

A review of NAPL source zone remediation efficiency and the mass flux approach

K. Soga^{a,*}, J.W.E. Page^a, T.H. Illangasekare^b

^a Department of Engineering, University of Cambridge, Cambridge, CB2 1PZ, UK

^b AMAX Distinguished Chair of Environmental Science and Engineering, Colorado School of Mines, Environmental Science and Engineering Division, Golden, CO 80303, USA

Available online 27 April 2004

Abstract

A number of previous studies are reviewed to examine the actual reduction of NAPL from source zones and the effectiveness of the specific technique of remediation used at sites under study. It has been shown that complete removal of the NAPL in free phase or residual is not possible due to the complex entrapment architecture of NAPLs at field sites. Consequently, the assessment of remediation efficiency should not be solely based on the reduction of entrapped NAPL mass from source zone. Instead, it should be based on the reduction of risk achieved through the lowering of the concentration of the dissolved constituents emanating from the entrapped NAPL during source zone clean-up. The prediction of the concentration in the plume requires a knowledge of the dissolution of NAPLs in the source zone. Attention is directed to the need for the understanding the mass transfer from entrapped NAPLs in the source zone before and after remediation. In this paper, the current knowledge of mass transfer processes from the non-aqueous phase to the aqueous phase is summarised and the use of mass flux measurements (monitoring the concentration of contaminants in aqueous phase due to source zone NAPL–groundwater mass transfer) is introduced as a potential tool to assess the efficiency of technologies used in source zone remediation. Preliminary results of numerical simulations reveal that factors such as source zone morphology as determined by the heterogeneity of the formation control the post-remediation dissolution behaviour, than the local mass transfer. Thus, accurate site characterization is essential for predicting NAPL dissolution and mass flux relationships as well as for assigning site-specific remediation target values.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Mass flux; Source zone; Remediation efficiency; Risk

1. Introduction

Accidental surface release and improper disposal of petroleum products (e.g. jet fuel, refinery wastes, diesel etc.) and volatile organic solvents are recognised as two of the most widespread causes of groundwater contamination by chemical compounds. In subsurface soil–water environments, these contaminants often persist as a separate phase due to their generally low solubility and hence are termed non-aqueous phase liquids (or NAPLs). NAPLs that are less dense than water, including many petroleum products, are termed light non-aqueous phase liquids (LNAPLs) and these commonly collect and pool at, or above, the water ta-

ble. The other type of NAPL is denser than water (DNAPL) and when spilled, migrates through the unsaturated zone continues on a downward migration through the water table under the influence of gravity into the saturated zone below. Chlorinated solvents used in industrial and manufacturing operations are a common form of this contaminant.

As surface water infiltrates and groundwater flows through the zone where NAPLs are entrapped (the NAPL source zone), small fraction of the NAPL slowly dissolves into the aqueous phase resulting in a dissolved contaminant plume downstream of the source zone as shown in Fig. 1. This can cause pollution of local water supplies and have detrimental effects on both human health and the ecological environment. Consequently, attention has been focused on the identification and characterization of the source zone and the plume, for the assessment of risk posed to the environment and subsequent measures to be taken to limit such

* Corresponding author. Tel.: +44-1223-332713; fax: +44-1223-33913.

E-mail address: ks@eng.cam.ac.uk (K. Soga).

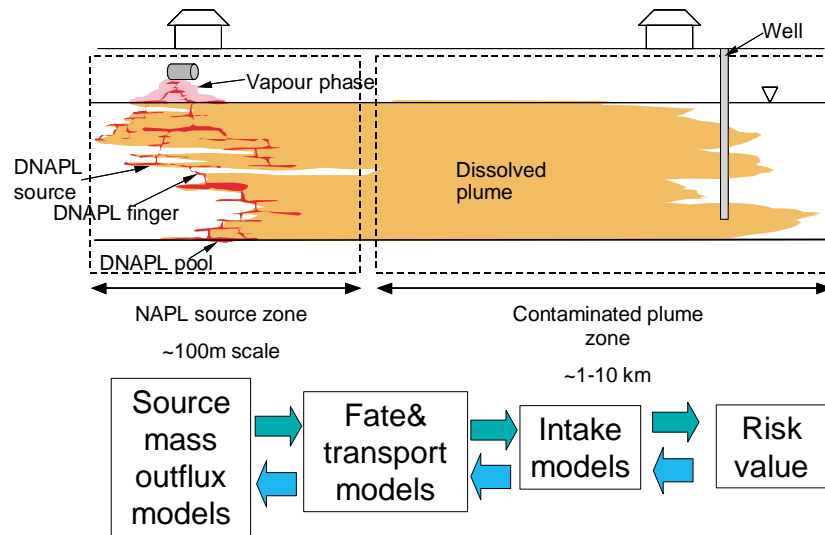


Fig. 1. Source and plume zones and risk evaluation.

effects. Much research is concerned with the development of remediation strategies to either (a) ‘remove’ the pure phase NAPL mass from within the ground (source zone remediation), or (b) ‘control’ or ‘treat’ the plume emanating from the source zone to reduce the concentrations in the groundwater to ‘safe’ levels (plume remediation). This paper focuses on the former approach of source zone remediation.

In this paper, a number of NAPL source zone remediation studies conducted at field sites are reviewed. Attention is focussed on the actual reduction of NAPL source mass and its effect on the downstream plume under conditions that are specific to the site. From this review of case studies, the intention is to demonstrate that it is very difficult or impossible to completely remove the NAPL mass from the source zone of the subsurface due to complex NAPL entrapment conditions, specifically in the case of DNAPLs. Consequently, there is a need to understand and possibly quantify the mass transfer from entrapped NAPL in the source zone into groundwater flowing through the source zone before and after remediation. Fig. 2 shows schematically the conditions that may exist before and after remediation where free phase NAPL is removed. The use of mass flux measurements (the rate of mass generated from the source zone) is introduced as a potential tool for assessing the efficiency of source zone remediation technologies. For this purpose,

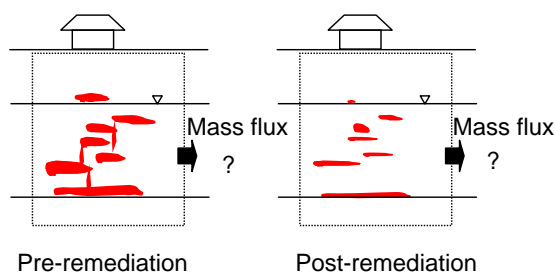


Fig. 2. Mass flux before and after remediation.

factors that control the mass flux emanating from the source zone undergoing remediation are examined. As field data are not adequate to make general conclusions, results from numerical simulations are used to examine this mass flux approach in greater detail.

2. NAPL source zone remediation efficiency

In attempts to completely remove, or at least substantially reduce the source zone NAPL content, a number of remediation technologies and strategies have been designed and employed to varying degrees of success. Initial attempts to remove contamination source zones generally relied on schemes based on pump-and-treat. Pump-and-treat techniques rely on increasing the groundwater flow in the source zone to enhance the dissolution of the NAPL and collection of the contaminated water through a recovery system for external treatment. However, it has been observed that such a method might still take decades or even longer to substantially reduce contamination levels due to the low aqueous solubility of NAPLs and large NAPL/water interfacial tensions [1]. Alternative techniques have therefore been developed. Research examining remediation of pure phase NAPL at various scales ranging from 1D column and 2D tank tests to full-scale field experiments are summarized in this section.

2.1. Chemical flushing

Although many experiments have been conducted using a variety of chemicals (e.g. surfactants, cosolvents, and complex agents) to enhance the solubility of NAPLs and to increase their mobility, there are noticeable differences in remediation efficiencies that are achievable under different experimental conditions.

Zhou and Rhue [2] screened 42 surfactants to examine their efficiency in removing a NAPL by increased solubilization. Using a range of surfactants and their combinations, between 92 and 98% of the PCE was removed from the test area by increasing NAPL solubility. Dwarakanath et al. [3] used homogeneous soil columns to identify anionic surfactants that recovered at least 99% of the contaminant during flooding and concluded sodium sulfosuccinate as one of the most effective surfactants. Earlier experiments by Pennell et al. [4] reported the removal of more than 99% of residual PCE if mobilization was the dominant mechanism. However, concerns have been raised about the dangers posed by re-mobilized NAPL migrating into previously uncontaminated aquifer regions.

Although the above levels of remediation efficiency might initially appear satisfactory, the test environments in the laboratory represented simplified systems that are not representative of much more complex field conditions. Only in very rare cases will a NAPL spill occur under subsurface conditions that can be assumed to be homogeneous; uniform groundwater flow will almost certainly never exist as will be simulated in simple laboratory columns. At actual field sites, the ground is likely to display varying degrees of heterogeneity and groundwater flow velocity.

A laboratory 2D flow-cell study by Oostrom et al. [5] considered the remediation of TCE spilled in a saturated heterogeneous medium using alternating periods of surfactant flushing and pump-and-treat. The NAPL saturations in the soil displayed only small decreases between each treatment period and pooled TCE was determined as the cause for this behaviour. After 3 weeks of pumping, only 60% of the spilled TCE volume was recovered, with the remainder re-mobilized and getting trapped in fine-grained material. In such entrapment conditions, the surfactant may only have limited accessibility to the pure phase NAPL and any remediation process will be restricted. Similar behaviour in the scale of a laboratory flow cell was demonstrated by Lunn and Kueper [6] and Saenton et al. [7].

At the field scale, Holzmer et al. [8] used sodium sulfosuccinate to investigate PCE removal in a shallow, low-permeability sand aquifer beneath a dry-cleaning facility. Although the surfactant-enhanced remediation removed 92% of the pure phase PCE from the relatively high permeability areas of the saturated zone, only 72% of the DNAPL mass was recovered from the entire soil volume that included an aquitard above the permeable zone. A set of field scale cosolvent flushing experiments was conducted by Annable et al. [9] in a hydraulically isolated test cell containing jet fuel and chlorinated solvents. A number of contaminants were identified as special targets, and more than 90% of their volume was removed during the test. However, the total NAPL mass removed from the cell estimated based on the known spill volume was around 75%. Jawitz et al. [10] conducted in situ alcohol flushing in a pilot-scale field test to recover PCE spilled at a dry-cleaning site. Although the PCE concentrations in the groundwater

after flushing were reduced by 92% in two-thirds of the sampling locations, the effectiveness of the flushing for pure phase removal was estimated to be only 62%.

2.2. *In situ chemical oxidation*

In situ chemical oxidation is based on the delivery of chemical oxidants to contaminated media, usually to convert the contaminants to innocuous products. For instance, potassium permanganate facilitates the oxidation of PCE and TCE to chlorides and carbon dioxide. Relatively few studies have explored the effects of chemical oxidation on the degradation of contaminants when present as pure phase NAPL in porous media.

Potassium permanganate was used by Schnarr et al. [11] to remediate PCE and TCE in both laboratory and controlled field tests. These two different environments highlight the limitations and difficulties encountered when remediation is conducted under heterogeneous field conditions. In homogeneous column experiments with uniform DNAPL saturation, recoveries ranged from 70 to 99%. The field tests were conducted at the Borden Canadian Forces base, a medium and fine-grained sandy aquifer with horizontal bedding features overlying a clay aquitard. When an isolated homogeneous source was created, 91% recovery of chloride ions was recorded. However, for a heterogeneous source, the mass recovery approached only 62% and this is largely due to the local geological heterogeneity and associated DNAPL distribution.

DNAPL source zones within low permeability media represent an even greater remediation challenge due to the poor access and strong mass transfer limitations. Siegrist et al. [12] considered a method of emplacing horizontal fracture zones filled with potassium permanganate (KMnO_4) in a TCE-contaminated field. The method showed remediation efficiencies of up to 99% for high localized concentrations (0.5–1.2 mg TCE/g soil), but after ten months, the average amount of TCE removed from the whole test site was 70% by mass. This inefficiency is mainly due to limited and inaccurate fracturing and restricted DNAPL-oxidant contact.

2.3. *Gas and steam treatment*

In situ air sparging is used to remove volatile organic compounds from both vadose and saturated soil zones of the subsurface by volatilisation. Braida and Ong [13] conducted a set of column experiments to investigate the remediation of VOC-contaminated soils. The observed mass removal rates ranged from 80 to 98%. However, the 1D setting of their experiments using only a single air channel is a very simplified and unrealistic representation of the flow and sizes of air channel encountered at the field-scale under heterogeneous conditions.

In another laboratory study, Rogers and Ong [14] used air sparging to study benzene removal from packed beds of three different-sized porous media placed in a small tank.

The coarser media were found to allow the greatest mass removal, but the efficiency was only 16.2%, and this decreased to just 7.6% for the finer-grained material. Due to the strong positive correlation between benzene removal rate and mean particle size, this technique will have variable degrees of effectiveness for highly heterogeneous aquifers. Waduge et al. [15] conducted soil tank experiments of air sparging remediation of a toluene source entrapped in various heterogeneous soil configurations. Removal rates ranged from 77 to 90% depending on the entrapment condition.

Limitations with the use of field scale air sparging were encountered by Benner et al. [16]. The field area was on the southern shore of Lake Michigan at a site that stored non-halogenated solvents including toluene, ethylbenzene and xylenes. Heterogeneity in the ground was characterized as peat and marl lenses within a coarsening-downwards sand sequence. At the end of remediation, microbial degradation had removed 23% by weight of the initial organic chemical mass and physical stripping was responsible for removing less than 6%. Thus, only 29% of the total NAPL mass was eliminated.

Thermal treatment technologies are also emerging as potential remediation techniques. Udell and McCarter [17] conducted 1D tests of pentachlorophenol (PCP) removal from soil using steam and recovered more than 80% by mass. Steam injection at high pressure was also used by Hadim et al. [18] to remove heating oil from contaminated soil. It was calculated that 86% of the oil had been successfully extracted from the ground. A study by Tse et al. [19] showed

that the desorption rate and water equilibrium concentrations of PCP could be enhanced by thermal treatment. The field test area was an old PCP manufacturing plant with soil hydraulic conductivities and total organic compound contents varying greatly with depth. After 6 months of steam injection and groundwater sampling, the PCP mass reduction in the soil was found to be in the range of 65.4–76.9%, with limited removal from the silty sand layers.

2.4. Summary

The source zone remediation studies used in this paper have been chosen from a much larger research database and the salient data has been plotted in Figs. 3 and 4. In Fig. 3, the percentage of maximum pure phase removal is plotted against the estimated volume of soils in source zone of the test area. The data has been selected from studies conducted at different experimental scales, ranging from 1D column experiments to full-scale 3D field tests. The efficiency of removal of the mass associated with the extent of the source zone is clearly displayed. The degree of source zone NAPL mass removal is limited to a small range of very high values for the reported column experiments. However, a wider range of efficiencies exists for field-scale remediation efforts as well as a decrease in the maximum possible remediation levels that are achieved when moving from the 1D column to the 3D field situations. The range of achievable source removal efficiencies (or uncertainty of mass removal) increases substantially when the scale gets larger. This suggests that

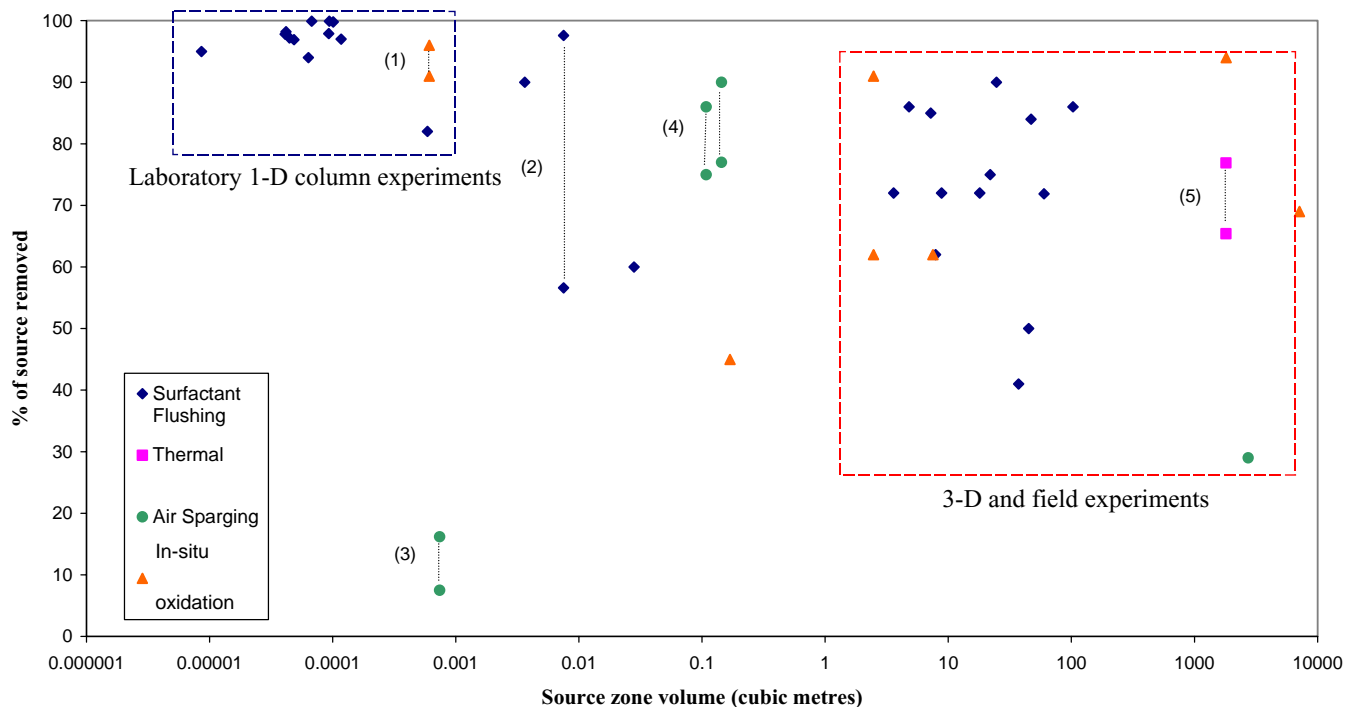


Fig. 3. Scale effect of NAPL removal efficiency of various source zone remedial technologies. Data from: [9, 16, 13, 46, 47, 48, 49, 50, 8, 51, 52, 10, 53, 22, 6(2), 24, 54, 55, 4, 56, 14(3), 57, 11(1), 19(5), 15(4), 58, 2]. References followed by a number in brackets represent experiments where a range of remediation efficiencies were obtained.

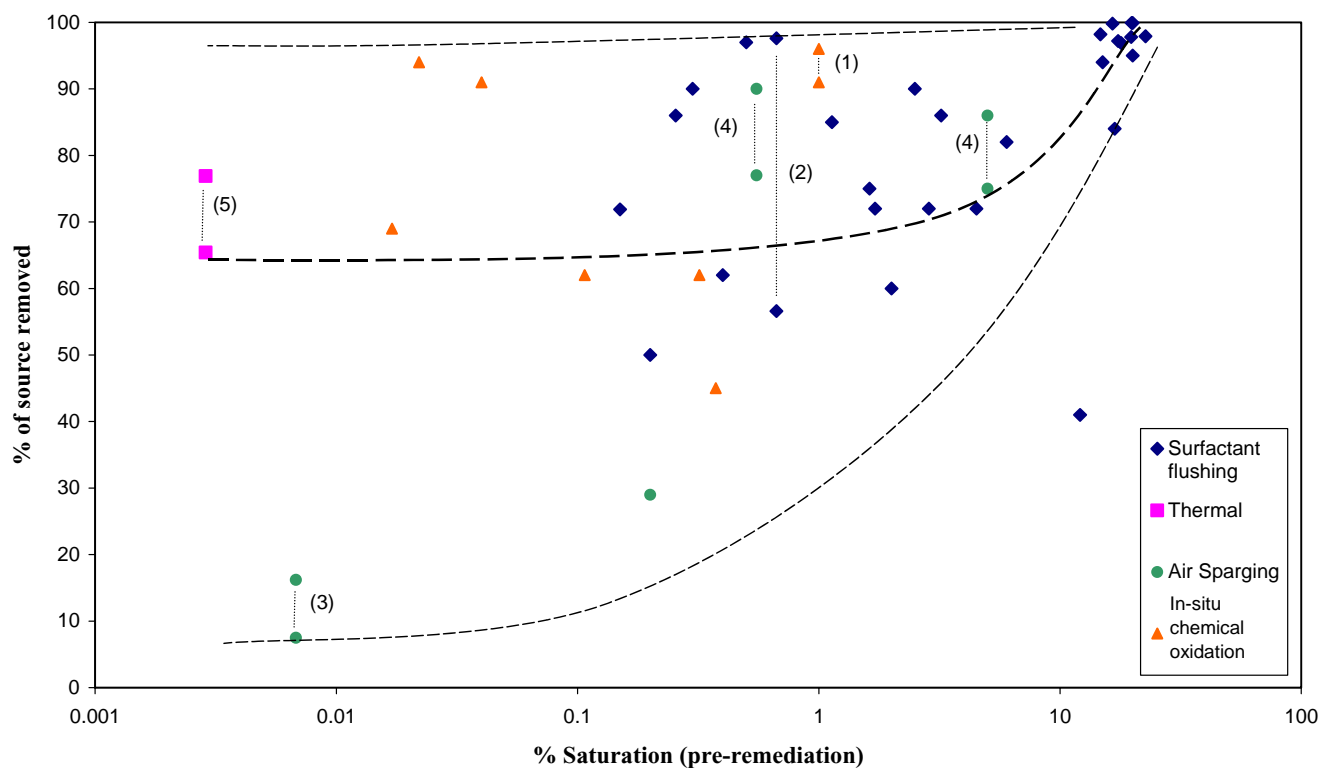


Fig. 4. Effect of initial NAPL saturation on NAPL removal efficiency.

there exists a significant uncertainty in upscaling from laboratory to actual field conditions.

In Fig. 4, the measured removal efficiency is correlated with the average source zone saturation prior to the commencement of any remediation efforts. By plotting a best-fit line through all the data points from different remediation technologies, it is clear that the source removal efficiency decreases as the average pre-remediation saturation value decreases. In fact, for typical field scale source saturations, on the average only 60% of the DNAPL mass/volume is removed. Furthermore, the degree of scatter in the data increases as the initial source zone saturation value becomes smaller. This highlights the limited and highly variable efficiencies of current source zone remediation techniques applied in the field scale.

3. The mass flux approach

3.1. Understanding mass flux from NAPL source

Based on the data from case studies presented in the previous section, it can be argued that the percentage of original NAPL mass removed (Fig. 3) may not be a good indicator of the efficiency of the technologies because the average pre-remediation NAPL saturations can be variable, as shown in Fig. 4. However, it is clear that high remediation efficiencies are achieved in 1D, homogeneous, well-characterized, uniform flow fields. At the field scale, such characteristics are

very rarely encountered and it is likely that a significant fraction of the contamination will still remain after treatment.

Accepting this field scale limitation, it is therefore necessary to consider what is an acceptable remediation level and more importantly, from the risk assessment terms, is the site 'safe' after source zone remediation has been performed? The effectiveness of remediation technologies should be evaluated by the risk reduction that is achieved by their application [20]. Therefore, it is proposed that remediation effectiveness should not be assessed in terms of the amount of NAPL removed from the source zone, but by measurement of the concentrations in the solute plume generated by mass transfer within the NAPL source zone.

The fundamental physical process for determining both pre- and post-remediation status of the solute plume is the mass transfer (both temporal and spatial) from the entrapped NAPL source. Therefore, for a given groundwater flow condition, the mass flux (i.e. the release rate of contaminant mass due to transfer from NAPL to the aqueous phase) leaving the source after remediation will determine whether the source is still a threat to groundwater. We call this the *mass flux-based remediation assessment method*. For instance, a technology might remove 85% of the source zone mass, but will the remaining 15% be enough to generate high aqueous phase NAPL concentrations and plumes identical to those from 100% source mass? If so, then the remediation has failed to achieve the desired goal of reducing risk by decreasing the concentrations in the downstream plume. The same hypothesis was presented and tested by Sale and McWhorter

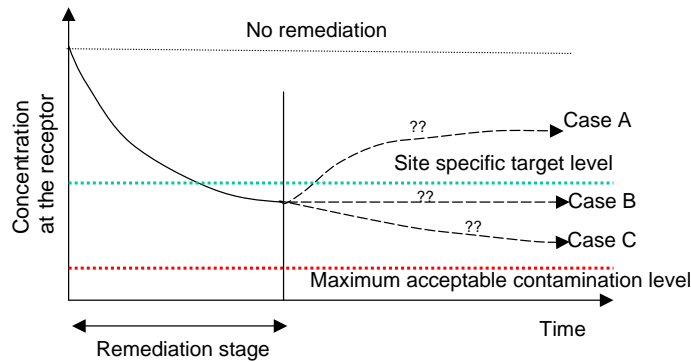


Fig. 5. Concentrations before and after remediation.

[21] for a hypothetical situation involving DNAPL pools in a uniform flow field. Alternatively, a 20% reduction in NAPL mass could be sufficient to change its subsurface distribution into a condition of significantly reduced mass transfer (such as a greatly reduced NAPL surface area) with a corresponding reduction in receptor risk.

Fig. 5 shows a schematic diagram of the change in concentration during and after source zone remediation. The concentration is measured at a downstream location (receptor), where the risk assessment is to be performed. For the change in concentration after remediation, three scenarios can be considered as shown in the figure; the concentration (i) increases (Case A), (ii) stays constant (Case B) or (iii) decreases (Case C). Case C is the most successful remediation method because the aqueous concentration continues to reduce with time towards the maximum acceptable concentration level. For Case A, although receptor concentrations after remediation are reduced, remediation will eventually fail. This could occur if the remediation method temporarily reduces the solute plume volume. How-

ever, the remaining pure phase source continues to generate dissolved contaminant mass and eventually its aqueous concentration starts to increase again (Scenario 1 in Fig. 6). On the other hand, Case C can occur if the source has been reduced to a volume that is small enough for the mass flux generated to be small. Therefore, in order to assess the effectiveness of remedial technologies using the mass flux approach, it is necessary to understand the mass transfer processes from the NAPL remaining after source zone remediation.

In order to measure the impacts of source treatment, or to understand the real risks posed by a residual source, it is essential to have accurate estimates of mass release from a source zone before and after treatment. The mass release rate can change as a function of time, and a key practical question is to understand how much reduction in time or monitoring of the system can be achieved by a source removal activity. Furthermore, there is a need to predict the future mass flux released from the source zone, which will allow site-specific remediation targets to be set.

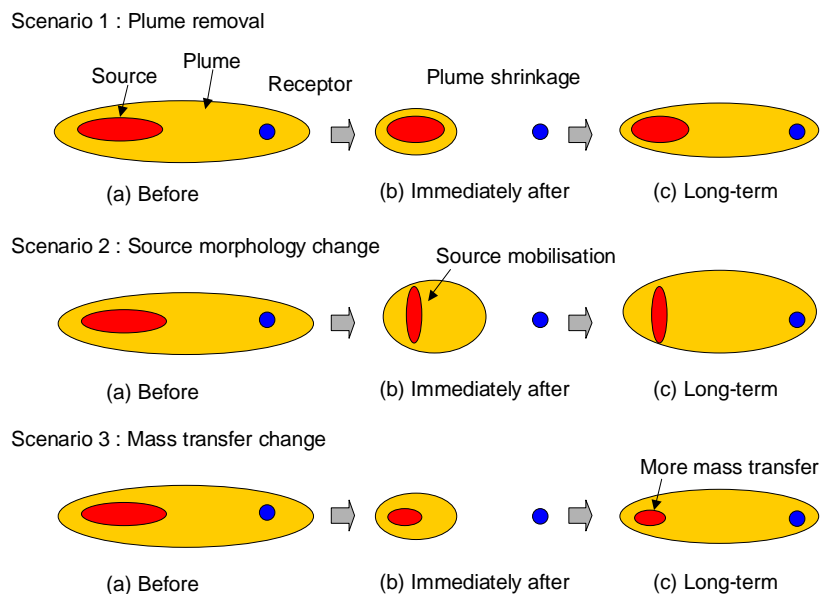


Fig. 6. Possible scenarios of Case A in Fig. 5.

In recent years, monitored natural attenuation (MNA) has become widely used for NAPL contaminated sites. There is little doubt that MNA will be used for many sites after aggressive source zone treatment. However, there are questions regarding the conditions under which MNA can be used with confidence. Combining temporal mass flux evaluation with estimates of natural attenuation capacity can allow us to develop meaningful risk-based source-plume management strategies. Hence, integrated modeling and measurement of both the mass flux from the post-remediation source and natural attenuation capacity of the subsurface environment will be essential.

3.2. Effect of source zone remediation activities on mass flux

Source zone remediation can change the NAPL source morphology, composition, and the chemical and biological environment. A possible scenario for Case A in Fig. 5 is source zone volume reduction combined with source zone spreading as shown as Scenario 2 in Fig. 6. The increase in the NAPL surface area available for mass transfer would potentially cause a gradual increase in post-remediation mass flux. Chemical, physical and biological changes of the NAPL properties followed by remedial actions (see Scenario 3 in Fig. 6) may increase or decrease the mass transfer rate from any NAPL source. Unfortunately, little is known about the influence of source zone treatment on mass flux and source zone architecture. Such information is critical for the evaluation of potential risk reduction and assessing the benefits of applying a particular remediation technology.

For certain chemical agents (cosolvents and surfactants), the interfacial tension between NAPL and the aqueous phase will decrease and NAPL can remobilise and move in the direction of gravity during the flushing stage [4]. Using a horizontally placed soil column, Kulasoorya et al. [22] compared the mass flux from a PCE source in a residual condition to that from a pooled condition created in the same column by injecting surfactant and mobilising the PCE. The mass flux reduced to half as the PCE mobilised and pooled on the bottom of the column, indicating the positive effect of mass flux reduction by PCE pooling on top of an impermeable boundary. Conversely, in tank experiments with a DNAPL spill in a stochastically heterogeneous soil model, Soga et al. [23] demonstrated the negative effect of increasing mass flux. DNAPL removal created a different end-point entrapment morphology (lower saturation zones with increased relative water permeability), resulting in a greater NAPL-water contact area generating aqueous phase concentrations that increased with time in previously uncontaminated areas.

Addition of chemical oxidants can cause the production of gases or precipitates that may reduce permeability or limit the delivery and mixing of the reagents. For example, MacKinnon and Thomson [24] found from a soil tank experiment that the formation and deposition of MnO_2 precipitates (produced during in situ reduction of chlorinated

solvents using permanganate) decreased the mass transfer of PCE into the aqueous phase. This is because MnO_2 deposits within the model aquifer decreased the velocity of water directly above the PCE pool and hence the overall mass transfer from the remaining PCE pool. They concluded that this limits the progress of pool oxidation during oxidant flushing and hence the formation of a PCE plume after treatment is inhibited. The implications of these findings are two-fold; MnO_2 precipitation may limit the process of pool oxidation, but also, from a positive perspective, it may inhibit the subsequent formation of a PCE plume. Furthermore, the oxidative environment can restrict bacterial growth and activity, creating unfavourable conditions for natural attenuation.

Remediation can impact water quality parameters such as the dissolved oxygen content and concentrations of soluble metals, pH, and dissolved solids. The biological environment in the source zone after remediation can affect the mass transfer rate. It is often believed that the source zone is likely to be toxic to dehalogenating bacteria. However, Seagren et al. [25] suggested that biodegradation of NAPL should increase the NAPL mass transfer rate because it can act as a reaction sink to increase the concentration gradient. Yang and McCarty [26] examined the factors affecting the dehalogenation of high concentrations of PCE using an anaerobic mixed culture, containing four groups of microorganisms. They showed that the PCE dissolution rate was five times greater than what could occur in the absence of biological dehalogenation, as predicted by the models of Seagren et al. [25]. Soil heterogeneities and DNAPL morphologies may also govern the extent and ability of microorganisms to access and degrade DNAPL constituents. Rogers and Logan [27] report that the presence of NAPL creates immobile water zones where bacteria retention decreases due to reduced collisions between bacteria and soil particles. This can possibly affect the mass transfer rate of DNAPL in natural formations.

4. Assessing mass flux from NAPL source zone in the field

4.1. Equilibrium and rate-limited mass transfer

The mass flux coming out from the 'remediated' or 'treated' source zone must be quantified for accurate risk assessment. Hence, the design and assessment of source zone removal technologies should focus on the ability of a specific technology to reduce the NAPL amount and morphology to a condition suitable for the mass flux observed downstream of the entrapment zone to meet an acceptable value. It is important to note that this value does not refer to a specific value of NAPL saturation, but a site-specific effective saturation defined by the state of the NAPL (controlled by the in situ conditions), and the entrapment morphology (determined by the site heterogeneity and spill condition).

The solubility limit of a NAPL at equilibrium with the aqueous phase represents an upper boundary for the aqueous phase contaminant concentration. This assumes that water leaving the region of the NAPL has a dissolved compound concentration at its maximum solubility (C_s) regardless of flow velocity and/or contact time between the mobile water and the immobile NAPL. However, field data indicates that contaminant concentrations in groundwater are lower than their corresponding equilibrium values [28,29]. Experimental investigations have shown that dissolution process is rate-limited [30–32]. This mass transfer \dot{M} ($\text{MT}^{-1}\text{L}^{-3}$) is often expressed by a linear model:

$$\dot{M} = K(C_s - C) \quad (1)$$

where C_s (ML^{-3}) is the solubility limit (equilibrium mass transfer) and C (ML^{-3}) is the current bulk aqueous concentration of the contaminant of interest. K (T^{-1}) is the overall mass transfer rate coefficient and is often related to the molecular diffusion coefficient and the interfacial area between NAPL and aqueous phases based on a single film model [30].

A variety of phenomenological mass transfer models based on laboratory column experiments are available and details of these correlations are widely cited in the literature [30–34]. The results of these studies highlight the ‘inadequacy of the local equilibrium approach to predict transient NAPL dissolution in column scale experiments’ [32]. Saba and Illangasekare [35] presented an up-scalable phenomenological mass transfer model for 2D flow fields under rate limited conditions and demonstrated the possible errors that can result from the use of 2D model to simulate dissolution in 2D flow fields.

4.2. Effect of NAPL morphology

Unstable fingering, preferential channelling and subsurface geological heterogeneities control the complex spatial distribution of NAPLs after a spill. The final NAPL distribution is present as zones of entrapment at low saturation (residual, ganglia and blobs) and high saturation (pools at permeability barriers and macro-scale entrapment zones resulting from capillary barriers). The mass outflux from the source zone is expected to be greatly influenced by the NAPL morphology due to complex migration and entrapment patterns and possible flow bypass around the pooled sources.

In contrast to the studies presented in the previous section investigating the mass transfer process from a uniformly distributed NAPL source under 2D flow conditions, studies by Johnson and Pankow [1] and Chrysikopoulos et al. [36] focused on the dissolution process from a 3D pooled NAPL. They measured the increase in boundary layer thickness from the upstream to downstream positions along the pool and illustrated the differences in dissolution behaviour depending on NAPL entrapment conditions (pool versus residual). Sale and McWhorter [21] developed a simple mathematical technique to assess mass transfer from NAPL

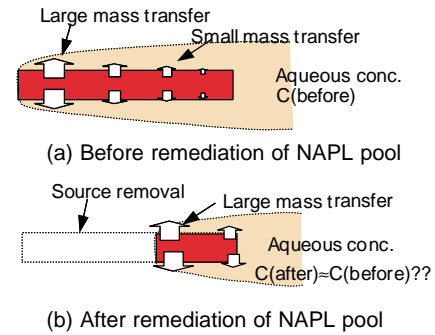


Fig. 7. Mass transfer from NAPL pool before and after remediation.

sources of different geometries. Assuming uniform groundwater flow through the source zone, they computed the mass transfer rate for three different geometries and demonstrated that the mass transfer of pooled NAPL occurs primarily at the leading edges as illustrated in Fig. 7 and is inhibited by interference from the upstream portion of the source for the remaining pool volume. Based on this, they concluded that that near-complete source removal is required to achieve meaningful and long-term improvements in groundwater quality.

4.3. Effect of field heterogeneity

Powers et al. [37] and Soerens et al. [38] used two-domain models to incorporate the flow bypassing effect and showed that much of the apparent non-equilibrium dissolution can be explained by irregular NAPL distribution and flow heterogeneity. This is generally regarded as one of the main failure mechanisms of pump-and-treat operations [39] and similar behavior has been observed during air-sparging [15].

Brusseau et al. [40] conducted intermediate-scale dissolution experiments and correlated quantitative 3D mathematical models of varying complexity to their results. They concluded that dissolution behaviour is controlled by larger scale factors such as non-uniform immiscible-liquid distribution, permeability variability, and sampling-associated dilution, and that local-scale mass transfer processes are generally of secondary importance. If flow bypassing is dominant and mass transfer rate coefficients can decrease with time generating lower than expected aqueous phase concentrations, it is of primary importance to have some understanding of the effects of heterogeneity and degree of flow bypassing that will occur. By quantifying the heterogeneity of the aquifer hydraulic properties and NAPL distribution, it is possible to predict non-equilibrium mass transfer as a lumped process in the source zone even if equilibrium mass transfer occurs at the local scale in the vicinity of the NAPL pools.

The conclusions of Sale and McWhorter [21] and Brusseau et al. [40] are especially relevant to field scale spills, where NAPL distribution is very much determined by the heterogeneity of the sub-surface. As field scale flow rates are often very low (i.e. 0.5 m per day represents an

upper bound), close to equilibrium NAPL concentrations can be expected at the local scale. Therefore, at the field scale, it is very likely that heterogeneity and NAPL distribution effects are dominant over local mass transfer effects.

4.4. Field scale simulations of mass flux

Despite all the research that has been reviewed here, a universally applicable theory for NAPL dissolution in field scale environments has not yet been presented. Research into the upscaling issue is still in the early stages. In order to demonstrate the effects of soil heterogeneity and complex NAPL entrapment conditions on mass flux generated from the source zone, multiphase flow-mass transfer modelling was performed. The modeling of the mass-flux relationship was achieved using a finite-difference multi-component simulator, UTCHEM, developed at the University of Texas, Austin [41].

The source zone was modeled as a 2D, rectangular test area 50 m long and 10 m thick with the aquifer volume divided into 10,000 blocks (each block being 0.5 m long and 0.1 m deep). 2D conditions were used in simulations primarily due to limitations in computational speed. Therefore the findings cannot be directly extrapolated to the actual field conditions where flow field is 3D. However, the results from this preliminary study demonstrate the potential use of the mass flux approach for remediation assessment.

Aquifer systems typically display stochastically varying soil hydraulic properties when formed by depositional processes [42]. Many studies (e.g. Woodbury and Sudicky [43]) have shown that the logarithm of the hydraulic conductivity value is normally distributed. The synthetic aquifer created for numerical simulations in this study assumes log-normal distribution of hydraulic conductivity. The horizontal and vertical correlation lengths of the soil properties in the test area were kept constant for each simulation. The stochastic parameters used in this study were (i) mean $\ln[k$ (in millidarcies)] = 9.2, (ii) variance ($\sigma_{\ln(k)}$) = 0.6, (iii) horizontal correlation length = 5.1 m and (iv) vertical correlation length = 0.21 m. Multiple permeability fields (or realisations) were generated using this set of parameters using the Turning Bands technique and two such realisations are shown in Fig. 8(a). A similar numerical approach was taken by Kueper and Frind [44], Dekker and Abriola [45] and Saenton et al., [7].

Tetrachloroethylene (PCE) was released into the saturated zone from a point source at the top of the test aquifer 15 m from the upstream boundary. The release rate was 0.005 m³ per day for a continuous period of 100 days. The spilled PCE was then allowed to migrate downwards into the aquifer and redistribute itself for 900 days under natural hydraulic conditions. At the end of this spill stage, the PCE is distributed both as pools and at residual saturation as shown in Fig. 8(b).

Each system was then subjected to natural groundwater flow conditions of 0.1 and 1 m per day, resulting in dissolved plumes down-gradient of the DNAPL source as shown in

Fig. 8(c). These dissolution stages of the modelling were each allowed to run for a time period of 3000 days. Various mass transfer models were applied to examine the effect of local scale mass transfer process and they include the local equilibrium model as well as the constant mass transfer rate coefficient model (with K values in Eq. (1) ranging from 100 to 1000 per day).

Using the dissolution stage output data, the temporal mass flux of dissolved DNAPL out of the source zone (i.e. at the downstream boundary of the test aquifer domain) can be computed. The evolution of mass flux with time is plotted in Fig. 9 for both 0.1 and 1.0 m per day flow conditions in Realisation 3. The initial increase is due to the delay in plume reaching to the source zone boundary, but then the mass flux decreases with time as the source depletes. The numerical results showed that the effect of different local scale mass transfer models ($K = 100$ or 1000 per day) was negligible for the given groundwater flow rates; the flow was slow enough for the mass transfer to be very close to the equilibrium condition (Eqbm in Fig. 9). A phenomenological model similar to the one proposed by Imhoff et al. [33] was also used and the result ($K = \text{var}$ in Fig. 9) was almost identical to those using the other mass transfer models. It should be noted that the overall mass transfer did become rate-limited when the flow rate was fast (e.g. 10 m per day) and the mass transfer rate coefficient value was small (e.g. $K = 1$ per day). However, this was considered to be out of range of typical field conditions.

Fig. 10 shows the evolution of mass flux with time for the 0.1 m per day flow condition simulations of the five realisations. Despite all five permeability fields possessing the same mean, variance and correlation length parameters, large variation in mass flux is observed due to different NAPL entrapment conditions. These numerical simulations show that heterogeneity and NAPL distribution effects are dominant over local mass transfer effects at the field scale for the ground water velocities examined.

In order to ascertain the effect of rate-limited behaviour, a non-dimensional source zone exit mass flux, \dot{M}_{ND} was used:

$$\dot{M}_{\text{ND}} = \frac{\dot{M}_x}{C_s \bar{v} A} \quad (2)$$

where \dot{M}_x is the computed mass flux at a given time, C_s the solubility limit, \bar{v} the mean Darcy's velocity, and A the cross sectional area of the downstream source zone boundary. The closer this number is to one, the overall mass transfer of the system is in equilibrium.

In Fig. 11, the computed normalized mass flux values are plotted as a function of PCE volume remained in the source zone. Data is presented from six different aquifer realisations and two ground water flow velocities. The data from the 1 m per day flow condition shows much larger decrease in PCE volume at the end of 3000 days compared to the data from the 0.1 m per day flow condition due to larger quantity of water available for dissolution. However, for a given PCE volume,

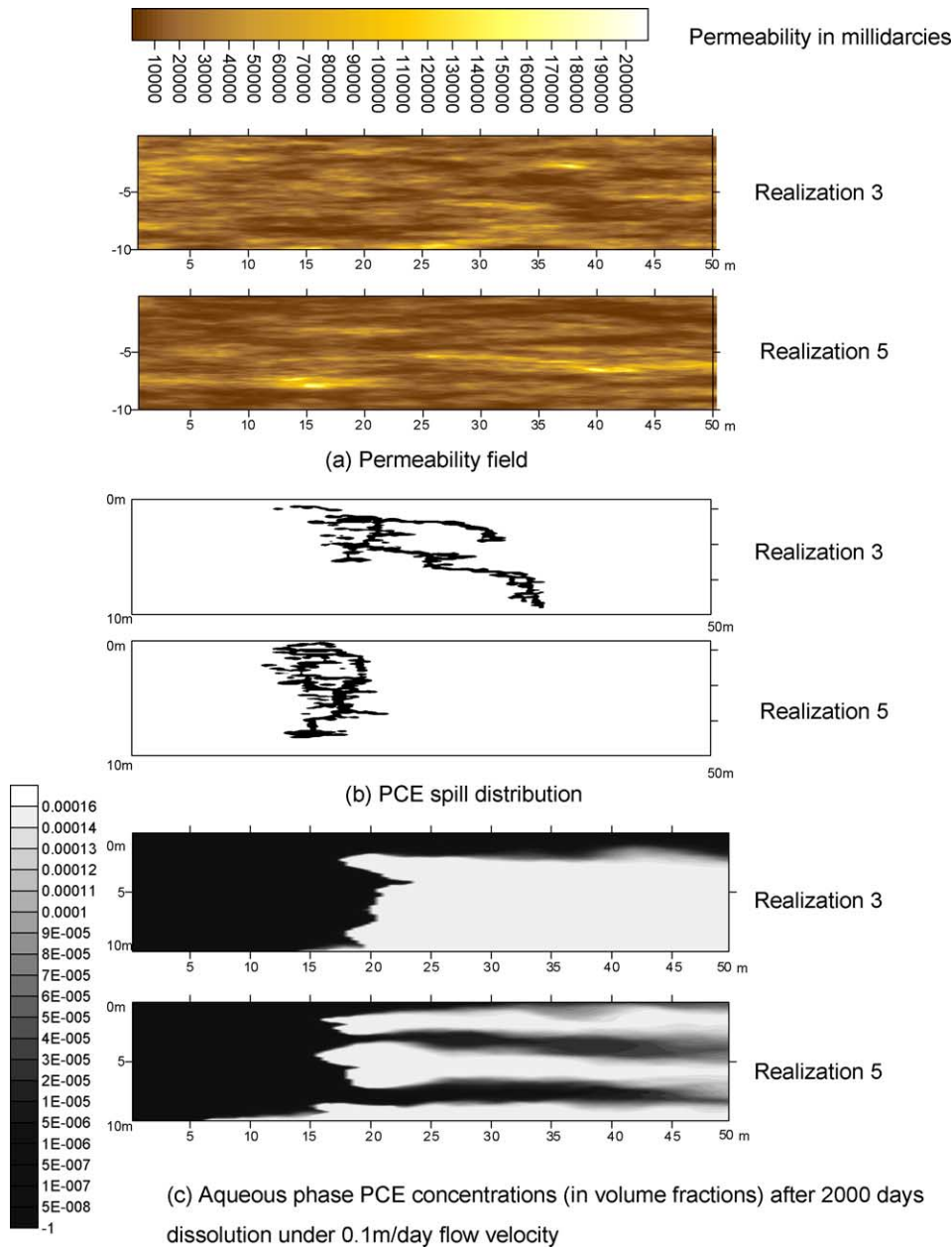


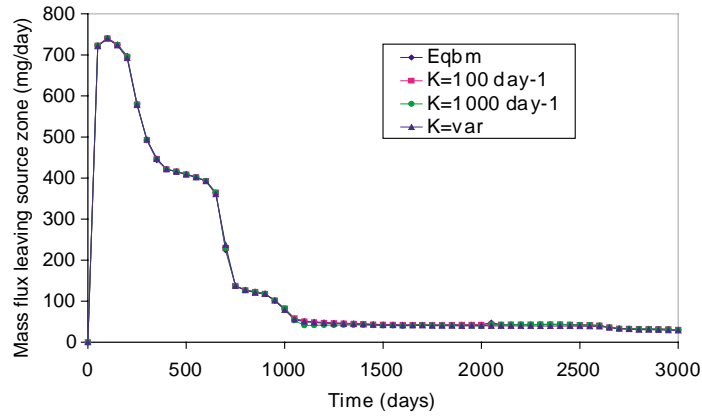
Fig. 8. Simulations of PCE spill and its dissolution in heterogeneous soil models for a source zone 50 m long and 10 m deep.

the normalised mass flux of each realisation is independent of ground water flow velocity.

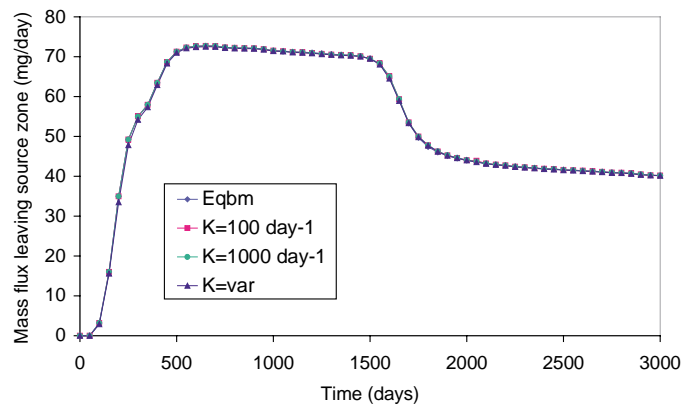
Some of the dissolution profiles in Fig. 11 display a single 'step-like' profile of rapid mass flux decrease with small PCE volume loss followed by a much more gradual, almost constant period of dissolution and then a more rapid decrease to low flux values (such as Realisation 1). The initially high and relatively constant mass flux during natural dissolution represents the dissolution of the residual PCE due to water flow through the low saturation DNAPL. When all of this has been removed from the source zone (approximately 175 l for Realisation 1 after about 400 days), only pooled PCE remains. Pools have very low mass transfer rates so the

mass flux decreases with only a small loss of PCE volume. Subsequent dissolution continues by advancing along the length of the pool with a near constant mass flux over a long period of time. A more complicated, 'step-like' pattern can be identified for Realisation 5 and this illustrates the effect of multiple pools as shown in Fig. 8. Individual pools will have different mass transfer rates and disappear at different times.

The level of remediation was modelled by uniform and blanket reductions in the amount of PCE present in the aquifer zone. Different levels of remediation were modelled by 0 (no remediation), 70, 90, 95 and 99 PCE volume removal. Hence, the spatial distribution of NAPL is the same,



(a) Flow velocity = 1 m/day



(b) Flow velocity = 0.1 m/day

Fig. 9. Computed mass flux with time for different mass transfer models. Note: all four data sets in each figure directly overlie each other.

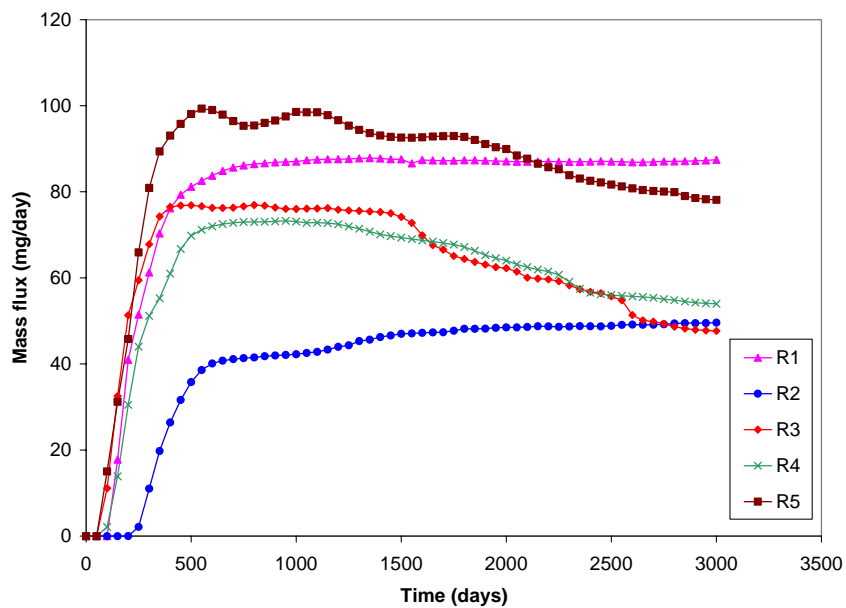


Fig. 10. Evolution of mass out flux with time for five realisations (0.1 m per day).

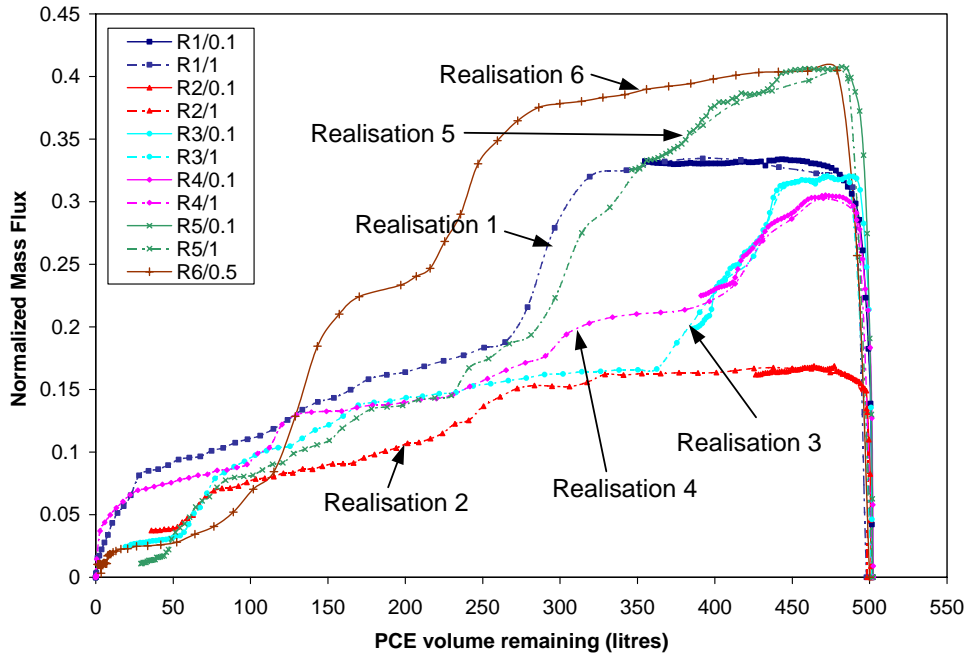


Fig. 11. Computed normalised mass out flux vs. PCE volume for six different realizations (RX/Y, where X is the realization number and Y is the average ground water velocity in m per day).

but the overall NAPL saturation is small. It should be noted that this uniform reduction is for demonstration purposes; the actual process of source zone remediation may change the characteristics of the NAPL entrapment condition.

Fig. 12 shows the dissolution paths of PCE remaining after various levels of remediation for Realization 6. The comparison between the post-remediation curves and the natural dissolution curve at the equivalent PCE volume shows the natural dissolution flux is small, whereas the post-remediation dissolution profiles are significantly greater. This disparity is greatest when the natural dissolu-

tion generates low mass flux values with significant PCE still present as pools. The spatial distribution of PCE in the remediation simulation is the same as that in the original spill. For the given volume of PCE left in the model, a much larger contact area between NAPL and ground water is present in the remediation simulation than in the natural dissolution curve. Hence, the dissolution curve seems to have a strong relationship to the DNAPL morphology in the source zone.

The end result of remediation will always contain some disparity away from the ideal (natural dissolution) condition and it is this variability that can be responsible for the

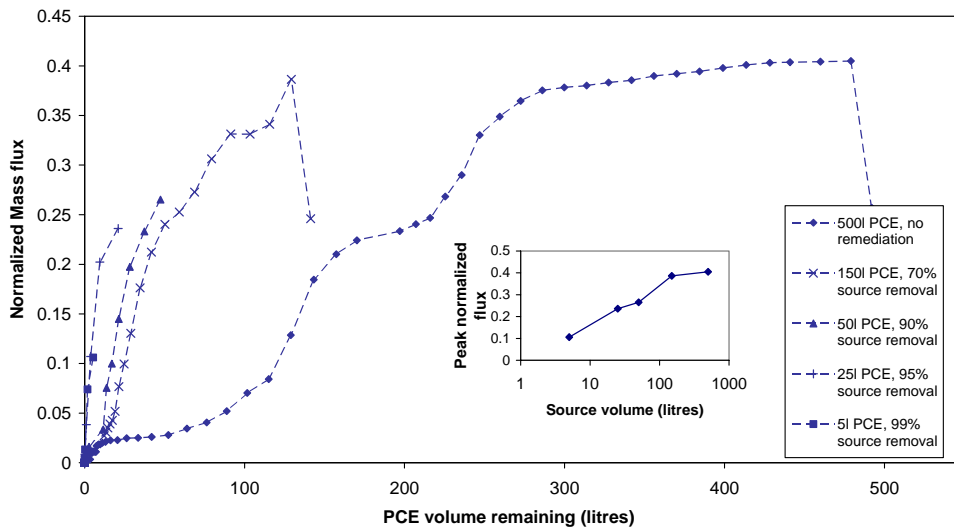


Fig. 12. Computed normalised mass out flux vs. PCE volume for various levels of remediation. The insert figure shows the peak normalized mass flux vs. the initial PCE volume determined from various level of original PCE volume of 500l.

elevated post-remediation profiles. In fact, the peak mass flux leaving the source zone after 70% PCE volume removal is of almost identical magnitude to that when no remediation strategies have been implemented. Thus, the change in NAPL distribution during dissolution has a greater influence on reducing PCE mass flux than the computed DNAPL volume reductions used to represent remediation. The data shown in the insert diagram of Fig. 12 suggests that at least 90% reduction in contaminant volume is required for any significant reduction in the post-remediation peak mass flux levels. Again, this highlights that the morphological distribution of NAPL is of primary importance compared to the actual NAPL volume. Accurate site characterisation is therefore essential for understanding the NAPL dissolution and associated mass flux relationships before any site-specific target values can be assigned or remediation technologies implemented.

5. Conclusions

Growth of the contaminated plume poses a significant threat to the groundwater system and is largely controlled by the rate of mass transfer and generation of aqueous phase contaminant concentrations in the source zone. Source removal efficiencies currently obtainable in the field are limited to about 60–70% and therefore there are significant uncertainties about the value of source zone remediation. That is, we do not know how well they will work and how they can be optimised. There is a need to define appropriate methods that can measure or define the “success” of such efforts (i.e. performance assessment). It is proposed that NAPL mass flux values can be used to assess and monitor remediation efficiency, to predict future site-specific behaviour, and to identify remediation targets. The design and assessment of source zone removal technologies should focus on the ability of a specific technology to reduce NAPL saturation to an acceptable condition so that the mass flux observed downstream of an entrapment zone meets an acceptable value.

After source zone remediation, the solute plume contaminant concentrations have typically been reduced to a level suitable for biological activities to naturally attenuate the contaminant in a more suitable environment than the pre-remediation condition. Source zone management strategies can be based on the combined mass flux approach together with estimates of natural attenuation capacity. Field scale simulations of dissolution processes from complex NAPL entrapment conditions show that an understanding of soil heterogeneity and initial NAPL morphology is essential for making field predictions based on mass flux and dissolution data. The results suggest that the dissolution curve seems to have a strong relationship to the DNAPL morphology in the source zone after remediation.

The impacts (positive or negative) of source zone remediation are highly dependent on the complex interactions between pre-treatment environmental conditions and treat-

ment process designs. There is a need to have sufficient understanding or guidance available to adequately predict and monitor these potential side effects. For successful source zone remediation, there is a need to evaluate (i) the type and duration of NAPL source removal technology, (ii) soil heterogeneities that control the local groundwater velocity, (iii) NAPL composition and morphology changes during remediation and (iv) contaminant attenuation downstream of the NAPL entrapment zone. The remediation target should be a site-specific, effective saturation defined by the state of the NAPL (as transformed by the in-situ conditions) and its entrapment morphology (as determined by the site heterogeneity and spill condition).

Acknowledgements

The work is partially supported by the UK Engineering and Physical Sciences Research Council (EPSRC) and is part of collaborative research between the University of Cambridge and the Colorado School of Mines under the US SERDP (The Strategic Environmental Research and Development Program).

References

- [1] R.L. Johnson, J.F. Pankow, Dissolution of dense chlorinated solvents into groundwater: 2. Source functions for pools of solvents, *Environ. Sci. Technol.* 26 (1992) 896–901.
- [2] M. Zhou, R.D. Rhue, Screening commercial surfactants suitable for remediating DNAPL source zones by solubilization, *Environ. Sci. Technol.* 34 (2000) 1985–1990.
- [3] V. Dwarakanath, K. Kostarelos, G.A. Pope, D. Shotts, H.W. Wade, Anionic surfactant remediation of soil columns contaminated by nonaqueous phase liquids, *J. Contam. Hydrol.* 38 (1999) 465–488.
- [4] K.D. Pennell, M. Jin, L.M. Abriola, G.A. Pope, Surfactant-enhanced remediation of soil columns contaminated by residual tetrachloroethylene, *J. Contam. Hydrol.* 16 (1994) 35–53.
- [5] M. Ostrom, C. Hofstee, R.C. Walker, J.H. Dane, Movement and remediation of TCE in a saturated heterogeneous porous medium 1: Spill behaviour and initial Dissolution, *J. Contam. Hydrol.* 37 (1999) 159–197.
- [6] S.R.D. Lunn, B.H. Kueper, Risk reduction during chemical flooding: preconditioning DNAPL density in-situ prior to recovery by miscible displacement, *Environ. Sci. Technol.* 33 (1999) 1703–1708.
- [7] S. Saenton, T.H. Illangasekare, K. Soga, T. Saba, T. Effects of source zone heterogeneity on surfactant enhanced NAPL dissolution and resulting remediation end-points, *J. Contam. Hydrol.* 59 (2002) 27–44.
- [8] F.J. Holzmer, G.A. Pope, L. Yeh, SEAR of PCE-DNAPL in low-permeability sand. *Treating Dense Nonaqueous-Phase Liquids (DNAPLs)*, Batelle Press, 1999.
- [9] M.D. Annable, P.S.C. Rao, R.K. Sillan, K. Hatfield, W.D. Graham, A.L. Wood, C.G. Enfield, Field-scale approach of in-situ cosolvent flushing: evaluation approach, in: *Proceedings of the ASCE Speciality Conference*, 1996, pp. 212–220.
- [10] J.W. Jawitz, R.K. Sillan, M.D. Annable, P.S.C. Rao, K. Warner, In situ alcohol flushing of a DNAPL source zone at a dry cleaner site, *Environ. Sci. Technol.* 34 (2000) 3722–3729.
- [11] M. Schnarr, C. Truax, G. Farquhar, E. Hood, T. Gonullu, B. Stickney, Laboratory and controlled field experiments using potassium

- permanganate to remediate trichloroethylene and perchloroethylene DNAPLS in porous media, *J. Contam. Hydrol.* 29 (1998) 205–224.
- [12] R.L. Siegrist, K.S. Lowe, L.C. Murdoch, T.L. Case, D.A. Pickering, In situ oxidation by fracture emplaced reactive solids, *J. Environ. Eng.* 125 (1999) 429–440.
- [13] W. Braidia, S.K. Ong, Modelling of air sparging of VOC-contaminated soil columns, *J. Contam. Hydrol.* 41 (2000) 385–402.
- [14] S.W. Rogers, S.K. Ong, Influence of porous media, airflow rate and air channel sparging on benzene removal during air sparging, *Environ. Sci. Technol.* 34 (2000) 764–770.
- [15] W.A.P. Waduge, K. Soga, J. Kawabata, Intermediate scale testing of air sparging/SVE system for remediation of NAPLs entrapped in heterogeneous soil, in: *Proceedings of the International Conference on Physical Modelling in Geomechanics*. St. John, Newfoundland, 2002.
- [16] M.L. Benner, S.M. Stanford, L.S. Lees, R.H. Mohtar, Field and numerical analysis of in-situ air sparging: a case study, *J. Hazardous Mater.* 75 (2000) 217–236.
- [17] K.S. Udell, M. McCarter, Treatability tests of steam-enhanced extraction for the removal of wood treatment chemicals from Visalia Pole Yard soils, Final Report Berkeley Environmental Restoration Centre, Berkeley, 1996.
- [18] A. Hadim, F.F. Shah, G.P. Korfiatis, Laboratory Studies of Steam tripping of NAPL-contaminated Soils, *J. Soil Contam.* 2 (1993) 37–58.
- [19] K.K.C. Tse, S.L. Lo, J.W.H. Wang, Pilot study of in-situ thermal treatment for the remediation of pentachlorophenol-contaminated aquifers, *Environ. Sci. Technol.* 35 (2001) 4910–4915.
- [20] R.A. Freeze, D.B. McWhorter, A framework for assessing risk reduction due to DNAPL mass removal from low permeability soils, *Ground Water* 35 (1997) 111–123.
- [21] T.C. Sale, D.B. McWhorter, Steady state mass transfer from single-component dense nonaqueous phase liquids in uniform flow fields, *Water Resources Res.* 37 (2001) 393–404.
- [22] I.H. Kulasooriya, K. Soga, D. Dai, T.H. Illangasekare, Effect of flow direction on enhanced surfactant remediation of DNAPL, in: *Proceedings of Fourth International Congress on Environmental Geotechnics*, Rio de Janeiro, 2002.
- [23] K. Soga, I.H. Kulasooriya, W.A.P. Waduge, T.H. Illangasekare, D. Dai, Surfactant remediation of DNAPL—column and tank experiments, in: *Proceeding of Environmental Geomechanics*, Monte Verita, Switzerland, 2002.
- [24] L.K. MacKinnon, N.R. Thomson, Laboratory-scale in situ chemical oxidation of a perchloroethylene pool using permanganate, *J. Contam. Hydrol.* 56 (2002) 49–74.
- [25] E.A. Seagren, B.E. Rittmann, A.J. Valocchi, Quantitative Evaluation of the Enhancement of NAPL-Pool Dissolution by Flushing and Biodegradation, *Environ. Sci. Technol.* 28 (1994) 833–839.
- [26] Y. Yang, P.L. McCarty, Biologically enhanced dissolution of tetrachloroethene DNAPL, *Environ. Sci. Technol.* 34 (2000) 2979–2984.
- [27] B. Rogers, B.E. Logan, Bacterial transport in NAPL-contaminated porous media, *J. Environ. Eng.* 126 (2000) 657–666.
- [28] D.M. Mackay, P.V. Roberts, J.A. Cherry, Transport of organic contaminants in groundwater, *Environ. Sci. Technol.* 19 (1985) 364–392.
- [29] J.W. Mercer, R.M. Cohen, A review of immiscible fluids in the subsurface: properties, models, characterization, and remediation, *J. Contam. Hydrol.* 6 (1999) 107–163.
- [30] C.T. Miller, M.M. Poirier-McNeil, A.S. Mayer, Dissolution of trapped nonaqueous phase liquids: mass transfer characteristics, *Water Resources Res.* 23 (1999) 2783–2793.
- [31] S.E. Powers, L.M. Abriola, W.J. Weber, An experimental investigation of nonaqueous phase liquid dissolution in saturated subsurface systems: steady state mass transfer rates, *Water Resources Res.* 28 (1992) 2691–2705.
- [32] S.E. Powers, L.M. Abriola, W.J. Weber, An experimental investigation of nonaqueous phase liquid dissolution in saturated subsurface systems: transient mass transfer rate, *Water Resources Res.* 30 (1994) 321–333.
- [33] P.T. Imhoff, P.R. Jaffe, G.F. Pinder, An experimental study of complete dissolution of a nonaqueous phase liquid in saturated porous media, *Water Resources Res.* 30 (1993) 307–320.
- [34] C. Khachikian, T.C. Harmon, Nonaqueous phase liquid dissolution in porous media: current state of knowledge and research needs, *Transport Porous Media* 38 (2000) 3–28.
- [35] T. Saba, T.H. Illangasekare, Effect of groundwater flow dimensionality on mass transfer from entrapped nonaqueous phase liquid contaminants, *Water Resources Res.* 36 (2000) 971–979.
- [36] C.V. Chrysikopoulos, K.Y. Lee, T.C. Harmon, Dissolution of a well defined trichloroethylene pool in saturated porous media: experimental design and aquifer characterization, *Water Resources Res.* 36 (2000) 1687–1696.
- [37] S.E. Powers, I.M. Nambi, G.W. Curry, Non-aqueous phase liquid dissolution in heterogeneous systems: mechanisms and a local equilibrium modelling approach, *Water Resources Res.* 34 (1998) 3292–3302.
- [38] T.S. Soeren, D.A. Sabatini, J.F. Harwell, Effects of flow bypassing and nonuniform distribution on the mass transfer characteristics of NAPL dissolution, *Water Resources Res.* 34 (1998) 1657–1673.
- [39] J.F. Keely, Performance evaluation of pump-and-treat remediations, US Environmental Protection Agency Report EPA/540/4-89/005, Washington DC, 1989.
- [40] M.L. Brusseau, Z. Zhang, N.T. Nelson, R.B. Cain, G.R. Tick, M. Ostrom, Dissolution of nonuniformly distributed immiscible liquid: intermediate-scale experiments and mathematical modeling, *Environ. Sci. Technol.* 36 (2002) 1033–1041.
- [41] M. Delshad, G.A. Pope, K. Sepehrnoori, A compositional simulator for modelling surfactant-enhanced aquifer remediation, *J. Contam. Hydrol.* 23 (1996) 303–327.
- [42] D. Russo, E. Bressler, Soil hydraulic properties as stochastic process. 1. Analysis of field spatial variability, *Soil Sci. Soc. Am. J.* 45 (1981) 682–687.
- [43] A.D. Woodbury, E.A. Sudicky, The geostatistical characteristics of the Borden Aquifer, *Water Resources Res.* 27 (1991) 533–546.
- [44] B.H. Kueper, E.O. Frind, Two-phase flow in heterogeneous porous media. 1. Model development, *Water Resources Res.* 27 (1991) 1049–1057.
- [45] T.J. Dekker, L.M. Abriola, The influence of field-scale heterogeneity on the surfactant-enhanced remediation of entrapped nonaqueous phase liquids, *J. Contam. Hydrol.* 42 (2000) 218–251.
- [46] S.R. Cline, O.R. West, R.L. Siegrist, W.L. Holden, Performance of in situ chemical oxidation field demonstrations at doe sites, in: *Proceedings of the in situ Remediation of the Geoenvironment Conference*, Minneapolis, MN, 5–8 October 1997.
- [47] S.H. Conrad, R.J. Glass, W.J. Peplinski, Bench-scale visualization of DNAPL remediation processes in analog heterogeneous aquifers: surfactant floods and in situ oxidation using permanganate, *J. Contam. Hydrol.* 58 (2002) 13–49.
- [48] V. Dwarakanath, Characterization and remediation of aquifers contaminated by nonaqueous phase liquids using partitioning tracers and surfactants. Ph.D. Dissertation, University of Texas, Austin, 1997.
- [49] J.C. Fountain, R.C. Starr, T. Middleton, M. Beikirch, C. Taylor, D. Hodge, A controlled field test of surfactant-enhanced aquifer remediation, *J. Ground Water* 34 (1996) 910–916.
- [50] G.J. Hirasaki, C.A. Miller, R. Szafranski, J.B. Lawson, N. Akiya, Surfactant/foam processes for aquifer remediation, in: *Proceedings of the SPE International Symposium on Oilfield Chemistry*, Houston, TX, 18–21 February 1997.
- [51] F.J. Holzmer, G.A. Pope, L. Yeh, Surfactant-enhanced aquifer remediation of PCE-DNAPL in low-permeability sand, in: *Proceedings of The Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, Monterey, CA, 22–25 May, 2002.
- [52] J.W. Jawitz, M.D. Annable, P.S.C. Rao, D. Rhue, Field implementation of a Winsor type I surfactant/alcohol mixture for in situ sol-

- ubilization of a complex LNAPL as a single-phase microemulsion, *Environ. Sci. Technol.* 32 (1998) 523–530.
- [53] K.M. Jerome, B. Riha, B.B. Looney, Final Report for Demonstration of In Situ Oxidation of DNAPL using the Geo-Cleanse Technology. US Department of Energy, Westinghouse Savannah River Company, Aiken, South Carolina, 1997.
- [54] R. Martel, R. Lefebvre, P.J. Gelinat, Aquifer washing by micellar solutions. 2. DNAPL recovery mechanisms for an optimised alcohol-surfactant solvent solution, *J. Contam. Hydrol.* 30 (1998) 1–31.
- [55] H.W. Meinardus, V. Dwarakanath, J. Ewing, G.J. Hirasaki, R.E. Jackson, M. Jin, J.S. Ginn, J.T. Londergran, C.A. Miller, G.A. Pope, Performance Assessment of NAPL remediation in heterogeneous alluvium, *J. Contam. Hydrol.* 54 (2002) 173–193.
- [56] M.J. Pitts, K. Wyatt, T.C. Sale, K.R. Piontek, Utilization of chemical-enhanced oil recovery technology to remove hazardous oily waste from alluvium, SPE/DOE paper no. 25153, in: Proceedings of the SPE International Symposium on Oilfield Chemistry, New Orleans, LA, 2–5 March, 1993.
- [57] M.J. Schnarr, G.J. Farquhar, An in-situ oxidation technique to destroy residual DNAPL from soil, in: Proceedings of the Third International Conference on Ground Water Quality on Subsurface Restoration, Dallas, TX, 21–24 June 1992.
- [58] C.M. Young, R.E. Jackson, M. Jin, J.T. Londergran, P.E. Mariner, G.A. Pope, F.J. Anderson, T. Houk, Characterization of a TCE DNAPL zone in alluvium by partitioning tracers, *Ground Water Monitoring and Remediation*, Winter 1999, 84–94.