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Evaluating the reliability of equilibrium dissolution assumption from residual gasoline in contact with water saturated sands

Greg Lekmine [a,*], Kaveh Sookhak Lari [a,c], Colin D. Johnston [a,b], Trevor P. Bastow [a], John L. Rayner [a], Greg B. Davis [a,b]

[a] *CSIRO Land and Water, Private Bag No. 5, Wembley, WA 6913, Australia*
[b] *School of Earth and Environment, University of Western Australia, Nedlands, WA 6009, Australia*
[c] *School of Engineering, Edith Cowan University, 270 Joondalup Drive, Joondalup, WA 6027, Australia*

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ABSTRACT

Understanding dissolution dynamics of hazardous compounds from complex gasoline mixtures is a key to long-term predictions of groundwater risks. The aim of this study was to investigate if the local equilibrium assumption for BTEX and TMBs (trimethylbenzenes) dissolution was valid under variable saturation in two dimensional flow conditions and evaluate the impact of local heterogeneities when equilibrium is verified at the scale of investigation. An initial residual gasoline saturation was established over the upper two-thirds of a water saturated sand pack. A constant horizontal pore velocity was maintained and water samples were recovered across 38 sampling ports over 141 days. Inside the residual NAPL zone, BTEX and TMBs dissolution curves were in agreement with the TMVOC model based on the local equilibrium assumption. Results compared to previous numerical studies suggest the presence of small scale dissolution fingering created perpendicular to the horizontal dissolution front, mainly triggered by heterogeneities in the medium structure and the local NAPL residual saturation. In the transition zone, TMVOC was able to represent a range of behaviours exhibited by the data, confirming equilibrium or near-equilibrium dissolution at the scale of investigation. The model locally showed discrepancies with the most soluble compounds, i.e. benzene and toluene, due to local heterogeneities exhibiting that at lower scale flow bypassing and channelling may have occurred. In these conditions mass transfer rates were still high enough to fall under the equilibrium assumption in TMVOC at the scale of investigation. Comparisons with other models involving upscaled mass transfer rates demonstrated that such approximations with TMVOC could lead to overestimate BTEX dissolution rates and underestimate the total remediation time.

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1. Introduction

Non-aqueous phase liquids (NAPL) such as petroleum hydrocarbon fuels present long-term risks of contamination in groundwater. After accidental release or leakage in natural environments, hydrocarbon contaminants infiltrate through soils to reach aquifers where LNAPL will typically volatilise and spread on the water table and release soluble components into groundwater via dissolution. Degradation of fuel components in groundwater environments is common (e.g., Patterson et al., 1993; Franzmann et al., 1999) but despite this plumes emanating from fuel releases can be extensive and prolonged (e.g., Davis et al., 1999; Sookhak Lari and Safavi, 2008) due to slow and persistent dissolution into groundwater.

Petroleum hydrocarbon dissolution is often described in terms of mass transfer at the NAPL/water interface assuming local equilibrium (Seagren et al., 1999; Sulaymon and Gzar, 2011) or rate limited mass transfer (Miller et al., 1990; Imhoff et al., 1994; Vasudevan et al., 2014). Both approaches to dissolution have been investigated in one dimensional column experiments for single components (Powers et al., 1992; Geller and Hunt, 1993) or synthetic multi-component mixtures (Borden and Kao, 1992; Garg and Rixey, 1999) from homogeneous NAPL pools or residual saturations (Lee and Chrysikopoulos, 2006). In porous media, rate-limited dissolution is a function of a mass transfer coefficient and the specific interfacial area between the water and the NAPL phase (Cho et al., 2005; Mobile et al., 2012). Due to difficulties inherent to accurate estimation of the interfacial area, lumped mass transfer coefficients have been defined through empirical mass transfer correlations to calibrate model predictions as a function of water pore velocities and NAPL saturations (Miller et al., 1990; Chrysikopoulos and Kim, 2000; Nambi and Powers, 2003). However, these

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[*] Corresponding author.
E-mail address: gregory.lekmine@csiro.au (G. Lekmine).

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unidirectional flow experiments are not fully representative of realistic field case situations in which channelling and flow bypassing may occur due to the morphology of sources as well as permeability and NAPL saturation heterogeneities which may have a non-negligible influence on mass transfer (Imhoff et al., 1996; Chen and Jawitz, 2009; Farthing et al., 2012; Kokkinaki et al., 2013). Oostrom et al. (2006) reported the most relevant two and three dimensional, intermediate scale experiments, focusing on aqueous dissolution processes (Eberhardt and Grathwohl, 2002) and those carried out to enhance remediation procedures (Jawitz et al., 1998; Palomino and Grubb, 2004). Most of the experiments investigated the dissolution of single (Saba et al., 2001) and multi-component DNAPL pools (Dela Barre et al., 2002; Roy et al., 2004).

Overall, few multi-dimensional, multi-component studies have been undertaken for gasoline dissolution. Voudrias and Yeh (1994) conducted the first two dimensional LNAPL pool dissolution experiment with toluene overlying water saturated sands. Results demonstrated that the vertical concentration gradient in the water phase was sharp and total dissolution would take decades in such configuration. From a similar design performed in three dimensions with benzene, Sulaymon and Gzar (2011) confirmed that transverse dispersion increases rate-limited mass transfer of benzene compared to column experiments in which the flow was usually forced in one direction through NAPL resident in the column. Other works with single components were also performed with residual entrapped LNAPL sources (Saba and Illangasekare, 2000) to quantify mass transfer rate correlations when horizontal fingering occurred for various lengths of entrapped zones of *p*-xylene. Two dimensional sand packs were also used to investigate dissolution kinetics due to the effects of permeability changes between an entrapped source zone and the surrounding material, geometry and perimeter of the source, as well as the grain size and the initial residual saturation (Nambi and Powers, 2000). Eberhardt and Grathwohl (2002) developed long-term experiment where dissolution was monitored for a year in three dimensional layered sands to estimate the reliability of Raoult's law to predict equilibrium aqueous concentrations, the influence of the flow velocity as well as the impact of the transverse dispersion on BTEX (benzene, toluene, ethylbenzene, xylenes) and PAHs (polycyclic aromatic hydrocarbons) dissolution from a coal tar pool.

No two-dimensional experiments of preferential dissolution of compounds from gasoline or complex gasoline-type mixtures have been reported. Such studies would need to consider complexities associated with variable saturations and interfacial water-NAPL surface areas, and preferential dissolution of the most soluble compounds, such as BTEX and TMBs (Lekmine et al., 2014). This would favour the increase in molar fractions of other aromatics and aliphatics during dissolution, changing the interactions between compounds over the course of dissolution (Vasudevan et al., 2016; Sookhak Lari et al., 2016a, 2016b). Together these features, coupled to gasoline initial composition, saturation, and permeability heterogeneities have a key role in local equilibrium and potential rate-limited dissolution (Grant and Gerhard, 2007).

The objective of this work is to evaluate the role of local heterogeneities on the reliability of the apparent equilibrium dissolution assumption verified at the scale investigation during dissolution from a fresh residual gasoline fuel in a two dimensional flow field with variable NAPL saturation. We developed a two dimensional laboratory experiment to quantify the dissolution sequence of BTEX and trimethylbenzene isomers (TMBs) from a gasoline at residual saturation focusing on two particular areas of interest: 1) in a homogeneous residual gasoline (NAPL) saturated zone and 2) in the transition zone from residual gasoline to full water saturated conditions. A multi-phase and multi-component model was built with TMVOC to evaluate the underlying processes, equilibrium assumption and heterogeneities governing the dissolution dynamics, and to determine temporal changes in BTEX molar fractions within portions of the residual NAPL contaminated and transition zones.

2. Experimental procedure

2.1. Experimental design

Tests were carried out in a two dimensional stainless steel tank of dimension 71 cm long × 30 cm high × 5.5 cm thick (Fig. 1). Five injectors equally spaced at 5 cm intervals were set on both edges and connected to vertical water wells (2 × 30 × 5.5 cm) separated from the sand pack in the tank by stainless steel screen meshes. A transparent glass window was set on the front wall to visually monitor packing, fluid emplacement and dissolution procedures. On the opposite wall 38 water sampling ports were installed, made of 1 mm (ID) tubing penetrating horizontally 2.5 cm into the container and sealed with a stainless micro-frit to prevent the NAPL phase contaminating water samples. The external parts of the sampling ports were sealed with fittings and septas. The tank was incrementally filled with wet washed sand ($d_{50} = 370\ \mu m$) under a constant small water head of 4 cm to ensure full water saturation and to limit the vertical segregation of the particles. Once fully packed, the top of the tank was hermetically sealed with a stainless steel lid containing five more injectors used to remove entrapped air and to inject the NAPL phase. A ceramic pump was used to impose a constant horizontal flow velocity from the influent water well into the saturated sands. Sand porosity was $\phi = 34\%$ giving a total pore volume of the sand pack PV = 4 L. The water saturated hydraulic conductivity, $Kw_{sat} = 3.74$ m/day, was estimated by setting up a constant head Marriott bottle on the inlet and measuring water loss over time in the outlet.

2.2. Establishment of residual saturation

A Marriott bottle containing 4 L of red dyed gasoline (fresh unleaded 91) was connected to the middle injection port on top of the lid while effluent tubings were connected to ports 17 and 23 (Fig. 1) near the base of the tank. A constant head difference of 50 cm between the water effluent and the gasoline induced downward gasoline movement and pore saturation. The head difference was low enough to maintain a relatively sharp interface between NAPL and water and fully saturate the whole length of the sand pack. The downward vertical flow was stopped once the medium was fully NAPL (gasoline) saturated from top to Z = 19.5 cm. The mass of water collected in the effluent and the mass of gasoline remaining in the bottle were weighed. Then a Marriott bottle containing tap water was connected to sampling ports 17 and 23 and the pressure head was reversed to −50 cm to induce an upward flush of the gasoline which was collected back into the Marriott bottle at the top of the tank. Flushing was stopped when only water appeared in the top outlet. Both bottles were weighed returning a total mass of residual gasoline remaining in the sand tank of 405 g which represented 23% of the pore space ($Sn_0 = 0.23$). Vertical distribution of the initial residual saturation could not be quantified but was visually estimated and then calibrated from modelling (Fig. 2a). Sn_o was assumed to be homogeneously distributed from the top of the sand to a depth of Z = 16 cm; largely along the full length of the medium. The transition zone was from Z = 16 cm with a maximal residual saturation of NAPL to a depth of Z = 19.5 cm where full water saturation (i.e. zero NAPL) was assumed. Inside this depth interval, visual observations and model calibration showed horizontal variations of Sn_o along the medium. Hence model estimates initially divided the transition zone into 3 sections with Sn_o decreasing from 23 to 3% for $0 < X < 23$ cm and $46 < X < 71$ cm while in the central section, $23 < X < 46$ cm, Sn_o vertically decreased from 23 to 12% (see Fig. 2a).

2.3. Dissolution procedure and analysis

After residual saturation was established the sand pack was left with no flow for 24 h to ensure equilibrium between the aqueous and NAPL phases. Initial dissolved concentrations were expected to follow

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