2 is ultimately controlled by equilibration with dissolved inorganic carbon (DIC) in the oceans (Box 1). By far most of the global DIC pool occurs in seawater, and as in most

inland waters, seawater DIC is predominantly composed of HCO_3^- and to a lesser degree carbonate (CO_3^{2-}) ions (hereafter referred to in sum as HCO_3^-). Most of this seawater HCO_3^- pool occurs in the deep oceans, and while it is by far the most abundant pool of actively cycling carbon in the biosphere, its equilibration with HCO_3^- in the ocean's surface waters is very slow.

Some of the HCO_3^- in the oceans precipitates as calcium carbonate (CaCO_3), both abiotically and by biogenic calcification, and becomes buried in the sediments (Box 1). Over long time scales (centuries to millennia), this deposition of precipitated carbonate minerals in marine sediments is balanced by riverine inputs of new HCO_3^- derived from mineral weathering in terrestrial watersheds, including carbonate minerals of marine sedimentary origin (limestone and dolomite) as well as silicate minerals of igneous origin (Berner et al. 1983). Over even longer time scales, tectonic uplift ultimately exposes new minerals on the continental land surfaces, albeit in a very spatially variable distribution (Martin 2017).

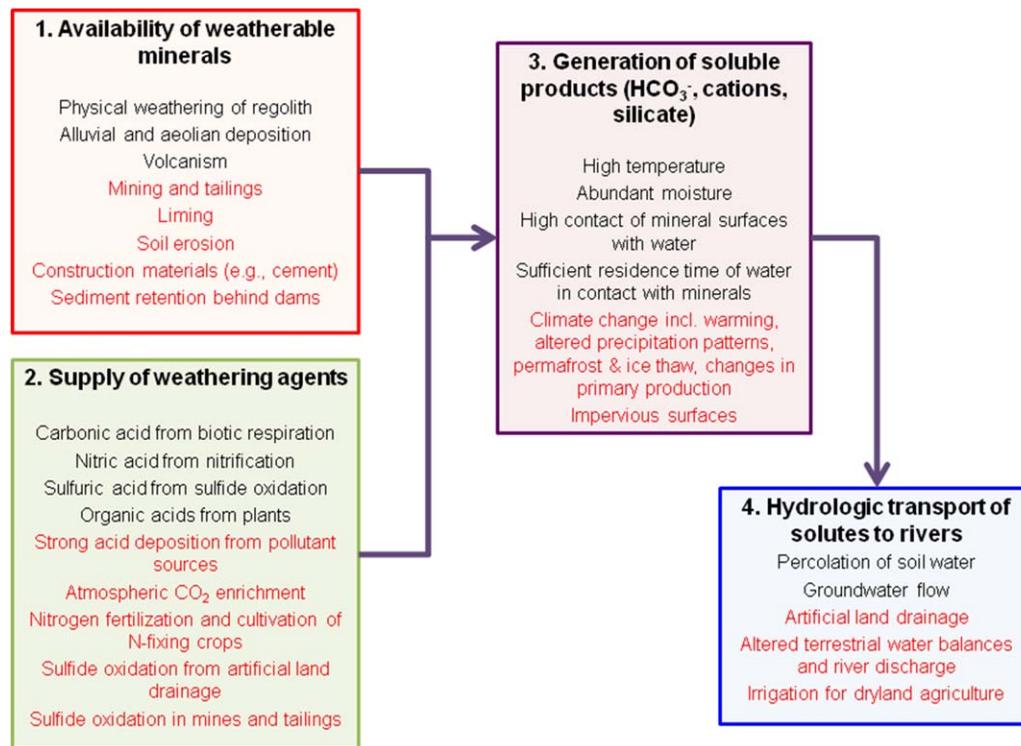


Fig. 1. Proximate controls on HCO₃⁻ fluxes from watersheds to the oceans. Red text indicates the major anthropogenic influences, most of which tend to increase HCO₃⁻ fluxes.

Alterations in the balance between inputs and losses of HCO₃⁻ in river systems thus have important implications for biogeochemical and ecological processes in inland waters and the oceans as well as for regulation of atmospheric CO₂ and climate. Human activities are increasingly altering terrestrial mineral weathering, land surface hydrology, and thus riverine fluxes of HCO₃⁻ to the oceans, with uncertain ramifications for biogeochemistry and feedbacks to climate. These alterations are also occurring concurrently with ocean acidification by increasing atmospheric CO₂, and changes in the riverine HCO₃⁻ fluxes can either offset or accelerate acidification in coastal waters (Semiletov et al. 2016). Although there is a building consensus that human activities are increasing riverine HCO₃⁻ fluxes, these anthropogenic influences are not currently considered in global carbon models or in water management. The purpose of this review is to summarize our comprehension of the controls on riverine HCO₃⁻ fluxes and discuss the evidence for how anthropogenic activities may be changing these fluxes.

Factors controlling production and transport of bicarbonate in watersheds

Chemical weathering of minerals to produce solutes is the ultimate source of HCO₃⁻ to rivers, and the nature and rates of chemical weathering in watersheds are often inferred from the hydrological export of HCO₃⁻ and other solute

products via rivers (Meybeck 1987; Gaillardet et al. 1999). The proximate controls on chemical weathering and solute export in watersheds are summarized in Fig. 1 (see also Brantley et al. 2011). The availability of weatherable minerals interacts with the supply of weathering agents under favorable conditions (e.g., temperature, moisture, mineral-water contact) to yield soluble products including HCO₃⁻, which are then subject to hydrologic transport into river systems (Fig. 1). The variable relative importance of these controls explains why the Earth's rivers range widely in their concentrations and fluxes of HCO₃⁻ and other major solutes derived from chemical weathering (Gibbs 1970; Kempe 1982).

The availability of minerals (Fig. 1, Mechanism 1) can control rates of chemical weathering in watersheds. Mineral availability is determined by the long-term balance between the input and output of minerals and their dissolution products in the weathering zone, which produces a spectrum from "fresh" to highly weathered soils (White and Brantley 2003). "Supply limitation," or the limitation of chemical weathering by the availability of weatherable minerals, is particularly evident in highly weathered, ancient landscapes of the humid tropics and subtropics, such as much of the lowland Amazon River basin where new minerals for weathering come only from the gradual degradation of the underlying regolith (Stallard and Edmond 1983). Tectonic uplift, erosion, and fluvial export and deposition of sediments can

also set long-term delivery rates of fresh material to the weathering zone and thereby impact weathering rates over geologic time scales (Raymo and Ruddiman 1992; Jacobson et al. 2003; Riebe et al. 2004; West et al. 2005) although recently a threshold to erosion-enhanced chemical weathering has been proposed (Gabet and Mudd 2009). At the other end of the spectrum are geologically young postglacial landscapes that still retain an abundance of readily weatherable silicate and carbonate minerals in soils, as well as terrains containing karst or carbonate-rich shale where large amounts of carbonate minerals are exposed to weathering (White and Blum 1995; Han and Liu 2004). In addition to natural processes, humans have altered the availability of minerals in the weathering zone through activities such as mining, water management, and construction, as discussed below.

Chemical weathering rates within the weathering zone can also be controlled by the supply of weathering agents (Fig. 1, Mechanism 2). The regulation of weathering reaction rates by the supply of weathering agents (i.e., protons) from both weak and strong acids has long been of interest to geochemists (Drever 1994). One of the main proton sources for weathering is carbonic acid (H_2CO_3), a weak acid produced when CO_2 dissolves in water (Box 1). Soil solutions tend to be supersaturated with dissolved CO_2 from root and microbial respiration and the reaction of carbonic acid with carbonate or silicate minerals consumes protons and yields HCO_3^- alkalinity and cations that are subject to hydrologic export from the weathering zone (Brantley et al. 2011). Other sources of protons to drive weathering reactions include weak organic (carboxylic) acids derived from vegetation and strong inorganic acids (mainly H_2SO_4 and HNO_3) derived from oxidation of sulfides and ammonium, respectively. All of these weathering agents are also produced by industrial activities and fossil fuel combustion (see below).

Numerous factors can influence the rates of reaction of these weathering agents with minerals (Fig. 1, Mechanism 3). For instance, the generation of soluble products from the reaction of protons with minerals is strongly regulated by temperature. Temperature is directly proportional to chemical weathering rates through its effects on mineral solubility and chemical reaction rates (Dessert et al. 2003). The temperature control on mineral weathering rates has been modeled using an Arrhenius function (White and Blum 1995) and shown to be a strong control of silicate mineral weathering rates through time and in cool climates (Millot et al. 2003). An important distinction between silicate and carbonate mineral equilibria is that carbonate minerals are less soluble at higher temperatures, and thus a warming climate may have opposing effects on weathering of these two kinds of minerals, although the atmospheric CO_2 enrichment that currently accompanies warming also plays a role by increasing proton availability. In addition to temperature, factors such as mineral surface area and soil water characteristics

can facilitate reactions of weathering agents and minerals (White et al. 1996).

The transport of solutes derived from mineral weathering out of the weathering zone is controlled by hydrology (Fig. 1, Mechanism 4). Infiltration and percolation of precipitation brings water to the weathering zone, while evapotranspiration removes soil water to the depth that plant roots occur. Hydrology also, in part, controls the residence time of water in the weathering zone (i.e., the rate of water throughput), and the balance between water throughput and mineral weathering rates is a critical control of riverine solute fluxes (Maher 2010). At low rates of water throughput (long water residence times in the weathering zone), mineral weathering will reach a near equilibrium with soil solutions, effectively putting a ceiling on solute concentrations and resulting in "transport limitation" of solute fluxes to rivers. At higher water throughput, if the input of protons and temperature remain constant, this transport limitation will be reduced, leading to higher fluxes. However, if the increase in water throughput continues, at some point the rate of mineral weathering will be at maximum and the system will become "reaction limited," in which case riverine fluxes will generally only increase if temperature or proton supply increase. Since mineral weathering rates increase with temperature, higher temperatures will lead to a system becoming transport limited at lower rates of water throughput and reaction limited at higher throughput. Thus anything that significantly alters the hydrology or temperature of the weathering zone may alter rates of chemical weathering and solute export, with anthropogenic climate change being one of the major drivers of both altered hydrology and temperature.

Bicarbonate can be retained within river systems if there is precipitation and storage of CaCO_3 , whether by biogenic calcification (e.g., shell production by mollusks) or abiotic calcite precipitation, effectively reversing the mineral weathering reaction (Box 1). Uptake of HCO_3^- by aquatic autotrophs (e.g., algae and submersed macrophytes) results in an equivalent molar change in H^+ and hence produces no net change in carbonate alkalinity, but it can indirectly promote carbonate precipitation by increasing pH. In alkaline stream systems draining glacial deposits of the Midwest U.S., Szramek and Walter (2004) concluded that although calcite precipitation can be observed seasonally, and accumulation of calcite produces readily visible marl deposits in headwater reaches, this back-precipitation of calcite was shown to have little influence on the annual export of HCO_3^- from those watersheds.

In productive reservoirs or natural lakes along rivers with alkaline waters that are saturated with respect to calcium carbonate, calcite may precipitate and some fraction may become buried indefinitely in sediment deposits, resulting in net retention of HCO_3^- . Most of the world's large rivers are too ionically dilute for calcite precipitation (Kempe 1982), but calcite does precipitate in some large reservoirs along

western U.S. rivers (e.g., Lake Powell on the Colorado River: Stackpoole et al. 2014; Stets et al. 2014) and in Lake Pepin, a large natural lake along the upper Mississippi River. Engstrom et al. (2009) analyzed sediment cores from Lake Pepin to show that carbonate deposition has increased in recent decades, presumably as a result of eutrophication, and that the retention of CaCO_3 is now $\sim 120,000 \text{ Mg yr}^{-1}$. Given the 2 : 1 molar ratio of HCO_3^- : CaCO_3 (Box 1), this would be equivalent to the sequestration of 29,000 Mg of HCO_3^- , a tiny percentage ($\sim 0.2\%$) of the annual HCO_3^- flux carried by the river to the ocean ($\sim 16 \text{ Tg yr}^{-1}$; see below). Thus it seems unlikely that calcite precipitation in transit through river systems has a major effect on HCO_3^- fluxes.

Anthropogenic disturbance and chemical weathering fluxes

A major challenge in chemical weathering studies is the existence of numerous and interacting abiotic and biotic processes that complicate the assessment of landscape level controls, and can obscure the net result of anthropogenic disturbances. Although there are clear examples where a dominant mechanism can be argued, and supported by models (Riebe et al. 2004; West et al. 2005), temporal and spatial variation in natural factors and human influences make generalizations difficult. Spatial variation in soil thickness and hydrologic flow paths create heterogeneity even in small watersheds (Oliva et al. 2003; Jin et al. 2010). Variation in climate can cause many systems to have seasonally or inter-annually variable water throughflow, which in turn affects water residence time and thus weathering rates (Johnson et al. 1969). Biological processes impart a myriad of controls on chemical weathering, and are subject to their own influences by climate, such as increased soil respiration with warming (Richter and Billings 2015). Below we discuss in more detail some of the most important ways in which human activity directly or indirectly influences the transport of inorganic carbon and other solutes derived from chemical weathering by rivers to the oceans.

Climate warming

As noted above, temperature directly affects rates of chemical weathering reactions. Anthropogenically driven, global climate change generally entails warming, and therefore would be expected to influence the supply of solutes including HCO_3^- in the weathering zone (Fig. 1). The effect of climate warming on solute fluxes is difficult to demonstrate outside of the lab but warming has been argued to increase fluxes from basalts (Dessert et al. 2003), granites (White et al. 1999; Oliva et al. 2003) and forested watersheds of the United States (Raymond 2017). Studies have shown that the weathering rates of non-carbonate minerals obey Arrhenius-type laws that describe the influence of temperature (Lasaga et al. 1994). This direct effect of temperature, however, will not influence all watersheds equally under

warming scenarios. Both White and Blum (1995) and Raymond (2017) showed transport limitation of the temperature effect at lower discharges. In transport-limited watersheds with low precipitation and therefore low water throughput, reactions within the weathering zone will already be close to equilibrium, and increases in temperature will have less of an influence on solute concentrations and transport to rivers.

The response of chemical weathering in watersheds to increasing temperature will also be highly dependent on the type of minerals in contact with water. Carbonate mineral weathering dominates overall solute export to the ocean. It was recently demonstrated that 70% of the global HCO_3^- flux originates from 10% of the Earth's surface, with substantial contributions not only from sedimentary carbonate rocks but also from watersheds and sediments with trace but appreciable levels of carbonate minerals (Hartmann et al. 2014b). In addition to weathering, temperature impacts the solubility of carbonates because they become less soluble at higher temperatures. There are also temperature effects on soil respiration, the source of dissolved CO_2 that controls soil solution pH, and these can be more important to fluxes than mineral solubility effects. Raymond (2017) found that forested watersheds with higher carbonate mineral abundance did indeed have larger riverine flux responses to increases in temperature compared to silicate-dominated watersheds, however there were no differences in the percentage changes between carbonate- and silicate-dominated watersheds.

Increasing temperature also has a number of other indirect effects on rates of chemical weathering and riverine solute export. Warming can lead to the melting of glaciers with consequent large increases in solute fluxes due to the export of these previously stored solutes (Gislason et al. 2009) and over longer time scales with the loss of glaciers, the biological production and development of soils on previously glaciated terrains would promote weathering and solute export. Temperature can also regulate evapotranspiration and therefore river discharge and HCO_3^- fluxes (Beaulieu et al. 2012). At the poles, increases in temperature are leading to permafrost thawing, bringing minerals into the weathering zone that have been frozen for thousands of years and thereby increasing HCO_3^- fluxes (Tank et al. 2012). Warming and permafrost thaw also lead to enhanced decomposition, leading to higher soil CO_2 and HCO_3^- concentrations (Striegl et al. 2007). Changing global climate is also expected to alter the amount and timing of rainfall on land, potentially increasing or decreasing solute fluxes depending on the region and environmental setting (Maher and Chamberlain 2014). To date the direct and indirect impacts of a warming climate on chemical weathering and solute export from watersheds have been proposed to be positive overall, leading to larger riverine fluxes of HCO_3^- to the oceans.

Mining

The impact of mining on mineral weathering depends on mineralogy, mining practices, geology, and the hydrologic setting. Mining can expose minerals to weathering by bringing them to the surface, and, in the case of subsurface mining, bringing water in contact with new mineral surfaces. A dominant mechanism for mining impact is the generation of sulfuric acid via the oxidation of metal sulfides (often pyrite, FeS_2) that become exposed during the mining process (Raymond and Oh 2009; Burrows et al. 2015). Very acidic mine drainage can be generated where the acid neutralizing capacity of tailings is insufficient to buffer the acid produced, decreasing downstream fluxes of HCO_3^- (Vesper et al. 2016). Where sulfuric acid production from sulfide oxidation comes into contact with abundant carbonate minerals, as for example in the case of overburden deposits from mountaintop removal for coal mining in the eastern U.S. (Lindberg et al. 2011), the acidity is consumed by reaction with carbonate minerals, and waters emanating from the tailings can contain high concentrations of calcium and sulfate from that reaction as well as HCO_3^- from further weathering of carbonate minerals (Mayo et al. 2000; Vengosh et al. 2013; Vesper et al. 2016). However the HCO_3^- concentrations in such waters reach an upper limit determined by the solubility of CaCO_3 in water within the tailings and, upon discharging into a stream, with the stream water that tends to be in equilibrium with the atmosphere.

There are still only a few in-depth studies of the net effects of mining on mineral weathering and solute fluxes. It is important to point out that in a sustainable future, with larger amounts of energy generated through renewable sources or relatively clean natural gas, the acidification of watersheds due to coal mining and burning should continue to decrease.

Agriculture

Agriculture can affect riverine HCO_3^- fluxes by changing the acid-base balance of soils, particularly where nitrogen fertilization results in elevated rates of nitrification, a chemolithotrophic microbial process that readily converts ammonium to HNO_3 in oxic soils and waters, producing 2 moles of H^+ for each mole of ammonium that it consumes. It was first argued by Semhi et al. (2000) that a large percentage of the HCO_3^- alkalinity in the Garonne River watershed of France originates from the dissolution of carbonate minerals by HNO_3 , which in turn is produced by nitrification of excess nitrogen in fertilized soils. Where native carbonate minerals exist in watersheds, the acidity produced by nitrification (or other proton sources) will enhance weathering rates and can result in an increase in HCO_3^- alkalinity as long as the availability of weatherable carbonate minerals is not exhausted and pH remains above ~ 6.5 (Kilham 1982; Perrin et al. 2008).

In less buffered agricultural soils, which tend to be in humid climates, nitrogen fertilization acidifies soils (Guo et al. 2010). To maintain pH in a favorable range for crop production, soil amendments containing carbonate minerals must be regularly added, a practice known as liming (Hamilton et al. 2007). The dissolution of carbonate minerals in agricultural soils can occur either via “carbonic acid weathering” (the reaction in Box 1), which dominates at $\text{pH} > 6.5$, or via reaction with strong acids when pH is lower. Only carbonic acid weathering produces HCO_3^- alkalinity, whereas strong acid weathering generates CO_2 . Limited evidence suggests that both reactions are important in agricultural soils of the upper Midwest U.S., and therefore a substantial fraction of the carbonate carbon in applied liming materials can ultimately be exported to rivers as HCO_3^- alkalinity (Hamilton et al. 2007).

The potential contribution of agricultural liming to riverine HCO_3^- fluxes can be estimated from the rate of lime application in the watershed, even though there remains considerable uncertainty in the relative importance of carbonic acid vs. strong acid dissolution. For example, $\sim 20 \text{ g m}^{-2} \text{ yr}^{-1}$ of CaCO_3 ($\sim 2.4 \text{ g of C m}^{-2} \text{ yr}^{-1}$) is applied each year to agricultural lands in the Ohio River watershed of the Midwest U.S. (Oh and Raymond 2006). Of the potential 4.8 g of C as riverine HCO_3^- that could be produced assuming carbonic acid weathering, Oh and Raymond (2006) found an increase in HCO_3^- fluxes of $\sim 3.75 \text{ g of C m}^{-2} \text{ yr}^{-1}$, or 78% of the potential. These ranges of lime weathering by carbonic acid overlap with estimates by Hamilton et al. (2007) and Semhi et al. (2000). In the United States there is $\sim 30 \text{ Tg of CaCO}_3$ equivalent applied for liming each year, resulting in a potential maximum HCO_3^- production of 7.2 Tg yr^{-1} , or a more likely flux of $\sim 5.4 \text{ Tg yr}^{-1}$ assuming $\sim 25\%$ of the applied liming materials dissolves by strong acid reactions. The total U.S. riverine flux of HCO_3^- is $\sim 35 \text{ Tg yr}^{-1}$ (Stets and Striegl 2012), and thus in the U.S. liming can account for $\sim 15\%$ of that total U.S. flux.

Extrapolating to the globe is difficult due to the lack of global liming statistics. In the U.S. nitrogen fertilizer use is $\sim 11 \text{ Tg N yr}^{-1}$ (Howarth et al. 2002), and thus there is a $\sim 1 : 3$ mass ratio of N to lime use (CaCO_3 equivalent), assuming liming is practiced on most fertilized soils. Global fertilizer use is $\sim 100 \text{ Tg N yr}^{-1}$ (Galloway et al. 2003), and assuming a similar fertilizer to lime ratio as in the U.S., global lime use could be $\sim 275 \text{ Tg yr}^{-1}$, resulting in a maximum contribution of 66 Tg yr^{-1} of riverine HCO_3^- flux. For conservative purposes one might assume a range of $40\text{--}70 \text{ Tg yr}^{-1}$.

Agricultural water management can also impact river fluxes. Water management for agriculture has dramatically altered the terrestrial water balance in many parts of the world, either by bringing new water to dry regions for irrigation or draining excessively wet regions to permit farming. In both cases the production and export of weathering products are subject to change, though only a few studies have

examined the implications for riverine HCO_3^- fluxes to the oceans.

Irrigation can increase water-mineral contact and rates of water throughput in the weathering zone, with consequences for chemical weathering rates and solute export (Fig. 1). Irrigation may entail pumping ancient water from deep aquifers or drawing from distant surface waters, representing a new water addition that can lead to greater water throughput in the weathering zone (e.g., Bohlke et al. 2007), often in arid or semi-arid landscapes replete with readily weatherable minerals. On the other hand, irrigation using local groundwater or surface waters may reduce river discharge (Barlow and Leake 2012), potentially reducing HCO_3^- fluxes.

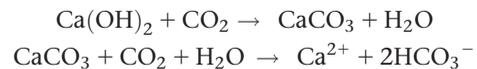
At the regional scale, widespread irrigation can alter rainfall patterns by increasing the downwind transport of evaporated irrigation water. In the Mississippi River watershed, it has been postulated that irrigation in the western Missouri River sub-watershed leads to higher summer rainfall over the downwind portion of the corn belt (Kustu et al. 2011), which could be partly responsible for the increase in HCO_3^- fluxes that has been observed in the Mississippi River (Raymond et al. 2008). The impact of irrigation on regional precipitation patterns is highly dynamic and will depend on the location of the irrigation and regional climate and air movements (Lo et al. 2013; Im et al. 2014).

Artificial drainage of farmland, often through networks of subsurface “tile drains” and open ditches, potentially increases riverine HCO_3^- fluxes. In addition to expanding the area of farmland with attendant increases in fertilization and liming, farmland drainage also changes rates of water throughput and bypasses longer soil flow paths to deliver shallow soil water directly to recipient streams (Blann et al. 2009; Schopka and Derry 2012). Drainage also creates oxidized conditions in soils that developed under intermittent or permanently reducing conditions, and often sulfuric acid produced by the weathering of accumulated iron sulfide minerals acts as a mineral weathering agent and consumes HCO_3^- in the soils or downstream waters (Smolders et al. 2006).

The global extent of artificial drainage for agriculture and other land uses is difficult to estimate. Even in the Midwest U.S., where estimates of the extent of drained farmland exist, it is difficult to determine the overall impact of land drainage on river discharge and HCO_3^- fluxes because climate and agricultural practices have also been changing, and we lack before-and-after studies since most drainage was put in place in the early 1900s. Nevertheless, it would be expected that artificial land drainage results in greater interaction between percolating water and weatherable minerals in the unsaturated soil layer, with weathering potentially augmented by acidity produced by sulfide oxidation where sulfide minerals have accumulated under water-saturated conditions in the past.

Concrete weathering

The built environment represents large-scale changes in surface mineralogy and hydrology that may be influencing HCO_3^- export to rivers. Much of the built environment is made of concrete containing cement. In the environment the weathering reaction of lime (Ca(OH)_2) in the cement with carbonic acid, which is known as carbonation (Chang and Chen 2006), results in the production of Ca^{2+} , HCO_3^- , and other ions. The weathering of cement to HCO_3^- by reaction with CO_2 is shown in these simplified reactions, showing the formation of CaCO_3 from lime, followed by the same CaCO_3 dissolution reaction as in Box 1:



Since concrete surfaces are often in direct contact with water, the potential for weathering is high, and solutes may readily be exported to rivers via stormwater drainage systems. Several studies have noted markedly higher fluxes of HCO_3^- in urban streams draining areas with higher impervious surface cover, much of which is presumably concrete (Barnes and Raymond 2009; Zeng et al. 2011; Kaushal et al. 2017; Moore et al. 2017). Recently total atmospheric CO_2 consumption due to concrete carbonation has been estimated at $0.25 \text{ Gt C yr}^{-1}$ (Xi et al. 2016). Given that an equimolar quantity of HCO_3^- is produced relative to the quantity of CO_2 that is consumed, the HCO_3^- production from cement weathering is potentially on a par with the riverine HCO_3^- flux (see below). It is currently difficult to determine how much of this cement-derived HCO_3^- is delivered to rivers but the potential exists that it is an important contributor to regional HCO_3^- fluxes.

Atmospheric deposition of acidity

In industrialized parts of the world, anthropogenic acidification of atmospheric deposition (both wet and dry) has resulted in large increases in the loading of acid weathering agents to watersheds (Fig. 1, Mechanism 2), primarily in the forms of sulfuric and nitric acids (Vet et al. 2014). In North America and Europe, efforts to reduce emissions of acid precursors (sulfur and nitrogen oxides) have yielded marked declines in the concentrations and rates of deposition of these acids, and the pH of precipitation has returned to close to pre-industrial values (Lajtha and Jones 2013). Acid deposition has been increasing in more recently industrialized regions, however, particularly in parts of China, India and elsewhere in east and south Asia. In addition, deposition of reduced nitrogen species (NH_4^+ and NH_3) is increasing in many agricultural parts of the world and can exceed that of nitrate (Vet et al. 2014); to the extent that this reduced nitrogen is not assimilated in watersheds it may be subject to nitrification and the resultant generation of nitric acid. In some regions of the world, particularly sensitive freshwater

lakes have been regularly limed in order to counteract the atmospheric deposition of acidity (Renberg et al. 1993).

The reaction of strong acids from atmospheric deposition with carbonate minerals in watersheds is similar to the effects of acid loading from mining, agriculture, and land drainage that are discussed above. One important difference is that atmospheric deposition impacts broad regions and often entails the transport of atmospheric pollution upwind and into relatively pristine headwater areas, whereas the aforementioned sources of acid loading mainly affect downstream waters.

When carbonate minerals are abundant in watersheds or sediments and the supply of weathering agents limits chemical weathering (Fig. 1, Mechanism 2), increased loading of strong acids via atmospheric deposition will enhance the dissolution of carbonates. As long as pH remains above ~ 6.5 there will be concomitant increases in carbonate alkalinity that can in turn increase riverine HCO_3^- fluxes (Kilham 1982). Such regions, which include some of the postglacial landscapes of the upper Midwest U.S. and much of south and east Asia, are generally regarded as insensitive to acidification because surface waters are well buffered (Duan et al. 2016), yet HCO_3^- fluxes may still be enhanced. Through the same process, acid deposition in contact with concrete surfaces in built-up areas can also produce a net source of HCO_3^- to rivers, as discussed above. If on the other hand the availability of weatherable carbonates (or concrete) in watersheds is limited, there will be a net consumption of HCO_3^- (generating CO_2) and the pH will eventually fall, potentially producing a decline in riverine fluxes. It is difficult to ascertain the net effect of these processes on global fluxes of inorganic carbon from rivers to the oceans.

Global estimates of riverine HCO_3^- fluxes and their changes over time

The most recent estimate of HCO_3^- fluxes to the ocean is $0.35 \text{ Pg C yr}^{-1}$ (Hartmann et al. 2014b). Are riverine HCO_3^- fluxes to the ocean increasing on the global scale? The large variation of riverine HCO_3^- export across watersheds and temporally within watersheds, coupled with multiple drivers of change and a paucity of long-term measurements, make this a difficult question to answer. The Mississippi River (U.S.A.) is the only large river that we are aware of with a long-term high-frequency record of HCO_3^- fluxes (Raymond et al. 2008). Bicarbonate concentrations and fluxes are clearly susceptible to human influence even at the scale of this very large river, which discharges $\sim 500 \text{ km}^3$ of water per year. The record—updated since it was first published by (Raymond et al. 2008)—shows that HCO_3^- fluxes have remained elevated and potentially even increased since the original analysis (Fig. 2). The current record has 100 yr of annual flux estimates within the time period of 1900–2015, calculated from daily measurements of total alkalinity. The

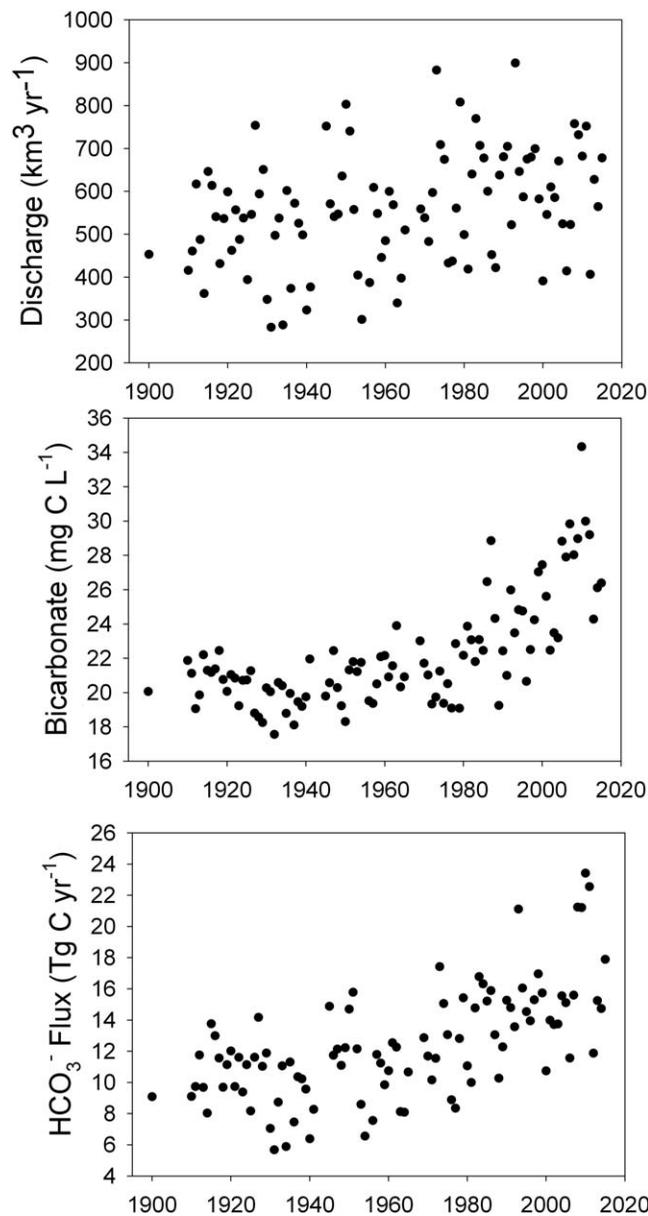


Fig. 2. Updated Mississippi watershed fluxes and bicarbonate concentrations. Methods are explained in Raymond et al. (2009), which presented these fluxes through 2004.

four highest annual HCO_3^- fluxes in this record all occurred after 2008.

The case of the Mississippi River exemplifies the difficulty in determining the relative importance of different drivers. There are many unexplained features in the annual flux time series, including a decrease in concentrations from 1900 to 1940, a period of low concentrations in the 1970s, and four consecutive years of high fluxes from 2008 to 2011 (Fig. 2). The river system is recovering from acid mine drainage produced by coal mining in the northeast portion of the watershed, is undergoing increasing urbanization, has had a

significant increase in agricultural production and associated use of fertilizers and lime, has seen large increases and then decreases in acid deposition, and has had a redistribution of precipitation and the associated discharge so that more of the annual discharge is coming from agricultural regions. The net result has been that HCO_3^- fluxes have increased from $10.8 \pm 1.7 \text{ Tg yr}^{-1}$ for the first 20 yr of record to $16.0 \pm 3.6 \text{ Tg yr}^{-1}$ for the last 20 yr, a remarkable $\sim 50\%$ increase. This increase in the concentration and flux of HCO_3^- from the largest U.S. river over the recent past has also been demonstrated in rivers of the eastern U.S. (Kaushal et al. 2013; Stets et al. 2014). Thus the trend of recent increasing HCO_3^- fluxes observed in the Mississippi River is evidently occurring across a broader region of the U.S., likely involving similar drivers.

Stets et al. (2014) argued that perhaps acidification is typical of the initial industrialization period, followed by mitigation of acid sources and a consequent alkalinity recovery in rivers in the post-industrialization period. This trend can be seen in some rivers of the United States that were sampled by the Clarke expedition in the early 20th century (Stets et al. 2014) and also through the reconstruction of alkalinity in Swedish lakes (Renberg et al. 1993). In many regions of the world, agriculture has also led to acidification where it was not counteracted by liming (Guo et al. 2010). Many regions of Asia are still in the initial phase of industrialization. The Mekong River of southeast Asia has increased in sulfate concentrations, potentially due to acid deposition, but shown no change in HCO_3^- concentration (Li and Bush 2015), and HCO_3^- fluxes have been lower in recent years due to drought and the filling of reservoirs, which have decreased water throughput (Li and Bush 2015). The Changjiang River of China is potentially highly influenced by anthropogenic acidity, which may be responsible for $\sim 20\%$ of weathering in its watershed (Chetelat et al. 2008). The Yellow River of China has also shown increases in the concentration of sulfate but not HCO_3^- and HCO_3^- fluxes have decreased due to water withdrawals (Chen et al. 2005). Thus many regions of the world seem to be still going through the acidification process. The idea of a peak of acidification with initial industrialization followed by recovery is also supported by a 130-yr record of calcium from the River Thames in England (Worrall et al. 2012).

Conclusions

Our understanding of the controls on HCO_3^- fluxes in rivers, including the interactions among climate, lithology and river chemistry, continues to improve. There is also a growing appreciation of the impact of human activities on HCO_3^- fluxes. Although we have identified a number of ways that human activities affect riverine HCO_3^- fluxes—and most of them would tend to increase fluxes—we still cannot estimate the net impact on the global scale. The conceptual model

put forward by Stets et al (2014) of an initial acidification during industrialization, followed by “alkalinization,” is compatible with a number of studies from around the globe. When viewed in this framework some proportion of the observed increases in riverine HCO_3^- fluxes may, in part, be a recovery toward pre-industrial fluxes.

In addition to reduced acidification owing to pollution control from mining and fossil fuel burning, a number of mechanisms that increase HCO_3^- fluxes have been discussed in this paper. Liming of agricultural fields to offset the acidification by fertilization and crop harvest can lead to increases in HCO_3^- fluxes. The global proliferation of concrete surfaces and attendant cement weathering also appears to have the potential to increase HCO_3^- fluxes at the regional scale. More broadly, increases in temperature and water throughput, two major changes associated with global climate change, will lead to an increase in HCO_3^- fluxes. The magnitude of the HCO_3^- flux response will be strongly influenced by how the hydrologic cycle responds to warming, and what percentage of the future energy portfolio is from the burning of coal, which is a particularly important source of anthropogenic acidification.

Currently the small number of studies is not sufficient to attempt quantification of the net impact of human disturbance on riverine HCO_3^- fluxes. More long time series of water chemistry in large rivers are needed. It is probable that additional long term data sets exist because total alkalinity, which can largely be ascribed to HCO_3^- , is a simple yet standard measurement made by water treatment facilities (Raymond et al. 2008). The scientific community needs to continue to collate river chemistry data into an open source database (e.g., the Global River Chemistry Database: Hartmann et al. 2014a). New high temporal resolution measurement methods are proving valuable for riverine biogeochemistry (Parker et al. 2007). Sensor technology for measuring components of the carbonate system are improving and need to be implemented in a manner that allows us to estimate the human contributions to HCO_3^- fluxes. Finally, isotopic approaches that allow for a better understanding of the processes important to chemical weathering (Han and Liu 2004) should be applied more broadly.

More research is urgently needed to understand how HCO_3^- fluxes may interact with atmospheric CO_2 and ocean acidification. In the past, the relationship between HCO_3^- fluxes and atmospheric CO_2 has arguably been approached in an overly simplistic manner. We now know that disturbances such as mining and liming can have different effects on atmospheric CO_2 sequestration depending on the parent lithology and degree of acidification. Furthermore, the fossil fuel costs, such as transportation of lime, of the anthropogenic activity need to be accounted for. Actions to enhance silicate mineral weathering by spreading finely ground material in regions with a favorable climate, which would potentially enhance riverine HCO_3^- fluxes, have been proposed as

a geo-engineering solution to help mitigate climate change (Moosdorf et al. 2014; Taylor et al. 2016). Whether intentionally enhanced or not, increased riverine HCO_3^- fluxes will potentially ameliorate ocean acidification in coastal waters to which the rivers discharge, as has been shown for mangrove wetlands (Sippo et al. 2016). We thus need to improve our ability to understand weathering responses to anthropogenic drivers to be able to assess the potential viability of this solution.

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