

# **Title: Addition of Alkalinity to Rivers: a new CO<sub>2</sub> 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  $\text{MtCO}_2\text{e yr}^{-1}$ , which amounts to  $\sim 10\%$  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,  
45 permanent and verifiable are urgently needed to reduce severe risks from climate change and reach  
net zero<sup>1</sup>; 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<sup>2</sup>. The landscape  
of CDR options include land-based approaches such as the application of alkaline materials to land  
50 (via Enhanced Rock Weathering (ERW))<sup>3</sup> and ocean-based approaches, such as Ocean Alkalinity  
Enhancement (OAE)<sup>4</sup> (Figure 1). As of yet, no CDR technologies exist for rivers, although recent  
calls have been made to integrate river management and climate change<sup>5,6</sup>. 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  
55 permanence, safety, societal acceptance, scalability, and we propose a framework for monitoring,  
reporting and verification (MRV).

Rivers are a hotspot for carbon flows<sup>7</sup>. Rivers and inland waters have been estimated to deliver  
approximately 0.96 PgCyr<sup>-1</sup> of organic and inorganic carbon from land areas to oceans via the  
land-to-ocean aquatic continuum (LOAC)<sup>8</sup>. Water draining from land surfaces delivers up to 18%  
60 of terrestrial gross primary production to inland waters via shunting of CO<sub>2</sub> from soils or organic  
carbon that is later mineralized to CO<sub>2</sub><sup>9-11</sup>, generating high pCO<sub>2</sub> (partial pressure of CO<sub>2</sub>) in some  
reaches (> 10,000 µatm)<sup>11</sup>. Carbonate alkalinity (CAIk) 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<sub>2</sub> from the atmosphere<sup>4</sup> (Equation 1). Large amounts (approximately  
65 0.4 PgC yr<sup>-1</sup>) of CAlk (comprising primarily HCO<sub>3</sub><sup>-</sup>) are leached from soils and bedrock and

delivered to oceans via the global inland water network<sup>8</sup>, driving the long-term carbonate-silicate cycles, Earth's natural regulator of atmospheric CO<sub>2</sub> and global temperature over geologic time<sup>12</sup> (Figure 1a). Upon arriving in the open water network, much of this dissolved inorganic carbon (DIC, comprising CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>) is evaded to the atmosphere as CO<sub>2</sub><sup>13,14</sup>, estimated as  
70 between 1.9 and 2.3 PgC yr<sup>-1</sup><sup>15</sup> and only a portion is exported via stable forms of Calk directly to the ocean for long-term storage<sup>8,11,14,15</sup>. Thus, rivers commonly have pCO<sub>2</sub> values well above atmospheric levels<sup>11,16</sup>. 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<sup>7,17</sup>, nor in global carbon budget accounting<sup>18,19</sup>.

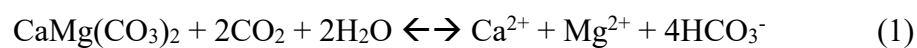
75 A prevalent view is that HCO<sub>3</sub><sup>-</sup> behaves conservatively once it has entered the open water network while transiting through rivers and inland waters<sup>8</sup> and that HCO<sub>3</sub><sup>-</sup> dominates DIC in most freshwaters<sup>20</sup>. However, pH controls the speciation of DIC into carbonate anions or CO<sub>2</sub>. When a volume of water containing HCO<sub>3</sub><sup>-</sup> is mixed with a volume of low pH water (below approximately pH 8.3), the low pH can convert stable HCO<sub>3</sub><sup>-</sup> to CO<sub>2</sub>, and thus be subject to evasion to the  
80 atmosphere (Figure 2). The range of natural river pH levels overlaps with the critical values pH 4.5-8.3 for carbonate speciation<sup>21</sup>. Thus, decreased pH, particularly around pH 5.5, where there is a sharp transition between CO<sub>2</sub> and HCO<sub>3</sub><sup>-</sup>, can increase carbon losses along the LOAC through increased CO<sub>2</sub> evasion, lowering HCO<sub>3</sub><sup>-</sup> exports to long-term storage in the oceans.

Human activities, such as fossil fuel burning and fertilizer application, have reduced base cation  
85 concentrations in soils and lowered pH and alkalinity of inland waters. Currently many rivers remain acidified with low alkalinity and pH<sup>22</sup>, despite reductions in acid emissions<sup>23,24</sup>. 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<sup>25,26</sup>. To save aquatic species at risk, such as Atlantic salmon (*Salmo salar*), from freshwater acidification, ground carbonate rocks have

90 been added to surface waters in river liming programs in North America and Europe for decades<sup>27–</sup>  
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<sup>27</sup> (Supplementary Data). However, the CDR potential of such alkaline additions to rivers  
95 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  
100 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  
105 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):



and examine chemical equilibria in response to application of dolomite to a range of natural river  
110 water chemistries and prescribed pCO<sub>2</sub> levels (reflecting the range of common fluvial values<sup>11</sup>  
from Nova Scotia, Canada (see Methods)). As expected, the carbonation weathering efficiency of  
the added dolomite increases with higher pCO<sub>2</sub> 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<sup>5</sup>.

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<sup>21</sup>, 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<sup>21,31</sup>. 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<sub>2</sub> evasion / increasing CO<sub>2</sub> 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<sub>2</sub> from the atmosphere as organic carbon<sup>32</sup>.

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<sub>3</sub><sup>-</sup> to convert to CO<sub>2</sub>, or 3) uptake of HCO<sub>3</sub><sup>-</sup> via photosynthesis<sup>33</sup> (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<sup>34</sup>.

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<sub>2</sub>, 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<sup>35</sup>.

**Permanence.** Once CAlk (mostly in the form of HCO<sub>3</sub><sup>-</sup>) reaches the ocean in river estuaries, the permanence of the carbon capture depends on the length of time HCO<sub>3</sub><sup>-</sup> remains in solution (i.e., that the reaction is not reversed), estimated as 10,000s of years<sup>8,36,37</sup>. Reverse reactions of carbonate weathering are less likely in areas where more rapid mixing and dilution occurs<sup>36,38</sup>,  
155 areas of lower salinity water<sup>21</sup>, and in cases where alkaline solutions are equilibrated with atmospheric CO<sub>2</sub> prior to addition to the oceans<sup>4</sup>. Freshwater plumes in the ocean are dilute, equilibrated with the atmosphere, and well-mixed, favouring carbon capture permanence of RiverCDR.

**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 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 RiverCDR MRV draws on standardized and well-established measurement techniques<sup>8,18</sup>. 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<sub>2</sub> by increased alkalinity in receiving ocean waters.

$$\Delta \text{CAI} = W + A - L - G \quad (2)$$

where

$\Delta \text{CAI}$  = increase in carbonate alkalinity at the river mouth relative to background

and is equivalent to CDR in  $[\text{Mass CO}_{2\text{eq}}] [\text{Time}]^{-1}$

$$W = \text{weathering-based CDR} = M * S * E_w * E_t$$

(3)



where

M = mass alkaline material added

S = stoichiometric relation of CDR vs tonnes alkaline material added

$E_w$  = carbonation weathering efficiency

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

$$A = \text{alkalinity-based CDR} = D + F \quad (4)$$

D = reduced loss of carbon inputs to treated river segment and receiving  
ocean waters =  $IC_{in} * \%R$

$IC_{in}$  = 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

F = reduced evasion of atmospheric CO<sub>2</sub> by increased alkalinity =  $SW * S$   
 $* k_w * ((pCO_2 \text{ before} - pCO_2 \text{ after})_{\text{water}} - (pCO_2)_{\text{atm}})$

(5)

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

S = solubility of CO<sub>2</sub> in water for given temperature and salinity conditions

$k_w$  = gas exchange velocity

$pCO_2$  = partial pressure of CO<sub>2</sub>

L = losses (Figure 3)

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

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$$\Delta \text{CAI} = ([\text{HCO}_3^-]_{\text{treatment}} - [\text{HCO}_3^-]_{\text{control}}) * Q - C \quad (6)$$

where

$[\text{HCO}_3^-]$  = concentration of bicarbonate and carbonate anions, compared to background levels in  $[\text{Mass CO}_2\text{e}] [\text{Length}]^{-3}$

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

C = the carbon added in any alkaline amendment (e.g.,  $\text{CaMg}(\text{CO}_3)_2$ ) in  $[\text{Mass CO}_2\text{e}] [\text{Time}]^{-1}$

To achieve net carbon removal, more dissolved CAI 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<sup>40</sup>. 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<sup>41</sup>, 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).

230 For all mineral amendment types, RiverCDR poses a risk if alkalinity were increased above ecosystem health thresholds<sup>42</sup>, 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.

235 **Scalability.** Global-scale hydrological modelling shows that the potential of CDR is in the 100s of Mt CO<sub>2e</sub> yr<sup>-1</sup> (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<sup>42</sup>. In this scenario, 240 RiverCDR has a potential of approximately 300 Mt CO<sub>2e</sub> yr<sup>-1</sup>.

**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<sup>27</sup>. Existing alkaline material dosers in Nova Scotia have a low land footprint (< 50 m<sup>2</sup>) and low energy costs 245 (< 600 kW·yr<sup>-1</sup>), 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<sup>32,39</sup>. 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<sub>2</sub>. 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<sup>32,34,44,45</sup>. 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<sup>46</sup>.

**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<sup>43</sup> 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 alkalization is lacking<sup>38</sup>. 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<sup>52</sup>, 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<sup>48</sup>. Increasing river alkaline exports may also deliver co-benefits to coastal fishing communities through reduced acidification of the ocean receiving waters<sup>49</sup>. RiverCDR directly delivers to estuaries, which are a hotspot for ocean acidification<sup>50,51</sup>. 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<sup>5</sup>. In acidic rivers, small-scale ERW-generated CAlk may be lost due to evasion<sup>21</sup>. Further, RiverCDR is well-suited for pairing with CO<sub>2</sub> capture technologies (DAC, BECCS, or flue gas) because RiverCDR provides a new way to sequester CO<sub>2</sub> captured by alkaline absorbants, and because the RiverCDR process is enhanced by increased pCO<sub>2</sub><sup>47</sup>.

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<sup>53</sup> and rising CO<sub>2</sub> in the atmosphere<sup>54</sup>, and possibly sulphur aerosol deposition from solar radiation management<sup>55</sup>. Direct human activity and climate change have already increased the land-to-river flux of organic and inorganic carbon by approximately 12%<sup>8,17</sup>, and this increasing trend is projected to continue to rise due to reductions to the soil carbon pool, CO<sub>2</sub> fertilization increasing terrestrial NPP, and via increased metabolism in lakes<sup>11,56</sup>. 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<sub>2</sub> 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 if applied correctly and at the right location. Rivers are a promising arena for CDR as they are hotspots for carbon exchange<sup>11</sup> with elevated pCO<sub>2</sub>, and therefore large amounts of CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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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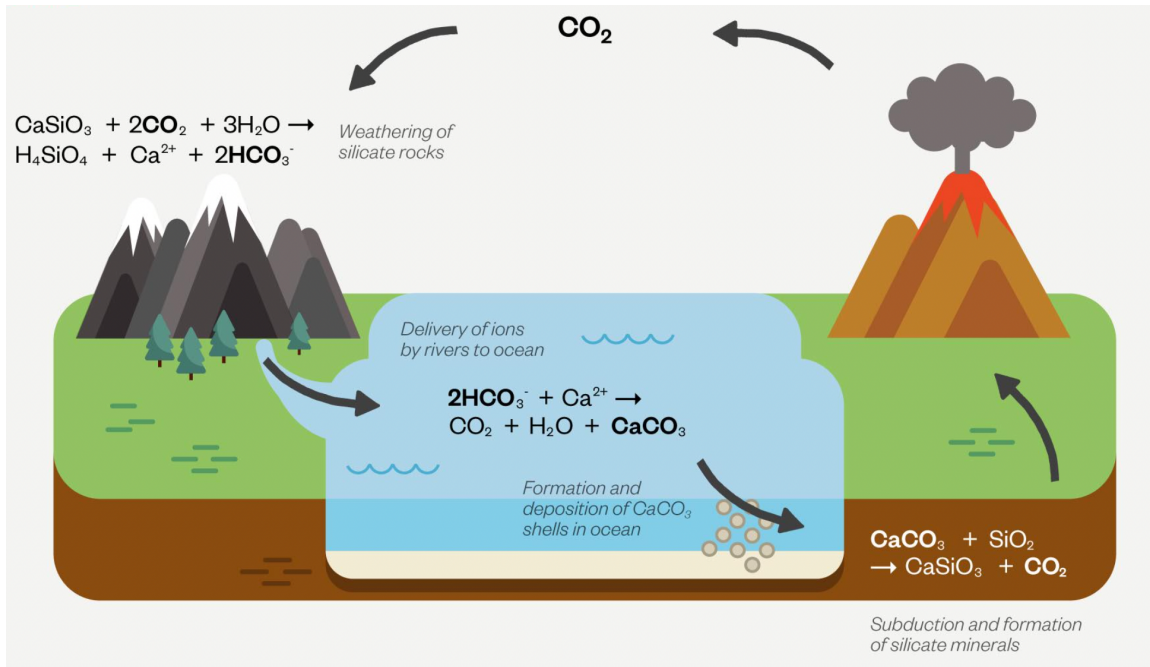
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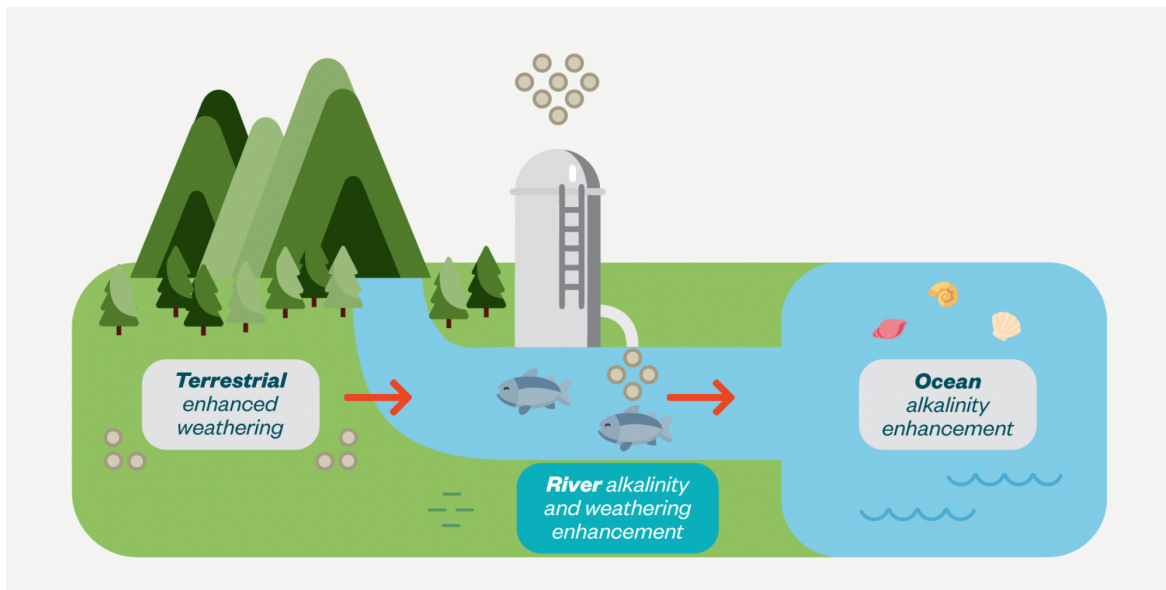
**TABLE 1.** RiverCDR risks associated with type of alkaline material used. H indicates high, M indicates medium, L indicates low, U indicates unknown.

	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

a)

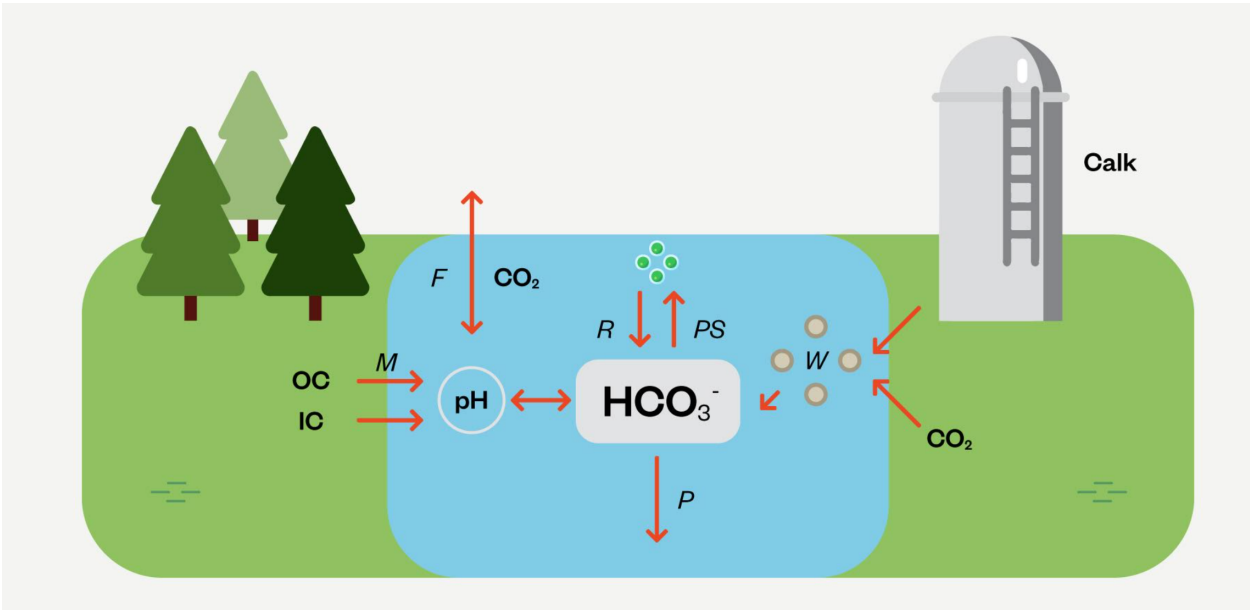


b)



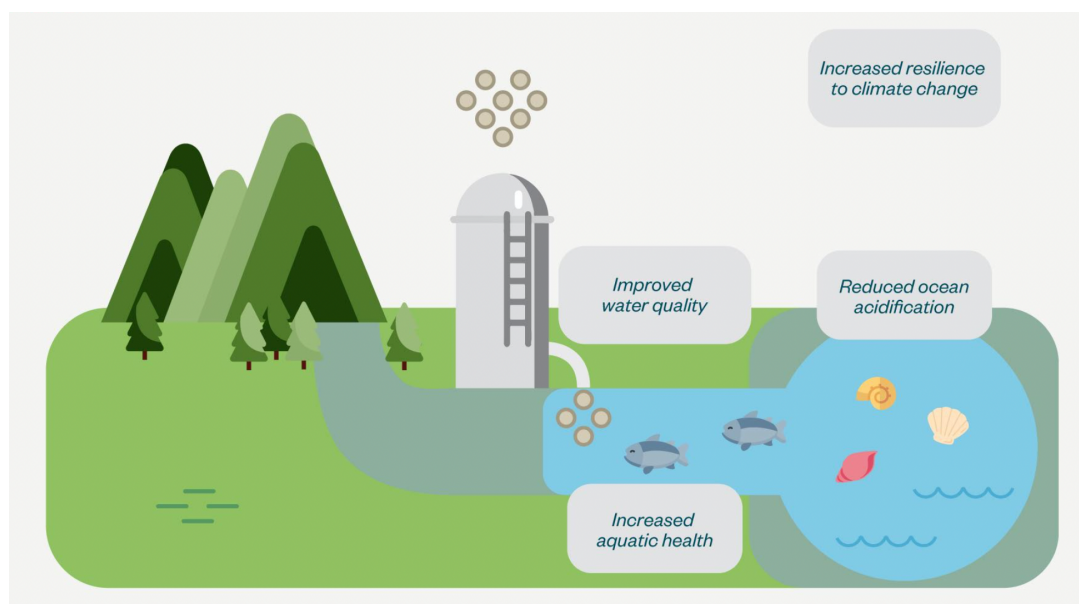
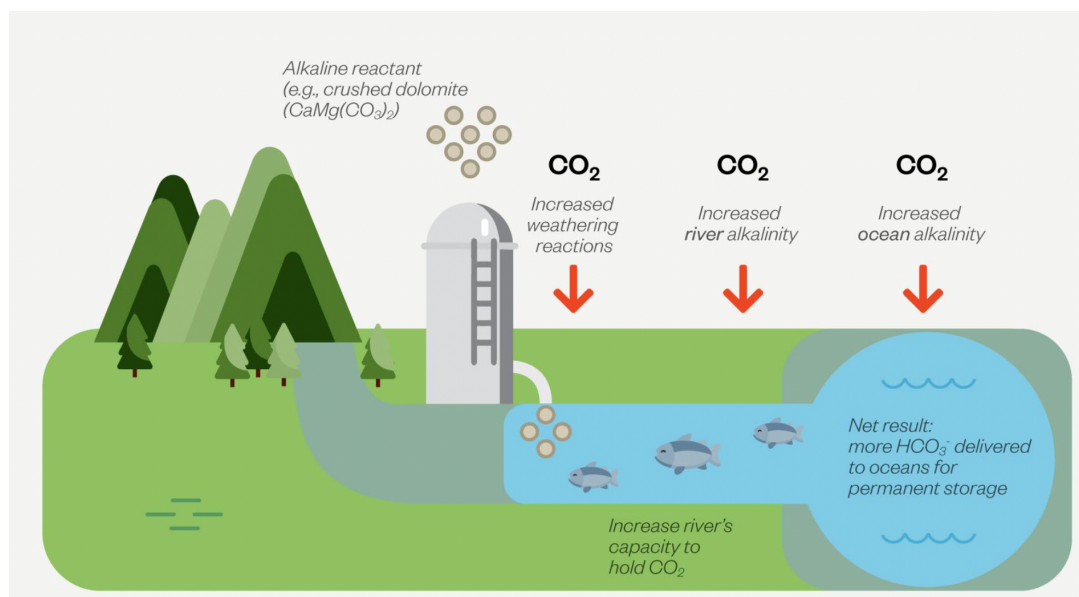
**Figure 1a)** The carbonate silicate cycle<sup>12</sup>, and **b)** existing (grey boxes) and new (turquoise box) CDR strategies that aim to increase alkalinity.



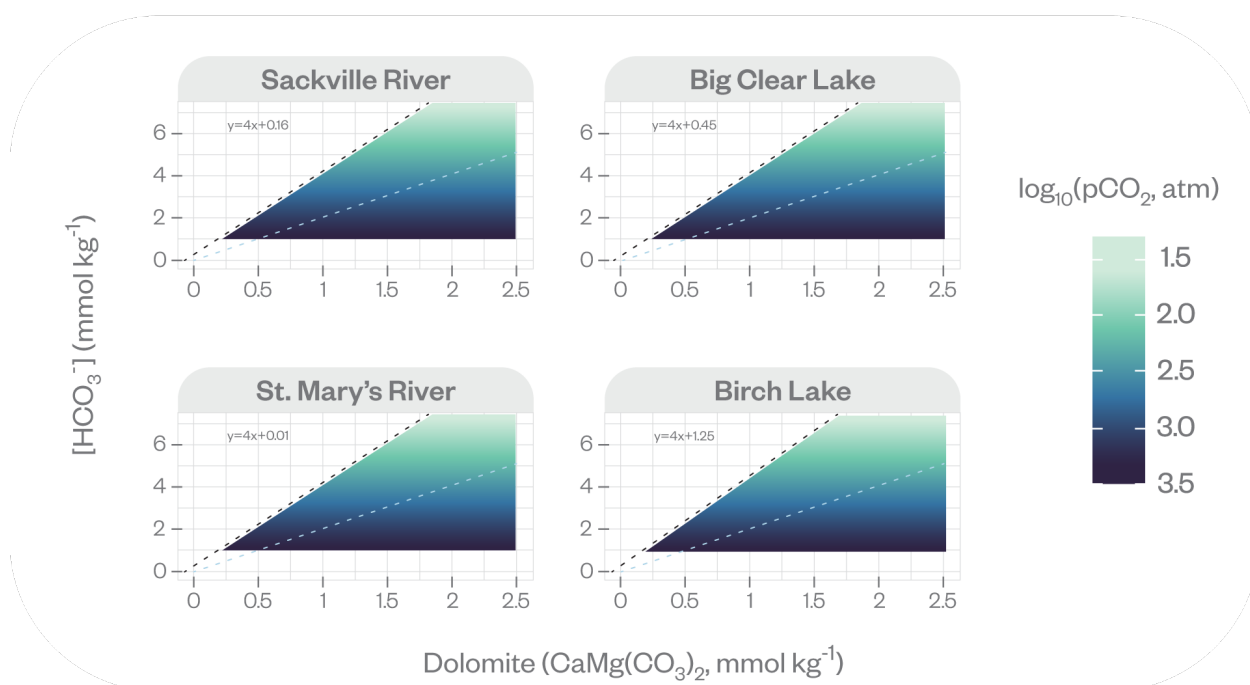


**Figure 2.** Inputs and outputs to carbonate alkalinity (CAlk) in rivers<sup>66,67</sup>. Here  $\text{HCO}_3^-$  represents Calk,  $PS$  represents photosynthesis,  $W$  represents inputs due to carbonation weathering,  $R$  represents respiration of organic matter,  $P$  represents precipitation of carbonate minerals,  $IC$  represents all forms of inorganic carbon inputs to the stream,  $M$  represents mineralization of dissolved organic carbon, and  $F$  represents  $\text{CO}_2$  invasion or evasion.

500



**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  $\text{HCO}_3^-$  as a function of dolomite addition, over a range of partial pressures of  $\text{CO}_2$  (see Methods). The dotted line and annotated linear equation,  $y = \beta_1 x + \beta_0$ , represent the stoichiometric ratio of bicarbonate to dolomite ( $\beta_1$ ), offset by the initial concentration of bicarbonate ( $\beta_0$ ). The 2:1 dotted line represents the amount of inorganic carbon added from the dolomite. For CDR to occur, the dosing and  $\text{HCO}_3^-$  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  $\text{CaCO}_3$ ), Al, Ca, Cl, Cu, Fe, K, Mn, Na, pH,  $\text{SO}_4$ , 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  $\text{CO}_2$  partial pressure. All simulations were run using PHREEQC (Version 3) in R with the PHREEQC database<sup>57,58</sup>. Several other contributed R packages were used for data cleaning and visualization<sup>59-62</sup>.

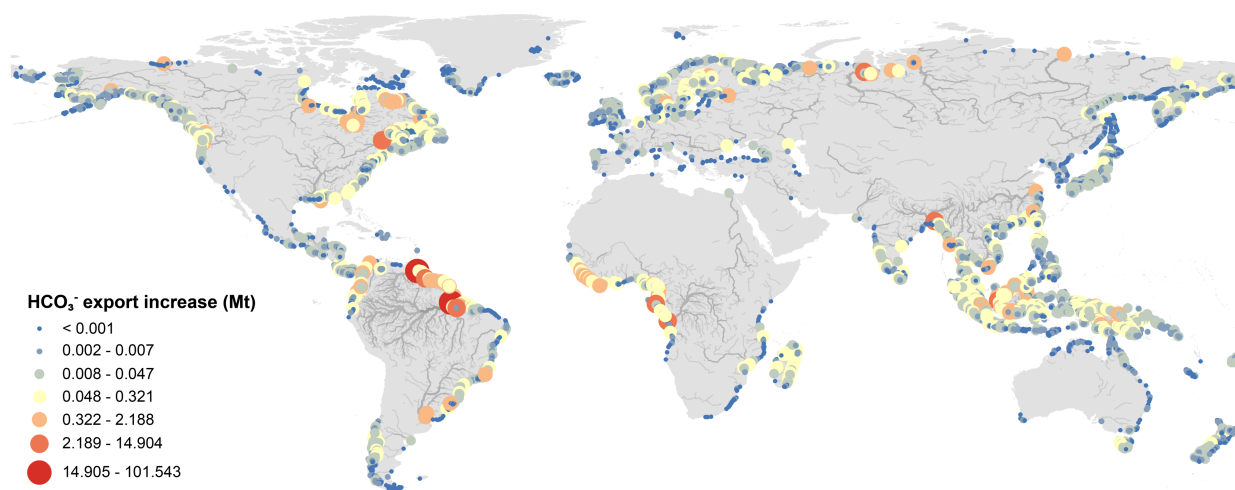
In our simulations, dolomite was added to solutions in equilibrium via the range of  $\text{pCO}_2$  that can be found in rivers and streams, from 400  $\mu\text{atm}$  of  $\text{CO}_2$  (approximately the partial pressure of  $\text{CO}_2$  in the atmosphere) to greater than 12,000  $\mu\text{atm}$ <sup>11</sup>.

### 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<sup>63,64</sup>. The database also includes an estimate of long-term average “naturalized” runoff and discharge, derived by downscaling coarse resolution ( $0.5^\circ$ ) runoff and discharge estimates of the global hydrological model WaterGAP (v2.2 as of 2014)<sup>65</sup>.

To generate a baseline scenario of  $\text{HCO}_3^-$ , a global map of present-day  $\text{HCO}_3^-$  concentrations<sup>42</sup> 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  $\text{HCO}_3^-$  concentration using mean annual river runoff for each watershed draining directly into the ocean. The mass flux of  $\text{HCO}_3^-$  at the outlet of the watershed was then calculated using long-term annual discharge from HydroSHEDS multiplied with the weighted mean  $\text{HCO}_3^-$  concentration.

To estimate the global potential if RiverCDR were applied to low alkalinity rivers, we simulated an increase of  $\text{HCO}_3^-$  concentration in low alkalinity areas (defined as less than 0.6 mMol) to a threshold of 0.6mMol, recalculated the  $\text{HCO}_3^-$  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 ( $\text{Mt CO}_2\text{e yr}^{-1}$ ) by raising low alkalinity watersheds ( $< 0.6 \text{ mmol/L}$ ) to threshold of  $0.06 \text{ mmol/L}$ .

## Reporting summary

### Code availability

560 Code and documentation for the PHREEQC code and global  $\text{HCO}_3^-$  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.

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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<sup>68</sup>. 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  $\text{HCO}_3^-$  anion. By contrast, a river with a pH of 4.5 holds only 0.13 mg/L of the DIC as  $\text{HCO}_3^-$  anion with the remainder as  $\text{CO}_2$  and therefore subject to loss through evasion (following Figure 2).