Journal of Contaminant Hydrology 153 (2013) 51–68

Contents lists available at ScienceDirect

Journal of Contaminant Hydrology

journal homepage: www.elsevier.com/locate/jconhyd

On the importance of diffusion and compound-specific mixing for groundwater transport: An investigation from pore to field scale

Massimo Rolle [a,b,*], Gabriele Chiogna [b,c], David L. Hochstetler [a], Peter K. Kitanidis [a]

[a] Department of Civil and Environmental Engineering, Stanford University, 473 Via Ortega, 94305 Stanford, CA, USA
[b] Center for Applied Geosciences, University of Tübingen, Hoelderlinstrasse 12, D-72074 Tübingen, Germany
[c] Department of Civil and Environmental Engineering, University of Trento, Via Mesiano 77, 38123 Trento, Italy

ARTICLE INFO

Article history:
Received 14 March 2013
Received in revised form 12 July 2013
Accepted 23 July 2013
Available online 8 August 2013

Keywords:
Diffusion
Mixing
Groundwater transport
Dilution index
Numerical modeling

ABSTRACT

Mixing processes significantly affect and limit contaminant transport and transformation rates in the subsurface. The correct quantification of mixing in groundwater systems must account for diffusion, local-scale dispersion and the flow variability in heterogeneous flow fields (e.g., flow-focusing in high-conductivity and de-focusing in low-conductivity zones). Recent results of multitracer laboratory experiments revealed the significant effect of compound-specific diffusive properties on the physical displacement of dissolved species across a representative range of groundwater flow velocities. The goal of this study is to investigate the role of diffusion and compound-specific mixing for solute transport across a range of scales including: (i) pore-scale (~10^{-2} m), (ii) laboratory bench-scale (~10^{0} m) and (iii) field-scale (~10^{2} m). We investigate both conservative and mixing-controlled reactive transport using pore-scale modeling, flow-through laboratory experiments and simulations, and field-scale numerical modeling of complex heterogeneous hydraulic conductivity fields with statistical properties similar to the ones reported for the extensively investigated Borden aquifer (Ontario, Canada) and Columbus aquifer (Mississippi, USA, also known as MADE site). We consider different steady-state and transient transport scenarios. For the conservative cases we use as a metric of mixing the exponential of the Shannon entropy to quantify solute dilution either in a given volume (dilution index) or in a given solute flux (flux-related dilution index). The decrease in the mass and the mass-flux of the contaminant plumes is evaluated to quantify reactive mixing. The results show that diffusive processes, occurring at the small-scale of a pore channel, strongly affect conservative and reactive solute transport at larger macroscopic scales. The outcomes of our study illustrate the need to consider and properly account for compound-specific diffusion and mixing limitations in order to accurately describe and predict conservative and reactive transport in porous media.

1. Introduction

The fate of pollutants in the subsurface is controlled by the complex interplay between physical and biogeochemical processes. For organic compounds typically present in contaminated groundwater, the most important biochemical processes are microbially-mediated redox reactions. Microorganisms can degrade oxidizable organic pollutants through a number of redox processes involving different terminal electron acceptors (e.g., Chapelle et al., 1995; Christensen et al., 2001; Rolle et al., 2008). Favorable conditions for some important degradation reactions occur at the fringe of contaminant plumes where soluble electron donors and acceptors come into contact

---

[*] Corresponding author at: Department of Civil and Environmental Engineering, Stanford University, 473 Via Ortega, 94305 Stanford, CA, USA. Tel.: +1 6507211118.
E-mail address: mrolle@stanford.edu (M. Rolle).

0169-7722/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jconhyd.2013.07.006

through mixing between the contaminant and the surrounding ambient water. At the plume fringe steep concentration gradients of dissolved reactants develop and have been observed at high-resolution monitored field sites (e.g., Amos et al., 2011; Davis et al., 1999; Prommer et al., 2009; Thornton et al., 2001; Tuxen et al., 2006). Insufficient mixing between dissolved reactants is increasingly recognized to control the overall contaminant transformation rates (e.g., Chiogna and Bellin, 2013; Cirpka et al., 2012; Kitanidis, 1994; Sanchez-Vila et al., 2007), and thus, the potential for natural attenuation and the performance of in situ engineered remediation. Therefore, correct characterization and quantification of mixing is of utmost importance to accurately describe reactive solute transport in groundwater. However, the heterogeneity of subsurface formations, the uncertainty and variability of initial and boundary conditions, the lack of resolution in groundwater monitoring and the scale of subsurface observations make adequate characterization quite challenging. A number of approaches and techniques have been proposed to describe conservative and reactive mixing at different scales (Dentz et al., 2011). Recently, considerable advances have been made in the study of mixing in subsurface environments thanks to the improvement of high-resolution site characterization and monitoring techniques (e.g., Anneser et al., 2008), the establishment of laboratory experiments in flow-through setups with the aim of studying coupled physical and (bio)degradation processes (e.g., Bauer et al., 2009a), and the development of pore-scale investigation of solute transport in porous media. The latter comprises microfluidic experiments (e.g., Willingham et al., 2008; Zhang et al., 2010) as well as pore-scale simulations. Detailed studies at the pore-scale have contributed to improved understanding of the fundamental interaction between physical and reactive processes in a number of relevant solute transport problems involving homogeneous reactions between dissolved species (e.g., Davison et al., 2012; Hochstetler and Kitanidis, 2013; Tartakovsky et al., 2009) and heterogeneous reactive systems with mineral precipitation and dissolution (e.g., Molins et al., 2012; Tartakovsky et al., 2008; Yoon et al., 2012). Often the results of such studies shed light on the limitations of continuum-scale descriptions traditionally adopted to describe solute transport in porous media (e.g., Battiato et al., 2009; Rolle et al., 2012; Tartakovsky et al., 2009). However, continuum-scale formulations are required to describe groundwater transport in practical applications; thus, it is important to develop formulations based on relationships among up-scaled parameters that are able to properly represent the effects of processes occurring at smaller scales.

A common finding of recent studies is the recognition of the crucial role of diffusive and local-scale dispersive processes. These processes are typically slow, thus leading to incomplete mixing in porous media and to the limitation of the overall degradation of contaminants released in groundwater systems. In particular, diffusion represents the only true mixing process in the subsurface since it affects both the entropy and the peak concentration of a solute plume (Kitanidis, 1994). Its contribution to local-scale dispersion and to the enhancement of such dispersion through flow variability in heterogeneous formations is critical for a correct characterization of mixing (Chiogna et al., 2011a). The importance of diffusion is also increasingly acknowledged in studies on persistence of contaminant plumes due to the back diffusion from silt and clay aquitards (e.g., Liu and Ball, 2002; Mackay and Cherry, 1989; Parker et al., 2008; Rasa et al., 2011).

Despite its primary importance, only a few modeling studies have emphasized the role of diffusion in contaminant transport in alluvial groundwater systems (e.g., Fiori et al., 2011; LaBolle and Fogg, 2001; LaBolle et al., 2008). Often the contribution of pore diffusion (i.e., the amount of diffusion that can occur in the pore space) is deemed irrelevant compared to mechanical dispersion. The latter quantifies the effects of velocity variability in the pore channels and is traditionally expressed with formulations independent of the diffusive properties of the transported solutes (e.g., Scheidegger, 1961). Recent laboratory investigation focusing on transverse hydrodynamic dispersion has shown that, at typical groundwater flow velocities, the contribution of pore diffusion is comparable to that of mechanical dispersion and cannot be neglected (e.g., Bauer et al., 2009b; Rolle et al., 2009). Moreover, multitracer experiments (Chiogna et al., 2010; Rolle et al., 2010) have demonstrated a compound-specific physical displacement in the transverse direction even at high flow velocity, which can only be described with a non-linear parameterization of mechanical dispersion retaining an explicit dependence on the aqueous diffusion coefficient of the transported species. Nevertheless, when molecular diffusion is explicitly considered in solute transport simulations, a constant diffusivity value (e.g., $\mathrm{D_{aq}} = 1 \times 10^{-9}\ \mathrm{m^2/s}$) is often assumed for every aqueous species. This is an approximation that, in our view, should be improved given that aqueous diffusion coefficients vary over more than one order of magnitude. Table 1 reports the aqueous diffusion coefficients of a number of dissolved species relevant to groundwater quality problems. The list of compounds presented in Table 1 is by no means exhaustive but it shows the range of variation of aqueous diffusivities of representative species in groundwater solute transport problems, with large organic molecules characterized by smaller diffusivities and small ions and dissolved gas molecules characterized by considerably higher values of D_{aq}.

The major goal of this study is to quantify the effects of diffusion for conservative and mixing-controlled reactive transport in groundwater. We restrict our analysis to two-dimensional flow-through systems and to non-sorbing dissolved compounds. We examine transient and steady-state conservative and reactive transport problems in homogeneous and complex heterogeneous porous media at different scales: (i) pore-scale (~10^{-2} m), (ii) laboratory bench-scale (~10^{0} m) and field-scale (~10^{2} m). We use numerical simulations and entropy-based metrics of mixing to quantitatively illustrate the key role of compound-specific mixing for conservative and reactive transport. Our analysis demonstrates the relevance of diffusion for solute transport at all scales. At the pore scale we show that compound-specific diffusive effects are very important not only at low but also at high flow velocity, in strongly advection-dominated regimes. Experimental observations and modeling confirm that compound-specific diffusion is significant also at the intermediate laboratory scale. Finally, numerical simulations in heterogeneous domains, with statistics consistent with those from extensively-investigated research sites, show a clear influence of compound-specific mixing for conservative and reactive transport also at the field scale.