COMMENTS ON "DIFFUSION AND ACCUMULATION OF CHLORIDE AND SODIUM IN LAKE ONTARIO SEDIMENT"


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In a recent paper, Lerman and Weiler [1] presented a diffusion model to describe the distribution of Na⁺ and Cl⁻ in the upper 30 cm of Lake Ontario sediment. The diffusion model assumes that the flux of ions is a function of the respective concentration gradients and (for Na⁺) some sediment reaction. However, the two species are charged ions and the electrical coupling between them should be taken into account. The electro-neutrality principle [2] requires that the total charge held by the solution should be zero at any point. This restriction modifies the fluxes of the ions so that the net charge transport across any cross-section is zero. It was shown by Vinograd and McBain in 1941 [3] that this requirement modifies the diffusion coefficient (defined as the ratio of total flux to concentration gradient) and that the diffusion coefficient of ions of a one-to-one electrolyte are identical even though the mobilities of the ions may be different. This problem has been discussed by Garrels et al. [4], who applied the results of Vinograd and McBain to the study of ionic diffusion in water-saturated rocks. A comprehensive treatment of the physical chemistry aspect of the problem is given by Robinson and Stokes [2].

It should be emphasized that the present problem is different from a case in which the diffusing ions can be considered traces in a concentrated solution. While it may be justified, in the latter case, to assume that the diffusion coefficient is constant [4], one cannot make the same assumption here since the diffusing ions constitute the major part of the salt.

Ionic transport in pore water of sediments can be studied either by using the appropriate electrolyte solutions or by employing a Fick's Law-type expression. This latter approach has been taken by Lerman and Weiler [1]. However, the quantitative results of such a treatment should be considered questionable unless one can show that ionic interaction in the sediment of Lake Ontario is negligible.

References
