



Research article

Scenario-based modelling of mass transfer mechanisms at a petroleum contaminated field site-numerical implications



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ABSTRACT

Knowledge about distribution of dissolved plumes and their influencing factors is essential for risk assessment and remediation of light non-aqueous phase liquid contamination in groundwater. Present study deals with the applicability of numerical model for simulating various hydro-geological scenarios considering non-uniform source distribution at a petroleum contaminated site in Chennai, India. The complexity associated with the hydrogeology of the site has limited scope for on-site quantification of petroleum pipeline spillage. The change in fuel composition under mass-transfer limited conditions was predicted by simultaneously comparing deviations in aqueous concentrations and activity coefficients (between Raoult's law and analytical approaches). The effects of source migration and weathering on the dissolution of major soluble fractions of petroleum fuel were also studied in relation to the apparent change in their activity coefficients and molar fractions. The model results were compared with field observations and found that field conditions were favourable for biodegradation, especially for the aromatic fraction (benzene and toluene (nearly 95% removal), polycyclic aromatic hydrocarbons (up to 65% removal) and xylene (nearly 45% removal). The results help to differentiate the effect of compositional non-ideality from rate-limited dissolution towards tailing of less soluble compounds (alkanes and trimethylbenzene). Although the effect of non-ideality decreased with distance from the source, the assumption of spatially varying residual saturation could effectively illustrate post-spill scenario by estimating the consequent decrease in mass transfer rate.

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1. Introduction

Restoration of contaminated aquifer to the regulatory standards is difficult even with the best engineering technologies due to the inherent heterogeneity of the subsurface system. This has led to the implementation of specific management strategies for the clean-up of contaminated sites (ARRA 2009; EPA, 2014). Effective design and implementation of *in-situ* remediation systems for petroleum spilled sites essentially require an understanding of the mechanisms controlling mass transfer and transport of non-aqueous phase compounds. Many petroleum contaminated sites contain mixtures of different aliphatic and aromatic compounds having considerable variations in their physico-chemical properties which

significantly influence their weathering rates (Bedient et al., 1999; Honghan et al., 2008; McCray et al., 2011; Thornton et al., 2013).

The prediction of non-aqueous phase liquid (NAPL) plume behaviour depends on the efficacy in quantifying the processes governing transformation and transport of dissolved compounds at a particular site (Honghan et al., 2008). At the field scale, NAPL migration is controlled by a complex combination of aquifer properties, NAPL properties, and other macro-scale features such as released volume of NAPL, local pumping effects and lithology (Mercer and Cohen, 1990; Divine et al., 2004). Therefore, site-specific mathematical models are necessary for investigating the dissolution and transport of NAPL compounds, which largely depend on the nature of the contaminant source and the initial fuel composition (Ostendorf and Kampbell, 1991; Zhu and Sykes, 2000; Vaezihir et al., 2012).

Previous studies have reported that dissolution mass transfer from residual sources at field sites can be at near equilibrium and the effective solubilities are generally estimated based on Raoult's

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law (Frind et al., 1999; Molson, 2000). However, estimation of mass transfer limiting conditions during dissolution of multi-component NAPL have shown that dissolution rate is highly influenced by the initial mass present in the non-aqueous phase at the source as well as the prevailing groundwater flow velocity (Frind et al., 1999; Johnson et al., 2003; Vasudevan et al., 2014a). Since the spilled gasoline fuel contains large number of aliphatic, aromatic and polycyclic aromatic hydrocarbon (PAH) compounds, the estimation of effective solubility as explained by Raoult's law seemed to be inadequate to represent the actual partitioning behaviour, which largely depends on the molecular interactions (Peters et al., 1999). Deviations from ideal behaviour (when activity coefficients deviating from unity) can be due to many reasons, including chemical heterogeneity of the components of the mixture and their respective molar volumes which are not incorporated into the common application of Raoult's law (McCray and Dugan, 2002; Lekmine et al., 2014). It is also important to determine the combined effect of sorption and biodegradation which can remove the dissolved organic compounds, thus improving the source clean-up strategies (Couto and Malta, 2008; Natarajan and Suresh Kumar, 2010). Hence understanding the spatial and temporal variation in the fuel composition (in terms of mole fractions and activity coefficients) during coupled mass transfer reactions plays a critical role in risk assessment related to their long term transport in the subsurface.

The quantification of available NAPL and its potential for migration can be generally described by volumetric NAPL saturations. It is well accepted that NAPL present at saturations exceeding residual saturation (S_r) are to be considered potentially mobile (ASTM, 1995; ITRC, 2009). Studies with soil core petro-physical testing at numerous sites have indicated that NAPL is rarely observed to exhibit significant mobility at saturations less than 20–25% (ITRC, 2009; Rousseau et al., 2012). The initial NAPL saturation at various fresh spilled sites may range from 10% to 20% based on the partitioning tracer studies (McCray and Brusseau, 1999; Divine et al., 2004; McCray et al., 2011). The estimation of field scale S_r , however, depends on the screening level of total petroleum hydrocarbon (TPH) concentration (mg/kg) (Rousseau et al., 2012). They observed that there is considerable deviation over 1 to 3 orders of magnitude when the NAPL saturations are calculated based on saturation concentration (effective aqueous solubility) as well as residual concentration (concentration in the NAPL phase). Thornton et al. (2013) used an empirical approach to address the transient nature of mass transfer at the source zone by exponentially correlating the molar fractions to the NAPL saturation. This assumption proved to be matching well for the soluble fractions even at long distance from the source zone. Most of the historical NAPL bodies are found to be stable/non-migrating due to a combination of factors including the dissipation of the pressure head at the time of release and water table fluctuations. This further immobilizes NAPL by progressively smearing the residual source over a greater vertical extent. Nonetheless, it can be ascertained that uniform distribution of residual NAPL over the entire domain seems to be superficial while estimating the extent of contamination as well as dissolution mass transfer.

The objective of the present work is to develop a mathematical model for predicting the transport of the dissolved plume along the predominant direction of groundwater flow at a fuel spill site by incorporating the spatial and temporal variation in spilled fuel composition. It is also aimed to check for possible deviation in the predicted dissolved concentrations due to non-ideal mass transfer considering the effects of dilution and weathering on the fuel composition. Using the model, it is aimed to study the effect of smearing and migration caused by water table fluctuations, by incorporating a spatially varying NAPL saturation scenario.

2. Materials and methods

2.1. Study area

The study location is a highly populated sub-urban area located in Tondiarpet in Chennai District of Tamil Nadu, India. Chennai district features flat topography with mild slope towards east which is part of the coastal plains of Tamil Nadu. The elevation at the location of the spill site is about 9 m above mean sea level (MSL). An underground pipeline for carrying petrol and diesel from the port to the distribution terminal of Bharat Petroleum Corporation Limited (BPCL) is running parallel to the Varadaraja Perumal Koil Street (VPK Street) at a depth of 1.5 m below ground level (BGL). There were news reports in 2013 about oil-contaminated bore wells around this site suspecting possible pipeline crack, which was later confirmed by the oil company based on their records. After the preliminary survey, the source was identified to be near the junction of Tiruvottiyur high road (T.H. Road) with VPK Street (Fig. 1).

2.2. Background data collection

2.2.1. Hydrogeology

The hydrogeology of the Tondiarpet area consists of various geological formations from ancient archean to recent alluvium, indicating the spatial and temporal heterogeneity in the degree of weathering. Groundwater is tapped mainly from the alluvium which extends to 27 m BGL where the bore wells with slotted pipes yield about 4–6 L per second (lps) (Ballukraya and Kalimuthu, 2010). Even though water table was found to be at a nominal depth of 10 m BGL, high rate of pumping by the local residents have substantially induced large fluctuations in the water table apart from seasonal effects such as storm water infiltration.

In order to understand the hydrogeology of the study area as well as to observe the changes in groundwater characteristics, 15 monitoring wells were installed around the spill site. The soil geology near the spill site is mainly characterized by alluvium deposits, predominantly sand with varying grain size up to a depth of 10 m BGL, beyond which silty clay observed up to a depth of 20 m BGL where it meets the hard rock. For all the monitoring wells in the study area, slotted pipes were used from a depth of 7 m to meet the uneven fluctuations in the water table. It was evident that NAPL smearing zone have already developed due to these fluctuations thereby extending residual fuel entrapment. The permeability of the aquifer material at a depth of 7 m ranges between 1.3 m/day to 2 m/day (Ballukraya and Kalimuthu, 2010). Based on the record of seasonal fluctuations in water table data between two monitoring wells which are at a distance of 855 m, the estimated hydraulic gradient was found to be varying from 0.001 to 0.003 over the year.

2.2.2. Features of spilled fuel

Presence of petroleum products in the subsurface was verified by the measurement of volatile organic carbon (VOC) content using a gas/VOC monitor (AreaRAE, Pune) for the soil samples collected at different depths. The analysis of soil samples collected near the water table showed high volatile solids (VS) concentrations, indicating the presence of trapped fuel in the capillary zone. The maximum value for VS observed near the spill source was 20 g/kg at a depth of 5.1 m for the monitoring well B. The ground water samples as well as fuel samples were collected from the exploratory bore wells using a disposable bailer. The analysis of aqueous samples from the monitoring wells indicated that concentrations of benzene, toluene, ethylbenzene and xylene were significantly high in all the samples along with traces of alkanes and naphthalene (Table 1). Nonetheless, as depicted in Fig. 1, the contamination has

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