

Factors influencing the transport and fate of contaminants in the subsurface *

M.L. Brusseau

Soil and Water Science Department, University of Arizona, 429 Shantz, Tucson, AZ 85721 (USA)

Abstract

The present status of research on the transport and fate of contaminants in the subsurface will be briefly reviewed. The discussion will center on solution-phase processes; other equally important processes (e.g., transformation reactions, vapor-phase processes, immiscible liquid-phase processes) are discussed in other papers presented in this issue.

Introduction

Hazardous waste sites, pesticide use, and the potential impact of human activities on drinking water quality have become prominent issues for the public. This concern has driven increased interest in and funding for research on the transport and fate of contaminants in the subsurface. As a result, many advances in this area have been made recently. However, there is still much left to discover and understand. This paper will briefly review the present status of the field, with a focus on the factors and processes that influence the transport and fate of contaminants in the subsurface. The discussion will center on solution-phase processes; other equally important processes (e.g., transformation reactions, vapor-phase processes, immiscible liquid-phase processes) are discussed elsewhere in this issue.

The outdated paradigm for solute transport

The transport of solute in porous media has been under investigation for quite some time. The paradigm that had been developed for solute transport and used as a basis for the development of mathematical models describing

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Correspondence to: M.L. Brusseau, Soil and Water Science Department, University of Arizona, 429 Shantz, Tucson, AZ 85721 (USA). Fax: (602) 621-1647.

solute transport included several fundamental assumptions. Among these assumptions were those of porous-media homogeneity and linear, instantaneous sorption. Research over the past 10 to 15 years has shown that these assumptions may often be invalid. Solute transport that does not conform to that predicted by the paradigm-based model can be considered as non-ideal. There are many factors that may cause non-ideal transport; these are presented in the next section.

Non-ideal solute transport

The various factors that may cause transport to be non-ideal are enumerated below; detailed discussions of these factors are provided in several recent reviews [1-3]. The focus is on solution and solid phases, given that other factors will be covered elsewhere.

Non-linear sorption

The distribution of the solute between sorbed and solution phases is characterized by the sorption isotherm. Several models have been proposed to describe isotherms, the appropriate one being a function of the particular application. Many solute transport models have been developed with the assumption that the sorption isotherm is linear. For many solutes this assumption will be invalid under certain conditions (cf. [4]).

Irreversible sorption

The sorption process is most often assumed to be reversible. However, this may not be the case under certain conditions. A review of many supposed instances of sorption hysteresis for organic compounds revealed that such observations may often be an artifact related to experimental conditions [3]. True irreversibility may, however, be exhibited for some systems.

Non-equilibrium sorption

The distribution of solute between the solution and solid phases has most often been assumed to be instantaneous in the development of transport models. A growing body of research has shown, however, that sorption of many solutes (especially organic compounds) is not instantaneous. The mechanism responsible for non-equilibrium is dependent on the system; for low-polarity organic compounds, the mechanism appears to involve an intrasorbent diffusion process (cf. [3,5-8]).

Sorption-capacity variability

Sorption capacity is all most always assumed to be spatially homogeneous when developing models, although it may often be spatially (and temporally) variable. There has been relatively little work done on characterizing the var-

iability of sorption capacity at the field scale, but what has been done demonstrates the existence of variability (cf. [9,10]).

Facilitated transport

There are several factors or processes that can reduce the affinity of a solute for the solid phase, thereby reducing retardation. This reduction in retardation leads to enhanced or facilitated transport. Organic solvents and colloidal matter are two components that can greatly enhance transport under certain conditions.

Hydraulic-conductivity variability

Hydraulic-conductivity homogeneity was one of the first assumptions that was relaxed in the development of solute transport models. There are several ways that have been proposed for representing hydraulic-conductivity heterogeneity, including stochastic, stratification, and two-domain approaches. Each approach has its advantages and disadvantages, and each has been proven successful for specific applications.

Other factors

Other factors, such as vapor-phase processes, immiscible liquid-phase processes, and transformation reactions, can cause transport to deviate from that expected based on models that do not account for the effects of these processes.

Field observations of non-ideal transport

Several field experiments have been performed to evaluate the transport of sorbing solutes under natural and induced hydraulic gradients. These experiments have yielded results that are inconsistent with the simplifying assumptions of porous-media homogeneity and instantaneous sorption that were described above. Personnel from the U.S. Department of Agriculture and the R.S. Kerr research center were involved in one of the first attempts to evaluate the field-scale transport of sorbing organic solutes in an aquifer. In two separate experiments, solutions containing DDT [11] and three herbicides (picloram, atrazine, trifluralin) [12] were first injected into and then extracted from a portion of the Ogallala aquifer. Non-ideal transport of the herbicides was manifest in a delayed approach to relative concentrations of one (i.e., "tailing"), whereas non-ideal transport of DDT was indicated by incomplete removal.

An experiment conducted to evaluate the behavior of organic solutes during groundwater recharge was reported by Roberts et al. [13]. Breakthrough curves for the tracers and the organic solutes, obtained at a monitoring well, exhibited tailing.

The dispersive and adsorptive properties of a sandy aquifer were evaluated by Pickens et al. [14], who performed a radial injection experiment with ^{131}I

as the non-reactive tracer and ^{85}Sr as the reactive tracer. Non-ideal transport of ^{85}Sr , which was manifest as tailed breakthrough curves, was attributed to rate-limited sorption.

The sorptive behavior of several organic solutes under induced-gradient conditions was evaluated in an experiment that was performed to assess the efficacy of flushing as a means to remediate a contaminated aquifer [15]. Contaminant profiles obtained from the experiment, which was performed using an injection-extraction well couplet, exhibited extended tails. This non-ideal behavior was attributed to rate-limited desorption.

An extensive field experiment designed to investigate solute transport in a sand aquifer under natural-gradient conditions was undertaken by personnel from Stanford University and the University of Waterloo [16-20]. Significant non-ideal transport was observed for the organic solutes, wherein the plumes decelerated with time. This temporal increase in retardation factors was postulated to result from rate-limited sorption, involving diffusion within microporous particles [16,19].

A natural-gradient tracer experiment reported by Garabedien et al. [21] was conducted to examine the transport of bromide and lithium in a sand and gravel aquifer. The enhanced longitudinal dispersion observed for lithium was attributed to physical and geochemical heterogeneity, specifically a negative correlation of hydraulic conductivity and sorption capacity. However, the potential of rate-limited sorption contributing to the non-ideal transport was not ruled out.

The results of a series of induced-gradient experiments performed as part of an effort to evaluate *in situ* bioremediation were recently reported [22]. Breakthrough curves for the organic solutes exhibited tailing, which was suggested to result from rate-limited sorption or hydraulic-conductivity heterogeneity. It is noteworthy that breakthrough curves for the non-reactive tracer also exhibited tailing.

The results of the experiments discussed above demonstrate that the transport of sorbing solutes at the field scale is characteristically non-ideal. The non-ideal behavior has been attributed to rate-limited sorption, hydraulic-conductivity heterogeneity, or sorption-capacity heterogeneity. In addition to these controlled experiments, there have been many anecdotal observations of non-ideal transport associated with aquifer restoration. For example, a typical observation for "pump-and-treat" systems is that the time and volume of water required to remove the contaminants is much greater than had been estimated in the planning stage. This type of phenomenon has been attributed to the effect of various non-ideality factors on transport.

Multi-factor non-ideality

We have seen evidence of non-ideal transport and have reviewed several factors that may cause such transport. It is possible, and often likely, that more

than a single factor may contribute to the observed non-ideal behavior, especially at the field scale. In response to this possibility, transport models are being developed that account for more than one source of non-ideality (i.e., multi-factor non-ideality models). Models that account for hydraulic-conductivity heterogeneity and sorption-capacity heterogeneity have been presented by Smith and Schwartz [23], Van der Zee and Van Riemsdijk [24], Garabedien et al. [21], Cvetkovic and Shapiro [25], and Kabala and Sposito [26]. Models that account for hydraulic-conductivity heterogeneity and rate-limited sorption have been presented by Bahr [27], Valocchi et al. [28], and Cvetkovic and Shapiro [25]. Models that account for hydraulic-conductivity heterogeneity, sorption-capacity heterogeneity, and rate-limited sorption have been presented by Bahr [27], Brusseau et al. [5,29], Sudicky et al. [30], and Des-touni and Cvetkovic [31].

These multi-factor non-ideality models will hopefully provide a more accurate description of solute transport under non-ideal conditions. The performance of these models, however, has yet to be evaluated, to any great extent, by using them to attempt to predict the results of field-scale experiments involving transport of sorbing solute. Until this has been done, the accuracy of these models will remain untested.

One model that has been evaluated for the ability to simulate field data is the one-dimensional model presented by Brusseau et al. [5]. This model accounts for the effects of porous media heterogeneity, which is represented by the two-domain approach, and for rate-limited sorption, which is represented as being a combination of instantaneous and rate-limited interactions. Brusseau [32] evaluated the performance of the model by attempting to predict data obtained from four field experiments performed under natural or induced gradients. The predictions produced with the multi-factor non-ideality model provided very good descriptions of breakthrough curves obtained from the experiments. The results of the analyses indicated that, while several factors appeared to have contributed in varying degrees to the non-ideal transport observed during the experiments, the impact of hydraulic-conductivity heterogeneity was important for all cases. For example, the effect of rate-limited sorption, which was postulated by Roberts et al. [19] to have caused the non-ideal transport for the Borden experiment, appears to have been a minor contributor in comparison to the effect of heterogeneity for the Borden experiment.

Considering that all parameter values were obtained independently for the predictions, it appears that the model may be used to simulate non-ideal transport of sorbing solutes at the field scale. Although the approach used to represent heterogeneity is simple in comparison to other approaches (e.g., stochastic), this model should be useful for situations where the extensive field data required to use more complex models are not available. Application of this one-dimensional model is obviously limited to systems that can be represented as one dimensional, such as breakthrough curves measured at monitoring wells.

Summary

Many of the assumptions inherent to the paradigm that has been the basis for the development and use of many solute transport models have been shown to be invalid. A new generation of models are being developed to address factors such as heterogeneity of porous media properties and non-equilibrium sorption. A complete description of solute transport will require models that account for multiple sources of "non-ideality".

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