

Mathematical modelling on transport of petroleum hydrocarbons in saturated fractured rocks

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Abstract. The present paper addresses critical issues that describe the dissolution mass transfer of petroleum hydrocarbons in a saturated subsurface system. The field procedure associated with the estimation of Light Non-Aqueous Phase Liquid (LNAPL) thickness in site monitor wells is revisited. A brief theory has been included on the composition and transport of petroleum hydrocarbons following an onshore oil spill in order to demonstrate the level of complexity associated with the LNAPL dissolution mass transfer even in a classical porous medium. However, such studies in saturated fractured rocks are highly complex and limited, and hence, deserve a special attention as the fate and transport of the petroleum hydrocarbons are not uncommon in saturated fractured rocks. In this context, an improved mathematical model has been proposed that will better describe the dissolution kinetics of petroleum hydrocarbons in saturated fractured rocks at the scale of a single fracture using dual-porosity concept. The lumped mass transfer coefficient in a classical porous medium proposed depends on mean grain size, while the same parameter has been replaced by an equivalent average thickness of fracture aperture that better describes the LNAPL dissolution rate in a coupled fracture-matrix system. A set of nonlinear coupled partial differential equations is deduced for a coupled fracture-matrix system in analogy with the differential equations of a classical porous medium. The proposed mathematical model may work well for the fracture aperture thicknesses varying between 100 and 500 microns with a relatively low Reynolds Number and initial NAPL saturation.

Keywords. Dissolution; petroleum hydrocarbon; LNAPL; fractured rock; mathematical model.

1. Introduction

Groundwater being the world's most extracted raw material, with withdrawal rates nearing 1000 km³ per annum (Zekster & Everett 2004; Shah 2009), environmental flows and ecosystem health are more dependent on groundwater than previously thought. On a global front, groundwater

resources correspond to one quarter of the total water withdrawals (Giordano 2009), and half of the total groundwater resources is used for potable water supply (United Nations 2003). Thus, the usage of groundwater keeps increasing as it is a common resource available to anyone with limited investment towards drilling and powering a well (Moench 2004). As per the statistics by Moench (2004) and Shah (2009), the Indian subcontinent has nearly 25 million wells, followed by United States (14 million wells) and China (nearly 4 million wells). These statistics clearly indicate that the groundwater resources are dwindling down at a much faster rate than anticipated, and the protection of the available groundwater resources should be one of the primary tasks of any developing country. Petroleum hydrocarbons being one of the most prevalent groundwater contaminants pollute the saturated subsurface system at well sites, service stations, refineries and farm sites, and subsequently cause serious environmental problems due to their widespread use. With reference to the protection of groundwater quality, the concept of epidemiological studies is becoming inevitable, which essentially evaluate the potential for health effects from exposures to petroleum hydrocarbons present in groundwater. The mobility and spreading of these petroleum hydrocarbons result from the historical presence, and its subsequent, fate and transport in a complex saturated porous medium. An estimation on the concentration of these contaminants as a function of space and time is very crucial in protecting the water-supply wells as well as water-distribution systems, and subsequently requires a sound understanding on the dissolution mass transfer of petroleum hydrocarbons in a saturated subsurface porous medium. In general, the sub-surface environment includes nearly homogeneous unconsolidated deposits such as gravel, sand, silt and clay; and highly heterogeneous consolidated materials such as fractured rock. However, the presence of silt and clay may impart significant heterogeneity even in unconsolidated deposits as they offer high resistance to flow of fluids (associated with the reduction of intrinsic permeability due to the smaller mean pore size) as well as to the transport of contaminants (associated with the enhancement of retardation due to the increased sorption with high specific surface area). The heterogeneity associated with the fractured rock formation is well-known and it results from the presence of high permeable fracture conduits embedded in between the low permeable solid rock-matrix. In addition, the site-specific parameters such as fracture-density, fracture-length, fracture-aperture thickness, fracture-spacing and dip dictates the extent and degree of local-scale heterogeneity, and subsequently implies that the distribution of contaminants in the sub-surface will be highly non-uniform. Such geological complexities at different scales directly influence the associated physical/chemical/biological processes of interests, and subsequently mitigate the dependence/reliability of model results. For example, (a) macroscopic Darcy's law may not be able to capture the microscopic or pore-scale heterogeneities; (b) steady state Darcy's may not be able to accommodate space and time dependent hydraulic conductivity; (c) extension of Darcy's law (meant for single-phase fluid flow) for multi-phase fluid flow using the concept of relative permeability of a particular phase (oil/water/gas) is highly debatable as intrinsic permeability does not depend on fluid property (unlike hydraulic conductivity); (d) the Representative Elementary Volume (REV) required for pore-scale mean capillary pressure and the larger-scale aquifer/reservoir mean pressure for multi-phase fluid flow may not be the same; (e) the same mathematical expression used for dispersion in analogy with diffusion in fractured rocks may not be valid; and (f) using a constant value of distribution coefficient (whether in Equilibrium sorption or in sorption kinetics) and the same bio-degradation rate throughout the simulation period may not reflect the reality depending on the type of sub-surface contaminants. Thus, both (hydro geological and modelling complexities associated with a saturated subsurface system has resulted in a limited understanding on the fate and transport of subsurface contaminants. In general, the sub-surface contaminants include naturally occurring and synthetic organic compounds, metals, ions, micro-organisms and

radio-nuclides. Since, petroleum hydrocarbons, which are associated with synthetic organic compounds are only sparingly soluble in aqueous phase (water), these contaminants generally exist in the saturated sub-surface system as a distinct liquid phase widely known as Non-Aqueous Phase Liquid (NAPL). The formation of residual NAPLs in the form of trapped disconnected blobs and ganglia of organic liquid in tiny sub-surface pore spaces by the action of capillary forces actually initiate the migration of NAPLs. The residual NAPL saturations are spatially variable at a given field site associated with the complex pore geometries along its flow path, and it becomes a function of pore size and pore connectivity or medium permeability. In addition to the medium property, fluid properties such as NAPL density, NAPL viscosity, interfacial tension and capillary pressure also dictate the formation of degree of residual NAPL. In general, residual NAPL saturations do not occupy more than one third of a pore space, while the lower limit of residual NAPL saturation can be as low as 1–2% of pore space. On the other hand, pooled NAPL, which represents a continuous mobile fluid distribution in the saturated subsurface contain NAPL saturations that occupy relatively more pore space (generally between more than one third to nearly three fourth of pore space). Thus, residual and pooled NAPL saturations distinctly differ in the sense that the relative permeability of residual NAPL is zero, while the same for pooled NAPL has a finite value, which is a function of amount of pooled NAPL saturation. Since, it is practically impossible to delineate the fractions of residual and pooled NAPL saturations at a given field site, the concept of Bulk Retention Capacity is used, which describes the ratio between NAPL and bulk volumes (Poulsen & Kueper 1992; Kuepur *et al* 1993; Brewster *et al* 1995). Understanding the transport of such petroleum hydrocarbons in a saturated porous medium still remains a challenging task as the dissolution mass transfer between LNAPL phase and aqueous phase is predominantly based on empirical relations as quantifying the dissolution mass transfer rate with reference to spatially and temporally varying NAPL-water interfacial area becomes a tedious task. The problem becomes further complex in the context of saturated fractured rocks, and the studies pertaining to the mathematical modelling that quantifies the dissolution mass transfer explicitly in fractured rocks is very limited. Thus, the objective of the present work is to brief on the composition and transport of petroleum hydrocarbons in a classical porous medium following an onshore oil spill; and to deduce a simplified mathematical model to estimate the dissolution mass transfer of petroleum hydrocarbons in saturated fractured rocks using dual-porosity concept.

2. Composition of petroleum hydrocarbons

Total Petroleum Hydrocarbons (TPH) can be described as the measurable amount of petroleum-based hydrocarbon mixture such as the concentrations of petroleum LNAPL constituents in soil and water samples; and thus, TPH is specifically associated with environmental sampling and analytical results, while Petroleum Hydro-Carbons (PHC) generally refers to hydrogen and carbon-containing compounds originating from crude oil. Crude oil is mainly composed of linear and branched alkanes, cyclo-alkanes and aromatics, while alkenes are associated with petroleum products deduced during refining of crude oil such as gasoline and diesel (Matar & Hatch 2000). PHCs can be simply classified as Mono-cyclic Aromatic Hydrocarbons (MAH) and Poly-cyclic Aromatic Hydrocarbons (PAH). Benzene, Toluene, Ethylbenzene, Xylene and Styrene, collectively referred to as 'BTEX + Styrene' or MAH, are highly toxic PHC compounds, and that they have a relatively low boiling point and molecular weight (volatile). The highly toxic PHC compounds also include benzo[a]pyrene, naphthalene and phenanthrene, which contain two or more fused rings of carbon atoms, generally referred to as PAH. PAHs are heavier and less volatile

than BTEX. In general, petroleum-contaminated soil and groundwater can be assessed using TPH Fraction and Indicator Approach as described by TPH Criteria Working Group (TPHCWG 1997). The TPH Fraction and Indicator Approach is based on the assessment of (a) individual petroleum-related constituents (indicators) using constituent-specific toxicity criteria; and (b) TPH fractions using fraction-specific toxicity criteria. In the absence of fraction-specific data, TPH mixtures, namely, TPH-GRO ($C_6 - C_{12}$) (purgeable) (volatile PHCs in water including BTEX + Styrene); TPH-DRO ($C_{10} - C_{20}$) (extractable) (extractable PHCs in water including applicable PAHs); and TPH-ORO ($C_{20} - C_{28}$) (extractable) (heavy extractable petroleum hydrocarbons in soil with the exception of certain PAHs) shall be assessed. The mechanisms of toxicity associated with these fractions significantly differ. Both MAH and PAHs are of great concern when assessing or remediating contaminated sites; and at least five samples of the excavated contaminated soil must be analysed for Volatile Petroleum Hydrocarbons (VPH), Light Extractable Petroleum Hydrocarbons (LEPH), Heavy Extractable Petroleum Hydrocarbons (HEPH), MAH and PAHs. In essence, PHCs, which is a complex mixture of alkanes, alkenes, alkynes and aromatics are mainly affected by weathering processes (such as dissolution in water, volatilization and photodegradation); and biodegradation (Potter & Simmons 1998). The focus of the present work is limited to the (LNAPL) dissolution in groundwater (i.e., in aqueous phase).

3. Transport of petroleum hydrocarbons in porous media

The release of Light Non-Aqueous Phase Liquids (LNAPLs) from underground storage tanks and pipeline ruptures form the major source of groundwater contamination by Petroleum Hydrocarbons (PHC) and these hydrocarbons exist as a separate, immiscible fluid phase in contact with groundwater (Powers *et al* 1992). Differences in the physical and chemical properties of groundwater and LNAPL result in the formation of a physical interface between these two immiscible fluids, and subsequently, prevent the mixing between the two (Newell *et al* 1995). In the event of an accidental oil spill from underground storage tanks or ruptured pipelines, oil (LNAPL) migrates vertically downwards in an unsaturated zone under the force of gravity, distributing itself in the form of both residual and pooled LNAPLs. During its coupled vertical as well as lateral migration, both residual and pooled NAPLs may vaporize leading to the formation of vapor plumes. When the depth to the groundwater table is large; the released LNAPL mass flux (spill) is not significant enough; and, when the vertical unsaturated hydraulic conductivity is not significant enough, then, there may not be any accumulation of the free product. On the other hand, when the above conditions are favourable, and volume of LNAPL release is significant, then the free product starts accumulating on the capillary fringe, and subsequently, the free product starts displacing the capillary fringe. As the pores within the capillary fringe is fully saturated with water; and since the density of immiscible LNAPL is lesser than water, further downward vertical migration of petroleum hydrocarbons beyond (top) capillary fringe is affected by the buoyant force exhibited within the capillary fringe. At this point, LNAPL requires a minimum critical LNAPL head (also called the entry pressure head) to enter into the capillary fringe zone. Having entered, LNAPL starts displacing the pore water within the pore spaces of capillary fringe laterally. The capillary rise associated with the entry pressure head may vary very widely (for example, 0.1 m for coarse sand; 0.5 m for fine sand; and 1 m for silt). Once the entry pressure head is overcome, petroleum hydrocarbons will begin to migrate in lateral direction as a continuous free-phase layer, but preferentially along the water table gradient, and thus, a fraction of LNAPL gets dissolved into the saturated groundwater system below the water table. On the

other hand, if the lateral migration of oil is slower than the rate at which the vertical migration of oil pours in, then the LNAPL spreading will not be unidirectional but radial. In such cases, the gravity force exceeds the buoyant force, and subsequently, the downward migration of oil into the groundwater aquifer increases. The moment the oil gets into the saturated zone (includes the thickness of capillary fringe above the water table), the oil (LNAPL) starts displacing the water from the pore spaces, and subsequently, NAPL saturation starts increasing. Thus, a large continuous-phase LNAPL mass initially displaces the groundwater (nearly vertically) underneath the source location, and hydrostatically depresses capillary fringe as well as the water table (Charbeneau 2000, 2003). With the reduction in LNAPL hydrostatic pressure (with time), the locally vertically depressed groundwater table slowly rebounds with the depleting LNAPL source. It should be noted here that both the geological units (just below the water table, and just above the water table but within the capillary fringe) are fully saturated with reference to water, while the pressure associated with them are positive normal pressure (towards gravity) and negative capillary pressure (against gravity), respectively. During the time period between the temporary displacement of groundwater table and its recovery, a significant fraction of LNAPL gets entrapped in that particular region of the porous system, and the saturation pertaining to the LNAPL fraction is termed as the residual LNAPL saturation, which is relatively difficult to estimate at the field-scale. It should be noted here that the residual hydrocarbons remain in the geological unit, while the free product spreads extensively. Thus, wettability controls the easiness with which LNAPL wets the geological unit (i.e., the solid grains); density controls the LNAPL product to float freely over the capillary fringe; and viscosity (in addition to LNAPL saturation; LNAPL gradient; LNAPL relative permeability and aquifer thickness) controls the mobility of dissolved LNAPLs within the saturated zone below the water table. It can also be noted that there is a threshold LNAPL layer thickness, up to which, the LNAPL transmissivity remains zero, beyond-which, the LNAPL transmissivity varies linearly with LNAPL layer thickness. Similarly, there is a threshold LNAPL saturation, up to which, LNAPL relative permeability remains zero, and beyond which, LNAPL relative permeability non-linearly varies with LNAPL saturation. It should also be noted that LNAPL does not float on the water table as pointed out by Poulsen & Kueper (1992) and they observed that the lower portion of LNAPL pool is at positive pressure (existing below the water table), while the LNAPL is at negative pressure above the LNAPL table (which exists at some location within the LNAPL pool). They also cautioned that the LNAPL at negative pressure may not be recoverable like the LNAPL at positive pressure using skimmer pumps in monitoring wells.

From Petroleum Engineering perspective, Bradley (1987) defined the residual saturation as the fluid that remained in an oil reservoir at its depletion. This residual saturation is a function of microscopic displacement efficiency (depends on capillary force, in addition to viscous and gravity forces); and macroscopic vertical as well as horizontal sweep efficiencies. While, from Environmental Engineering perspective, Mercer & Cohen (1990) defined the residual saturation as the saturation at which NAPL becomes discontinuous and is immobilized by capillary forces under ambient groundwater flow conditions. Thus, it can be noted here that both the above definitions for residual saturation is associated with a non-zero capillary pressure resulting from field-scale forced imbibition induced by groundwater flow (associated with a groundwater gradient), while Freeze & McWhorter (1997) defined the residual saturation as the non-wetting phase saturation at zero capillary pressure at the terminus of the spontaneous imbibition curve based on drainage and imbibitions experiments. Thus, there is a marginal difference between laboratory and field-scale measurements of residual saturations. In this context, Kueper *et al* (1993) pointed out that caution should be exercised when measuring a residual saturation in the laboratory and applying it to a field condition. Further, it can be noted the resultant residual LNAPL saturation

following an oil spill is a function of initial (maximum) residual LNAPL saturation, which in turn depends on LNAPL pressure history. However, LNAPL does not develop a high capillary pressure as in the case of a petroleum reservoir because the groundwater table is associated with a shallow unconfined aquifer with an insignificant hydrostatic excess pressure. In addition, the LNAPL components such as benzene, toluene, ethyl-benzene and xylenes are only slightly soluble in groundwater. This clearly indicates that the removal of entrapped petroleum hydrocarbons from a saturated subsurface system is extremely difficult as LNAPLs represent potential long term sources for continued groundwater contamination. Hence, understanding the behaviour of LNAPLs in a saturated subsurface system is crucial for the selection and implementation of an effective clean up strategy.

De Pastrovich *et al* (1979) demonstrated that the larger apparent LNAPL thickness within the monitoring well is associated only with the free liquid hydrocarbons (where LNAPL fraction is greater than residual saturation), while (2–10 times) smaller actual LNAPL thickness of the aquifer formation forms only a (top) fraction of the apparent LNAPL thickness. It can be noted that the measured water table inside the well becomes the bottom boundary, while the air-LNAPL interface becomes the top boundary for the apparent LNAPL thickness. The actual LNAPL thickness in the formation is embedded in between the zones of LNAPL capillary rise on the top; and water capillary rise on the bottom, and these zones contain LNAPL fraction which are at or below residual saturation.

The apparent LNAPL thickness in the monitoring well can be approximated as a function of entry pressure head (API 2004; Charbeneau *et al* 1995, 1999; Charbeneau 2000, 2003) as expressed in Eq. (1).

$$b_{nc} = \left(\frac{\sigma_{nw}}{1 - \rho_r} - \frac{\sigma_{an}}{\rho_r} \right) \frac{h_d}{\sigma_{aw}}. \quad (1)$$

In Eq. (1), b_{nc} represents (critical) LNAPL thickness in monitoring well; σ_{nw} represents LNAPL-water interfacial tension; σ_{an} represents air-LNAPL surface tension; σ_{aw} represents air-water surface tension; and ρ_r represents LNAPL specific gravity; and h_d represents the entry pressure head. Having approximated the value of apparent LNAPL thickness, the actual LNAPL thickness in the formation can be expressed as a function of apparent LNAPL thickness in the monitoring well (Lenhard & Parker 1990) as given in Eq. (2).

$$D_o = \frac{r_{ro} b_{ao} H_o}{(r_{ro} b_{ao}) - b_{ow} (1 - r_{ro})}. \quad (2)$$

In Eq. (2), D_o represents the actual thickness of LNAPL in the formation; H_o represents the apparent LNAPL thickness in the monitoring well; r_{ro} represents density of LNAPL; b_{ao} represents air/oil scaling factor $\left(= \frac{S_{aw}}{S_{ao}} \right)$; b_{ow} represents oil/water scaling factor $\left(= \frac{S_{aw}}{S_{ow}} \right)$; S_{aw} represents surface tension of uncontaminated water; S_{ao} represents surface tension of LNAPL; and $S_{ow} (= S_{aw} - S_{ao})$ represents interfacial tension between water and LNAPL. Thus, the presence of LNAPL in a saturated porous medium is determined primarily by the measurement of LNAPL in monitoring wells (EPSRP 2012). However, the better characterization of LNAPL needs additional parameters such as (a) soil/rock texture; (b) pore size and geometry; (c) hydrogeologic factors such as pore water content, hydraulic conductivity, water table fluctuations and the type of the concerned aquifer; (d) fluid properties such as fluid density, viscosity and interfacial tension; (e) soil–fluid interaction properties such as capillary pressure and relative permeability. It should also be noted that the hydraulic recovery of LNAPL may not result in complete elimination of LNAPL, while the residual LNAPL may continue to be a source of contaminants of concern. Thus, a well-established procedure to address the contamination

of groundwater by petroleum hydrocarbons at the larger field scale is followed conventionally through (a) understanding the nature and intensity of LNAPL sources; (b) physical characteristics and chemical composition of LNAPL at and away from sources; (c) areal and volumetric distribution of LNAPL mass; (d) geological and hydro-geological factors influencing the spatial and temporal distribution of LNAPL mass; (e) transport behaviour of LNAPL mass with reference to the resultant direction of groundwater flow considering local scale heterogeneities; (f) the rate at which LNAPL mass gets dissolved and vaporized at various depths with reference to the location of groundwater table. However, it may not be practically feasible to gather all the above information to start with, and subsequently, requires professional judgement even in classical porous medium, and the extension of these concepts to saturated fractured rocks is associated with much more complexity.

4. Transport of petroleum hydrocarbons in fractured media

The onshore oil spill of petroleum hydrocarbons during its transportation through buried pipelines is not uncommon in countries like India, which is characterized by two thirds of hard rocks. Onshore oil spills over such fractured geologic deposits will find its way through a complex network of rock fractures to the biosphere. The immiscible fluid migration within this network is dictated by the dominant influences of viscous, capillary and gravitational forces. As soon as the released oil spill reaches the saturated hard rocks, the LNAPL mass flux will be transported continuously until the same gets trapped as residual ganglia in fracture apertures with a relatively higher thickness (say, more than 10 microns), while the mobility of LNAPL is finally restricted by dominant capillary forces associated with fracture apertures of reasonably small thicknesses (say, less than 1–10 microns). Since the rock mass is fully saturated with groundwater, the trapped LNAPL mass slowly starts dissolving into water phase. This dissolution mass transfer within the connected fracture network forms an oil plume. Since the associated solubility of petroleum hydrocarbons are relatively low, the dissolution mass transfer of LNAPL mass flux takes a relatively larger time level (sometimes, several decades together) and subsequently act as a potential long-term source of groundwater contamination. In addition, it is extremely difficult to delineate the spatial distribution of LNAPL mass fluxes within the rock mass as all the fractures do not by default transmit fluid masses, but only those fractures with proper connectivity, i.e., the fluids migrate through preferential pathways having least frictional resistance to fluid flow. Thus, remediation strategies in saturated fractured rock masses are not straight forward as it is feasible in a classical porous medium. This is because neither transport of petroleum hydrocarbons in saturated rock fractures is clearly understood nor the conventional remediation technologies applied in a classical porous medium such as in-situ air sparging, pump-and-treat and soil vapor extraction are clearly understood in fractured rock masses. In particular, the dissolution mass transfer within a fracture aperture is significantly affected by residence time of LNAPL mass fluxes within the fracture and its associated matrix diffusion, in addition to the basic parameters such as thickness of fracture aperture, mean fluid velocity within the fracture, and the porosity and effective diffusion coefficient of rock-matrix. Further, the mass flux exchange between a high permeable fracture and low permeable rock-matrix will be significantly influenced by the nature of roughness and curvature of fracture walls, and in turn, the fluid mass transfer from fracture to rock-matrix will be varying spatially along the high permeable fracture. In addition, depending on the dip (or inclination) of fracture, the gravity effect will play a crucial role in mobilizing the LNAPL mass fluxes. For example, if the fracture is significantly dipped with a relatively larger hydraulic gradient between the inlet and outlet of a particular

fracture, then the residence time available within that fracture will be minimal and the LNAPL mass fluxes will be flushed out with a relatively faster rate. However, releases of such free phase LNAPL masses will be associated with fracture apertures with a relatively larger thickness, while the LNAPL mass flux held by dominant capillary effect in relatively smaller fracture apertures will not be removed even with a higher hydraulic gradient as they are held strongly by capillary effects and not dictated by gravity effects, and hence, the associated mass transfer will be diffusion controlled. Thus, understanding the concept of dissolution mass transfer rate of entrapped LNAPL mass fluxes even at the scale of single fracture remains a challenging task and subsequently, it will provide a better insight for a larger field scale applications.

The saturated fractured rock mass is conceptualized as a set of regular, low permeable rock-matrix blocks embedded in between high permeable fractures as conceptualized by Warren & Root (1963). Although the conceptualization consists of both vertical as well as horizontal fractures, the present focus is restricted to transport of petroleum hydrocarbons in a single horizontal fracture with its associated rock-matrix. The transport of solutes considering advection, dispersion, matrix diffusion and linear/non-linear sorption have already been investigated by the author at the scale of a single fracture with its associated rock-matrix (Suresh Kumar & Sekhar: 2005; Suresh Kumar & Ghassemi 2005; Sekhar *et al* 2006; Suresh Kumar *et al* 2006, 2008; Sekhar & Suresh Kumar 2006; Ghassemi & Suresh Kumar 2007; Suresh Kumar 2008, 2009, 2014; Natarajan & Suresh Kumar 2010, 2011; Renu & Suresh Kumar 2012). In the context of oil spill, the dissolution mass transfer of petroleum hydrocarbons (LNAPL dissolution) plays a crucial role in addition to the above mentioned transport processes. In a fracture-matrix coupled system, the oil spill enters into the high permeability fracture at the fracture inlet, i.e., at the intersection of a horizontal and a vertical fracture. As a LNAPL and a hydrophobic organic, petroleum hydrocarbons is relatively immiscible with the water phase. Thus, the rate at which the dissolution mass transfer occurs is significantly slow such that even small volumes of petroleum hydrocarbons act as long-term sources of groundwater contamination. The present study focuses on the LNAPL release as soon as it reaches the saturated zone of fractured formation. Since the time associated with the dissolution process is too long, the dissolution mass transfer of LNAPL into its aqueous phase is generally described by mass transfer kinetics as against equilibrium mass transfer. This mass transfer kinetics is mathematically described by the well-known film theory, where the mass of petroleum hydrocarbons is transferred through a thin film (interface) or boundary layer separating the LNAPL and water phase. Due to the presence of interface, mass is first transferred from bulk LNAPL phase to the interface followed by the mass transfer from the interface to the bulk aqueous phase. For single component dissolution, it can be safely assumed that the diffusion of the single component within the LNAPL phase is fast enough to achieve the equilibrium, and subsequently, the concentration at the interface may be assumed to be at its steady state solubility level. It should be noted here that for multi-component dissolution, the diffusion resistance offered by each component may not be the same, and sometimes, it may be significant as well. In such cases, it may not be fair to expect the concentration of each component at the interface to be at its solubility level, and this is one of the reasons why Raoult's law deviates significantly when describing multi-component dissolution mass transfer. Thus, for single component dissolution mass transfer within a single fracture, there will be only one type of resistance to mass transfer across the interface and hence, a single-resistance linear driving force model can safely be assumed as described in Eq. (3).

$$J = K_L^f \left(C_{\text{interface}}^f - C^f \right) \Rightarrow J = K_L^f \left(C_S^f - C^f \right). \quad (3)$$

In Eq. (3), J represents LNAPL mass flux within the high permeable fracture ($\text{ML}^{-2}\text{T}^{-1}$); K_L^f represents the overall mass transfer rate within the fracture from the LNAPL-water interface to the water phase (LT^{-1}); C_S^f represents the water solubility of the respective LNAPL component (ML^{-3}); C^f represents the bulk fracture concentration in the aqueous phase (ML^{-3}). The concentration difference between the interface and the bulk aqueous phase concentration within the fracture dictates the driving force for dissolution. For multi-component dissolution, the driving force may not be the same for all the components of interest, and subsequently, it might lead to multi-resistance nonlinear driving force between the interface and the bulk aqueous phase. In addition, the assumption of linear driving force model of dissolution mass transfer for single component LNAPL dissolution may not be valid when the thickness of the fracture aperture falls below the range between 1 and 10 μm , in which case the fluid flow is governed by the capillary effect and not by positive pressure differential or gravity effects. Further, it should be noted that Eq. (3) is applicable at the Representative Elementary Volume (REV) scale in a classical porous medium, where fundamental aquifer properties such as porosity and hydraulic conductivity can effectively be averaged. However, in a coupled fracture-matrix system, high permeable fracture and low permeable rock-matrix are treated as two different continuums, and subsequently, single-resistance linear driving force model within a high permeable fracture is analogous to a dissolution mass transfer mechanism within a pipe with 100% porosity. In the absence of tortuosity within a fracture, dissolution mass transfer mechanism within a high permeable fracture needs to be treated much carefully with reference to the dissolution mass transfer mechanism associated with a porous medium. The additional factors which will significantly influence the dissolution mass transfer within a fracture includes (a) the mean fracture aperture thickness in case of fracture with smooth walls; (b) the spatial variation of fracture aperture thickness for fractures with undulated fracture walls; (c) the roughness of fracture walls; (d) the mean fluid velocity within the fracture that decides the residence time of LNAPL-water liquids; (e) the mean radius of LNAPL blobs with reference to the thickness of fracture aperture; (f) the density and viscosity of LNAPL fluid; (g) the porosity and effective diffusion coefficient of low permeable rock-matrix. In essence, the mass transfer rate K_L^f will be determined not only by the LNAPL-water interface coupled with the combined effects of conventional advective and diffusive forces, but also by the combined effects of all the above mentioned factors. In addition, since the thickness of fracture aperture is significantly small, the role of van der Waals forces nearer to the fracture wall may be significant, and the influence of van der Waals forces on the resultant dissolution mass transfer needs to be investigated. Thus, the analysis of mass fluxes at the fracture-matrix interface will be very critical in the sense that the delineation of interface mass fluxes resulting from dissolution mass transfer and matrix diffusion will be extremely difficult. Unlike porous media, in a coupled fracture-matrix system, depending on the radius of LNAPL blobs, the velocity of LNAPL blobs with its associated gravity settling effect may also play a crucial role. Hence, in the expression for dissolution mass transfer rate K_L^f provided by Miller *et al* (1990) as given in Eq. (4), estimation of both average mass transfer coefficient, k_{la} [L/T]; and the effective specific interfacial area per unit volume of porous media, a^n [L^2L^{-3}] may not be directly applicable in a coupled fracture-matrix system. For example, the parameter a^n needs to be described as the effective specific interfacial area per unit surface area of fracture wall a^n [L^2L^{-2}], and in turn, the expression for mass transfer rate will marginally get modified to take into account the thickness of the fracture aperture, $2b$ [L] as given in Eq. (5). It should be noted that the dimension of fracture aperture appears in Eq. (5) as this dimension is

highly insignificant in comparison with other two dimensions, which constitute the fracture volume.

$$K_L = (k_{la}) (a^n), \quad (4)$$

$$K_L = (k_{la}) (a^n) (2b). \quad (5)$$

However, the parameters k_{la} and a^n will still be spatially and temporally varying as a function of (a) fracture-matrix geometry; (b) local scale hydrodynamics associated with a typical coupled fracture-matrix system; and (c) LNAPL characteristics both at the fracture inlet (as a source) and within the fracture volume. In addition, in a coupled fracture-matrix system, it is extremely difficult to delineate the 'inactive' NAPL surface areas, especially along the fracture-matrix interface. Given the varying nature of fracture aperture walls, the mass transfer rate within the high permeable fracture will be highly time dependent.

The concept of applying Local Equilibrium Assumption (LEA) for LNAPL dissolution mass transfer in a single fracture assuming the establishment of thermodynamic equilibrium throughout the interphase including both LNAPL and water layers may not be appropriate within a fracture as possible in a classical porous medium. This is because in a coupled fracture system, if the source is assumed to be available only at the fracture inlet, then, there is no feasibility of assuming LEA away from the LNAPL source. Even if the source is assumed to mix continuously with the aqueous phase within the fracture, the LNAPL mass within the fracture volume in the form of (different sizes of) blobs may try to settle down non-uniformly spatially due to gravity effects, and in turn LEA assumption may be ruled out completely. In essence, dissolution of LNAPL may not instantaneously result in aqueous concentrations equal to the solubility limit of respective LNAPL. In addition, the diffusive mass transfer from high permeable fracture to low permeable rock-matrix clearly curtails the concept of infinite dissolution mass transfer rate within the fracture. As a result, both the parameters k_{la} and a^n needs to be estimated explicitly. Thus, the mass flux from LNAPL to the aqueous phase is not only governed by the rate at which the equilibrium concentration of concerned LNAPL mass at the interface boundary is removed by advection, diffusion, dispersion, sorption and biodegradation, but also by the intensity of matrix diffusion, which depends on porosity and effective diffusion coefficient of rock-matrix, and the fluid residence time within the fracture (which is a function of mean fluid velocity). In essence, the larger mean fluid velocity associated with the high permeable fracture, a larger transverse dispersivity resulting from differential advection or matrix diffusion and a smaller LNAPL pool associated with the smaller thickness fracture aperture may over-estimate the dissolution mass transfer rates, and hence, the applicability of local equilibrium assumption is far from reality in saturated fractured rocks. In this context, non-equilibrium expressions as given in Eqs. (4) and (5) can be used to predict LNAPL dissolution at the microscopic scale. However, estimating the LNAPL-water interfacial area is extremely difficult at the microscopic scale, and hence, both the parameters k_{la} and a^n are lumped together and treated as a single entity described as a Lumped Mass Transfer Coefficient (K_L). Powers *et al* (1991) deduced an alternate relation to quantify K_L in terms of a dimensionless number called the modified Sherwood number (Sh'), which essentially relates the dissolution mass transfer at the LNAPL-water interface to the mass transfer away from the interface as expressed in Eq. (6).

$$Sh' = \frac{K_L d_m^2}{D^*}. \quad (6)$$

In a typical classical porous medium, D^* represents the free molecular diffusion coefficient of the concerned LNAPL and d_m represents the mean grain size. However, in a coupled fracture-matrix

system, d_m will be replaced by the mean thickness of fracture aperture (2b), and subsequently, Eq. (6) gets modified to Eq. (7).

$$Sh' = \frac{K_L (2b)^2}{D^*}. \quad (7)$$

Right from Miller *et al* (1990) to Nambi & Powers (2003), several researchers have developed empirical correlations for the modified Sherwood number as a function of Reynolds Number (or mean fluid velocity) and NAPL saturation, and all these models essentially allows a single dissolution rate, and subsequently, they may not be able to capture all field scale heterogeneities at all time levels. However, an improved model was suggested by Brusseau (1992) to take into account both LEA (fast) and limited mass transfer (slow) sites, and Hamed *et al* (2000) provided the respective empirical relations for mass transfer coefficients. Grant & Gerhard (2007) introduced the concept of thermodynamic interfacial area model as against the conventional empirical dissolution mass transfer models, which essentially requires only rock and fluid properties and the capillary pressure – saturation curves, and this particular physically based model applicable at the macroscopic scale does not require any calibration as provided in Eq. (8). In addition, in their study, it was assumed that the variations in mass transfer rates result only from variations in interfacial area associated with a relatively small pressure gradient along with the consideration of a constant mass transfer coefficient. In a coupled fracture-matrix system, the mass transfer dynamics will be very complex resulting from (a) higher mean fluid velocity associated with the high permeable fracture; (b) additional mass loss from the fracture associated with matrix diffusion; (c) a larger hydraulic gradient associated with the inclined fractures; and (d) the preferential nature of fluid flow through fractures.

$$a(S_w) = (\theta) \left(\frac{\Phi_{NW}(S_w)}{\sigma_{NW}} \right). \quad (8)$$

In Eq. (8), θ represents the aquifer porosity; $\Phi_{NW}(S_w)$ represents the area under the capillary pressure – saturation curve at a given saturation; σ_{NW} represents interfacial tension between LNAPL and the aqueous phase; and $a(S_w)$ represents the effective specific interfacial area per unit volume of porous media. Since, the porosity in a single fracture amounts to unity, the interfacial area in saturated fractured rocks always remain larger with reference to that in a classical porous medium. However, the effectiveness of the above thermodynamic interfacial area models under advective dominant transport systems, associated with fractured rocks still remains a question.

Kinetic expressions were introduced by several researchers for the cases with heterogeneous LNAPL distributions in order to estimate the dissolution mass transfer rates. For example, Sherwood–Gilland model (Miller *et al* 1990; Imhoff *et al* 1993; Powers *et al* 1994; Saba & Illangasekare 2000; Nambi & Power 2003) relates the modified Sherwood Number with aqueous velocity and NAPL saturation, in the absence of an explicit NAPL-water interfacial area as provided in Eq. (9).

$$Sh' = \frac{K_L d_m^2}{D^*} = b \text{Re}^c S_N^d. \quad (9)$$

In Eq. (9), b, c and d represent the empirical coefficients (Kokkinaki 2013); d_m represents the mean grain size; Re represents the Reynolds Number; and S_N represents the NAPL saturation. The value of K_L is estimated from Eq. (9) and the same is substituted in Eq. (3) in order to deduce the LNAPL mass flux. The different set of expressions for Sherwood Number in the form of Eq. (9) are tabulated and compared in table 1.

Table 1. Various Sherwood–Gilland models in the form of $Sh' = b Re^c S_N^d$ with their respective applicability ranges for Reynolds Number and NAPL saturation.

Reference	Sh' Model	Applicability range	System
Nambi & Powers (2003)	$(37.15) Re^{0.61} S_N^{1.24}$	Re: 0.018–0.134 S_N : 0.01–0.35	2D
Saba & Illangasekare (2000)	$(8) Re^{0.28} S_N^{1.04}$	Re: 0.0015–0.01 Mean S_N : 0.22	2D
Powers <i>et al</i> (1994)	$(44.75) Re^{0.53} S_N^{0.94}$	Re: 0.034–0.588 S_N : 0.001–0.197	1D
Imhoff <i>et al</i> (1993)	$(75.5) Re^{0.71} S_N^{0.87}$	Re: 0.0012–0.021 S_N : 0–0.16	1D
Miller <i>et al</i> (1990)	$(216) Re^{0.75} S_N^{0.6}$	Re: 0.005–0.1 S_N : 0–0.21	1D

From table 1, it is clear that the Sherwood Number expressions are mainly dependent on Reynolds Number as well as NAPL saturation. Keeping aside the initial NAPL saturation which depends on the nature and intensity of oil spill, Reynolds Number, and in turn, the mean fluid velocity plays a crucial role in deciding the resultant Sherwood Number, based on which the dissolution rate K_L will be computed. This mean fluid velocity in a saturated fractured rock mass is highly dependent on the hydraulic behaviour of rock fractures, which is again dependent on the geometry of void space or fracture aperture thicknesses. The deduction of this mean fluid velocity in fractured rock masses becomes very critical as the fluid flow through fractures cannot be described by linear Darcy flow with negligible inertial effects (resulting from ignoring the details on fracture geometry and fracture surface roughness), while nonlinear fluid flow better describes the fluid flow through fractures, where inertial forces become dominant with reference to the viscous forces, while the hydraulic gradient varies nonlinearly with the mean fluid velocity. From table 1, it can be seen that the upper limit of Reynolds Number is relatively higher for the model cases by Powers *et al* (1994) and Miller *et al* (1990); and to some extent by Nambi & Powers (2003). In describing fluid flow through rock fractures, the concept of nonlinear fluid flow becomes increasingly dominant with a relatively larger Reynolds Number. For high fluid flow rates through fractures, the description of mean fluid velocity, i.e., the momentum conservation equation as expressed in Eq. (10) becomes increasingly complex as the resultant equation involves a complex function of mean fluid velocity and hydrodynamic pressure as provided by Brush & Thomson (2003). The resultant fluid flow equation resulting from coupling mass and momentum conservation equations is further complicated in describing fluid flow through fractures as it is nearly impossible to find a fracture replicating the smooth parallel walled aperture; and the rock fractures are generally characterized by the complicated fracture network geometry.

$$\rho (\vec{u} \cdot \nabla) \vec{u} = \mu \nabla^2 \vec{u} - \nabla p. \quad (10)$$

In Eq. (10), \vec{u} represents flow velocity vector; ρ represents the fluid density; and p represents the hydrodynamic pressure. Thus, the assumption of insignificant inertial effects with reference to the viscous and pressure forces is hypothetically introduced in describing fluid flow through a smooth parallel plate fractures, and the resultant mean fluid velocity is computed based on the linear stokes equation. In one-dimensional fluid flow, the total volumetric flow rate through a single fracture is described as a function of cube of mean fracture aperture, widely known as Poiseuille flow (or Cubic Law) with a uniform pressure gradient between smooth parallel plates

(Witherspoon *et al* 1980) and the expression for the same is provided by Eq. (11). The respective expression for mean fluid velocity is given by Eq. (12).

$$Q = -\frac{W(2b)^3}{12\mu}\nabla p = -\frac{k}{\mu}A\nabla P, \quad (11)$$

$$\bar{V} = -\frac{k}{\mu}\nabla p. \quad (12)$$

In Eq. (12), k represents the intrinsic permeability, which is a function of square of mean fracture aperture; and μ represents the fluid viscosity. However, Eqs. (11) and (12) are applicable only for fluid flow with low flow rates, where a linear relationship is maintained between fluid flow rate and the pressure gradient. Thus, the direct applicability of Sherwood–Gilland models (that includes a higher Reynolds Number) to saturated fractured rocks remains a question. On the other hand, the efficiency of the above models can be tested for nonlinear fluid flow through fractures using the Forchheimer’s law (Bear 1972; Moutsopoulos 2009) that take into account the energy losses resulting from both viscous as well as inertial forces, and the respective nonlinear relation between the fluid flow rate and the pressure gradient is provided in Eq. (13). The advantage of using Forchheimer’s law for high fluid flow rates not only better describes the nonlinear fluid flow through fractures but it also boils down to linear Darcy’s law for low flow rates.

$$-\nabla p = AQ + BQ^2. \quad (13)$$

In Eq. (13), A represents the coefficient that describes the energy loss due to viscous forces, while the coefficient B describes the energy loss due to inertial forces. This ratio between viscous and inertial forces known as Reynolds Number is described as a function of fracture aperture thickness of an idealized parallel smooth fracture (Zimmerman *et al* 2004); and the fracture width, which is normal to the direction of pressure gradient, and the respective expression for the Reynolds Number is provided in Eq. (14), assuming a unit fracture width.

$$\text{Re} = \frac{\rho\bar{V}D}{\mu} = \frac{\rho\bar{V}(2b)}{\mu} = \frac{\rho Q}{\mu}. \quad (14)$$

It can be inferred from table 2 that most of the existing models can be applied in saturated rocks, when the mean fluid velocity within the fracture ranges between 10 and 100 m/day for fracture aperture thickness with 100 microns, while the velocity range for higher fracture apertures marginally increases (say, 1–100 m/day). Table 2 takes into account the influence of Re only, while the consideration of NAPL saturation will further filter the applicability of the existing models.

The mathematical model used to describe the transport of an oil spill (LNAPL-water system) within a high permeable fracture is analogous to the expressions provided by Zhang & Brusseau (1999) and Clement *et al* (2004). Several researchers have provided the mathematical models that describe the rate limited sorption and biodegradation (for example, Clement *et al* 2004). In general, two sets of equations are required to address the transport within the mobile dissolved aqueous phase and the immobile NAPL phase. The expression for mass transfer rate constant requires the estimation of initial maximum dissolution rate constant and its associated exponent (Powers *et al* 1994; Clement *et al* 2004). Having found the dissolved aqueous phase concentration within the fracture, then, rate limited diffusive mass flux is applied at the fracture-matrix interface, followed by the diffusive mass transport within the low permeable

Table 2. Applicability of existing Sherwood–Gilliland models for saturated fractured rocks based on Reynolds Number.

\bar{V} (m/s)	2b (μm)	Re	Sherwood–Gilliland model applicability
1.0e–07	100	0.00001	None
1.0e–06	100	0.0001	None
1.0e–05	100	0.001	None
1.0e–04	100	0.01	Nambi & Powers (2003); Saba & Illangasekare (2000); Imhoff <i>et al</i> (1993); Miller <i>et al</i> (1990)
1.0e–03	100	0.1	Nambi & Powers (2003); Powers <i>et al</i> (1994); Miller <i>et al</i> (1990)
1.0e–07	500	0.00005	None
1.0e–06	500	0.0005	None
1.0e–05	500	0.005	Saba & Illangasekare (2000); Imhoff <i>et al</i> (1993); Miller <i>et al</i> (1990)
1.0e–04	500	0.05	Nambi & Powers (2003); Powers <i>et al</i> (1994); Miller <i>et al</i> (1990)
1.0e–03	500	0.5	Powers <i>et al</i> (1994)

solid rock-matrix. The complete mathematical model that describes the coupled fluid flow and transport of petroleum hydrocarbons is summarized as given in Eqs. (15)–(26).

The transport of a petroleum hydrocarbons emanating from saturated fractured rocks contaminated with residual LNAPL products is given by Eq. (15).

$$\theta_a^f \frac{\partial C_a^f}{\partial t} + \theta_n^f \frac{\partial C_n^f}{\partial t} + \rho_n^f \frac{\partial \theta_n^f}{\partial t} = \frac{\partial}{\partial x} \left(\theta_a^f D_L^f \frac{\partial C_a^f}{\partial x} \right) - q^f \frac{\partial C_a^f}{\partial x}. \quad (15)$$

In Eq. (15), C_a^f represents the dissolved aqueous phase concentration; C_n^f represents the LNAPL phase concentration; θ_a^f represents the volumetric water content within the high permeable fracture; θ_n^f represents the volumetric LNAPL content; ρ_n^f represents LNAPL density within the fracture; q^f represents the Darcy flux within the fracture; and D_L^f represents the longitudinal dispersion coefficient along the fracture. Eq. (15) represents the mass balance equation for the dissolved aqueous phase, while the mass balance equation for the LNAPL phase is given by Eq. (16).

$$\theta_n^f \frac{\partial C_n^f}{\partial t} = \alpha_{mt}^f (C_a^f - C_n^f) = -\alpha_{mt}^f (C_n^f - C_a^f). \quad (16)$$

In Eq. (16), α_{mt}^f represents the first order mass transfer coefficient for diffusion. The LNAPL-water dissolution within the fracture is described by a similar first order mass transfer process as expressed in Eq. (17).

$$\rho_n^f \frac{\partial \theta_n^f}{\partial t} = K_{La}^f (C_a^f - C_s^f) = -K_{La}^f (C_s^f - C_a^f). \quad (17)$$

Substituting Eqs. (16) and (17) in Eq. (15) yields the non-linear partial differential equation that describes the transport of dissolved aqueous phase concentration of LNAPL within the high permeable fracture as given by Eq. (18), where K_{La}^f represents the aqueous phase dissolution rate constant within the fracture; and C_s^f represents the saturation concentration of LNAPL within the fracture.

$$\theta_a^f \frac{\partial C_a^f}{\partial t} = \frac{\partial}{\partial x} \left(\theta_a^f D_L^f \frac{\partial C_a^f}{\partial x} \right) - q^f \frac{\partial C_a^f}{\partial x} + \alpha_{mt}^f (C_n^f - C_a^f) + K_{La}^f (C_s^f - C_a^f). \quad (18)$$

The primary dependent variable in Eq. (18) corresponds to C_a^f , while the same equation has an additional unknown C_n^f which needs to be guessed to start with, before solving Eq. (19).

The changes in the LNAPL mass within the fracture can be modelled using Eq. (19).

$$\frac{\rho_w^f}{\theta^f} \frac{\partial C_n^f}{\partial t} = -K_{La}^f (C_s^f - C_a^f). \quad (19)$$

In Eq. (19), ρ_w^f represents the density of aqueous phase fluid, which results from replacing the dry bulk density of soil matrix associated with the classical porous medium; and θ^f represents the fracture porosity.

The LNAPL dissolution rate constant can be estimated from Eq. (20), where $C_n^{f^o}$ represents the initial mass fraction of the residual LNAPL within the fracture; K_{La}^{\max} represents the initial maximum dissolution rate constant within the fracture; and β represents the empirical constant.

$$K_{La}^f = K_{La}^{\max} \left(\frac{C_n^f}{C_n^{f^o}} \right)^\beta. \quad (20a)$$

The initial maximum dissolution rate constant depends on Reynolds Number, molecular diffusivity of LNAPL in water and the mean fracture aperture thickness as given by Eq. (22).

The term K_{La}^f in Eq. (20a) represents the mass transfer rate constant within the fracture, while the same equation is generally expressed as given in Eq. (20b) in a typical classical porous medium (Clement *et al* 2004).

$$K_{La} = 4.13 \text{ Re}^{0.598} \left(\frac{d_{50}}{d_m} \right)^{0.673} U_{in}^{0.369} \left(\frac{D_m}{d_{50}^2} \right) \left(\frac{C_N}{C_N^0} \right)^\beta. \quad (20b)$$

The exponent β in Eq. (20b) can be computed from the empirical equation provided by Powers *et al* (1994) as given in Eq. (20c) and this expression is valid only in a porous medium, while a modified expression is required to express the same exponent β in a fractured reservoir.

$$\beta = 0.518 + 0.114 \left(\frac{d_{50}}{d_m} \right) + 0.10 U_{in}. \quad (20c)$$

However, Eq. (20b) cannot be applied as such in describing the NAPL dissolution within a fracture. The terms d_{50} , d_m and d_{50} in Eq. (20b), which are applicable only in a porous medium needs to be replaced while applying for a fractured aquifer in terms of its mean aperture thickness $2b$. In this context, in a coupled fracture-matrix system, the medium grain diameter (d_m) is assumed to be equal to (d_{50}), which is again equal to the mean thickness of fracture aperture

($d_m = d_{50} = d_{10} = d_{60} = 2b$). Thus, the term $\left(\frac{d_{50}}{d_m}\right)^{0.673}$ in Eq. (20b) becomes equal to unity, while the term uniformity index also becomes unity as given in Eq. (21).

$$U_{in} = d_{60}/d_{10} = 2b/2b = 1. \quad (21)$$

Thus, the modified equations representing $K_{La}^{f\max}$ and β (applicable in a fractured aquifer) are given in Eqs. (22) and (23), respectively.

$$K_{La}^{f\max} = 4.13 \operatorname{Re}^{0.598} \left(\frac{D_m^f}{(2b)^2} \right), \quad (22)$$

$$\beta = 0.518 + 0.114 + 0.1 = 0.732. \quad (23)$$

In Eq. (22), D_m^f represents molecular diffusivity of LNAPL in aqueous phase; and $2b$ represents the mean fracture aperture thickness. Eq. (23) represents that the value of β becomes a constant and it is equal to 0.732, with the assumption that the ratio $\left(\frac{d_{50}}{d_m}\right)$ and U_{in} in Eq. (20b) are equal to unity based on ($d_m = d_{50} = d_{10} = d_{60} = 2b$). Substituting Eq. (23) in Eq. (20), the expression for K_{La}^f is provided in Eq. (24).

$$K_{La}^f = K_{La}^{f\max} \left(\frac{C_n^f}{C_n^{f^o}} \right)^{0.732}. \quad (24)$$

The typical value of β in a classical porous medium varies between 0.5 and 1.0 as predicted by Powers *et al* (1994), and subsequently, the deduced value of β in a coupled fracture-matrix system also falls in that range without any ambiguity.

Having deduced the dissolved aqueous phase concentration within the fracture, the fluid mass exchange between high permeable fracture and low permeable rock-matrix at the fracture-matrix interface can be described as given in Eq. (25). The diffusive mass flux as given in Eq. (25) is normal to the fracture axis and it is applicable only at the fracture-matrix interface. It should be noted that the variable C_a^m needs to be guessed first before solving Eq. (26), and then, the same parameter needs to be iterated until convergence is achieved between guessed and computed values of C_a^m after solving Eq. (26).

$$\frac{\partial C_a^f}{\partial t} = - \frac{\theta_m D_{eff}}{b} \frac{\partial C_a^m}{\partial y} \Big|_{y=b}. \quad (25)$$

In Eq. (25), θ_m represents the porosity of rock-matrix, while D_{eff} represents the effective diffusion coefficient of rock-matrix. The one-dimensional diffusive mass transfer normal within the rock-matrix is represented by Eq. (26).

$$\frac{\partial C_a^m}{\partial t} = D_{eff} \frac{\partial^2 C_a^m}{\partial y^2}. \quad (26)$$

The numerical implication of the proposed mathematical model is quite important. In Eq. (18), the parameter θ_a^f represents the volumetric water content within the fracture, which is equal to the fracture porosity (equal to unity) in a single fracture. Eq. (18) holds good as long as θ_n^f is assumed to be significantly small. As a result, the Darcy flux and the mean fluid velocity

within the fracture remains the same. Thus, the Sherwood–Gilland models proposed by Miller *et al* (1990); Imhoff *et al* (1993); Powers *et al* (1994); and Saba & Illangasekare (2000) can be safely applied in a coupled fracture-matrix system, while the proposed model by Nambi & Powers (2003) may not be applicable as it includes a relatively higher LNAPL saturation. A higher LNAPL saturation implies a significant reduction in volumetric water content, and in turn, Eq. (18) needs to be solved with extreme care. For example, for higher LNAPL saturations, Eq. (18) gets transformed into Eq. (27).

$$\left(\theta_a^f + \theta_n^f\right) \frac{\partial C_a^f}{\partial t} = \frac{\partial}{\partial x} \left(\left(\theta_a^f + \theta_n^f\right) D_L^f \frac{\partial C_a^f}{\partial x} \right) - q^f \frac{\partial C_a^f}{\partial x} + \alpha_{mt}^f \left(C_n^f - C_a^f\right) + K_{La}^f \left(C_s^f - C_a^f\right). \quad (27)$$

Rearranging Eq. (27) yields Eq. (28).

$$\frac{\partial C_a^f}{\partial t} = \frac{\partial}{\partial x} \left(D_L^f \frac{\partial C_a^f}{\partial x} \right) - \left(\frac{q^f}{\left(\theta_a^f + \theta_n^f\right)} \right) \frac{\partial C_a^f}{\partial x} + \left(\frac{\alpha_{mt}^f \left(C_n^f - C_a^f\right)}{\left(\theta_a^f + \theta_n^f\right)} \right) + \left(\frac{K_{La}^f \left(C_s^f - C_a^f\right)}{\left(\theta_a^f + \theta_n^f\right)} \right) \quad (28)$$

From Eq. (28), it is clear that the magnitude of mean fluid velocity becomes a function of LNAPL saturation, which keeps varying with time. Thus, varying mean fluid velocity with a constant longitudinal dispersion coefficient does not correlate well. On the other hand, the last two terms on RHS of Eq. (28) also gets significantly affected by the presence of higher LNAPL saturation. Thus, the proposed equations can be verified only when the LNAPL saturation is low (2–10%), and the equations may not be appropriate for conditions with significant LNAPL saturation (greater than 20%), while the model results need careful analysis on the interpretation of results for LNAPL saturation range between 10 and 20%. In addition, a higher fracture aperture thickness may not be associated with proper fracture-matrix coupling as anticipated. For example, when higher values of fracture aperture thicknesses are considered for numerical simulation (say, $2b > 500$ microns), the flow regime within the high permeable fracture becomes highly complex in the sense that the behaviour of fluids nearer to the fracture walls may not be the same with that of the fluids that are transported along the centre of the fracture axis. For very large fracture aperture thickness (say, $2b > 1000$ microns), the fluid flow behaviour will not follow a Darcian approach. Hence, the proposed model may work well for the fracture aperture ranges between 100 and 500 microns. However, this range of fracture aperture is associated with higher mean fluid velocity as discussed earlier in table 2. This implies that Eq. (18) may remain hyperbolic dominant despite the presence of LNAPL dissolution mass transfer and matrix diffusion. In such cases, the continuity of fluid mass fluxes at the fracture-matrix interface plays a very crucial role in determining the efficiency of the numerical model. On the other hand, for the cases of fracture apertures with less than 1 micron thickness, the fluid flow driving mechanism within the fracture becomes very complex, and the proposed model can not be used for such very low fracture apertures. In essence, the numerical model can produce better results for the proposed mathematical model for a relatively low Reynolds Number as well as low initial LNAPL saturation (2–10%).

5. Conclusions

This article has addressed the critical issues that describe the dissolution mass transfer of petroleum hydrocarbons in a saturated subsurface system. A brief theory has been included on the composition and transport of petroleum hydrocarbons following an onshore oil spill. An

improved mathematical model has been proposed that will better describe the dissolution kinetics of petroleum hydrocarbons in saturated fractured rocks at the scale of a single fracture using dual-porosity concept. The following conclusions have been drawn from the present study.

- (i) Both geological and modelling complexities associated with a saturated subsurface system has led to the limited understanding on the fate and transport of the subsurface contaminants, in general; and petroleum hydrocarbons, in particular.
- (ii) Residual NAPL saturations depend on both aquifer properties (pore geometry, pore size and pore connectivity/medium permeability) and fluid properties (NAPL density, NAPL viscosity, interfacial tension and capillary pressure) with a zero relative permeability, while pooled NAPLs represent a continuous mobile fluid distribution with a finite value of relative permeability.
- (iii) Albeit the actual LNAPL thickness in the formation can be expressed as a function of an apparent LNAPL thickness in the monitoring well, additional parameters including aquifer/rock properties (soil/rock texture, pore geometry, pore size, and pore connectivity); fluid properties (density, viscosity and interfacial tension); hydrogeological properties (pore water content, hydraulic conductivity, water table fluctuations and type of aquifer); and solid–fluid interaction properties (capillary pressure and relative permeability) are required to better characterize LNAPLs.
- (iv) The lumped mass transfer coefficient proposed by Powers *et al* (1991) depends on mean grain size associated with a classical porous medium, while the same parameter has been replaced by an equivalent average thickness of fracture aperture (2b), that better describes the LNAPL dissolution rate in a coupled fracture–matrix system.
- (v) A set of nonlinear coupled partial differential equations is deduced for a coupled fracture–matrix system in analogy with the differential equations of a classical porous medium.
- (vi) The proposed mathematical model may work well (a) for the fracture aperture thicknesses varying between 100 and 500 microns; (b) for low Reynolds Number; and (c) low initial NAPL saturation.

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