COMMENT

Rate of carbon dioxide transport across air–water boundaries in lakes

In their paper "Mechanisms that regulate growth rates of phytoplankton in Shagawa Lake, Minnesota," Megard and Smith (1974) include an estimate of the rate of invasion of carbon dioxide based on the assumption that the net increment of particulate organic carbon per day must be supported by invasion of CO_2 from the air. Their estimate amounts to 840 mg m^{-2} day^{-1}.

Megard and Smith do not recognize that there is a barrier to CO_2 invasion across the air–water boundary that severely limits this kind of transport into a lake. Bohr (1899) studied this barrier, using a stirring device that renewed the air–water interface as rapidly as possible without entraining air bubbles. In such well stirred water surfaces the coefficient of transport across the boundary had an average value of 0.0023 cm s^{-1}. I have frequently duplicated Bohr's experiment using lake waters, and my students routinely do so in classes. We use a variable speed stirring motor to achieve the stirring rate which renews the surface as rapidly as possible without entraining air bubbles.

It seems likely that lakes are subject to similar surface renewal rates only on fairly breezy days. During high winds, whitecaps are generated that increase the surface brought into air contact considerably, and the effective transfer coefficient may be as high as 0.01 cm s^{-1}. But on calm days the rate of surface renewal is much lower than in Bohr's experiment and the transfer coefficient is probably considerably less than 0.001.

Several years ago I published computations for the CO_2 invasion rate for western Lake Erie (Verduin 1956), using Bohr's coefficient, and obtained a daily transfer of 26 mmol m^{-2} (312 mg). I pointed out that the actual invasion rate probably averages considerably less than this in Lake Erie, and the same is true for Shagawa Lake.

Wood (1974) has gathered and tabulated data from several sources which bear on the boundary layer problem. He points out an erroneous CO_2 transport estimate by Morton et al. (1972) that resulted from their failure to take account of the carbon reservoir within the medium.

There is evidence in the data of Megard and Smith showing that Shagawa Lake does not replenish its CO_2 supply from the air on a daily basis, but that the bicarbonate pool supports the photosynthetic process to a large extent. The conversion of $Ca(HCO_3)_2$ to $CaCO_3$ by photosynthetic removal of CO_2 from the bicarbonate, with an attendant rise in pH, is the primary source of carbon for phytoplankton pulses. In their table 1 Megard and Smith show that the pH rose to 10.2 in July and 9.7 in August. A Δ pH of one unit represents approximately 2 g of carbon removal from the bicarbonate in one cubic meter of water (Moore 1939; Deffeyes 1965). Thus it is obvious that the bicarbonate reservoir in 10 m of water will support a large phytoplankton pulse, and nocturnal vertical mixing will usually replenish the high pH surface waters before the next day's photosynthetic demands begin.

When pH values are as high as 9 or 10 one can be sure that CO_2 is absorbed from the air, but in small lakes the rate of transport is probably less than 200 mg C m^{-2} day^{-1}.

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Reply to comment by J. Verduin

Invasion of carbon from the atmosphere must have equalled the daily increment of POC in the mixed layer (840 mg m^{-2} day^{-1}) if dissolved carbon did not enter from deeper water and if the quantity of dissolved carbon in the mixed layer did not change from day to day (ignoring diurnal oscillations). We do not know whether these conditions were met in Shagawa Lake, because rates of invasion from deep water and quantities of dissolved carbon in the mixed layer were not measured. The rate of invasion from the atmosphere is probably somewhat lower than our estimate, as we point out, but it probably exceeds Verduin's limit.

The rate of invasion of DIC from the atmosphere was 24–60 mmol m^{-2} day^{-1} (270–720 mg m^{-2} day^{-1}) at a lake in Ontario when the quantity of phytoplankton in the mixed layer was about 50% of the quantity in the mixed layer of Shagawa Lake at the climax of the bloom. Net changes of DIC from day to day were negligible, despite large diurnal oscillations, and the influx from deep water to the mixed layer was also negligible (Schindler and Fee 1973). Our estimate is therefore not unreasonable.

The high pH in Shagawa Lake and in the Ontario lake corresponds to very low partial pressures of CO_2, which may be four orders of magnitude below saturation in the Ontario lake. Because p_{CO_2} is low, and because the phytoplankton withdraw DIC from the water as it enters from the atmosphere (and deep water), the coefficient for transport of CO_2 across the air–water boundary is greater than the coefficient imposed by purely physical processes in the laboratory experiment discussed by Verduin.

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Reference

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Factors affecting gas exchange in natural waters

The rate of CO_2 exchange between atmosphere and surface water is an extremely complex process. It is greatly affected by at least three factors: the difference in CO_2 concentration between atmosphere and surface water; turbulent mixing (which is a direct function of wind velocity, and usually expressed as a boundary layer thickness or transfer coefficient); and chemical enhancement, by reaction of CO_2 with