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Natural source zone depletion of LNAPL: A critical review supporting modelling approaches

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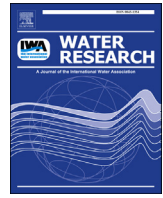
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Review

Natural source zone depletion of LNAPL: A critical review supporting modelling approaches



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ABSTRACT

Natural source zone depletion (NSZD) of light non-aqueous phase liquids (LNAPLs) includes partitioning, transport and degradation of LNAPL components. NSZD is being considered as a site closure option during later stages of active remediation of LNAPL contaminated sites, and where LNAPL mass removal is limiting. To ensure NSZD meets compliance criteria and to design enhanced NSZD actions if required, residual risks posed by LNAPL and its long term behaviour require estimation. Prediction of long-term NSZD trends requires linking physicochemical partitioning and transport processes with bioprocesses at multiple scales within a modelling framework. Here we expand and build on the knowledge base of a recent review of NSZD, to establish the key processes and understanding required to model NSZD long term. We describe key challenges to our understanding, inclusive of the dominance of methanogenic or aerobic biodegradation processes, the potentially changeability of rates due to the weathering profile of LNAPL product types and ages, and linkages to underlying bioprocesses. We critically discuss different scales in subsurface simulation and modelling of NSZD. Focusing on processes at Darcy scale, 36 models addressing processes of importance to NSZD are investigated. We investigate the capabilities of models to accommodate more than 20 subsurface transport and transformation phenomena and present comparisons in several tables. We discuss the applicability of each group of models for specific site conditions.

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1. Introduction

Natural source zone depletion (NSZD) of light non aqueous phase liquids (LNAPLs) in subsurface environments comprises the superposition and linking of several natural processes which result in LNAPL mass loss. The processes include movement of the parent LNAPL relative to air, soil and water phases; the partitioning of LNAPL components (e.g., benzene) into other phases (air, water, soil), and degradation through biochemical reactions. The magnitude of rates of NSZD is a critical decision-making parameter to compare to active remediation endpoints at LNAPL impacted sites (Sookhak Lari et al., 2018b). Furthermore, a good estimate of the NSZD rate results in an appropriate estimate of the longevity and associated risks of the contamination (Blanc et al., 1996; Davis et al. 1999, 2009; Garg et al., 2017; Mulligan and Yong, 2004; Rivett et al., 2011).

The history of NSZD as an emerging remediation approach, and the paradigm shift from Monitored Natural Attenuation (MNA, focusing on fate and transport of dissolved-phase hydrocarbon plumes in the saturated zone) to NSZD was reported in Garg et al. (2017), where key publications Johnson et al. (2006) and ITRC (2009) were highlighted. In particular, the paradigm shift from MNA to NSZD was due to the finding that rates of degradation and mass loss in the vadose zone were being found to be orders of magnitude higher than MNA in groundwater (Garg et al., 2017). Historically, estimates of mass loss and biodegradation had been undertaken separately for groundwater, for vadose zones and through direct LNAPL fingerprinting.

LNAPLs can consist of a range of different petroleum product types (including, gasolines, jet fuels, kerosenes, diesels, lube oils, coal tars and crude oils) which are likely to undergo NSZD at differing rates due to their differing compositions and environmental factors. Depending on their solubility and vapour pressure, LNAPL components may partition into groundwater or the soil gas phase prior to biodegradation or perhaps biodegrade without entering the aqueous phase (for example for alkanes) (Abreu et al., 2009; Ng et al. 2014, 2015). The rate of NSZD is a function of the complexity of the LNAPL distribution in the subsurface (Christensen and Larsen, 1993; Sookhak Lari et al., 2018b), the partitioning attributes of components in the LNAPL (Lang et al., 2009; Lekmine et al., 2017; Vasudevan et al., 2016a), geo-physical properties of media, fluid flow conditions (Sookhak Lari et al., 2016a), types of microorganisms and their predators (Franzmann et al., 1999), availability of nutrients and electron acceptors (Wiedemeier et al., 1999a) and ambient parameters such as pH and temperature (Garg et al., 2017). Biodegradation and partitioning processes can result in compositional changes to the LNAPL and an apparent stepwise depletion of components in a specific order, based on their susceptibilities to biodegradation and partitioning (Christensen and Larsen, 1993; Peters and Moldowan, 1993; Volkman et al., 1984), suggesting that different compound types undergo NSZD at different rates. Together, these processes form a highly non-

linear system to investigate (Blagodatsky and Smith, 2012; Blanc et al., 1996; Garg et al., 2017; Miller et al., 2013).

Traditional approaches for monitoring and determining the rate of NSZD (also used for MNA) include measuring several indicators of the biotic processes (Franzmann et al. 1999, 2002), either at site scales (Chaplin et al., 2002; Johnson et al., 2006) or through pore-scale sampling (Hallett et al., 2013). Commonly, these include measuring the abundance of electron acceptors (mainly with a focus on oxygen, nitrate, sulfate and reactions products such as ferrous iron and methane) required for biological respiration, fermentation and methanogenesis (Garg et al., 2017). The latter is reported to be the dominant LNAPL mass loss reaction at many sites (Garg et al., 2017). Furthermore, various approaches have been used to collect and measure soil gas (Sookhak Lari et al., 2017; Sweeney and Todd Ririe, 2017) and determine the proportionality of important compounds such as oxygen, carbon dioxide and methane. These indicators are then converted through stoichiometric approaches to determine the degree of NSZD (Amos et al., 2005; Chaplin et al., 2002; Cohen et al., 2016; Davis et al. 1998, 2013; Eichert et al., 2017; Johnson et al., 2006; Lahvis et al., 1999; Lundegard and Johnson, 2006). Also pilot tests are widely used to estimate the rate of NSZD in typical site conditions (Dobson et al., 2007; Rockhold et al., 2005).

Despite field-scale measurements and pilot tests providing vital data regarding current rates of NSZD at a site, it is not trivial to extrapolate the data and predict long-term rates as NSZD rates can differ due to differing LNAPL compositions, extents of weathering and environmental factors. Indeed, the complex mix of processes, combined with weathering and biodegradation can significantly impact the composition and longevity of a LNAPL (Meckenstock et al., 2015).

Modelling biotic degradation of chemicals in porous media is a field of study in various engineering applications. Examples include municipal landfills (Lowry et al., 2008; Visscher and Cleemput, 2003), storage of greenhouse gases (Ebigbo et al., 2010), enhanced oil recovery (Landa-Marbán et al., 2017; Li et al., 2011), natural attenuation and biodegradation in groundwater plumes (Prommer et al. 1999, 2002) and intrusion of biodegradable volatile organic compounds through the vadose zone into buildings (Akbariyeh et al., 2016; Knight and Davis, 2013; Parker, 2003).

Here we focus on key understandings that allow modelling NSZD of LNAPLs (Karapanagioti et al., 2003; Mulligan and Yong, 2004; Rivett et al., 2011). Under four broad groupings we discuss 21 critical processes affecting the rate of NSZD. We discuss how different modelling strategies address or accommodate these processes. We provide a critical review of the capabilities of 36 models that may have application to modelling NSZD. We investigate to what extent these models address each of the 21 processes, and recommend a limited number with capability for further application and development. The analysis is presented in several tables to ease comparison of the models.

In Section 2 we discuss major processes affecting NSZD,

categorized into four main groups. Different modelling strategies to model these processes are discussed in Section 3. In Section 4 we discuss capabilities of available models with respect to accommodating the processes discussed in Section 2.

2. Critical processes affecting NSZD

Fig. 1 depicts 21 of the major subsurface processes (both physical and biological) which may affect the overall rate of NSZD (Blanc et al., 1996; Garg et al., 2017; Mulligan and Yong, 2004; Rivett et al., 2011; Sookhak Lari et al., 2018b). A brief description of these (and relevant references) is also provided in Table 1. In this section we describe the key features of the processes in relation to NSZD and the necessity for modelling. We categorize the processes into four broad groups: (i) physicochemical processes governing fluid transport; (ii) LNAPL partitioning and compositional changes; (iii) NSZD processes in the vadose zone and groundwater; and (iv) fundamental microbiological processes underpinning effective NSZD.

2.1. Physicochemical processes governing fluid transport

Subsurface multi-phase transport of fluids, including LNAPL, vapour, soil gas and groundwater flow, has considerable impact on the rate of NSZD. Spatial and temporal dynamics of the fluids alter saturation and interphase surface area in the porous media. This consequently affects the rate of mass transfer between phases and influences partitioning of the LNAPL compounds into other phases, as well as the rate and type of biochemical reactions.

Multi-phase fluid dynamics in the subsurface is a complex function of fluid characteristics and ambient parameters. A key

parameter affecting LNAPL transport (and consequently vapour and soil gas flow; see e.g. (Sookhak Lari et al., 2016a; Sweeney and Todd Ririe, 2017)) is the characteristics of the LNAPL release. Chronic or catastrophic release incidents at different depths cause different morphology and evolution paths of the LNAPL plume. These also affect the volume of trapped, residual and free LNAPL as well as the LNAPL composition (Sookhak Lari et al., 2016b).

Another key controlling feature is the soil formation. The soil-moisture characteristic parameters (Lenhard and Parker, 1990; Sookhak Lari et al., 2018b), the heterogeneity of the formation (Johnston and Trefry, 2009), and the permeability and hydraulic conductivity (Sookhak Lari et al., 2017) are among the soil intrinsic features affecting subsurface fluid flow. For instance, the soil van Genuchten parameters have a great impact on capillary pressure and vertical distribution of LNAPL in the soil profile (Lenhard et al., 2018; Sookhak Lari et al., 2018b). These also impact the volume of trapped and residual LNAPL and the interphase surface area between different fluid pairs (Lenhard et al., 2018). Furthermore, ambient phenomena such as biofilm growth (or even gas bubble formation as a result of biological processes) are believed by some researchers to alter the soil intrinsic features such as permeability and hydraulic conductivity (Amos and Mayer, 2006; Tartakovsky et al., 2013).

LNAPL physical characteristics, such as viscosity and density, have been shown to significantly impact distribution, recovery and NSZD of the LNAPL (Lenhard and Parker, 1990; Sookhak Lari et al., 2015, 2018b). Along with the soil-moisture characteristic curve parameters, density and viscosity are the major parameters determining LNAPL plume evolution and distribution. The value of density and viscosity of the LNAPL may significantly change as a result of NSZD (compositional changes) and biogenic heat

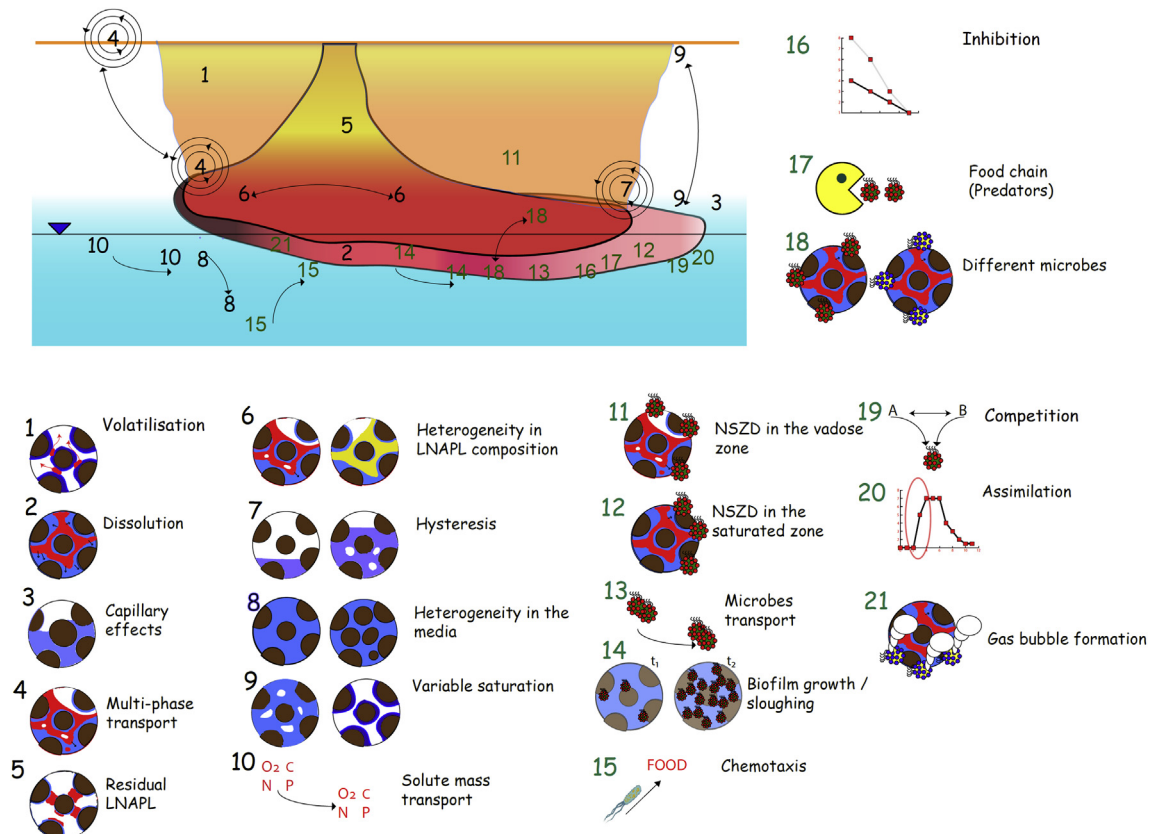


Fig. 1. Some of the major processes and parameters in NSZD.

Table 1

Brief description of the processes and parameters depicted in Fig. 1 (Blanc et al., 1996; Bradford et al., 2014; Sookhak Lari et al., 2016a).

#	Process	#	Process
1	Volatilisation	12	NSZD in the saturated zone
2	Dissolution	13	Microbes transport
3	Capillary effects	14	Biofilm growth/sloughing
4	Multi-phase transport	15	Chemitaxis
5	Residual LNAPL	16	Inhibition
6	Heterogeneity in the LNAPL composition	17	Food chain (predators)
7	Hysteresis	18	Different microbes
8	Heterogeneity in the media	19	Competition
9	Variable saturation	20	Assimilation
10	Solute mass transport	21	Gas bubble formation - Ebullition
11	NSZD in the vadose zone		

formation (e.g., due to biological activities) (Beyer et al., 2016; Sookhak Lari et al. 2016a, 2018a).

Groundwater dynamics also play a significant role. Soil water or capillary hysteresis depends on the saturation path history and is a function of variations in the groundwater table elevation, e.g. during the initial penetration of the LNAPL or following seasonal water table fluctuations. It alters the relative permeability of the soil and the capillary pressure – saturation relationship. It is shown that hysteresis can considerably change the morphology and homogeneity of the LNAPL plume. Furthermore, water table fluctuations increase the volume of immobile LNAPL (residual or trapped LNAPL) (Lenhard et al., 2018; Pasha et al., 2014; Sookhak Lari et al., 2016a). Immobile LNAPL is not easily recoverable through active remediation approaches and may remain as an ongoing source of contamination (Lekmine et al., 2017). Groundwater flow also augments the rate of LNAPL dissolution into the aqueous phase. The magnitude of the interphase mass transfer of mass is a function of the interfacial velocity of the fluids (Lekmine et al., 2017; Sookhak Lari et al., 2015).

Depending on the dynamics of an LNAPL plume in the subsurface, a suitable strategy for modelling NSZD should accommodate a number, or all of the above processes and parameters. For instance, multi-phase transport may be of particular importance for modelling an evolving LNAPL plume subjected to variable groundwater table, compared to a quasi-static subsurface condition. Similarly, LNAPLs comprising highly-partitioning components may require a multi-component modelling strategy.

2.2. LNAPL partitioning and compositional changes

The composition of LNAPLs can vary dramatically in their properties, components and carbon ranges depending on the product type (crude oil, gasoline, kerosene, jet fuels, diesel and lube oil range products). Major partitioning processes that an LNAPL can undergo in the subsurface will depend on the proportion of volatile, non-volatile, soluble, insoluble and the carbon skeleton configuration (complexity) of components that comprise the LNAPL.

Partitioning of LNAPL components into other phases (volatilisation and dissolution) can result in significant changes to the composition due to physical processes (Brauner et al., 2004). These may alter the LNAPL properties, such as increasing the viscosity,

and alter the potential transport of LNAPL through the porous media (Newell et al., 1995). Physical losses of the volatile and soluble components generally affects the lighter components < C10, with the aromatic and aliphatic components both affected by volatilisation and mainly the aromatics affected by dissolution into water, with partitioning of LNAPL into gas and water phases largely governed by Raoult's law and the mole fractions of the components in the LNAPL (Lekmine et al., 2017). For example, LNAPL components, such as benzene, toluene, ethylbenzene, and xylenes, have lower molecular weights and higher solubilities compared to other constituents (Vasudevan et al., 2016a). These are readily volatilised and partition into groundwater, thus leaving behind heavier molecular weight constituents in the source zone (Suthersan et al., 2017). See also the discussion in Section 2.4.

Gasolines are the main product types affected by volatilisation and dissolution because they contain a high proportion of volatile (C4 to C10 components) and water soluble compounds (aromatics; mainly alkylbenzenes). So for fresh gasolines the major early changes to the composition are largely due to volatilisation and dissolution depending on the subsurface environment and the contact with groundwater. Over time such processes may allow a weathered gasoline to eventually resemble kerosene. On the other hand, crude oils (and mixtures of different product types) are more complicated and can vary dramatically in their compositions and range from light products (like gasoline) to heavy products (like lube oils) and any combination of light, medium and heavy product types (gasoline, kerosene, diesel and lube oil).

Mass losses and NSZD rates the LNAPL has experienced can often be calculated from compositional changes in LNAPLs using a conservative tracer over a specified time period. The conservative tracers used can vary and selection of a conservative tracer is generally based on it being one of the most non-volatile, water insoluble and biodegradation resistant components present in the LNAPL samples in sufficient relative abundances to measure. Concentration increases of the selected conservative tracers in the LNAPL samples allow losses to partitioning and biodegradation to be calculated (Baedecker et al., 2018; Douglas et al. 1996, 2012; Johnston et al., 2007). Despite this providing estimates of the current rate of LNAPL mass loss, it does not estimate rates over future years (e.g. over decades). Therefore, key features of LNAPL partitioning and compositional changes during NSZD need to be

embedded into NSZD models.

2.3. NSZD processes in the vadose zone and groundwater

Extensive investigations have been carried out over the last 20–30 years on partitioning of LNAPL components to groundwater (dissolution) and into the vadose zone (volatilisation) and their subsequent biodegradation and attenuation. Along with biodegradation and compositional changes in the LNAPL itself, these primarily constitute the NSZD processes. Linking these partitioning and biodegradation processes holistically across the water saturated and unsaturated zones is a primary challenge.

LNAPL resides across these zones (Johnston and Trefry, 2009; Lenhard and Parker, 1990; Tomlinson et al., 2017) and seasonal and other transient affects vary LNAPL and water saturations and air-filled porosities (and relative interfacial areas and flow dynamics) to yield variable component concentrations, fluxes and biodegradation above and below the water table (Davis et al., 1993; Steffy et al., 1995). These also commonly drive the risk profile of an LNAPL source, but also feed the mass loss mechanisms of NSZD.

For dissolved contaminant plumes, MNA is an accepted biodegradation remedial strategy. A broad range of science has been brought together to quantify MNA processes in groundwater; multiple electron acceptors such as oxygen, nitrate, sulfate, iron and manganese oxides, and methanogenic processes (Davis et al., 1999; Dolfing et al., 2008; Essaid et al. 2011, 2015; Patterson et al., 1993; Rivett and Thornton, 2008; Wiedemeier et al., 1999b), novel ways of determining degradation rates (Gillham et al., 1990; Thierrin et al., 1995), and the role of microorganisms (Franzmann et al., 2002).

Commonly, the feasibility of the application of MNA as a site closure option assumes the LNAPL source has been or is being removed (WADWER, 2004). Huntley and Beckett (2002) indicated that almost all LNAPL mass removal was required in a homogeneous aquifer to decrease plume concentrations (Huntley and Beckett, 2002). Removal of LNAPL mass to such a degree was often not feasible, apart from shallow and readily accessible LNAPL sources. In contrast and through describing a general discharge versus mass model, Falta et al. (2005) determined that if aquifers indeed were heterogeneous, then the mass flux of dissolved components into a groundwater plume from a NAPL source decreased in proportion to the mass removed from the NAPL source zone (Falta et al., 2005). Exponential decay of a source where mass discharge is proportional to source mass has also been considered (Newell et al., 1996). For groundwater MNA, commonly the complexity of the LNAPL distribution, its saturation and its depletion over time has not been accommodated in models. These traits and the underlying processes are critical to capture in a conceptual and actual model of NSZD.

In soils and vadose zones, gas transport and its compositional change and biotransformation have been topics of research for many decades (Barber et al., 1990; Gliński and Stepniński, 1985). The connection to LNAPL sources and mass loss has a more recent history due to the threats posed to human health by potential inhalation of hydrocarbon vapours in buildings (Abreu and Johnson, 2005, 2006; Patterson and Davis, 2009) and possible production of methane. Research on petroleum vapours focused on its biodegradation to quantify the mitigated threat compared to chlorinated vapours that may persist more in vadose zones (Davis et al., 2004). Key to mitigating petroleum vapour threats was the availability of oxygen in the subsurface to sustain biodegradation (Davis et al. 2005, 2009; DeVaul, 2007; Knight and Davis, 2013; Lahvis et al., 1999; Ostendorf and Kampbell, 1991; Patterson and Davis, 2009). In some studies, methane was the hydrocarbon that was being biodegraded by the available oxygen, rather than volatile

components of the LNAPL such as benzene, toluene, etc. (Garg et al., 2017; Lundegard et al., 2008). There appears ample evidence that in some circumstances methane is the dominant hydrocarbon in the vadose zone above an LNAPL (Garg et al., 2017) and in other cases VOCs are dominant (Davis et al., 2005). In some cases neither VOCs nor methane seem present, whereby biodegradation processes may occur in close proximity to the LNAPL itself where it is distributed across the capillary fringe and/or into the vadose zone (Davis et al. 1998, 2013).

Apart from the fundamental transport and biodegradation mechanisms in the vadose zone, triggers for the dominance of methanogenesis compared to the volatilisation of other VOCs as drivers of mass depletion (or neither) during NSZD need to be embedded into models of NSZD. Over time the dominance of VOCs (perhaps associated with a recent release) or methane as the major mass loss from LNAPL may transition from one to the other. Models need to be able to accommodate this.

Apart from partitioning from the LNAPL and subsequent processes in groundwater and vadose zones, critical to quantifying NSZD processes is also understanding of the partitioning behaviour of gases and volatile compounds within and across the capillary fringe (Barber and Briegel, 1987; Barber et al., 1990). Beyond the downgradient edge of LNAPL zones reactions within a dissolved groundwater plume may continue to produce methane and carbon dioxide and/or release volatile compounds such as benzene that may migrate vertically upwards towards the water table and capillary fringe. Some studies sought to quantify transfer mechanisms and attenuation in this zone which is sometimes quite dynamic (Barber et al., 1990; McCarthy and Johnson, 1993; Rivett et al., 2011). A model of NSZD should also be able to consider such features.

2.4. Fundamental microbiological processes

The microbial degradation of petroleum hydrocarbons has been widely explored using single or mixed cultures in the laboratory (Salanitro, 2001), with degradation pathways described for alkanes, alkenes, isoalkanes, cycloalkanes, polyaromatic, heterocyclic and BTEX compounds (Salanitro, 2001). Biodegradation of petroleum LNAPLs can result in an apparent stepwise depletion of compounds in a specific order, based on their susceptibilities to biodegradation (Abreu et al., 2009; Christensen and Larsen, 1993; Kaplan et al., 1996; Peters and Moldowan, 1993; Volkman et al., 1984; Wade, 2001). Fuel types are variably affected by biodegradation in the subsurface; gasoline contains a greater mass of relatively highly volatile and soluble components which would subsequently degrade in the vadose zone soil or groundwater; whereas kerosene, diesel and lube oils contain mainly semi and non-volatile compounds (typically with carbon ranges > C9). Despite the limited volatile or soluble components, diesel for example has been reported to have all of the n-alkanes removed after approximately 20 years due to biodegradation under some conditions (Christensen and Larsen, 1993), leaving more complex compound types like branched and cyclic alkanes unaltered at this extent of biodegradation.

An open question here is regarding the NSZD of different compound types (long chained alkanes, short chained alkanes, branched alkanes, aromatics, resin and asphaltenes), for example as modelled by Ng et al. (2015) and Ng et al. (2014), and ambient parameters controlling long-term rates of NSZD. We try to highlight the necessity of understanding the complexity and interaction of such parameters while considering modelling strategies for NSZD.

These recent models assume the non-volatile dissolved organic carbon (NVDOCs) (or polar compounds) present in the groundwater are sourced from the partial degradation of aromatics, resin

and asphaltenes (Ng et al., 2014) or only aromatics (Garg et al., 2017; Ng et al., 2015) based on work by Thorn and Aiken (1998). However, recent data from the site shows that after 30 years that the aromatics (alkylbenzenes and naphthalenes) like the alkylcyclohexanes and isoprenoids were the most recalcitrant components measured in the LNAPL (Baedecker et al., 2018), which may suggest the aromatics are not be the source of the NVDOCs. The resins (or the more water soluble portion of the resins) are a potential source of the NVDOCs, as the Bemidji crude oil contains 4%–6% resins (Eganhouse et al., 1993). The resins do not seem to have been investigated as a source of the NVDOCs and contain the components (combinations of a range of functional groups such as alcohols, ketones, aldehydes and carboxylic acids) that could partition NVDOCs directly from the LNAPL to groundwater.

Related to this is the in place biodegradation of insoluble components of LNAPL like n-alkanes which change the composition of LNAPL itself. Intrinsically, we perceive biodegradation to occur in a water phase, but LNAPLs contain components that are largely insoluble. Investigations suggest that microbial communities are capable of residing in residual water at the LNAPL interface and access these 'insoluble' components via biosurfactant, emulsification and associated mechanisms, all of which are expected to enhance the rates of biodegradation (Marchant and Banat, 2012). The conceptual understanding is microbial communities reside in water surrounded by the LNAPL and access the LNAPL directly or create micelles (smaller components of LNAPL) preferentially 'consuming' LNAPL portions and leaving modified residual levels of LNAPL behind, e.g., without the n-alkanes. These complexities need to be further investigated and incorporated into models where we are seeking to predict LNAPL NSZD and LNAPL weathering features over decadal timeframes.

The rate of NSZD through biodegradation is also impacted and can vary depending on the ambient conditions present at the site, contaminant bioavailability and chemical composition, microbial community composition and electron acceptors available to the microbial community to utilise (Davis et al., 1999; Franzmann et al., 2002; Röling and van Verseveld, 2002). In addition, the biodegrading microbial community itself has been shown to depend on other factors such as temperature (Rayner et al., 2007), pH or salinity (Shelton et al., 2014) which affects the presence of degrading organisms, microbial activity, and the biodegradation rate (Shelton et al., 2016). At highly contaminated legacy sites, low biodegradation rates can also result from the presence of toxic contaminant concentrations, accumulation of toxic metabolites and low bioavailability of the contaminant or other unfavourable environmental conditions (Ham et al., 2004; Liang et al., 2009; Prommer et al., 2002).

Recharge and transport of micronutrients through the vadose zone can also have an effect on biodegradation. At the Bemidji site, the amount of weathering of the crude oil was higher in zones with higher recharge from the ground surface (Bekins et al., 2005; Garg et al., 2017). This showed the potential effect of the transport of microbial growth nutrients (through downward fluid flow), most likely phosphorus. Gray et al. (2010) also indicated that adding inorganic growth essentials (nutrients) could enhance methanogenesis. Similarly, Aldén et al. (2001) and Gallego et al. (2001) described the addition of nutrients (nitrogen and phosphorous) to improve microbial growth and bioremediation.

The discussion above shows that in the natural environment, at micro-scales the exact mechanism(s) of biodegradation is quite complex and not fully understood (Meckenstock et al., 2015; Schmidt et al., 2017). There is promise to understand underlying patterns of the microbial community composition, activity and function through molecule and other advanced techniques (Kimes et al., 2013; Mason et al., 2014; Yergeau et al., 2015), but embedding

molecular and genetic information in scaled models seems a future activity. However, an average response of microorganisms to the abundance of substrates and other growth and maintenance prerequisites is well-established at meso and macro scales. Microorganisms use LNAPL compounds as a source of energy and/or carbon, along with nutrients, electron acceptors and enzymes for catabolism and anabolism (together metabolism). Biotic processes are mainly through aerobic and anaerobic respiration (e.g. nitrate, sulfate or methanogenesis) or fermentation (the carbon source also acts as the electron acceptor) (Blanc et al., 1996; Garg et al., 2017). The native microbial community has been demonstrated to be readily capable of degrading LNAPL, however changes in the LNAPL composition (due to biotic and abiotic processes) may also result in changes in associated microbial community composition and diversity due to enhancement of niche degrading microbes or recalcitrance and/or toxicity of the LNAPL and residual products (Bruckberger et al., 2018; Salanitro, 2001).

Types and sequences of the biotic processes depend on multiple factors including the complexity and age/weathering of LNAPL chemicals, abundance of the electron acceptors and reduction potential of the aquifer, temperature (most favourable range is 20 °C–30 °C), and pH (most favourable range is near neutral condition) can play significant roles in NSZD (Blanc et al., 1996; Garg et al., 2017). Less critical factors seemed to be parameters relating to predation by protozoans and biofilm sloughing since there may be less impact on the rate of biodegradation (Essaid et al., 2015; Garg et al., 2017). It is still not very clear as to the role of chemotaxis and whether this enhances the rate of degradation due to enabling organism to access less bioavailable LNAPL products (Adadevoh et al., 2017; Wang et al., 2016).

3. Modelling strategies

The necessity of modelling critical parameters affecting NSZD was discussed in the previous section. In general, individual or combinations of NSZD processes have been modelled through three different modelling strategies (Karapanagioti et al., 2003; Miller et al., 2013) including mass balance models, analytical approaches and numerical simulations. Hybrid models benefiting from a combination of these have also been applied.

Mass balance models are site-specific models and simplify site conditions both temporally and spatially (Adamson and Newell, 2009; Newell and Adamson, 2005; Ng et al., 2014). Basic mass conservation equations are utilised without linking NSZD processes to flow or mass transport. Such models are useful as a basis for further detailed analytical and numerical studies, or to give preliminary estimates of process rates (Johnson et al., 2006; Verginelli and Baciocchi, 2013).

Analytical models rely on solutions to simplified differential equations describing the system. As such solutions only exist for certain conditions, analytical models are only applicable for cases where the model assumptions hold. These are mostly equilibrium conditions in the flow field, simplified representations for reactions, and symmetry of the problem (Berlin et al., 2015; Bouchard et al., 2011; Chen et al., 2016).

Numerical models approximate a solution to the governing differential equations through discretization techniques. These models are computationally more demanding and require more effort to implement. However, their flexibility (in comparison with analytical models) in dealing with multiple processes and parameter variability is significant (Miller et al., 2013). Numerical models can be further categorized based on their representations of the NSZD processes and parameters.

3.1. The scale of the problem

Numerical modelling of physio-chemical processes and microbial activities in porous media can be either at a molecular-scale (Wu and Coulon, 2016), pore-scale (Schmidt et al., 2017) or a meso- and macro-scale (Sookhak Lari et al., 2018a). The physics of micro-scale flow and mass transport have been extensively addressed in the literature (Liu and Mostaghimi, 2017). However, pore-scale understanding of microbial growth and biochemical reactions is yet to be developed (Meckenstock et al., 2015).

Pore-scale modelling of microbial growth is mostly conducted through direct simulation of individual microorganisms (Wu and Coulon, 2016), modified Lattice Boltzman (LB) equations or pore network modelling (Yan et al., 2017). However, morphology of biological colonies and mutation in their genes are among the existing ambiguities (Schmidt et al., 2017; Xiong et al., 2016). Also pore-scale mass transfer limitations (in particular into the biofilm) is poorly understood (Gharasoo et al., 2015; Liu and Mostaghimi, 2017; Xiong et al., 2016). These prohibit adequate approaches for upscaling the understandings from a pore-scale to meso- and macro-scales (Bahar et al., 2016; Ebigo et al., 2010; Tartakovsky et al., 2013).

NSZD is mostly modelled at a Darcy scale. In such case, the Navier-Stokes and continuity equations are averaged for the flow field. Similarly, biochemical processes are modelled through empirical correlations mimicking an average behaviour of microbial populations (Rivett et al., 2011). These are studied in more details in Section 3.3.1.

3.2. Flow field representation

At a pore-scale, either a Navier-Stokes equation or its simplified versions (Stokes equation or Hagen–Poiseuille equation) are used for direct simulation of single or multi-phase flow field. Approaches like LB are also used to minimize computational costs (Yan et al., 2017). However, such a detailed level of calculation is still not practical for macro (e.g., field) scales.

The flow field at a macro scale is modelled based on the conceptual model of the site. This may vary from analytical models to Darcy and transport equations for the saturated zone, Richards and transport equations for saturated and unsaturated zones and two and multi-phase flow and transport equations for the entire domain (Miller et al., 2013). Details of these models are presented in Section 4.

3.3. Modelling microorganisms

Microbial processes and growth models are either unstructured or structured. In unstructured growth models, only one indicator of the microbial population is studied; usually the mass or number of the microbes. On the other hand, various features of the microbes are studied in structured models. These may include the structure of their Deoxyribonucleic acid (DNA) and Adenosine Tri-Phosphate (ATP) (Blanc et al., 1996; Tartakovsky et al., 2013).

Microbial growth models can also be segregated or unsegregated. For segregated models, individual microbes and their behaviour are studied. In contrast, unsegregated models study an average representation of the microbial colonies in the form of a continuum. Models for NSZD are mostly unstructured and unsegregated (Blanc et al., 1996).

Most of the NSZD models consider microbes as a biofilm attached to the grains. However, there are models considering a concentration of floating microorganisms. Movement of these are modelled in the form of an advection-diffusion process and sometimes, their 'precipitation' is also included through

application of the Stokes law (Bradford et al., 2014). Microbial chemotaxis (in which microorganisms actively chase and move towards a 'food' source, regardless of the flow field) has also been modelled through modified advection-diffusion equations (Adadevoh et al., 2017; Wang et al., 2016).

3.3.1. Mathematical representation of biotic processes at a Darcy scale

Biochemical reactions are either at equilibrium or time-dependant (kinetic) (Blanc et al., 1996; Rivett et al., 2011) and sometimes instantaneous (Davis et al., 2009). A zero-order reaction is expressed as:

$$\frac{dS}{dt} = \text{constant} \quad (1)$$

in which S represents the substrate [M/L³] and t is time [T]. The non-dimensional Sherwood, Peclet and Damkohler numbers are used to identify to what extent the assumption of zero-order reactions hold (Barry et al., 2002; Rifai and Bedient, 1990; Sookhak Lari and Moeni, 2015).

A commonly assumed kinetic reaction for substrate consumption is first-order:

$$\frac{dS}{dt} = \alpha_1 S \quad (2)$$

where α_1 is a constant. A single Monod equation (the Michaelis–Menten equation with a time-varying term for biomass population) is the most popular equation describing the substrate consumption rate as a function of the biomass:

$$r_s = \frac{dS}{dt} = -kX \left(\frac{S}{K_s + S} \right) \quad (3)$$

where X is the biomass concentration [M/L³], K_s is the half-saturation [M/L³] and

$$k = \frac{\mu_{\max}}{Y} \quad (4)$$

where μ_{\max} is the maximum specific growth rate [T⁻¹] and Y is the biomass yield coefficient (Blanc et al., 1996). The microbial growth is limited by the excess amount of substrate:

$$r_s = -kX \left(\frac{S}{K_s + S + S^2/k_i} \right) \quad (5)$$

where k_i is a constant. Also for a non-competitive inhibitor (e.g. end product),

$$\begin{cases} r_s = \frac{-kX}{I} \left(\frac{S}{K_s + S} \right) \\ I = 1 + \frac{C_i}{k_i} \end{cases} \quad (6)$$

$$\begin{cases} r_s = -kX \left(\frac{S}{K_s I + S} \right) \\ I = 1 + \frac{C_i}{k_i} \end{cases} \quad (7)$$

or

$$\begin{cases} r_s = -kX \left(\frac{S}{K_s + S} \right) I \\ I = 1 - \frac{c_i}{k_i} \end{cases} \quad (8)$$

where I is an inhibiting factor and c_i is the concentration of the non-competitive inhibitor. Other forms of modelling inhibition are presented in the literature (Blanc et al., 1996).

More advanced representations for the substrate utilization rate (and counterpart microbial growth rate) include the abundance of electron acceptors (Barry et al., 2002; Battistelli, 2004):

$$r_s = -kX \left(\frac{S}{K_s + S} \right) \prod_{i=1}^N \left(\frac{A_i}{K_{A_i} + A_i} \right) \quad (9)$$

where A_i is the concentration of the electron acceptor i and K_{A_i} is its half-saturation. The competition process for two substrates is represented as (Huang et al., 2006; RERP, 2000);

$$\begin{cases} r_{s_1} = \frac{k_1 X S_1}{K_{s_1} + S_1 + K_{s_1} \frac{S_2}{K_{s_2}}} \\ r_{s_2} = \frac{k_2 X S_2}{K_{s_2} + S_2 + K_{s_2} \frac{S_1}{K_{s_1}}} \end{cases} \quad (10)$$

where k_1 , k_2 , K_{s_1} and K_{s_2} are constant values.

The first-order growth of biomass is used in some models;

$$\frac{dX}{dt} = \alpha_2 X \quad (11)$$

where α_2 is a constant. In more sophisticated models, the substrate utilization and biomass formation are connected through the yield coefficient. The Monod-based growth and decay of the biomass can simply be represented by:

$$\frac{dX}{dt} = \mu_{max} X \left(\frac{S}{(K_s + S)} \right) - bX \quad (12)$$

where b [T^{-1}] is the first-order decay coefficient. However, infinite growth of the biomass is impossible. Some models have options to limit the biomass growth. For a multi-component Monod-based equation, this can be expressed as:

$$\frac{dX}{dt} = \frac{\mu_{max} X}{I_b} \left(\frac{S}{(K_s + S)} \right) \prod_{i=1}^N \left(\frac{A_i}{(K_{A_i} + A_i)} \right) - bX \quad (13)$$

where I_b is the inhibitor for biomass formation. If $I_b = 1$ there is no growth limit. Otherwise, the growth inhibitor is usually expressed as

$$I_b = 1 + \frac{X}{k_b} \quad (14)$$

where k_b is a constant, or

$$I_b = \frac{\rho_X}{\beta - X} \quad (15)$$

where β is a constant and ρ_X is the biomass density [M/L^3].

4. Available models

Depending on the problem and phenomenon to be studied, subsurface modelling is conducted through various approaches (Freedman et al., 2017; Rivett et al., 2011). Table 2 introduces 36 models. The table presents the models' capabilities in dealing with NSZD processes and parameters depicted in Fig. 1. Also in Table 3, the complexity of the biodegradation module in each model is referenced to the governing equations in Section 3.3.1. The information in both tables are based on the models features introduced in theoretical reports (if available) and relevant publications reporting application of the models. Further capabilities of some models, as e.g., amendments to open-source codes, may also exist. Below we categorize these models based on their representation of the flow field and discuss the conditions under which the models may be applicable. We also discuss the emerging needs and tools for representative modelling of NSZD at the end of this section.

4.1. Analytical models

Analytical models have been used to study the partitioning of LNAPL compounds (Hers et al., 2000) and their biodegradation (Lahvis et al., 1999; Luo et al., 2015; Siddique et al., 2008) in groundwater and in vadose zone soils. The analytical models in Table 2 are those with biodegradation modules and include BIOCHLOR, BIOSCREEN, BRKNAPL, ECOSYS, REMCHLOR, REMFUEL and R-UNSAT. The models include zero or first order reactions to model biodegradation (except for BRKNAPL). These are mostly 1-dimensional models with limited capabilities for modelling flow and mass transport. In general, no biomass growth or multi-component reactions are considered. However, BIOSCREEN has an option to model plume attenuation by entering key electron acceptors. Also BIOCHLOR simulates the generation of chlorinated solvent degradation products.

There are also some other analytical models in the literature (with no capability of modelling biodegradation) which are used as parts of other modelling packages (i.e. to form hybrid models) for NSZD (Essaid et al., 2011; Fernández et al., 2016; Gallo and Hassanizadeh, 2002; Jacques et al., 2008; Marruffo et al., 2012; Yoon et al., 2009).

Despite inherent limitations of analytical models, some notable application of these also exist; for example modelling first-order decay of BTEX by BIOSCREEN (Jeong et al., 2005), biological and Monod-based decay of phenanthrene in a batch experiment (no-flow) by BRKNAPL (Sandrin et al., 2006), first-order decay of ethylene dibromide and 1,2-dichloroethane plumes at a site by REMCHLOR (Henderson et al., 2009) and identifying unsaturated zone biodegradation mass removal rates at Bemidji site by calibrating R-UNSAT (Essaid et al., 2011).

Also some separate analytical modelling approaches have been undertaken of vadose zone partitioning and biodegradation, which are mostly based on derivation of solutions to the transport equations in the vadose zone (Baehr, 1987; Lahvis et al., 1999).

4.2. Saturated flow and transport models

Saturated flow models (Darcy equation) mimic the aqueous phase flow regime in the saturated zone (Miller et al., 2013; Zheng and Wang, 1999);

$$S_s \frac{\partial H}{\partial t} = \nabla \cdot (\mathbf{K} \cdot \nabla H) + S^w \quad (16)$$

where S_s is the specific storage, H indicated the hydraulic head [L], t is the time [T] and \mathbf{K} represents the hydraulic conductivity tensor.

Table 2
Capabilities of the models with respect to the phenomena depicted in Fig. 1. Y: Yes; N: No; R: Refer to the Comments; Ref.: Reference; A: Analytical model; Nu: Numerical model.

#	Model	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	A/ Nu	Comments	Ref.	
1	3DMM	Y	Y	Y	Y	Y	Y	N	Y	Y	Y	Y	Y	Y	N	Y	N	N	Y	N	N	N	Nu		(Huang et al., 2006; Yu et al., 2010)	
2	BIOCHLOR	N	N	N	N	N	N	N	N	Y	N	Y	N	N	N	N	N	N	N	N	N	N	N	A	3D dispersion/1D advection.	(Aziz et al., 2002; Falta, 2008; Mulligan and Yong, 2004)
3	BIOMOC	N	N	N	N	N	N	Y	N	Y	N	Y	N	R	N	Y	N	Y	N	N	N	N	Nu	First order growth and decay of microbes with no effect on the media.	(Essaid and Bekins, 1997; Essaid et al., 2011, Essaid et al., 2003)	
4	BIONAPL3D	N	Y	N	N	N	N	Y	N	Y	N	Y	R	R	N	Y	N	Y	N	N	N	N	Nu	Growth and first order decay of the biomass with no effect on the media.	(Freitas et al., 2011a, Freitas et al., 2011b; Molson et al., 2002a; Molson and Frind, 2000; Molson et al., 2002b; Vaezihir et al., 2012)	
5	BIOPLUMEIII	N	N	N	N	N	N	N	N	Y	N	Y	Y	Y	N	N	N	N	N	N	N	N	Nu		(Mulligan and Yong, 2004; Rafai et al., 1998; Suarez and Rifai, 2004)	
6	BIOREDOX	N	R	N	N	N	N	Y	N	Y	N	Y	R	N	N	N	N	N	N	N	N	N	Nu	Based on MT3DMS. Dissolution is modelled as a boundary condition in MT3DMS	(Carey, 1998; Mulligan and Yong, 2004)	
7	BIOSCREEN	N	R	N	N	N	N	N	Y	N	Y	N	N	N	N	N	N	N	N	N	N	N	A	Dissolution is modelled as a boundary condition	(Jeong et al., 2005; Mulligan and Yong, 2004; Newell et al., 1996)	
8	BIOSLURP	Y	Y	Y	Y	Y	N	Y	Y	Y	Y	N	N	N	N	N	N	N	N	N	N	N	Nu		(Mulligan and Yong, 2004; Scientific-Software-Group, 1984)	
9	BRKNAPL	N	Y	N	N	N	N	N	N	N	Y	N	Y	N	Y	N	N	N	N	N	N	N	A		(Sandrin et al., 2006)	
10	COMSOL	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	Nu	Multi-physics package	(Adadevoh et al., 2017; COMSOL, 2017; Wang et al., 2016)	
11	ECOSYS	N	N	N	N	N	N	N	R	Y	Y	N	N	N	N	N	Y	N	N	N	N	N	A	Diffusion based transport. Mostly applied for nitrification/denitrification	(Blagodatsky and Smith, 2012; Grant et al., 1993)	
12	GSIM	N	R	N	N	N	N	Y	N	Y	N	Y	R	Y	N	Y	N	Y	N	N	N	N	Nu	Based on RT3D. Growth and first order decay of the biomass with no effect on the media.	(Gomez and Alvarez, 2010; Gomez et al., 2008)	
13	HP1	N	Y	R	N	N	N	N	Y	Y	R	Y	R	R	N	Y	N	Y	N	N	N	N	Nu	Richards equation for the flow field. Also heat transfer equation. A combination of HYDRUS1D/PHREEQC-2. Growth and first order decay of the biomass with no effect on the media.	(Jacques and Šimunek, 2005; Jacques et al., 2008)	
14	HYDROGEOC-HEM	N	N	R	N	N	N	Y	Y	Y	R	Y	N	Y	N	R	N	R	R	R	N	Nu	Richards equation for the flow field. Also heat transfer equation. Options for highly customized biochemical reactions.	(Fang et al., 2011; Yeh et al., 2004)		
15	MIN3P	N	Y	R	N	Y	N	N	Y	Y	Y	R	Y	Y	Y	N	Y	N	Y	R	R	Y	Nu	Richards equation for the flow field. Options for customized biochemical reactions.	(Amos and Mayer, 2006; Broholm et al., 2005; Maier and Grathwohl, 2005; Mayer et al., 2002; Miles et al., 2008)	
16	MIN3PDUSTY	R	Y	R	R	Y	N	N	Y	Y	Y	Y	Y	Y	N	Y	N	Y	R	R	Y	Nu	Based on MIN3P. Also included transport in the gas phase.	(Molins and Mayer, 2007; Sihota and Mayer, 2012)		
17	MISER	Y	Y	Y	Y	Y	N	Y	Y	Y	Y	Y	R	R	N	Y	N	N	N	N	N	Nu	Two dimensional model. Growth and first order decay of the biomass with no effect on the media.	(Rathfelder et al., 2000)		
18	MOFAT	Y	Y	Y	Y	Y	N	Y	Y	Y	Y	N	N	N	N	N	N	N	N	N	N	N	Nu		(Gaganis et al., 2004; Karapanagioti et al., 2003; Katyal et al., 1991)	
19	MT3DMS	N	R	N	N	N	N	Y	N	Y	N	Y	R	R	N	N	N	N	N	N	N	N	Nu	A modified version is assessed. Dissolution is modelled as a boundary condition. First order growth and decay of microbes with no effect on the media. Microbial transport is not directly possible.	(Xu et al., 2015; Zheng and Wang, 1999)	
20	NAPL SIMULATOR	Y	Y	Y	Y	Y	N	Y	Y	Y	Y	Y	N	N	N	N	N	N	N	N	N	N	Nu	Two dimensional model.	(Guarnaccia et al., 1997; Karapanagioti et al., 2003; Yang et al., 2013)	
21	OPENGEOSYS	N	Y	R	N	N	N	Y	Y	Y	R	Y	R	R	N	Y	N	N	N	N	N	N	Nu	Richards equation for the flow field. Growth and first order decay of the biomass with no effect on the media.	(Beyer et al., 2016; Popp et al., 2015)	
22	PFLOTTRAN	N	Y	Y	R	N	N	N	Y	Y	Y	Y	Y	Y	N	Y	N	R	R	R	N	Nu	Richards equation/considerations for two-phase flow. Options for customized biochemical reactions.	(Hammond et al., 2014)		
23	PHT3D	N	R	N	N	N	N	Y	N	Y	N	Y	R	R	N	Y	N	N	N	N	N	N	Nu	Based on MT3DMS. Dissolution is modelled as a boundary condition. Growth and first order decay of the biomass with no effect on the media.	(Appelo and Rolle, 2010; Barry et al., 2002; Ng et al., 2015)	
24	REMCHLOR	Y	Y	N	N	N	N	N	N	R	R	R	N	N	N	N	N	N	N	N	N	N	A	Analytical representations.	(Falta and Kueper, 2014; Falta et al., 2007; Henderson et al.,	

Table 2 (continued)

#	Model	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	A/ Nu	Comments	Ref.	
25	REMFUEL	N	Y	N	N	N	N	N	N	N	R	N	Y	N	N	N	N	N	N	N	N	N	N	A	Analytical representations.	(Falta et al., 2012)
26	RT3D	N	R	N	N	N	N	N	Y	N	Y	N	Y	R	R	N	Y	N	N	N	N	N	N	Nu	Based on MT3DMS. Dissolution is modelled as a boundary condition. Growth and first order decay of the biomass with no effect on the media.	(Clement, 1997; Lu et al., 1999; Mulligan and Yong, 2004)
27	R-UNSAT	R	R	N	R	N	N	N	Y	Y	N	Y	N	N	N	N	N	N	N	N	N	N	N	Nu/ A	Partitioning through boundary conditions. Gas diffusion and aqueous advection/dispersion are the main transport mechanisms. Monod kinetics is an option.	(Essaid et al., 2011; Karapanagioti et al., 2003; Lahvis and Baehr, 1997)
28	SEAM3D	N	R	N	N	N	N	N	Y	N	Y	N	Y	R	R	N	Y	N	Y	Y	N	N	N	Nu	Based on MT3DMS. Dissolution is modelled as a boundary condition. Growth and first order decay of the biomass with no effect on the media.	(Widdowson, 2004; Widdowson et al., 2002)
29	STOMP	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	N	N	N	N	N	N	N	N	N	N	N	Nu	Growth and first order decay of the biomass with no effect on the media.	(White and McGrail, 2005; Yoon et al., 2009)
30	SURFACT	Y	Y	R	R	N	N	N	Y	Y	Y	Y	Y	R	R	N	Y	N	N	N	N	N	N	Nu	Based on RT3D. Richards equation for the aqueous flow plus gas transport equations. Growth and first order decay of the biomass with no effect on the media.	(Mulligan and Yong, 2004; Panday and Huyakorn, 2008)
31	SWMS3D	N	N	R	R	N	N	N	Y	Y	Y	Y	Y	N	R	N	N	N	N	N	N	N	N	Nu	Richards equation for the aqueous flow plus gas diffusion. Growth and first order decay of the biomass with no effect on the media.	(Alfnes et al., 2004; Simbnek et al., 1995)
32	TMVOC	Y	Y	Y	Y	Y	R	Y	Y	Y	Y	Y	N	R	N	R	N	R	R	N	N	N	N	Nu	Hysteresis in modified versions. TMVOC V3.0 includes the biochemical modelling capabilities in TMVOCBIO.	(Falta and Kueper, 2014; Jung et al., 2017; Pruess and Battistelli, 2002; Sookhak Lari et al., 2016a; Sookhak Lari et al., 2018a)
33	TMVOCBIO	Y	Y	Y	Y	Y	R	Y	Y	Y	Y	Y	N	R	N	Y	N	Y	Y	N	N	N	N	Nu	Hysteresis in modified versions. Growth and first order decay of the biomass with no effect on the media.	(Battistelli, 2004; Jung and Battistelli, 2016; Jung et al., 2017)
34	TOUGHREAC-T-N	N	N	R	R	N	N	N	Y	Y	Y	Y	N	R	N	Y	N	Y	N	N	N	N	N	Nu	Richards equation for the aqueous flow. Diffusion in the gas. Only vertical flows. Growth and first order decay of the biomass with no effect on the media. Designed to model soil nitrogen cycle.	(Blagodatsky and Smith, 2012; Maggi et al., 2008; Xu et al., 2004)
35	UG	N	Y	N	N	N	N	N	Y	N	Y	N	Y	N	N	N	Y	N	N	N	N	N	N	Nu	A multi-physics package. An application of the model is reported here.	(Watson et al., 2005)
36	UTCHEM	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	N	Y	N	Y	N	Y	Y	N	N	N	Nu		(RERP, 2000; Yang et al., 2013)	

Also S^w in equation (16) is the source term. Many such models implement forms of the advection-dispersion equation to model multi-species solute mass transport. For a single component:

$$\frac{\partial(C)}{\partial t} = \nabla \cdot (\mathbf{D} \cdot \nabla C) - \nabla \cdot (\mathbf{v} C) + r \tag{17}$$

where C is the concentration [ML^{-3}], \mathbf{v} is the Darcy velocity vector [LT^{-1}] and \mathbf{D} is the dispersion tensor [L^2T^{-1}]. The sink/source term is also represented by r [$\text{ML}^{-3}\text{T}^{-1}$]. Discussions on the rate-limited and equilibrium interphase mass transfer are also presented in Section 4.4.

Linking relevant groundwater transport and attenuation processes together to form saturated flow models for NSZD was attempted for multiple soluble species in the 1990s (Clement et al., 1998), with more sophisticated geochemical models being developed to accommodate all electron acceptor/donor and ancillary reactions (Prommer et al., 1999) and to understand the limitations and complexities of controls on plume MNA. Such controls include reactions on the fringes of plumes governed by small scale lateral dispersivities leading to limited mixing of dissolved LNAPL components and electron acceptors (Ham et al., 2004), and the implications of seasonal and transient effects (e.g., Prommer et al. (2002)). Since the 1990s, similar concepts have been applied in a number of saturated flow models to study NSZD.

Well known models in this category are BIOMOC, BIOREDOX, BIOPLUMEIII, BIONAPL3D, GSIM, MT3DMS, PHT3D, RT3D and SEAM3D. Among these, PHT3D has a strong capability for accommodating and calculating geochemical conditions including pH. BIOMOC, BIONAPL3D, GSIM and SEAM3D are able to consider different types of microorganisms. BIOPLUMEIII and RT3D can consider transport of microorganisms through an advection-diffusion equations. As introduced in Table 3, the models include different forms of Monod-based equations for biochemical reactions.

Saturated flow models are applicable for steady LNAPL plumes in which the equilibrium or rate-limiting dissolution process can be modelled as a boundary condition and also, partitioning into the gaseous phase is negligible. A number of notable field or pilot scale applications of these models to study aspects of NSZD include sequential use of electron acceptors at Bemidji site by BIOMOC (Essaid et al., 2011), field scale first-order decay of benzene by BIOPLUMEIII (Suarez and Rifai, 2004), field scale Monod-based decay of various gasoline ingredients by BIONAPL3D (Freitas et al., 2011b; Molson et al., 2002a; Vaezihir et al., 2012), anaerobic degradation of organic matters at Bemidji site by PHT3D (Ng et al., 2015) and a series of Monod-based BTEX degradation processes at a site in USA by RT3D (Lu et al., 1999). In addition to the models named above, some in-house codes have also been used to

Table 3
NSZD biodegradation equations (Section 3.3.1) applied in each of the models in Table 2.

#	Model	Eqs.	Ref.	Comment	#	Model	Eqs.	Ref.	Comment
1	3DMM	9; 13; 10; 6; 15	(Huang et al., 2006; Yu et al., 2010)		17	MISER	9; 13; 8; 15	(Rathfelder et al., 2000)	N = 3
2	BIOCHLOR	2	(Falta, 2008; Mulligan and Yong, 2004)		18	MOFAT	2	(Gaganis et al., 2004; Karapanagioti et al., 2003)	
3	BIOMOC	9; 13; 6; 14	(Essaid et al., 2011, Essaid et al., 2003)		19	MT3DMS	9; 13	(Xu et al., 2015)	N = 2
4	BIONAPL3D	9; 13; 6; 14	(Freitas et al., 2011b; Molson et al., 2002a, Molson et al., 2002b; Vaezihir et al., 2012)		20	NAPL SIMULATOR	2	(Karapanagioti et al., 2003; Yang et al., 2013)	
5	BIOPLUMEIII	9; 13	(Mulligan and Yong, 2004; Suarez and Rifai, 2004)	N = 2, I ₀ = 1	21, 22	OPENGEOSYS, PFLOTRAN	e.g., 9; 13; 7	(Popp et al., 2015; Hammond et al., 2014)	Options for customized reactions.
6	BIOREDOX	9; 13	(Mulligan and Yong, 2004)		23	PHT3D	9; 13; 7	(Appelo and Rolle, 2010; Barry et al., 2002; Ng et al., 2015)	
7	BIOSCREEN	2; 1 (instant reaction)	(Mulligan and Yong, 2004)		24	REMCHLOR	2	(Falta and Kueper, 2014; Henderson et al., 2009)	
8	BIOSLURP	2	(Mulligan and Yong, 2004)		25	REMFUEL	1; 2; 3	(Falta et al., 2012)	
9	BRKNAPL	9; 13; 5	(Sandrin et al., 2006)	N = 2	26	RT3D	9; 13; 6	(Lu et al., 1999; Mulligan and Yong, 2004)	
10	COMSOL	N/A	(Adadevoh et al., 2017; Wang et al., 2016)	Arbitrary	27	R-UNSAT	2	(Essaid et al., 2011; Karapanagioti et al., 2003)	
11	ECOSYS	9; 13; 14	(Blagodatsky and Smith, 2012)	N = 2	28	SEAM3D	5; 9; 13; 10; 6	(Widdowson, 2004)	N = 2
12	GSIM	9; 13; 6; 15	(Gomez and Alvarez, 2010)		29	STOMP	9; 13	(Yoon et al., 2009)	
13	HP1	9; 13; 6	(Jacques et al., 2008)		30	SURFACT	9; 13; 6	(Mulligan and Yong, 2004)	
14	HYDROGEOCHEM	N/A	(Fang et al., 2011)	Options for highly customized biochemical reaction	31	SWMS3D	9; 13	(Alfnes et al., 2004)	N = 2
15	MIN3P	e.g., 9; 13; 6; 10	(Amos and Mayer, 2006; Broholm et al., 2005; Maier and Grathwohl, 2005; Mayer et al., 2002; Miles et al., 2008)	Options for customized biochemical reaction.	32	TMVOC	2	(Falta and Kueper, 2014; Jung et al., 2017; Sookhak Lari et al., 2016a; Sookhak Lari et al., 2018a)	Includes TMVOCBIO features in version 3.0
16	MIN3PDUSTY	9; 13; 6	(Molins and Mayer, 2007; Sihota and Mayer, 2012)	Options for customized biochemical reaction.	33	TMVOCBIO	9; 13; 5; 7; 10; 14	(Battistelli, 2004; Jung et al., 2017)	
					34	TOUGHREAC-T-N	9; 13; 7	(Blagodatsky and Smith, 2012; Maggi et al., 2008)	N = 2
					35	UG	9; 7; 10	(Watson et al., 2005)	Arbitrary. An application is mentioned here.
					36	UTCHEM	9; 13; 7; 10; 15	(RERP, 2000; Yang et al., 2013)	N = 3

study NSZD in fully-saturated conditions (Jahan et al., 1999; Vasudevan et al., 2016b).

4.3. Unsaturated flow and transport models

Unsaturated flow models are based on the Richards equation (and constitutive relationships for the flow field) to mimic the aqueous phase flow regime in the saturated and unsaturated zones (Miller et al., 2013; Panday and Huyakorn, 2008)

$$S_s S_w \frac{\partial H}{\partial t} + \varepsilon \frac{\partial S_w}{\partial t} = \nabla \cdot (\mathbf{K} \cdot \nabla (H + z)) + S^w \quad (18)$$

where ε is the porosity, z is the elevation [L] and S_w is the water saturation [–]. Constitutive relationships are required to relate the hydraulic conductivity, saturation and pressure head (including capillary effects). Transport equations like that in equation (17) apply. Models in this category include PFLOTRAN, HP1, HYDROGEOCHEM, MIN3P, MIN3PDUSTY, OPENGEOSYS, SURFACT, SWMS3D and TOUGH2REACT-N. A number of these models include gas diffusion/transport through the vadose zone (e.g., PFLOTRAN,

MIN3PDUSTY, SURFACT and SWMS3D).

Among these models, SURFACT was developed based on RT3D and therefore, inherits the parent model capabilities including options for transport of microorganism. Models MIN3P and HYDROGEOCHEM include options to introduce customized biochemical reaction kinetics. MIN3P also enables the user to model gas bubble formation in the aqueous phase as a result of biochemical reactions. PFLOTRAN is an open source and parallel flow and multicomponent reactive transport code with options for complex biochemical reactions.

Unsaturated flow models are applicable for steady LNAPL plumes and residuals in which the equilibrium or rate-limiting dissolution and evaporation process can be modelled as boundary conditions. Notable field or pilot scale application of these models to study NSZD processes include dynamic changes in microbial characteristics at a bioremediation site in Colorado USA by a modified version of HYDROGEOCHEM (Fang et al., 2011), multi-component Monod-based degradation at a kerosene-contaminated site in Germany by MIN3P (Miles et al., 2008) and multi-component Monod-based degradation of toluene and o-

xylylene at a site in Norway by SWMS3D. In-house codes have also been used to study NSZD in unsaturated flow fields (Abreu et al., 2009; Molins et al., 2010; Rockhold et al. 2004, 2005). In particular, a generalised representation of biochemical reactions is applied in an unsaturated flow and transport model (Mayer et al., 2002).

4.4. Two-phase and multi-phase models

Two phase and multi-phase flow models are able to model the flow of aqueous and gaseous phases (for two phase models) and gaseous, aqueous and LNAPL phases (for three-phase models). For multicomponent models, the mass balance equation is (Miller et al., 2013; Pruess and Battistelli, 2002)

$$\frac{\partial C^i}{\partial t} + \nabla \cdot \left[\sum_{\beta=1}^{N_p} (C_{\beta}^i \mathbf{v}_{\beta} - \mathbf{D} \nabla C_{\beta}^i) \right] = r^i \quad (19)$$

where i and β refer to the component number i and phase β respectively (with N_p as the total number of phases). The velocity is calculated through the Darcy law equation;

$$\mathbf{v}_{\beta} = -k \frac{k_{r\beta}}{\mu_{\beta}} (\nabla P_{\beta} - \rho_{\beta} \mathbf{g}) \quad (20)$$

with constitutive relationships to relate, relative permeability of each phase, pressure (P , including capillary) and the phase saturation. Here, k and $k_{r\beta}$ are the absolute and relative permeability to phase β [L^2] and $[-]$ respectively), ρ_{β} and μ_{β} are the density [ML^{-3}] and viscosity of phase β [$ML^{-1}T^{-1}$] and \mathbf{g} is the acceleration vector [LT^{-2}]. Most of the models also include partitioning, either by considering equilibrium conditions (Raoult's and Henry's law) or through rate-limited mass transfer;

$$R = -M_k (C_{\beta}^i - C_{\beta}^{i,eq}) \quad (21)$$

where M_k is the mass transfer coefficient for species i across the boundary layer [LT^{-1}] and C_{β}^i and $C_{\beta}^{i,eq}$ are the mass concentrations in the bulk aqueous solution and at equilibrium, respectively. R is then the rate of mass transfer [$ML^{-2}T^{-1}$]. The mass transfer coefficient is determined through empirical or analytical Sherwood number correlations (RERP, 2000; Sookhak Lari et al., 2015). The models we investigate in Table 2 include 3DMM, BIOSLURP, MISER, MOFAT, NAPL-SIMULATOR, STOMP, TMVOC, TMVOCBIO and UTCHEM. Among these, MISER, NAPL-SIMULATOR and MOFAT are two-dimensional. UTCHEM, TMVOC and TMVOCBIO have options for high performance computing and parallel-processing. UTCHEM and TMVOCBIO are able to model heat transport, complex biochemical reactions, inhibitors and different microorganisms. Competitive reactions are possible in these two, as well as 3DMM. UTCHEM is also able to model microbes transport and their growth effects on the media.

Multi-phase models usually require greater computational resources to be applied. Despite their significant modelling capabilities, these requirements limit their application to study the dynamics of LNAPL in subsurface systems, active remediation approaches and NSZD (Falta and Kueper, 2014; Miller et al., 2013; Sookhak Lari et al., 2018a; Sookhak Lari et al., 2019). A number of notable field or pilot scale applications of these models to study NSZD processes includes Monod-based degradation of BTEX in a pilot test to study bioremediation by 3DMM (Huang et al., 2006), single-component first-order decay of a mixture of volatile organic compounds in the vadose zone by MOFAT (Gaganis et al., 2004) and

first-order degradation of benzene in an anonymous coastal alluvial site subjected to hysteresis (water table fluctuations) by NAPL SIMULATOR (Yang et al., 2013). In-house codes have also been used to study two and multi-phase cases of NSZD (Gallo and Manzini, 2001; Hron et al., 2015).

4.5. Multi-physics models

Multi-physics package are adjustable and multi-purpose scientific software for numerical approximation of user-specified systems of partial differential equations (Miller et al., 2013). Most packages can be implemented on clusters and supercomputers to conduct parallel-processing calculations. However, application of such tools to model NSZD is not extensive. Multi-physics packages such as COMSOL and UG have been used to model subsurface biochemical reactions at pore and macro scales. Pore-scale processes like chemotaxis have been modelled through application of COMSOL (Adadevoh et al., 2017; Wang et al., 2016). UG has also been used to model multi-component Monod-based degradation of various hydrocarbons in saturated flows both at pilot and field scales (Watson et al., 2005).

4.6. Emerging needs and tools for representative modelling

The previous sections have revealed the current level of complexity that existing modelling frameworks can handle. Among these, multi-phase multi-component models are able to address some of the more critical transport and partitioning phenomena required to describe NSZD processes. Models like TMVOCBIO and UTCHEM include options for simulating heat generation and transport, variations in pH, degradation and partitioning to different phases (Jung and Battistelli, 2016; RERP, 2000). As these require massive computational effort, a number of multi-phase multi-component models are now configured as parallel-processing versions, enabling application of clusters and supercomputers to conduct heavy simulations (Jung et al., 2017). Regardless, application of these to address all processes applicable to NSZD and even active remediation is not yet common (Sookhak Lari et al., 2018a, Sookhak Lari et al., 2018b; 2019) especially over long time periods (decades) and at fine spatial scales.

The sequence and type of biochemical reactions which can be modelled are determined through built-in libraries in simulation packages. These are based on the current level of understanding from application and observations (Garg et al., 2017). As previously discussed the current concepts for the class and sequence of reactions as e.g. in Ng et al. (2014) and Ng et al. (2015) may include assumptions that may need further focus to ensure assumptions about LNAPL weathering over long time periods is accurately accommodated in models. Similarly, research advances regarding other key NSZD processes whilst informing models of NSZD processes and their evolution over time, will challenge the ability of currently available models. Accommodating all process concurrently and accurately in one code and being able to deliver simulations in a timely manner seems still a future challenge.

In order to link site-scale observations and built-in libraries in numerical models, time and length scales are inevitably integrated and therefore, some information and/or prediction accuracy may be lost. Key to progress will be the scalability of micro and meso-scale experimentation to elucidate NSZD processes at field scale. These can be used to better quantify relationships between ambient parameters (pH, temperature etc.), types of hydrocarbons and reactions (e.g., exact mechanism of complex syntrophic fermentation/methanogenic reactions) and geo-physical features at short time and length scales. This provides improved insights for modelling purposes, with less assumptions. Furthermore, pore

scale simulations may also provide additional understandings regarding the dynamics of biochemical reactions and microorganisms (e.g., biofilm growth and sloughing, mutation in genes and food chain (not in any of the models)) as a function of flow field characteristics, and therefore a better upscaling (from pore scale to Darcy scale) of the governing equations (Bahar et al., 2016; Tartakovsky et al., 2013; Wang et al., 2016; Xiong et al., 2016). Advanced mathematical approaches, like converting the governing partial differential equations into their Lattice Boltzmann representations can also significantly reduce the pore scale computational costs (Yan et al., 2017).

5. Conclusions

Active remediation of sites contaminated with LNAPL is an expensive and often prolonged task. The efficiency of active remediation decreases over time and may become less than the rate of NSZD (Garg et al., 2017). This provides a motivation to consider NSZD as a continuous and passive clean-up option, with insignificant side effects and reduced costs. However, it is vital to measure current and estimate future rates of NSZD. To enable a comparison with active remediation efforts and also to estimate the longevity of risk factors and LNAPL itself, the long term effectiveness of NSZD needs to be quantified. This enjoins a NSZD modelling approach.

We provide a critical review across the literature on the key processes that might need to be considered in conceptual and actual models of NSZD. Compositional changes of LNAPL due to partitioning and subsequent biodegradation and further weathering means NSZD rates are likely to change over decadal time frames. Various classes of chemicals might control the long term rate of LNAPL NSZD. Methanogenesis may dominate at some time periods (Garg et al., 2017) as might aerobic biodegradation of volatile compounds in vadose zone soils (Davis et al., 2005). MNA in groundwater might also be a dominant process at some point of time despite seemingly orders of magnitude biodegradation rate differences at other points in time. LNAPL fingerprinting and changes in composition provides indicators of historic weathering – and in part provides measures of the scale of volatilisation, dissolution and intrinsic biodegradation, and overall mass loss. The key understandings are in place, but transitions between times of dominant NSZD processes need refinement, as do the geochemical and hydrogeological conditions under which they may occur and be dominant. Coupled to this are differences predicated by product type (gasoline, crude, diesel, etc), and scale and size of release events.

A significant gap exists in upscaling micro-scale biological processes to meso and macro scales (Schmidt et al., 2017). Even though Darcy-scale lumped-parameter equations have been widely used to quantify the NSZD processes at pilot and field scales, the physiochemical understanding of the processes is yet to be improved. A number of existing questions have been presented in the literature (Garg et al., 2017; Schmidt et al., 2017). Furthermore, processes like assimilation and existence of food chains have rarely been studied at Darcy scales. This is mostly due to the lack of appropriate mathematical representations. Averaging and verifying the pore-scale governing equations may be of some help (Xiong et al., 2016). We noted the necessity for models capable of handling extremely complex syntrophic fermentation/methanogenic reactions that are sensitive to ambient parameters not typically included in transport models (e.g., pH and temperature). We highlighted the needs for meso scale experiments and pore scale simulations to provide more universal input libraries and upscaled governing equations for modelling NSZD.

Multi-phase multi-component models have rarely been used to

study NSZD. Across 36 models considered these seem to have a strong basis for future NSZD modelling. Despite their strong modelling capabilities, application of these models requires an adequate level of team expertise in the geo-physics, geo-chemistry and geo-biology. Often, access to supercomputing and parallel processing facilities is needed. However, it has been shown that detailed field-scale multi-phase and multi-component transport phenomena can be modelled through such modelling frameworks (Miller et al., 2013; Sookhak Lari et al., 2016a; Sookhak Lari et al., 2018a). Linking these to the relevant level of microbial, geochemical and biodegradation processes, under potentially transient subsurface conditions remain challenges for long term estimation of NSZD and LNAPL longevity, but a challenge that needs to be addressed.

Advanced computational algorithms are progressively implemented in simulators to reduce computational costs of modelling highly nonlinear systems. Advances in parallel processing clusters and supercomputers promise improved capabilities of the models to investigate complex interconnected biochemical reactions (Miller et al., 2013). Machine learning can be used to analyse massive data collected from field measurements to shape site-specific models for NSZD (Wu and Coulon, 2016). These seem to form the basis for new generations of representative NSZD models that can address the challenges outlined.

Finally, it is recognised that NSZD processes operate concurrently with active remedial efforts at LNAPL sites. An appropriately capable code could be used to simulate mass removal via both approaches and to determine at what stage NSZD becomes the dominant mass removal mechanism compared to active mass removal efforts (Sookhak Lari et al., 2018a, Sookhak Lari et al., 2018b; 2019). This provides the basis for decisions around proceeding with active remediation at LNAPL impacted sites, or transitioning to a NSZD site-closure regime.

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