River chemistry constraints on the carbon capture potential of surficial enhanced rock weathering

Shuang Zhang [1]* **Noah J. Planavsky** [2,3] **Joachim Katchinoff** [2] **Peter A. Raymond** [3,4]
Yoshiki Kanzaki [5] **Tom Reershemius** [2] **Christopher T. Reinhard** [5]

[1]Department of Oceanography, Texas A&M University, College Station, Texas
[2]Department of Earth and Planetary Sciences, Yale University, New Haven, Connecticut
[3]Yale Center for Natural Carbon Capture, Yale University, New Haven, Connecticut
[4]Yale School of the Environment, Yale University, New Haven, Connecticut
[5]School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia

Abstract

Technologies and approaches that remove and sequester carbon dioxide (CO_2) from Earth's atmosphere are likely to play a significant role in mitigating anthropogenic climate disruption in the coming century. Enhanced rock weathering (ERW) on the land surface is one extensively discussed approach toward carbon dioxide removal (CDR), but the capacity of rivers to carry dissolved products derived from ERW without CO_2 re-release is largely unexplored, hindering a full understanding of the life cycle of ERW and its associated maximum CDR potential. Here, we use a conceptual model built upon river/stream carbonate chemistry to estimate the upper limits on the carbon transport potential (CTP) of rivers and groundwaters. Our model yields a riverine CTP ranging between 0.26–0.89 $GtCO_2$ yr^{-1} for the United States and 7.1–21.3 $GtCO_2$ yr^{-1} globally for accelerated silicate weathering, and between 0.090–0.37 $GtCO_2$ yr^{-1} for the United States and 2.5–8.8 $GtCO_2$ yr^{-1} globally for accelerated carbonate weathering. Although these limits will be challenging to achieve in practice, our results support the notion that the transport of dissolved constituents in surface waters is unlikely to be a primary bottleneck limiting the CDR potential of ERW. This supports the notion that accelerated mineral weathering should be considered as an additional component of greenhouse gas mitigation portfolios. However, future research on the kinetics of ERW reactions and river responses, along with consideration of possible added CO_2 emissions by activities needed to accomplish ERW, are needed for a more realistic quantification of the net CDR via ERW in the land–soil–river system.

Carbon dioxide removal (CDR) from Earth's atmosphere is now widely viewed to be a key component of efforts to stabilize atmospheric CO_2 and prevent significant degradation of surface environments. For instance, all pathways delineated by the Intergovernmental Panel on Climate Change (IPCC) as having the potential to limit global warming since the preindustrial period to 1.5°C with little to no overshoot require CDR on the order of 100–1000 $GtCO_2$ over the next century (Köhler et al. 2010; Taylor et al. 2016; Strefler et al. 2018; Rogelj et al. 2018). Importantly, active CDR is projected with high confidence to be required even in pathways with rapid and deep cuts to anthropogenic emissions (Fuss et al. 2014; Gasser et al. 2015). A range of potential CDR approaches (also termed "negative emissions technologies") is currently being considered, including coastal "blue" carbon (Johannessen and Macdonald 2016), enhanced sequestration of organic carbon in natural and/or managed terrestrial ecosystems (Griscom et al. 2017), inorganic carbon sequestration in agricultural soils (Beerling et al. 2020), and sequestration of carbon in a variety of geologic reservoirs (Bui et al. 2018), among others. However, all currently proposed CDR techniques are subject to significant constraints imposed by available land, financial cost, environmental impact, and conceptual or technological maturity (Fuss et al. 2018). There is, therefore, an obvious impetus to develop a

Additional Supporting Information may be found in the online version of this article.

portfolio of strategies that can most effectively maximize CDR potential while navigating existing and emerging technological, logistical, and ethical constraints (Rau 2019).

Enhanced rock weathering (ERW) in Earth surface environments is based on naturally occurring weathering processes of silicate and carbonate rocks. It is one potential means of carbon capture and sequestration, with potentially significant co-benefits for food production and natural ecosystems (Beerling et al. 2018, 2020). The underlying principle of this CDR strategy is straightforward—because Earth's long-term carbon cycle is fundamentally regulated by storage and release of carbon by rock weathering (Berner 2004), selectively enhancing certain rock weathering processes has the potential to remove vast quantities of CO_2 from the atmosphere (Seifritz 1990; Köhler et al. 2010; Hartmann et al. 2013; Kelemen et al. 2020). For instance, CO_2 in Earth's atmosphere reacts with silicate minerals in basalt (shown here as congruent dissolution of pyroxene) to become dissolved bicarbonate (HCO_3^-):

$$\begin{aligned} Mg_xCa_yFe_{1-x-y}SiO_3 + 2CO_2 + 3H_2O \\ \rightarrow xMg^{2+} + yCa^{2+} + (1-x-y)Fe^{2+} + 2HCO_3^- + H_4SiO_4. \end{aligned} \quad (1)$$
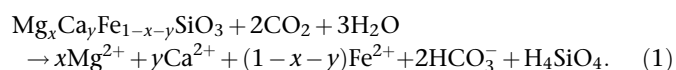
Weathering of carbonate minerals will similarly consume CO_2 and produce HCO_3^-:

$$Ca_xMg_{(1-x)}CO_3 + CO_2 + H_2O \rightarrow xCa^{2+} + (1-x)Mg^{2+} + 2HCO_3^-. \quad (2)$$
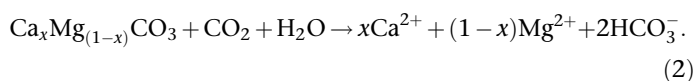
So long as the produced HCO_3^- remains stable, these weathering reactions sequester CO_2 from the atmosphere and result in negative radiative forcing. However, on geologic timescales the precipitation of ions (e.g., Ca^{2+} and Mg^{2+}; produced by weathering processes and transported via runoff to the oceans) will re-release CO_2 back to the atmosphere:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O. \quad (3)$$
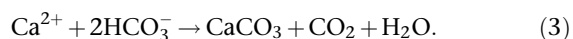
The residence time of bicarbonate in the ocean is on the order of 10^5 yr, resulting in the conventional view that the storage lifetime of this process is effectively permanent on human timescales (Renforth and Henderson 2017; Middelburg et al. 2020). On geologic timescales silicate weathering coupled to carbonate formation (Eqs. 1, 3), results in net removal of CO_2 from the atmosphere, while natural carbonate weathering coupled with carbonate formation (Eqs. 2, 3) is ultimately CO_2-neutral.

For HCO_3^- generated in the rock weathering process, the addition of proton equivalents (acidity) from species other than carbonic acid results in conversion back to CO_2:

$$H^+ + HCO_3^- \rightarrow CO_2 + H_2O. \quad (4)$$
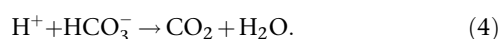
Notable potential sources of non-carbonic acidity include sulfuric acid, derived from atmospheric SO_2 deposition or oxidative weathering of sulfide minerals (Bufe et al. 2021), and nitric acid produced from oxidation of ammonium-based fertilizer (Hamilton et al. 2007). If non-carbonic acidity drives release of CO_2, the result in the case of silicate weathering is a decreased efficiency of CO_2 sequestration (Eqs. 1, 4), while for carbonate weathering it can potentially represent a net CO_2 source to the atmosphere (Eqs. 2, 4) (Oh and Raymond 2006; Hamilton et al. 2007).

Natural rock weathering on land currently removes ~ 1 $GtCO_2$ yr^{-1} from the atmosphere (Ciais et al. 2014). ERW approaches are designed to augment this CO_2 sink. However, building from the above framework for geochemical CO_2 consumption and re-release it is clear that the carbonic acid system in soils, rivers, and surface oceans is central to understanding the efficiency, potential, and ultimate cost of CDR through ERW. Most previous estimates of CDR potential through ERW have focused on upscaling of process-based models of local mineral dissolution within soils (Hartmann and Kempe 2008; Beerling et al. 2020; Goll et al. 2021). Here, we provide a new perspective on this problem by focusing instead on the capacity of rivers (as well as groundwaters) to carry dissolved products from ERW without CO_2 re-release. The logic is: if excess amounts of the solutes (e.g., Ca, Mg, Na, K, HCO_3^-) derived from ERW enter the river system, the saturation state of calcium carbonate (Ω) might surpass the thermodynamic threshold required for carbonate precipitation (eq. 3), which will re-release CO_2 back to the atmosphere and counteract the efficiency of CDR via ERW. In other words, there is a threshold of alkalinity input beyond which calcium carbonate precipitation will occur, and this should impose an effective upper limit on CDR. We argue that constraining the upper limit on the carbon transport potential (CTP) river/stream systems and groundwaters can help to inform coherent, quantitative targets that may be useful for optimization strategies and exploration of environmental impacts. Similar potential upper limits on capture have been useful in shaping dialogue about carbon capture via organic carbon (Griscom et al. 2017; Roe et al. 2021), but to date have been lacking for surficial ERW.

Materials and procedures

River quality datasets

Our model for estimating CTP relies on well-documented aqueous geochemical datasets, with a focus on river/stream chemistry in the contiguous United States and on a global scale (U.S. Geological Survey 2016). Our primary database for the United States (*see* Supporting Information) contains 3560 sites for stream/river data. To expand the data beyond the contiguous United States, we employ the global river chemistry database GLORICH (Hartmann et al. 2014), which contains data from more than 1.27 million samples and over 18,000 sampling locations, including a range of dissolve solute species in addition to catchment characteristics. We employ a modified GLORICH dataset that passes a series of filtering

criteria (*see* Supporting Information), resulting in data for 3365 locations worldwide.

An iterative geochemical model for estimating riverine CTP

We use an iterative thermodynamic numerical model to estimate upper limits on CTP. We begin with initial dissolved solute chemistry (Fig.1) and calculate the initial Ω for each site (Fig. 2). We then iteratively add ions derived from simulated congruent rock weathering (assuming a given rock feedstock is dissolved within 1 yr) to each river until the local river reaches a specified Ω for calcite precipitation. We employ two scenarios when simulating river responses to ERW. One is defined as the "closed" scenario (assuming no CO_2 degassing occurs in the river following simulated ERW) and the other is defined as "degassed" scenario (assuming additional CO_2 degassing occurs in the river following simulated ERW) (see Supporting Information). Conceptually, our numerical model results in an estimate of the maximum quantity of cations and alkalinity that can be stored in rivers before the onset of carbonate formation and commensurate re-release of CO_2. With that in mind, these values do not correspond to a maximum extent of CDR through surficial rock weathering—they represent the point at which there would be a significant drop in the amount of CO_2 captured per ton of rock dissolved. We focus here on three potential feedstocks for ERW—calcite ($CaCO_3$), dolomite ($Ca_{0.5}Mg_{0.5}CO_3$), and flood basalt ($Na_{0.11}K_{0.01}Fe(II)_{0.14}Mg_{0.22}Ca_{0.22}Al_{0.38}Fe(III)_{0.05}SiTi_{0.02}O_{3.33}$) (Marini 2006). According to mineral stoichiometry and the stoichiometries of

Eqs. 1 and 2, the maximum CDR (i.e., the molar amount of CO_2 that can be captured per mole of ERW substrate if dissolved congruently) is 1 mol of CO_2 per mol of calcite or dolomite (Mg + Ca = 1 mol; 1 * 1 = 1), and 1.28 mol of CO_2 per mol of flood basalt (Mg + Ca + Fe (II) = 0.58 mol; Na + K = 0.12 mol; 0.58 * 2 + 0.12 = 1.28).

It is worth noting that stoichiometric release of the cations from rock feedstocks is unlikely to occur in nature. A variety of processes, including incongruent dissolution of the minerals themselves, plant uptake of released ions, or retention of cations in the soil, could decrease the proportion of major cations (e.g., Ca and Mg) that ultimately reach river/stream systems. These processes are expected to drive an increase of CTP compared with our current model setup, as they will tend to lower $[Ca^{2+}]$ in solution and thus decrease carbonate saturation state. This makes the estimates presented here conservative (*see* Supporting Information for relevant model simulation). In the case of basalt, dissolved Fe(II) will probably be oxidized and thus change the acid/base balance. However, during initial rock dissolution, Fe(II) still plays the same role as Ca and Mg in terms of atmospheric CO_2 consumption. In addition, since Fe(II) is only 20% of the major cation load in flood basalt (in terms of mol), the influence of Fe(II) oxidation on the acid/base balance should not alter our main conclusions (*see* Supporting Information for relevant model simulation). Integration of the mean added rock mass for each site from our iteration model, the CDR for each rock type, and the river discharge, allows us to calculate the CTP on regional (United States) or global scales (*see* Supporting Information).
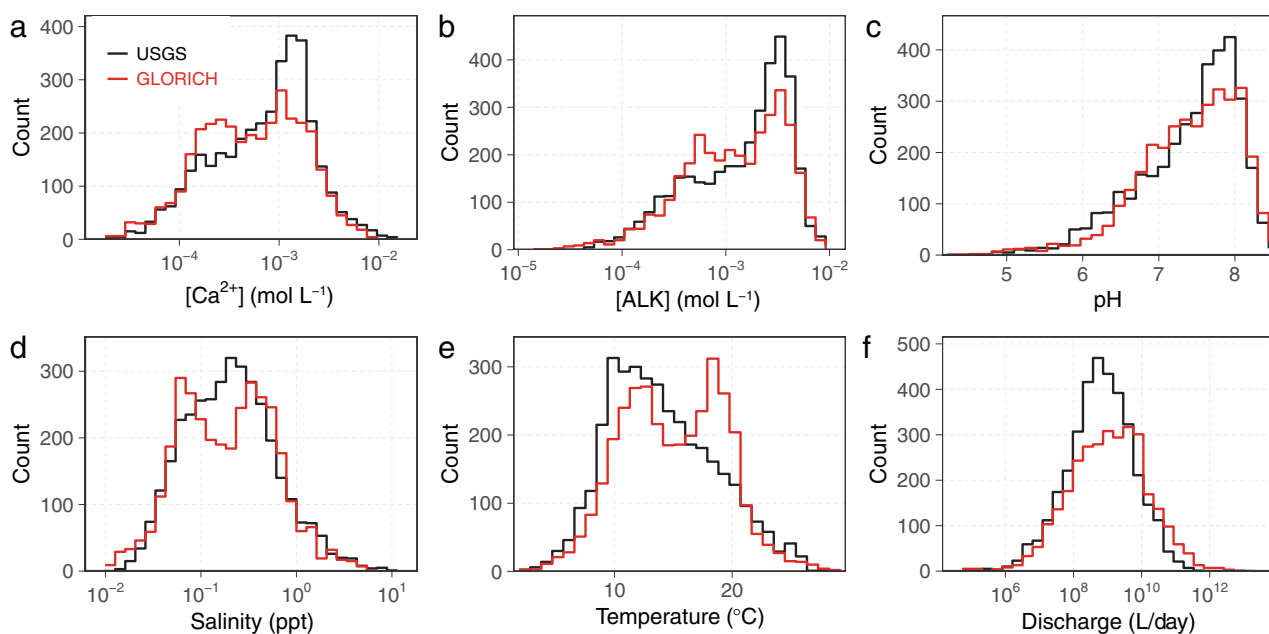

Fig. 1. Frequency distributions of initial solute, temperature, and salinity data for river/stream data in the U.S. and GLORICH datasets. Shown are the key parameters for the iterative model discussed in the text, including (**a**) dissolved Ca^{2+}, (**b**) alkalinity (ALK), (**c**) pH, (**d**) salinity, (**e**) temperature, and (**f**) discharge.
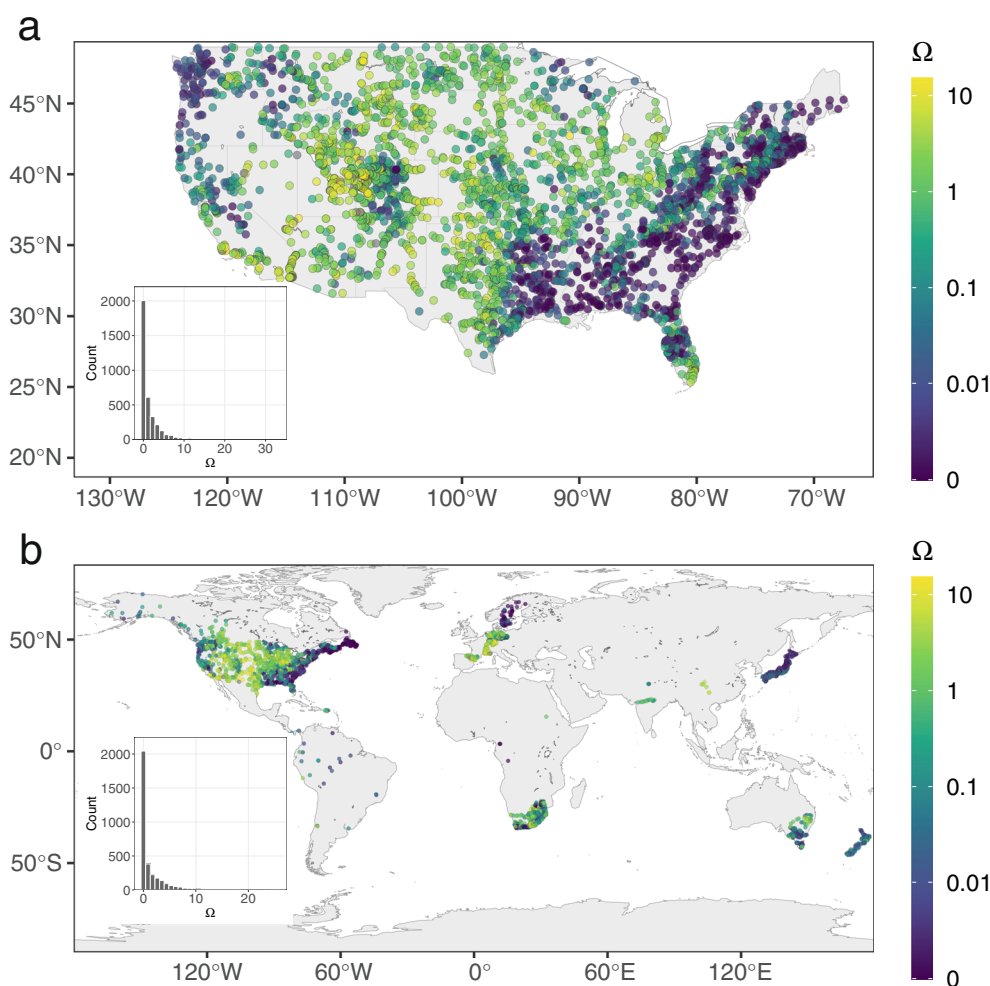
Fig. 2. Site locations for stream/river data from (**a**) the contiguous United States and (**b**) global river chemistry data. Color scale for symbols denotes fluid calcite saturation state (Ω) prior to simulated enhanced rock weathering.

Initial, iterative, and final saturation states (Ω) after simulated ERW are calculated based on solute chemistry, temperature, and salinity according to:

$$\Omega = \frac{[Ca^{2+}][CO_3^{2-}]}{K_{sp}}, \qquad (5)$$

where K_{sp} represents the apparent solubility product for calcite corrected for site-specific temperature and salinity (Zeebe and Wolf-Gladrow 2001) and brackets denote concentration. We explore a range of threshold calcite saturation states between 5 and 25, which is meant to capture both weakly over-saturated stream/river systems and systems with relatively high saturation states that approach or exceed in-situ carbonate formation and CO_2 re-release. For comparison, carbonate precipitation in river waters is generally observed to be negligible at $\Omega < 10$ (Suarez 1983; Herman and Lorah 1987; Neal 2002; Szramek and Walter 2004), and extremely high

saturation states ($\Omega > 45$) are sometimes observed without extensive carbonate precipitation. Indeed, high measured rates of carbonate precipitation in rivers are generally limited to settings where turbulent flow and elevated evaporation transiently boost saturation state, such as in upper course falls and hydrothermal systems (Arenas-Abad et al. 2010). In addition, the presence of soluble reactive phosphate, suspended material, and organic acids have all been shown to inhibit carbonate precipitation, which is implicitly considered when using a high saturation threshold (e.g., when $\Omega > 10$).

Although the exact role of groundwater in regulating the global carbon cycle has been largely underexplored compared with the river systems, subsurface silicate weathering in groundwater systems might also serve as a significant carbon sink (Zhang and Planavsky 2020). By integrating the geochemistry of 2007 sites for groundwaters across the contiguous United States and global groundwater flux estimates (Luijendijk et al. 2020; Zhang and Planavsky 2020), we also

provide first-order estimates of the potential for groundwaters to transport the dissolved constituents of ERW without leading to subsurface mineral precipitation (see Supporting Information). Note that the global groundwater flux estimate used in this study is the terrestrially derived net groundwater discharging to the ocean and should not be confused with the regional groundwater discharging into river waters.

Model limitations

The conceptual model in this study aims to provide a first-order estimate of the carbon transport potential of river/stream systems and groundwaters. Although we consider our estimates to be robust and likely conservative, there are some limitations to our conceptual framework. First, we are only simulating alkalinity and cation addition and are agnostic about the factors controlling local dissolution/release. Therefore, it is important not to view our calculated carbon transport potential as synonymous with a feedstock application rate. Second, a range of factors could potentially impact the composition of solutes from ERW during transport to rivers. Although we have evaluated several scenarios to test the potential impact of these processes on our estimates of CTP—for instance, Ca and Mg uptake by secondary mineral formation and plant growth and Fe(II) oxidation (see Supporting Information)—the detailed alteration of solute composition from soil to river is difficult to simulate. Third, our conceptual model does not equate to a net CDR, which will instead be determined by the maximum CDR potential (controlled by the combined impacts of local feedstock dissolution, plant uptake, secondary mineral formation, and downstream CTP as estimated in this study) minus extra CO_2 emissions (mining + comminution + transport + application). Considering extra CO_2 emission during mining, crushing/grinding, transporting, and spreading of rock powder on land should decrease the overall net CDR efficiency, largely depending on the choice of source rocks and comminution techniques (Renforth 2012; Moosdorf et al. 2014; Strefler et al. 2018). In any case, further exploration of the kinetics of feedstock dissolution and secondary mineral formation in soil in a reaction-transport framework (Taylor et al. 2016; Beerling et al. 2020; Kantzas et al. 2022; Kanzaki et al. 2022), understanding the impacts of processes in the soil-to-river continuum, and better constraints on CO_2 emissions during the large-scale implementation of ERW will all be critical for the continued development of a holistic picture of ERW as a CDR strategy.

Carbon transport potential for enhanced silicate rock weathering

Extensive deployment of enhanced silicate weathering on both regional and global scales would be required to reach elevated carbonate saturation states in stream/river systems (Fig. 3). In other words, there is significant CTP with silicate rock as a feedstock without the river system precipitating carbonate phases. For instance, at a nominal saturation state of
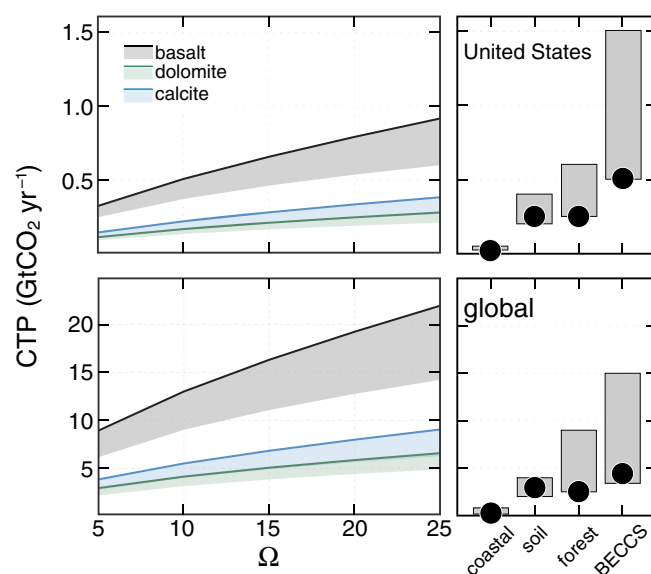

Fig. 3. River/stream CTP for the contiguous United States (top) and globally (bottom). Estimates are shown for calcite, dolomite, and flood basalt as feedstocks for ERW. Solid lines denote the upper end of the 95% confidence interval of Monte Carlo resampling of "closed" model runs, while the bottom edges of the shaded envelope denote the lower end of 95% confidence interval of Monte Carlo resampling of "degassed" model runs (see Supporting Information). Shown at right are estimates of carbon capture potential (units on its *y*-axis are the same as those of the CTP estimates on the left) for a range of other NETs derived from a recent community assessment (National Academies of Sciences, Engineering, and Medicine 2019). Additional NETs include sequestration in coastal "blue" carbon ("coastal"), soil carbon sequestration in agricultural systems ("soil"), carbon sequestration associated with afforestation/reforestation and improved forest management practices ("forest"), and BECCS. Gray boxes show ranges for estimated CDR potential, while filled circles show values determined to be "safe"—that is, levels of deployment that would, with high confidence, not be expected to cause adverse societal, economic, and environmental impacts.

$\Omega = 10$ with flood basalt as a feedstock, our model predicts an upper CTP of 0.39–0.48 $GtCO_2$ yr^{-1} (mean value) for the United States and 10.0–12.2 $GtCO_2$ yr^{-1} globally, with a range in upper CTP of 0.26–0.89 $GtCO_2$ yr^{-1} for the United States and 7.1–21.3 $GtCO_2$ yr^{-1} globally when considering a larger saturation state range of $\Omega = 5$–25 (Fig. 3). Our model predicts substantial CTP using silicate rock as a feedstock even at very modest saturation-state thresholds—at $\Omega = 5$, U.S. and global gross CTP are comparable to or greater than the estimated CDR potential of coastal "blue" carbon capture, carbon sequestration achievable in agricultural soils or through forest management, and bioenergy with carbon capture and sequestration (BECCS) (Fig. 3).

One important caveat associated with quantifying CTP using all river samples is that interaction of various species in the inland river networks might modify the Ω in connected downstream river/stream systems. To mitigate this issue, we use an alternative model to estimate CTP based on river
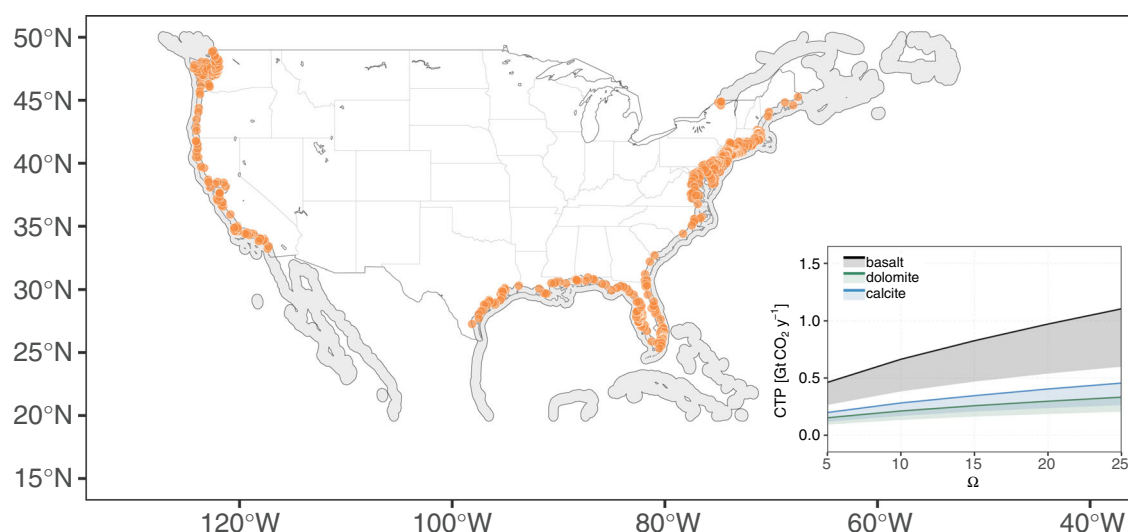
Fig. 4. Distribution of river/stream data close to the U.S. coastline (within 50 km to the coastline). Inset shows the CTP estimate based only on river/stream chemistry of coastal samples. Estimates are shown for calcite, dolomite, and flood basalt as feedstocks for ERW. Solid lines denote the upper end of the 95% confidence interval of Monte Carlo resampling of "closed" model runs, while the bottom edges of the shaded envelope denote the lower end of 95% confidence interval of Monte Carlo resampling of "degassed" model runs.

samples close to U.S. coast (defined here as the 50 km buffer zone around the U.S. coastline). This alternative estimate of CTP (Fig. 4) is actually somewhat higher than our estimate using all U.S. river samples (e.g., 0.58 and 0.48 GtCO$_2$ yr^{-1}, respectively, at a nominal saturation state of $\Omega = 10$ and with flood basalt as a feedstock), indicating that our baseline estimate of CTP is conservative.

Compared with the river system, groundwater CTP is less well-constrained but is potentially also significant. For the same nominal saturation state ($\Omega = 10$), our model predicts global CTP for groundwaters of up to 1.6 GtCO$_2$ y^{-1} using flood basalt as a feedstock for ERW (*see* Supporting Information). Overall fluid fluxes and major/trace element chemistry of groundwaters represent an important frontier for future research (Santos et al. 2021), and accurate diagnosis of groundwater CTP will require the development of more robust constraints on regional and global groundwater discharge fluxes and solute chemistry (Zhang and Planavsky 2020). Nevertheless, our results indicate that there may also be significant potential for long-term CO$_2$ storage in groundwaters through ERW.

Potential for enhanced carbonate rock weathering

Enhanced carbonate rock weathering—using calcite and/or dolomite as a feedstock for ERW—has a lower CTP for a given threshold saturation state than enhanced silicate weathering (Fig. 3). This is a natural result of the weathering stoichiometries of each phase (Eqs. 1, 2). However, our estimated CTP for enhanced carbonate rock weathering is comparable to estimates for safe deployment of a range of other CDR approaches (Fig. 3), even at relatively low threshold saturation states. For instance, we estimate global CTP for enhanced carbonate rock

weathering at $\Omega = 5$ of 2.7–3.5 GtCO$_2$ yr^{-1} depending on whether the feedstock for ERW is calcite or dolomite. This can be augmented by global groundwater with CTP values up to ~ 0.43 GtCO$_2$ yr^{-1} using carbonate feedstocks at $\Omega = 5$ (*see* Supporting Information).

There is potentially a significant difference in the downstream impacts of ERW using carbonate rock relative to silicates. In the case of using silicate feedstock, the conversion of HCO$_3^-$ to CO$_2$ via non-carbonic acidity can drive down overall capture efficiency (e.g., ton[s] of CO$_2$ sequestered per ton of silicate rock), but even in the most extreme case will at worst be CO$_2$-neutral (Eqs. 1, 4). In contrast, ERW using carbonate feedstocks—regularly implemented in managed agricultural systems as "liming"—has the potential to be a net CO$_2$ source (West and McBride 2005; Hamilton et al. 2007; Lynch et al. 2021) via the release of HCO$_3^-$ from carbonate rock and its subsequent conversion to CO$_2$ with non-carbonic acidity (Eqs. 2, 4). Indeed, IPCC guidelines for greenhouse gas inventories treat agricultural liming as a net CO$_2$ source to the atmosphere (IPCC 2006). However, our database for U.S. surface waters strongly indicates that the vast majority of carbonate-dominated catchments—across agricultural and mixed land (e.g., natural, rural, suburban, and urban) environments—act as net CO$_2$ sinks on a short-term basis (e.g., not considering long-term carbonate precipitation and CO$_2$ re-release in the ocean on timescales greater than $\sim 10^4$ yr), even with extensive liming already occurring in agricultural catchments (Fig. 5).

Solute chemistries in both agricultural and mixed-use systems indicate dissolution of carbonate rock and export of alkalinity from the critical zone (c.f., Hamilton et al. 2007),
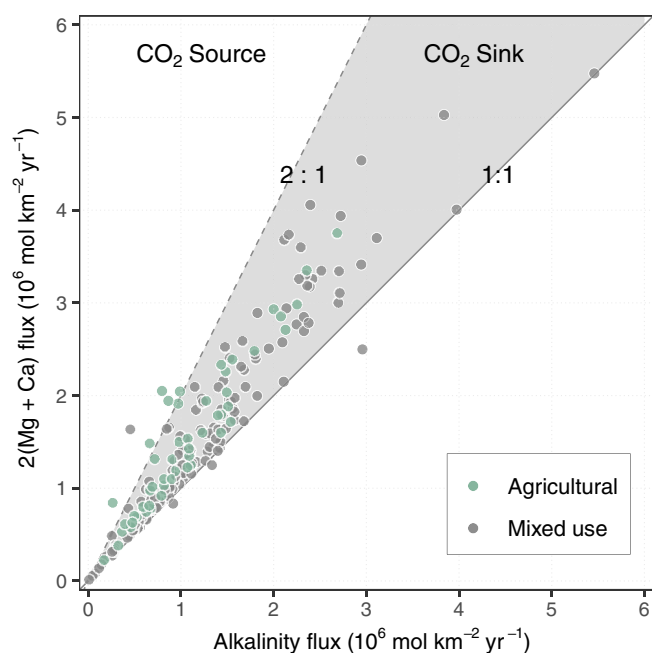
Fig. 5. Comparison of fluxes of carbonate alkalinity (predominantly as HCO_3^-) and major cations (shown here as twice the combined flux of dissolved Ca^{2+} and Mg^{2+}) for rivers in our database draining carbonate-dominated catchments. The lower line depicts the 1:1 ratio expected for dissolution occurring exclusively with carbonic acid, while the upper line depicts the 2:1 stoichiometry of calcite/dolomite. Catchments that plot in the shaded region (labeled "CO_2 sink") show strong evidence for dissolution of carbonate minerals together with capture of soil CO_2 as carbonate alkalinity. Catchments plotting in the region above the 2:1 line (labeled "CO_2 source") represent carbonate mineral dissolution together with conversion of HCO_3^- to CO_2. The carbonate rock proportion is derived from (Hartmann and Moosdorf 2012) and land use categories (i.e., agricultural vs. mixed use) are derived from (Tuanmu and Jetz 2014) (see Supporting Information).

suggesting that the net conversion of rock-derived carbon to CO_2 due to non-carbonic acidity does not play a major role in the overall carbon budget in carbonate-dominated environments on the catchment scale. This is consistent with field observations at the local scale that indicate overall CO_2 capture during liming of row crops (Oh and Raymond 2006; Hamilton et al. 2007). Better accounting of non-carbonic acidity in managed systems and coupling of ERW with practices that limit acidity production will be an important avenue of future work. However, assuming non-carbonic acidity is largely neutralized through current liming practices (Hamilton et al. 2007), additional carbonate application and weathering in agricultural settings could actually be a net carbon sink on timescales less than $\sim 10^3$–10^4 yr.

Implications of modeled carbon transport potential for deployment of ERW

Conceptually, our model is designed to provide an estimate of the upper limits on CDR potential for ERW as constrained by the river capacity without CO_2 re-release. In other words,

our model does not consider other bottlenecks in the CDR potential of ERW, such as limited dissolution of feedstock at application sites. However, we consider this estimate useful for a number of reasons. First, it provides an upper bound on conceivable deployment level. Although significant effort will be required to evaluate practical net CDR across a range of socioeconomic scenarios, feedstocks, and deployment styles, it is unlikely that ERW will be capable of achieving CDR in excess of the estimates presented here. This represents a key starting point for placing boundaries on the relative impacts of ERW deployment across a range of socioeconomic and climate scenarios. For instance, one potential path toward surpassing these limits would be significant weathering of ultramafic material or mafic minerals, but ultramafic and or mafic minerals have a higher potential for trace metal contamination of surface waters and soils (Hartmann et al. 2013; Amann et al. 2020) and are likely to be more costly to mine and transport (Kelemen et al. 2020). Second, our CTP estimates are broadly comparable with existing top-down estimates of ERW capture potential across the tropical land over the next century (on the order of ~ 15 GtCO$_2$ yr^{-1}) (Taylor et al. 2016). The global riverine CTP estimates for flood basalt application surpass recent estimates of CDR via ERW in agricultural settings (Strefler et al. 2018; Beerling et al. 2020), even when our model is run at relatively low saturation state thresholds. This provides support for the notion that cropland ERW will not face a bottleneck during transport of dissolved weathering products to the oceans. However, it also suggests that in many areas it would be worthwhile to explore inexpensive enhanced weathering application in settings beyond croplands (Goll et al. 2021) and other means of agricultural ERW (e.g., ERW in agroforestry and in lower-impact manure management practices).

To our knowledge, our modeling results represent the first regional and global estimates of carbon transport potential using carbonate feedstocks, with estimates suggesting the possibility of significant capture via carbonate-based ERW. Despite obvious risks, there are socioeconomic and logistical considerations supporting the notion that carbonate-based ERW should be further evaluated for incorporation into greenhouse gas mitigation portfolios. Dissolution rates of carbonates are roughly three orders of magnitude more rapid than those of basaltic rock under the same conditions (Morse and Arvidson 2002; Kelemen et al. 2020) and long-term decline in dissolution kinetics caused by surface passivation often observed in silicate weathering (Daval et al. 2018) will be less of an issue for carbonate feedstocks. Furthermore, carbonate rock exposure is two to four times that of basalt at Earth's surface (Hartmann and Moosdorf 2012; Goldscheider et al. 2020), and carbonate quarries are widely distributed given the common use of carbonate in aggregate and in concrete production. In addition, waste fines from crushed limestone production could provide an inexpensive source of enhanced carbonate weathering. Critically, it is worth stressing that surficial enhanced carbonate weathering could

occur in reactors instead of via diffuse application of carbonates in soils, which would limit the potential for back reaction and CO_2 re-release (Rau et al. 2007).

Conclusions

Our results reinforce the notion that ERW has significant CDR potential (Beerling et al. 2020; Goll et al. 2021), and suggest that the carbon transport potential of river/stream systems and groundwaters is unlikely to be a bottleneck in scaling net CDR. Indeed, both for the United States and at a global scale our model highlights enhanced silicate rock weathering as having gross CTP rivaling or exceeding most other CDR approaches currently being assessed. Furthermore, our results indicate that ERW using carbonate rock as a feedstock may have significant CDR scope, along with a range of possible co-benefits and socioeconomic advantages. Overall, these considerations suggest that both silicate- and carbonate-based ERW approaches should be thoroughly assessed for cost, downstream environmental impacts, and longevity of capture with the aim of near-term deployment at the gigaton scale.

Data availability statement

The data and code are hosted at https://zenodo.org/record/5034798#.YpqD6OzMKsA.

References

Amann, T., J. Hartmann, E. Struyf, W. de Oliveira Garcia, E. K. Fischer, I. Janssens, P. Meire, and J. Schoelynck. 2020. Enhanced weathering and related element fluxes—A cropland mesocosm approach. Biogeosciences **17**: 103–119. doi:10.5194/bg-17-103-2020

Arenas-Abad, C., M. Vázquez-Urbez, G. Pardo-Tirapu, and C. Sancho-Marcén. 2010. Chapter 3: Fluvial and associated carbonate deposits, p. 133–175. *In* A. M. Alonso-Zarza and L. H. Tanner [eds.], Developments in sedimentology. Elsevier.

Beerling, D. J., and others. 2018. Farming with crops and rocks to address global climate, food and soil security. Nat. Plants **1**: 138–147. doi:10.1038/s41477-018-0108-y

Beerling, D. J., and others. 2020. Potential for large-scale CO_2 removal via enhanced rock weathering with croplands. Nature **583**: 242–248. doi:10.1038/s41586-020-2448-9

Berner, R. A. 2004. The phanerozoic carbon cycle: CO_2 and O_2, 1st ed. Oxford Univ. Press.

Bufe, A., N. Hovius, R. Emberson, J. K. C. Rugenstein, A. Galy, H. J. Hassenruck-Gudipati, and J.-M. Chang. 2021. Co-variation of silicate, carbonate and sulfide weathering drives CO_2 release with erosion. Nat. Geosci. **14**: 211–216. doi:10.1038/s41561-021-00714-3

Bui, M., and others. 2018. Carbon capture and storage (CCS): The way forward. Energ. Environ. Sci. **11**: 1062–1176. doi:10.1039/C7EE02342A

Ciais, P., and others. 2014. Carbon and other biogeochemical cycles, p. 465–570. *In* O. Edenhofer and others [eds.], Climate change 2013. Cambridge Univ. Press.

Daval, D., C. Calvaruso, F. Guyot, and M.-P. Turpault. 2018. Time-dependent feldspar dissolution rates resulting from surface passivation: Experimental evidence and geochemical implications. Earth Planet. Sci. Lett. **498**: 226–236. doi:10.1016/j.epsl.2018.06.035

Fuss, S., and others. 2014. Betting on negative emissions. Nat. Clim. Change **4**: 850–853. doi:10.1038/nclimate2392

Fuss, S., and others. 2018. Negative emissions—Part 2: Costs, potentials and side effects. Environ. Res. Lett. **13**: 063002. doi:10.1088/1748-9326/aabf9f

Gasser, T., C. Guivarch, K. Tachiiri, C. D. Jones, and P. Ciais. 2015. Negative emissions physically needed to keep global warming below 2°C. Nat. Commun. **6**: 7958. doi:10.1038/ncomms8958

Goldscheider, N., and others. 2020. Global distribution of carbonate rocks and karst water resources. Hydrgeol. J. **28**: 1661–1677. doi:10.1007/s10040-020-02139-5

Goll, D. S., and others. 2021. Potential CO_2 removal from enhanced weathering by ecosystem responses to powdered rock. Nat. Geosci. **1–5**: 545–549. doi:10.1038/s41561-021-00798-x

Griscom, B. W., and others. 2017. Natural climate solutions. PNAS **114**: 11645–11650. doi:10.1073/pnas.1710465114

Hamilton, S. K., A. L. Kurzman, C. Arango, L. Jin, and G. P. Robertson. 2007. Evidence for carbon sequestration by agricultural liming. Global Biogeochem. Cycl. **21**. doi:10.1029/2006GB002738

Hartmann, J., and S. Kempe. 2008. What is the maximum potential for CO_2 sequestration by "stimulated" weathering on the global scale? Naturwissenschaften **95**: 1159–1164. doi:10.1007/s00114-008-0434-4

Hartmann, J., and N. Moosdorf. 2012. The new global lithological map database GLiM: A representation of rock properties at the Earth surface. Geochem. Geophys. Geosyst. **13**: Q12004. doi:10.1029/2012GC004370

Hartmann, J., A. J. West, P. Renforth, P. Köhler, C. L. De La Rocha, D. A. Wolf-Gladrow, H. H. Dürr, and J. Scheffran. 2013. Enhanced chemical weathering as a geoengineering strategy to reduce atmospheric carbon dioxide, supply nutrients, and mitigate ocean acidification. Rev. Geophys. **51**: 113–149. doi:10.1002/rog.20004

Hartmann, J., R. Lauerwald, and N. Moosdorf. 2014. A brief overview of the GLObal RIver Chemistry Database, GLORICH. Proc. Earth Planet. Sci. **10**: 23–27. doi:10.1016/j.proeps.2014.08.005

Herman, J. S., and M. M. Lorah. 1987. CO_2 outgassing and calcite precipitation in Falling Spring Creek, Virginia, U.S.A. Chem. Geol. **62**: 251–262. doi:10.1016/0009-2541(87)90090-8

IPCC. 2006. 2006 IPCC guidelines for national greenhouse gas inventories—IPCC. IPCC.

Johannessen, S. C., and R. W. Macdonald. 2016. Geo-engineering with seagrasses: Is credit due where credit is given? Environ. Res. Lett. **11**: 113001. doi:10.1088/1748-9326/11/11/113001

Kantzas, E. P., and others. 2022. Substantial carbon drawdown potential from enhanced rock weathering in the United Kingdom. Nat. Geosci. **1–8**: 382–389. doi:10.1038/s41561-022-00925-2

Kanzaki, Y., S. Zhang, N. J. Planavsky, and C. T. Reinhard. 2022. Soil Cycles of Elements simulator for Predicting TERrestrial regulation of greenhouse gases: SCEPTER v0.9. Geoscientific Model Development. **15**: 4959–4990. doi:10.5194/gmd-15-4959-2022

Kelemen, P. B., N. McQueen, J. Wilcox, P. Renforth, G. Dipple, and A. P. Vankeuren. 2020. Engineered carbon mineralization in ultramafic rocks for CO_2 removal from air: Review and new insights. Chem. Geol. **550**: 119628. doi:10.1016/j.chemgeo.2020.119628

Köhler, P., J. Hartmann, and D. A. Wolf-Gladrow. 2010. Geoengineering potential of artificially enhanced silicate weathering of olivine. PNAS **107**: 20228–20233. doi:10.1073/pnas.1000545107

Luijendijk, E., T. Gleeson, and N. Moosdorf. 2020. Fresh groundwater discharge insignificant for the world's oceans but important for coastal ecosystems. Nat. Commun. **11**: 1260. doi:10.1038/s41467-020-15064-8

Lynch, J., M. Cain, D. Frame, and R. Pierrehumbert. 2021. Agriculture's contribution to climate change and role in mitigation is distinct from predominantly fossil CO_2-emitting sectors. Front. Sustain. Food Syst. **4**. doi:10.3389/fsufs.2020.518039

Marini, L. 2006. Geological sequestration of carbon dioxide: Thermodynamics, kinetics, and reaction path modeling, 1st ed. Elsevier Science.

Middelburg, J. J., K. Soetaert, and M. Hagens. 2020. Ocean alkalinity, buffering and biogeochemical processes. Rev. Geophys. **58**: e2019RG000681. doi:10.1029/2019RG000681

Moosdorf, N., P. Renforth, and J. Hartmann. 2014. Carbon dioxide efficiency of terrestrial enhanced weathering. Environ. Sci. Technol. **48**: 4809–4816. doi:10.1021/es4052022

Morse, J. W., and R. S. Arvidson. 2002. The dissolution kinetics of major sedimentary carbonate minerals. Earth Sci. Rev. **58**: 51–84. doi:10.1016/S0012-8252(01)00083-6

National Academies of Sciences, Engineering, and Medicine. 2019. Negative emissions technologies and reliable sequestration: A research agenda. The National Academies Press.

Neal, C. 2002. Calcite saturation in eastern UK rivers. Sci. Total Environ. **282–283**: 311–326. doi:10.1016/S0048-9697(01)00921-4

Oh, N.-H., and P. A. Raymond. 2006. Contribution of agricultural liming to riverine bicarbonate export and CO2 sequestration in the Ohio River basin. Global Biogeochem. Cycles **20**. doi:10.1029/2005GB002565

Rau, G. H. 2019. The race to remove CO_2 needs more contestants. Nat. Clim. Change **9**: 256. doi:10.1038/s41558-019-0445-5

Rau, G. H., K. G. Knauss, W. H. Langer, and K. Caldeira. 2007. Reducing energy-related CO_2 emissions using accelerated weathering of limestone. Energy **32**: 1471–1477. doi:10.1016/j.energy.2006.10.011

Renforth, P. 2012. The potential of enhanced weathering in the UK. Int. J. Greenhouse Gas Control **10**: 229–243. doi:10.1016/j.ijggc.2012.06.011

Renforth, P., and G. Henderson. 2017. Assessing ocean alkalinity for carbon sequestration. Rev. Geophys. **55**: 636–674. doi:10.1002/2016RG000533

Roe, S., and others. 2021. Land-based measures to mitigate climate change: Potential and feasibility by country. Glob. Chang. Biol. **27**: 6025–6058. doi:10.1111/gcb.15873

Rogelj, J., and others. 2018. Mitigation pathways compatible with 1.5°C in the context of sustainable development, v. **82**. IPCC.

Santos, I. R., and others. 2021. Submarine groundwater discharge impacts on coastal nutrient biogeochemistry. Nat. Rev. Earth Environ. **1–17**: 307–323. doi:10.1038/s43017-021-00152-0

Seifritz, W. 1990. CO_2 disposal by means of silicates. Nature **345**: 486. doi:10.1038/345486b0

Strefler, J., T. Amann, N. Bauer, E. Kriegler, and J. Hartmann. 2018. Potential and costs of carbon dioxide removal by enhanced weathering of rocks. Environ. Res. Lett. **13**: 034010. doi:10.1088/1748-9326/aaa9c4

Suarez, D. L. 1983. Calcite supersaturation and precipitation kinetics in the Lower Colorado River, All-American Canal and East Highline Canal. Water Resour. Res. **19**: 653–661. doi:10.1029/WR019i003p00653

Szramek, K., and L. M. Walter. 2004. Impact of carbonate precipitation on riverine inorganic carbon mass transport from a mid-continent, forested watershed. Aquat. Geochem. **10**: 99–137. doi:10.1023/B:AQUA.0000038960.63501.5b

Taylor, L. L., and others. 2016. Enhanced weathering strategies for stabilizing climate and averting ocean acidification. Nat. Clim. Change **6**: 402–406. doi:10.1038/nclimate2882

Tuanmu, M.-N., and W. Jetz. 2014. A global 1-km consensus land-cover product for biodiversity and ecosystem modelling. Global Ecology and Biogeography **23**: 1031–1045. doi:10.1111/geb.12182

U.S. Geological Survey. 2016. National Water Information System data available on the World Wide Web (Water Data for the Nation), accessed Apr, 2021, at URL [http://waterdata.usgs.gov/nwis/].

West, T. O., and A. C. McBride. 2005. The contribution of agricultural lime to carbon dioxide emissions in the United States: Dissolution, transport, and net emissions. Agr. Ecosyst. Environ. **108**: 145–154. doi:10.1016/j.agee.2005.01.002

Zeebe, R. E., and D. Wolf-Gladrow. 2001. CO$_2$ in seawater: Equilibrium, kinetics, isotopes, v. **65**, 1st ed. Elsevier Science.

Zhang, S., and N. J. Planavsky. 2020. Revisiting groundwater carbon fluxes to the ocean with implications for the carbon cycle. Geology **48**: 67–71. doi:10.1130/G46408.1

Acknowledgments

Conflict of Interest

The authors declare no competing interests.