GROUND WATER

Editorial

Beyond the K_d Approach

by Patrick V. Brady[a] and Craig M. Bethke[b]

In our efforts to predict the mobility of contaminants in the surface, we hydrologists were for many years forced to rely upon a number of computational simplifications in our work. Whether due to a paucity of input data, limited computing power, or the lack of applicable theory, we have at various times assumed that water tables remain static, that single values of porosity and permeability represent the properties of heterogeneous soils and sediments, and that single-parameter sorption coefficients, commonly known as K_d values, can describe ion sorption.

Advances in our understanding of physical hydrology in tandem with increases in computing power have, over roughly the past five years, allowed us to relax some of these simplifications. Transport models accounting for shifting water tables and heterogeneous media, once the domain of academic research, are now commonly applied to real-world problems. As a result, our models yield more realistic predictions than previously thought possible.

Yet even many of the most advanced modeling studies continue to treat what is in many cases the most significant chemical process affecting contaminant mobility—ion sorption to soil and aquifer solids—in terms of K_d values. We argue (on page 435) for incorporating a treatment of ion sorption more rigorous than the K_d approach because we now have the necessary theoretical framework and computational tools. More importantly, we show that in many cases we cannot predict contaminant mobility or engineer ground water cleanup correctly if we fail to do so.

A K_d distribution coefficient lumps the effects of a number of complex chemical processes into a single value, which we for convenience take as constant. The value for a single ion along a given aquifer, however, can vary with changing ion concentration or chemical conditions by many orders of magnitude. The attraction of assuming a single-valued K_d is clear: this assumption allows the differential equation describing contaminant transport to be cast in a particularly simple form, readily amenable to analytic and numerical solution. Permeability, another parameter that ranges over many orders of magnitude, can many times represent successfully the overall behavior of a system with a single value. There are, however, few field studies attesting to the accuracy of the constant-K_d approach for ionic species like heavy metals and radionuclides, and those that do exist do not appear fully relevant to many of today's more troublesome contaminants.

The K_d approach works best for contaminants that sorb weakly to soil and aquifer solids, are present in low concentration, participate in few reactions, and occur in a ground water system where chemical conditions such as contaminant concentration and pH vary little. Most heavy metals and many of the cationic radionuclides, however, sorb rather strongly to a variety of surfaces, especially the oxy-hydroxides of transition metals, and react to form various species and complexes. As a result, the K_d approach cannot be expected to describe sorption effectively for these two important classes of contaminants.

We (on page 435) use the example of inorganic Pb to show that K_d-based transport models give results that are not only quantitatively inaccurate, but qualitatively wrong. The K_d-based models greatly overestimate plume advance, understate the difficulty in removing contaminants from the subsurface, and fail to anticipate a "tail" of contamination in discharge from the contaminated zone that persists indefinitely. These inaccuracies are sufficient to lead (in the absence of other overriding criteria, such as past experience) to bad decisions in designing environmental remediation or protection projects.

Abandoning the K_d approach for a more theoretically sound treatment of ion sorption is an important and necessary step that we in our profession must take if we are to predict contaminant movement in a meaningful manner. Langmuir isotherms and the more general surface complexation approach describe ion sorption at specific sites according to balanced chemical reactions. These theoretically sound and well-established elements of modern surface chemistry are beginning to be applied outside academia to problems of contaminant transport. James Davis and co-workers (Davis et al. 1998), for example, used the surface complexation approach to explain Zn^{2+} movement at Otis Air Force Base, and John Zachara and co-workers (Zachara et al. 1995) used the method to examine subsurface transport of ^{60}Co. Turner and Pabalan (1999) applied it to consider sorption at the proposed nuclear waste repository at Yucca Mountain, Nevada.

We as a profession are in a position to move beyond the K_d approach. Versatile reactive transport codes such as PHREEQ-C, HYDROGEOCHEM, and XT have become available in recent years, and have been applied successfully to a variety of problems. Computing power sufficient to carry out chemically realistic reactive transport simulations is now widely available: the computing power of yesterday's mainframe supercomputers is available on personal computers.

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Our profession is called on to provide quantitative analyses of contaminant migration in order to estimate (1) risks to human health and the general ecology, (2) the potential success (and the consequences of failure) of expensive cleanup actions, (3) the risk associated with residual contamination after cleanup, and (4) the optimum siting of monitoring and sentinel wells. In each case, the rewards of correct prediction and the costs of inaccuracy, both direct and in terms of damage to the profession, are considerable.

The results of our study (page 435) suggest that the easy fiction of single-parameter sorption coefficients has in fact become an inconvenient and perilous burden. It is no longer logical for us to carry this burden when advances in the application of surface complexation theory, the advent of powerful reactive transport codes, and the widespread availability of fast personal computers make available predictive models of contaminant transport in the subsurface more accurate and useful than previously considered possible.

References

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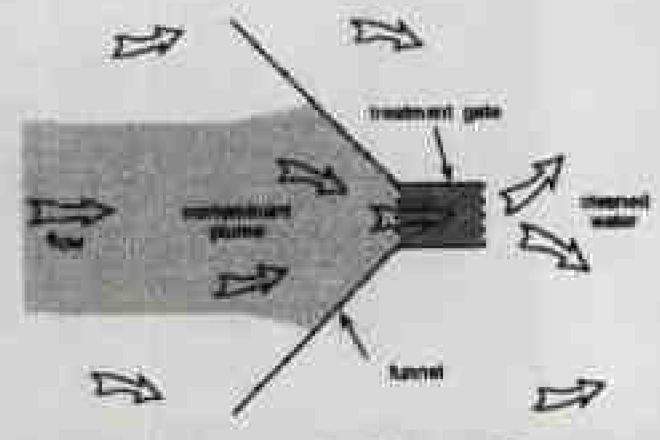

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