Anthropogenic influences on riverine fluxes of dissolved inorganic carbon to the oceans

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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 circumneutral 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,
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 (CO₂) 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 CO₂ 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 HCO₃⁻ and to a lesser degree carbonate (CO₃²⁻) ions (hereafter referred to in sum as HCO₃⁻). Most of this seawater HCO₃⁻ 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 HCO₃⁻ in the ocean’s surface waters is very slow.

Some of the HCO₃⁻ in the oceans precipitates as calcium carbonate (CaCO₃), 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 HCO₃⁻ 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).
Alterations in the balance between inputs and losses of HCO$_3^-$ 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 CO$_2$ and climate. Human activities are increasingly altering terrestrial mineral weathering, land surface hydrology, and thus riverine fluxes of HCO$_3^-$ to the oceans, with uncertain ramifications for biogeochemistry and feedbacks to climate. These alterations are also occurring concurrently with ocean acidification by increasing atmospheric CO$_2$, and changes in the riverine HCO$_3^-$ 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 HCO$_3^-$ 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 HCO$_3^-$ 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 HCO$_3^-$ to rivers, and the nature and rates of chemical weathering in watersheds are often inferred from the hydrological export of HCO$_3^-$ 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 HCO$_3^-$, 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 HCO$_3^-$ 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 and others 2003; Riebe and others 2004; West and others 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 ($\text{H}_2\text{CO}_3$), 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 and others 2011). Other sources of protons to drive weathering reactions include weak organic (carboxylic) acids derived from vegetation and strong inorganic acids (mainly H$_2$SO$_4$ 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 and others 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 and others 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 and others 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 ~ 120,000 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 (~ 0.2%) of the annual HCO$_3^-$ flux carried by the river to the ocean (~ 16 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 (Giselson 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, FeS₂) 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 HCO₃⁻ (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 HCO₃⁻ from further weathering of carbonate minerals (Mayo et al. 2000; Vengosh et al. 2013; Vesper et al. 2016). However the HCO₃⁻ concentrations in such waters reach an upper limit determined by the solubility of CaCO₃ 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 HCO₃⁻ fluxes by changing the acid-base balance of soils, particularly where nitrogen fertilization results in elevated rates of nitrification, a chemo-lithotrophic microbial process that readily converts ammonium to HNO₃ 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 HCO₃⁻ alkalinity in the Garonne River watershed of France originates from the dissolution of carbonate minerals by HNO₃, 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 HCO₃⁻ 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 pH > 6.5, or via reaction with strong acids when pH is lower. Only carbonic acid weathering produces HCO₃⁻ alkalinity, whereas strong acid weathering generates CO₂. 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 HCO₃⁻ alkalinity (Hamilton et al. 2007).

The potential contribution of agricultural liming to riverine HCO₃⁻ 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, ~20 g m⁻² yr⁻¹ of CaCO₃ (~2.4 g of C m⁻² 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 HCO₃⁻ that could be produced assuming carbonic acid weathering, Oh and Raymond (2006) found an increase in HCO₃⁻ fluxes of ~3.75 g of C m⁻² 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 ~30 Tg of CaCO₃ equivalent applied for liming each year, resulting in a potential maximum HCO₃⁻ production of 7.2 Tg yr⁻¹, or a more likely flux of ~5.4 Tg yr⁻¹ assuming ~25% of the applied liming materials dissolves by strong acid reactions. The total U.S. riverine flux of HCO₃⁻ is ~35 Tg yr⁻¹ (Stets and Striegl 2012), and thus in the U.S. liming can account for ~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 ~11 Tg N yr⁻¹ (Howarth et al. 2002), and thus there is a ~1:3 mass ratio of N to lime use (CaCO₃ equivalent), assuming liming is practiced on most fertilized soils. Global fertilizer use is ~100 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 ~275 Tg yr⁻¹, resulting in a maximum contribution of 66 Tg yr⁻¹ of riverine HCO₃⁻ flux. For conservative purposes one might assume a range of 40–70 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 quantify 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 carbonatation (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:

\[
\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}
\]

\[
\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-
\]

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 carbonatation has been estimated at 0.25 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 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 ~ 500 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 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 $10.8 \pm 1.7$ Tg yr$^{-1}$ for the first 20 yr of record to $16.0 \pm 3.6$ 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 $\text{HCO}_3^-$ 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.

References


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