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Title: Addition of Alkalinity to Rivers: a new CO₂ Removal Strategy

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One-Sentence Summary: Addition of alkalinity to rivers is a previously unexplored but promising new tool to aid our global mission to reduce serious risks from climate change while restoring aquatic habitats.

Abstract

In addition to rapid reductions of greenhouse gas emissions, large scale carbon dioxide removal (CDR) is needed to limit severe climate warming. While recent CDR efforts have focused on land surfaces and oceans, rivers have not yet been explored as a CDR medium. Here, we examine the CDR potential of the addition of alkaline materials to rivers (RiverCDR). We synthesize knowledge gained from long-term studies of river liming that demonstrate significant improvements to water quality, fish populations and overall ecosystem health and combine it with regional and global modeling approaches. We find RiverCDR can permanently sequester carbon through both increasing carbonation weathering reactions (enhanced weathering) and increasing rivers' and receiving ocean water's capacity to retain dissolved inorganic carbon (increased alkalinity). Our thermodynamic modelling demonstrates the potential to use carbonate rocks for RiverCDR: a safe and inexpensive source of alkalinity. Our global scale modelling shows that while staying within safe limits RiverCDR has the potential to permanently store hundreds of $MtCO_{2e}$ yr^{-1}, which amounts to ~10% of current conventional land-based CDR methods (mostly reforestation and afforestation) and exceeds other novel CDR technologies such as biochar. To further explore opportunities, we propose a simple system for monitoring reporting and verification at the river mouth, using standardized hydrological approaches. We recommend that RiverCDR be added to our current options for CDR, as it has the potential to drawdown carbon while enhancing biodiversity and ecosystem functions, employment, and local livelihoods, if done correctly, and in the right locations.

Main

Carbon dioxide removal (CDR) technologies that are effective, affordable, scalable, safe, permanent and verifiable are urgently needed to reduce severe risks from climate change and reach net zero[1]; however, our current available CDR options are far from sufficient to meet these goals. We urgently need to develop new CDR methods, particularly those that minimize land requirements and energy consumption and that can scale up rapidly and cheaply[2]. The landscape of CDR options include land-based approaches such as the application of alkaline materials to land (via Enhanced Rock Weathering (ERW))[3] and ocean-based approaches, such as Ocean Alkalinity Enhancement (OAE)[4] (Figure 1). As of yet, no CDR technologies exist for rivers, although recent calls have been made to integrate river management and climate change[5,6]. Here, we propose a new CDR pathway, RiverCDR: a technology that artificially accelerates dissolution of alkaline materials in rivers. We examine how it may achieve CDR and meet key net-zero goals such as permanence, safety, societal acceptance, scalability, and we propose a framework for monitoring, reporting and verification (MRV).

Rivers are a hotspot for carbon flows[7]. Rivers and inland waters have been estimated to deliver approximately 0.96 PgCyr-[1] of organic and inorganic carbon from land areas to oceans via the land-to-ocean aquatic continuum (LOAC)[8]. Water draining from land surfaces delivers up to 18% of terrestrial gross primary production to inland waters via shunting of CO_2 from soils or organic carbon that is later mineralized to CO_2[9–11], generating high pCO_2 (partial pressure of CO_2) in some reaches (> 10,000 μatm)[11]. Carbonate alkalinity (CAlk) is produced from carbonation weathering, a set of well-known mineral dissolution reactions of carbonate and silicate rocks that increase CAlk and promote a transfer of CO_2 from the atmosphere[4] (Equation 1). Large amounts (approximately 0.4 PgC yr-[1]) of CAlk (comprising primarily HCO_3^-) are leached from soils and bedrock and

delivered to oceans via the global inland water network[8], driving the long-term carbonate-silicate cycles, Earth's natural regulator of atmospheric CO_2 and global temperature over geologic time[12] (Figure 1a). Upon arriving in the open water network, much of this dissolved inorganic carbon (DIC, comprising CO_2, HCO_3^- and CO_3^{2-}) is evaded to the atmosphere as CO_2[13,14], estimated as between 1.9 and 2.3 $PgC\ yr^{-1}$ [15] and only a portion is exported via stable forms of CAlk directly to the ocean for long-term storage[8,11,14,15]. Thus, rivers commonly have pCO_2 values well above atmospheric levels[11,16]. This lateral land-to-ocean carbon transport via inland waters and rivers has only recently been conceptualized in detail and is not well represented in the current generation of land carbon models[7,17], nor in global carbon budget accounting[18,19].
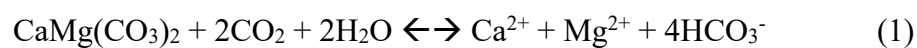
A prevalent view is that HCO_3^- behaves conservatively once it has entered the open water network while transiting through rivers and inland waters[8] and that HCO_3^- dominates DIC in most freshwaters[20]. However, pH controls the speciation of DIC into carbonate anions or CO_2. When a volume of water containing HCO_3^- is mixed with a volume of low pH water (below approximately pH 8.3), the low pH can convert stable HCO_3^- to CO_2, and thus be subject to evasion to the atmosphere (Figure 2). The range of natural river pH levels overlaps with the critical values pH 4.5-8.3 for carbonate speciation[21]. Thus, decreased pH, particularly around pH 5.5, where there is a sharp transition between CO_2 and HCO_3^-, can increase carbon losses along the LOAC through increased CO_2 evasion, lowering HCO_3^- exports to long-term storage in the oceans.

Human activities, such as fossil fuel burning and fertilizer application, have reduced base cation concentrations in soils and lowered pH and alkalinity of inland waters. Currently many rivers remain acidified with low alkalinity and pH[22], despite reductions in acid emissions[23,24]. This lack of recovery is due to both the continued exceedance of critical loads of acid deposition and the slow recruitment of critical base cations in catchment soils[25,26]. To save aquatic species at risk, such as Atlantic salmon (*Salmo salar*), from freshwater acidification, ground carbonate rocks have

been added to surface waters in river liming programs in North America and Europe for decades[27–30] (Supplementary Data). These programs use 'lime dosers' to obtain a cost-effective, precise and continuous dispersal of alkaline materials directly to rivers. Lime dosing has been successful in raising pH and base cation concentrations above threshold concentrations needed for ecosystem health[27] (Supplementary Data). However, the CDR potential of such alkaline additions to rivers has not yet been explored.

Here we combine the concepts of river liming and CDR and identify the potential of a new negative-emission technology, RiverCDR. We define RiverCDR as the direct addition of ground alkaline materials to river waters using methods that favour carbonation weathering reactions (Figure 3a). RiverCDR is thus a strategy to artificially accelerate the dissolution of alkaline minerals to increase delivery of CAlk to the oceans via rivers for long-term storage. In RiverCDR, carbon may be drawn down via two main pathways: carbonation weathering and increased alkalinity along the treated water plume. The captured carbon is then transported by the river to oceans for long-term storage (Figure 3a).

By mapping out the thermodynamic and stoichiometric limits of carbonation weathering, we find that RiverCDR is possible with carbonate minerals as the alkaline amendment, but that not all dosing/river chemistry conditions will generate CDR. Here we consider the case of the carbonate mineral dolomite (Equation 1):

$$CaMg(CO_3)_2 + 2CO_2 + 2H_2O \longleftrightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^- \qquad (1)$$

and examine chemical equilibria in response to application of dolomite to a range of natural river water chemistries and prescribed pCO_2 levels (reflecting the range of common fluvial values[11] from Nova Scotia, Canada (see Methods)). As expected, the carbonation weathering efficiency of the added dolomite increases with higher pCO_2 of the receiving water for a given dose (Figure 4).

Carbon capture is not achieved at low doses, particularly when stronger (mineral/organic) acids are present in higher concentrations (represented by a lowered y-intercept of the stoichiometric limit) (Figure 4), setting a dose-limit below which CDR would not occur. Another limit is the 2:1 line here, representing the amount of carbon introduced into the water from the carbonate minerals. Favourable geochemical conditions are those in which added alkaline material undergoes carbonation weathering reactions that are spontaneously driven forward[5].

For small amounts of alkalinity added, the initial pH must be above the pH_0, the transition region between mineral acidic and alkaline waters, but carbon capture can be achieved in mineral acidic waters at higher rates of alkaline material addition[21], suggesting that RiverCDR is possible in acidified rivers, especially in locations with high pCO_2. Thus, in rivers where $pH < pH_0$ dosing rates of carbonate minerals must be sufficient to avoid carbonate rocks becoming a CO_2 source in rivers, especially those with elevated strong acid concentrations[21,31]. Most river water chemistries, if below saturation, can favour spontaneous forward reactions of carbonate weathering reactions (e.g., Equation 1), even for carbonate minerals, given sufficient pCO_2 and dosing rates.

We also identify physical characteristics that promote weathering in rivers. Rivers promote chemical disequilibrium at point inputs of alkaline material through continuous refreshing of water via advective import. And the hydraulics of running water systems with high surface roughness favour dissolution reaction kinetics, as turbulence promotes disruption of chemically-equilibrated films developing around the weathering front. Further, elevated shear stress along the riverbed promotes suspension of particles in the water medium.

We identify another pathway for CO_2 drawdown in RiverCDR via increased alkalinity in the receiving river and ocean waters which increases their ability to store CO_2 (Figure 3a). Increased alkalinity increases pH, which promotes the conversion of CO_2 to HCO_3^-, thereby reducing pCO_2

(decreasing CO_2 evasion / increasing CO_2 invasion) in the treated water plume and facilitating the retention and delivery of DIC to the ocean. Furthermore, as we discuss below, the addition of alkalinity to rivers increases biological productivity in acidified rivers and estuaries, removing additional CO_2 from the atmosphere as organic carbon[32].

140 Losses to CAlk generated through carbonation weathering may occur via three paths in rivers: 1) reverse reactions in which a carbonate mineral is precipitated, 2) mixing with a minerally acidic body of water causing HCO_3^- to convert to CO_2, or 3) uptake of HCO_3^- via photosynthesis[33] (Figure 2). Carbonate precipitation results when saturation limits are exceeded and would reverse the alkalinity and CDR generated. A recent modelling study estimated that calcite saturation limits do 145 not pose a large constraint for CDR in rivers[34].

In summary, the feasibility of RiverCDR depends on the distance of the addition point from the ocean, the type of minerals applied, and the river hydraulic and chemical properties (pCO_2, pH, alkalinity, temperature, dissolved constituents, and saturation limits) at the addition point and downstream that govern the likelihood of the reaction Equation 1 to take place or to be reversed. 150 Here, we review how RiverCDR may meet established CDR criteria[35].

Permanence. Once CAlk (mostly in the form of HCO_3^-) reaches the ocean in river estuaries, the permanence of the carbon capture depends on the length of time HCO_3^- remains in solution (i.e., that the reaction is not reversed), estimated as 10,000s of years[8,36,37]. Reverse reactions of carbonate weathering are less likely in areas where more rapid mixing and dilution occurs[36,38], 155 areas of lower salinity water[21], and in cases where alkaline solutions are equilibrated with atmospheric CO_2 prior to addition to the oceans[4]. Freshwater plumes in the ocean are dilute, equilibrated with the atmosphere, and well-mixed, favouring carbon capture permanence of RiverCDR.

160   **Verifiability**. For a CDR technology to be able to be part of the carbon market it must provide

transparent MRV of the net amount of carbon captured. We have developed an MRV for

RiverCDR based on changes in carbonate alkalinity export rates calculated at a single point at the

river mouth (Equation 6). In doing so, we avoid having to use forward mass balance calculations

that include all the sources and sinks of carbonate alkalinity in rivers (Equation 2-5, Figure 2) that

165   would be highly uncertain due to difficulty in estimating variables such as gas transfer velocities

and short-term changes in carbonation weathering efficiencies. At-a-point river mouth flux

estimations integrate all upstream carbonate alkalinity inputs and outputs such as photosynthesis,

precipitation, and other unanticipated gains and losses (Figure 2), as rivers transport dissolved and

suspended constituents from the watershed to a single outlet point (i.e., the river mouth). Our

170   RiverCDR MRV draws on standardized and well-established measurement techniques[8,18]. This

RiverCDR MRV calculation (Equation 6) is conservative because it does not account for increased

organic carbon stores associated with increased primary production or biomass associated with

higher trophic levels and does not include carbon drawdown of CO_2 by increased alkalinity in

receiving ocean waters.

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$$\Delta CAlk = W + A - L - G \tag{2}$$

where

$\Delta CAlk$ = increase in carbonate alkalinity at the river mouth relative to background

and is equivalent to CDR in [Mass CO_{2eq}] [Time]$^{-1}$

180   W = weathering-based CDR = $M * S * E_w * E_t$

$$\tag{3}$$

where

     M = mass alkaline material added

     S = stoichiometric relation of CDR vs tonnes alkaline material added

185   E_w = carbonation weathering efficiency

     E_t = CAlk transport efficiency to ocean, as a function of %R

A = alkalinity-based CDR = D + F   (4)

     D = reduced loss of carbon inputs to treated river segment and receiving

190   ocean waters = ICin * %R

     ICin = inorganic carbon inputs into treated reach via groundwater, surface

     water, or organic carbon mineralization

     %R = the percentage increase in dissolved inorganic carbon (DIC) as

     bicarbonate instead of CO as a function of river pH

195   F = reduced evasion of atmospheric CO_2 by increased alkalinity = SW * S

     * kw * ((pCO_2 before - pCO_2 after)$_{water}$ - $(pCO2)_{atm}$))

        (5)

     SW = area of surface water in treated river and ocean plumes

     S = solubility of CO_2 in water for given temperature and salinity conditions

200   k_w = gas exchange velocity

     pCO_2 = partial pressure of CO_2

L = losses (Figure 3)

G = grey emissions produced by the supply chain of alkaline material (mining + grinding + transport + dosing)

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$$\Delta CAlk = ([HCO_3^-]_{treatment} - [HCO_3^-]_{control}) * Q - C \qquad (6)$$

where

$[HCO_3^-]$ = concentration of bicarbonate and carbonate anions, compared to background levels in [Mass CO_{2e}] [Length]$^{-3}$

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Q = river discharge in [Length]^3 [Time]$^{-1}$

C = the carbon added in any alkaline amendment (e.g., $CaMg(CO_3)_2$) in [Mass CO_2e] [Time]$^{-1}$

To achieve net carbon removal, more dissolved CAlk must be delivered to the river mouth than was added in the mineral amendments (Figure 4).

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Safety. We identify potential risks of RiverCDR to aquatic ecosystems and identify that the safety of RiverCDR depends on the type of material added, the nature of the receiving waters, the dose/method of application, and the ecology of the selected river. We review numerous long-term studies of lime dosing in acidified rivers and summarize how addition of carbonate minerals impact aquatic ecosystems (Supplementary Data). While the impact of the addition of carbonate minerals to rivers is generally considered safe and is well known (Supplementary Data), the impact of other alkaline materials on aquatic ecosystems is not well-studied and poses added risk (Table 1). Addition of strong bases, such as CaO and MgO, can cause rapid rises in pH leading to fish kills and ecological harm[40]. Addition of silicate minerals, particularly of those which undergo

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225 incongruent weathering where secondary minerals are formed, poses risks for release of potentially toxic metals such as nickel and chromium to rivers and estuaries[41], for production of clays that can cloud river water or clog river substrates, and for silicosis from inhalation by humans during RiverCDR operations (Table 1).

For all mineral amendment types, RiverCDR poses a risk if alkalinity were increased above 230 ecosystem health thresholds[42], particularly for systems that have species at risk which are acidophilic. RiverCDR would also pose a risk to aquatic health if the dosing method was not continuously managed and produced large swings in pH/water chemistry. To reduce potential risks to ecosystem health from RiverCDR dosing must be precisely calculated and executed, and river biogeochemistry and ecology must be well-understood.

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Scalability. Global-scale hydrological modelling shows that the potential of CDR is in the 100s of Mt CO_{2e} yr^{-1} (Methods Figure 1). We consider a scenario where RiverCDR is applied to low alkalinity rivers (<0.6 mM) across the globe, the amount of CAlk generated is limited to stay within safe limits (0.6 mM) to avoid a shift in microbiological communities[42]. In this scenario, 240 RiverCDR has a potential of approximately 300 Mt CO_{2e} yr^{-1}.

Affordability. Affordability of RiverCDR is aided by its simplicity and its ability to use readily available and inexpensive feedstock. Dosing technology is already well developed[27]. Existing alkaline material dosers in Nova Scotia have a low land footprint (< 50 m^2) and low energy costs 245 (< 600 kW·yr^{-1}), which are provided by solar and wind renewable energy while river advection transports the captured carbon downstream of the addition point to the river mouth. A range of alkaline materials could achieve RiverCDR via carbonation weathering, such as silicate rock

minerals, and industrial minerals[32,39]. Alkaline minerals must be milled to small particle sizes (e.g., < 0.07 mm) so they can remain in suspension in the river until dissolution is complete. Thus, carbon costs are incurred during transportation of alkaline material to the sites and during the milling process. As with ERW and OAE, a potential for reusing waste materials exists, such as waste dust in the aggregate industry, or in unused dolomite in the cement industry. A challenge for RiverCDR, as with ERW and OAE, is the transport costs of feedstock to deployment sites.

RiverCDR provides an opportunity to use carbonate rocks as feedstock for significant capture and storage of atmospheric CO_2. Our finding that river water chemistry provides a thermodynamically favourable medium for carbonate rocks to undergo spontaneous carbonation weathering opens up new opportunities to lower risks and costs for CDR (Table 1). The ability to use carbonate feedstock is attractive because carbonate minerals weather congruently (e.g., do not generate clay minerals), contain fewer metal impurities than silicate rocks, and dissolve orders of magnitude faster than silicate minerals under the same conditions[32,34,44,45]. Further, carbonate rock requires no additional processing (e.g., does not require heating) and may require less energy for transport because carbonate quarries are widely available globally[46].

Uncertainties. Further research is needed on the impacts of alkaline additions on nitrogen cycling, cyanobacterial blooms and dissolved humic substances in rivers, including possible increased mineralization of dissolved organic carbon[43] and effects of cation exchange processes during humic flocculation in estuaries. The ecological impacts of the addition of alkalinity to circumneutral rivers is yet unexplored. Information on regional or local impacts of estuarine alkalinization is lacking[38]. Further research is needed on the ecosystem effects and general site risks involved in the addition strong bases to rivers (Table 1); this uncertainty has caused concern

in ocean application of alkaline materials[52], highlighting the importance of community consultation and support.

Co-Benefits / Social acceptability. Social acceptability of RiverCDR is supported by its potential to deliver co-benefits to the communities where it is deployed (Figure 3b). Long-term studies show that addition of carbonate materials to these rivers can reverse the impact of freshwater acidification and provide a range of ecosystem and societal benefits, depending on the site-specific context and the method used (Supplementary Data). In fact, the addition of alkalinity to many rivers is urgently needed to save species at risk from extirpation and increase aquatic ecosystem productivity and biodiversity[48]. Increasing river alkaline exports may also deliver co-benefits to coastal fishing communities through reduced acidification of the ocean receiving waters[49]. RiverCDR directly delivers to estuaries, which are a hotspot for ocean acidification[50,51]. The co-benefits at the local-watershed scale of CDR application may increase opportunities to improve ecological justice of CDR and for community-based efforts and leadership by Indigenous peoples.

We find that RiverCDR can complement other CDR methods. RiverCDR may help increase the efficacy of ERW that is dependent on the ability of rivers to transport the products of weathering reactions to the ocean for storage[5]. In acidic rivers, small-scale ERW-generated CAlk may be lost due to evasion[21]. Further, RiverCDR is well-suited for pairing with CO_2 capture technologies (DAC, BECCS, or flue gas) because RiverCDR provides a new way to sequester CO_2 captured by alkaline absorbants, and because the RiverCDR process is enhanced by increased pCO_2[47].

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Carbon fluxes from land to rivers are projected to increase with climate change. And agents of acidification that disrupt the land-to-ocean transport of carbon are projected to increase with climate change, including increased intensity of precipitation[53] and rising CO_2 in the atmosphere[54], and possibly sulphur aerosol deposition from solar radiation management[55]. Direct human activity and climate change have already increased the land-to-river flux of organic and inorganic carbon by approximately 12%[8,17], and this increasing trend is projected to continue to rise due to reductions to the soil carbon pool, CO_2 fertilization increasing terrestrial NPP, and via increased metabolism in lakes[11,56]. Our findings suggest that RiverCDR may increase the ability of rivers to maintain the delivery of land-based carbon to oceans, and therefore reduce CO_2 evasion, under these projected future stresses.

In conclusion, here we have identified a new negative-emission technology, RiverCDR, that may add to the CDR strategies needed to achieve net zero. We show how RiverCDR can contribute to climate action while providing demonstrated co-benefits such as increased freshwater ecosystem health and alleviation of freshwater and ocean acidification acidification if applied correctly and at the right location. Rivers are a promising arena for CDR as they are hotspots for carbon exchange[11] with elevated pCO_2, and therefore large amounts of CO_2 to capture. Rivers have physical and chemical conditions that favour carbonation weathering reaction kinetics and reduced likelihood of carbonate precipitation of alkalinity delivered to the ocean. Thermodynamic modelling shows a potential use of carbonate rocks in rivers to remove CO_2 from the atmosphere. By being applied at a point and driven by gravity, RiverCDR minimizes land use and minimizes energy consumption. Due to the history of alkalinity addition to rivers to reduce acidification threats to species at risk, the technology is relatively mature and well-understood. RiverCDR thus may meet leading CDR criteria, such as affordability, scalability, permanence, safety, and verifiability (i.e., the ability to simply quantify the CO_2 removed) placing it among current options

of promising CDR strategies. RiverCDR thus may provide an opportunity to restore water resources and lower greenhouse gases to combat severe climate change, supporting progress towards three Sustainable Development Goals (SDGs): SDG6 Clean Water and Sanitation, SDG13, Climate Action, and SDG14, Life Below Water.

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References

1. Lee, H. *et al.* Synthesis Report of the IPCC Sixth Assessment Report (AR6): Summary for Policymakers. (2023).

2. Ho, D. T. Carbon dioxide removal is not a current climate solution — we need to change the narrative. *Nature* **616**, 9–9 (2023).

3. Beerling, D. J. *et al.* Farming with crops and rocks to address global climate, food and soil security. *Nature plants* **4**, 138–147 (2018).

4. Hartmann, J. *et al.* Stability of alkalinity in ocean alkalinity enhancement (OAE) approaches – consequences for durability of CO_2 storage. *Biogeosciences* **20**, 781–802 (2023).

5. Knapp, W. J. & Tipper, E. T. The efficacy of enhancing carbonate weathering for carbon dioxide sequestration. *Frontiers in Climate* **4**, (2022).

6. Rahman, M. F. *et al.* As the UN meets, make water central to climate action. *Nature* **615**, 582–585 (2023).

7. Ciais, P. *et al.* Empirical estimates of regional carbon budgets imply reduced global soil heterotrophic respiration. *National Science Review* **8**, nwaa145 (2021).

8. Regnier, P., Resplandy, L., Najjar, R. G. & Ciais, P. The land-to-ocean loops of the global carbon cycle. *Nature* **603**, 401–410 (2022).

9. Battin, T. J. *et al.* Biophysical controls on organic carbon fluxes in fluvial networks. *Nature Geosci* **1**, 95–100 (2008).

10. Johnson, M. S. *et al.* CO2 efflux from Amazonian headwater streams represents a significant fate for deep soil respiration. *Geophysical Research Letters* **35**, (2008).

11. Liu, S. *et al.* The importance of hydrology in routing terrestrial carbon to the atmosphere via global streams and rivers. *Proceedings of the National Academy of Sciences* **119**, e2106322119 (2022).

345   12. Berner, R. A. & Kothavala, Z. Geocarb III: A Revised Model of Atmospheric CO2 over

Phanerozoic Time. *American Journal of Science* **301**, 182–204 (2001).

13. Tranvik, L. J. *et al.* Lakes and reservoirs as regulators of carbon cycling and climate.

Limnology and Oceanography **54**, 2298–2314 (2009).

14. Raymond, P. A. *et al.* Global carbon dioxide emissions from inland waters. *Nature* **503**, 355–

350   359 (2013).

15. Battin, T. J. *et al.* River ecosystem metabolism and carbon biogeochemistry in a changing

world. *Nature* **613**, 449–459 (2023).

16. Aufdenkampe, A. K. *et al.* Riverine coupling of biogeochemical cycles between land,

oceans, and atmosphere. *Frontiers in Ecology and the Environment* **9**, 53–60 (2011).

355   17. Lauerwald, R., Regnier, P., Guenet, B., Friedlingstein, P. & Ciais, P. How Simulations of the

Land Carbon Sink Are Biased by Ignoring Fluvial Carbon Transfers: A Case Study for the

Amazon Basin. *One Earth* **3**, 226–236 (2020).

18. Casas-Ruiz, J. P. *et al.* Integrating terrestrial and aquatic ecosystems to constrain estimates of

land-atmosphere carbon exchange. *Nat Commun* **14**, 1571 (2023).

360   19. Friedlingstein, P. *et al.* Global Carbon Budget 2022. *Earth System Science Data* **14**, 4811–

4900 (2022).

20. Schlesinger, W. H. & Bernhardt, E. S. *Biogeochemistry (Fourth Edition)*. (Academic Press,

2020).

21. Bertagni, M. B. & Porporato, A. The Carbon-Capture Efficiency of Natural Water

365   Alkalinization: Implications For Enhanced weathering. *Science of The Total Environment*

838, 156524 (2022).

22. Rotteveel, L., Heubach, F. & Sterling, S. M. The Surface Water Chemistry (SWatCh) database: a standardized global database of water chemistry to facilitate large-sample hydrological research. *Earth System Science Data* **14**, 4667–4680 (2022).

370

23. Clair, T. A., Dennis, I. F., Scruton, D. A. & Gilliss, M. Freshwater acidification research in Atlantic Canada: a review of results and predictions for the future. *Env.Rev.* **15**, 153–167 (2007).

24. Monteith, D. T. *et al.* Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature* **450**, 537 (2007).

375

25. Whitfield, C. J., Watmough, S. A., Aherne, J. & Dillon, P. J. A comparison of weathering rates for acid-sensitive catchments in Nova Scotia, Canada and their impact on critical load calculations. *Geoderma* **136**, 899–911 (2006).

26. Lacoul, P., Freedman, B. & Clair, T. Effects of acidification on aquatic biota in Atlantic Canada. *Env.Rev.* **19**, 429–460 (2011).

380

27. Henrikson, L. & Brodin, Y. Liming of surface waters in Sweden — a synthesis. in *Liming of Acidified Surface Waters* (eds. Henrikson, L. & Brodin, Y.) (Springer, 1995). doi:10.1007/978-3-642-79309-7_1.

28. Clair, T. A. & Hindar, A. Liming for the mitigation of acid rain effects in freshwaters: a review of recent results. *Env.Rev.* **13**, 91–128 (2005).

385

29. Raymond, P. A. & Oh, N.-H. Long term changes of chemical weathering products in rivers heavily impacted from acid mine drainage: Insights on the impact of coal mining on regional and global carbon and sulfur budgets. *Earth and Planetary Science Letters* **284**, 50–56 (2009).

30. Vesper, D. J., Moore, J. E. & Adams, J. P. Inorganic carbon dynamics and CO2 flux associated with coal-mine drainage sites in Blythedale PA and Lambert WV, USA. *Environ Earth Sci* **75**, 340 (2016).

31. Taylor, L. L. *et al.* Increased carbon capture by a silicate-treated forested watershed attenuated by acid deposition. *Biogeosciences* **18**, 169–188 (2021).

32. Renforth, P. & Campbell, J. S. The role of soils in the regulation of ocean acidification. *Philosophical Transactions of the Royal Society B: Biological Sciences* **376**, 20200174 (2021).

33. Morel, F. M. M. *et al.* Zinc and carbon co-limitation of marine phytoplankton. *Nature* **369**, 740–742 (1994).

34. Zhang, S. *et al.* River chemistry constraints on the carbon capture potential of surficial enhanced rock weathering. *Limnology and Oceanography* **67**, S148–S157 (2022).

35. Frontier Climate. Frontier Climate. https://frontierclimate.com/.

36. Rau, G. H. CO2 Mitigation via Capture and Chemical Conversion in Seawater. *Environ. Sci. Technol.* **45**, 1088–1092 (2011).

37. Archer, D. Fate of fossil fuel CO2 in geologic time. *Journal of Geophysical Research: Oceans* **110**, (2005).

38. Kirchner, J. S., Lettmann, K. A., Schnetger, B., Wolff, J.-O. & Brumsack, H.-J. Carbon capture via accelerated weathering of limestone: Modeling local impacts on the carbonate chemistry of the southern North Sea. *International Journal of Greenhouse Gas Control* **92**, 102855 (2020).

39. Hartmann, J. *et al.* Enhanced chemical weathering as a geoengineering strategy to reduce atmospheric carbon dioxide, supply nutrients, and mitigate ocean acidification. *Rev.Geophys.* **51**, 113–149 (2013).

40. CBC, R. B. 'Total devastation': Dozens of fish killed in North, West Vancouver streams | CBC News. *CBC* https://www.cbc.ca/news/canada/british-columbia/trout-kill-in-north-shore-streams-1.4652572 (2018).

41. Haque, F., Chiang, Y. W. & Santos, R. M. Risk assessment of Ni, Cr, and Si release from alkaline minerals during enhanced weathering. *Open Agriculture* **5**, 166–175 (2020).

42. Iversen, L. L. *et al.* Catchment properties and the photosynthetic trait composition of freshwater plant communities. *Science* **366**, 878–881 (2019).

43. Hart, K. A., Sterling, S. M. & Halfyard, E. A. Application of dolomite to forested catchments in Nova Scotia improves water quality (but more is needed to meet all targets). (In prep.).

44. Morse, J. W. & Arvidson, R. S. The dissolution kinetics of major sedimentary carbonate minerals. *Earth-Science Reviews* **58**, 51–84 (2002).

45. Kelemen, P. B. *et al.* Engineered carbon mineralization in ultramafic rocks for CO2 removal from air: Review and new insights. *Chemical Geology* **550**, 119628 (2020).

46. Hartmann, J. & Moosdorf, N. The new global lithological map database GLiM: A representation of rock properties at the Earth surface. *Geochemistry, Geophysics, Geosystems* **13**, (2012).

47. Caldeira, K. & Rau, G. H. Accelerating carbonate dissolution to sequester carbon dioxide in the ocean: Geochemical implications. *Geophysical Research Letters* **27**, 225–228 (2000).

48. Sterling, S. M. *et al.* Ionic aluminium concentrations exceed thresholds for aquatic health in Nova Scotian rivers, even during conditions of high dissolved organic carbon and low flow. *Hydrology and Earth System Sciences* **24**, 4763–4775 (2020).

49. Renforth, P. & Henderson, G. Assessing ocean alkalinity for carbon sequestration. *Reviews of Geophysics* **55**, 636–674 (2017).
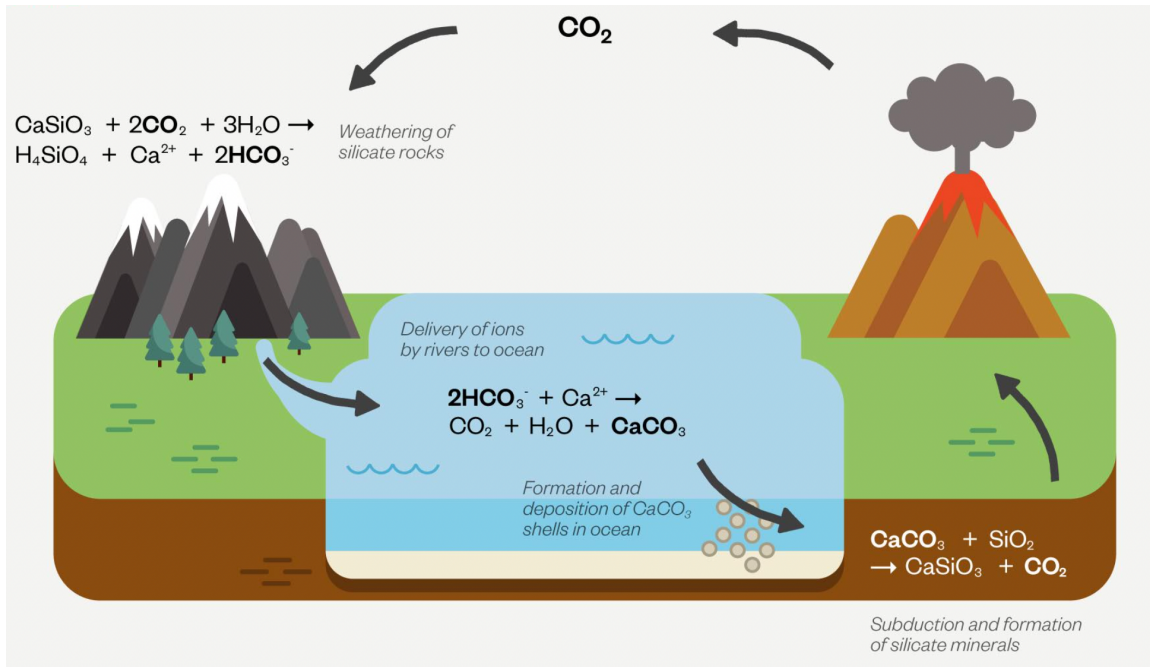
50. Azetsu-Scott, K. *et al.* Calcium carbonate saturation states in the waters of the Canadian Arctic Archipelago and the Labrador Sea. *Journal of Geophysical Research: Oceans* **115**, (2010).

51. Bianucci, L. *et al.* Sensitivity of the regional ocean acidification and carbonate system in Puget Sound to ocean and freshwater inputs. *Elementa: Science of the Anthropocene* **6**, 22 (2018).

52. BBC. Protest calls for St Ives Bay chemical test delay. *BBC News* (2023).

53. Chemke, R., Ming, Y. & Yuval, J. The intensification of winter mid-latitude storm tracks in the Southern Hemisphere. *Nat. Clim. Chang.* **12**, 553–557 (2022).

54. Phillips, J. C. *et al.* The Potential for CO_2-Induced Acidification in Freshwater: A Great Lakes Case Study. *Oceanography* **28**, 136–145 (2015).

55. Ricke, K. Solar geoengineering is scary - that's why we should research it. *Nature* **614**, 391 (2023).

56. Hasler, C. T. *et al.* Biological consequences of weak acidification caused by elevated carbon dioxide in freshwater ecosystems. *Hydrobiologia* **806**, 1–12 (2018).

57. Charlton, S. R., Parkhurst, C. A. & Appelo, C. A. J. phreeqc: R Interface to Geochemical Modeling Software. (2023).

58. Dunnington, D. tidyphreeqc: Tidy Geochemical Modeling Using PHREEQC. (2022).

59. Wickham, H. *et al.* Welcome to the Tidyverse. *Journal of Open Source Software* **4**, 1686 (2019).

60. Dunnington, D. chemr: R Data Structures for Chemistry Data. (2022).

61. Vaughan, D. & Dancho, M. furrr: Apply Mapping Functions in Parallel using Futures. (2022).

62. Wickham, H. & Bryan, J. readxl: Read Excel Files. (2023).

460   63. Lehner, B. & Grill, G. Global river hydrography and network routing: baseline data and new

approaches to study the world's large river systems. *Hydrological Processes* **27**, 2171–2186

(2013).

64. Lehner, B., Verdin, K. & Jarvis, A. New Global Hydrography Derived From Spaceborne

Elevation Data. *Eos, Transactions American Geophysical Union* **89**, 93–94 (2008).

465   65. Döll, P., Kaspar, F. & Lehner, B. A global hydrological model for deriving water availability

indicators: model tuning and validation. *Journal of Hydrology* **270**, 105–134 (2003).

66. Wallin, M. Evasion of CO2 from Streams: Quantifying a Carbon Component of the Aquatic

Conduit in the Boreal Landscape. (Swedish University of Agricultural Sciences, 2011).

67. Atekwana, E. A. & Krishnamurthy, R. V. Seasonal variations of dissolved inorganic carbon

470   and δ13C of surface waters: application of a modified gas evolution technique. *Journal of*

Hydrology **205**, 265–278 (1998).

68. Lerman, A. & Mackenzie, F. T. Carbonate Minerals and the CO2-Carbonic Acid System. in

Encyclopedia of Geochemistry: A Comprehensive Reference Source on the Chemistry of the

Earth (ed. White, W. M.) 206–226 (Springer International Publishing, 2018).

475   doi:10.1007/978-3-319-39312-4_84.

480

TABLE 1. RiverCDR risks associated with type of alkaline material used. H indicates high, M indicates medium, L indicates low, U indicates unknown.

	Level of Knowledge	Introduction of heavy metals	Increased river turbidity	Deposition of fines on riverbed gravel habitat	Risk of rapid increases of river pH	Risk of silicosis when inhaled
Calcite / Dolomite minerals	H	L	L	L	M	L
Pure olivine minerals	L	L	L	L	L	L
Alkali metal oxides	L	L	L	L	H	L
Alumino-Silicate minerals	L	M	H	H	L	H
Cement Kiln Dust	L	H	L	L	H	U

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490   **a)**

b)

Figure 1a) The carbonate silicate cycle[12], and **b)** existing (grey boxes) and new (turquoise box) CDR strategies that aim to increase alkalinity.
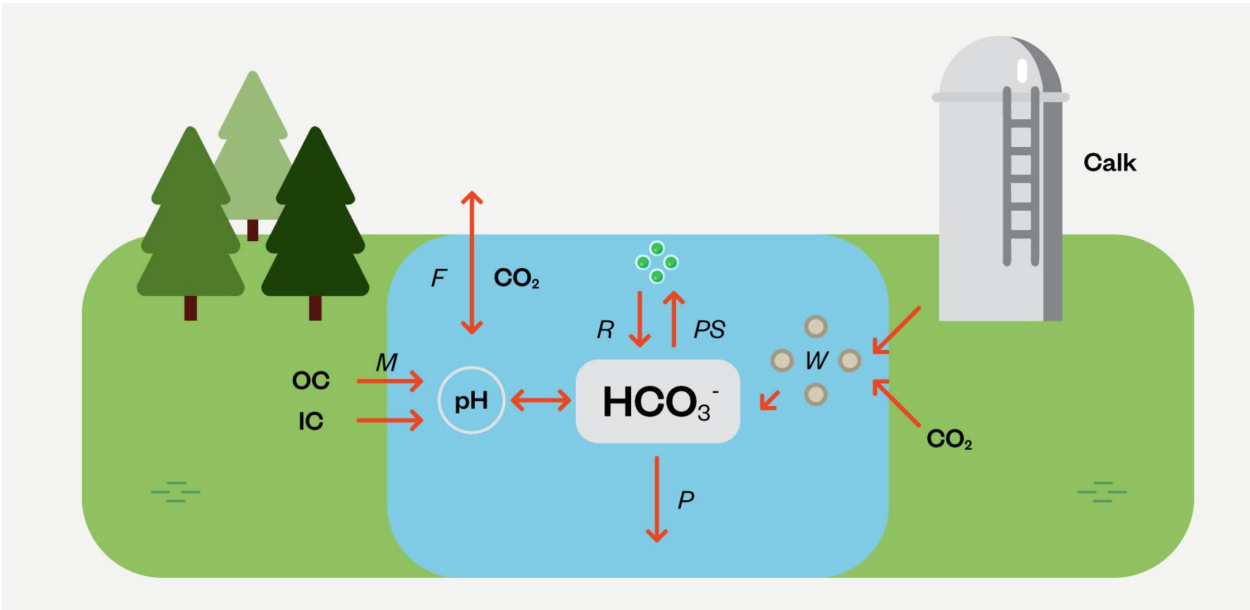
Figure 2. Inputs and outputs to carbonate alkalinity (CAlk) in rivers[66,67]. Here HCO_3^- represents Calk, *PS* represents photosynthesis, *W* represents inputs due to carbonation weathering, *R* represents respiration of organic matter, *P* represents precipitation of carbonate minerals, *IC* represents all forms of inorganic carbon inputs to the stream, *M* represents mineralization of dissolved organic carbon, and *F* represents CO_2 invasion or evasion.
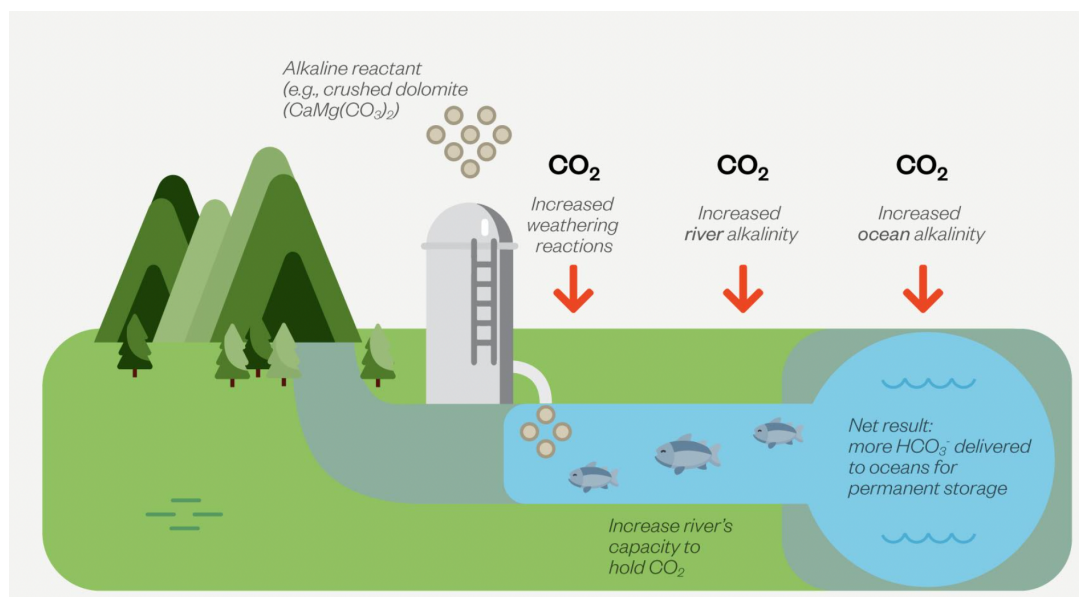
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Figure 3. a) Mechanisms of carbon dioxide drawdown from addition of alkalinity to rivers. **b)** co-benefits of addition of carbonate minerals to acidified rivers.
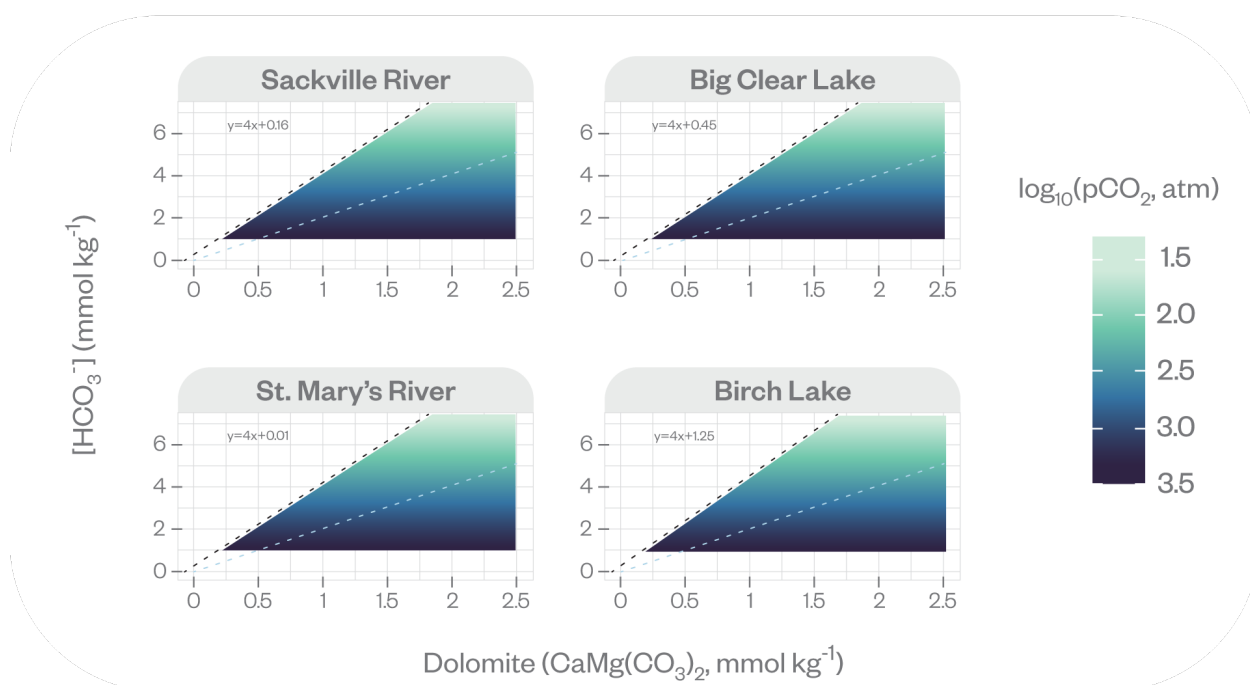
Figure 4. Thermodynamic predictions of Molal concentration of HCO_3^- as a function of dolomite addition, over a range of partial pressures of CO_2 (see Methods). The dotted line and annotated linear equation, $y=\beta_1 x+\beta_0$, represent the stoichiometric ratio of bicarbonate to dolomite (β_1), offset by the initial concentration of bicarbonate (β_0). The 2:1 dotted line represents the amount of inorganic carbon added from the dolomite. For CDR to occur, the dosing and HCO3- response must occupy the space between the two lines.

Methods

Thermodynamic modelling of CDR potential in rivers from alkalinity additions

Model solutions representing four neutral to acidic freshwater systems in Nova Scotia (the Sackville, Roseway, and St Mary's Rivers, Shortts Lake) and four alkaline systems in Ontario (Arab, Big Clear, Big Salmon, and Birch Lake) were characterized by measured alkalinity (as $CaCO_3$), Al, Ca, Cl, Cu, Fe, K, Mn, Na, pH, SO_4, and Zn. Alkalinity was below detection in Roseway River, and so a value of zero was imputed. Each solution was equilibrated with (1) dolomite in varying amounts and (2) a gas phase with a fixed CO_2 partial pressure. All simulations were run using PHREEQC (Version 3) in R with the PHREEQC database[57,58]. Several other contributed R packages were used for data cleaning and visualization[59–62].
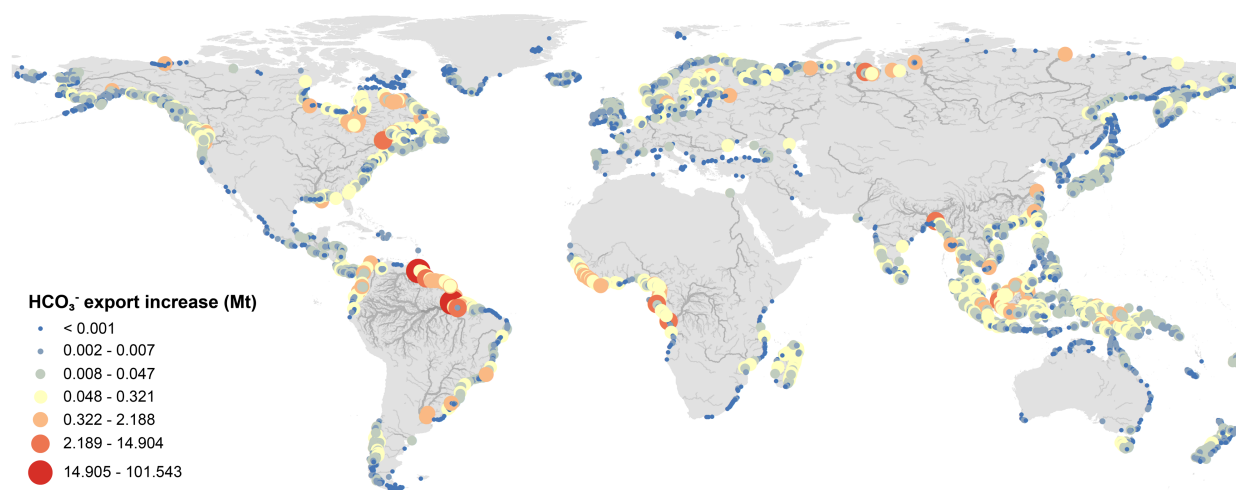
In our simulations, dolomite was added to solutions in equilibrium via the range of pCO_2 that can be found in rivers and streams, from 400 µatm of CO_2 (approximately the partial pressure of CO_2 in the atmosphere) to greater than 12,000 µatm[11].

Forecasting global potential of RiverCDR

The HydroSHEDS global hydrographic framework applied in this study includes a digital elevation dataset with flow direction and flow accumulation grids at a spatial resolution of 15 arc-seconds (approximately 500 m pixel resolution at the equator) that were derived from a digital elevation dataset at 3 arc-second resolution (approximately 90 m resolution at the equator) using automated and manual processing steps[63,64]. The database also includes an estimate of long-term average "naturalized" runoff and discharge, derived by downscaling coarse resolution (0.5°) runoff and discharge estimates of the global hydrological model WaterGAP (v2.2 as of 2014)[65].

To generate a baseline scenario of HCO_3^-, a global map of present-day HCO_3^- concentrations[42] was resampled to the target spatial resolution of 15 arc-seconds. Smaller data gaps in the original layers were filled using nearest-neighbor spatial allocation techniques. Next, we calculated the weighted mean HCO_3^- concentration using mean annual river runoff for each watershed draining directly into the ocean. The mass flux of HCO_3^- at the outlet of the watershed was then calculated using long-term annual discharge from HydroSHEDS multiplied with the weighted mean HCO_3^- concentration.

To estimate the global potential if RiverCDR were applied to low alkalinity rivers, we simulated an increase of HCO_3^- concentration in low alkalinity areas (defined as less than 0.6 mMol) to a threshold of 0.6mMol, recalculated the HCO_3^- export for each watershed, and finally calculated the difference from the baseline scenario. The results at the watershed scale were summarized at country, continental, and global scales (Methods Figure 1).

Methods Figure 1. Amount of CDR increase (Mt CO_{2e} yr^{-1}) by raising low alkalinity watersheds (< 0.6 mmol/L) to threshold of 0.06 mmol/L.

Code availability

560   Code and documentation for the PHREEQC code and global HCO_3^- flux data are publicly available

at (https://github.com/bentrueman/river-cdr.).

Author contributions:

     Conceptualization: SMS (lead), EAH

565   Methodology: SMS (lead), EAH, GG, BL

     Investigation: SMS (lead), EAH

     Visualization: SMS (lead), BT (Figure 4), GG (Methods Figure 1).

     Funding acquisition: SMS

     Project administration: SMS

570   Supervision: SMS

     Writing – original draft: SMS

     Writing – review & editing: SMS, EAH, BT, GG, KH, BL

     Supplementary Data: KH, SMS, EAH

575   **Competing interests:** Competing interests of the authors. SMS and EAH and sit on the board and

hold equity in a carbon dioxide removal company (CarbonRun). SMS and EAH have filed a patent

related to carbon dioxide removal in rivers.

Acknowledgments:

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Supplementary Information

Supplementary Data. Database of studies on the impact of river liming on water quality, ecosystems, and society [see attached excel spreadsheet entitled Supplementary Data].

Supplementary Note: illustration of the sensitivity of CAlk to changes in pH commonly found in rivers. The speciation of inorganic carbon as a function of pH[68]. To illustrate, we compare two rivers each receiving 10 mg/L of DIC. A river with a pH of 7.5 holds 9.3 g of the DIC as HCO_3^- anion. By contrast, a river with a pH of 4.5 holds only 0.13 mg/L of the DIC as HCO_3^- anion with the remainder as CO_2 and therefore subject to loss through evasion (following Figure 2).