Journal of Contaminant Hydrology 158 (2014) 78–92

Contents lists available at ScienceDirect

Journal of Contaminant Hydrology

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

Laboratory-scale in situ bioremediation in heterogeneous porous media: Biokinetics-limited scenario

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ARTICLE INFO

Article history:
Received 3 June 2013
Received in revised form 6 January 2014
Accepted 7 January 2014
Available online 16 January 2014

Keywords:
In situ bioremediation
Biokinetics
Dispersion

ABSTRACT

Subsurface heterogeneities influence interfacial mass-transfer processes and affect the application of in situ bioremediation by impacting the availability of substrates to the microorganisms. However, for difficult-to-degrade compounds, and/or cases with inhibitory biodegradation conditions, slow biokinetics may also limit the overall bioremediation rate, or be as limiting as mass-transfer processes. In this work, a quantitative framework based on a set of dimensionless coefficients was used to capture the effects of the competing interfacial and biokinetic processes and define the overall rate-limiting process. An integrated numerical modeling and experimental approach was used to evaluate application of the quantitative framework for a scenario in which slow-biokinetics limited the overall bioremediation rate of a polycyclic aromatic hydrocarbon (naphthalene). Numerical modeling was conducted to simulate the groundwater flow and naphthalene transport and verify the system parameters, which were used in the quantitative framework application. The experiments examined the movement and biodegradation of naphthalene in a saturated, heterogeneous intermediate-scale flow cell with two layers of contrasting hydraulic conductivities. These experiments were conducted in two phases: Phase I, simulating an inhibited slow biodegradation; and Phase II, simulating an engineered bioremediation, with system perturbations selected to enhance the slow biodegradation rate. In Phase II, two engineered perturbations to the system were selected to examine their ability to enhance in situ biodegradation. In the first perturbation, nitrogen and phosphorus in excess of the required stoichiometric amounts were spiked into the influent solution to mimic a common remedial action taken in the field. The results showed that this perturbation had a moderate positive impact, consistent with slow biokinetics being the overall rate-limiting process. However, the second perturbation, which was to alleviate inhibition and increase the biodegradation rate, enhanced the overall biotransformation rate to a greater degree.

1. Introduction

Bioremediation offers great potential for cleaning up environmental contaminants because it can treat them in situ with little disturbance to the contaminated matrix, and the contaminants can often be completely mineralized to inorganic materials (Head, 1998). Furthermore, bioremediation is relatively inexpensive compared to other remedial technologies such as incineration, soil washing, and pump and treat (Hughes et al., 1997; Singleton, 1994). However, the success of in situ bioremediation is made technologically challenging by the inherently complex and heterogeneous nature of the subsurface environment (National Research Council, 1993). These physical and chemical heterogeneities of the

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http://dx.doi.org/10.1016/j.jconhyd.2014.01.001

subsurface occur at several scales and affect in situ bioremediation by controlling the availability of nutrients and substrates that drive the microbiological processes. This is important because many field and laboratory studies suggest that a large fraction of pollutants present in environmental systems are unavailable for microbial degradation (Alexander, 1994; Beck et al., 1995). Therefore, not understanding or accounting for the interactions between these scale-dependent physical/chemical heterogeneities and microbiological processes may reduce the effectiveness of field-scale in situ bioremediation (Rittmann et al., 1994). Indeed, reviews of field methods available for bioremediation have concluded that consideration of scale-dependent phenomena, such as mass transport and interfacial transfer mechanisms, is a prerequisite to success in the field (Sturman et al., 1995).

The physical and chemical heterogeneities in the subsurface create interfaces where strong contrasts in physical and chemical properties exist over short distances (e.g., aqueous–solid interfaces, aqueous–non-aqueous phase liquid (NAPL) interfaces, and aqueous–aqueous interfaces in solution chemistry). The strong contrasts at these interfaces control moisture flux, nutrient fluxes, and redox conditions, which in turn drive the distribution and activity of microbes in the subsurface (Brockman and Murray, 1997; McMahon and Chapelle, 1991). As a result, these processes can impact in situ bioremediation because they influence the rates of substrate flux, mixing and the microbial ecology. Therefore, it is very important to identify the rate limiting process in the design and operation of in situ bioremediation systems so that these systems can be appropriately engineered to enhance the overall rate of contaminant removal.

In response to this need, Johnson et al. (2013) and Song and Seagren (2008) presented a quantitative framework, based on a set of dimensionless numbers, to capture the effects of the competing interfacial and biokinetic processes and define the overall rate-limiting process for a given application of in situ bioremediation. As noted by Bosma et al. (1997), although slow biokinetics are often assumed to limit in situ biodegradation, physical/chemical processes are actually rate-limiting in many cases. Consistent with this conclusion, based on the analysis of Johnson et al. (2013) and others (e.g., Maier and Grathwohl, 2006), it appears that transverse dispersion is the rate-limiting process in many in situ bioremediation scenarios with readily biodegradable contaminants. For example, Song and Seagren (2008) demonstrated this for the case of naphthalene in an intermediate-scale flow cell (ISFC) system that contained two porous media layers of contrasting hydraulic conductivities. Similarly, sorption and desorption may also limit in situ biodegradation, especially for contaminants with strong sorptive interactions with subsurface soils, or under inhibitory conditions (Brusseau et al., 1991; Bouwer et al., 1994; Guerin and Boyd, 1992; Guerin and Boyd, 1997; Johnson et al., 2013; Mulder et al., 2000; Rijnaarts et al., 1990; Volkering et al., 1993). Finally, NAPL contaminant sources can limit contaminant bioavailability as a result of interphase mass-transfer limitations and partitioning into a NAPL, which can reduce the aqueous concentration of organic compounds and biodegradation rates (Fu et al., 1996; Ghoshal et al., 1996; Labare and Alexander, 1995; Yang et al., 1995).

Nevertheless, despite the many situations in which mass transfer processes are the overall rate-limiting process, there are situations in which the in situ biokinetics is the overall rate-limiting process. In cases where this is true, knowledge of biodegradation kinetics is essential for evaluation of contaminant fate in the subsurface and can provide useful insight into the favorable range of important environmental parameters for improvement of the microbiological activities, and enhancement of the in situ contaminant biodegradation rate (Tabak and Govind, 1997). In fact, improvement of the biodegradation rate via biostimulation (e.g., addition of electron donors, electron acceptors, and nutrients) and bioaugmentation are often practiced in the field. As noted above, these perturbations will not be successful if biokinetics are not limiting, but many field tests have been conducted to evaluate the effects of biostimulation and bioaugmentation on the overall rate of in situ bioremediation and have successfully demonstrated enhanced bioremediation (Eguchi et al., 2001; Major et al., 2002; Salanitro et al., 2000).

Key situations in which the in situ biokinetics are likely to be the overall rate-limiting process include when the key microbial populations are inhibited and/or substrate limited, as in this work, or present in insufficient numbers. For example, electron acceptors (e.g., oxygen, nitrate, and sulfate) are often introduced into groundwater to enhance degradation of electron-donor contaminants, such as petroleum hydrocarbons (Anderson and Lovley, 2000; Hunkeler et al., 1999; Knapp and Faison, 1997; Salanitro et al., 2000), and electron donors are commonly added to create reduced conditions and stimulate reductive dechlorination of chlorinated solvents, either via direct injection of hydrogen into an aquifer (Aziz et al., 2003), or through indirect addition of hydrogen in the form of a fermentable carbon source such as lactate, fumarate, propionate, methanol, molasses, vegetable oils and cheese whey (e.g., Aulenta et al., 2005; Dyer et al., 2003; Ellis et al., 2000; Hageman et al., 2004; Hoelen et al., 2006; Romer et al., 2003). Similarly, biostimulation via nutrient addition has also been illustrated at the field-scale (Gallego et al., 2001; Menendez-Vega et al., 2007). In addition, bioaugmentation has been strategically applied in difficult-to-degrade chlorinated solvent plumes through the addition of cultures enriched with *Dehalococcoides* spp., the only bacterial group known to perform complete reductive dechlorination of chlorinated ethenes (Adamson et al., 2003; Hood et al., 2008; Krumins et al., 2009; Major et al., 2002; Scheutz et al., 2008; Tas et al., 2009).

The goal of this study was to perform an integrated modeling and experimental analysis of the impact of slow biokinetics on the transport and biodegradation of dissolved contaminants in an intermediate-scale flow cell (ISFC) system that contained two porous media layers of contrasting hydraulic conductivity. The fundamental hypothesis of this work is that the previously developed quantitative framework (Johnson et al., 2013; Song and Seagren, 2008) can be used to identify the overall rate-limiting process for bioremediation and predict what engineering action will effectively enhance the in situ biodegradation rate. This quantitative framework was evaluated by quantifying the key physicochemical and microbiological processes, and theoretically and experimentally investigating their interactions.

2. Theory

The saturated groundwater flow velocities, v_i, were calculated using Darcy's law and the hydraulic-head values obtained