



Analysis of kinetic adsorption of solutes in groundwater using Random Walks and the Telegraph equation

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ABSTRACT. Transport of kinetic non-equilibrium adsorbing solutes in groundwater has been investigated. When N_f and N_a (functions of x and t) denote concentrations of particles in free (mobile) and adsorbed state, respectively, the model leads to two coupled partial differential equations. In one dimension:

$$\begin{aligned}\partial_t(N_f) + v\partial_x(N_f) &= -\lambda N_f + \mu N_a \\ \partial_t(N_a) &= \lambda N_a - \mu N_a\end{aligned}$$

where λ and μ are state change rates, or transition probabilities per unit of time. A term describing hydrodynamic dispersion, i.e. $D \partial_{xx}^2(N_f)$, has been omitted here. In a moving coordinate system where x replaces $x - vt\mu/(\lambda + \mu)$, we can rewrite the system after using $N_f + N_a = u$, $N_f - N_a = w$ and after eliminating w . This leads to:

$$(\lambda + \mu)\partial_t u = \lambda\mu \frac{v^2}{(\lambda + \mu)^2} \partial_{xx}^2 u - \partial_{tt}^2 u - v \frac{\lambda - \mu}{(\lambda + \mu)^2} \partial_{xt}^2 u$$

This equation looks like the Telegraph equation. In fact, for $\lambda = \mu$ it equals the Telegraph equation exactly. Similar models appear in the literature in a variety of fields (chemotaxis, heat exchange, chromatography) and a solution is available at least since the 1950's (e.g. Goldstein [2]; Giddings and Eyring [1]). For early times the solution behaves as a wave travelling with a finite speed, while for large times it converges to a Fickian dispersion model with an apparent dispersion coefficient $D^* = \lambda\mu v^2/(\lambda + \mu)^3$. An attractive feature of the telegraph model is that the unrealistic unlimited propagation, so typical of the diffusion model, remains absent. Although for $\lambda \neq \mu$ the equation differs slightly from the classical telegraph equation, the system still behaves essentially in the same way.

The two-dimensional case has been analyzed accordingly and a solution is presented. When, for early times this solution is compared to a 2-D Fickian transport solution some additional anomalies appear. These may very well explain the so-called tailing effect which quite often is observed in field experiments. Accordingly, the paper presents a stochastic procedure (Random Walk) to simulate and visualize the system. Several examples of Random Walk simulations will be presented.

References

- [1] J.C. Giddings and H. Eyring. A molecular dynamic theory of chromatography. *J. Phys. Chem.*, 59:416–421, 1955.
- [2] S. Goldstein. On diffusion by discontinuous movements and on the telegraph equation. *Quart. J. Mech. Appl. Math.*, VI:129–156, 1951.