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A review on dissolution of multi-component non-aqueous phase liquids: recent studies, mechanisms and mass transfer limitations

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ABSTRACT

Dense non-aqueous phase liquids (DNAPLs) are considered as priority pollutants in groundwater systems due to their low solubility and high toxicity even at low concentrations. The impact of their accidental release is irreversible as they mix with groundwater through dissolution such that complete remediation of the aquifer is nearly impossible. In this paper, the current status of research and recent developments in the experimental, analytical and mathematical approaches to study the dissolution of multi-component DNAPL compounds in the saturated, homogeneous/heterogeneous porous media are summarised. It is observed that most of the earlier investigations have been confined to single-component dissolution either in lab-scale or *in-situ* studies. The existing mass transfer correlations are insufficient to estimate the dissolution rate of DNAPLs in a multi-component system where the velocity and non-aqueous phase liquids saturation are differently influenced by the aquifer heterogeneity. Considering the variability in the distribution pathways, a realistic quantification of the morphology and surface area of DNAPLs is quite challenging. Based on the insights from the recent literature, it is envisaged that a combination of solubility enhancement and remobilisation techniques can be further expanded to optimally remediate the contaminated sites.

Keywords: Aquifer remediation; Dissolution; Effective solubility; Mass transfer; Multi-component DNAPL; Raoult's law

1. Introduction

Contamination of underground water resources by accidental spills or leaks of non-aqueous organic liquids is a common problem observed in most countries. Though non-aqueous phase liquids (NAPL) generally do not mix thoroughly with water, most of the NAPLs of concern are partially miscible and soluble in water [1]. It is of grave concern due to the long-term chemical activity of components in the subsurface environment giving rise to potential health hazards for human beings. Dictated by the pertaining hydrogeology, these compounds reach the saturated groundwater aquifers through infiltration, where, depending on the density, they may prefer to stay at the water table (and light NAPL pools, for example, petroleum products) or at the bottom of the aquifer or any low-permeable strata (as dense NAPL pools, for example, chlorinated solvents) [2,3].

In order to understand the extent of groundwater contamination issues by NAPLs and to suggest/evaluate suitable remediation plans, it is important to understand the

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typical hydro-geo-chemical nature of the NAPL compounds in the heterogeneous subsurface environment. One of the basic characteristics that determine their fate and transport in the saturated porous/fractured media is the aqueous solubility (at equilibrium) where the potentially soluble mass is partitioned through dissolution. The phenomena of NAPL dissolution have captured the attention of many hydrogeologists across the world during the past few decades and a considerable number of theories and models are developed distinctly to address various types of complexities in evaluating the interphase mass transfer conditions [4–7]. The basic disparity among the approaches is, however, attributed to the status of mass transfer, where an equilibrium condition can be expected only when there are no obvious limitations for dissolution mass exchange [5–9]. On the other hand, the kinetic (rate-limited) approach is mostly preferred when the NAPL is present in discontinuous blobs or trailing away from the spilled pool source [10–12]. Therefore, a conceptual model for a fair geometrical representation of NAPL distribution in the subsurface in inevitable to discuss further on the dissolution mechanism (Fig. 1).

As seen in Fig. 1, the amount of spill, the extent of spread, the quantum of pooling and the residence time of any NAPL compound can influence the dissolution mass transfer, which also depends on a number of inherent physico-chemical characteristics of the compound, such as solubility, density, temperature, viscosity, volatility etc. (Table 1). Most of the spills are associated with multiple NAPLs together, causing them to compete among themselves for effective mass transfer. The equilibrium aqueous concentration of a particular NAPL thus obtained is termed as effective solubility, which depends on its mole fraction in the mixture of NAPLs present together.

The literature to-date shows that most of the theoretical, as well as experimental research is focused on single-component dissolution systems, considering the NAPL as a single entity. For modeling the transient dissolution, most of the widely used correlations use NAPL saturation as a surrogate for the surface area since it was difficult to measure the surface area experimentally [24,25]. As the NAPL front travels along some preferential pathways, the residual saturation results in dissolution fingering along those paths that may control the overall rate of dissolution [14]. The problem is further complicated when there are multiple compounds having significant differences in their mole fraction, allowing those compounds having better partitioning coefficients to preferentially dissolve at a faster rate. However, the overall rate of dissolution in such cases will be limited by the rate of the slowest (significant) compound in the NAPL mixture. It is therefore obvious to consider that NAPL is not a single entity but is composed of many phenolic and polyaromatic hydrocarbons, as in the case of creosote [15]. However, as far as the mas transfer phenomena are concerned, very little emphasis has been given to the multi-component dissolution studies in the earlier literature.

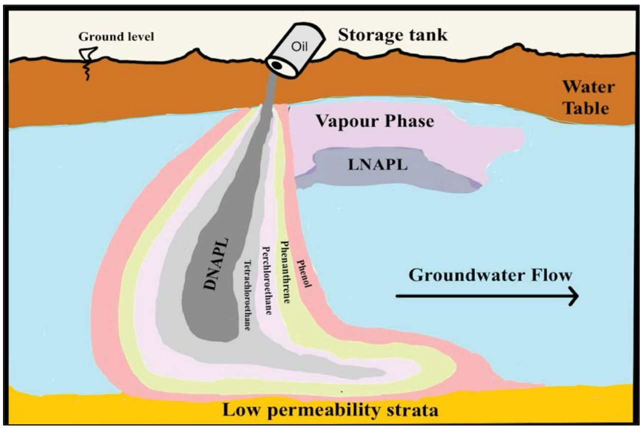

Fig. 1. Schematic representation of NAPL partitioning and distribution in the subsurface.

The necessity of preparing this review was understood by conducting a literature survey using the SCOPUS survey tool with "NAPL" and "Dissolution" as keywords. There were only about 442 articles published between the year 1990 to 2021, which include review papers, research articles and book chapters. There are no recent review articles focusing on dissolution of multi-component NAPLs. Also, it is to be noted that the concept of dissolution is not limited to environmental engineering but has been studied in various other domains such as chemistry/chemical engineering, earth and planetary sciences, agricultural and biological sciences (Fig. 2).

From the literature, it is evident that limited studies have addressed the problem of multi-component dense non-aqueous phase liquids (DNAPL) dissolution during the recent past decades, despite the advancements in computational and analytical tools. Considering this research gap, the present article aims to discuss recent investigations to update our understanding of multi-component DNAPL dissolution. The following sections/review will sequentially emphasis the (i) limitations in initial approaches, (ii) advancements in estimating effective solubility, (iii) solubility enhancement techniques, (iv) combined effects of DNAPL dissolution with degradation and (v) development of analytical solutions for mass transfer models.

2. Conceptual models of DNAPL dissolution

2.1. Dissolution of single-component DNAPL

Several earlier studies on single-component NAPL dissolution are based on a simplifying assumption of a steady source at a constant equilibrium strength [16]. Siegel and Pfannkuch [17] derived one of the first empirical mass transfer correlations for dispersed oil globules in typical porous media based on experimental data [18]. Most of the earlier studies on NAPL dissolution models were based on concepts of idealized spheres and cylinders in packed bed columns. Many researchers have proposed correlations between the heat transfer coefficient (HTC) and its similar mass transfer coefficient (MTC) and Peclet number (Pe) [16,17]. NAPL dissolution study has been modelled as isolated spheres that shrink with dissolution as explained by "Two-Film Theory" as represented in Fig. 3 [22,23].

A few researchers have derived correlations for equilibrium NAPL dissolution using dimensional analysis and experimental data to choose the model, which is also widely used in other studies [19–21]. In the case of DNAPL,

Table 1
Important physical and chemical properties of some of the common NAPLs

S. No.	Compound	Solubility@25°C (mg/L)	Density@20°C (g/cc)	Molecular mass (g/mol)	Solvent-water partitioning coefficient (–)	References
			DNAPL			
1.	Tetrachloromethane	810	1.590	153.82	2.83	[2]
2.	Trichloromethane	8,090	1.490	119.38	2.49	[3]
3.	Dichloromethane	19,800	1.330	84.93	1.25	[2]
4.	Chlorobenzene	500	1.11	112.56	2.64	[4]
5.	Trichloroethylene	1,099	1.463	131.4	2.51	[5]
6.	1,1,2-Trichloroethane	1,554	1.34	133.4	2.48	[6]
7.	Phenol	82,800	1.07	94.11	1.46	[7]
8.	Naphthalene	30	1.14	128.17	3.30	[8]
			LNAPL			
9.	Benzene	1,640	0.877	78.11	2.13	[9]
10.	Toluene	520	0.867	92.14	2.75	[10]
11.	Ethylbenzene	184	0.86	106.17	3.14	[11]
12.	*p*-Xylene	171.1	0.89	106.16	3.17	
13.	*m*-Xylene	106	0.86	106.16	3.20	
14.	*o*-Xylene	180	0.88	106.16	3.13	
15.	1,2,4-Trimethylbenzene	65.4	0.87	120.19	3.67	
16.	1,3,5-Trimethylbenzene	48.2	0.87	120.19	3.66	
17.	1,2,3-Trimethylbenzene	60	0.90	120.19	3.67	[8]
18.	Styrene	300	0.909	104.15	3.67	
19.	3-Ethyltoluene	40	0.90	120.19	2.95	
20.	Indene	20	0.997	116.16	6.70	
21.	2-Methylindene	20	0.971	130.19	3.42	

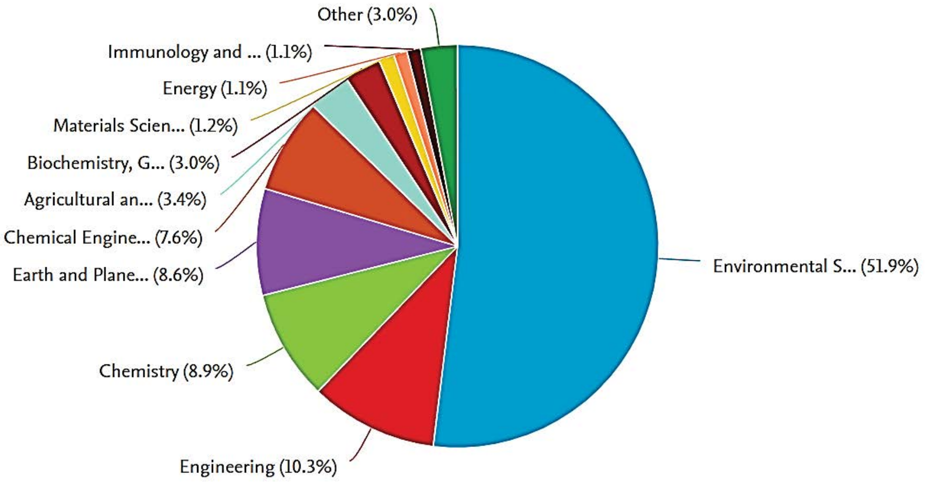

Fig. 2. Application of the concept of NAPL dissolution in diverse fields of study.

say trichloroethane (TCE), a similar approach has been employed to model the partitioning into various surrounding phases such as soil, air, water, suspended solids, biota, and sediments [22].

Under equilibrium conditions, the pure phase NAPL dissolves from the available pool of mass to the accompanying groundwater completely up to the limit of its aqueous phase solubility (which is a function of temperature). The resulting aqueous phase concentration can be expressed as:

$$C_a = K_{ow} C_{sat} \tag{1}$$

where C_a is the aqueous phase concentration (ML^{-3}), C_{sat} is the saturated concentration (at equilibrium partitioning) of the compound (ML^{-3}), and K_{ow} is the organic-water partitioning coefficient.

However, suppose there are any constraints on the mass transfer. In that case, the dissolution becomes rate-limited, and the interfacial area becomes reduced, resulting in a reduction in NAPL saturation in the available pore space. A first-order expression can be used to represent the kinetics of dissolution:

$$R^{n}_{\text{diss}} = K_{\text{nw}}\left(C_{\text{sat}} - C_{a}\right) \tag{2}$$

where R is the mass transfer rate ($ML^{-3}\cdot T^{-1}$), and K_{nw} is the transient dissolution mass transfer coefficient from the non-aqueous phase to the aqueous phase (T^{-1}).

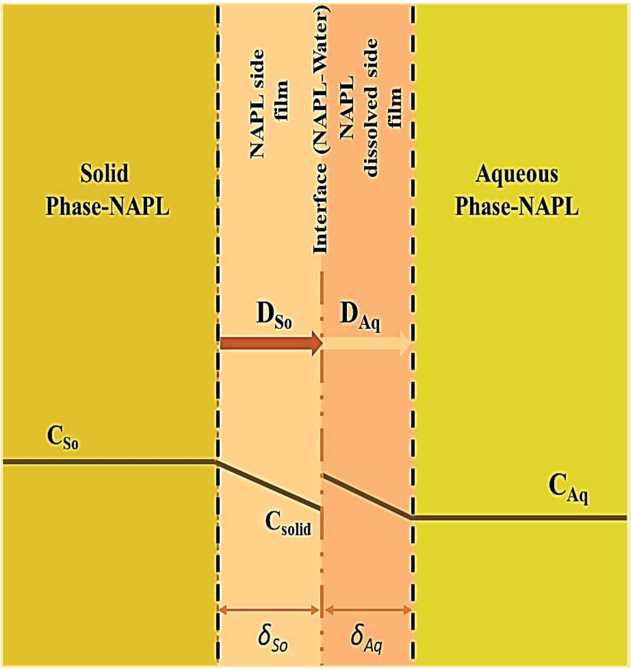

Fig. 3. Mass transfer zones for NAPL dissolution using two-film mass transfer model [6].

As evident from the mechanics of mass transfer, one part of NAPL molecules dissolves in the aqueous phase while another part of water molecules dissolves in the non-aqueous (organic) phase. Due to the hydrophobic nature of the NAPL molecule, the dissolution is retarded. Fig. 4 could depict the dissolving process of a single-component NAPL in water, represented as solid brown circles and blue circles, respectively in a closed system.

Understanding the mass transfer process when the NAPL flows through a saturated heterogeneous porous media is an intricate process [23]. The fate of NAPL within the porous media involves the following crucial mechanisms such as (a) solute advection, (b) dissolution mechanism and (c) solute diffusion/dispersion. When water flows through the saturated media, a non-equilibrium state tends to occur due to the dilution effect, resulting in further NAPL contamination. To retain the equilibrium state of the solution, some of the entrapped NAPL mass dissolves into the water. Further, while the dissolved NAPL is transferred from one place to another, the advection front of water will influence the dissolution, making it a key mechanism of the system. The mechanism of NAPL dissolution serves two roles in the overall NAPL mass transfer. First, the mechanism causes a reduction of NAPL, and second, it increases the dissolved concentration throughout the flow pathways. The former role could aid in removing NAPL from porous media, while the latter would increase the permeability of the media. Further, there is a third step, where solute diffusion/dispersion occurs to migrate NAPL from higher concentration regions to lower concentration regions. In a nutshell, NAPL dissolution is driven by a combination of advection components and dispersive components [24].

2.2. Dissolution of multi-component DNAPL

A more realistic approach is the consideration of multiple NAPL compounds being simultaneously available for interphase mass transfer. According to Raoult's law, the effective solubility of each component in the mixture depends on the available mass (or mole fraction) and its pure phase solubility. Multi-component NAPLs are organic liquids containing more than one chemical entity possessing similar/dissimilar chemical properties. A multi-component

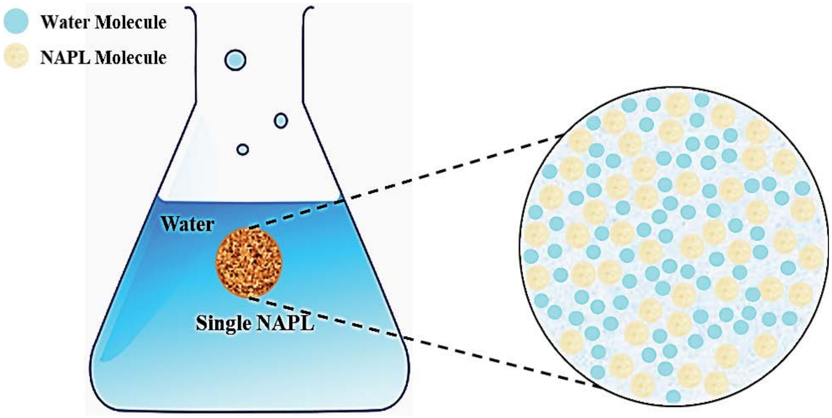

Fig. 4. Schematic representation of single-component NAPL dissolution.

batch system is shown in Fig. 5, where the solid circle with purple (say A) and brown colour (say B) represents two different NAPLs while the solid blue (say C) represents a water molecule. A similar investigation on multi-component NAPL dissolution can be carried out in continuous flow system as shown in Fig. 6 [25,26]. During the process of dissolution, both NAPLs tends to behave ideally (follows Raoult's law) if component A and B possess similar chemical structure, as observed by Banerjee (1984) and the same was referred to by Chrysikopoulos and Lee [27]. A summary of the research studies based on the dissolution using Raoult's law (Table 2).

On the other hand, if A and B have dissimilar structures and specific mole fractions, the dissolution phenomena observed are non-ideal [32,33]. Some other reasons for the non-ideal nature could be attributed to the difference in molecular structure, polarity, and molar volume [26,34]. This non-ideal nature of the component in a mixture of NAPL is generally represented by an activity coefficient term [35]. It is a dimensionless correction term coefficient where higher deviations in their values from unity imply higher non-ideal behaviour [14].

Under equilibrium conditions, the effective solubility of a component in a DNAPL mixture can be expressed as:

$$C_{\text{sat}_i} = C^0_{\text{sat}_i} X_{n_i} \tag{3}$$

where $C_{\text{sat}}{}^0$ is the pure phase solubility of compound 'i' in the aqueous phase (ML^{-3}) and X_{ni} is its mole fraction in the non-aqueous phase (–).

The aqueous phase solubility is also a function of relative chemical activity of the individual component.

$$X_s^w = \frac{X_s^o \gamma_s^o}{\gamma_s^w} \tag{4}$$

where g represents the activity coefficient, *o* represents non-aqueous, *w* represents aqueous phase, and the letter *s* represents pure, single-component NAPL. As the contribution of water molecules dissolving in the NAPL phase is very insignificant, the second term, the numerator of Eq. (4), approximately equals 1.

As observed by Banerjee (1984), NAPL with low solubility in groundwater depicted the most negligible interaction with other NAPL components and hence was unaffected by the presence of co-solute, which makes the NAPL dissolution ideal. Schwarzenbach found that only 0.008% of molecules of *n*-octane participated in the dissolution process at equilibrium, causing the solvent least interacting with water molecules [28]. The activity coefficient of individual elements in multi-component NAPL mixtures composed of distinct components can be estimated using the UNIFAC model [35].

$$C_s^w = C_{\text{sat}_s} X_s^0 \gamma^0_{s\left(X_s^0\right)} \tag{5}$$

The equation for NAPL in which the components are composed of chemically similar structures can be generalized.

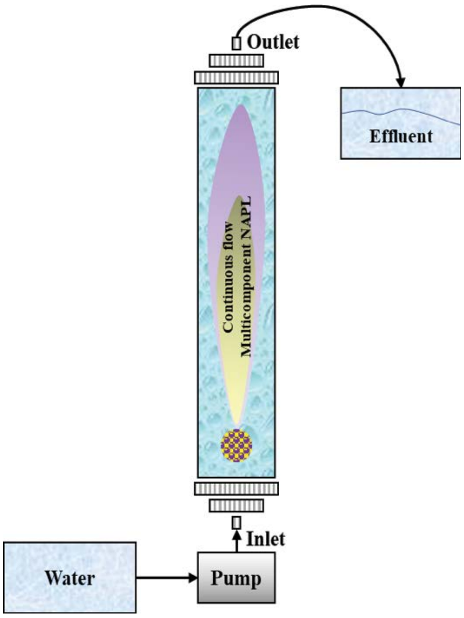

Fig. 6. Schematic representation of multi-component DNAPL dissolution in column studies.

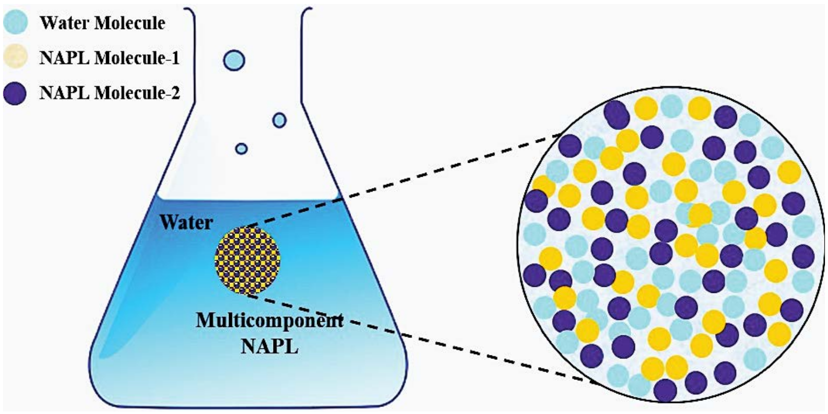

Fig. 5. Schematic representation of multi-component DNAPL dissolution.

Table 2
Summary of the works related to Raoult's law

NAPL used	Findings	References
Phenanthrene; naphthalene	Predicted and experiment data of dissolution followed Raoult's law.	[7]
TCA; TCE	Dissolution of mixture of NAPL followed Raoult's law. In other words, ideal behaviour of solution was observed with increase in mole fraction of NAPLs and hence following Raoult's law. The study fails to consider changes in activity coefficient while calculating activity coefficient.	[28]
BTEX; petroleum hydrocarbons	A linear relationship was found to exist between the deviations in aqueous concentrations and activity coefficients from their Raoult's law-based values for all compounds.	[29]
Methyl tert-butyl ether (MTBE); BTEX	MTBE dissolution followed Raoult's law. Measured activity coefficient for benzene in BTEX deviated from Raoult's law.	[30]
Creosote residual amounts	Non-equilibrium approach is more suitable.	[15]
Toluene/benzene ethylbenzene/ toluene; ethylbenzene/benzene	Ratio mass estimation (RME) was used instead of Raoult's law model.	[31]

$$C_s^w = C_{\mathrm{sat}_s} X_s^0 \tag{6}$$

However, such simplifications in case of a complex mixture of petrochemicals can result in errors in estimating effective solubility up to two-folds (Feenstra 1990). In case of transient dissolution, the resulting aqueous concentration also depends on the resistance offered by film at the interface as well as the composition of NAPL [36].

In such cases, residual saturation will come into the picture. This represents the multi-component scenario, as all the compounds can occupy the same pore volume defined by the residual saturation. Nonetheless, the change in mole fraction influences the effective solubility as well as the remaining mass distribution in the NAPL phase, which in turn affects the dissolution mass transfer coefficient. It is moreover important to realize that effective solubility can be an active function of time-dependent mole fraction. Hence, the temporal change in concentration can be expressed:

$$\frac{dC_i}{dt} = -F_v X_i \tag{7}$$

where C_i is the concentration of component 'i', F_v is the flow rate, and X_i is the mole fraction.

In support of these assumptions, some studies are discussed. The concentration of 1,1,2-trichloroethane (TCA) in a mixture of TCA and TCE was found to be less, which is directly proportional to the difference in their solubilities [42]. A similar investigation was conducted by Lee and Chrysikopoulos [28] using a semi-analytical procedure. Lee and Chrysikopoulos [33] studied the combined effect of transport and pool dissolution of multi-component DNAPL in a stratified porous (heterogeneous) media. They considered a layer of sand over the clay to resemble an aquifer layered with an aquitard. The activity coefficient was observed to increase with a decrease in mole fraction. The concentration of tetrachloroethene (PCE) increased gradually while that of 1,1,2-TCA decreased due to the difference in their effective solubility values. It is also reported that the distribution of NAPL is greater in statistically anisotropic subsurface formations than in saturated subsurface (only sand) formations of homogenous properties.

In case of multi-component light NAPLs such as benzene, toluene, ethylbenzene, xylene (BTEX), tracking one compound has helped in interpreting the history of other compounds though the interpretation is complicated. The results from the study can be used to generalise the process of dissolution for various hydrophobic organic compounds present in a multi-component NAPL [37,38].

Dissolution characteristics of an ideal ternary NAPL mixture demonstrated the relative importance of the mixture's internal and external mass transfer resistances and ideality on multi-component NAPL dissolution at the pore and intermediate scales. Vasudevan et al. [29], investigated the effect of compositional heterogeneity on the multi-component NAPL dissolution and inferred the unique role of the bulk compound (filler) in driving the non-ideality.

Brahma and Harmon [6] the ideal behaviour of the mixture of NAPL was studied for TCE, PCE and TCA. The investigation made use of a diffusion-based dissolution model based on hydrodynamic theory. This approach demonstrated intra-NAPL diffusion coefficients for ideal and non-ideal ternary solvent examples. The results of the study indicate that the hydrodynamic approach was more applicable to chlorinated organic solvents (DNAPLs). The most significant effects of non-ideality were observed for more soluble components, that is, when considered as an ideal mixture. These components (TCE and TCA) can be disappeared from the NAPL pool more slowly in the diffusion model simulation, whereas while including the non-ideality, the TCE and octanol were able to disappear more quickly. It is important to note that these simulations employed unrealistically large and impenetrable blobs to exploit the potential importance of hydrodynamic diffusion. Thus, the differences in dissolution times are over-estimated in the realm of NAPL residual but may represent the magnitude of the anticipated effect [6]. A summary of the research studies based on the experimental as well as analytical tools is provided herewith (Tables 3 and 4).

Table 3
Short summary of experimental studies on single and multi-component dissolution

S. No.	NAPL type	Model type or method	Experimental conditions/ expressions/assumptions	Major findings	References
Single-component studies					
1.	Trichloroethylene	Residual/dead-end pool dissolution	Entrapped residual blobs (gravity fingering), pooling in a dead-end fracture	A new mass transfer relation as a power law function of Peclet number and the remaining mass percentage was successfully matched to the Sherwood number. The lesser mass transfer could be due to low porous media.	[39]
2.	Tetrachloroethylene	Steady-state dissolution	3D fractured-rock network, ambient groundwater condition	Mass transfer coefficient (K_L) has a positive and significant relation with NAPL-water interfacial area and NAPL saturation. Similar correlations were found for dissolution carried out in porous media.	[40]
3.	Trichloroethene	Heterogeneous-source model	Column study: inner diameter: 2.1 cm; length; 7 cm	The heterogeneous 1D source model was validated with the data from column experiments. The developed model was relatively feasible and successful in simulating multistage dissolutions as observed in column and flow cells set-up.	[26]
4.	Methyl tert-butyl ether	1D model	Column study: inner diameter: 3.8 cm; length: 40 cm, velocity: 3–4 mL/min	Dissolution increased with higher velocity and reduced with greater initial MTBE. Smaller the grain size, higher the dissolution rate. The rate of dissolution is prolonged in the presence of trichloroethylene.	[41]
5.	Tetrachloroethene; trichloroethene	Simulation analysis	Coupling of dissolution, sorption and biodegradation	Dissolution, partition and degradation of DNAPL were considered. The developed framework is suitable for combined effects of 3 reactive transport mechanisms and for designing the remediation of the contaminated site.	[42]
Multi-component studies					
1.	Phenanthrene; naphthalene; phenanthrene; 2,3-benzofuran; phenol; *m*-cresol; 1-naphthol; phenoxathiin	Continuously stirred flow-through reactor	Single-compound; multi-compound	A numerical model with a variable activity coefficient was developed (by following the mass balance equation and Raoult's law). The actual and predicted profiles of solutes in the aqueous phase were quite similar. Raoult's law assumption did not hold good for a multi-component system. The numerical model is useful for measuring activity coefficients in complicated organic mixtures.	[7]
2.	Industrial creosote residual-PAH	Physical and mathematical model	Inner diameter: 1.0 cm; length: 9–15 cm; velocity: 3–4 mL/min; contact time; groundwater velocity	A few elements of creosote reached equilibrium in a shorter duration following Raoult's law. To consider complete dissolution of creosote, water to creosote volume ratio was supposed to be which is quite higher. Due to a very high value of water/oil ratio (greater than 2,70,000), water flushing cannot be recommended as an economic remedial measure.	[15]

Table 3 (Continued)

Table 3

S. No.	NAPL type	Model type or method	Experimental conditions/ expressions/assumptions	Major findings	References
3.	BTEX; trimethyl-benzene (TMB) isomers of LNAPL	Multi-component solution model	Fresh, weathered, and synthetic gasoline	In the research, the effect of compositional change of NAPL (fresh, weathered, and synthetic gasoline mixtures) on the activity coefficient was investigated. The fresh and weathered gasoline had an activity coefficient between 1.0 and 1.2, depicting slight ideal behaviour.	[32]
4.	Creosote	Analytical model coupled dissolution with phase transport	Fractured environment; spatially homogeneous source	A model on dissolution of components of creosote coupled with transport was developed and was studied using the analytical solution and Laguerre series. The constituents of creosote have varied dissolution and diffusion property, for example, phenol (8.70×10^4 g/m^3) and polycyclic aromatic hydrocarbons (PAH) ($2.54 \times 10^1 - 3.14 \times 10^1$ g/m^3). The model is most applicable to screening-level calculations.	[43]
5.	Methyl tert-butyl ether (MTBE); BTEX	1D laboratory model	Batch and column studies; inner diameter: 4 cm; length: 19 cm	The observed NAPL followed equilibrium dissolution behaviour over a concentration range of four to five orders of magnitude. The requirement of pore volume increased three times to reduce the MTBE concentration to less than 100µL. Raoult's law assumption for methyl tert-butyl ether (MTBE) in gasoline mixture holds good.	[30]
6.	Benzene; trichloroethylene; chloropropane; toluene	2D dimensional FEM (extended multiphase flow model)	***Assumption***: Local chemical equilibrium ***Gas pressure gradient***: Negligible	The mass transfer rate and fluid density updating have the most negligible impact during highly transient migration periods. For long-term simulations, cumulative dissolution to the water phase and volatilisation to the gas phase account for more significant proportions of the total mass.	[44]
7.	Trichloroethylene; perchloroethylene	Analytical model in subsurface media	Column study (silica sand and alkali sand)	Dissolution of TCE and PCE possessing high and low solubility was carried out in 5 sand-packed column setups. TCE and PCE reached 600 and 110 mg/L on 40th day, which is less than their saturation concentration. This may be due to the dominant dilution effect, differential hydrophobicity, and density. The analytical model was in good agreement with the experimental data.	[45]
8.	BTEX	Numerical model and low order spatial moment analysis	Homogenous and isotropic groundwater flow	Spatial moment analysis shows that sorption retards the dissolution of BTEX and, mostly, on benzene and toluene due to their higher solubility. There is an influence of aerobic degradation in dissolving BTEX and transport during the early stages. The temporal distribution shows that the concentration profile on BTEX reduced in the presence of sorption and biodegradation, which can be considered as interaction factors.	[46]

3. Limitations on the initial approaches of single and multi-component DNAPL dissolution studies

Most of the DNAPL spills are remote, and it becomes difficult to study the dissolution which is due to the heterogeneity of the strata. In addition, the assumption of local equilibrium being invalid for varied conditions [53]. A similar instance was found in a study where transport and dissolution of 1,2-dichloroethane (1,2-DCA) were simulated in a 2D sandbox apparatus. In this study, the size of the box failed to replicate the scale of the field, resulting in a limiting correlation from the lab-scale experiment to site

Table 4
Short summary of analytical/numerical studies on single and multi-component dissolution

S. No.	NAPL studied	Model used	Experimental conditions	Equations developed	Findings and inference	References
			Single-component Studies			
1.	Trichloroethylene	Empirical model	Non-destructive visualization technology	2D micromodel: $Sh = 1.98 \cdot Re^{0.79}$ 3D packed bed: $Sh = 11.06 \cdot Re^{0.56}$ Sh – Sherwood number	NAPL saturation reduced from 24.5% to 9.5% in 10 h. After 10 h of a continuous water flow, most blobs disappeared, as seen in the 2D image and the could be due to dissolution. MTC was higher for the packed-bed system than the micromodel due to the inherent pore structure.	[47]
2.	Tetrachloroethylene	Conceptual model (linear driving force model)	Fractional wettability, porous media	Sherwood number: $Sh = 1.15 \cdot Re^{0.654}$ Sc – Schmidt number	Increased tetrachloroethylene wet sand fraction results in extended dissolution. This was followed by increased rates of concentration reduction and more persistent subsequent low-concentration tailing. The proposed model required additional data input.	[48]
3.	1,3,5-Trifluro-benzene	Laboratory scale: Sherwood–Gilland model		Sherwood number: $Sh'_{SG} = \frac{K_L^{SG} \cdot d_m^2}{D^*}$	Relative behaviour of the five models is demonstrated to be dependent on system and source zone features. Through theoretical analysis, comparing Sherwood–Gilland type models to a process-based, thermodynamic dissolution model, it is shown that the coefficients of the Sherwood–Gilland models can be related to measurable soil properties.	[49]

Table 4 (Continued)

Table 4

S. No.	NAPL studied	Model used	Experimental conditions	Equations developed	Findings and inference	References
4.	Tetrachloroethylene	MISER (Michigan soil-vapor extraction remediation) model	2D, 3D phase model, intermediate and strong wettability condition	Mass exchanged per unit time per unit volume between the NAPL and aqueous phases can be expressed as: $E_{\text{ow}} = \frac{-\partial\left(\varepsilon S_o \rho_o\right)}{\partial t} = k_{\text{ow}}\left(\alpha A^t_{\text{ow}} + \beta A^c_{\text{ow}}\right)$ k_{ow} – Film mass transfer coefficient; A^t_{ow} – NAPL-water interfacial area per unit volume (entrapped ganglia); A^c_{ow} – NAPL-water interfacial area per unit volume (continuous NAPL phase); C_e – Equilibrium solubility concentration; α and β – Parameters to account for fraction of the interfacial area is exposed to mobile water	Dependency on soil wettability and the spatial distribution of NAPL. Large distribution results in faster dissolution due to increased access to flowing water.	[50]
Multi-component studies						
1.	Organic pollutant (lab study)	Phenomenological model	Velocity, DNAPL saturation (constant), interfacial area, porous media	Sherwood number $\text{Sh}' = 12\,\text{Re}^{0.75} \cdot \theta_n^{0.6} \cdot S^{0.5}$	Mass transfer rate coefficient is directly proportional to the aqueous phase velocity. There is no relationship between grain size and a parameter as a surrogate measure of NAPL distribution.	[21]
2.	Trichloroethene; tetrachloroethene; 1,1,2-trichloroethane	Diffusion model with spherical blob surface	2D model, ternary NAPL, pore-scale and intermediate-scale experiments	$\frac{\partial M_i}{\partial t} = k_f \cdot A_t \cdot \left(c_i^* - c_i^\infty\right)$ M_i = Mass of NAPL; K_f = Mass transfer coefficient;	The non-ideal mixture results in significant mass loss during dissolution due to the increased effective solubility of its components. The dissolution time remained almost the same for the ideal combination.	[6]
3.	Hydrofluoroether (HFE-1700)	2D-tank reconstructed aquifer	DNAPL saturation, hydraulic condition	Relationship between Sherwood number and Reynold's number. $\text{Sh} = \alpha \cdot \text{Re}\beta^1 \cdot S_m\beta^2 \cdot \text{Re}\beta^2 \cdot (P/A)\beta^3 \cdot I_y\beta^4$	The proposed correlation can be used to assess non-aqueous phase liquid (NAPL) dissolution rates over a wide range of saturation (residual and non-residual) conditions and different aqueous phase velocities within the NAPL source zone.	[51]

Table 4 (Continued)

Table 4

S. No.	NAPL studied	Model used	Experimental conditions	Equations developed	Findings and inference	References
4.	Ethyl acetate/butyl acetate Butyl acetate/amyl acetate	Two-chamber micropipette-based method	Assumption: Approximation of reduced surface area and homogeneous mixing (ideal)	Mass flux individual component: $\frac{dm_i}{dt} = A_{\text{frac}_i} D_i \left(c_i - c_s\right) \left\{ \frac{1}{R} + \frac{1}{\sqrt{\pi D_i t}} \right\}$	This modified model can accurately predict the dissolution of microdroplets for the ethyl acetate/butyl acetate and butyl acetate/amyl acetate systems, given the solubility and diffusion coefficients of each pure component in water initial droplet radius. The dissolution of microdroplet (multi-component NAPL) was in good agreement with modified Epstein–Plesset model. However, model fail for macro-droplets.	[52]

conditions [54]. Further, when in case of a saturated porous media, if the degree of saturation of NAPL is low, it is difficult for a NAPL capillary pressure-saturation model to describe the intrusion and emission behaviour of NAPL [55]. Accordingly, the model needs to be upgraded by considering transition phenomena in the system. Based on this update, a new concept which describes the relationship between capillary pressure and degree of saturation was developed [56]. In a study investigated by Fortin et al. [112], the dissolving sphere model described the removal of NAPL from the subsurface by conventional technologies is difficult. Therefore, to address this issue, a mathematical technique referred to as the multiple analytical source superposition technique (MASST) was developed. The approach is computationally efficient for a uniform flow condition. However, the major limitation here is that real-time scenarios are much more complex than what is accounted for in the system [57].

Considering an equilibrium model is quite easy to use and can account for every NAPL mass but fails to account for heterogeneity (physical/chemical) by mass transfer limitation causing tailing. Moreover, while considering the two-site model, the limit could be that it can partially complement with mass transfer limited region. Further, the multi-site model, where only one coefficient is considered for each site, needs optimization by considering many parameters. [58]. Most of the earlier studies have used simplified models, whereas the field scenarios are much more complex [59–61].

3.1. Equilibrium and non-equilibrium conditions

Several contrasting reports have been published discussing whether equilibrium is achieved during DNAPL dissolution. It was reported that small lengths of NAPL in the range of few centimeters were sufficient to reach equilibrium [12]. The time required to reach equilibrium was around 15 min (Siegel and Pfannkuch [17]). Several studies have suggested that equilibrium conditions always existed in columns [21,62]. However, later studies have found that non-equilibrium conditions could exist for short contact time, as reported by Garg & Rixey [38] Steefel & Lasaga [63]. They also theoretically showed that non-equilibrium conditions could be found for short contact time, mainly for large NAPL blobs and high velocities, which was further proved experimentally in short columns at high velocity. Several other studies as well reported non-equilibrium dissolution at high velocities. Equilibrium can be expected at lower velocities, typically at ~10 m/y, and dilution could cause an apparent non-equilibrium state. Studies show non-equilibrium conditions existed in a two-dimensional tank dissolution experiment [64]. It has further been suggested that much of the apparent non-equilibrium could be explained using models that account for heterogeneity [65]. Though non-equilibrium is possible at high velocities, most groundwater conditions could have equilibrium dissolution, and apparent non-equilibrium could be due to subsequent three-dimensional dilutions and mixing. Dissolution of NAPL can be at steady-state or transient dissolution [13]. When the concentration of dissolved NAPL reaches a constant value, it is called steady-state dissolution, while the concentration of dissolved NAPL changes with time is called transient dissolution. Usually, dissolution is a steady-state for residually saturated NAPL until a critical NAPL saturation (or surface area) is reached. The concentration of NAPL reduces continuously and may exhibit long tailing. The transition from steady-state to transient dissolution has not been explored and can play an essential role in remediation modelling.

3.2. Factors affecting mass transfer kinetics

The earlier studies showed that mole fractions of lower concentration significantly affected mass transfer [66]. Later a significant portion of earlier research, for example, [12,19,21,67], has shown that groundwater velocity, NAPL saturation and its distribution in pores, fracture aperture and length have remarkable effects on mass transfer kinetics [39,68]. A study conducted by Bradford and Abriola [48] to investigate dissolution in porous media proved that dissolution behaviour relies on soil parameters such as wettability and mean grain size distribution. Later, the results were demonstrated considering the dissolution of NAPL for the long term. In further studies, it was found that NAPL volume and surface area was crucial parameter in dissolution kinetics. Furthermore, it was observed that the ideal mixture of NAPL obeys first-order kinetics and was function of the solubility of a mixture of NAPL [69,70]. In another study, a mathematical model was developed considering the dual porosity concept, which further illustrated dissolution kinetics of petroleum hydrocarbon in a saturated aquifer system [71].

3.3. Tools for estimating interfacial area

The surface area of the NAPL-water interface is an essential parameter that is hard to estimate. Prasad Saripalli et al. [72] proposed that sodium dodecylbenzene sulfonate can be used as an interfacial tracer material to measure NAPL-water interfacial area in column experiments called the "Interfacial tracer technique". The limitation of this method is that it is inaccurate, involves many assumptions, and provides an approximate interfacial area. Later the investigation was also carried out following mobilisation by "Chemical Flooding" [73].

Further, the use of synchrotron X-ray micro-tomography and interfacial partitioning tracer tests showed that the values obtained from tracer tests were more significant, as demonstrated by Brusseau et al. [74]. In their study, microtomography data were collected before and after the tracer test. Detailed analysis of data depicted that the surfactant tracer caused the least impact on the fluid-phase configuration and interfacial areas under conditions associated with typical laboratory applications. The difference between the tracer test and X-ray microtomography was due to the failure of the methods to resolve interfacial area associated with microscopic surface heterogeneity. These techniques were later extended for residual saturation, vadose zone with single and multiple component NAPL [25,75].

4. Scope of controlled experiments in estimating effective solubility

4.1. Effective solubility for ideal and non-ideal mixtures

The chemical similarity of components of NAPL can cause the dissolution to behave ideally. In a recent study, Mackay et al. [62] showed that fugacity could be used to determine the effective solubility of a component within a DNAPL mixture. Effective solubility of structurally similar NAPL can be predicted, but in a couple of studies, 10%–30% of deviation was observed, and for mixtures of aliphatic and aromatic compounds, a deviation of about 25% to 50% from their ideal concentrations was observed [76,77]. A similar deviation of about 41% in effective solubility can be observed in a representative gasoline mixture [11,32].

4.2. Variability in experimental conditions as a cause of disparity in dissolution

As shown in Table 3, the experimental studies on the dissolution of single and multi-component NAPL are quite different for different compounds, for example, trichloroethylene, tetrachloroethylene, 1,3,5-triflurobenzene, which could have led to the disparity in dissolution behavior in various studies. The studies on these compounds are carried out in batch and column mode to understand the dissolution of single and multi-component systems [78–80]. Further, contaminant transport by the dissolution of single and multi-component DNAPL in mixed porous media was investigated and modelled in a few studies [75,76]. Lee and Chrysikopoulos [33] investigated NAPL dissolution in porous formations. The results illustrate that, pool shrinkage was time-dependent and accounted for reducing the DNAPL pool surface area. Further, aquitards reduced dissolved NAPL concentrations in aquifers significantly. The model moreover predicts that the transport of dissolved NAPL is slower in anisotropic aquifers than inhomogeneous aquifers.

The dissolution of benzene, toluene, xylene, and naphthalene (BTXN) from trapped NAPL was investigated by Garg and Rixey [38] for a low source length (L) to interstitial velocity (v) ratio. This was to ensure that dissolution was mass transfer limited (MTL). The toluene dissolution data was fitted to the model, and the process of dissolution can be generalised for components of NAPL. The study further helped in predicting the dissolution history of individual compounds of petrochemical hydrocarbons [38]. Investigation of the dissolution behaviour of non-ideal gasoline spills was reported by Vasudevan et al. [11]. The study revealed that lighter aliphatic components present in gasoline significantly affected effective solubility, resulting in 20% deviations from the measured values of the batch study. Dissolution of binary NAPL pool was studied over a broad range of pore water velocities varying from 0.1 to 60 m/d. Prediction of model were based on local equilibrium and mass transfer limited model. The experimental results depict that the local equilibrium model holds best fit, the concentration decreased for the pore velocity ranging from 0.01–1 m/d and later the values were constant for the pore velocity between 1–100 m/d [36].

The solubility of chlorophenols as a function of pH was investigated by Arcand et al. [82]. It was found that, for an increase of 1 pH unit from pH 5, solubility increased by 10 times. Also the solubility was constant below pH 4. The experimental data was in congruent with the literature. Popp et al. [83] investigated the temperature dependency of NAPL solubility and its timely emission in the source zone using a simulation model tool for porous media, OGS which coupled thermal, hydraulic and geochemical processes.

The simulation results of GS model showed a good fit for 1D and 2D experiments; nevertheless, were overestimated for the 1D experiment. This model could be implemented for studies of varied nature accounting for temperature. Zhou et al. [84] studied a physical model of NAPL dissolution to predict the dissolution rate coefficient in a completely saturated environment, and it was stated in terms of the modified Sherwood number (Sh') and is a function of Peclet (Pe) number. For forecasting NAPL dissolution rate coefficients, the model offers an alternative to actual correlations.

An investigation on dissolution phenomena of DNAPL trapped in saturated media for styrene and trichloroethylene was conducted by Powers et al. [19]. The study indicated that coarser soil traps more NAPL than finer soil and deviation from equilibrium concentration was found to be a function of aqueous phase velocity, and its shift varied for different soils. Yang et al. [85] developed a model for the multiphase transport of NAPL in the subsurface. The model simulation results indicate the rate of dissolution as a function of the size NAPL blob and hydrodynamic conditions. Moreover, the model was successful in predicting dissolution for toluene, and the results were in line with available experimental data. Nambi and Powers [86] investigated a 2D dissolution on entrapment in heterogeneous environments, and the results demonstrate that the concentration of effluent was less than equilibrium for a greater NAPL saturation value. This difference in effluent concentrations in the system was due to aqueous phase flow patterns within a heterogeneous system.

5. Analytical solutions in understanding the mechanics of dissolution

The method to solve the advection–dispersion equation with dissolution primarily involves Laplace or Fourier transformation to the dissolution experimental data on saturated porous media. It is evident from the literature that various studies on single and multi-component dissolution in saturated media involve ideal and non-ideal conditions in their investigations. A few studies have also focused on multi-component dissolution in fractured porous media. A summary of analytical/numerical studies on single and multi-component dissolution is given in Table 4.

One of the first analytical solutions for DNAPL dissolution in one-dimensional groundwater flow was given by Leij et al. [87]. The solutions to three-dimensional are complicated to use. Leij et al. [88] developed an analytical solution for 3D NAPL dissolution using Green's function method. Several others used the greens method to account for the dissolution of NAPL. By using the mass superposition technique, an analytical solution for NAPL dissolution is developed [57]. Some of the important studies and their major conclusions are discussed.

In an earlier study around the 1990s, the dissolution kinetics of NAPL was studied by Mackay et al. [62] where they observed that the NAPL component with higher solubility (hydrophilic), for example, benzene, chlorobenzene etc. are depleted rapidly and consumed lesser volume of water. The ones with lower solubility, for example, toluene, *p*-xylene etc., depleted slowly after consuming more water (pore volumes). However, the least soluble (hydrophobic) NAPL component, for example, biphenyl, did not deplete within the observed durations. A semi-analytical instead of a numerical approximation method was used to study the transport of mixture 1,1,2-TCA and TCE for a hypothetical contaminated site [27]. Results depict that 1,1,2-TCA solubilisation was faster as compared to TCE, leading to lower 1,1,2-TCA mole fractions. The incorporated method accounts for the change in activity coefficient (non-aqueous phase) in multi-component dissolution, making it more accurate than previous studies.

A semi-analytical method was formulated by Lee [89] to investigate the dissolution of a multi-component NAPL mixture in the shape of a rectangular prism assuming interaction between the components within the source. The results indicated that equilibrium aqueous-phase concentrations could be achieved for individual components as a function of time. These methods can be used to plan and understand experiments in homogeneous sub-surfaces in a laboratory setup. Hansen and Kueper [90] an analytical solution to predict multi-component NAPL dissolution was investigated. The expression for multi-component NAPL represented both transient aqueous concentration in equilibrium and prevailing mass of each NAPL component as it dissolves. However, the analysis was restricted to ideal NAPL mixture only.

In a dissolution experiment conducted by Detwiler et al. [91] for varying fracture aperture and entrapped NAPL (TCE) geometry, a computational "Depth-Averaged" model that incorporates fluid flow, transport of the dissolved NAPL, interphase mass transfer, and the corresponding NAPL-water-interface movement as fundamental parameters was developed. The digital images from the light transmission techniques recorded the advancement of TCE distribution and was comparable with experimental data. Results suggest that the model can be used to understand the dissolution relating to aperture, phase and hydrodynamic.

A 2D analytical model for the dissolution of 1,1,2-TCA pool in a saturated media was developed in the form of a single integral for Laplace transforms and Fourier transforms [91]. The solution worked for NAPL pools that were denser and lighter than water. Under controlled laboratory circumstances, the model effectively replicated the reactions of a TCA pool at the bottom of a two-dimensional porous media. Green's function method (GFM) was used to solve the advection–dispersion equation due to because of the ease of handling initial and boundary conditions and its relative simplicity in formulating solutions for multi-dimensional problems [92]. The function may be used to solve a different problem that involves equilibrium and non-equilibrium transport in semi-infinite and infinite mediums. Furthermore, very general and concise expressions for the solute concentration are possible with the GFM, particularly for multi-dimensional problems [88].

Analytical solutions were derived for 3D transport due to the dissolution of single-component NAPL pools in fully saturated and homogenous porous media and were suitable with unidirectional interstitial velocity. The elongated pool of NAPL along the interstitial flow direction was shown to have a greater concentration and was proportional to the

Sherwood number [93]. Additionally, a finite difference approach was used to develop an analytical solution for a 3D model of multi-component (1,1,2-trichloroethane and trichloroethylene) dissolution. The findings were consistent with their past research [28]. Lee and Chrysikopoulos [28] investigated the multi-component dissolution of NAPL contaminant pools in saturated porous media and developed a more efficient semi-analytical method that required less computation than the previous method. Further, the model predicts erroneous results if changes in multi-component NAPL activity coefficients are neglected [27]. All these analytical solutions aid in the planning and interpreting experiments in laboratory-packed beds and the verification of sophisticated numerical models.

6. Comparative evolution of dissolution enhancement techniques

The DNAPLs such as creosote, diesel fuel, coal tar etc., generally exist in complex form and the natural dissolution process of theses contaminants is time-consuming. Therefore, enhancement of the dissolution rate of DNAPL is required. With improvement in dissolution rate, there will be an ample quantity of dissolved NAPL easily available in the liquid phase, which can further be remediated with appropriate technology. Due to the poor solubility of the NAPL contaminants in subsurface and their comparatively strong capillary forces in the aquifer, traditional remediation techniques like pump and treat are inefficient and uneconomical for on-site circumstances [94]. With advances in technology, researchers have developed different solubility enhancement techniques. A short summary of dissolution enhancement techniques for single and multi-component NAPL is given in Table 5.

6.1. Surfactants for dissolution enhancement

Most of the research has investigated various surfactants for enhanced dissolution of entrapped NAPL chemicals, for example, biosurfactant, ionic and non-ionic surfactant, *in-situ* flushing using co-solvents etc. The former involves mixing surfactants of optimum concentration with NAPL, and the latter requires injection of co-solvent into the contaminant source zone to enhance the dissolution of the NAPL. Further, the application reduces its interfacial tension to make it more mobile. In the 1990s, NAPL dissolution enhancement was studied for the first time by Chevalier et al. [95] using a non-ionic surfactant in a saturated soil media. Results of the investigation depict that the use of surfactant improved the aqueous phase permeability of the media. Another study by Liu and Chang [96] investigated the effect of surfactant (sodium dodecyl sulphate, Triton X-100 and Brij 35) on the solubility of chlorophenols. It was further learned that the solubility of chlorophenol was a function of hydrophobicity. The adsorption of chlorophenols onto clayey adsorbent in the presence of surfactant showed a decreasing trend, which could be attributed to hydrophobic interaction.

In a study carried out by Mccray and Brusseau [97], cyclodextrin (a non-toxic sugar-based molecule) was used for *in-situ* remediations of multi-component NAPL pollutants. According to the findings, the pollutants that are most soluble in the cyclodextrin solution would have high initial aqueous concentrations. These will be the ones, which gets quickly dissolved from the NAPL. This finding was supported by an investigation carried out by Carroll and Brusseau [70]. In their study, they demonstrated significant solubility improvement and a rise in mass-removal rates for multi-component NAPL for 10% cyclodextrin solution. The increase in multi-component solubility was however, inversely related to the increase in single-component aqueous solubility. In some cases, hydroxypropyl-beta-cyclodextrin has enhanced the solubility of organics, heavy metals, and radioisotopes. The major hindrance in this technique was the choice of appropriate cyclodextrin type and the limited availability of cyclodextrin, which makes it a bit expensive.

6.2. Co-solvents for dissolution enhancement

Alcohol groups of lower and higher molecular weight, say ethanol, 1-propanol, and 2-propanol, are widely used as co-solvents. The reason being their higher solubility and water-miscibility. This leading to improved solubilisation and mobilisation of chlorinated solvents trapped in the subsurface. Before beginning the remediation operation, selecting the proper flushing agent is a crucial step. This is because the removal behaviour of each pollutant varies significantly depending on the flushing agent utilised [98,99]. Several other studies have demonstrated the efficacy of *in-situ* co-solvents flushing as a technique for improved NAPL removal from the subsurface. The *in-situ* flushing can effectively help in the design of remediation technologies [99–102].

6.3. Advanced methods for dissolution enhancement

There are few evidence on usage of ultrasonic waves for NAPL removal from the subsurface zone by means of enhancing solubility. However, more research is needed in this area. Further, the enhancement of NAPL dissolution as a function of soundwaves also need to be studied. NAPL Kim and Wang [103] carried out an investigation to study the impact of ultrasound on NAPL/oil removal. The results indicate that there was significant influence of waves on pollutant removal and the degree of reduction was a function of sonication power, flow rate, and type of soil. Sonication power directly correlated with pollutant extraction for high flow rates and was limited until cavitation was achieved. The effectiveness of sonication decreases with the flushing rate but eventually becomes constant under higher flow rates.

Microbial or biological enhancement of solubility of tetrachloroethene was studied by Glover et al. [104] in a laboratory-scale experiment. The findings of investigation suggest that solubility was inverse function of flow rate and got enhanced by factor of 1.5 and so is the mass transfer rate. Few more studies investigated impact of sound/acoustic waves on enhancement of dissolution are also found and is represented in Table 5 [105]. New technologies such as steam flooding, air sparging, and soil vapour extraction have been developed in response to the demand for alternate NAPL remediation approaches [47,106].

Table 5
Short summary of dissolution enhancement techniques for single and multi-component NAPL

NAPL used	Enhancement method	Experimental conditions/ parameters	Findings/inferences	References
TCE; 1,2-DCA	Dissolution and dechlorination	Column study: inner diameter: 4.8 cm; length: 60 cm	Under dynamic conditions and in the presence of microbial consortium, the dechlorination process resulted in the bio-enhanced dissolution of tetrachloroethylene.	[107]
PCE	Acoustic enhancement	Pore-water velocity measurements at a frequency of 75 Hz	The dissolution of perchloroethylene was increased 3-folds for 75 Hz due to the oscillatory motion of pore water velocity. The sound waves also immobilized the perchloroethylene, thus affecting the dissolution mass transfer.	[108]
p-Xylene	Tween-80	Heterogeneous media	The steady-state concentrations were lesser than the aqueous (equilibrium) solubility, indicating rate-limited mass transfer.	[109]
TCE	Dissolution with dechlorination	Batch reactor with zero-valent iron nanoparticle	Zero-valent iron nanoparticles (nZVI) could not cause DNAPL dissolution/mass-depletion rate for a concentration of 10 g/L. The rate of reaction was found to be inversely proportional to longevity. With the increase in the rate of reaction, there was an increase in the dechlorination rate and hence a reduction in pollutant concentration.	[110]
PCE	Ethanol with water as co-solvent	Ethanol/water co-solvents in the presence of airflow rate	Co-solvent/air flooding with a higher airflow rate resulted in higher perchloroethylene removal, attributed to improved distribution of co-solvent in the pore network. The reduction was more significant with a higher co-solvent/water ratio.	[102]
TCE	Dissolution by dechlorination bacteria	Batch reactor (biotic and abiotic) at $T = 20°C$ and using dechlorination bacteria	Dissolution of TCE was enhanced 4-folds in biotic reactor with bacteria as compared to abiotic reactor. The mass transfer coefficient (K_m) is found to be a function of temperature.	[111]
Binary mixture of benzene and TCE; TCE and DCM; DCM and toluene	Natural remobilisation/mixing	Natural remobilization	The change in density of benzene/TCE at a ratio of 25:75 leads to natural remobilisation. For TCM/DCM, there was no natural remobilisation as their densities had not made much difference. For DCM/toluene, difference in density has induced downward displacement. The results indicate that natural remobilisation may be an active mechanism with implications for site evaluation and remediation. The ultimate transformation from a DNAPL to an LNAPL may induce an upward displacement.	[9]
Aromatic hydrocarbons	Dissolution and microbial degradation	Density and viscosity	A significant quantity of metabolites related to the degradation of phenanthrene (styrene, diethyl, triethyl benzene, etc.) was reported at the contaminated tar site, indicating the existence of suitable microbes.	[8]
Mixture of NAPL	Surfactant (cyclodextrin)	Equilibrium aqueous concentration $C_i^A = C^{\mathrm{oW}} \cdot {}_iX^N \cdot {}_i\gamma^N \cdot \left(\frac{\gamma_i^{\mathrm{oA}}}{\gamma_i^A}\right) \cdot E_i$	Maximum contaminant concentration in the elution curves coincides with the occurrence of maximum concentration of cyclodextrin, followed by a gradual decline. The results indicate enhanced dissolution behaviour of multi-component organic pollutants.	[97]

Table 5 (Continued)

Table 5

NAPL used	Enhancement method	Experimental conditions/ parameters	Findings/inferences	References
1,1,2-TCE; PCE	Acoustics waves	Multi-component NAPL Ganglia; Column study: inner diameter: 2.5 cm; length-30 cm	Enhancement in dissolution was found to be directly proportional to the frequency of the acoustic wave. The NAPL mixture with less solubility had a more significant enhancement in the presence of square waves instead of sinusoidal or triangular sound waves.	[105]
o-Xylene; *o*-dichlorobenzene	Ethoxylated alcohol	Expression for the NAPL mass dissolution (macroscopic): $\rho_n \frac{\partial \eta}{\partial t} = -k_l \cdot \left(C^* - C\right)$	The use of surfactant (ethoxylated alcohol) resulted in 90% removal of chemicals in the first 10 PV in a column experiment, followed by a steady removal efficiency for the next 20 PV. The dissolution of *o*-Xylene and *o*-dichlorobenzene increased by a factor of 30 and 55, respectively.	[112]
PCE, TCE	Anaerobic mixed culture	Batch and column study in presence of methanogens and homo-acetogens	DNAPL dissolution rate was significantly enhanced when directly coupled with biological de-halogenation.	[113]
Ethyl acetate; butyl acetate	Dissolution with growth (multi-component system)	Local thermodynamic equilibrium and linearization models	Ideal components behave similarly, whereas non-ideal constituents show a significant difference in solubility as well as diffusivity.	[114]
1,2-DCA; TCE; PCE.	Hydroxypropyl-β-cyclodextrin; sodium dodecyl sulfate; ethanol	Column study: inner diameter: 2.2 cm; length: 7 cm	Raoult's law was applicable for elution of multi-component DNAPL under lower power enhanced-solubilisation agents such as water, HPCD, MCD, while the results were erroneous with high power enhanced solubilisation agents such as ethanol and sodium dodecyl sulfate.	[115]

6.4. Limitations of dissolution enhancement

The observed main limitations while using surfactant solutions for *in-situ* soil washing are that there is no accurate method to quantify the required surfactant. Inaccuracy will lead to excess surfactant usage, causing pores to clog due to the dispersion of soil particles by surfactant solution. To avoid the issue of clogging, some studies used electron donors. Further, it will result in high energy consumption and lower soil permeability. In addition, low surfactant recovery adds to the operation's cost and can create further contamination of the soil with the surfactant.

7. Critical challenges in understanding DNAPL dissolution with degradation

NAPL degradation is found in field conditions due to microbial action. The dissolution coupled with degradation in these cases is more complex and there are several challenges in understanding DNAPL dissolution with degradation. The daughter products of degraded halogenated NAPL can repartition back into the NAPL phase and can also influence the dissolution of the parent NAPL [116]. The effect of daughter products on the dissolution of NAPL could be significant but has been less investigated so far. The formation of daughter products by microbial degradation can potentially enhance the rate of dissolution of NAPL and can deplete the aqueous-phase concentration of the parent NAPL, as well as increase the concentration gradient for dissolution, as represented in Fig. 7 [117]. For example, a study carried out by Carr et al. [117] showed that the formation of daughter products by microbial degradation enhanced the dissolution of PCE by a factor of 16 times [118] and increased the PCE removal rate by approximately 14-fold.

The dissolution characteristics of a NAPL mixture containing methyl tert-butyl ether (MTBE), BTEX, 1,2,4-trimethyl benzene, and octane were studied [10,30,38,119]. They found that MTBE dissolved in an ideal manner (i.e., followed Raoult's law). However, other NAPLs (BTEX, 1,2, 4 trimethyl benzene and octane) dissolved non-ideally to some extent [120]. The effect of repartitioning of hydrocarbons during the dissolution of NAPL was studied [121]. They also investigated the in-series interactions of DCM (dichloromethane) and TCE (trichloroethane) during dissolution. Further, they found upstream DCM can repartition into the downstream TCE and thereby delay the dissolution of TCE. The DCM plume, therefore, can get retarded due to its repartitioning into the downstream NAPL (TCE) [121]. Ignoring the daughter product repartition in NAPL could cause significant laboratory and field prediction errors.

Researchers suggest that up to 60% of the product mass could be repartitioned into NAPL even at a modest NAPL saturation of 2% [122]. The daughter products can also repartition themselves back into the NAPL phase and influence the dissolution of the parent compound. There have been

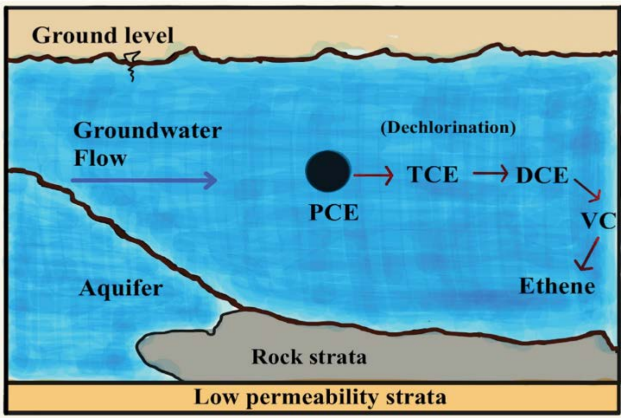

Fig. 7. Formation of daughter products in the degradation of a typical DNAPL (PCE).

limited studies on the effect of repartitioning of daughter products on the dissolution of NAPL. Ramsburg et al. [122] quantified the dissolution and partitioning of DCE (dichloroethane) and VC (vinyl chloride) between NAPL and water in batch experiments. They found that the partitioning could be approximately described by Raoult's law analogy (RLA). Ramsburg et al. [123] also studied the partitioning of DCE into PCE using column experiments. They modeled kinetic mass transfer during multi-component DNAPL dissolution using correlations developed in previous studies by Imhoff and Powers [63,124] for single-component dissolution. However, the model does not consider the change in the constitution of NAPL during dissolution and assumes a constant NAPL constitution during dissolution. Several other studies have focused more on the biological aspects of daughter product formation and not on the physical dissolution and repartitioning [104,125,126]. The influence of daughter products on the dissolution of NAPL is a promising research area that needs further understanding to investigate the efficacy of remediation plans.

8. Conclusions and future scope

This review attempts to provide a brief overview of the single and multi-component dissolution mechanisms carried out in different conditions and to study their mass transfer limitations. The dissolution of NAPL has continued to attract contemporary researchers in the field of environmental, biological, and petrochemical fields. Still, there are significant areas which require further advancement in order to optimize the field applications of various remediation techniques.

A fundamental method to estimate the NAPL surface area has not emerged so far. The effect of NAPL architecture and heterogeneities on the dissolution must be further investigated. Studies on the investigation of the influence of coupled physical and chemical heterogeneity on the entrapment and dissolution behaviour of residual NAPL are required.

Equally, there is a need to quantify wettability parameters in natural soils and subsurface formations and investigate dissolution behaviour in heterogeneous natural environments. Further study is required in NAPL source zone detection, modeling heterogeneity, etc.

It is difficult to quantify the extent of mass transfer limitations for *in-situ* dissolution and effective solubility of single and multi-component NAPL. A model that can simulate the change from steady-state to transient dissolution is yet to be developed. Understanding multiple-stage dissolution from a complex source with greater heterogenic structure is challenging research. A robust method that can predict the dissolution of NAPL for such conditions is the need of the hour.

Knowledge of the movement and dissolution mechanisms of pure-phase DNAPL and the migration of the aqueous-phase plumes are comparatively limited in fractured geologic media. The extension of the dissolution model presented in all systems, as well as to media containing entrapped and pooled NAPL, warrants further examination. Novel solubility enhancement techniques for improving dissolution and natural remobilisation can be discovered.

Further, more research is to be focused on understanding the kinetics of multi-component dissolution. Most of the remediation plans for the contaminated sites include only one of the available techniques depending upon the budget, soil type, site requirements etc. Hence studies on the combination of techniques to remediate the contaminated sites can also be further expanded.

Symbols

P_e — Peclet number
C_a — Aqueous phase concentration, mg/L
C_{sat} — Saturated concentration, mg/L
K_{ow} — Organic-water partitioning coefficient
R — Mass transfer rate, g/m^3·min
K_{nw} — Transient dissolution mass transfer coefficient
C_{sat}^0 — Pure phase solubility, mg/L
X_{ni} — Mole fraction in the non-aqueous phase
g — Activity coefficient
C_i — Concentration of component, mg/L
K_L — Mass transfer coefficient, cm/min
Sh — Sherwood number
Re — Reynold's number
Sc — Schmidt's number
E_{ow} — Mass exchanged per unit time per unit volume, g/m^3·min
k_{ow} — Film mass transfer coefficient, cm/min
A^t_{ow} — NAPL-water interfacial area per unit volume, cm^{-1}
A^c_{ow} — NAPL-water interfacial area per unit volume, continuous NAPL phase

Abbreviations

NAPL — Non-aqueous phase liquids
LNAPL — Light non-aqueous phase liquids
DNAPL — Dense non-aqueous phase liquids
HTC — Heat transfer coefficient
MTC — Mass transfer coefficient
TCE — Trichloroethane/Trichloroethylene

TCA — 1,1,2-Trichloroethane
BTEX — Benzene, toluene, ethylbenzene, xylene
PCE — Tetrachloroethene
MTBE — Methyl tert-butyl ether
PAH — Polycyclic aromatic hydrocarbons
TMB — Trimethylbenzene
MISER — Michigan soil-vapor extraction remediation
HFE-1700 — Hydrofluoroether
DCA — 1,2-dichloroethane
MASST — Multiple analytical source superposition technique
BTXN — Benzene, toluene, xylene, and naphthalene
MTL — Mass transfer limited
DCM — Dichloromethane
VC — Vinyl chloride

References

[1] A.A. Keller, M.J. Blunt, P.V. Roberts, Behavior of nonaqueous phase liquids in fractured porous media under two-phase flow conditions, Transp. Porous Media, 38 (2000) 189–203.

[2] J.W. Roy, J.E. Smith, R.W. Gillham, Laboratory evidence of natural remobilization of multi-component DNAPL pools due to dissolution, J. Contam. Hydrol., 74 (2004) 145–161.

[3] M.O. Rivett, R.M. Allen-King, A controlled field experiment on groundwater contamination by a multi-component DNAPL: dissolved-plume retardation, J. Contam. Hydrol., 66 (2003) 117–146.

[4] R.G. McLaren, E.A. Sudicky, Y.J. Park, W.A. Illman, Numerical simulation of DNAPL emissions and remediation in a fractured dolomitic aquifer, J. Contam. Hydrol., 136–137 (2012) 56–71.

[5] Y.C. Lee, T.S. Kwon, J.S. Yang, J.W. Yang, Remediation of groundwater contaminated with DNAPLs by biodegradable oil emulsion, J. Hazard. Mater., 140 (2007) 340–345.

[6] P.P. Brahma, T.C. Harmon, The effect of multi-component diffusion on NAPL dissolution from spherical ternary mixtures, J. Contam. Hydrol., 67 (2003) 43–60.

[7] L. Liu, U. Maier, P. Grathwohl, S.B. Haderlein, Contaminant mass transfer from NAPLs to water studied in a continuously stirred flow-through reactor, J. Environ. Eng., 138 (2012) 826–832.

[8] J.A. Van Leeuwen, N. Hartog, J. Gerritse, C. Gallacher, R. Helmus, O. Brock, J.R. Parsons, S.M. Hassanizadeh, The dissolution and microbial degradation of mobile aromatic hydrocarbons from a Pintsch gas tar DNAPL source zone, Sci. Total Environ., 722 (2020) 137797, doi: 10.1016/j.scitotenv.2020.137797.

[9] J.W. Roy, J.E. Smith, R.W. Gillham, Natural remobilization of multi-component DNAPL pools due to dissolution, J. Contam. Hydrol., 59 (2002) 163–186.

[10] S. Lesage, S. Brown, Observation of the dissolution of NAPL mixtures, J. Contam. Hydrol., 15 (1994) 57–71.

[11] M. Vasudevan, C.D. Johnston, T.P. Bastow, G. Lekmine, J.L. Rayner, I.M. Nambi, G. Suresh Kumar, R. Ravi Krishna, G.B. Davis, Effect of compositional heterogeneity on dissolution of non-ideal LNAPL mixtures, J. Contam. Hydrol., 194 (2016) 10–16.

[12] P.T. Imhoff, P.R. Jaffé, G.F. Pinder, An experimental study of complete dissolution of a nonaqueous phase liquid in saturated porous media, Water Resour. Res., 30 (1994) 307–320.

[13] S.E. Powers, L.M. Abriola, W.J. Weber, An experimental investigation of nonaqueous phase liquid dissolution in saturated subsurface systems: transient mass transfer rates, Water Resour. Res., 30 (1994) 321–332.

[14] A. Patmonoaji, Y. Hu, M. Nasir, C. Zhang, T. Suekane, Effects of dissolution fingering on mass transfer rate in three-dimensional porous media, Water Resour. Res., 57 (2021) e2020WR029353, doi: 10.1029/2020WR029353.

[15] M.W. Priddle, K.T.B. MacQuarrie, Dissolution of creosote in groundwater: an experimental and modeling investigation, J. Contam. Hydrol., 15 (1994) 27–56.

[16] J.W. Mercer, R.M. Cohen, A review of immiscible fluids in the subsurface: properties, models, characterization and remediation, J. Contam. Hydrol., 6 (1990) 107–163.

[17] D.I. Siegel, H.O. Pfannkuch, Silicate dissolution influence on Filson Creek chemistry, northeastern Minnesota, Geol. Soc. Am. Bull., 95 (1984) 1446–1453.

[18] D.M. Ward, O. Trass, A.I. Johnson, Mass transfer from fluid and solid spheres at low Reynolds numbers: Part II, Can. J. Chem. Eng., 40 (1962) 164–168.

[19] W.J. Powers, S.E. Abriola, L.M. Weber, An experimental investigation of nonaqueous phase liquid dissolution in saturated subsurface systems: steady-state mass transfer rates, Water Resour. Res., 28 (1992) 2691–2705.

[20] P.T. Imhoff, M.W. Farthing, C.T. Miller, Modeling NAPL dissolution fingering with upscaled mass transfer rate coefficients, Adv. Water Resour., 26 (2003) 1097–1111.

[21] A.S. Miller, C.T. Mcneill, P. Mayer, Dissolution of trapped nonaqueous phase liquids' mass transfer characterstics, Water Resour. Res., 25 (1990) 2783–2796.

[22] Y. Cohen, P.A. Ryan, Multimedia modeling of environmental transport: trichloroethylene test case, Environ. Sci. Technol., 19 (1985) 412–417.

[23] A. Luciano, P. Viotti, M.P. Papini, Laboratory investigation of DNAPL migration in porous media, J. Hazard. Mater., 176 (2010) 1006–1017.

[24] L.D. Stewart, J.C. Chambon, M.A. Widdowson, M.C. Kavanaugh, Upscaled modeling of complex DNAPL dissolution, J. Contam. Hydrol., 244 (2022) 103920, doi: 10.1016/j.jconhyd.2021.103920.

[25] H. Li, L. Zhao, X. Gao, X. Li, Experimental investigation of methyl tert-butyl ether dissolution in saturated porous media, Chin. J. Chem. Eng., 23 (2015) 1685–1690.

[26] Z. Guo, A.E. Russo, E.L. DiFilippo, Z. Zhang, C. Zheng, M.L. Brusseau, Mathematical modeling of organic liquid dissolution in heterogeneous source zones, J. Contam. Hydrol., 235 (2020) 103716, doi: 10.1016/j.jconhyd.2020.103716.

[27] C.V. Chrysikopoulos, K.Y. Lee, Contaminant transport resulting from multi-component nonaqueous phase liquid pool dissolution in three-dimensional subsurface formations, J. Contam. Hydrol., 31 (1998) 1–21.

[28] K.Y. Lee, C.V. Chrysikopoulos, Numerical modeling of three-dimensional contaminant migration from dissolution of multi-component NAPL pools in saturated porous media, Environ. Geol., 26 (1995) 157–165.

[29] M. Vasudevan, I.M. Nambi, G. Suresh Kumar, Scenario-based modelling of mass transfer mechanisms at a petroleum contaminated field site-numerical implications, J. Environ. Manage., 175 (2016) 9–19.

[30] W.G. Rixey, S. Joshi, Dissolution of MTBE From a Residually Trapped Gasoline Source. A Summary of Research Results, American Petroleum Institute, 2000.

[31] J.F. Devlin, J.R. Barbaro, A method of estimating multi-component nonaqueous-phase liquid mass in porous media using aqueous concentration ratios, Environ. Toxicol. Chem., 20 (2001) 2443–2449.

[32] G. Lekmine, T.P. Bastow, C.D. Johnston, G.B. Davis, Dissolution of multi-component LNAPL gasolines: the effects of weathering and composition, J. Contam. Hydrol., 160 (2014) 1–11.

[33] K.Y. Lee, C.V. Chrysikopoulos, NAPL pool dissolution in stratified and anisotropic porous formations, J. Environ. Eng., 124 (1998) 851–862.

[34] D. Schaefer, Determinability of NAPL mass by measuring concentrations downstream of a contaminant source, Environ. Earth Sci., 67 (2012) 2459–2467.

[35] M.C. Padgett, G.R. Tick, K.C. Carroll, W.R. Burke, Chemical structure influence on NAPL mixture nonideality evolution, rate-limited dissolution, and contaminant mass flux, J. Contam. Hydrol., 198 (2017) 11–23.

[36] E.A. Seagren, T.O. Moore, Nonaqueous phase liquid pool dissolution as a function of average pore water velocity, J. Environ. Eng., 129 (2003) 786–799.

[37] J.T. Geller, J.R. Hunt, Mass transfer from nonaqueous phase organic liquids in water-saturated porous media, Water Resour. Res., 29 (1993) 833–845.

[38] S. Garg, W.G. Rixey, The dissolution of benzene, toluene, *m*-xylene and naphthalene from a residually trapped non-aqueous phase liquid under mass transfer limited conditions, J. Contam. Hydrol., 36 (1999) 313–331.

[39] Z. Yang, A. Niemi, F. Fagerlund, T. Illangasekare, R.L. Detwiler, Dissolution of dense non-aqueous phase liquids in vertical fractures: effect of finger residuals and dead-end pools, J. Contam. Hydrol., 149 (2013) 88–99.

[40] K.E. Christensen, P.W. Altman, C. Schaefer, J.E. McCray, Steady-state DNAPL dissolution in three-dimensional fractured sandstone network experiments, J. Environ. Eng., 141 (2015) 04014047, doi: 10.1061/(asce)ee.1943-7870.0000871.

[41] H. Li, L. Zhao, X. Gao, X. Li, Experimental investigation of methyl tert-butyl ether dissolution in saturated porous media, Chin. J. Chem. Eng., 23 (2015) 1685–1690.

[42] T.P. Clement, T.R. Gautam, K.K. Lee, M.J. Truex, G.B. Davis, Modeling of DNAPL-dissolution, rate-limited sorption and biodegradation reactions in groundwater systems, Biorem. J., 8 (2004) 47–64.

[43] S.K. Hansen, B.H. Kueper, A new model for coupled multi-component NAPL dissolution and aqueous-phase transport, with application to creosote dissolution in discrete fractures, Water Resour. Res., 50 (2014) 58–70.

[44] J.J. Kaluarachchi, J.C. Parker, Modeling multi-component organic chemical transport in three-fluid-phase porous media, J. Contam. Hydrol., 5 (1990) 349–374.

[45] M.T. Gönüllü, Modelling dissolution of an organic mixture in the subsurface, Water Res., 30 (1996) 649–653.

[46] R. Valsala, S.K. Govindarajan, Interaction of dissolution, sorption and biodegradation on transport of BTEX in a saturated groundwater system: numerical modeling and spatial moment analysis, J. Earth Syst. Sci., 127 (2018) 53, doi: 10.1007/s12040-018-0950-3.

[47] Y. Hu, A. Patmonoaji, H. Xu, K. Kaito, S. Matsushita, T. Suekane, Pore-scale investigation on nonaqueous phase liquid dissolution and mass transfer in 2D and 3D porous media, Int. J. Heat Mass Transfer, 169 (2021) 120901, doi: 10.1016/j.ijheatmasstransfer.2021.120901.

[48] S.A. Bradford, L.M. Abriola, Dissolution of residual tetrachloroethylene in fractional wettability porous media: Incorporation of interfacial area estimates, Water Resour. Res., 37 (2001) 1183–1195.

[49] A. Kokkinaki, D.M. O'Carroll, C.J. Werth, B.E. Sleep, An evaluation of Sherwood–Gilland models for NAPL dissolution and their relationship to soil properties, J. Contam. Hydrol., 155 (2013) 87–98.

[50] S.A. Bradford, K.M. Rathfelder, J. Lang, L.M. Abriola, G.E. Brown, Entrapment and dissolution of DNAPLs in heterogeneous porous media, J. Contam. Hydrol., 67 (2003) 133–157.

[51] A. Luciano, G. Mancini, V. Torretta, P. Viotti, An empirical model for the evaluation of the dissolution rate from a DNAPL-contaminated area, Environ. Sci. Pollut. Res., 25 (2018) 33992–34004.

[52] J.T. Su, D. Needham, Mass transfer in the dissolution of a multi-component liquid droplet in an immiscible liquid environment., Langmuir, 29 (2013) 13339–13345.

[53] I.M. Nambi, S.E. Powers, Mass transfer correlations for nonaqueous phase liquid dissolution from regions with high initial saturations, Water Resour. Res., 39 (2003), doi: 10.1029/2001WR000667.

[54] B. Wu, H. Li, X. Du, L. Zhong, B. Yang, P. Du, Q. Gu, F. Li, Correlation between DNAPL distribution area and dissolved concentration in surfactant enhanced aquifer remediation effluent: a two-dimensional flow cell study, Chemosphere, 144 (2016) 2142–2149.

[55] K. Nakamura, M. Kikumoto, Modeling water–NAPL–air three-phase capillary behavior in soils, Soils Found., 54 (2014) 1225–1235.

[56] K. Nakamura, M. Kikumoto, New concept to describe three-phase capillary pressure–degree of saturation relationship in porous media, J. Contam. Hydrol., 214 (2018) 1–15.

[57] T.C. Sale, D.B. McWhorter, Steady-state mass transfer from single-component dense nonaqueous phase liquids in uniform flow fields, Water Resour. Res., 37 (2001) 393–404.

[58] M.M. Hamed, P.D. Nelson, P.B. Bedient, A distributed-site model for non-equilibrium dissolution of multi-component residually trapped NAPL, Environ. Modell. Software, 15 (2000) 443–450.

[59] F. Wang, M.D. Annable, J.W. Jawitz, Field-scale prediction of enhanced DNAPL dissolution based on partitioning tracers, J. Contam. Hydrol., 152 (2013) 147–158.

[60] J.C. Parker, E. Park, Modeling field-scale dense nonaqueous phase liquid dissolution kinetics in heterogeneous aquifers, Water Resour. Res., 40 (2004) 1–12.

[61] M.O. Rivett, S. Feenstra, J.A. Cherry, A controlled field experiment on groundwater contamination by a multi-component DNAPL: creation of the emplaced-source and overview of dissolved plume development, J. Contam. Hydrol., 49 (2001) 111–149.

[62] D. Mackay, W. Ying Shiu, A. Maijanen, S. Feenstra, Dissolution of non-aqueous phase liquids in groundwater, J. Contam. Hydrol., 8 (1991) 23–42.

[63] C.I. Steefel, A.C. Lasaga, Chapter 16 – Evolution of Dissolution Patterns: Permeability Change Due to Coupled Flow and Reaction, D.C. Melchior, R.L. Bassett, Eds., Chemical Modeling of Aqueous Systems II, ACS Symposium Series, ACS Publication, Washington D.C., 1990, pp. 212–225. Available at: https://doi.org/10.1021/bk-1990-0416.ch016

[64] S.E. Powers, I.M. Nambi, G.W. Curry, Non-aqueous phase liquid dissolution in heterogeneous systems: mechanisms and a local equilibrium modeling approach, Water Resour. Res., 34 (1998) 3293–3302.

[65] T.S. Soerens, D.A. Sabatini, J.H. Harwell, Effects of flow bypassing and nonuniform NAPL distribution on the mass transfer characteristics of NAPL dissolution, Water Resour. Res., 34 (1981) 63–65.

[66] R.C. Borden, C.-M. Kao, Evaluation of groundwater extraction for remediation of petroleum-contaminated aquifers, Water Environ. Res., 64 (1992) 28–36.

[67] S.E. Powers, L.M. Abriola, J.S. Dunkin, W.J. Weber, Phenomenological models for transient NAPL-water mass-transfer processes, J. Contam. Hydrol., 16 (1994) 1–33.

[68] E.L. DiFilippo, K.C. Carroll, M.L. Brusseau, Impact of organic-liquid distribution and flow-field heterogeneity on reductions in mass flux, J. Contam. Hydrol., 115 (2010) 14–25.

[69] L. Liu, F. Wu, S. Haderlein, P. Grathwohl, Determination of the subcooled liquid solubilities of PAHs in partitioning batch experiments, Geosci. Front., 4 (2013) 123–126.

[70] K.C. Carroll, M.L. Brusseau, Dissolution, cyclodextrin-enhanced solubilization, and mass removal of an ideal multi-component organic liquid, J. Contam. Hydrol., 106 (2009) 62–72.

[71] V. Renu, G.S. Kumar, Numerical modeling on benzene dissolution into groundwater and transport of dissolved benzene in a saturated fracture-matrix system, Environ. Processes, 3 (2016) 781–802.

[72] K. Prasad Saripalli, H. Kim, P. Suresh, C. Rao, M.D. Annable, Measurement of specific fluid−fluid interfacial areas of immiscible fluids in porous media, Environ. Sci. Technol., 31 (1997) 932–936.

[73] K.P. Saripalli, M.D. Annable, P.S.C. Rao, Estimation of nonaqueous phase liquid−water interfacial areas in porous media following mobilization by chemical flooding, Environ. Sci. Technol., 31 (1997) 3384–3388.

[74] M.L. Brusseau, H. Janousek, A. Murao, G. Schnaar, Synchrotron X-ray microtomography and interfacial partitioning tracer test measurements of NAPL-water interfacial areas, Water Resour. Res., 44 (2008) 1–9.

[75] A.G. Karaoglu, N.K. Copty, N.H. Akyol, S.A. Kilavuz, M. Babaei, Experiments and sensitivity coefficients analysis for multiphase flow model calibration of enhanced DNAPL dissolution, J. Contam. Hydrol., 225 (2019) 103515, doi: 10.1016/j.jconhyd.2019.103515.

[76] S. Feenstra, Aqueous concentration ratios to estimate mass of multi-component NAPL residual in porous media, Present. to Univ. Waterloo FbKiment Thesis Requir. Degree Dr. Philos., 1997.

[77] V.M. Vulava, L.D. McKay, M.M. Broholm, J.F. McCarthy, S.G. Driese, G.S. Sayler, Dissolution and transport of coal

tar compounds in fractured clay-rich residuum, J. Hazard. Mater., 203–204 (2012) 283–289.

[78] Z. Gong, K. Alef, B.M. Wilke, P. Li, Dissolution and removal of PAHs from a contaminated soil using sunflower oil, Chemosphere, 58 (2005) 291–298.

[79] M.G. Mahmoodlu, E.M. Pontedeiro, J.S. Pérez Guerrero, A. Raoof, S. Majid Hassanizadeh, M.T. van Genuchten, Dissolution kinetics of volatile organic compound vapors in water: An integrated experimental and computational study, J. Contam. Hydrol., 196 (2017) 43–51.

[80] B. Agaoglu, T. Scheytt, N.K. Copty, Laboratory-scale experiments and numerical modeling of cosolvent flushing of multi-component NAPLs in saturated porous media, J. Contam. Hydrol., 140–141 (2012) 80–94.

[81] K.Y. Lee, C.V. Chrysikopoulos, Dissolution of a well-defined trichloroethylene pool in saturated porous media: experimental results and model simulations, Water Res., 36 (2002) 3911–3918.

[82] Y. Arcand, J. Hawari, S.R. Guiot, Solubility of pentachlorophenol in aqueous solutions: The pH effect, Water Res., 29 (1995) 131–136.

[83] S. Popp, C. Beyer, A. Dahmke, N. Koproch, R. Köber, S. Bauer, Temperature-dependent dissolution of residual non-aqueous phase liquids: model development and verification, Environ. Earth Sci., 75 (2016) 1–13.

[84] D. Zhou, L.A. Dillard, M.J. Blunt, A physically based model of dissolution of nonaqueous phase liquids in the saturated zone, Transp. Porous Media, 39 (2000) 227–255.

[85] X. Yang, L.E. Erickson, L.T. Fan, A discrete blob model of contaminant transport in groundwater with trapped non-aqueous phase liquids, Chem. Eng. Commun., 154 (1996) 33–57.

[86] I.M. Nambi, S.E. Powers, NAPL dissolution in heterogeneous systems: an experimental investigation in a simple heterogeneous system, J. Contam. Hydrol., 44 (2000) 161–184.

[87] F.J. Leij, T.H. Skaggs, M.T. Van Genuchten, Analytical solutions for solute transport in three-dimensional semi-infinite porous media, Water Resour. Res., 27 (1991) 2719–2733.

[88] F.J. Leij, E. Priesack, M.G. Schaap, Solute transport modeled with Green's functions with application to persistent solute sources, J. Contam. Hydrol., 41 (2000) 155–173.

[89] K. Lee, Transport of dissolved contaminants originating from a rectangular prism-shaped, multi-component nonaqueous-phase liquid source in saturated porous media, Environ. Geol., 43 (2002) 132–137.

[90] S.K. Hansen, B.H. Kueper, An analytical solution to multi-component NAPL dissolution equations, Adv. Water Resour., 30 (2007) 382–388.

[91] R.L. Detwiler, H. Rajaram, R.J. Glass, Nonaqueous-phase-liquid dissolution in variable-aperture fractures: development of a depth-averaged computational model with comparison to a physical experiment, Water Resour. Res., 37 (2001) 3115–3129.

[92] F.J. Leij, M.T.H. Van Genuchten, Analytical modeling of nonaqueous phase liquid dissolution with Green's functions, Transp. Porous Media, 38 (2000) 141–166.

[93] C.V. Chrysikopoulos, Three-dimensional analytical models of contaminant transport from nonaqueous phase liquid pool dissolution in saturated subsurface formations, Water Resour. Res., 31 (1995) 1137–1145.

[94] C.A. Peters, C.D. Knightes, D.G. Brown, Long-term composition dynamics of PAH-containing NAPLs and implications for risk assessment, Environ. Sci. Technol., 33 (1999) 4499–4507.

[95] L.R. Chevalier, S.J. Masten, R.B. Wallace, D.C. Wiggert, Experimental Investigation of surfactant-enhanced dissolution of residual NAPL in saturated soil, Groundwater Monit. Rem., 17 (1997) 89–98.

[96] J.C. Liu, P.S. Chang, Solubility and adsorption behaviors of chlorophenols in the presence of surfactant, Water Sci. Technol., 35 (1997) 123–130.

[97] J.E. Mccray, M.L. Brusseau, Cyclodextrin-enhanced *in-situ* flushing of multiple-component immiscible organic liquid contamination at the field scale: analysis of dissolution behavior, Environ. Sci. Technol., 33 (1999) 89–95.

[98] R.W. Falta, C.M. Lee, S.E. Brame, E. Roeder, J.T. Coates, C. Wright, A.L. Wood, C.G. Enfield, Field test of high molecular weight alcohol flushing for subsurface nonaqueous phase liquid remediation, Water Resour. Res., 35 (1999) 2095–2108.

[99] T.I. Ladaa, C.M. Lee, J.T. Coates, R.W. Falta, Cosolvent effects of alcohols on the Henry's law constant and aqueous solubility of tetrachloroethylene (PCE), Chemosphere, 44 (2001) 1137–1143.

[100] R.A. Kanaly, K. Watanabe, Multiple mechanisms contribute to the biodegradation of benzo[a]pyrene by petroleum-derived multi-component nonaqueous-phase liquids, Environ. Toxicol. Chem., 23 (2004) 850–856.

[101] J.W. Jawitz, D. Dai, P.S.C. Rao, M.D. Annable, R.D. Rhue, Rate-limited solubilization of multi-component nonaqueous-phase liquids by flushing with cosolvents and surfactants: modeling data from laboratory and field experiments, Environ. Sci. Technol., 37 (2003) 1983–1991.

[102] S.W. Jeong, A.L. Wood, T.R. Lee, Enhanced removal of DNAPL trapped in porous media using simultaneous injection of cosolvent with air: influencing factors and removal mechanisms, J. Hazard. Mater., 101 (2003) 109–122.

[103] Y.U. Kim, M.C. Wang, Effect of ultrasound on oil removal from soils, Ultrasonics, 41 (2003) 539–542.

[104] K.C. Glover, J. Munakata-Marr, T.H. Illangasekare, Biologically enhanced mass transfer of tetrachloroethene from DNAPL in source zones: experimental evaluation and influence of pool morphology, Environ. Sci. Technol., 41 (2007) 1384–1389.

[105] C.V. Chrysikopoulos, E.T. Vogler, Acoustically enhanced multi-component NAPL ganglia dissolution in water saturated packed columns, Environ. Sci. Technol., 38 (2004) 2940–2945.

[106] ITRC, Evaluating Natural Source Zone Depletion at Sites with LNAPL, The Interstate Technology & Regulatory Council, Columbia, 2009, pp. 1–76.

[107] M. Chen, L.M. Abriola, B.K. Amos, E.J. Suchomel, K.D. Pennell, F.E. Löffler, J.A. Christ, Microbially enhanced dissolution and reductive dechlorination of PCE by a mixed culture: Model validation and sensitivity analysis, J. Contam. Hydrol., 151 (2013) 117–130.

[108] C.V. Chrysikopoulos, E.T. Vogler, Acoustically enhanced ganglia dissolution and mobilization in a monolayer of glass beads, Transp. Porous Media, 64 (2006) 103–121.

[109] S. Saenton, T.H. Illangasekare, K. Soga, T.A. Saba, Effects of source zone heterogeneity on surfactant-enhanced NAPL dissolution and resulting remediation end-points, J. Contam. Hydrol., 59 (2002) 27–44.

[110] F. Fagerlund, T.H. Illangasekare, T. Phenrat, H.J. Kim, G.V. Lowry, PCE dissolution and simultaneous dechlorination by nanoscale zero-valent iron particles in a DNAPL source zone, J. Contam. Hydrol., 131 (2012) 9–28.

[111] S. Lee, Enhanced dissolution of TCE in NAPL by TCE-degrading bacteria in wetland soils, J. Hazard. Mater., 145 (2007) 17–22.

[112] J. Fortin, W.A. Jury, M.A. Anderson, Enhanced removal of trapped non-aqueous phase liquids from saturated soil using surfactant solutions, J. Contam. Hydrol., 24 (1997) 247–267.

[113] Y. Yang, P.L. Mccarty, Biologically enhanced dissolution of tetrachloroethene DNAPL, Environ. Sci. Technol., 34 (2000) 2979–2984.

[114] S. Chu, A. Prosperetti, Dissolution and growth of a multi-component drop in an immiscible liquid, J. Fluid Mech., 798 (2016) 787–811.

[115] G.R. Tick, J.R. Harvell, D. Murgulet, Intermediate-scale investigation of enhanced-solubilization agents on the dissolution and removal of a multi-component dense nonaqueous phase liquid (DNAPL) source, Water Air Soil Pollut., 226 (2015) 371, doi: 10.1007/s11270-015-2636-7.

[116] F.H. Chapelle, L.J. Kauffman, M.A. Widdowson, Modeling long-term trends of chlorinated ethene contamination at a

public supply well, J. Am. Water Resour. Assoc., 51 (2015) 1–13.

[117] C.S. Carr, S. Garg, J.B. Hughes, Effect of dechlorinating bacteria on the longevity and composition of PCE-containing nonaqueous phase liquids under equilibrium dissolution conditions, Environ. Sci. Technol., 34 (2000) 1088–1094.

[118] N. Cope, J.B. Hughes, Biologically-enhanced removal of PCE from NAPL source zones, Environ. Sci. Technol., 35 (2001) 2014–2021.

[119] M.O. Rivett, S. Feenstra, Dissolution of an emplaced source of DNAPL in a natural aquifer setting, Environ. Sci. Technol., 39 (2005) 447–455.

[120] A.E. Russo, M.K. Mahal, M.L. Brusseau, Nonideal behavior during complete dissolution of organic immiscible liquid, J. Hazard. Mater., 172 (2009) 208–213.

[121] C. Serralde, M.O. Rivett, J.W. Molson, Interaction of Multiple In-Series DNAPL Residual Source Zones: Implications for Dissolution, Repartitioning and DNAPL Mobilization at Contaminated Industrial Sites, IAHS, UKCEH Wallingford, Oxfordshire OX10 8BB, UK, 2008, pp. 388–395.

[122] C.A. Ramsburg, C.E. Thornton, J.A. Christ, Degradation product partitioning in source zones containing chlorinated ethene dense non-aqueous-phase liquid, Environ. Sci. Technol., 44 (2010) 9105–9111.

[123] C.A. Ramsburg, J.A. Christ, S.R. Douglas, A. Boroumand, Analytical modeling of degradation product partitioning kinetics in source zones containing entrapped DNAPL, Water Resour. Res., 47 (2011), doi: 10.1029/2010WR009958.

[124] T. Saba, T.H. Illangasekare, J. Ewing, Investigation of surfactant-enhanced dissolution of entrapped nonaqueous phase liquid chemicals in a two-dimensional groundwater flow field, J. Contam. Hydrol., 51 (2001) 63–82.

[125] P.L. Morrill, B.E. Sleep, D.J. Seepersad, M.L. McMaster, E.D. Hood, C. LeBron, D.W. Major, E.A. Edwards, B. Sherwood Lollar, Variations in expression of carbon isotope fractionation of chlorinated ethenes during biologically enhanced PCE dissolution close to a source zone, J. Contam. Hydrol., 110 (2009) 60–71.

[126] Y. Yang, P.L. McCarty, Comparison between donor substrates for biologically enhanced tetrachloroethene DNAPL dissolution, Environ. Sci. Technol., 36 (2002) 3400–3404.