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Impact of chemically enhanced diffusion on dissolved inorganic carbon stable isotopes in a fertilized lake

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[1] At high pH the chemical reaction of CO_2 with OH^- can significantly increase the mass transfer of CO_2 between air and water. The reaction of CO_2 with OH^- strongly fractionates carbon isotopes in comparison to simple diffusion. These processes, chemically enhanced diffusion (CED) and chemically enhanced fractionation (CEF), greatly influence the carbon budgets and carbon isotope ratios for water bodies with high pH. Using floating chambers, we estimated mass transfer coefficients for CO_2 and a nonreactive gas, CH_4, in an experimentally eutrophied lake. The mass transfer coefficient estimated from CH_4 flux did not vary greatly between measurements (k_{600} = 1.83 ± 0.33 cm h^{-1}; mean ±1 SD) and agreed well with other independent estimates of mass transfer. The mass transfer coefficient of CO_2, however, was chemically enhanced by 3.5- to 7.5-fold. This enhancement was related to pH and temperature but was slightly higher than predictions from an existing model. We determined the role of CEF by modifying a model of CED to include both carbon isotopes (^{12}C and ^{13}C). A whole-lake addition of inorganic ^{13}C to Peter Lake created dynamics in $\delta^{13}C$-dissolved inorganic carbon (DIC) and provided a test of the new model. The value of $\delta^{13}C$-DIC decreased from approximately −9‰ to −21‰, a result that was well predicted by the model including CEF but could not be duplicated when CEF was omitted. Thus CED and CEF influenced the mass balance of air-water CO_2 exchange and had isotopic consequences for DIC. Although CEF is considered inconsequential for mean oceanic conditions, this model could be applied to marine systems for inorganic carbon modeling in areas where pH is elevated or physical mass transfer is limited because of low turbulence.

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