

technical bulletin

CL:AIRE technical bulletins describe specific techniques, practices and methodologies relevant to sites in the UK. This bulletin introduces the concept of natural source zone depletion. It includes a description of the processes controlling depletion rates, how these rates are measured and outlines its potential significance at UK LNAPL sites.

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An Introduction to Natural Source Zone Depletion at LNAPL Sites

1. INTRODUCTION

Sources of hazardous chemicals in the subsurface may pose significant risks to human health and the environment. Of particular concern are light non-aqueous phase liquid (LNAPL) source zones that may contain considerable chemical mass, and pose potential risks via direct exposure to LNAPL, vapour migration / intrusion and dissolved-phase impact to controlled waters. Spills of hydrocarbon fuels and oils form the most common examples. Remediation of such sites requires effective source zone management to achieve successful outcomes.

'Natural source zone depletion' (NSZD) describes the naturally occurring processes that collectively result in the depletion of chemical contaminant mass from a (LNAPL) source zone. Over time, source zone depletion typically results in decreased receptor risks and eventual source exhaustion. Dissolution and vapourisation physically deplete the LNAPL by mass transfer of chemical constituents to the aqueous (groundwater) and gaseous (soil gas) phases. Degradation of NAPL constituent chemicals may also occur due to chemical reaction or biodegradation; hydrocarbon fuel/oil constituents are particularly susceptible to the latter.

Recent research in North America has prompted interest to more thoroughly assess LNAPL NSZD occurrence and evaluate its potential significance to LNAPL site management¹. Underestimation of NSZD rates, due to neglecting the gaseous contribution to depletion, has been a key driver. Substantial quantities of gas may be emitted from anaerobic petroleum hydrocarbon biodegradation processes, especially methanogenesis (Garg *et al.*, 2017; Lundegard and Johnson, 2006). Several guidance documents on the assessment of NSZD occurrence and its potential significance to remediation programmes have been recently published (API, 2017; ITRC, 2018 (updating ITRC (2009); CRC CARE, 2018).

The purposes of this bulletin introducing NSZD at LNAPL sites are to:

- Introduce and raise awareness of NSZD and outline its potential significance;
- Outline the key processes controlling NSZD rates and recent research advances;
- Outline recent approaches to measuring NSZD, particularly the gaseous component;
- Consider the varied roles of emerging NSZD technology use in the remediation life cycle; and
- Review the challenges and needs yet to be overcome.

2. SIGNIFICANCE OF NSZD OCCURRENCE

Assessing the rates and timescales of NSZD occurrence is critical to managing LNAPL-contaminated sites since the contributing processes of dissolution, vapourisation and biodegradation may:

- Significantly reduce impacts over time due to reductions in source zone LNAPL mass, LNAPL saturation of the pore space, and the mobility of the LNAPL;
- Assist definition of a more precise conceptual site model (CSM) and key physical, chemical, and biological processes that control contaminant transport and potential impacts;
- Progressively lower risks arising from the mobility of the LNAPL, for instance, risks of subsurface LNAPL discharge to a receiving water course;
- Progressively reduce contaminant fluxes that sustain both the subsurface vapour and groundwater plume thereby leading to reduced receptor risks and gradual plume shrinkage;
- Influence the timeframes over which plume remediation options such as monitored natural attenuation (MNA) or other *in situ* technologies need to be employed to protect receptors; and
- Influence decision-making on the need for active remediation technologies that may deliver faster (but partial) source zone removal, but may not generate significant risk-reduction when compared to natural depletion processes alone.

3. KEY PROCESSES CONTROLLING NSZD EXPRESSION

Understanding the key processes that control NSZD rates and their individual relative contribution to source-mass depletion are considered a priority for remediation selection and design, for risk assessors and/or regulators. The key processes - dissolution, vapourisation, volatilisation and biodegradation for LNAPL sites - are illustrated in the LNAPL CSM shown in Figure 1. It is convenient to consider here the overall expression of NSZD by segregating source depletion contributions to (Palaia and Fitzgibbons, 2017):

- the aqueous expression of NSZD below the water table, and
- the gaseous expression of NSZD above the water table.

Some of the key processes influencing each expression are introduced below with a greater focus on the gaseous expression where current research advances have been made.

¹ LNAPL NSZD is broadly similar in concept to the 'engineered bioreactor' concept applied in waste management to generate methane from landfills (often for energy production) and accelerate stabilisation of degradable wastes, and on which research has been undertaken in UK and Europe over a number of decades.

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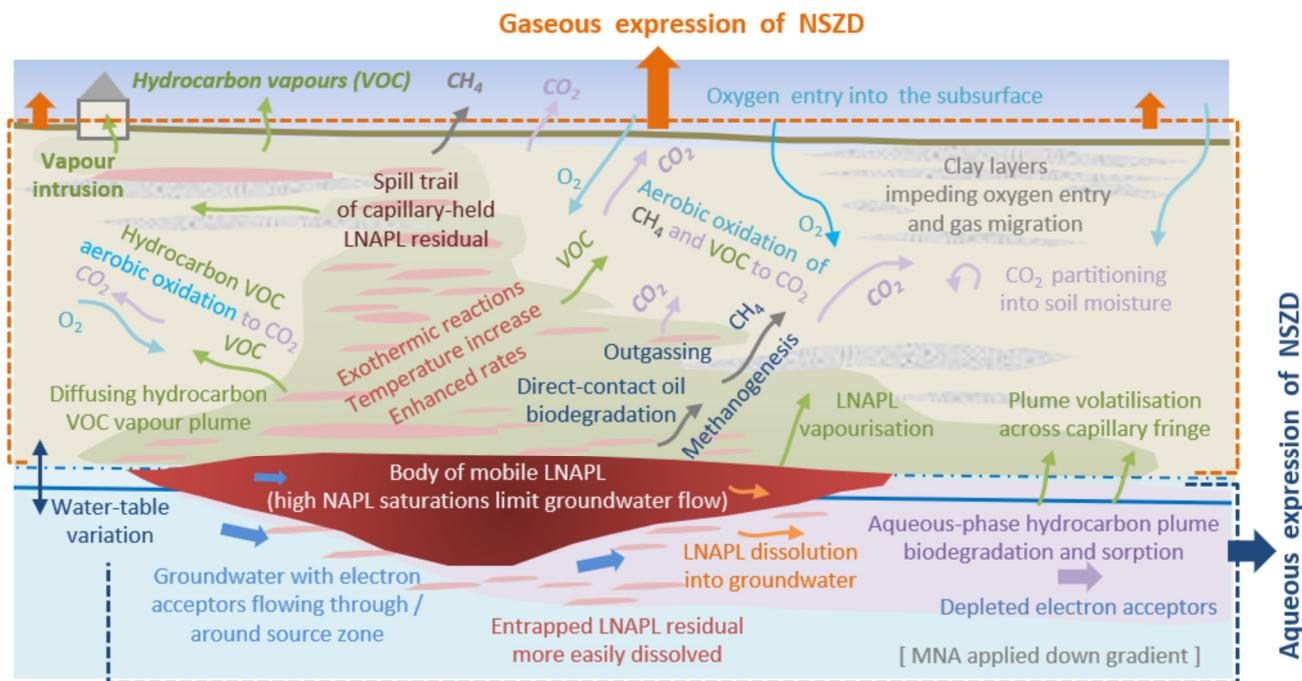


Figure 1. Conceptual site model showing processes above and below the water table generating gaseous and aqueous expressions of NSZD. The possible breakthrough of various gases (CH_4 , CO_2) and hydrocarbon (volatile organic compound, VOC) vapours at ground surface is also shown.

3.1 Aqueous Expression of NSZD

The aqueous expression of NSZD originates from dissolution of soluble LNAPL chemical constituents into flowing groundwater or infiltrating water contacting the LNAPL. Greatest fluxes are expected from dissolution of LNAPL droplets/ganglia dispersed within the saturated (groundwater) zone. This more dispersed, more accessible, source term arises from:

- Some LNAPL invasion below the water table during original release; and
- Mobile LNAPL resting on a rising water table becoming entrapped as capillary-held residual LNAPL.

A fluctuating water table hence represents an important mechanism for the enhancement of NSZD rates as it transfers LNAPL mass from the main body of buoyant mobile LNAPL (through which groundwater flow is limited by high LNAPL saturations) to the underlying zone of groundwater flow. Dissolution (and vapourisation) of individual chemicals from a multi-component (multi-chemical) LNAPL may occur at different rates, based on a chemical's physical properties (solubility, vapour pressure) and its changing molar proportion within a depleting LNAPL (Thornton *et al.*, 2013).

Significant biodegradation of dissolved-phase hydrocarbons may occur prior to plumes reaching even nearby monitoring wells. This hydrocarbon mass loss needs to be allowed for in the estimation of the aqueous expression of NSZD that should be based upon both the observed hydrocarbon concentration flux monitored and the additional hydrocarbon flux equivalent already biodegraded. The significance of biodegradation is well understood, especially at sites implementing MNA (Environment Agency, 2000) with an established research literature of petroleum hydrocarbon biodegradation / natural attenuation. Methodologies within that literature may be

used to estimate biodegraded hydrocarbon component contributions to the aqueous expression of NSZD (albeit recognising data collection in MNA site assessments is geared to assessing receptor protection, rather than source zone depletion (Environment Agency, 2000; National Research Council, 2000)).

A mass budgeting approach is used whereby estimates of the dissolved hydrocarbon transformation losses are based upon differences observed between monitoring-well transects bridging the source-zone flow-path. Electron acceptors (oxygen, nitrate, sulfate) consumed by hydrocarbon oxidation or else soluble by-products generated (ferrous iron, manganese, dissolved CH_4 and CO_2) are evaluated and then stoichiometrically converted to equivalent hydrocarbon losses based upon a representative chemical(s) within the LNAPL. For example, the hydrocarbon mass loss due to aerobic oxidation may be calculated from the site-observed oxygen consumption and knowing that the aerobic oxidation of decane ($\text{C}_{10}\text{H}_{22}$) (for instance) to CO_2 degrades 0.29 kg of decane per kg of O_2 consumed. An estimate of the overall aqueous expression of NSZD rate is hence typically made at a site 'control plane' of monitoring wells just downgradient from a source determining the rates of hydrocarbon mass loss attributed there to aerobic and anaerobic processes as well as any continuing mass flux of hydrocarbon concentrations still monitored.

3.2 Gaseous Expression of NSZD

The gaseous expression of NSZD originates from vapourisation of LNAPL chemical constituents into soil gas in the unsaturated zone (also known as the vadose zone) above the water table. Vapour plume concentrations may diffuse or advect in the soil gas radially and towards ground surface thereby posing potential vapour intrusion risks. Vapourisation rates will be influenced by the

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distribution of LNAPL initially present. Water table movement may lead to movement of LNAPL into parts of the unsaturated zone and enhance vapourisation from the LNAPL as well as volatilisation, the transfer of dissolved-phase contaminant in the aqueous-phase groundwater to the vapour-phase soil gas. Biodegradation, again though, has a particularly significant influence upon the gaseous expression of NSZD. However, that contribution has been largely overlooked until recently and is considered below (Garg *et al.*, 2017; Suthersan *et al.*, 2015).

Diffusive, but biodegradation-attenuated, transport of vapour concentrations is a significant process at hydrocarbon LNAPL sites. Key process-related controls illustrated in Figure 2 include:

- Diffusion control occurs as air-phase diffusion coefficients for volatile organic compounds (VOCs) are around four orders of magnitude greater than aqueous-phase coefficients, causing diffusion of vapours to be inhibited by high water contents in the soil porosity;
- Advective gaseous flux influences, e.g. where methane (CH_4) generation is sufficiently high to create pressure gradients, or service trenches provide transmissive conduits;
- Steep concentration (diffusion) gradients develop between the LNAPL and ground surface driving contaminant vapour and gas transport towards surface;
- Critically though, vapour contaminant breakthrough at ground surface, even over an unsaturated zone thickness of a few metres, may be prevented, or attenuated, due to biodegradation;
- Continual entry and replenishment of O_2 from ground surface allows shallow subsurface aerobic biodegradation of volatile hydrocarbons (including CH_4) to CO_2 gas;
- Subject to seasonal or daily climate variation causing front movements vertically, quasi-steady state fronts of O_2 and CO_2 and hydrocarbon contaminant profiles may establish in the unsaturated zone as fluxes equate; and

- Increased temperatures and thermal gradients from exothermic biodegradation reactions may enhance rates of vapourisation, volatilisation, diffusion, biodegradation and advection.

The Molins *et al.* (2010) modelling study of the intensively studied Bemidji (Minnesota) oil spill field site illustrates many of these processes.

Anaerobic hydrocarbon biodegradation, in particular methanogenesis, has proven to be a key process leading to measurement of significant amounts of emitted gas, analogous to landfill processes where putrescible wastes (rather than LNAPL) undergo methanogenesis. Key controls include (Figure 2):

- High LNAPL-organic loading leading to highly reduced portions of the saturated and unsaturated zone resulting in methanogenesis and CH_4 and CO_2 gas production predominantly in the pore space adjacent to the LNAPL;
- Transport of buoyant gas bubbles containing CH_4 (and CO_2) generated from LNAPL within the saturated zone may occur to the unsaturated zone;
- CH_4 gas and volatile hydrocarbon vapours meeting an invading atmospheric oxygen front from ground surface may be aerobically biodegraded removing CH_4 and O_2 from the soil gas and generating CO_2 and elevated temperatures.

Direct-contact oil biodegradation within the LNAPL body is now recognised as significant. In particular, 'direct outgassing' may occur whereby production and release of CH_4 and CO_2 from biodegradation of the oil occurs within the immediate pore space adjacent to the oil. Uptake of hydrocarbon molecules into microorganisms may occur via: uptake of the more soluble hydrocarbons dissolved in the aqueous phase; uptake of hydrocarbon micro-droplets pseudo-solubilised by a biosurfactant from the organism; and uptake to microorganisms that grow in fatty acids in direct contact with larger hydrocarbon drops

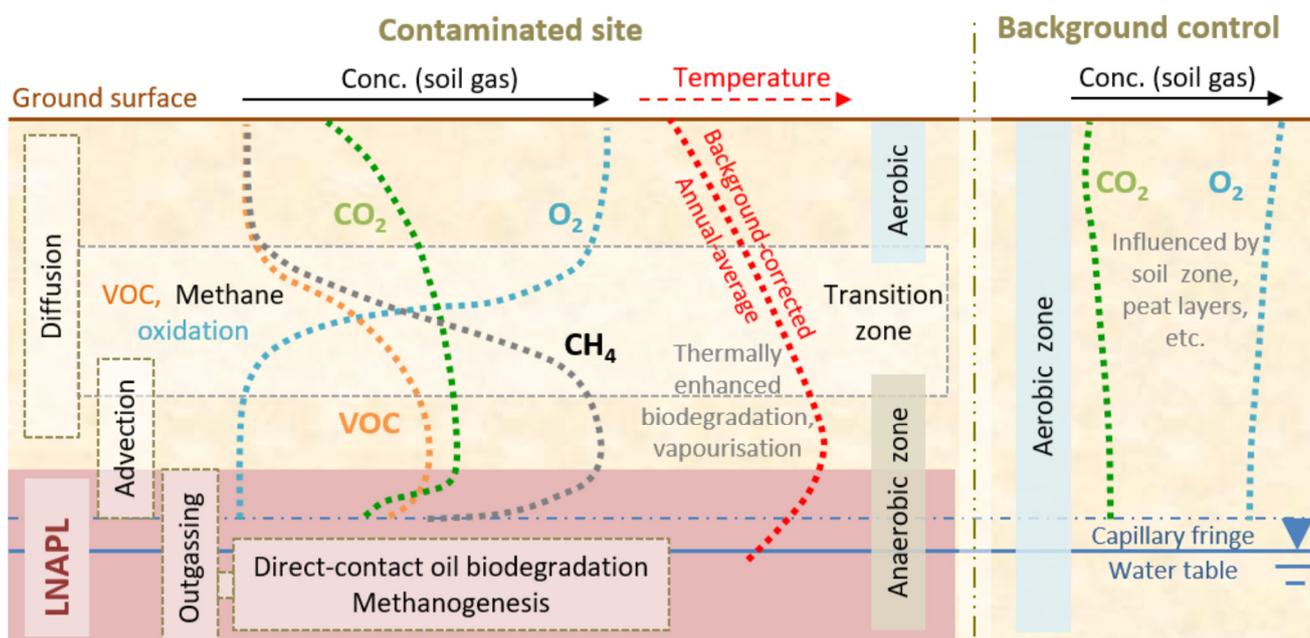


Figure 2. Illustration of processes controlling vertical chemical concentrations in the soil gas between the water table and ground surface arising from the gaseous contribution to NSZD of a biodegradable and volatile LNAPL containing VOCs. A background area free of contamination is also shown.

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(Hua and Wang, 2014). The latter two processes counter the belief that biodegradation of source zone mass is limited by dissolution from the LNAPL to the aqueous phase, and, importantly allows less soluble hydrocarbons to biodegrade. Supporting evidences include (Meckenstock *et al.*, 2014; Hua and Wang, 2014; Ng *et al.*, 2014, 2015):

- Bemidji crude oil spill site evidence of direct outgassing of CH₄ and CO₂ involving, notably, low solubility compounds (e.g. alkanes) that biodegraded within the LNAPL body;
- Modelling suggested 70% of carbon loss from the oil could be attributed to direct outgassing; and
- High rates of biodegradation in a bulk oil body containing only minuscule water droplets.

4. MEASURING NSZD RATES – RECENT ADVANCES

Historically, estimation of NSZD rates has been made at MNA sites where changes in dissolved-phase hydrocarbon and electron acceptor concentrations upgradient and downgradient of the source zone are used within a traditional electron acceptor mass balance model approach to estimate a rate (Section 3.1; Environment Agency, 2000; ITRC, 2009). However, it should be recognised:

- Such estimates only quantify the aqueous contribution to (expression of) NSZD;
- Downgradient measurements closer to the source zone are preferred as these may give a more accurate estimate of the NSZD aqueous component due to the increased uncertainties associated with more distant downstream data favoured for demonstrating natural attenuation occurrence and receptor protection in MNA (i.e. a tension exists between NSZD and MNA needs); and
- Historical sole reliance upon this estimate to mistakenly quantify total NSZD has led to source depletion rates being significantly underestimated as the gaseous contribution, now increasingly recognised to dominate (or prove significant) was ignored.

Site methods are required that reliably quantify the gaseous component of NSZD and measure the combined gaseous mass flux of volatile hydrocarbon vapour and gaseous products arising from biodegradation that may be directly attributed to LNAPL source zone mass depletion. Measurements based on the degradation products arising, such as CO₂, should consider unrelated background contributions that may complicate that signature. Also, gaseous depletion rate measurements are not practical at the LNAPL source interface, but made within the overlying unsaturated zone, or at ground surface. Methods are based on using soil gas flux data (gradient, passive flux trap or dynamic closed chamber methods), temperature data (biogenic heat method), or more recently, using LNAPL compositional change data (CRC CARE, 2018). The most commonly adopted methods are introduced below.

The gradient method – assesses the changes in the vertical distribution of soil-gas constituents (O₂, CO₂, CH₄ and vapour-phase petroleum hydrocarbon) in the unsaturated zone above the LNAPL source via soil gas sampling probes. Concentration gradients obtained are combined with estimates or field measurements of the effective diffusion coefficient for the soil gas, and the gaseous mass flux then calculated using Fick's first law of diffusion. Stoichiometric

conversion of the biodegradation product mass flux then allows an estimate of the rate of LNAPL mass depletion. The method was first applied to estimate NSZD by Johnson *et al.* (2006) and Lundegard and Johnson (2006).

CO₂ efflux methods – measure CO₂ flux in the soil gas via flux chambers or traps typically deployed at ground surface. It is assumed that all petroleum hydrocarbon vapours, including CH₄, in the unsaturated zone are converted to CO₂ and that the NSZD rate can be estimated stoichiometrically based on the biodegradation of a representative hydrocarbon. Two methods have been developed to measure CO₂ flux - the passive CO₂ flux trap method (McCoy *et al.*, 2014) and the dynamic closed chamber method (Sihota and Mayer, 2012).

Biogenic heat methods – recognise hydrocarbon biodegradation is an exothermic process and that the reaction heat flux generated can be thermodynamically equated to a NSZD rate. The thermal gradient is obtained from unsaturated zone temperature depth profiles, and after correction for (seasonally variant) background temperature influence or any non-hydrocarbon related heat effects, the NSZD rate is estimated by dividing the heat flux by the enthalpy (heat) of reaction for a site-relevant biodegradation reaction stoichiometry (CRC CARE, 2018).

Determination of the overall NSZD rate is hence non-trivial and demands field measurements and data interpretation to be carefully undertaken cognisant of the inherent process-based complexities. With increased availability of case study data, it is now possible to quote typical NSZD rates. Garg *et al.* (2017) provide a representative median NSZD rate (as contaminant volume of LNAPL depleted per unit area per year) of approximately 16,000 litres/hectare/year (based on data from 25 sites), equivalent to 1.6 litres/m²/year. This equates to a removal of around 6 mm of *in situ* LNAPL thickness per year (for a 25% porosity soil); hence NSZD may, in time, gradually deplete significant volumes. Significant temporal and spatial variation in rates noted by Garg *et al.* (2017) does however underline the need for site-specific NSZD rate assessment.

5. ROLE OF NSZD WITHIN THE SITE REMEDIATION LIFE CYCLE

Considering the role of NSZD within the site remediation life cycle:

- NSZD may be implemented as a standalone or contributing remedy; and
- NSZD rates may be used for a variety of decision-making purposes, ranging from technology selection and implementation to system shutdown or site closure.

These roles are introduced below with an illustrative conceptualisation of the role of NSZD within the site remediation life cycle shown in Figure 3.

5.1 Development of the LNAPL Conceptual Site Model

Evolving the LNAPL Conceptual Site Model (CSM) through the site remediation life cycle progression is central to the successful management of LNAPL impacted sites. Understanding the dynamic significance of NSZD is a key aspect of the model evolution. Initially a

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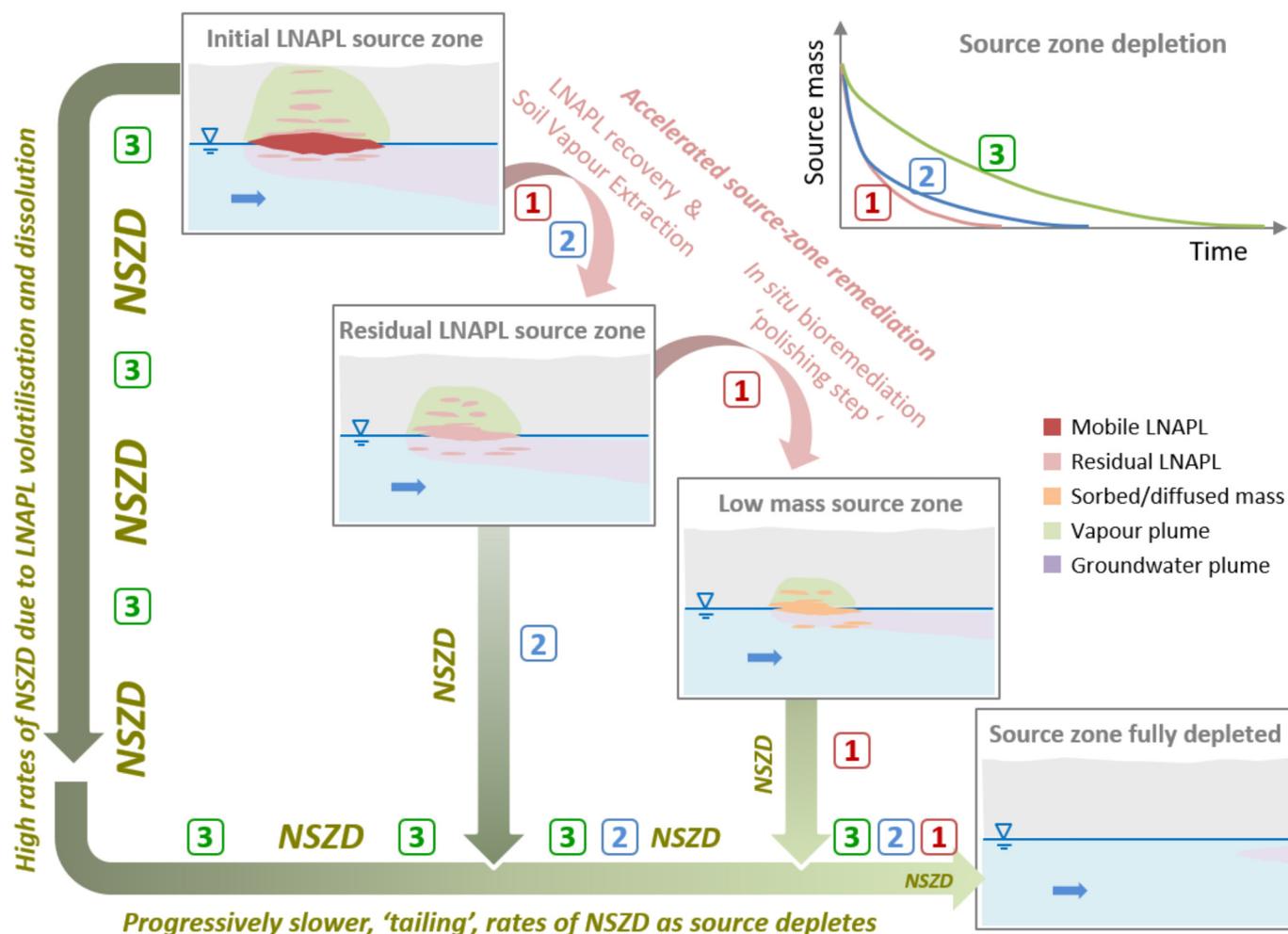


Figure 3. Conceptualisation of the roles of NSZD within the site remediation life cycle. Three numbered pathways are illustrated that rely to varying degrees on NSZD; pathway [3] is completely reliant, pathway [2] is intermediate, and pathway [1] is the least reliant, mainly following an accelerated source-zone remediation pathway.

qualitative screening may perhaps be undertaken to assess whether the probable rate of NSZD is sufficient to address LNAPL risks posed (which is quite probably unlikely). In later iterations of the CSM through the remedial alternatives evaluation, technology selection, design, implementation and performance assessment stages, there is a probable shift in assessment complexity, which may demand additional quantitative spatially- and time-integrated NSZD data in order to more accurately estimate contaminant mass depletion rates and support decision-making on NSZD adoption or the selection of alternative remedies.

5.2 Remediation Technology Selection, Design, Implementation and Performance

NSZD serving as a remedy, or measurement of NSZD rates may be employed in one or more of the following roles (adapted from ITRC (2018) and Palaia and Fitzgibbons (2017)):

A baseline or benchmark to compare the relative benefit of NSZD to other remediation technologies (e.g. by comparing an LNAPL skimming system's mass removal rates to those from NSZD, or supporting a sustainability assessment of future remediation by evaluating the net-benefit of additional remediation compared to NSZD) (Fig. 3);

A primary or standalone remedy at older sites where LNAPL-related impacts are stable (and not of concern), potential receptors are not at risk, and NSZD timeframes are consistent with the goals of the site owner and within regulatory requirements;

A component of a remedy, where NSZD is the primary remedy component for portions of the LNAPL zone, and engineered remediation systems are focused on those portions of the LNAPL footprint where more aggressive removal is required to meet remedial goals;

A final step in a treatment train, where there is remedy transition to NSZD as a long-term risk management approach after other remedial technologies have achieved their design objectives (and mass fluxes from the source or downgradient concentrations are now judged sufficiently low);

To evaluate active remediation progress, for instance, periodic NSZD measurements can be taken during static, re-equilibration periods in areas of residual hydrocarbons during an active remediation programme;

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To mark an endpoint for an active remediation, NSZD rates, with appropriate monitoring to ensure performance objectives have been met, can be used to support a decision for system shutdown.

Within the above selection process, it is critical to compare the sustainability benefits realised from accelerated source zone removal possible from an array of technologies, with those accrued from simply allowing a source zone to deplete naturally, either in part or as a standalone remedy.

6. CHALLENGES AND RESEARCH NEEDS

Various challenges and research needs require consideration to more fully develop our understanding of NSZD and its potential relevance to LNAPL site management, including the following:

Technology Application

- Each NSZD measurement method has its unique procedure and inherent assumptions. Direct comparison of results arising from different measurement approaches can be challenging:
 - ◊ Further side-by-side method comparisons are hence required at real sites with varying geological complexity
- The value of bulk hydrocarbon-based NSZD data for assessment of remedial timeframes to achieve chemical-specific (e.g. benzene) remediation criteria is limited:
 - ◊ Assessing the contributions of various hydrocarbon constituent classes (or at least the key constituents of potential concern) is thus required (CL:AIRE, 2017)
- Temporal decline in NSZD rates is complex to predict and depends on the evolving LNAPL configuration where rates may also vary between the individual chemical constituents of the LNAPL:
 - ◊ Improved prediction of the temporal decline of key chemical-specific risk drivers is required within the overall NSZD
- A dearth of long-term NSZD studies causes long-term changes in NSZD rates to be unclear:
 - ◊ Long-term case study demonstrations are hence required
- Uncertainties also exist in the short-term variability of NSZD rates and hence site-specific controls due to the following possible processes (and others) require assessment:
 - ◊ Seasonal variation, water infiltration dynamics, cold/warm temperature cycles in the subsurface
- Evaluating NSZD monitoring technologies in more challenging site environments is required, such as:
 - ◊ Fractured bedrock sites, particularly with porous rock matrix with significant water-table fluctuation (e.g. the Cretaceous Chalk)
 - ◊ Unsaturated zones of insufficient thickness for complete oxidation of hydrocarbon vapours and CH₄
 - ◊ Impervious ground cover, low permeability - wet unsaturated zone, and particularly cold-climate sites

Site Management

- Due to the exponential decline, or tailing, in source zone mass and mass depletion rates, the timeframes for NSZD to achieve complete source zone depletion may be long and require alternative site management strategies (e.g. institutional control) which should be recognised in the remedial options evaluation to allow recommendation of complementary or different remedies
- Preferred metrics and protocols require development to assist decision-making on:
 - ◊ The appropriate timing and site conditions for transitioning to NSZD and the monitoring required
 - ◊ Acceptance of NSZD occurrence and its sufficiency to deplete the source zone, but without the need for further confirmatory monitoring due to the low receptor risks now involved
- Decision-making on monitoring requirements for the various NSZD options employed, including:
 - ◊ Temporal frequency, spatial density and configuration, reasonable costs
- Implications for site owner liabilities and their transfer
- Regulatory acceptance of NSZD and the development of the regulatory-management frameworks required:
 - ◊ Development of a NSZD Assessment Guide is recommended (analogous to Environment Agency R&D Publication 95 for MNA)

7. CONCLUSIONS

NSZD is becoming increasingly important for those involved in the management of sites contaminated by LNAPLs. The principal NSZD processes are direct mass transfer via LNAPL vapourisation, LNAPL dissolution, volatilisation of mass transferred to the aqueous phase and, in particular, biodegradation. Critically too, there is growing evidence that the gaseous contribution to NSZD, hitherto largely overlooked, appears dominant over the aqueous contribution. This has led to significant effort to better measure that gaseous expression of NSZD at sites. These processes occur, to some degree, at all LNAPL-release sites. Therefore, understanding them, quantifying them and evaluating their effectiveness is an important part of sustainable remediation options appraisal. Whilst NSZD shows significant promise in terms of being used to benchmark the performance of alternative remediation technologies and underpin its optimal and appropriate use as a site remedy, there remains significant need for further research and associated longer-term datasets, which could be achieved by establishing demonstration sites in multiple hydrogeological settings.

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For further information please contact the authors:
 Dr Michael Rivett, GroundH₂O Plus Ltd - rivett@groundh2oplus.co.uk
 Dr Rob Sweeney, CL:AIRE - rob.sweeney@claire.co.uk

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