Closing the inland water carbon cycle

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Inland water carbon dioxide emissions mirror the ocean's carbon uptake and are driven not only by ecosystem heterotrophy but also by chemical equilibration and calcification.

Research on the global carbon cycle has traditionally considered two active compartments (land and ocean) vertically exchanging carbon dioxide with a third compartment, the atmosphere. In 1992, Sarmiento and Sundquist (*1*) identified the need to include the lateral transfer of carbon from land to the ocean via streams, rivers, lakes, and reservoirs to accurately budget the ocean's carbon cycle. Specifically, a fraction of the riverine carbon delivered to the ocean is outgassing, implying that the preindustrial ocean was a source rather than a sink of carbon and that the ocean's present-day carbon sequestration is larger than the net flux of carbon dioxide across the air-sea interface into the ocean.

Fifteen years later, Cole *et al.* (*2*) articulated the implications of this lateral carbon flux for land biosphere carbon budgets. They showed that inland waters bury substantial carbon in reservoirs, lakes, and floodplains and emit large quantities of carbon dioxide and methane and thus act as a carbon sink and a carbon source. Cole *et al.* (*2*) estimated that about twice as much carbon enters inland waters as is exported to the sea and inferred that net atmosphere–to–land biosphere fluxes should be higher. The resulting paradigm shift (rivers are active rather than passive pipes transferring carbon from land to sea) has stimulated much research on carbon cycling in inland waters, particularly regarding carbon dioxide emissions. Estimates of inland water carbon dioxide emissions (0.8 to 3.3 Pg C year^{-1}) are on par with the oceans' carbon uptake (2.8 Pg C year^{-1}), but poorly constrained (*2*, *3*), because of spatial and temporal heterogeneity in aquatic ecosystems and the multiple processes governing carbon dioxide release.

Carbon dioxide exchanges across the air-water interface are the result of three processes and their interactions (Fig. 1): outgassing because of re-equilibration to atmospheric carbon dioxide levels, the metabolic balance between gross primary production and respiration, and the balance of carbonate mineral precipitation and dissolution (*4*). Outgassing is a major process in streams, rivers, reservoirs, and lakes receiving groundwaters that are initially exposed to high partial pressures of carbon dioxide in soils or surface waters that are enriched with dissolved inorganic carbon (*5*). The carbon eventually emitted due to equilibration gets imported in inorganic form from upstream systems. If respiration exceeds primary production, i.e., more organic carbon is consumed than produced, then the ecosystem is heterotrophic and a local source of carbon dioxide. Inland waters receive dissolved and particulate organic carbon from upstream aquatic and adjacent terrestrial systems that stimulate heterotrophy. The resulting excess of carbon dioxide production over consumption supports most of the global carbon dioxide emission (*6*). Calcification results in the release of one mole of carbon dioxide per mole of calcium carbonate precipitated and involves the consumption of calcium and bicarbonate ions (*4*, *7*).

These processes are coupled with the consequence that carbon dioxide outgassing following equilibration can induce calcification. Moreover, a one-to-one relationship does not exist between emission and either net ecosystem production or calcification because carbon dioxide emission is governed by the gradient across the air-water interface. Consequently, an autotrophic ecosystem (producing oxygen and consuming carbon dioxide) can still release carbon dioxide to the atmosphere because of excess carbon dioxide imported from elsewhere or generated during calcification.

In this issue, Many *et al.* (*7*) demonstrate that calcification supports carbon dioxide emission in Lake Geneva and provide strong arguments that this mechanism is important in various lakes globally. Lake Geneva is autotrophic with a positive net ecosystem production, hence carbon dioxide consumption, of 105 Gg C year^{-1}. Nevertheless, the lake emits carbon dioxide (~12 Gg C year^{-1}) because more carbon dioxide is generated during chemical equilibration of the dissolved carbonate system (~100 Gg C year^{-1}) and by calcification (~20 Gg C year^{-1}). The study reinforces that dissolved inorganic carbon delivery to lakes is a pivotal factor governing carbon dioxide emissions (*5*, *8*) and that carbon dioxide released by calcification is used by primary producers and emitted to the atmosphere (*4*, *8*). Many *et al.* (*7*) argue that freshwater scientists should integrate the organic and inorganic carbon cycling processes to accurately quantify carbon flows in inland waters.

However, closing inland-water carbon cycles by integrating the organic and inorganic carbon components requires not only databases comprising dissolved and particulate organic and inorganic carbon but also more precise reporting of data relevant to calculating carbonate equilibria. Researchers often report bicarbonate concentrations rather than dissolved inorganic carbon (the total of carbonic acid, bicarbonate, and carbonate ions) and alkalinity (the excess of proton acceptors over donors due to charge balancing). Calcification implies that two units of alkalinity are consumed, and one unit of dissolved inorganic carbon is released (*4*). Without fully resolving the dissolved carbonate equilibria, it will be challenging to understand and quantify calcification in

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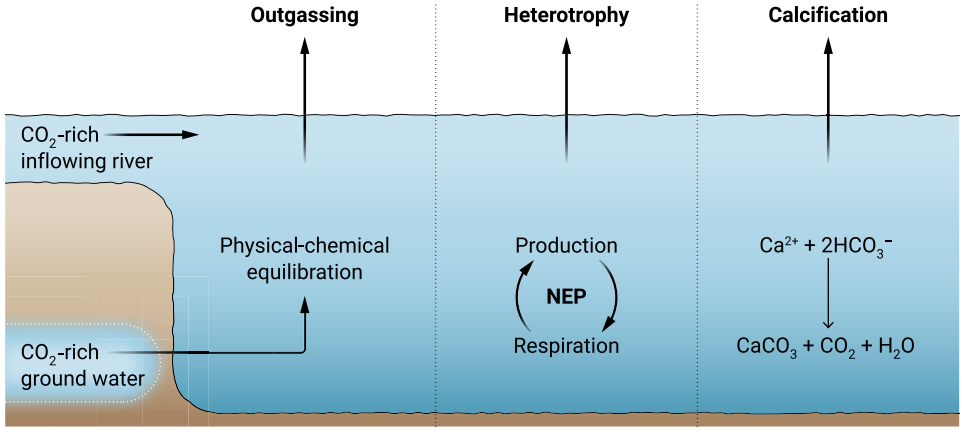

Fig. 1. Carbon dioxide emissions are the result of outgassing due to physical-chemical equilibration, ecosystem heterotrophy [i.e., negative net ecosystem production (NEP) = gross primary production minus respiration], and calcification. Illustration credit: Austin Fisher/*Science Advances*.

global inland waters. Even if dissolved inorganic carbon and alkalinity are both reported, carbonate equilibria calculations remain challenging because a fraction of the alkalinity may be organic, introducing bias (overestimation of carbon dioxide partial pressures).

Most dissolved inorganic carbon in inland waters originates from autotrophic and heterotrophic respiration in soils and groundwaters and a small part from the atmosphere. Plant and soil respiration generates carbon dioxide. A portion of the carbon dioxide reacts with silicate and carbonate rocks and leads to the formation of alkalinity (bicarbonate and carbonate, the charged forms of dissolved inorganic carbon); another part remains in the form of carbon dioxide. The latter is readily emitted upon entering surface waters because of equilibration. The alkalinity part is often considered unreactive in downstream aquatic ecosystems and is used by earth scientists as a proxy for chemical weathering intensity. However, calcification consumes alkalinity. Because of this action, alkalinity fluxes to the ocean may underestimate global chemical weathering if inland water calcification is indeed a major process, as shown by Many *et al.* (*7*).

Calcification is an important process in freshwater systems as shown by the widespread occurrences of travertine and lacustrine carbonate deposits, recent assessments of lake carbon budgets (*7*, *8*), and the ubiquitous occurrence of calcifying organisms in lakes (*6*, *8*, *9*). Calcification occurs both in the pelagic and benthic domains of inland waters. Benthic calcifiers are quite diverse and include phototrophs such as cyanobacteria, microalgae, and macroalgae (e.g., charophytes), as well as heterotrophs (e.g., bivalves and ostracods). Phytoplankton serve as nucleation sites for calcification in supersaturated waters (*9*). Saline lakes emit substantial quantities of carbon dioxide, partly due to calcification (*10*).

To meet climate targets, carbon dioxide removal from the atmosphere is needed. One potential climate solution is terrestrial-enhanced weathering. The rationale is that readily weatherable rocks or minerals such as olivine, wollastonite, and lime can be added to soils to stimulate the transformation of respired carbon dioxide into alkalinity (bicarbonate and carbonate ions), which is then transported with the water to the sea. The oceanic residence time of alkalinity is on the order of 100,000 years, implying that carbon will not return to the atmosphere within climate-relevant timescales. However, calcification in lakes and other inland waters transforms part of the alkalinity into calcium carbonate minerals and carbon dioxide. This calcification-induced carbon dioxide release limits the efficacy of terrestrial enhanced weathering as a carbon capture technique. It also complicates the verification of carbon sequestration because this loss of additional alkalinity happens downstream at large distances and with a significant delay. A global assessment of the role of calcification in inland water carbon cycling and in constraining the carbon capture potential of terrestrial enhanced weathering requires the development of mechanistic models for inland water carbon cycling. These models should incorporate the balance between primary production and respiration and fully resolve the inorganic carbon cycle, including calcification, as pioneered for Lake Geneva (*7*).

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