

Comment on "Salt-Pump Mechanism for Contaminant Intrusion into Coastal Aquifers"

Dror *et al.* (1) claimed that the diffusion rate of organic molecules into pure water increases by at least an order of magnitude in the presence of dissolved sodium chloride. This is surprising, because diffusion coefficients (D) in water are rather species-insensitive. For many ions and organic molecules of the size used as contaminant models (1), D (25°C) varies only within the range 0.5×10^{-5} to $\sim 2 \times 10^{-5}$ cm² s⁻¹ (2, 3). This insensitivity arises because D is controlled largely by the hydrodynamic radius of the diffusing particle and the viscosity of the liquid (4). In (1), the order-of-magnitude change in flux is ascribed to "salting out," wherein solubilities of species in water are reduced and activity coefficients are increased by the addition of ionic solutes. However, both saline and freshwater sources are saturated with respect to the contaminants, so that the activity (the product of activity coefficient and concentration) is the same. Consequently, no increase of diffusion flux would be expected in these experiments.

Analysis of data presented in (1) indicates that diffusion cannot be responsible for the observations. Transport is measured between two stirred chambers containing water, separated by a barrier of sand 20 mm thick. When the source side is saltwater, without contaminants, and the collector contains deionized water, salt appears rapidly in the collector. Approximately 16% of the infinite-time concentration builds up in 15 min. Normal liquid diffusion experiments on this scale take several days (5).

If the process were only diffusion, there would be a steady change with time in the concentration profile through the barrier, following the diffusion laws (4). Curves for this [figure 27.10 in (4)] can be used with known D values for NaCl (6) to estimate the travel

into the barrier. After 15 min, the concentration 7 mm into the barrier has not yet reached 1% of the source concentration, so it is difficult to see how any detectable diffusion-driven penetration to the collector can have occurred in this time. Alternatively, because the apparatus approximates to a diaphragm cell for determining D (5), the data points can be used to estimate values for D (NaCl) using the integrated expressions for such a device [(7) and equation 4.89 in (5)], if the effects of the sand are ignored initially. The values for the first two points shown by Dror *et al.* [figure 1B in (1)] are $D = 4.4 \times 10^{-3}$ cm² s⁻¹ and $D = 4.1 \times 10^{-3}$ cm² s⁻¹, a factor of 300 greater than the accepted value (6, 8), $D = 1.478 \times 10^{-5}$ cm² s⁻¹ (25°C). Not only is there a very serious absolute discrepancy, but subsequent points show a systematic trend, with an almost monotonic decrease down to about $D = 1.8 \times 10^{-3}$ cm² s⁻¹, so the effect is decreasing as the experiment proceeds. True diffusion should generate only random fluctuations in successive values.

Making rough estimates for the effects of the sand, it seems probable that the initial "diffusion constant" from this measurement would be about four orders of magnitude higher than the true one. Something other than diffusion is driving this salt migration.

In the main experiment, there are organic contaminants in the saline solution, as both saturated solution and suspended microdroplets. These compounds are transported to the collector chamber at approximately the same relative rate as for the salt. This suggests that the transport mechanisms for salt and organic contaminants are the same and are probably macroscopic. In (1), irregularities in the concentration curves were ascribed to transport of microdroplets. If that is true, it can only be

due to macroscopic flow, because droplets would diffuse at rates much lower even than the solution species.

Some driving force for this flow is needed. When both chambers contain water, transport between them is slow, but a difference in salt concentration between the two produces rapid transport, which slows as the differential salt concentration decreases. Two possible explanations can be suggested. First, because the two chambers contain solutions of different density, there will be a hydrostatic force (9) driving the denser liquid through the lower half of the barrier, with a matching flow in the reverse direction in the upper half, analogous to a thermal convection current. Second, the stirring of different solutions may produce a differential hydrodynamic force, driving liquid through the barrier. This could be an effect of density or of viscosity.

Until these points can be cleared up, the environmental implications in (1) need to be treated with reserve.

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References and Notes

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2. D. R. Lide, Ed., *CRC Handbook of Chemistry and Physics* (CRC Press, Boca Raton, ed. 81, 2000), tables 5.95, 6.192.
3. The hydrogen and hydroxyl ions are special cases and move much faster.
4. P. W. Atkins, *Physical Chemistry* (Oxford Univ. Press, Oxford, ed. 3, 1986), pp. 674–682.
5. P. J. Dunlop, B. J. Steel, J. E. Lane, in *Techniques of Chemistry*, A. Weissberger, B. W. Rossiter, Eds. (Wiley, New York, 1972), pp. 205–350.
6. *Landolt-Bornstein Tables* (Springer, Berlin, 1969), vol. 5a, p. 616.
7. It has been assumed that change in concentration is linearly proportional to the conductivity change shown on figure 1B in (1). The interface area is needed, and because the supporting online material for (1) does not specify which rectangular face connects the two cells, the largest has been assumed. Any alternative choice increases the discrepancy found.
8. Value is for the average concentration in the two vessels; see p. 263 in (5).
9. It is assumed that the barrier is vertical.

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