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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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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 water and OH^- ions, supplementing carbon transfer.

These factors may be conveniently combined into a simple "stagnant film" model of gas exchange, which appears to represent the transfer of gases between atmosphere and water as well as more complex models (reviewed by Danckwerts 1970).

The highest values for the differences in CO_2 between atmosphere and surface water in nature are likely to be found in nutrient-enriched soft-water lakes, such as Shagawa Lake and Lake 227. Due to algal demand for CO_2, the concentration of dissolved inorganic carbon in Lake 227 is often lower than in the best acidified, boiled, double-distilled water. The P_{CO_2} in surface waters is thus effectively zero, and the concentration difference between atmosphere and water is equal to the atmospheric concentration of CO_2. In more typical bicarbonate waters the gradient is much smaller, and the CO_2 difference is detectable only by the most sensitive chemical techniques. In most oligotrophic lakes, losses of CO_2 exceed incomes from the atmosphere. This is undoubtedly due to the input of organic matter from the drainage basin, which decomposes in the lakes.

Maximum values for turbulent mixing occur in large lakes and oceans. In the stagnant film gas exchange model the effect of turbulence is expressed as a mass transfer coefficient, $M = D/Z$. D is the diffusion coefficient for a given gas (1.91×10^{-5} cm^2 s^{-1} for CO_2 at 25°C: Broecker 1974). The remaining parameter, Z, is the stagnant boundary layer referred to by Verduin. M can be measured, using carbon-14 (e.g. Craig 1957; Broecker 1963), radon-222 (e.g. Broecker 1965) or helium-3 (T. Torgerson unpublished data). The thickness of the stagnant boundary layer calculated from such measurements has ranged from 20 μm for the North Pacific (Peng et al. 1974) to 800 μm in lakes (Thurber and Broecker 1970). Z is known to decrease in proportion to the square of the wind velocity at the water surface (Kanwisher 1963; Emerson 1975*b*; Broecker and Peng 1974).

The chemical enhancement factor (E) reached measured values of 5 to 10 in Lake 227. The theoretical maximum was 21! (Emerson 1975*a*). The mechanism for enhancement is complex, but was treated in detail by Emerson (1975*a*).

In general, the higher the pH of surface waters or the thicker the stagnant boundary layer (Z), the greater the enhancement factor (E) will be. This is simply because of the increased probability of invading CO_2 reacting with OH^- ion in passing through a thicker boundary layer with a higher concentration of OH^- ion.

Putting all of the above together, the flux of CO_2 across the air–water interface (F) is equal to

$$F = E(D/Z)(C_A - C_L).$$

Broecker (1974) gives a clear and concise introduction to the topic.

The highest values of CO_2 flux recorded in nature are for the ocean, where all measurements fall in the range 0.33 to 1.08 g C m^{-2} day^{-1} for annual averages (Arnold and Anderson 1957; Bolin and Eriksson 1959; reviewed by Broecker and Peng 1974). These are for a system where values of turbulent mixing are maximum, but values for differences in CO_2 between atmosphere and surface water and for chemical enhancement are low. It is thus clear that natural values are possible that are far in excess of Verduin's (1975) predictions and greater than Megard and Smith's (1974) measurements as well.

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Announcement

Second International Symposium on Paleolimnology

The 2nd International Symposium on Paleolimnology will be held in northern Poland at Mikołajki, in the Mazurian Lake District, on 14–20 September 1976. The meeting is being sponsored by the International Association of Theoretical and Applied Limnology, the Quaternary Research Committee of the Polish Academy of Sciences, the Polish Hydrobiological Society, and the Institute of Geological Sciences of the Polish Academy of Sciences. The integrating topics for the 3 days are, African paleolimnology and paleoclimatology, impact of man on aquatic systems, and sediments and sedimentation processes.

Excursions will be in the Mazurian and other northern Polish lake areas.

Chairman of the International Committee is Prof. David G. Frey, Department of Zoology, Indiana University, Bloomington 47401 USA. Interested persons can obtain further information by writing to Dr. Frey or to the secretary of the Polish Organizing Committee: Dr. Barbara Marciniak, Zakład Nauk Geologicznych PAN, Al. Żwirki i Wigury 93, 02-089 Warszawa, Poland.