Guidance on Natural Source Zone Depletion

April 2024

CL:AIRE

ISBN: 978-1-905046-44-7

Published by CL:AIRE, Reading Business Centre, Fountain House, Queens Walk, Reading, RG1 7QF. Email: enquiries@claire.co.uk

Acknowledgements
This guidance has been written by James Rayner of Geosyntec and steered by a collaborative technical review group incorporating representatives from industry, consultancy, and regulators across the devolved administrations. CL:AIRE would like to gratefully acknowledge the Environment Agency for their seed funding for this project. The final document has kindly been reviewed and supported by the Environment Agency, Natural Resources Wales, Scottish Environment Protection Agency and the Northern Ireland Environment Agency (NIEA), an agency within the Department of Agriculture, Environment and Rural Affairs (DAERA). CL:AIRE would also like to thank its Technology and Research Group for their peer review of the document prior to publication.

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Report Citation
It is recommended citation to this report is made as follows:

CL:AIRE, 2024. Guidance on Natural Source Zone Depletion. CL:AIRE, Reading. ISBN 978-1-905046-44-7. Download at https://www.claire.co.uk/nszd

Executive Summary

Natural source zone depletion (NSZD) can be a sustainable risk-management strategy for petroleum hydrocarbon light non-aqueous phase liquids (LNAPLs) impacting the subsurface. NSZD refers to the combination of naturally occurring processes – biodegradation, vaporisation, volatilisation and dissolution – that act to reduce LNAPL mass, saturation and mobility in the subsurface. NSZD processes are expressed through effluxes of soil gas, vapour and heat in the unsaturated zone, within a groundwater plume and in the changing composition of the weathering LNAPL. Expressions of NSZD can be monitored to estimate rates of LNAPL mass depletion. Several NSZD monitoring technologies have been developed, that are in common use, and continue to evolve. The rate of natural LNAPL depletion is typically dominated by losses to the gaseous phase generated through biodegradation, which can be in the order of thousands to tens of thousands of litres of LNAPL per hectare per year. With ongoing evolution of monitoring technology, NSZD is now recognised as a viable alternative to, or component of, active remediation strategies for LNAPL impacted sites.

Recent advances in NSZD are captured in this document, alongside a decision-making framework, to provide technical guidance for practitioners, regulators and liability owners on the science and practical considerations for the application of NSZD-based risk-management strategies in the UK.

The framework is a three-stage procedure, designed to mesh with existing risk-management procedures, such as Land Contamination Risk Management (LCRM) used in England, Wales and Northern Ireland. The stepwise framework includes:

1. **Screening** NSZD feasibility by confirming that LNAPL and NSZD processes do not pose risks to receptors, and evaluating technical, practical, economic, sustainability and regulatory constraints;
2. **Demonstration** that the rate of NSZD can achieve remediation objectives, through good quality data collection supporting defensible conceptualisation of NSZD processes; and
3. **Implementation** of a long-term performance monitoring programme to confirm that NSZD continues to be protective of receptors and capable of achieving remediation objectives, resulting in eventual closure of risk-management measures for LNAPL.

Understanding NSZD requires development and evolution of an advanced conceptual site model for LNAPL and associated risks. This may influence the scope and duration of other *in situ* remediation options and/or demonstrate that active remediation will not provide substantially increased benefits over natural processes alone. NSZD may provide a stand-alone strategy, where risks are adequately managed, or be used alongside or as part of a sequence of remediation solutions, including monitored natural attenuation, for petroleum hydrocarbon impacts to the subsurface. Alternatively, NSZD assessments or monitoring can be applied for a variety of other decision-making purposes within the remediation site lifecycle.

Monitoring NSZD represents a long-term commitment to LNAPL risk management in the order of years to decades. If circumstances change, and NSZD is no longer protective of receptors or viable to all stakeholders, then contingency measures may be required,

including consideration of remediation alternatives to NSZD. Engagement with the regulator is required throughout the decision-making process regarding NSZD as a risk-management strategy for LNAPL impacted sites.

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1. Introduction

1.1 Why Natural Source Zone Depletion is Important

Natural source zone depletion (NSZD) is the term used to describe the collective, naturally occurring processes of dissolution, vaporisation, volatilisation and biodegradation that result in observable reductions in mass, saturation and mobility of light non-aqueous phase liquid (LNAPL), most commonly oils and fuels, within the subsurface. Rates of LNAPL mass depletion due to NSZD can be significant (e.g. Johnson *et al*., 2006; Garg *et al*., 2017; crcCARE, 2020; Smith *et al*., 2022), often in the order of thousands to tens of thousands of litres of LNAPL per hectare per annum (L/Ha/a).

With the rapid and ongoing evolution of this field and complementary advances in site characterisation and monitoring technologies, NSZD is now recognised as a viable alternative and long-term risk-management strategy for environmental liabilities involving LNAPLs. Evaluating NSZD can be significant to the sustainable management of LNAPL contaminated sites. Understanding NSZD requires development and evolution of an advanced conceptual site model (CSM) that describes physical, chemical and biogeochemical processes that control LNAPL distribution, mobility and migration potential, and aqueous, gaseous and vapour fluxes. This level of understanding is required to demonstrate that risks are adequately managed, now or in the future, and assess whether NSZD can achieve remediation objectives. Consideration of NSZD may influence the scope and duration of other *in situ* remediation options and/or demonstrate that active remediation will not provide substantially increased benefits, including risk reduction, over natural processes alone.

Uptake of NSZD, and associated research, has predominantly taken place in the USA and Australia, and several guidance documents on its assessment and application to remediation programmes have been published (ITRC, 2009; API, 2017; ITRC, 2018; crcCARE, 2018). To date, NSZD-based risk management within the UK and Europe has been relatively limited, perhaps due to a combination of challenges and remaining gaps in understanding of NSZD processes, that recent research and case studies have begun to address (e.g. CL:AIRE, 2019; Concawe, 2020; Smith *et al*., 2021; CL:AIRE, 2023a; CL:AIRE, 2023b; Statham *et al*., 2023;). NSZD has been demonstrated to be significant at these sites and will therefore be an underlying driver towards achieving LNAPL site remediation objectives in the UK and Europe. This document captures the recent advances in NSZD to provide technical guidance for practitioners, regulators, liability owners and other stakeholders on the science and practical considerations for NSZD-based risk-management strategies in the UK.

This guidance document aims to outline:

- Key processes controlling NSZD (Section 1.2 and Appendix 1);
- Current approaches to measuring NSZD processes and evaluating mass depletion rates (Section 1.3, Appendix 1 and Appendix 2);
- The roles of NSZD in the remediation lifecycle (Section 1.4); and

- A decision-making framework for selecting, designing and implementing NSZD at UK sites (Section 2 and Appendix 3).

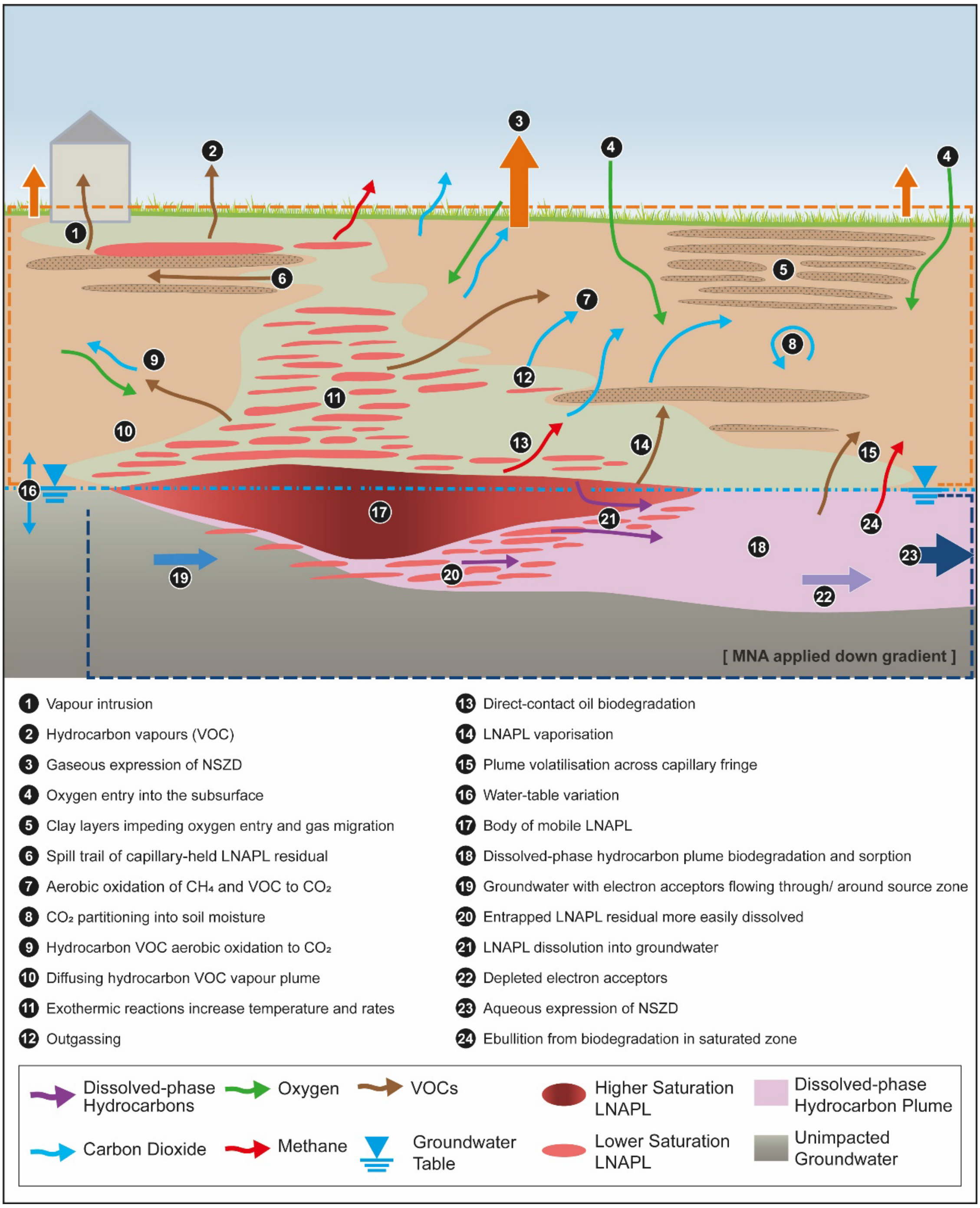
Assessing NSZD requires knowledge and experience in the characterisation of LNAPLs, multi-phase flow (NAPL, water, gas/vapour), natural attenuation and reactive transport in the unsaturated and saturated zones. Anyone responsible for assessing and implementing NSZD should be suitably qualified and experienced, such as required under the definition of a ‘competent person’ in the Land Contamination Risk Management procedures (LCRM; Environment Agency, 2023) used in England, Wales and Northern Ireland.

At the time of writing (December 2023), this document is a collation of the current understanding of NSZD. Given the rapid evolution of this field, its contents cannot be considered as definitive, and the reader may wish to research additional resources as these become available. However, consideration of the procedural guidance contained in this document would demonstrate the reasonable practice and care expected of professional practitioners.

1.2 Overview of NSZD Processes

Understanding the processes that control NSZD is critical to the selection, design and implementation of NSZD-based risk-management strategies for LNAPL contaminated sites. The key physical and biological attenuation processes – biodegradation, vaporisation, volatilisation and dissolution – affect the rates of mass depletion. NSZD processes are expressed in gaseous and aqueous phases and compositional changes within the LNAPL (Figure 1.1).

NSZD processes are introduced below, with additional information presented in Appendix 1.



① Vapour intrusion
② Hydrocarbon vapours (VOC)
③ Gaseous expression of NSZD
④ Oxygen entry into the subsurface
⑤ Clay layers impeding oxygen entry and gas migration
⑥ Spill trail of capillary-held LNAPL residual
⑦ Aerobic oxidation of CH_4 and VOC to CO_2
⑧ CO_2 partitioning into soil moisture
⑨ Hydrocarbon VOC aerobic oxidation to CO_2
⑩ Diffusing hydrocarbon VOC vapour plume
⑪ Exothermic reactions increase temperature and rates
⑫ Outgassing
⑬ Direct-contact oil biodegradation
⑭ LNAPL vaporisation
⑮ Plume volatilisation across capillary fringe
⑯ Water-table variation
⑰ Body of mobile LNAPL
⑱ Dissolved-phase hydrocarbon plume biodegradation and sorption
⑲ Groundwater with electron acceptors flowing through/ around source zone
⑳ Entrapped LNAPL residual more easily dissolved
㉑ LNAPL dissolution into groundwater
㉒ Depleted electron acceptors
㉓ Aqueous expression of NSZD
㉔ Ebullition from biodegradation in saturated zone

Figure 1.1: Conceptual site model showing unsaturated and saturated zone processes generating gaseous and aqueous expressions of NSZD (after CL:AIRE, 2019).

Gaseous expression of NSZD results from vaporisation and biodegradation of LNAPL and sorbed-phase chemical constituents, and volatilisation and biodegradation of dissolved-phase constituents. These processes produce methane, carbon dioxide and hydrocarbon vapours and lead to vertical diffusive transport of carbon dioxide, methane and hydrocarbon vapours through the unsaturated zone. Biodegradation within the LNAPL-impacted saturated zone and anaerobic portions of overlying unsaturated zone occurs predominantly by methanogenesis. To the extent that oxygen infiltrates the unsaturated zone, vertically migrating methane and hydrocarbon vapours, and even

LNAPL, are aerobically biodegraded. This oxygen depleting process attenuates hydrocarbon vapours and LNAPL mass, while generating carbon dioxide and heat.

Aqueous expression of NSZD originates from the dissolution of soluble LNAPL and sorbed-phase chemical constituents into groundwater or infiltrating water (CL:AIRE, 2019). Biodegradation (oxidation) of dissolved-phase hydrocarbons consumes electron acceptors (oxygen, nitrate, iron oxides/oxyhydroxides, sulfate and manganese oxides) and generates soluble by-products (ferrous iron, manganese (II), dissolved methane, non-volatile dissolved organic compounds and dissolved inorganic carbon). Biodegradation can be significant, even over short distances from the LNAPL, such that the aqueous expression of NSZD will typically comprise dissolved organic carbon and/or dissolved inorganic carbon components with residuals of terminal electron accepting processes.

Depletion of volatile, soluble and/or bioavailable LNAPL constituents result in compositional changes in LNAPL. Extensive studies looking at the effects of weathering processes (dissolution, volatilisation, biodegradation etc.) on hydrocarbon fuels have demonstrated that compositional changes follow predictable trends, which can therefore be used as reliable indicators of NSZD (DeVaull *et al*., 2020). Physical losses of the volatile and soluble constituents generally affect the lighter (<C10) aromatic and aliphatic components in hydrocarbon LNAPL, with partitioning governed by Raoult's Law and the mole fractions of the NAPL components. Hydrocarbon constituents are variably susceptible to biodegradation but research indicates a hierarchy based on constituent structure, whereby *n*-alkanes are expected to biodegrade first, followed by alkylcyclohexanes, isoprenoids and polycyclic aromatic hydrocarbons (Kaplan *et al*., 1996).

In addition to compositional factors, multi-phase transport (NAPL, water and soil gas) and other processes govern the expression and rates of NSZD, including:

1. NAPL physical properties – NAPL viscosity and density affect initial LNAPL distribution in the subsurface and can change over time due to NSZD processes, resulting in compositional changes and biogenic heat;

2. LNAPL source architecture – the characteristics of the LNAPL release and subsequent distribution of residual and mobile LNAPL volumes;

3. Groundwater dynamics – influencing initial distribution and subsequent redistribution of LNAPL;

4. Physical and biogeochemical heterogeneities – the nature and distribution of prevailing redox conditions are controlled by the type and exchange of electron acceptors, which are in turn influenced by physical and biogeochemical heterogeneities (e.g. low permeability layers, hardstanding, variations in soil moisture content, soil mineralogy and microbial communities);

5. Subsurface temperatures – biodegradation rates are reduced and dissolution of migrating carbon dioxide and hydrocarbon vapours in soil moisture enhanced at lower temperatures compared to drier, warmer conditions, that could arise from seasonal variations, climate change and/or anthropogenic sources, such as sewers.

While NSZD of petroleum hydrocarbons is ubiquitous in the environment, these constraints present challenges to the characterisation and monitoring of relevant processes.

1.3 Measuring NSZD Occurrence and Rates

Advances in NSZD monitoring methods allow rates to be estimated from data describing gaseous and aqueous expressions of NSZD and/or LNAPL compositional changes. These methods support the theoretical, qualitative and quantitative assessment of NSZD rates. Each method has limitations and biases, and their suitability to monitor NSZD should be evaluated with consideration to the LNAPL CSM.

The NSZD monitoring methods in common use are introduced below, with supporting information provided in Appendix 2.

Three approaches for monitoring NSZD processes in the unsaturated zone have received widespread use:

- The gradient method – uses measurements of oxygen, methane and carbon dioxide taken at discrete depths using nested soil gas sampling probes or within monitoring well screens installed above the LNAPL (API, 2017; ITRC, 2018; crcCARE, 2018). Soil gas measurements, corrected for non-NSZD contributions, are used to estimate diffusive fluxes through the unsaturated zone, which are then stoichiometrically equated to rates of hydrocarbon biodegradation and thus NSZD (Figure 1.2);

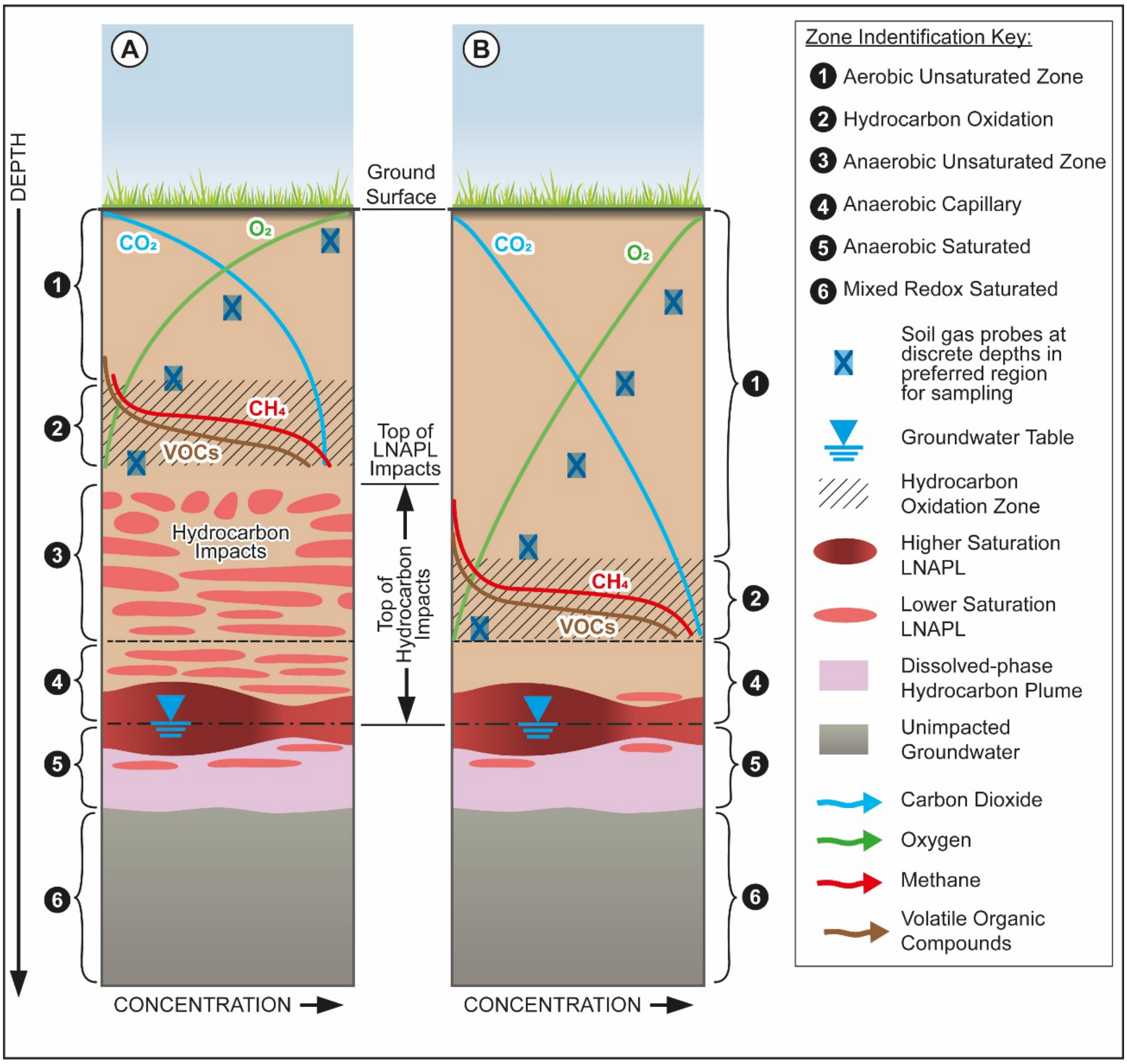


Figure 1.2: Conceptualisation of soil gas vertical profiles with schematic gradient method monitoring setups for (A) sites with shallow LNAPL impacts above the water table; and (B) sites without shallow LNAPL impacts (after API, 2017). Reproduced courtesy of the American Petroleum Institute.

- Gaseous efflux methods – measure soil gas flux using a trap or chamber installed in the surface or shallow subsurface. The gaseous flux is equated to a NSZD rate based on reaction stoichiometry for biodegradation of a representative hydrocarbon compound (e.g. decane). Two methods have been developed (Figure 1.3 and Figure 1.4):
    - the passive CO_2 flux trap (McCoy *et al*., 2015) is deployed for a period of several days to collect carbon dioxide on an adsorbent material. Laboratory analysis provides time-averaged measurements of carbon dioxide (Figure 1.3);
    - the dynamic closed chamber (Sihota and Mayer, 2012) is an active monitoring technique using a vacuum pump connected to a surface-mounted chamber to collect and pass soil gas (carbon dioxide, methane etc.) through a field gas analyser. Measurements typically span minutes and multiple measurements spanning multiple days are typically required to derive time-weighted averages.

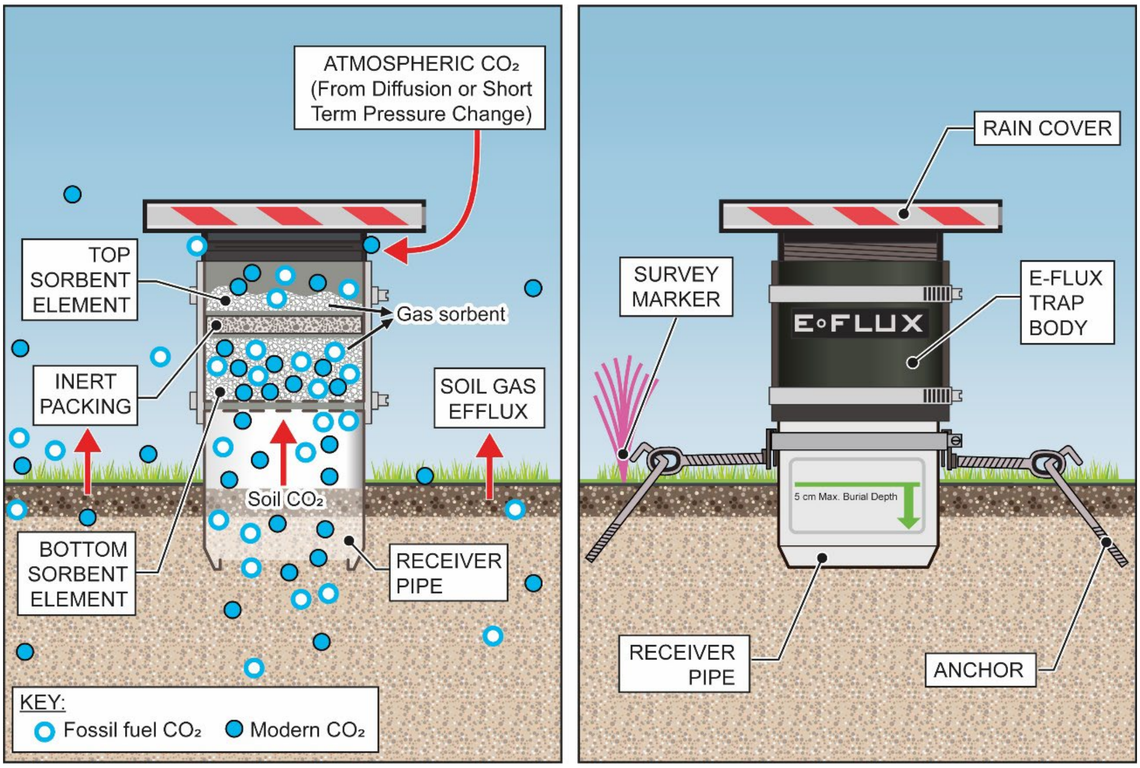


Figure 1.3: Passive CO_2 flux trap. Schematic process diagram and example site deployment (Source: E-Flux).

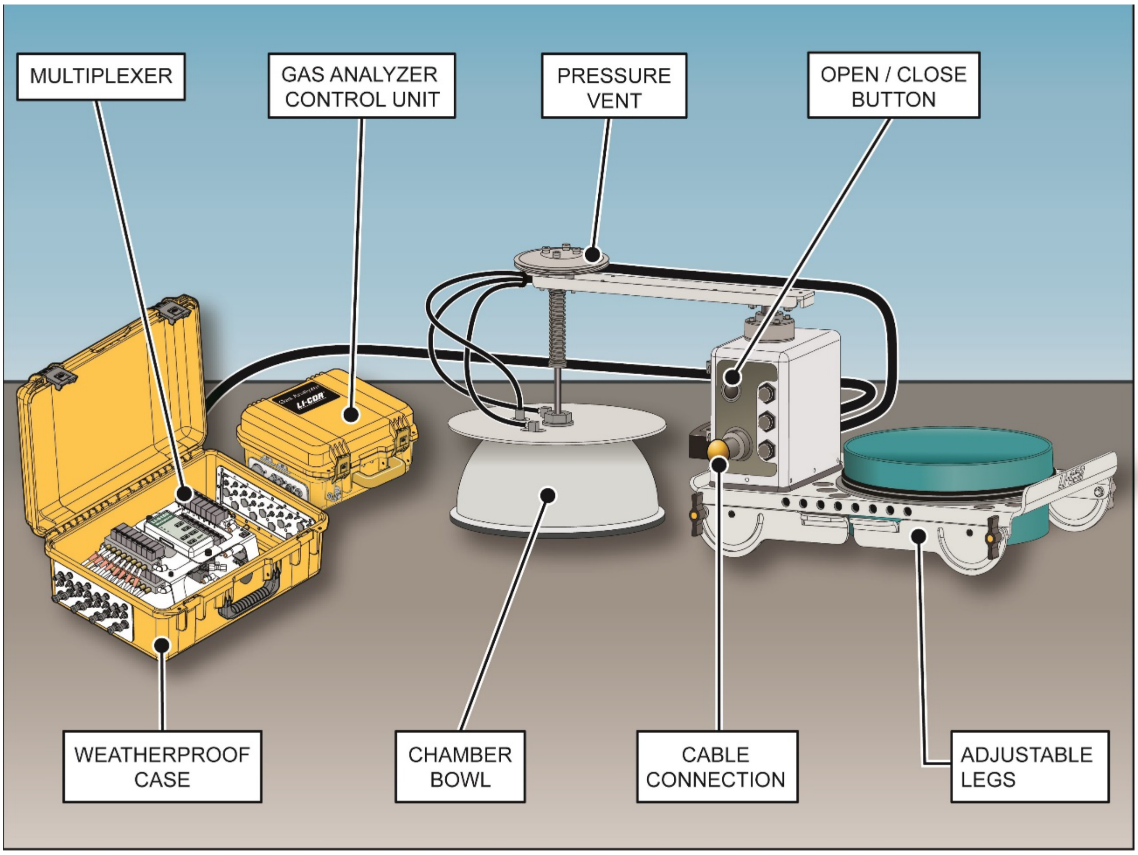


Figure 1.4: Example dynamic closed chamber site setup (Source: LI-COR Environmental).

- Biogenic heat methods – biodegradation of LNAPL, hydrocarbon vapours and methane, in particular aerobic oxidation, are exothermic reactions releasing energy in the form of heat (Figure 1.5). The thermal gradient from hydrocarbon biodegradation is determined by taking soil temperature measurements at discrete depths (Sale *et al*., 2018; Warren and Bekins, 2015; Karimi Askarani *et al*., 2018; Kulkarni *et al*., 2020; Ganna *et al*., 2022; Kulkarni *et al*., 2022) using strings of thermistors/thermocouples or button-type temperature loggers. The thermal flux, inferred from the thermal gradient, can be equated stoichiometrically to a NSZD rate. Soil temperature measurements can be collected continuously over periods spanning hours to years, advancing understanding of the temporal variability in aerobic biodegradation to NSZD rates (e.g. Thermal NSZD®, 2016; Walker *et al*., 2020).

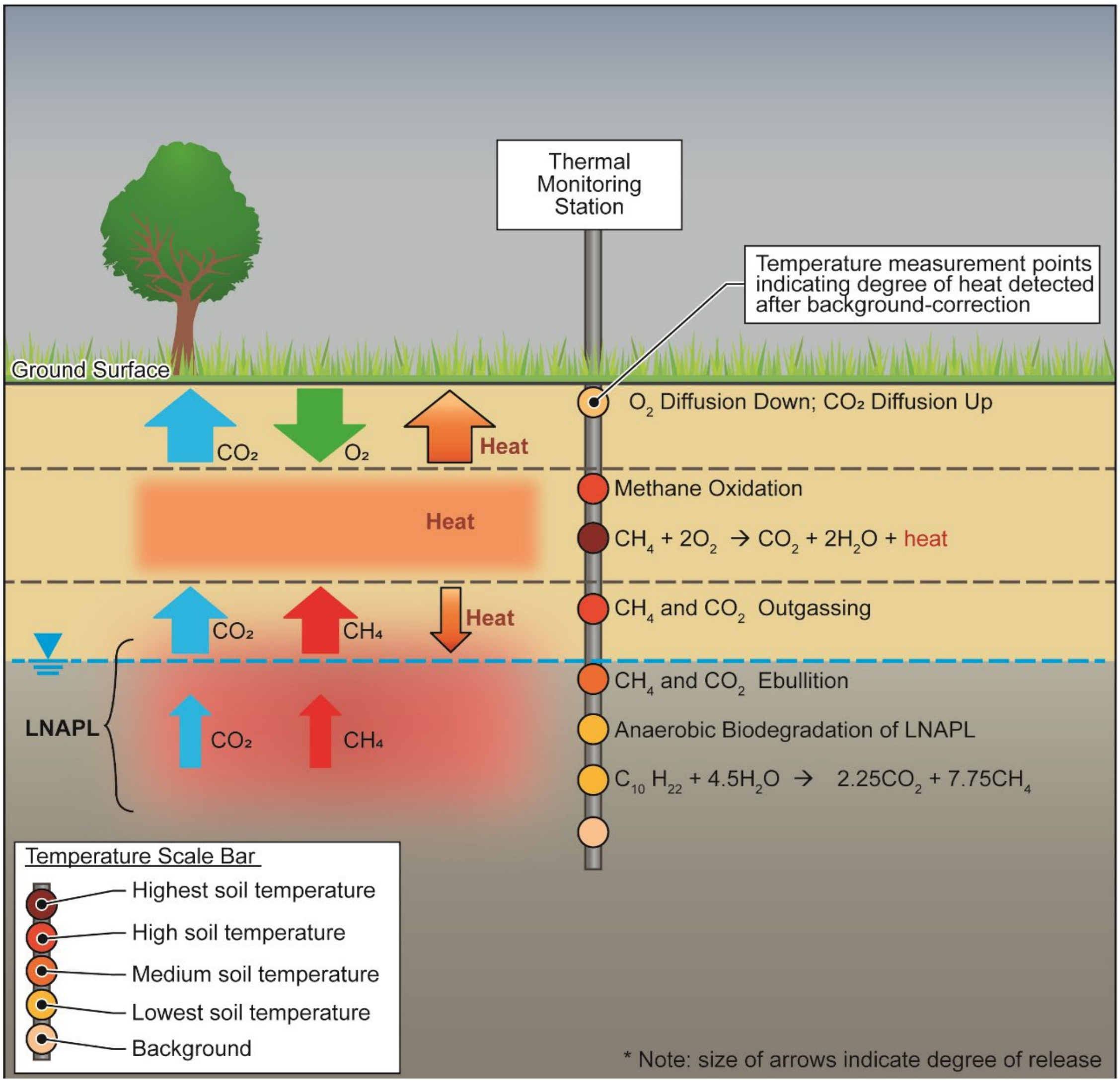


Figure 1.5: Schematic of a biogenic heat method monitoring and theory (modified from Thermal NSZD®, 2016).

The unsaturated zone monitoring methods provide estimates of bulk hydrocarbon LNAPL depletion rather than depletion of potentially risk-driving constituents of potential concern (COPC). Each of the unsaturated zone monitoring methods require corrections for non-NSZD related contributions to soil gas or soil temperature. Previously corrections based on "background" measurements taken outside the area of LNAPL impact were required. Recent advances include development of alternative methods to address background corrections, for example use of carbon 14 (^{14}C) isotope techniques with gradient and gaseous efflux methods (e.g. McHugh *et al*., 2020; Smith *et al*., 2021), and a "single stick" computational method for transforming soil temperature data into NSZD rates without background correction (Karimi Askarani and Sale, 2020).

Aqueous expression of NSZD is commonly monitored using established methods for assessing contaminant plume dynamics in groundwater (e.g. ITRC, 2009; ITRC, 2010; crcCARE, 2018; CL:AIRE, 2024), as illustrated in Figure 1.6.

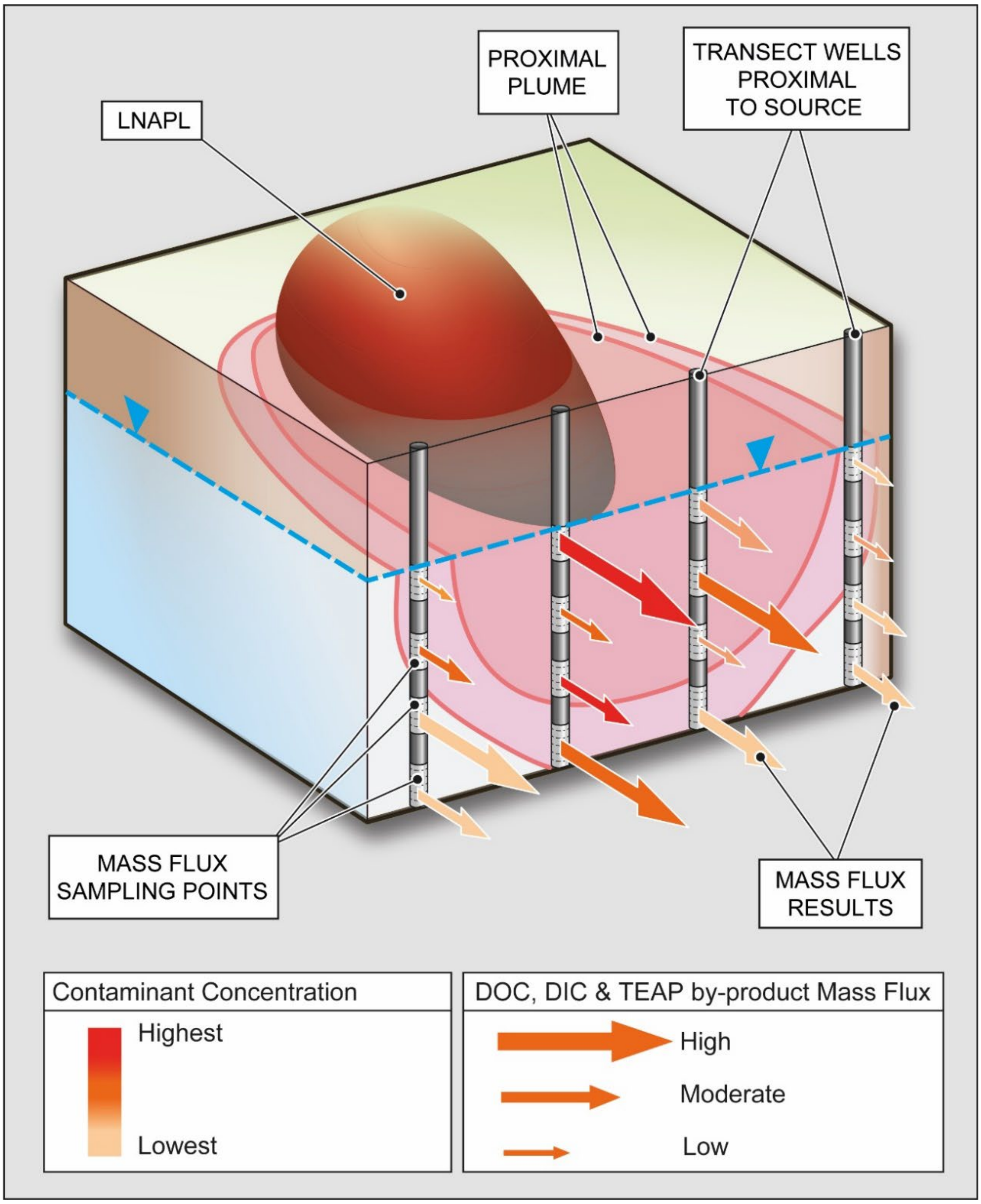


Figure 1.6: Schematic of groundwater monitoring well transect for assessment of mass discharge in groundwater from LNAPL (ITRC, 2010). DOC refers to dissolve organic carbon constituents (hydrocarbons); DIC refers to dissolved inorganic carbon species; TEAP refers to terminal electron accepting processes.

The occurrence and rate of LNAPL depletion through dissolution (aqueous expression) may be estimated by:

- Assessing spatial and temporal trends in hydrocarbon concentration data in groundwater proximal to the LNAPL source (crcCARE, 2018);
- Mass balance of hydrocarbons and geochemical indicators for biodegradation, such as the method provided by National Research Council (2000) and extended by ITRC (2009); or
- Carbon balance (Mackay *et al*., 2018) of measurements of dissolved organic carbon and dissolved inorganic carbon.

In addition to providing bulk estimates of LNAPL depletion through dissolution into groundwater, groundwater monitoring techniques permit evaluation of the depletion of potentially risk-driving COPCs within the LNAPL, if this is an objective.

Where monitoring of gaseous and/or aqueous expressions of NSZD using these techniques is challenging, compositional change and emerging methods provide alternative or supporting means to estimate rates of NSZD:

- Compositional change methods (crcCARE, 2018; DeVaull *et al*., 2020) utilise analytical data for LNAPL constituents and LNAPL physical properties with literature or measured multi-phase flow parameters to equate changes in COPCs, biomarkers or other parameters with NSZD rates. These methods provide another means to monitor depletion of risk-driving COPCs, should this be an objective of a NSZD risk-management strategy.
- Degassing methods (Amos *et al*., 2005) use the observed depletion of dissolved nitrogen gas and argon in groundwater to assess methanogenesis and the rate of NSZD in the saturated zone. This method has potential application to NSZD where conditions prevent the full gaseous efflux from reaching the ground surface and/or reliable measurement of variations in soil gas concentrations vertically in the unsaturated zone (e.g. a shallow water table or confined system, where saturated conditions extend above the LNAPL).

Physical and biogeochemical heterogeneities and confounding background effects are common factors that contribute to variability in NSZD rates. As with many environmental monitoring procedures, NSZD rates are “estimates” and should be considered with one order of magnitude precision (API, 2017; crcCARE, 2018). The varying assumptions and biases between different NSZD monitoring methods mean that estimates will rarely match precisely, as illustrated in Figure 1.7. It is suggested that two or more methods are used, where site conditions permit, to provide convergent lines of evidence for NSZD with acknowledgement of uncertainty in the rate of LNAPL depletion.

The estimation of NSZD rates is non-trivial and requires data collection and analysis to be carefully undertaken, with consideration to the complexity of the processes under evaluation, spatial and temporal variability, and the limitations and biases inherent in each estimation method (CL:AIRE, 2019).

Representative NSZD rates are provided by multiple authors. A selection are summarised in Table 1.1 that indicate NSZD will gradually deplete significant volumes of LNAPL. Spatial and temporal variation in NSZD rates is noted by multiple authors (e.g. Sihota *et al*., 2016; Eichert *et al*., 2017; Garg *et al*., 2017 ; crcCARE, 2020), and stresses the need for site-specific measurements, in particular where NSZD processes may be affected by challenging site conditions (e.g. Concawe, 2020; Smith *et al*., 2021).

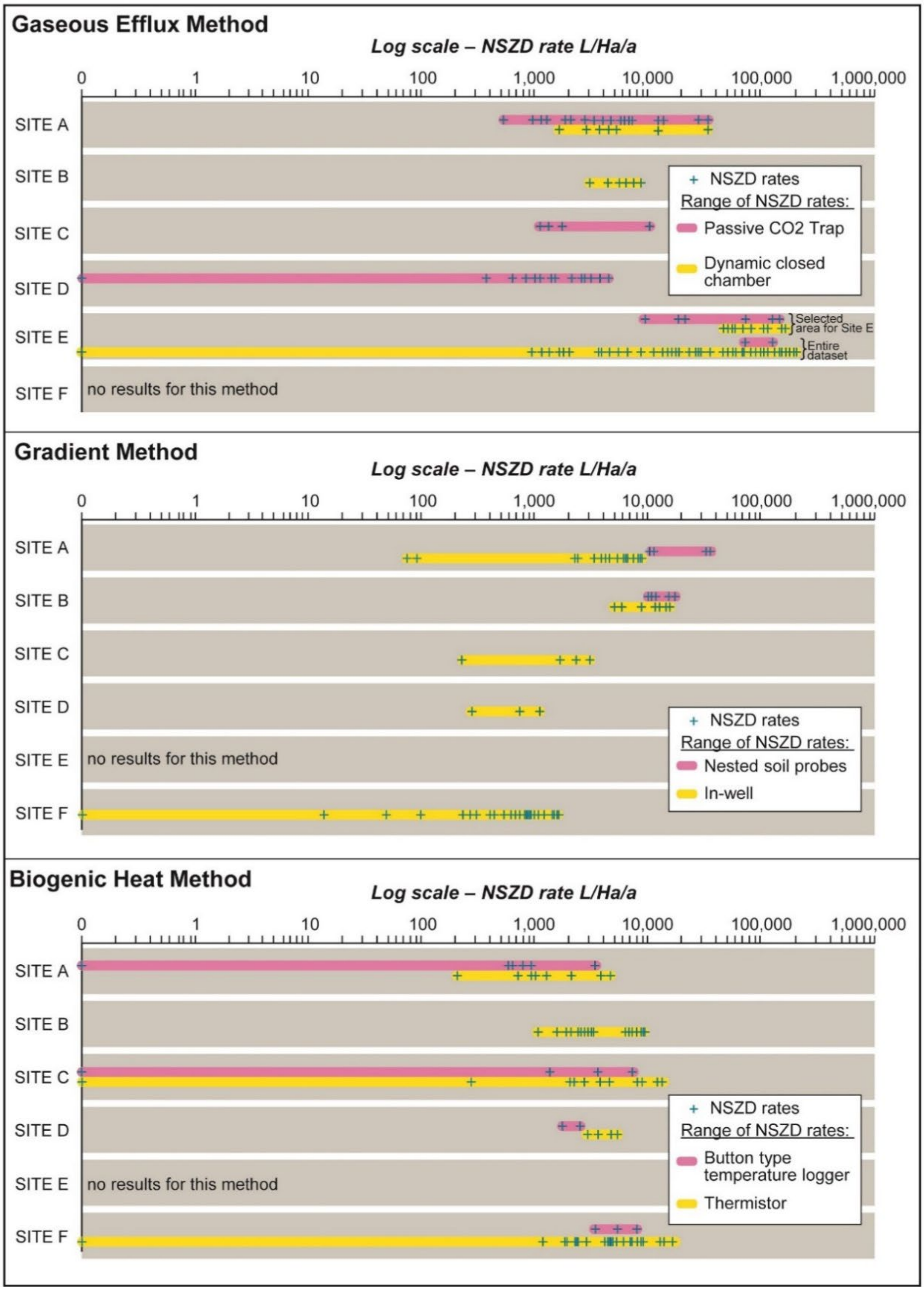


Figure 1.7: Comparison of NSZD rates in litres of LNAPL per hectare per year (L/Ha/a) across six sites by method (adapted from Rayner *et al*., 2020). This study demonstrates different techniques for measuring rates of NSZD were variable both spatially and temporally. This is an expected outcome given the non-uniform distribution of LNAPL across a source zone and seasonal impacts of variations in parameters affecting NSZD processes such as water table elevation and unsaturated zone moisture contents.

Table 1.1: Average NSZD rate measurements from site case studies.

Fuel/oil	LNAPL Volume Depletion Rate (L/Ha/a)	Equivalent LNAPL Formation Thickness Depletion Rate* (mm/a)	Equivalent Petroleum Hydrocarbon Concentration in Soil Depletion Rate* (mg/kg/a)	Reference
Crude	200 to 600	≈0.1 to 0.2	≈0.03 to 0.09	Lundegard & Johnson, 2006
	15,000	≈6.1	≈2.4	Sihota *et al.*, 2011
	2,900 to 10,300	≈1.2 to 4.2	≈0.46 to 1.6	Sihota *et al.*, 2016
	1,000 to 17,000	≈0.4 to 6.9	≈0.15 to 2.7	Rayner *et al.*, 2020
Condensate	Up to 36,000	≈14.7	≈5.7	Rayner *et al.*, 2020
Gasoline	Up to 15,000	≈6.1	≈2.4	Rayner *et al.*, 2020
	260 to 54,000	≈0.1 to 22	≈0.04 to 8.6	Smith *et al.*, 2021
Diesel	6,000 to 14,000	≈2.4 to 5.7	≈1.0 to 2.2	Rayner *et al.*, 2020
	Up to 13,000	≈1.1	≈0.43	Rayner *et al.*, 2020
	460 to 2,700	≈0.2 to 1.1	≈0.07 to 0.43	Smith *et al.*, 2021
Mixed fuels	2,800 to 29,000	≈1.1 to 12	≈1.6 to 11	Garg *et al.*, 2017
	Up to 5,100	≈2.1	≈0.8	Rayner *et al.*, 2020
Jet fuel	47,300 to 165,000	≈19 to 67	≈7.5 to 26	Rayner *et al.*, 2020

* Calculated for illustrative purposes only, assuming soil porosity of 25%, soil bulk density of 2.0 g/cm^3, LNAPL density 0.8 g/cm^3 and LNAPL smear zone thickness of 1 m.

1.4 NSZD in Site Remediation Lifecycle

NSZD can be applied as a stand-alone risk-management strategy for LNAPL where it can be demonstrated that risks are adequately managed and natural processes can achieve timebound remediation objectives. Alternatively, NSZD assessments or monitoring can be applied for a variety of other decision-making purposes within the remediation site lifecycle. These concepts are illustrated in Figure 1.8 and introduced below (CL:AIRE, 2019):

- A baseline or benchmark with which to assess the benefit of active remediation alternatives compared to natural processes, i.e. as part of a sustainability assessment using the SuRF-UK framework (CL:AIRE, 2010; CL:AIRE, 2020a);
- A component of a remediation or risk-management strategy, where NSZD is implemented alongside active remediation and/or monitored natural attenuation (MNA) for portions of the LNAPL where potential risks to receptors are adequately managed;
- Following active remediation, where the selected technologies have achieved their design objectives enabling transition to a passive long-term risk-management approach (e.g. Statham *et al.*, 2023);
- Evaluating progress or the endpoint for active remediation that can be used to support a decision to shut down.

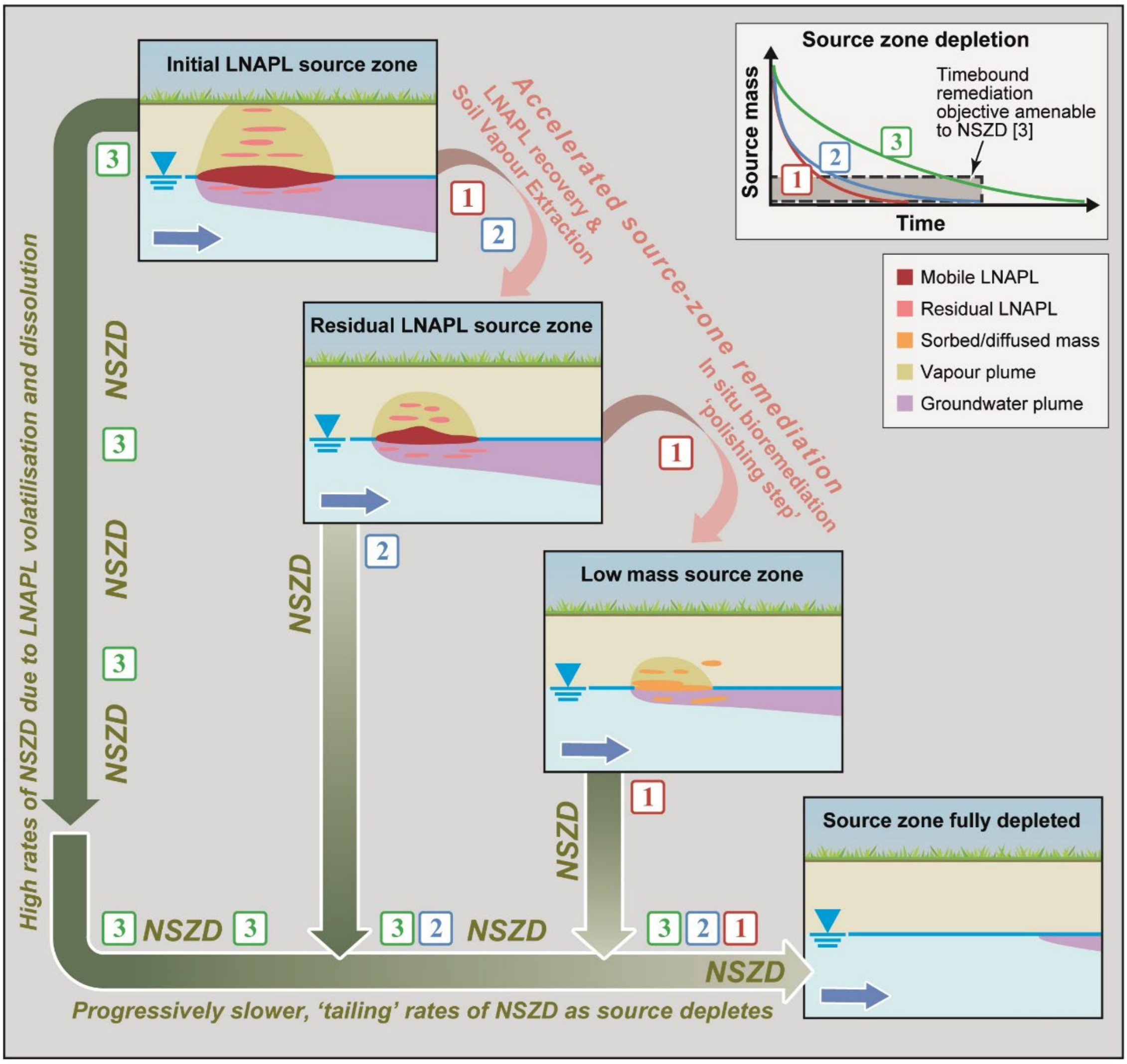


Figure 1.8: Schematic of possible roles of NSZD within the site remediation lifecycle (after CL:AIRE, 2019). The numbered pathways indicate varying reliance on NSZD to achieve source zone remediation: [1] limited NSZD, mostly active remediation; [2] moderate NSZD and active remediation; and [3] NSZD only.

NSZD could be considered at three stages of the site remediation lifecycle, such as that defined in LCRM (Environment Agency, 2023):

1. In advancing conceptualisation of potential contaminant linkages from generic to detailed quantitative risk assessment (LCRM Stage 1 Tier 2 to Tier 3);
2. Comparing NSZD with other potential remediation technologies in an Options Appraisal (LCRM Stage 2); and/or
3. In transition from active remediation to a passive risk-management strategy during remediation and verification (LCRM Stage 3).

The selection, design and implementation of NSZD as a risk-management strategy relies upon the development of an advanced CSM for LNAPL demonstrating understanding of relevant NSZD processes and associated risks to identified receptors. Assessing NSZD processes informs the CSM, but the NSZD strategy relies upon the CSM for validation.

The initial NSZD CSM will focus upon characterising potential contaminant linkages associated with LNAPL, soil gas, vapour and groundwater, with only theoretical or semi-quantitative evaluation of relevant processes. With increased quantitative understanding of NSZD, the CSM can advance to demonstrate NSZD occurrence with sufficient confidence to estimate LNAPL depletion rates using suitable techniques, and finally support the design and verify the performance of a long-term monitoring strategy that adequately manages risks, while achieving remediation objectives.

CSMs for potential contaminant linkages associated with LNAPL that are informed by preliminary or generic quantitative risk assessments, for example using generic assessment criteria (CL:AIRE, 2014; Nathanail *et al.*, 2015; SoBRA, 2017) or gas screening values (British Standards Institution, 2019), could misrepresent potential risks to receptors. Initial assessments of NSZD should inform the conceptualisation of potential contaminant linkages required to perform detailed quantitative risk assessment:

- LNAPL mobility and migration potential;
- soil gas and hydrocarbon vapour flux, reactive transport and intrusion potential; and/or
- solute reactive transport.

Additional quantitative spatially- and temporally-integrated NSZD data are needed to achieve the higher level of assessment complexity required to appraise this technology against remediation alternatives, should this be required. The effort expended to advance the CSM for NSZD should also inform conceptualisation for active remediation alternatives in the source zone, and advance demonstration of the viability of MNA in the groundwater plume (CL:AIRE, 2024).

NSZD represents an extension of established MNA practices for groundwater plumes (CL:AIRE, 2024) to hydrocarbon LNAPL source zones. The combination of NSZD in the LNAPL source zone and MNA in the dissolved-phase plume, with appropriate monitoring to assure attainment of performance objectives, may constitute the final step in remediation of a LNAPL release site (ITRC, 2018). However, while related, combined monitoring of NSZD and MNA may not be required for all LNAPL risk-management strategies, the scope being driven by site-specific remediation objectives. For example, MNA alone may be appropriate where understanding LNAPL distribution, mobility, longevity and gaseous efflux are not material to the management of identified risks. Similarly, MNA is not required for NSZD where potential risks to groundwater and groundwater-dependent receptors are absent.

2. NSZD Decision-making Framework

2.1 Approach

The approach for assessing and implementing NSZD as a remediation and long-term management strategy for LNAPL is a three-stage process involving structured decision-making and iterative data collection and analysis, undertaken as part of broader options appraisal, remediation and verification. The three stages are summarised in Figure 2.1 and this chapter, with supporting information provided in Appendix 3.

1. **Screening** – the purpose of screening is to understand whether a LNAPL contaminated site is likely to be conducive to evaluating and monitoring NSZD, based on technical, practical, legal and economic constraints (e.g. LCRM Stage 2 Step 1 remediation feasibility study [Environment Agency, 2023]). The process is designed to be completed using the CSM from detailed investigation and risk assessment of LNAPL, groundwater, vapour and soil gas (e.g. LCRM Stage 1 [Environment Agency, 2023]);
2. **Demonstration** – this stage is used to advance the CSM to establish whether NSZD is occurring at significant rates and capable of achieving remediation objectives, and to determine which monitoring methods allow NSZD processes, and risks to receptors, to be assessed throughout the programme with an adequate degree of confidence. Demonstration will require NSZD-specific data collection and the development of a refined, process-based CSM describing NSZD processes;
3. **Implementation** – performance monitoring is required to verify that NSZD is occurring as expected and that receptors are protected throughout the risk-management programme. Monitoring can cease once the remediation objectives have been achieved. Validation of the programme will be supported by a CSM demonstrating LNAPL mass depletion and reduction of aqueous and gaseous fluxes that meet remediation criteria.

Implementing a NSZD monitoring strategy represents a potentially long-term commitment to LNAPL risk management in the order of years to decades. Engagement between practitioners and liability owners with the regulator is required during all stages of the process to confirm the suitability of NSZD to all stakeholders, whose requirements may evolve during the remediation programme.

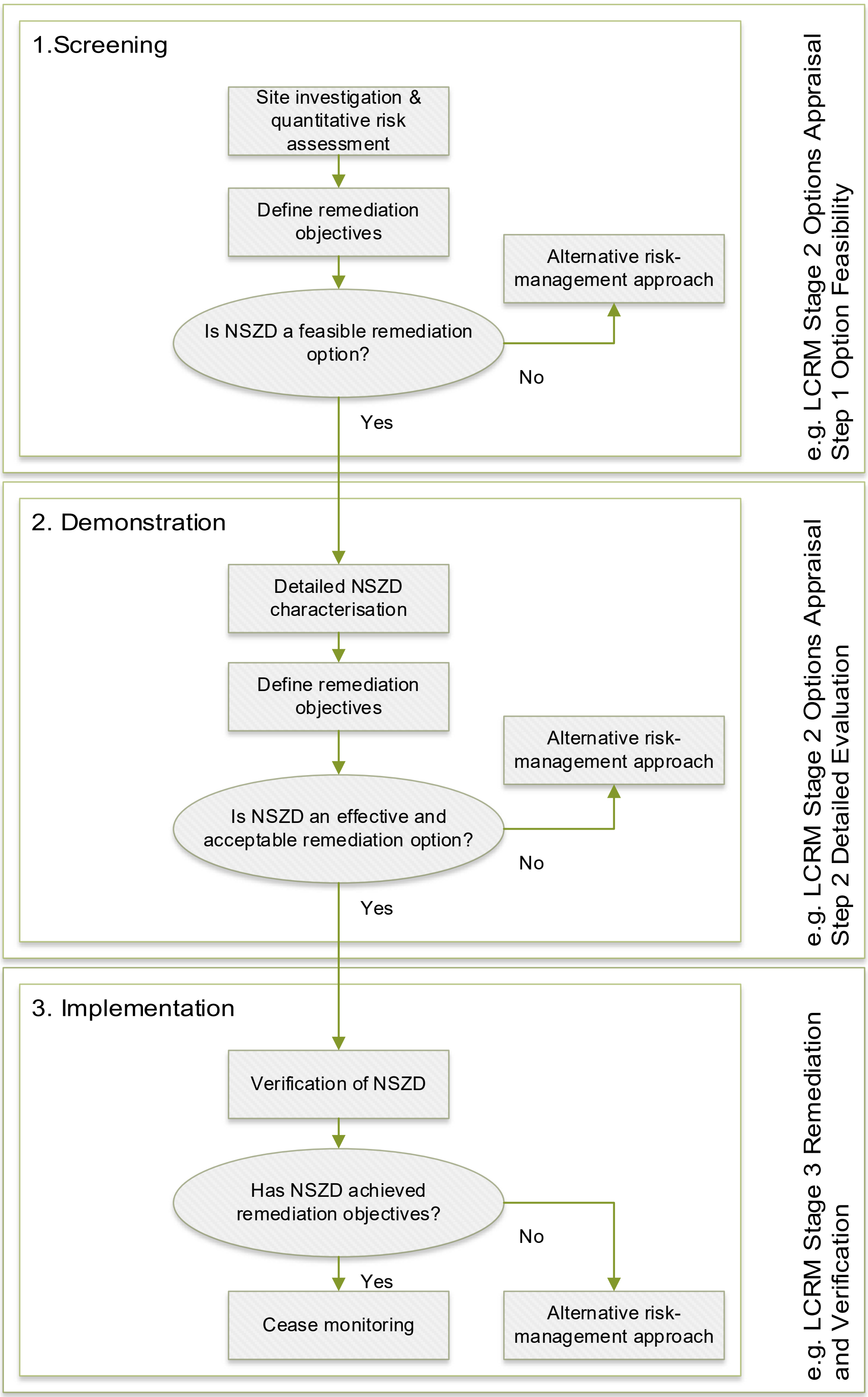


Figure 2.1: Overall procedure for assessment and implementation of NSZD.

2.2 Screening

The first stage in assessing NSZD as a potential risk-management option is to consider whether LNAPL and NSZD processes pose risks to receptors, then assess whether NSZD is likely to be feasible as a remediation solution. The screening procedure is illustrated in Figure 2.2 and relies upon a defensible CSM assessing potential contaminant linkages concerning LNAPL, groundwater, vapour and soil gas to evaluate constraints on the feasibility of monitoring NSZD for risk-management purposes.

To identify potentially suitable sites for NSZD-based risk management, the screening procedure should consider:

- Technical constraints – will receptors remain protected from LNAPL and NSZD processes generating vapours, soil gas and groundwater impacts for the duration of the risk-management programme? Can NSZD processes be characterised and monitored reliably for *in situ* conditions?
- Practicability – is there adequate time and access to areas of the site to assess the performance of NSZD, including long-term access to monitoring locations should a NSZD-based strategy be implemented? Can alternative NSZD monitoring technologies be used to overcome access constraints, while meeting data quality objectives for measuring NSZD processes?
- Economic viability – is NSZD likely to be efficient, in terms of cost, time and effort over the lifetime of the risk-management programme, compared to other feasible remediation options (CL:AIRE, 2021)?
- Sustainability – is NSZD likely to be more sustainable than other feasible remediation options, when assessed against the sustainability criteria described by SuRF-UK (CL:AIRE, 2010; CL:AIRE, 2021)? Are environmental and social impacts of NSZD and long-term monitoring activities small compared to shorter-term, intensive remediation?
- Regulatory constraints – is NSZD compliant with relevant legislation and guidance for remediation of LNAPL and management of risks associated with land contamination?

Monitoring NSZD is a long-term strategy spanning years to decades, for which holistic guidance on land stewardship and sustainable remediation provided by NICOLE and SuRF-UK provide several factors for consideration including:

- Managing and monitoring land contamination to ensure land industrial areas can be effectively and efficiently used, improved and/or returned to another long-term use. Unused or underused industrial land can be used for example for societal benefits, such as storing water, storing energy, or production of biomass, or contributing to biodiversity goals. This also entails a continued effort to prevent new contamination (NICOLE, 2018).
- The ethics and intergenerational equity of using long-term risk-management strategies such as NSZD to address environmental liabilities that could potentially be addressed sooner (SuRF-UK Indicator SOC 2 ‘Ethics and equity’).
- The ability of long-term strategies such as monitoring NSZD to continue to be effective risk-management options, where changes in land use, ownership and/or due to climate change are plausible future scenarios during completion of the

programme (SuRF-UK Indicator ECON 5 ‘Lifespan and flexibility’). NSZD-based risk management may be vulnerable to effects of climate change and resiliency is a consideration for feasibility evaluation at candidate NSZD sites (CL:AIRE, 2022).

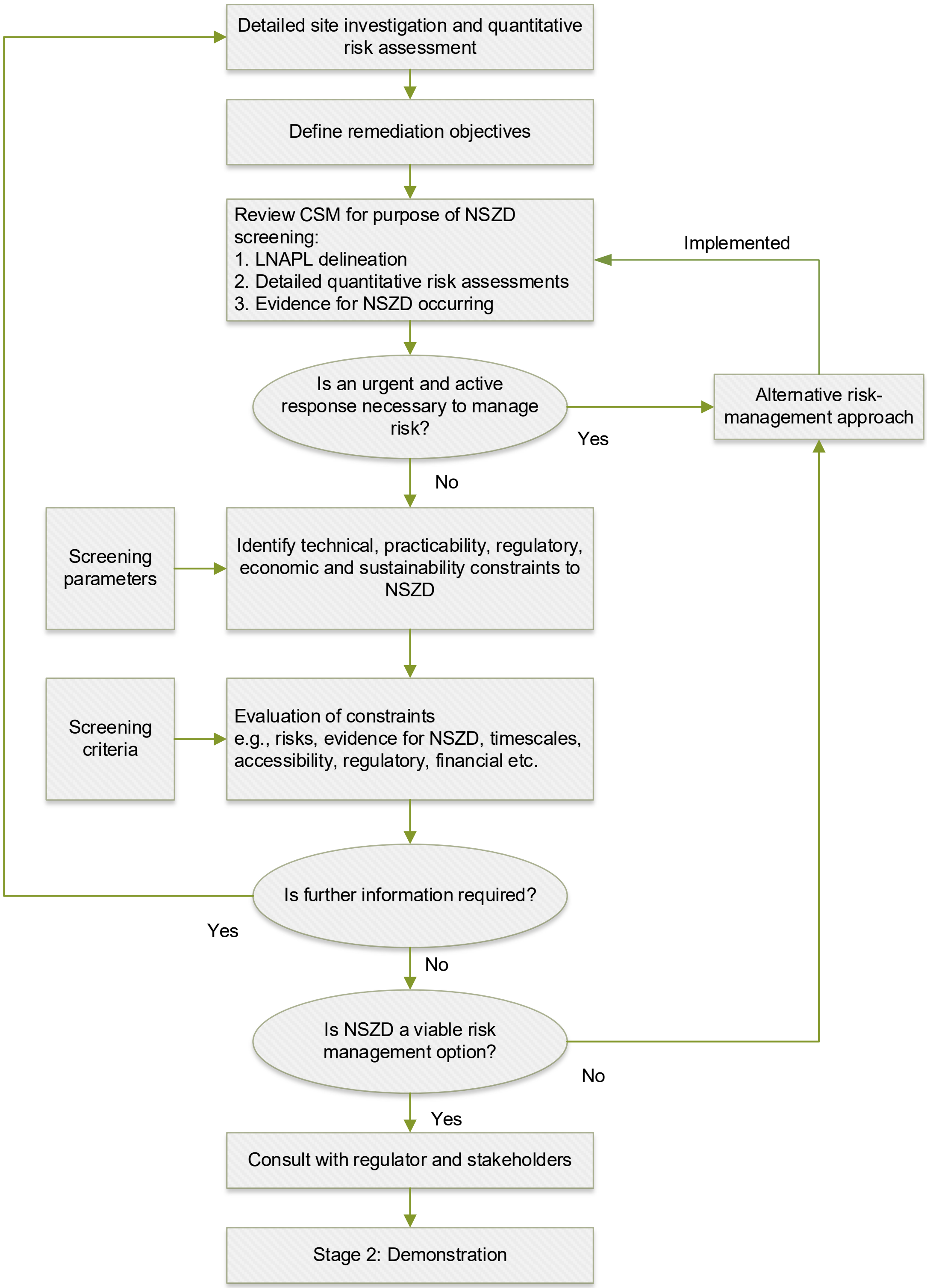


Figure 2.2: Stage 1 NSZD screening.

Evaluation of the constraints on NSZD presented in Table 2.1 is recommended as the starting point for appraising whether NSZD will likely be protective of receptors for the duration of the risk-management programme. If one or more of the conditions listed is characteristic of the LNAPL under consideration, an alternative risk-management approach is likely to be required to address relevant contaminant linkages.

Table 2.1: Risk-based constraints precluding NSZD as a feasible stand-alone option.

Constraint	Probably infeasible condition
Primary source of LNAPL impact to subsurface	LNAPL release continuing
Vapour intrusion and/or soil gas risk from LNAPL	Indoor air concentrations exceed risk-based criteria in LNAPL impacted areas, or LNAPL separation distance below occupied space or building structure <1 m (USEPA, 2015; Card *et al*., 2019; Energy Institute, 2023)
Groundwater and groundwater-dependent receptor risk from LNAPL	Receptors at imminent risk of impact from migrating LNAPL and/or dissolved-phase plume
Groundwater Source Protection Zones (SPZ)	LNAPL lies within SPZ I or SPZ II

Table 2.2 presents NSZD screening criteria covering technical, practical, economic, regulatory and sustainability constraints that provide means to complete an initial assessment of the feasibility of NSZD for a given LNAPL source.

Table 2.2: Constraints on the feasibility of NSZD.

Constraint	Probably feasible	Possibly feasible	Potentially infeasible
LNAPL delineation	Fully delineated	Partially delineated	Poorly delineated
LNAPL migration potential	Immobile, not migrating	Mobile, not migrating	Mobile and migrating
Subsurface heterogeneity (effect on ability to reliably monitor NSZD expressions)	“Homogeneous”	Moderate heterogeneity (e.g. layered porous media)	Complex heterogeneity (e.g. permeable stringers, fractured bedrock, services including sewers, conduits/ tunnels including mine shafts/adits)
Naturally elevated soil gas concentrations	Low soil organic matter Non-calcareous soil/rock Deep fossil/petrogenic source absent		High soil organic matter Calcareous soil/rock present Deep fossil/petrogenic source present

Constraint	Probably feasible	Possibly feasible	Potentially infeasible
Unsaturated zone thickness (z)	1 m < z < 30 m (after API, 2017) Stable water table, small fluctuations	1 m < z < 30 m Water table fluctuations periodically submerge LNAPL	1 m > z > 30 m, i.e. thin or thick unsaturated zone
Ongoing active remediation	No active remediation		Interference from nearby remediation in unsaturated zone (e.g. soil vapour extraction)
Evidence for NSZD occurrence	Elevated gaseous flux or soil temperature in LNAPL impacted areas Plume of elevated dissolved-phase concentrations, electron acceptors depleted		Gaseous flux, soil temperature and/or dissolved-phase plume indistinguishable from background
Timebound remediation objectives	Remediation objectives achievable with NSZD alone		Remediation objectives are not achievable with NSZD
Level of confidence in CSM	High – comprehensive dataset spatially and temporally informing high level understanding of NSZD processes		Low – limited dataset spatially and temporally, inadequate information for LNAPL or NSZD
Acceptability to the regulator	No policy objection		Policy objections in principle
NSZD monitoring locations	Access confirmed for on-site and off-site monitoring in the long term	Access possible for on-site and off-site monitoring in the long term	Limited / no access
Financial provisions	Long-term, legally-binding budget secured	Long-term, non-legally binding budget secured	No long-term budget in place
Objectives of landowner	Long-term interest in site (>10 years)	Medium-term interest (>3 to 10 years)	Short-term ownership / developer (<3 years)

Constraint	Probably feasible	Possibly feasible	Potentially infeasible
Location of liability	LNAPL within land ownership boundary	LNAPL on boundary with third party	Outside land ownership boundary (in third party land)
Sustainability	More sustainable than alternative options		Less sustainable than alternative options

Where evaluation of most of the constraints indicates a NSZD-based strategy is probably or possibly feasible, NSZD could be considered as part of a broader remediation options appraisal to identify the preferred risk-management approach.

Where current site circumstances indicate NSZD is potentially infeasible, consideration should be given to which constraints are material to this outcome and could be overcome with additional characterisation and/or design. For example:

- Low confidence in the CSM, poor LNAPL delineation etc. may potentially be resolved through identifying and addressing prioritised data gaps;
- Complex heterogeneity and/or naturally elevated soil gas concentrations do not preclude NSZD but will influence monitoring technology selection and how NSZD rates are estimated. Overcoming challenging ground conditions is an active research area for NSZD.

2.3 Demonstration

Stage 2 requires additional, detailed site characterisation to develop the CSM to:

- Demonstrate advanced, site-specific understanding of the nature and extent of predominant NSZD processes;
- Determine which NSZD monitoring methods are appropriate to the site and observed biogeochemical processes and can be appropriately applied to provide reliable estimates for LNAPL depletion rates;
- Support comparison of NSZD with other remediation alternatives (LCRM Options Appraisal);
- Confirm that potential risks to receptors are being effectively managed and, if receptors cannot be protected, what measures will be required to address this issue.

The procedure to demonstrate viability of NSZD is illustrated in Figure 2.3.

Environmental data that meet relevant data quality objectives are required to support reliable site conceptualisation and NSZD rate estimation. Appendix 2 and Appendix 3 present supporting information for the investigation of LNAPL sites and NSZD processes, including considerations, strengths and weaknesses of commonly used NSZD monitoring technologies.

Initial investigations of NSZD should characterise the LNAPL and terminal electron accepting processes (TEAPs) acting upon the LNAPL and gaseous and aqueous NSZD by-products. The scope of initial investigations may include:

- Surveys of soil gas, hydrocarbon vapours and/or temperature, indicating the nature of gaseous expressions of NSZD within the unsaturated zone (e.g. Ririe and Sweeney, 2022);
- Characterisation of source mass discharge in groundwater, indicated by the combined fluxes and spatial integration of dissolved organic carbon, dissolved inorganic carbon and TEAP by-products;
- Analyses of LNAPL composition and physical properties.

Further to advancing process understanding and initial site-specific estimates of NSZD rates, initial investigations should indicate which monitoring technologies might be expected to provide reliable measurements of NSZD processes and rate estimates for each LNAPL source. Ideally, at least two methods should be identified to monitor expressions of NSZD and provide independent estimates of total LNAPL depletion rates (e.g. Wozney *et al*., 2022). This provides a level of confidence in NSZD similar to the multiple lines of evidence approach used to demonstrate viability of MNA (CL:AIRE, 2024). Process understanding and NSZD rates can be compared with anticipated performance of remediation alternatives as part of remediation options appraisal.

If initial investigations affirm that NSZD is occurring at significant rates and can be reliably monitored, spatially- and temporally-integrated data collection will be required to advance understanding of process variability and uncertainty in NSZD estimates. The typical frequency and duration of monitoring depends on the objectives and scope of the investigations. Where gaseous and/or aqueous expressions of NSZD are being investigated, multiple monitoring events spanning approximately 1 year will be required to estimate the annual NSZD rate (API, 2017; crcCARE, 2018).

It is recommended that practitioners engage with the regulator and other stakeholders to agree the scope of data collection and analysis that demonstrate the viability and application of NSZD in its defined role within a risk-management strategy. Regular reporting demonstrating NSZD performance against remediation objectives and describing changes in the CSM may be required, the scope and frequency of which should be agreed with the regulator.

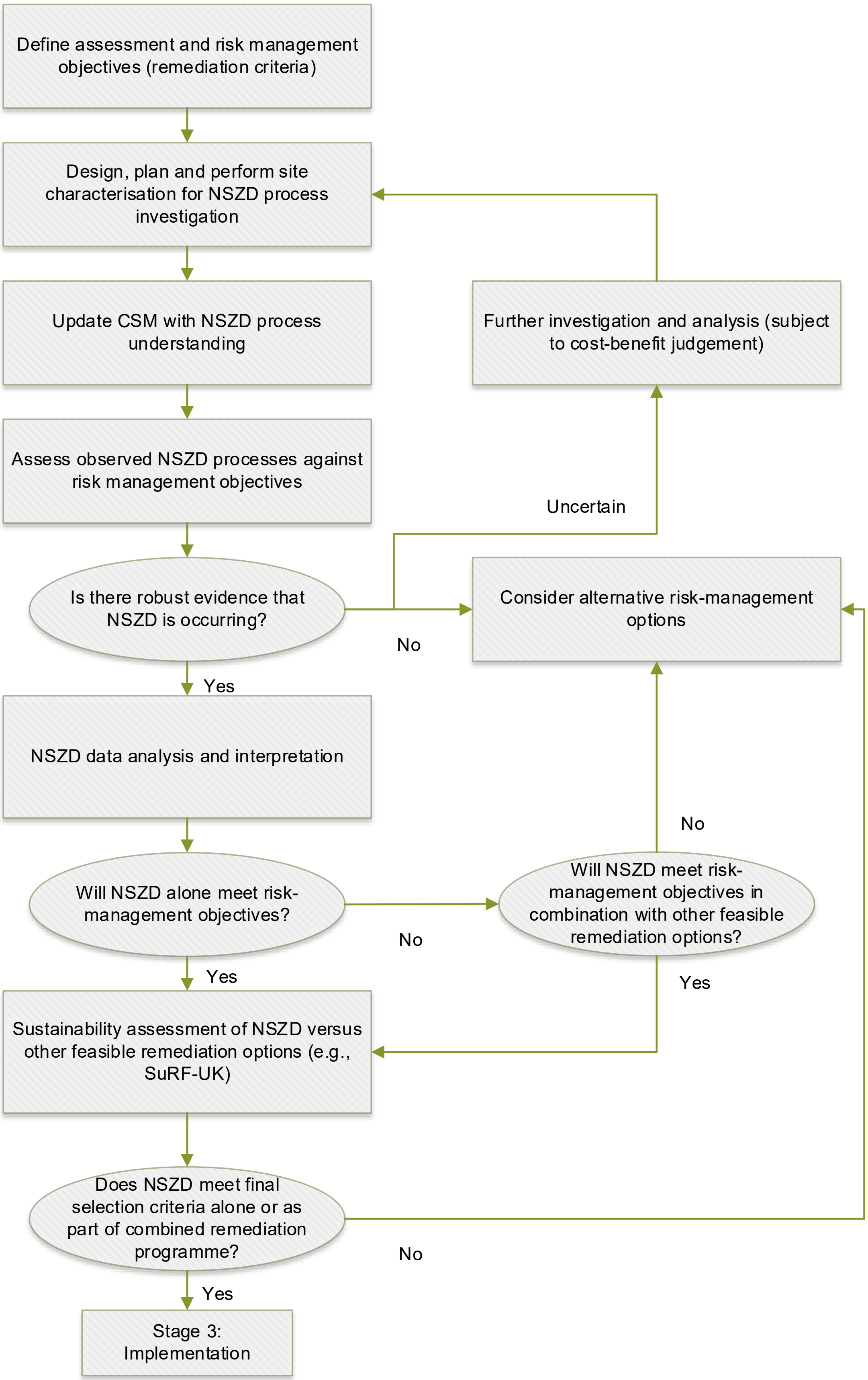


Figure 2.3: Demonstration of NSZD.

2.4 Implementation

If the regulator and stakeholders support the implementation of a NSZD-based strategy to manage LNAPL impacts to the subsurface, a performance monitoring plan should be developed that aims to:

- Continue demonstration of the occurrence of NSZD at rates that will achieve remediation objectives;
- Confirm that receptors remain protected for the duration of the programme; and
- Support decision-making to either close the monitoring programme, continue monitoring or trigger contingency measures if the risk profile and/or NSZD rates adversely change.

The procedure for implementation of NSZD is illustrated in Figure 2.4. The strategy objectives should be established at the outset, with remediation criteria defined to support assessment of the programme endpoint. Since the implementation of NSZD is contingent on prior demonstration that the risks to receptors are effectively managed, the primary performance objectives (and criteria) for NSZD may not be risk-based (e.g. reduction in soil gas, vapour and/or groundwater concentrations to meet risk-based target values) as is typically the case for active remediation programmes. Rather, performance objectives and criteria could concern other goals and key performance indicators (KPI) for regulators and other stakeholders. NSZD monitoring data may not therefore be directly comparable to remediation criteria. Establishing performance metrics, based on the types of data collected, is recommended to assist with demonstrating that NSZD remains effective.

Monitoring NSZD represents a long-term commitment to LNAPL risk management. Consideration of plausible future changes to site conditions, such as redevelopment and the effects of climate change, may influence remediation objectives and performance assessment.

The scope of monitoring should reflect the CSM, including measurement of process-relevant parameters by suitable techniques at representative monitoring locations, that support reliable estimation of NSZD rates and risks to receptors. The duration of monitoring, typically of the order of years to decades, will be proportional to the extent of LNAPL and associated risks should the effectiveness of NSZD change. Depending on the variability of NSZD, monitoring could be less frequent than required for Stage 2 and reduce with time as long-term trends are established. A contingency plan should be developed that identifies what actions will be taken if NSZD fails or circumstances change. Practitioners should liaise with the regulator and stakeholders to agree the monitoring strategy in advance of implementation.

Assessors will need to review NSZD monitoring data as it is collected to confirm risks are appropriately managed and track performance against relevant metrics. The long-term source depletion trend may take several years to become apparent. It is suggested that an evaluation period is established to assess NSZD performance against remediation criteria and objectives. NSZD performance should be reported to stakeholders, including the regulator, to confirm that the programme continues to meet expectations and needs, which may change over time. As a minimum, the scope and frequency of reporting should be agreed with the regulator. Once remediation objectives have been achieved, the monitoring programme can close with agreement of the regulator and other stakeholders. Monitoring should continue for another evaluation period if NSZD continues to be effective and the programme is expected to reach its endpoint within the agreed timeframe. Practitioners may consider reviewing the monitoring scope at the end of each evaluation period, which may indicate opportunities to rationalise the programme with agreement of the regulator and stakeholders.

If NSZD is successful, a closure report will verify the effectiveness of the strategy (Environment Agency, 2023). Verification relies upon a lines of evidence approach, informed by the CSM and performance monitoring data to demonstrate that further monitoring or remediation is unnecessary.

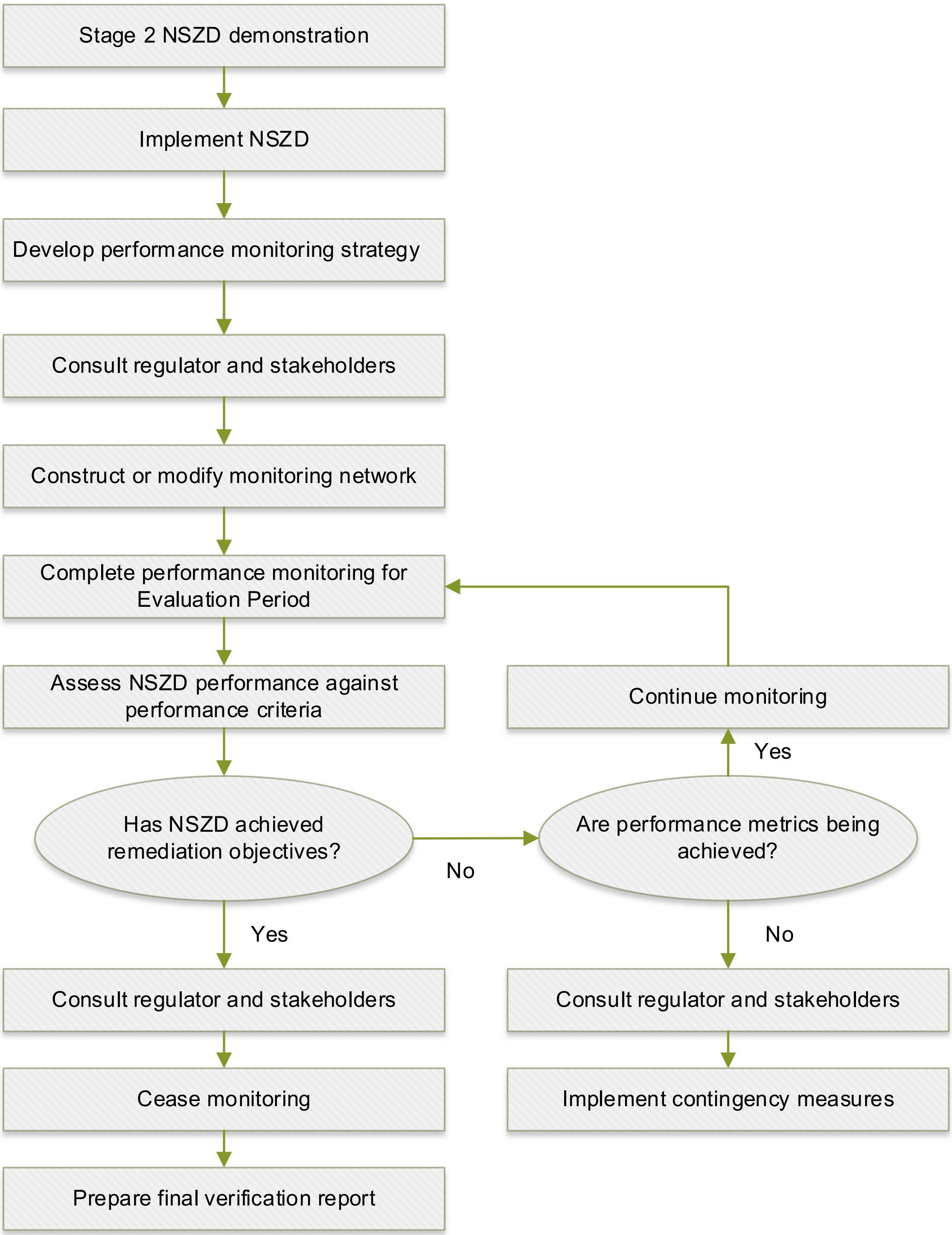


Figure 2.4: Implementation of NSZD-based monitoring strategy.

3. Future of NSZD

NSZD extends the application of attenuation-based risk-management strategies of hydrocarbon contamination from the groundwater plume (MNA) to LNAPL source zones. Investigation and monitoring NSZD has been performed at relatively few sites in the UK and Europe, perhaps due to challenging site conditions. However, an increasing number of case studies are emerging that indicate NSZD is still significant (e.g. Concawe, 2020; Smith *et al.*, 2021; Statham *et al.*, 2023; CL:AIRE, 2023a; CL:AIRE, 2023b). These studies highlight the effects of complex ground conditions on the NSZD measurement techniques, which can influence NSZD rate estimates. These complexities are not unique to the UK or Europe, and an increased understanding of NSZD performance will more ably demonstrate the potential for its application to sustainable risk-management strategies at such sites.

The key challenges to NSZD relevant to the UK are subjects of ongoing research. This aims to further understand the effects of site conditions on NSZD but also to advance experience and capabilities to characterise NSZD under challenging conditions, predict long-term behaviour and effective management of risks to receptors throughout the remediation site lifecycle.

NSZD is a rapidly evolving field. The key areas of focus for research and development include:

- NSZD screening methods that may efficiently assess prevailing conditions and processes, and indicative rates (e.g. Amos *et al.*, 2005; Ririe and Sweeney, 2022);
- Evolving monitoring technologies, specifically how and where these are used, to manage uncertainties in NSZD rate estimation more effectively (e.g. Karimi Askarani and Sale, 2020; Cozens *et al.*, 2019; Blotevogel *et al.*, 2021, Karimi Askarani *et al.*, 2021, Verginelli and Baciocchi, 2021);
- Understanding the long-term behaviour of NSZD, addressing challenges of short-term variability, to support development of predictive capabilities (e.g. Sookhak Lari *et al.*, 2022; Davis *et al.*, 2022);
- Developing supporting technologies to enhance the rate of NSZD for sites where sustainable, attenuation-based remediation is desirable but conditions are sub-optimal to achieve remediation objectives (e.g. Siciliano *et al.*, 2016; Murphy *et al.*, 2022).

Given the ongoing evolution of NSZD, the reader may wish to research additional resources as these become available. However, consideration of the procedural guidance contained in this document would demonstrate the reasonable practice and care expected of professional practitioners.

Appendix 1: NSZD Processes

A1.1 Overview

Understanding the key processes that control NSZD is critical to the selection, design and implementation of NSZD as a risk-management strategy for LNAPL impacted sites. Following release into the environment, petroleum hydrocarbon constituents in LNAPL are subject to multiple processes and reactions that control LNAPL distribution, partitioning and degradation (Rivett *et al*., 2011; Sookhak Lari *et al*., 2019), that can ultimately affect the nature and rate of NSZD (Figure A1.1).

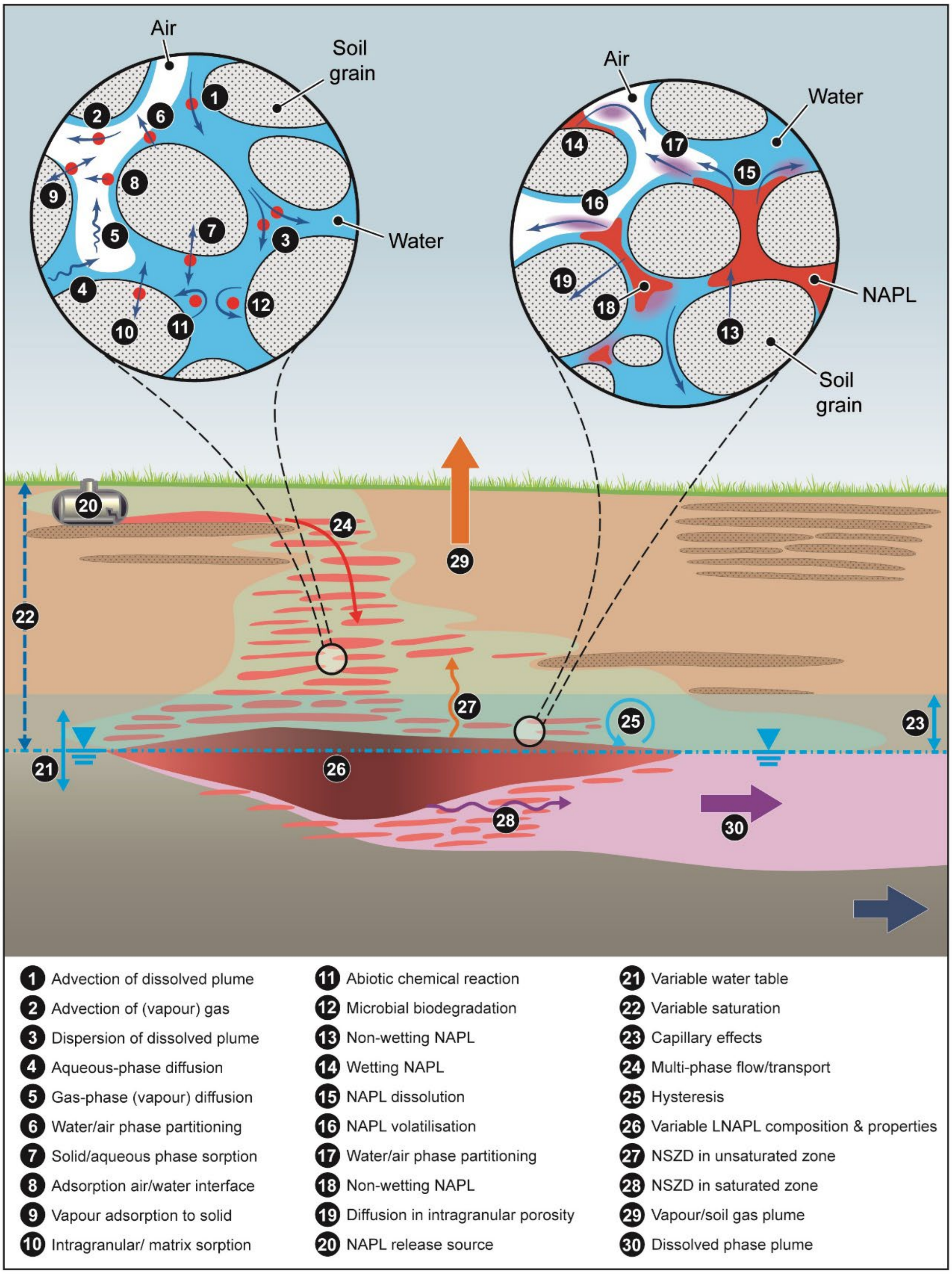


Figure A1.1: Major subsurface processes affecting NSZD (after Rivett *et al*., 2011; after CL:AIRE, 2019; after Sookhak Lari *et al*., 2019). Reproduced from the Journal of Contaminant Hydrology, Rivett *et al*., Copyright (2011), with permission from Elsevier.

It is convenient to consider the overall expression of NSZD in terms of contributions to source depletion indicated by (CL:AIRE, 2019):

- Aqueous expression – dissolution and biodegradation of soluble LNAPL components in groundwater or infiltrating water contacting LNAPL; and
- Gaseous expression – LNAPL biodegradation causing gaseous efflux and vaporisation of volatile LNAPL components.

The key processes influencing aqueous and gaseous expression of NSZD are introduced below.

A1.2 Aqueous Expressions of NSZD

The key processes contributing to aqueous expression of NSZD include (ITRC, 2009; API, 2017; crcCARE, 2018; ITRC, 2018; CL:AIRE, 2019):

- Dissolution of soluble LNAPL and sorbed-phase constituents generating a plume within the saturated zone;
- Biodegradation of the dissolved-phase plume, which occurs via terminal electron accepting processes (TEAPs – aerobic respiration, nitrate reduction, iron reduction, manganese reduction, sulfate reduction and methanogenesis) forming soluble by-products of ferrous iron, manganese, carbon dioxide and methane.

A conceptual model for these processes is illustrated in Figure A1.2.

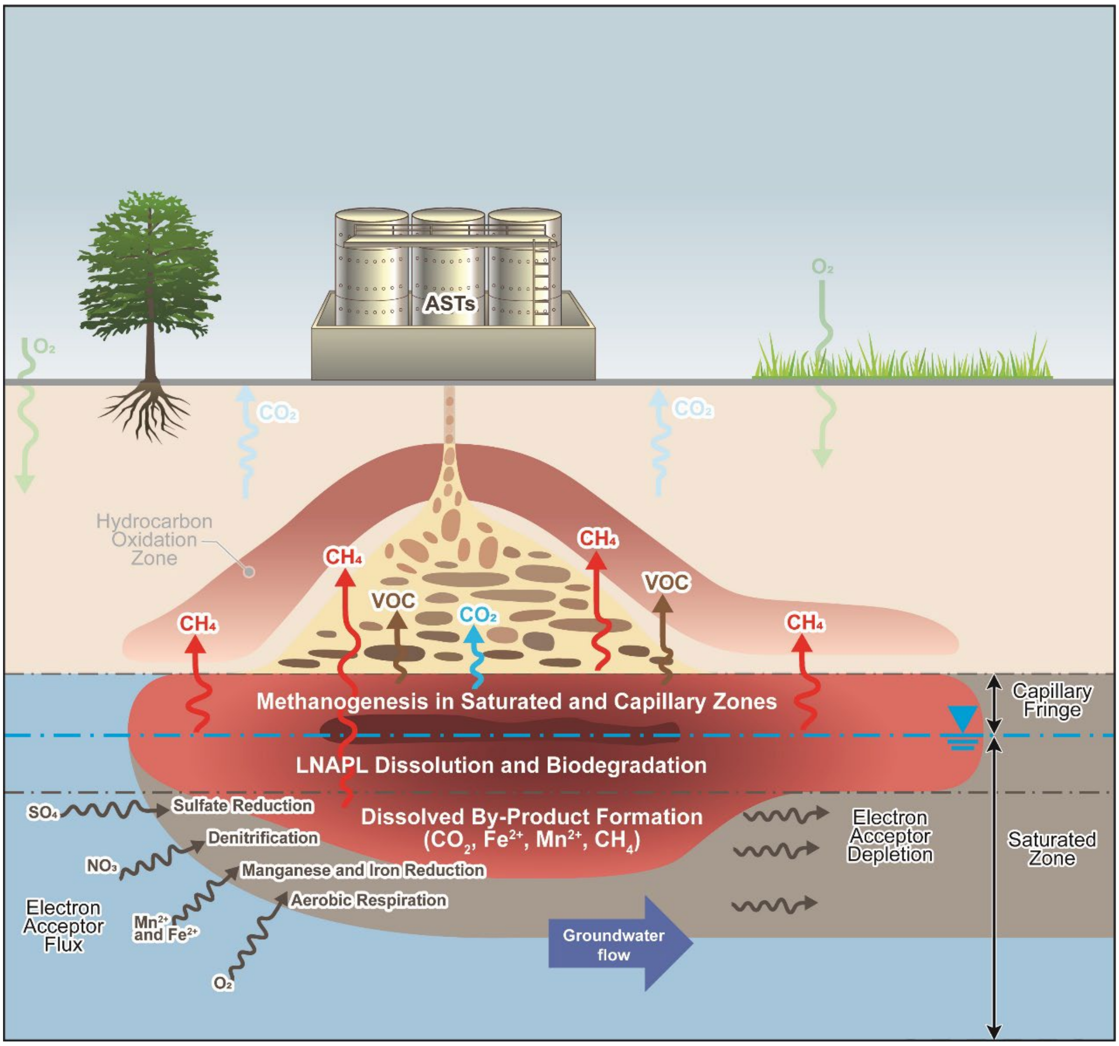


Figure A1.2: Conceptualisation of processes contributing to aqueous expression of NSZD (API, 2017). Reproduced courtesy of the American Petroleum Institute.

Processes contributing to the aqueous expression of NSZD are well documented in scientific literature (e.g. National Research Council, 2000; ITRC, 2009). LNAPL constituents dissolve into flowing groundwater according to Raoult's Law. The effective solubility of a LNAPL constituent represents the maximum equilibrium concentration in groundwater resulting from dissolution of a multicomponent NAPL. Raoult's Law defines the effective solubility (S^e_i) as the product of the pure phase solubility (S_i) of a constituent i and its mole fraction (X_i) (ITRC, 2009):

$$S^e_i = X_i \cdot S_i$$

As soluble LNAPL constituents are depleted through dissolution, their mole fractions and effective solubilities decrease.

Dissolved-phase hydrocarbons are available for biodegradation, that can occur via several TEAPs. The effects of TEAPs are often apparent in comparisons of groundwater monitoring data collected upgradient and immediately downgradient of the LNAPL; soluble electron acceptors (dissolved oxygen, nitrate and sulfate) become depleted and by-products of iron (II), manganese (II), carbon dioxide and methane generated. The assumed sequence of TEAPs is predicated upon the enthalpy of each reaction, where oxygen is used first, followed by nitrate, iron, manganese, sulfate and finally carbon. However, syntrophic behaviour and methane generation (methanogenesis) can occur in the presence of other electron acceptors (Gieg *et al.*, 2014). Depletion of soluble electron acceptors is observed in the fringes of dissolved-phase hydrocarbon plumes (Wilson *et al.*, 2004), whereas electron acceptors derived from the aquifer material itself (iron minerals, manganic minerals, carbonates etc.) can occur within the plume fringes and core.

Within the LNAPL-impacted saturated zone, biodegradation generally proceeds to a methanogenic state except where biodegradation is not electron acceptor limited. Methanogenesis of petroleum hydrocarbons produces both carbon dioxide and methane. Methane is considerably less soluble than carbon dioxide. Methane plumes within the unsaturated zone overlying hydrocarbon impacts in the saturated zone are common, due to volatilisation, outgassing and ebullition (Section A1.3). In systems where other TEAPs are the prevailing biodegradation mechanism, an abundance of carbon dioxide or dissolved inorganic carbon species may be present.

A1.3 Gaseous Expressions of NSZD

Gaseous efflux is now recognised as the predominant indicator for NSZD of petroleum hydrocarbons. The key processes contributing to gaseous expression of NSZD are (API, 2017; crcCARE, 2018, ITRC, 2018, CL:AIRE, 2019):

- Anaerobic biodegradation of LNAPL and dissolved-phase hydrocarbons within the saturated zone generating methane and/or carbon dioxide;
- Aerobic biodegradation of LNAPL in the unsaturated zone generating carbon dioxide and heat;
- Vaporisation of LNAPL, and volatilisation of sorbed and dissolved-phase hydrocarbon constituents into the unsaturated zone generating a vapour plume;
- Upward transport of carbon dioxide, methane, hydrocarbon vapours and heat through the unsaturated zone;
- Aerobic biodegradation of methane and hydrocarbon vapours generating carbon dioxide and heat.

A conceptual model for these processes is illustrated in Figure A1.3.

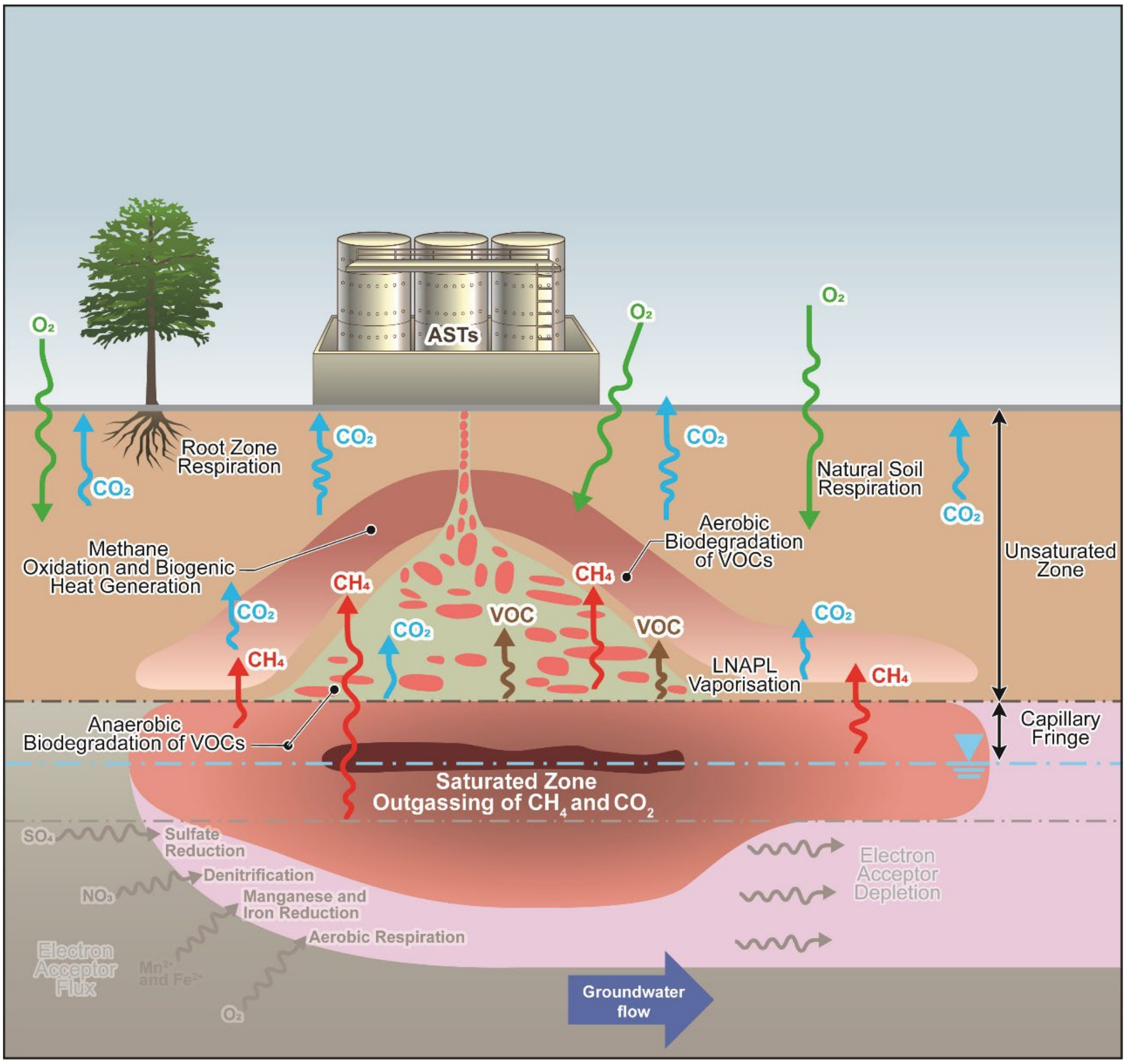


Figure A1.3: Conceptualisation of processes contributing to gaseous expression of NSZD (API, 2017). Reproduced courtesy of the American Petroleum Institute.

Biodegradation processes are the principal contributor to gaseous expression of NSZD:

- Methanogenesis (anaerobic biodegradation) is the dominant attenuation process observed in many LNAPL systems. Notable studies include Lundegard and Johnson (2006) and Ng *et al.* (2015). Methanogenesis is part of a complicated, multiple step syntrophic process (Garg *et al.*, 2017), where fermenters biodegrade hydrocarbons forming dissolved hydrogen and/or acetate and methanogens utilise the products of fermentation to form methane (Gieg *et al.*, 2014). While thermodynamic theory suggests that all electron acceptors should be depleted before methanogenesis can take place, observations and microbial process research indicate some syntrophic behaviour, resulting in methanogenesis in the presence of other electron acceptors (Gieg *et al.*, 2014).
- Direct outgassing is the term used to describe production and release of methane and carbon dioxide from direct contact biodegradation of oil in the saturated zone and unsaturated zone. Direct outgassing is produced from oil constituents that biodegrade within the pore space adjacent to entrapped oil (Ng *et al.*, 2015).

- Ebullition is the transport of gas bubbles generated in the saturated zone into the unsaturated zone. Ebullition is expected to be a significant process at sites where LNAPL is present in the saturated zone, due to the predominance of methanogenesis and the limited solubility of methane in groundwater.
- Aerobic biodegradation of hydrocarbons is a significant unsaturated zone process where atmospheric oxygen diffuses into the subsurface, producing carbon dioxide and heat:
    - On the basis that systems are commonly electron acceptor limited, an anaerobic core typically forms around the hydrocarbon impact mirroring the distribution of TEAPs in the saturated zone. Garg *et al*. (2017) therefore suggests aerobic biodegradation may be important for new LNAPL releases, before electron acceptors have depleted. McHugh *et al*. (2020) presents an exception, where aerobic biodegradation of LNAPL was demonstrated in a deep basalt aquifer (>100 m) where oxygen was present throughout the unsaturated zone.
    - Aerobic biodegradation of methane and hydrocarbon vapours can occur in the unsaturated zone above LNAPL (e.g. Davis *et al*., 2009). Amos *et al*. (2011) demonstrated that oxygen depletion in the unsaturated zone was predominantly due to methane oxidation, rather than biodegradation of hydrocarbon vapours.

Vaporisation of LNAPL constituents occurs according to Raoult's Law. LNAPL constituents vaporise into air-filled pore space within the unsaturated zone according Raoult's Law, like the process described above, where the effective vapour pressure (P_{eff}^{i}) is defined as the product of the pure phase vapour pressure (P_i) of a constituent i and its mole fraction (X_i):

$$P_{eff}^{i} = X_i \cdot P_i$$

As volatile LNAPL constituents are depleted through vaporisation, their mole fractions and effective vapour pressures decrease.

Dissolved-phase gases and volatile hydrocarbons volatilise from the capillary fringe according to Henry's Law, contributing to the overall vapour pressure above the LNAPL. The dimensionless form of Henry's Law Constant (H') is the ratio of dissolved-phase (C_s) and vapour phase (C_v) concentrations:

$$H' = C_v / C_s$$

Soil gas and hydrocarbon vapour transport in the unsaturated zone is predominantly by diffusion (ITRC, 2007; ITRC, 2018; CL:AIRE, 2018; Card *et al*., 2019). Diffusion occurs between zones of high concentration to low concentration. The diffusive flux (J) is controlled by the effective diffusion coefficient (D_v^{eff}), that expresses the ability for a compound to diffuse through porous media:

$$J = D_v^{eff} \cdot (dC/dz)$$

In addition to upward diffusion of methane, carbon dioxide and hydrocarbon vapours, downward diffusion of oxygen from the surface is a contributory process to the formation of a methane and hydrocarbon oxidation zone above LNAPL.

Analogous to diffusion, thermal conduction is the predominant transport process for biogenic heat generated from aerobic biodegradation of LNAPL, methane and hydrocarbon vapours in the unsaturated zone. Heat is transported from zones of high temperature to lower temperatures (dT/dz). The thermal flux (q_H) is constrained by the thermal conductivity of the porous media (K_H) and can be estimated by Fourier's First Law:

$$q_H = K_H \cdot (dT/dz)$$

Advection is the movement of bulk soil gas from areas of higher pressure to areas of lower pressure due to the presence of a pressure gradient. For NSZD, advection may be more important when the rate of soil gas generation from methanogenic biodegradation is high (ITRC, 2018) or in close proximity to buildings (typically over tens of centimetres). The relative contribution of advection to overall soil gas transport appears to be small, even at sites where high rates of methanogenesis have been observed (e.g. approximately 15% at the Bemidji research site, Minnesota [Molins *et al*., 2010; Sihota and Mayer, 2012]).

A1.4 Controls on NSZD Expression

Following release to ground, multi-phase (NAPL, water and soil gas) transport and other processes control LNAPL distribution, saturation and propensity for NSZD (Figure A1.4).

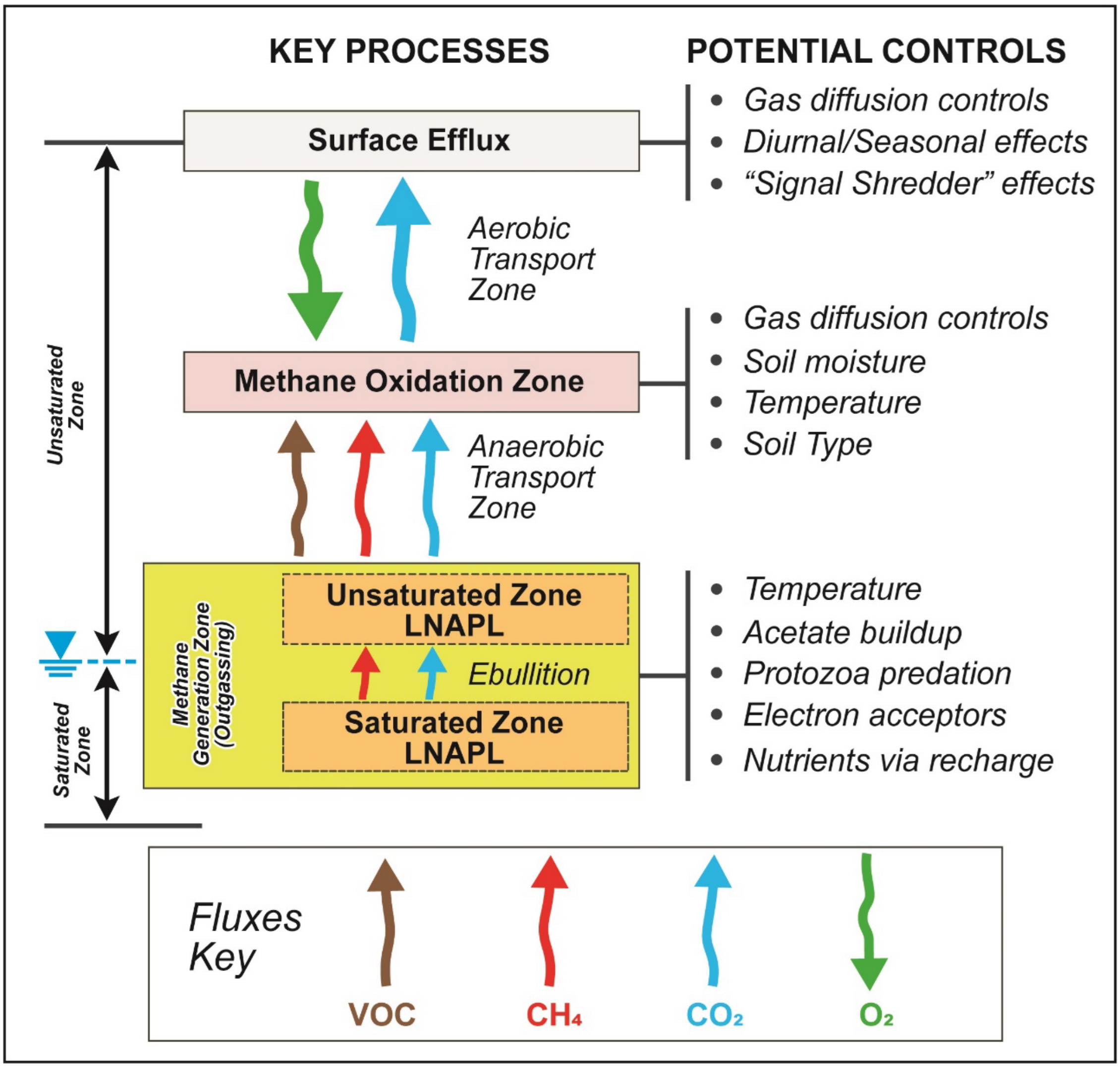


Figure A1.4. Controls on NSZD processes (Garg *et al*., 2017).

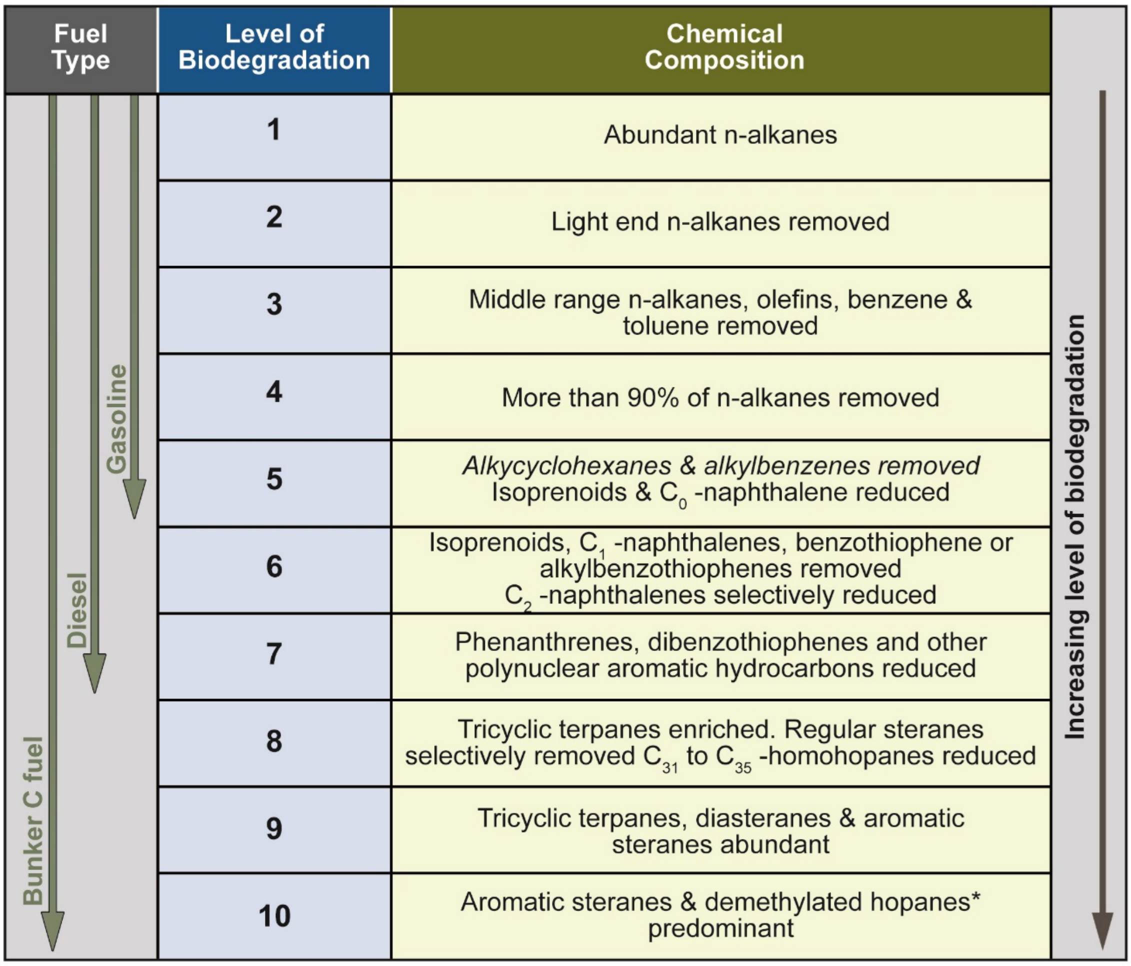
Factors that could ultimately influence the expression of NSZD are introduced below.

1. LNAPL source architecture – the characteristics of the LNAPL release and subsurface hydraulic properties influence source zone architecture, including the volumes and extent of residual and mobile LNAPL, as well as its composition (Sookhak Lari *et al*., 2019). The greater interphase contact area of residual compared to mobile NAPL may make the residual volume of LNAPL susceptible to higher rates of mass transfer to aqueous and vapour phases, depending on subsurface conditions. NAPL viscosity and density affect initial LNAPL distribution in the subsurface and can change over time due to NSZD processes, resulting in compositional changes and biogenic heat.

2. Groundwater dynamics – water table elevation is significant in determining the initial distribution and subsequent redistribution of LNAPL saturation, and expression of NSZD. Water table fluctuations can smear LNAPL, increasing the volume of residual LNAPL, and increasing mass transfer from NAPL to aqueous and vapour phases. Van de Ven *et al*. (2021) observed immediate changes in surface efflux of carbon dioxide and methane up to 3- and 344-times higher than baseline conditions resulting from simulated lowering of that water table in a sand tank containing LNAPL.

Subsequently, carbon dioxide efflux settled at a quasi-steady state 1.4 to 1.6 times higher than the baseline. Raising the water table resulted in reduced rates of gaseous efflux, by 0.4 to 0.9 times of the baseline. The study demonstrates the effects of dynamic changes in water table that may confound field measurements of gaseous efflux and NSZD rate estimation, in particular where data collection is limited to a single event and the effects of short-term and long-term variability are not considered. Dynamic water table conditions could result from climate change and should therefore be considered for the interpretation of NSZD data (Section A3.3).

3. NAPL composition – hydrocarbon products are highly complex and variable mixtures (Potter and Simmons, 1998). Dissolution and vaporisation of individual constituents from hydrocarbon LNAPL will 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). Physical losses of the volatile and soluble constituents generally affect the lighter <C10 aromatic and aliphatic components in hydrocarbon LNAPL. Hydrocarbon LNAPL is also variably susceptible to biodegradation in the subsurface, depending on the component bioavailability, microbial population and availability of suitable electron acceptors. Biodegradation of petroleum hydrocarbons has been extensively studied with degradation pathways described for alkanes, alkenes, isoalkanes, cycloalkanes, polycyclic aromatic and heterocyclic compounds as well as benzene, toluene, ethylbenzene and xylenes (BTEX) (Salanitro, 2001). Biodegradation of LNAPLs can result in an apparent stepwise depletion of compounds in a specific order (Figure A1.5) based on their susceptibility to biodegradation (Kaplan *et al*., 1996). The bioavailability and composition of LNAPL constituents, along with the types of electron acceptors available for the microbial community to use, is therefore a factor impacting biodegradation and NSZD rates, which may vary with time.



Level of Biodegradation	Chemical Composition
1	Abundant n-alkanes
2	Light end n-alkanes removed
3	Middle range n-alkanes, olefins, benzene & toluene removed
4	More than 90% of n-alkanes removed
5	*Alkycyclohexanes & alkylbenzenes removed* Isoprenoids & C_0 -naphthalene reduced
6	Isoprenoids, C_1 -naphthalenes, benzothiophene or alkylbenzothiophenes removed C_2 -naphthalenes selectively reduced
7	Phenanthrenes, dibenzothiophenes and other polynuclear aromatic hydrocarbons reduced
8	Tricyclic terpanes enriched. Regular steranes selectively removed C_{31} to C_{35} -homohopanes reduced
9	Tricyclic terpanes, diasteranes & aromatic steranes abundant
10	Aromatic steranes & demethylated hopanes* predominant

* Present under certain conditions only.

Figure A1.5: Change in gasoline, diesel fuel and Bunker C composition during biodegradation (Kaplan *et al*., 1996). © 1996 John Wiley & Sons, Inc.

4. Availability of electron acceptors – hardstanding and/or low permeability layers in soil or bedrock overlying the LNAPL can limit the infiltration of electron acceptors and nutrients in recharge (saturated zone) or gaseous diffusion (unsaturated zone). In the unsaturated zone of these systems, aerobic biodegradation of methane and hydrocarbon vapours, generating carbon dioxide and heat, may therefore be limited (e.g. Cozens *et al*., 2019; Smith *et al*., 2021). Alternative electron acceptors may sustain NSZD where these are abundant and bioavailable (e.g. ferric iron or sulfate in soil or bedrock minerals, from diffuse agricultural pollution or leaking sewers etc.). Such conditions may be confounding when compared with typical conceptual models for NSZD, which may be oxygen-limited but still exhibit elevated concentrations of carbon dioxide. Oxygen is toxic to methanogens even at low concentrations (Garg *et al*., 2017). NSZD of methanogenesis-dominated systems may be effectively stopped by introduction of air to the subsurface due to change in land use, remediation etc.

5. Nutrients – microbial communities are reliant upon nutrients in recharge and soil or bedrock mineralogy, as well as electron acceptors, for biodegradation of hydrocarbons. Phosphate is a key nutrient, the bioavailability of which is largely controlled by redox and speciation. Siciliano *et al*. (2016) demonstrated that anaerobic hydrocarbon biodegradation rates were correlated with abundance of

adsorbed phosphate, and phosphate minerals brushite and newberyite, where newberyite inhibited microbial activity and biomass growth. Characterising phosphate speciation may be a significant step to understanding the potential for NSZD or enhancing LNAPL biodegradation.

6. Soil moisture – microbial activity is limited in drier soils (e.g. Yadav and Hassanizadeh, 2011). Increased rates of NSZD have been observed in semi-arid soils after rainfall events (McAlexander and Sihota, 2019) but very wet soils can act as a barrier for gaseous diffusivity and stop influx of oxygen from the surface. The effective diffusivity of soil gases is strongly influenced by soil moisture. Garg *et al.* (2017) calculated the expected range of NSZD rates for representative soil types and moisture contents (≈200 to 100,000 L/Ha/a). The calculated range corresponds to the range of site-wide average NSZD rates observed at 25 field sites. Variable soil moisture due to potential effects of climate change could be significant for measuring NSZD expressions and rate estimation (Section A3.3).

7. Temperature – several studies have identified correlation between soil temperature and hydrocarbon biodegradation or NSZD rates (e.g. Sihota *et al*., 2016; Kulkarni *et al*., 2017; Eichert *et al*., 2017). Favourable temperatures are between 20 and 30 degrees Celsius (°C), which exceeds typical ambient soil temperatures in northwest Europe (≈10°C). Diurnal and seasonal variation in soil temperatures may influence NSZD rates, in particular for shallow LNAPL sources which may be more susceptible to changes in ambient air temperatures. Sihota *et al*. (2016) observed complex seasonal variation in surficial efflux of carbon dioxide, with peak rates of NSZD occurring in winter and natural soil respiration dominating in summer.

8. Biodegradation pathways and inhibition – Garg *et al*. (2017) summarises studies where differing methanogenic pathways were observed or inferred for crude oil and refined-product biodegradation – hydrogenotrophic methanogenesis (hydrogen oxidisation coupled with carbon dioxide reduction) or acetoclastic methanogenesis (converting acetate to methane). Biological effects of inhibition due to acetate build-up control and reduce overall hydrocarbon degradation rates compared to thermodynamic controls. Volatile hydrocarbons may also inhibit methanogenic LNAPL biodegradation; Sherry *et al*. (2014) observed methanogenesis of weathered crude oil at approximately twice the rate of unweathered oil.

Appendix 2: NSZD Monitoring Technologies

A2.1 Overview

Direct measurement of NSZD is currently infeasible; rather, research has focused upon developing technologies that allow expressions of NSZD to be monitored, from which rates can be estimated using analytical procedures. These include methods relying upon data collection in the unsaturated zone, either at surface or in the subsurface, and saturated zone to estimate the contributions to NSZD indicated by gaseous and aqueous expressions. The overall NSZD rate is the sum of gaseous and aqueous expressions. Methods that track compositional changes in the LNAPL itself provide an alternative or complementary technology to assess NSZD occurrence and estimate overall rates.

Where quantitative estimation of overall NSZD rates is required, at least two methods should be used in parallel, with the aim of providing complementary lines of evidence for NSZD (e.g. Smith *et al*., 2021; Wozney *et al*., 2022). Monitoring technologies should be deployed in multiple locations around the year to assess spatial and temporal variations, if site-scale annual estimates of NSZD rates are required. The NSZD monitoring technologies in common use are introduced below.

A2.2 Rates from Measurements of Gaseous Expressions of NSZD

Four methods have been developed that rely upon measurements of soil gas or thermal parameters in the unsaturated zone to estimate rates for the gaseous expression of NSZD using analytical procedures.

Gradient method

The gradient method uses measurements of oxygen, methane and carbon dioxide taken at discrete depths using soil gas sampling probes installed above the LNAPL (API, 2017; ITRC, 2018; crcCARE, 2018). Soil gas measurements, corrected for non-NSZD contributions, are used to estimate diffusive fluxes through the unsaturated zone, which are then stoichiometrically equated to rates of hydrocarbon biodegradation and thus rates of NSZD (e.g. Johnson *et al*., 2006; Lundegard and Johnson, 2006).

The gradient method can be used for short- and long-term measurement of gas flux (API, 2017). Since this method uses measurements of three soil gases affected by NSZD, the gradient method can be used in two ways:

- Estimation of carbon dioxide efflux (production), cross-checked against oxygen influx (consumption); or
- Estimation of methane efflux alone.

This flexibility supports application of the gradient method to diffusion-dominated systems that exhibit methane oxidation in the unsaturated zone due to exchange with atmospheric oxygen, and to systems where oxygen influx is limited (e.g. due to hardstanding, low permeability or variations in soil moisture content) and methane persists throughout much of the unsaturated zone.

The gradient method is based on Fick's 1st Law of Diffusion:

$$J = D_v^{eff} \cdot (dC/dZ)$$

where J is the steady-state diffusive flux (g/m^2-soil/s), dC/dZ is the soil gas concentration gradient (g/m^3-m) or change in gas concentration (C, g/m^3) over change in depth (Z, m), and D_v^{eff} is the effective vapour diffusion coefficient (m^2/s), that is specific to the soil and gas being measured. It is typically annotated with a subscript that specifies the gas (e.g. D_{O2}^{eff} is the effective diffusion coefficient for oxygen).

The NSZD rate (R_{NSZD}, g/m^2/d) is estimated from the background corrected diffusive flux (J_{NSZD}, µmol/m^2/s) by:

$$R_{NSZD} = J_{NSZD} \cdot m_r \cdot MW \times 10^{-6} \times 86400$$

Where m_r is the stoichiometric molar ratio for oxidisation of an indicator hydrocarbon (e.g. decane, $C_{10}H_{22}$), MW is the molar weight of the of the representative hydrocarbon (g/mol).

Correction for background contributions is simply the total diffusive flux minus the flux associated with natural soil respiration and other non-NSZD sources (e.g. landfill, coal mine workings, deep petrogenic sources etc.).

Two main assumptions underpin the gradient method:

- Soil gas flux is predominantly by diffusion; and
- Unsaturated zone is homogeneous and isotropic.

Research indicates that these assumptions are not limiting and support use of the gradient method at most sites (API, 2017; crcCARE, 2018). While homogeneous and isotropic conditions are uncommon in the subsurface, the variability in effective diffusion coefficient can be addressed by taking measurements with consideration to the heterogeneity and/or by developing weighted-average diffusivity values (crcCARE, 2018).

The following general procedure is recommended for use of the gradient method for a single monitoring location (API, 2017; crcCARE, 2018):

1. Install multi-level soil gas sampling probes;
2. Soil gas sampling to measure oxygen, carbon dioxide, methane and hydrocarbon vapour concentrations;
3. Estimate soil gas concentration gradients;
4. Compensate observed measurements for the oxygen consumption and carbon dioxide production unrelated to NSZD (background);
5. Calculate the NSZD flux.

A typical monitoring setup for the gradient method is illustrated in Figure A2.1.

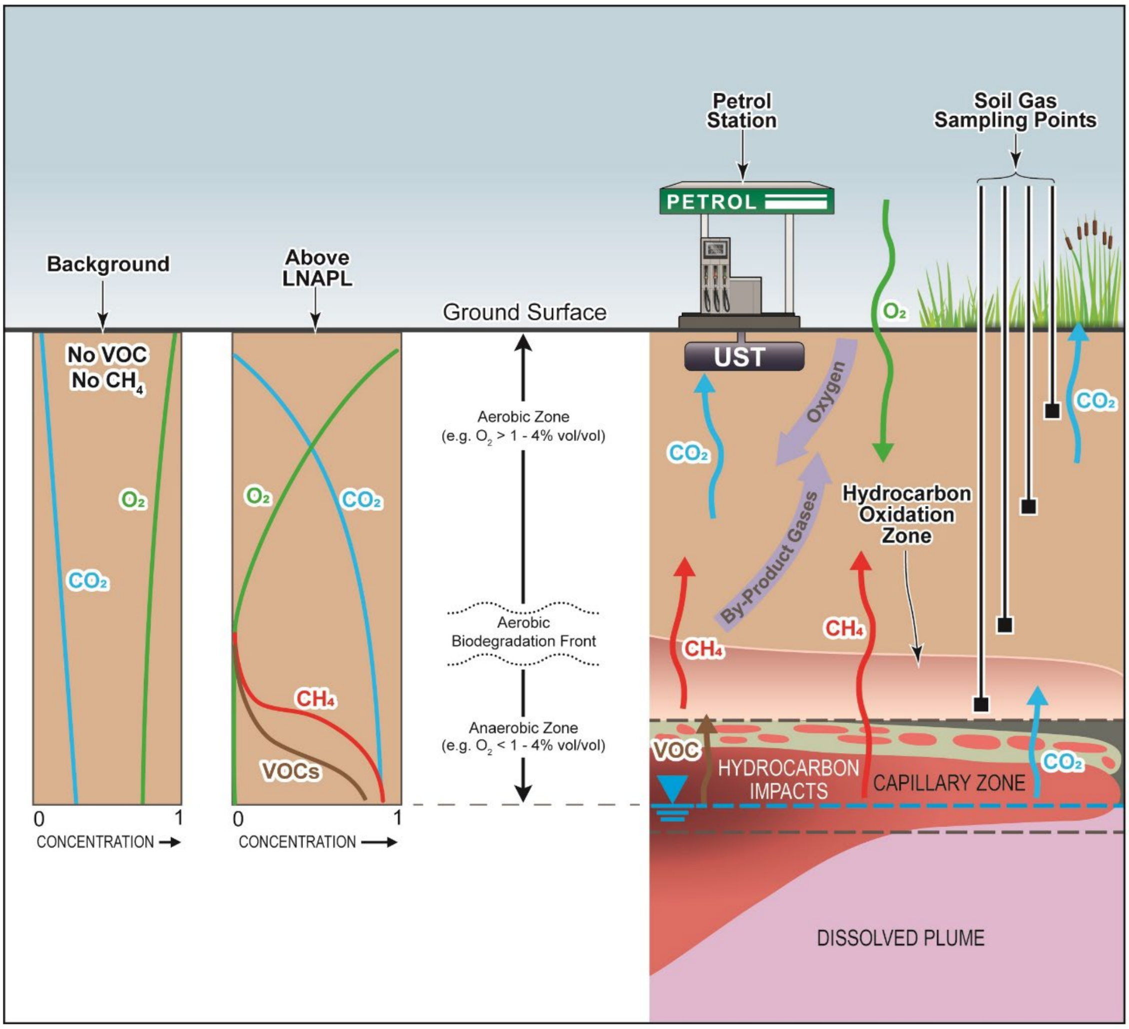


Figure A2.1: Schematic of gradient method monitoring setup (crcCARE, 2018).

Procedures for collection of soil gas and vapour samples are provided in BS 8576:2013 (British Standards Institution, 2013), BS 8485:2015 + A1:2019 (British Standards Institution, 2019), API (2017) and crcCARE (2018). Procedural checklists and a worked example of NSZD rate calculation using the gradient method for a typical methane oxidisation system is appended in crcCARE (2018). Considerations for calculation of the NSZD rate for oxygen limited systems, i.e. where methane is present to shallow depth in the unsaturated zone, is presented in API (2017). Example applications of the gradient method at field sites are provided by Ririe and Sweeney (2014), Ng *et al*. (2015), Concawe (2020), crcCARE (2020), McHugh *et al*. (2020) and Smith *et al*. (2021).

Considerations for use of the gradient method:

- An appropriate number of monitoring locations for soil gas vertical profiling is required that meet data quality objectives to appraise the spatial variability in NSZD rates;
- Monitoring locations should include areas above the LNAPL and in unimpacted background areas (if ^{14}C analysis is not used);
- Diffusive soil gas flux estimated by the gradient method represents a snapshot in time. Multiple, repeat measurements will be required to assess the annual variability;

- Appropriate quality assurance/quality control (QA/QC) measures (e.g. BS 8576:2013 British Standards Institution, 2013; USEPA, 2006) are necessary to confirm the data collected meets data quality objectives for precision, accuracy, representativeness, completeness, comparability and sensitivity (PARCCS);
- crcCARE (2018) presents alternative methods for soil gas sampling, for example using existing gas and groundwater monitoring wells, if new, dedicated apparatus cannot be installed. If existing groundwater monitoring wells are being considered for soil gas sampling, practitioners should review the information provided by crcCARE (2018) to ensure this approach is suitable for the intended application and site;
- The effective diffusion coefficient can be from empirical methods or site-specific measurement. Where *in situ* tracer tests are used to estimate variability in effective diffusion coefficients, these should be performed concurrently with soil gas sampling;
- The effective diffusion coefficient is affected by soil moisture, after rain and seasonally. Consideration should be given to performing monitoring during dry periods and repeating *in situ* tracer tests with each monitoring event;
- Confirmation that advection is negligible may be required to satisfy data quality objectives for use of the gradient method at some sites. Pressure or nitrogen tracer tests are recommended alongside soil gas monitoring;
- The calculation procedure described by crcCARE (2018) assumes linear concentration profiles with depth for carbon dioxide and oxygen. Verginelli and Baciocchi (2021) suggest that this approach may underestimate NSZD rates by an order of magnitude and developed an alternative gradient calculation method using a first-order reaction model that matched field measurement data from nine NSZD sites (Figure A2.2);
- The use of ^{14}C methods provides an alternative means to compensate for soil gas flux unrelated to NSZD processes, that does not require sampling in unimpacted areas. ^{14}C analysis is beneficial as it avoids the need for additional sampling in unimpacted areas, which may be on land owned by a third party. The gradient method samples could be analysed as described by CL:AIRE (2021) or measurements could be paired with the passive flux trap to obtain the specialist analysis.

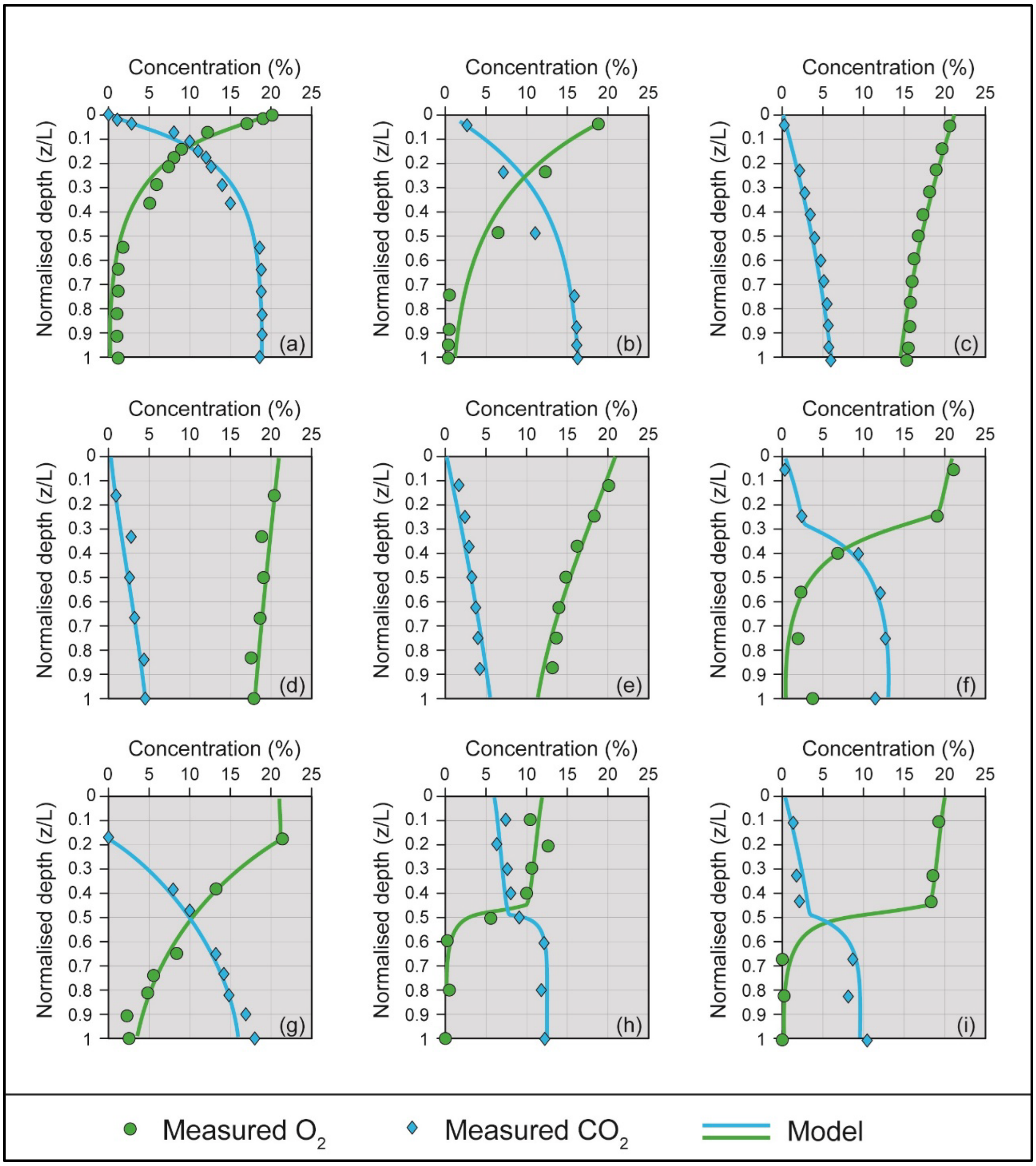


Figure A2.2: Comparison of simulated oxygen and carbon dioxide concentrations (Verginelli and Baciocchi, 2021) and as a function of normalised depth (z/L) and the data observed in the field by different authors: (a) Davis *et al*. (2005), (b) Lundegard and Johnson (2006), (c) Pasteris *et al*. (2002), (d) crcCARE (2018), (e) Chaplin *et al*. (2002), (f) Fischer *et al*. (1996), (g) Lahvis *et al*. (1999), (h) Hers *et al*. (2000) and (i) Lundegard *et al*. (2008). Reproduced from the Journal of Contaminant Hydrology, Verginelli and Baciocchi, Copyright (2021), with permission from Elsevier.

Passive flux trap

The passive flux trap is deployed at or in the near surface to collect carbon dioxide migrating upwards through the unsaturated zone on an adsorbent material. The uptake of carbon dioxide onto a known surface area for a known period of time enables the estimation of carbon dioxide gas flux. The carbon dioxide flux needs to be corrected for contributions unrelated to NSZD. Then, the rate of NSZD can be determined by stoichiometric conversion for a representative petroleum hydrocarbon.

Deployment of passive flux traps is typically performed over periods of up to two weeks. Passive flux traps were developed in academia and were later commercialised by E-Flux, LLC.

The surficial carbon dioxide flux (J, $g_{CO2}/m^2/d$) is estimated by:

$$J_{CO2} = M_{CO2} / A / t$$

where M_{CO2} is the carbon dioxide mass trapped (g), A is the cross-sectional area of the trap (m^2) and t is the deployment period (d).

The NSZD rate (R_{NSZD}, g/m²/d) is estimated from the background corrected surficial carbon dioxide flux (J_{CO2}, $g_{CO2}/m^2/d$) by:

$$R_{NSZD} = J_{CO2} \cdot m_r \cdot MW_{HC} / MW_{CO2}$$

Where m_r is the stoichiometric molar ratio for oxidisation of an indicator hydrocarbon (e.g. decane, $C_{10}H_{22}$), MW is the molar weight of the of the representative hydrocarbon (g/mol) and MW_{CO2} is the molar weight of carbon dioxide (g/mol).

Correction for background contributions is simply the total carbon dioxide flux minus the flux associated with natural soil respiration and other non-NSZD sources (e.g. landfill, coal mine workings, deep petrogenic sources etc.).

The key assumptions of the passive flux trap:

- Carbon dioxide flux is vertical;
- Carbon dioxide flux is attributable (or can be apportioned) to NSZD processes.

The following general procedure is recommended for use of the passive flux trap for a single monitoring location (API, 2017; crcCARE, 2018):

- Deploy the passive flux trap;
- Retrieve the passive flux trap and submit to a specialist laboratory;
- Perform laboratory analysis of carbon dioxide (and ^{14}C if being used to assess contributions from NSZD and other sources);
- Assess the carbon fractions associated with NSZD and non-NSZD sources and compensate the NSZD carbon flux;
- Calculate the NSZD rate.

Instructions for the installation of passive flux traps are provided by crcCARE (2018) and the manufacturer E-Flux. The use of passive flux traps requires a specialist laboratory. While other methods are available to compensate for carbon dioxide flux unrelated to NSZD, ^{14}C analysis is considered to be beneficial as it avoids the need for additional sampling in unimpacted areas, which may be on land owned by a third party.

A worked example of NSZD rate calculation using passive flux traps is appended in crcCARE (2018). Example demonstrations of passive flux trap deployments at field sites are provided by Concawe (2020), crcCARE (2020), McHugh *et al.* (2020), and Smith *et al*. (2021).

Considerations for use of passive flux traps:

- An appropriate number of monitoring locations for carbon dioxide flux measurements is required that meets data quality objectives to appraise the spatial variability in NSZD rates;
- The monitoring locations are accessible and will be protected for the duration of the deployment (2 weeks typically);
- Monitoring locations should include areas above the LNAPL (and in unimpacted background areas if ^{14}C analysis is not being used);
- For sites where the ground surface is hardstanding or compacted, installing passive flux traps may create a chimney effect and result in overestimation of NSZD rates. It is suggested that pressure equalisation measures are used with passive flux traps for these conditions (e.g. Concawe, 2020; Smith *et al.*, 2021);
- Passive flux traps can be used at sites where advective and diffusive soil gas transport is occurring;
- Passive flux traps may not be suitable for monitoring NSZD rates at sites where atmospheric oxygen exchange is limited, i.e. methane is present at shallow depth.

Dynamic closed chamber

The dynamic closed chamber (Sihota and Mayer, 2012) is an active monitoring technique that measures soil gas efflux at the ground surface. The dynamic closed chamber uses a vacuum pump connected to a surface-mounted chamber to collect and pass soil gas (carbon dioxide, methane etc.) through a field gas analyser. The timed rate of change in soil gas concentrations is used to calculate the soil gas flux. The soil gas flux is equated to NSZD rate through stoichiometric conversion for a representative petroleum hydrocarbon. Measurements typically span minutes and multiple measurements spanning multiple days are typically required to derive time-weighted averages. Dynamic closed chamber systems are commercially available from multiple vendors.

Since the dynamic closed chamber is a direct measure of soil gas concentrations and flux, it has few assumptions that can bias rate estimation. This method is versatile, insofar as it can be used to estimate NSZD rates from carbon dioxide efflux (for systems with observed oxygen exchange) or methane efflux (for systems with limited oxygen exchange).

The surficial soil gas flux (J, g/m^2/d) is estimated by:

$$J = dC/dt \cdot V / A$$

where dC/dt is the change in soil gas concentration (g/m^3) over time, t, V is the volume of the chamber (m^3) and A is the cross-sectional area of the chamber (m^2).

The NSZD rate (R_{NSZD}, g/m^2/d) is estimated from the background corrected surficial soil gas flux ($J_{gas,}$ g/m^2/d) by:

$$R_{NSZD} = J_{gas} \cdot m_r \cdot MW_{HC} / MW_{gas}$$

Where m_r is the stoichiometric molar ratio for oxidisation of an indicator hydrocarbon (e.g. decane, $C_{10}H_{22}$), MW is the molar weight of the of the representative hydrocarbon (g/mol) and MW_{gas} is the molar weight of measured soil gas (carbon dioxide or methane, g/mol).

Correction for background contributions is simply the total flux of soil gas measured minus the flux associated with natural soil respiration and other non-NSZD sources (e.g. landfill, coal mine workings, deep petrogenic sources etc.).

The following general procedure is recommended for use of the dynamic closed chamber for a single monitoring location (API, 2017; crcCARE, 2018):

- Install chambers and allow re-equilibration (>16 hours);
- Perform soil gas efflux survey using the dynamic closed chamber system;
- Perform data validation;
- Assess contributions to gaseous efflux from NSZD and non-NSZD sources (background);
- Calculate the NSZD rate.

Procedures for the installation of dynamic closed chambers are provided by API (2017), crcCARE (2018) and system manufacturers (e.g. LI-COR). A worked example of NSZD rate calculation using dynamic closed chamber with carbon dioxide flux data is appended in crcCARE (2018). Considerations for calculation of the NSZD rate using methane flux data are presented in API (2017), i.e. for systems with limited oxygen exchange in the unsaturated zone.

Considerations for use of the dynamic closed chamber method:

- An appropriate number of monitoring locations for soil gas vertical profiling is required that meets data quality objectives to appraise the spatial variability in NSZD rates;
- Monitoring locations should include areas above the LNAPL and in unimpacted background areas (if ^{14}C analysis is not used);
- Diffusive soil gas flux estimated by the gradient method represents a snapshot in time. Multiple, repeat measurements will be required to assess the annual variability;
- Appropriate QA/QC measures (e.g. BS 8576:2013 British Standards Institution, 2013; USEPA, 2006) are necessary to confirm the data collected meets data quality objectives for PARCCS;
- For sites where the ground surface is hardstanding or compacted, installing dynamic closed chambers may be challenging without excessive disturbance that can influence soil gas flux measurements;
- The dynamic closed chamber can be used at sites where advective and diffusive soil gas transport is occurring;
- The use of ^{14}C methods provides an alternative means to compensate for soil gas flux unrelated to NSZD processes, that does not require sampling in unimpacted areas. ^{14}C analysis is beneficial as it avoids the need for additional sampling in unimpacted areas, which may be on land owned by a third party. Soil gas samples collected on the downstream side of the gas analyser could be analysed for ^{14}C as described by CL:AIRE (2021) or paired with the passive flux trap to obtain the specialist analysis.

Biogenic heat methods

Biogenic heat methods estimate the thermal gradient from hydrocarbon biodegradation from soil temperature measurements taken at discrete depths (Sale *et al*., 2018; Warren and Bekins, 2015; Karimi Askarani *et al*., 2018; Kulkarni *et al*., 2020; Ganna *et al*., 2022; Kulkarni *et al*., 2022). The thermal flux, inferred from the thermal gradient, is equated to NSZD rate by stoichiometric conversion for a representative petroleum hydrocarbon. Soil temperature measurements can be collected as snapshots in time or continuously to assess temporal variability in NSZD.

Biogenic heat methods rely upon measurement of excess heat from exothermic NSZD reactions, principally aerobic oxidation of hydrocarbons. Other dominant NSZD biodegradation reactions, i.e. methanogenesis, are not strongly exothermic. Soil temperature profiles in soil above LNAPL where oxygen exchange and other electron acceptors are limited may be confounding and result in underestimation of NSZD rates.

The thermal flux is analogous to the diffusive flux and can be estimated using Fourier's First Law:

$$q_H = K_T \cdot dT/dZ$$

where q_H is the steady-state conductive heat flux (J/m^2-soil/s), dT/dZ is the temperature gradient (°K/m), and K_T is the thermal conductivity of the soil (J/m/s/°K) that is specific to the soil within the hydrocarbon oxidation zone.

Correction for background contributions to subsurface temperature is simply the soil temperature profile measured in the LNAPL impacted area minus the soil temperature measured in a nearby unimpacted area, with similar surface cover, lithology, at the same depth below surface and with alternative heat sources absent (e.g. sewers, mine shaft/adit etc.). Alternative methods for background correction of soil temperatures include mathematical procedures, such as the "single stick" method described by Karimi Askarani and Sale (2020).

The NSZD rate (R_{NSZD}) is calculated from the background corrected heat flux (q_H) and enthalpy of reaction (ΔH^o):

$$R_{NSZD} = q_H / \Delta H^o$$

The enthalpies of oxidation of methane (43.9 kilojoules per gram [kJ/g]) and octane (44.8 kJ/g) are similar (API, 2017). As such it is common to estimate R_{NSZD} from the ΔH^o for methane, assuming that this reaction represents oxidisation of all hydrocarbons (LNAPL, hydrocarbon vapours and methane).

The biogenic heat method relies on the assumption of instantaneous reaction for methane oxidation (Davis *et al*., 2009) and complete conversion of all petroleum hydrocarbons to carbon dioxide (Stockwell, 2015). The kinetics of biodegradation can be complex with many concurrently occurring processes (see Garg *et al*., 2017). However, to date it has been assumed that the net effect of these collective microbiological processes is a zero-order (constant) biodegradation rate. This may represent an over-simplification of long-term behaviour, where the zero-order rate coefficient is expected to decrease at later stages of NSZD.

The main assumptions underpinning NSZD rate estimation from biogenic heat methods are:

- Soil is homogeneous and isotropic;
- The biogenic heat source is at quasi-steady state and constant;
- Heat conduction is the dominant mechanism for heat transfer in the unsaturated zone;
- Exothermic reactions are instantaneous and complete, including methane oxidation.

Multiple studies suggest that these assumptions are not limiting (crcCARE, 2018). The method relies upon assigning thermal parameter values that are representative of the formation within which the heat flux is observed, that can be obtained using site-specific measurements and/or a range of literature values. The quasi-steady state condition generating a constant heat source is considered true for sites with LNAPL at middle to late-stage (Tracy, 2015), as is likely the case for most sites being considered for NSZD.

The following general procedure is recommended for use of biogenic heat methods for a single monitoring location (crcCARE, 2018):

- Install soil temperature measurement devices;
- Log soil temperatures for an extended period of time;
- Estimate the soil thermal conductivity;
- Calculate the average temperature by depth and compensate for temperature unrelated to NSZD processes;
- Estimate the thermal gradient;
- Calculate the NSZD rate.

A typical biogenic heat method monitoring setup is presented in Figure A2.3.

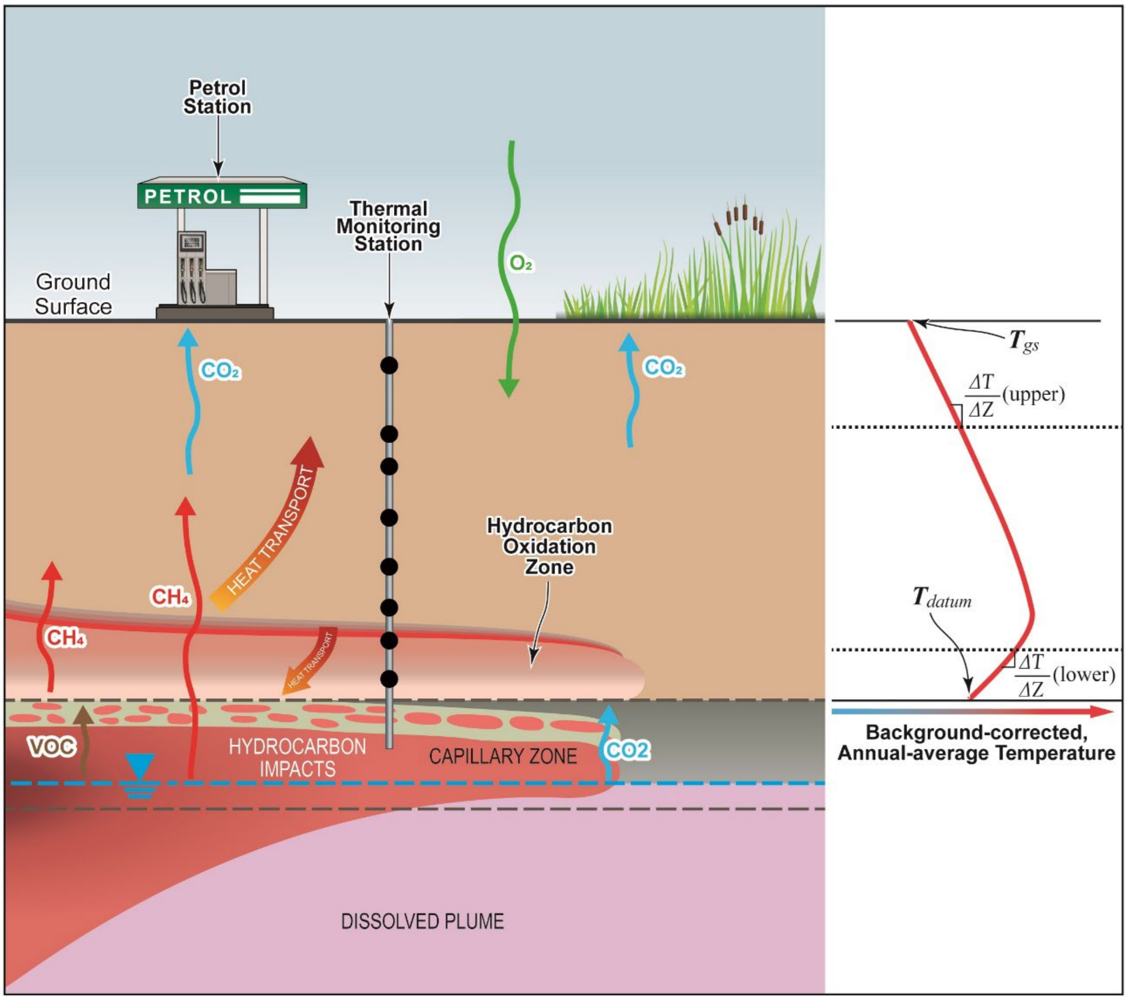


Figure A2.3: Schematic of a biogenic heat method monitoring setup and a typical background corrected NSZD temperature profile (crcCARE, 2018).

crcCARE (2018) compares the attributes of seven tools for making screening-level and quantitative estimates of NSZD rates from subsurface temperature monitoring (Johnston *et al.*, 2007; Sweeney and Ririe, 2014; Warren and Bekins, 2015; Thermal NSZD®, 2016; Bio-Therm®, 2017). A worked example of NSZD rate calculation using a biogenic heat method is appended in crcCARE (2018). Example applications of biogenic heat methods at field sites are provided by Sweeney and Rire (2014), Concawe (2020), crcCARE (2020), McHugh *et al.* (2020) and Smith *et al.* (2021).

Considerations for use of biogenic heat methods:

- An appropriate number of monitoring locations for soil temperature vertical profiling is required that meet data quality objectives to appraise the spatial variability in NSZD rates;
- Monitoring locations should include areas above the LNAPL and in unimpacted background areas (if mathematical background compensation procedures are not used);
- Various soil temperature measurement and biogenic heat calculation options are available. Each should be reviewed and the preferred approach selected based on the data needs and site constraints;

- Temperature data can be collected using various techniques:
    - Dedicated thermistor strings installed in a borehole and backfilled, wired to a data logger at surface;
    - Using an existing monitoring well with a thermocouple and reel;
    - Using an existing monitoring well with self-contained thermal data loggers.
- Data logging approaches provide advantages over manual techniques where repeated measurements are required to assess variability in rates and/or renewed access is problematic. Some data logging systems relay information to the internet, allowing remote access and control;
- Appropriate QA/QC measures are necessary to confirm the data collected meets data quality objectives for PARCCS (USEPA, 2006);
- NSZD rates from single measurements are considered screening-level only. Collection of multiple soil temperature profiles, at a frequency of 1 month to 1 year is recommended to address uncertainties in estimated rates (crcCARE, 2018);
- The thermal conductivity can be estimated using either laboratory testing, calculations, literature values (e.g. Sweeney and Ririe, 2014; crcCARE, 2018) or *in situ* monitoring (e.g. Karimi Askarani *et al*., 2021). In heterogeneous media, volume-weighted or geometric averaging of thermal conductivities for different soil types may be appropriate;
- The use of mathematical procedures provides an alternative method to compensate for soil temperature anomalies unrelated to NSZD (e.g. Karimi Askarani and Sale, 2020).

A2.3 Rates from Measurement of Aqueous Expressions of NSZD

Aqueous expression refers to the dissolution of LNAPL in groundwater. The dissolved-phase discharge in groundwater downgradient of the LNAPL source zone will be subject to some level of natural attenuation. Natural attenuation in groundwater occurs through a combination of physical and biogeochemical processes that act to reduce the contaminant mass, concentration and/or toxicity in groundwater (CL:AIRE, 2024).

Methods to estimate the mass depletion rate in groundwater through dissolution of LNAPL within the saturated zone include:

- Use of dissolved contaminant concentration trends (USEPA, 2009; Wilson, 2011; crcCARE, 2018);
- Mass budget methods (e.g. National Research Council, 2000; Johnson *et al*., 2006; ITRC, 2009; Mackay *et al*., 2018).

Groundwater monitoring wells to be used for this purpose should be installed immediately downgradient of the LNAPL. Groundwater sampling should be performed to obtain representative samples for determination of dissolved-phase hydrocarbons and geochemical parameters; groundwater samples containing NAPL will mislead NSZD rate estimation. Sampling groundwater from monitoring wells in which LNAPL has accumulated is unlikely to meet this data quality objective and should be avoided. It is recommended that analytical data are also reviewed to confirm that the concentrations reported by the laboratory are not impacted by NAPL.

Dissolved-phase concentration trends

The aqueous expression of NSZD can be estimated using analytical concentration data for COPC in groundwater samples, and limited data for physical properties for the saturated zone.

The first-order point attenuation rate coefficient (k_{point}) indicates the rate of degradation of COPC and is determined from analysis of COPC concentrations in groundwater versus time (Figure A2.4), commonly performed for evaluation of MNA. The procedure for calculation of k_{point} is described by Newell *et al*. (2002), ITRC (2013), CL:AIRE (2024) and other guidance cited in this document.

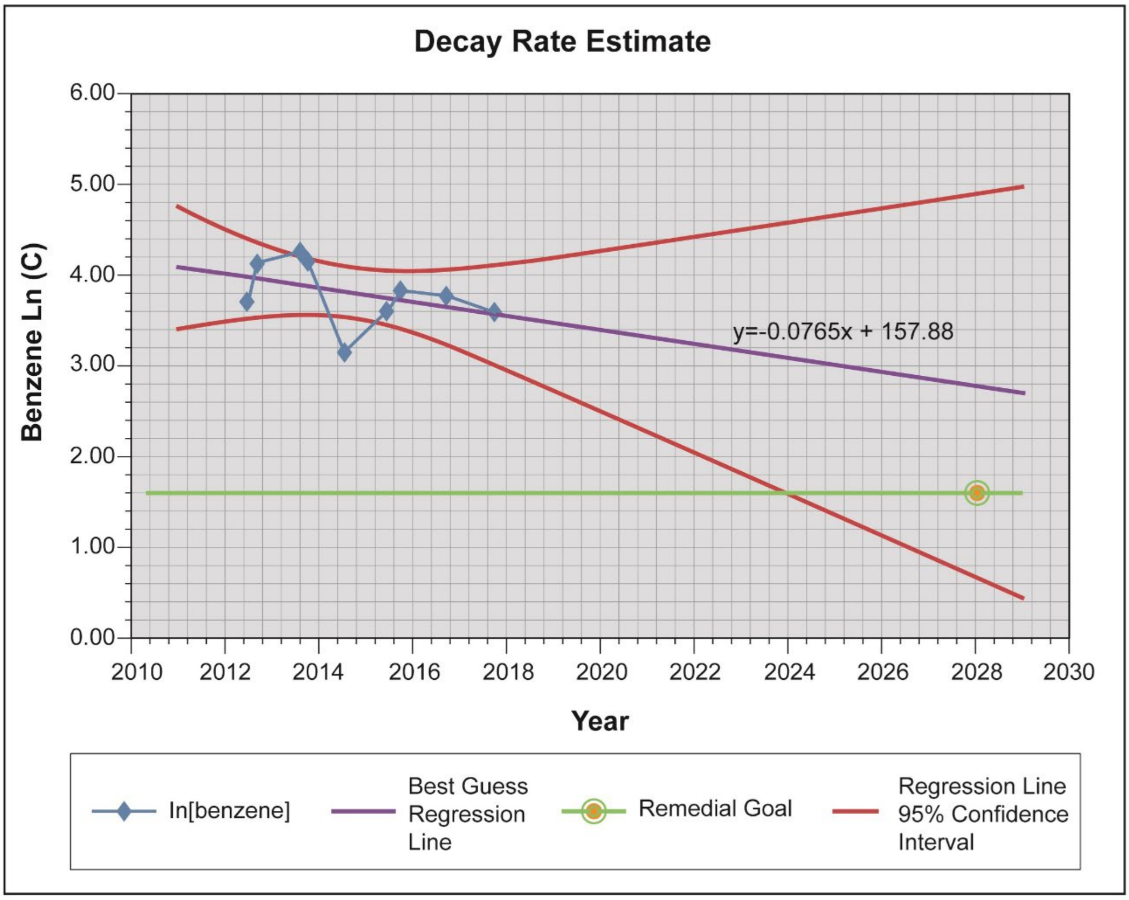


Figure A2.4: Decay rate estimate using dissolved contaminant concentrations (benzene) and the regression function (crcCARE, 2018).

Once the rate constant is estimated, it can then be used to calculate the NSZD rate due to aqueous expression, specific to a COPC as shown below.

$$R_{COPC\text{-}aq} = -k_{point} \cdot \theta_w \cdot h_{gw}$$

where $R_{COPC\text{-}aq}$ is the chemical-specific NSZD rate ($g_{COPC}/m^2/a$), θ_w is water-filled porosity (m^3/m^3), and h_{gw} is the saturated thickness of the plume (m^3/m^2).

Furthermore, the bulk NSZD rate due to aqueous expression can be estimated by:

- The sum of $R_{COPC\text{-}aq}$ for multiple constituents, where k_{point} is calculated for each constituent expressed in consistent concentration units, for example by conversion to micromolar concentrations (µmol/L) or by conversion to micrograms carbon per litre (µg C/L); or
- Using measurements of bulk petroleum hydrocarbon concentrations such as provided by Total Petroleum Hydrocarbons analysis of groundwater samples.

Mass budget methods

Mass budgeting methods estimate the rate of LNAPL mass depletion in groundwater as the sum of rate of dissolution and rate of biodegradation. Mass budgeting methods integrate COPC and geochemical concentration data to estimate the ongoing *in situ* biodegradation of hydrocarbons. These procedures are based on the change in electron acceptor and metabolic by-product concentrations observed between upgradient (background) and hydrocarbon plume areas, and stoichiometry of hydrocarbon biodegradation reactions (crcCARE, 2018).

The measured aqueous species affecting the rate of mass depletion processes described by the mass budget method are conceptualised in Figure A2.5.

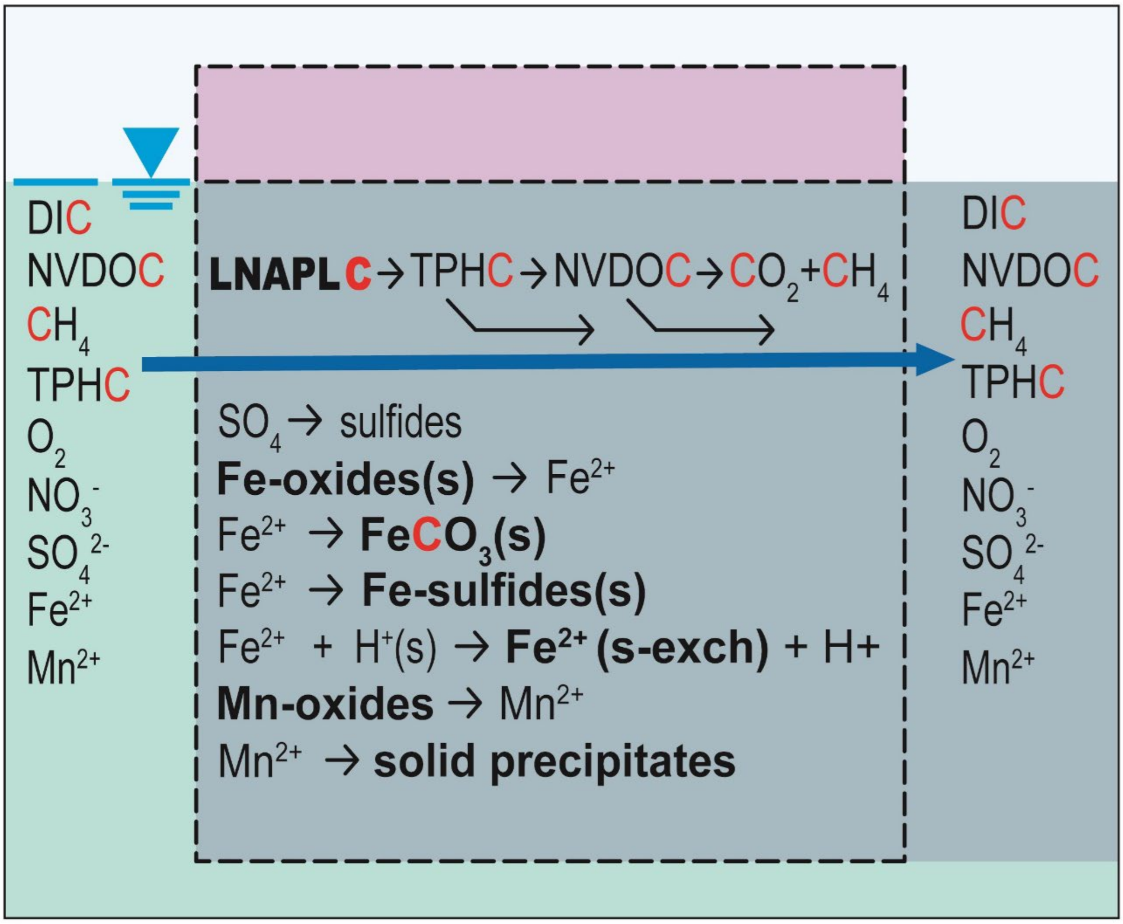


Figure A2.5: Conceptualisation of the species and processes potentially affecting the mass budget methods for estimating the groundwater NSZD rate (Mackay *et al.*, 2018). © 2018 John Wiley & Sons, Inc. DIC refers to dissolved inorganic carbon, NVDOC refers to non-volatile dissolved organic carbon, TPH refers to Total Petroleum Hydrocarbons.

The fundamental basis for mass budgeting is presented by National Research Council (2000), as modified by ITRC (2009):

$$R^{C}_{depletion\text{-}sat} = R^{C}_{dissolution\text{-}sat} + R^{C}_{bio\text{-}sat}$$

Where $R^{C}_{depletion\text{-}sat}$ is the mass depletion rate due to aqueous expression of NSZD, $R^{C}_{dissolution\text{-}sat}$ is the LNAPL dissolution rate into groundwater and $R^{C}_{bio\text{-}sat}$ is the hydrocarbon biodegradation rate indicated by TEAPs in groundwater.

The LNAPL dissolution rate is equivalent to the source mass discharge of dissolved-phase hydrocarbons. There are three fundamental methods to measure source mass discharge (*D*) (ITRC, 2010):

1. Transect methods, integrating concentration and groundwater flow data for individual monitoring locations;
2. Well capture/pumping test methods, using recovered concentration data with extraction rates; and
3. Passive flux meters, which are a technology used to estimate groundwater and mass flux directly in monitoring wells (Hatfield *et al.*, 2004; CL:AIRE, 2020b).

Methods to estimate the biodegradation rate from TEAPs and other indicators of hydrocarbon biodegradation are provided by National Research Council (2000) and ITRC (2009). These methods rely upon parameterisation of biodegradation reactions using stoichiometric ratios (refer to ITRC, 2009). Biodegradation of decane ($C_{10}H_{22}$) by TEAPs is commonly used to represent a wide range of petroleum hydrocarbon products for determining rates of NSZD. However, consideration should be given to selecting other indicator compounds for specific fuel types. For example, Smith *et al.* (2021) based NSZD rate estimates for gasoline on stoichiometric coefficients for octane (C_8H_{18}) and for diesel on stoichiometric coefficients for hexadecane ($C_{16}H_{34}$).

A worked example of mass budgeting methods is provided by crcCARE (2018).

Data collection and analysis can appear onerous for application of mass budgeting methods. The carbon budget method (Mackay *et al.*, 2018) provides an alternative to the mass budgeting methods described by National Research Council (2000) and ITRC (2009) that considers only the inputs and outputs of soluble carbon containing compounds and the change in carbon-containing species in the source control volume (Figure A2.6).

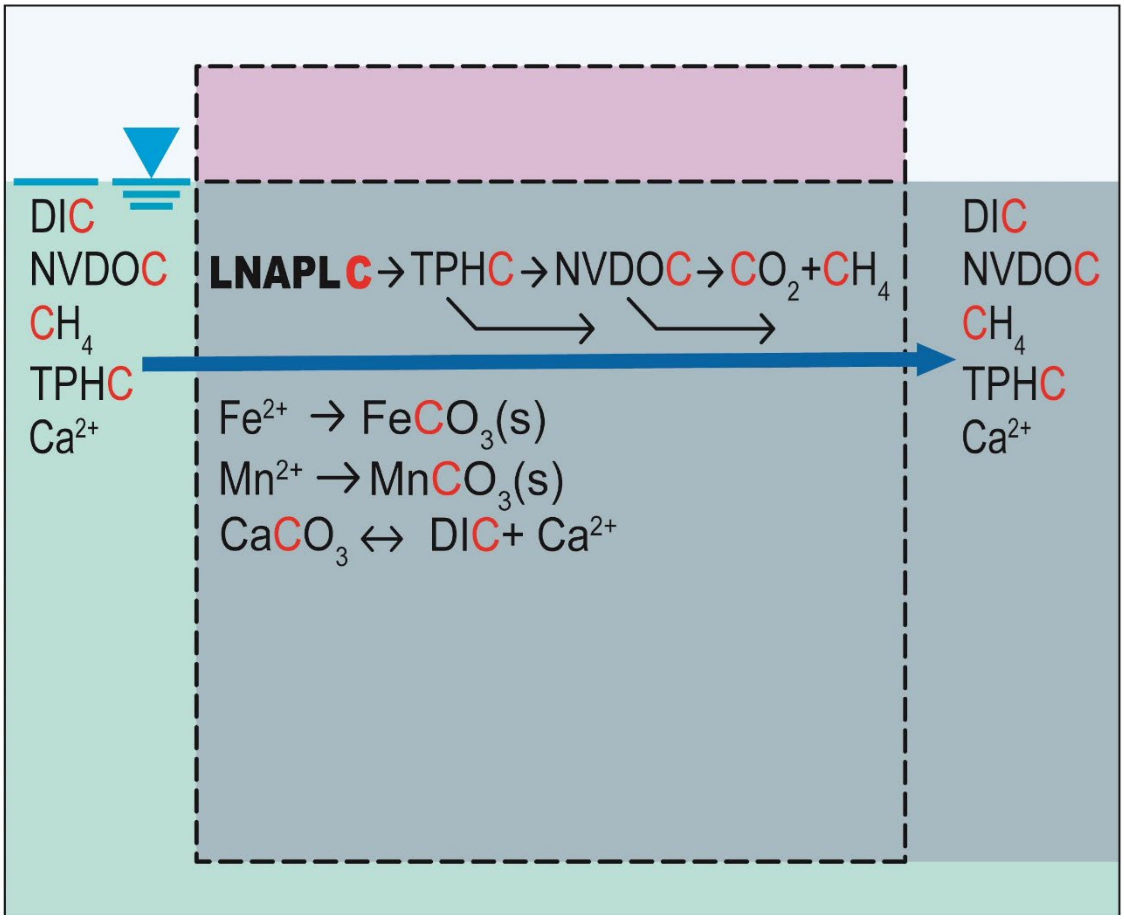


Figure A2.6: Conceptualisation of the carbon budget method for estimating the groundwater NSZD rate (Mackay *et al*., 2018). © 2018 John Wiley & Sons, Inc. C refers to expressing species in terms of carbon equivalents. DIC refers to dissolved inorganic carbon, NVDOC refers to non-volatile dissolved organic carbon, TPH refers to Total Petroleum Hydrocarbons.

Mackay *et al*. (2018) presents a comparison of mass budget and carbon budget methods and demonstrates the potential value in simpler data collection and analysis for estimation of bulk rates of aqueous expression of NSZD. Where constituent-specific NSZD rates are sought, the mass budgeting procedures described by crcCARE (2018) could be applied.

A2.4 Rates from Measurement of LNAPL Composition

LNAPL compositional change methods provide an alternative, complementary or confirmatory means to estimate overall NSZD rates to monitoring gaseous and/or aqueous expressions of NSZD. The method requires periodic sampling and analysis of LNAPL from soil and/or monitoring wells. Quantification of indicator compounds, such as COPCs and conservative markers, and physical properties of the LNAPL is required, as well as data collection and analysis to support estimation of the LNAPL formation thickness.

The key assumptions of compositional change methods are:

- Regression of chemical content of the LNAPL, corrected for mass depletion, against time, is representative of NSZD;

- LNAPL samples collected from groundwater monitoring wells and/or soil samples are representative of the source zone; and
- The NSZD rate is representative of all NSZD processes (refer to Appendix 1).

The overall NSZD rate for an individual COPC in LNAPL ($R_{COPC\text{-}LNAPL}$, $g_{COPC}/m^2/d$) estimated by compositional change is given by:

$$R_{COPC\text{-}LNAPL} = dm_{COPC}/dt \cdot \rho_{LNAPL} \cdot D_{LNAPL}$$

Where dm_{COPC}/dt is the change in mass fraction of a chemical constituent in the LNAPL normalised for a conservative marker (g_{COPC}/g_{LNAPL}) over time, t (d), ρ_{LNAPL} is the LNAPL density (g/m^3) and D_{LNAPL} is the specific volume of LNAPL *in situ* (m^3/m^2).

The normalised chemical constituent mass fraction (dm_{COPC}, g_{COPC}/g_{LNAPL}) may be calculated as:

$$dm_{COPC} = m_{COPC\text{-}0} - m_{COPC\text{-}t} \cdot m_{marker\text{-}0}/m_{marker\text{-}t}$$

Where m_{COPC} the mass fraction of the constituent (g_{COPC}/g_{LNAPL}), m_{marker} is the mass fraction of a conservative marker (g_{marker}/g_{LNAPL}), subscript *-0* indicates the initial time (i.e. fresh oil) or an earlier time than subscript *-t*, which denotes a later time (d).

The general procedure for completing the LNAPL compositional change analysis is summarised by crcCARE (2018):

- Retrieve intact soil cores and LNAPL sampling from monitoring wells or subsurface soil;
- Laboratory analysis of LNAPL for COPCs, conservative markers and physical properties;
- Laboratory analysis on intact soil cores to determine pore fluid saturation and hydraulic properties, or estimate soil water retention from physical properties (e.g. Mishra *et al*., 1989);
- Regression of normalised mass fraction data against time;
- Calculate the LNAPL specific volume (API, 2007; Concawe, 2022);
- Integrate estimates of COPC-specific NSZD rates with the LNAPL specific volume to estimate the overall NSZD rate.

A worked example of the LNAPL compositional method is provided by crcCARE (2018). DeVaull *et al*. (2020) presents two examples of this method performed on two case study site datasets.

Considerations for application of LNAPL compositional change methods to estimate overall NSZD rates:

- The chemical composition of LNAPL is highly variable, vertically and horizontally. An appropriate number of samples is necessary to generate a representative NSZD rate;
- A specialist NAPL laboratory will be required to determine pore fluid saturation and hydraulic properties, in suitably preserved intact soil cores (e.g. API, 1998);
- A commercial laboratory with capability to perform forensic analyses on LNAPL may be required to quantify COPCs and conservative markers;

- Selection of the conservative marker is non-trivial and requires consideration of the type of LNAPL, state of weathering, state of alteration due to biodegradation, constituent abundance in the LNAPL etc. Example conservative markers include *n*-alkanes hopane, pristane and phytane (refer to Douglas *et al*., 1996; Douglas *et al*., 2012; Baedecker *et al*., 2018; DeVaull *et al*., 2020). DeVaull *et al*. (2020) describes a marker selection procedure based on multiple trials of regression analysis with various candidate constituents, culminating the selection on analyses satisfying statistical criteria confirming the reliability of the regression models;
- Timescales for discernible changes in the mass fraction of target chemical constituents are in the order of years. Long-term NSZD kinetics are likely complex and may not be adequately well-represented by linear (zero-order) trends over extended timescales. DeVaull *et al*. (2020) developed non-linear (first-order) rate coefficients from regression of compositional data for the Bemidjii crude oil release site, Minnesota (Essaid *et al*., 2011);
- Estimates for NSZD rates based on multiple COPCs can be integrated to provide an estimate of the overall NSZD rate for LNAPL. An example procedure is provided in DeVaull *et al*. (2020).

A2.5 Method Selection and Deployment

Selection of a NSZD monitoring method or methods is a site-specific decision based on the objectives of data collection (including data quality objectives) and site conditions, as indicated by the CSM. Subsurface conditions, as well as those at the surface, will influence method selection. Specifically, the nature of expressions of NSZD in the unsaturated zone, heterogeneity and accessibility are leading factors constraining the suitability of one method over another. Method selection for Screening, Demonstration and/or Implementation purposes (refer to Section 2) may differ as the CSM evolves.

Aspects of the LNAPL CSM and how these relate to NSZD processes and monitoring are summarised in Table A2.1. A comparison of the six NSZD monitoring methods introduced is provided in Table A2.2.

Table A2.1: Key elements of the LNAPL CSM and how they relate to NSZD measurement (after API, 2017; crcCARE, 2018). Reproduced courtesy of the American Petroleum Institute and crcCARE.

Element	Relation to NSZD
Lateral extent of LNAPL	Forms the area of the NSZD investigation – monitoring outside the LNAPL footprint can generally be considered background if there are data to document no hydrocarbon impacts at depth. Multiple releases/separate LNAPL bodies on the same site or deep LNAPL with tortuous soil gas transport pathways, for example, may require adaptation of the NSZD monitoring programme.
Vertical extent of LNAPL	NSZD occurs only in hydrocarbon-impacted areas. The rate may vary based on the amount of LNAPL present and where it occurs in the subsurface, although these effects remain a subject of study.
Type of LNAPL and fluid density	Conversion of biodegradation by-product vapour flux to a NSZD rate requires a stoichiometric conversion using a hydrocarbon representative of the LNAPL mixture. Conversion to a volumetric-based NSZD rate requires the LNAPL density.
Depth to groundwater and water table fluctuation	NSZD monitoring using these vapour phase-related methods can only be performed in the unsaturated zone above the hydrocarbon impacted soil. The effects of LNAPL submergence on NSZD rates is uncertain. Consider timing NSZD measurements at extremes of seasonal high and low water table for site-specific assessment of this potential effect.
Ambient temperature clime	At sites with shallow hydrocarbon source zones (e.g. <6 m; Sweeney and Ririe, 2014) or significant changes in groundwater temperatures, NSZD rates may vary with seasonal change in soil temperatures. At these types of sites, ambient temperature changes affect soil temperature. Effects of root zone activity on shallow soil gas profiles and flux is highest during the warmer, vegetation growing season. In certain climes, competent ground ice may limit shallow soil vapour flux when this is present. Ground frost is often permeable and does not necessarily restrict soil gas exchange with the atmosphere. Consider the temperature and water table elevation effects in parallel as there can often be optimum times to measure when water tables are lowest and soil temperatures highest.

Element	**Relation to NSZD**
Depth to top of hydrocarbon impacts in soil	The top of the hydrocarbon impacts will drive soil gas concentration profiles and determine where gradient method monitoring should be located. Layers of shallow zones of petroleum in soil, separated by “clean” soil, above the bulk of the hydrocarbon mass in the LNAPL smear zone, for example, may confound data interpretation from the gradient method.
Soil type and moisture content	Movement of hydrocarbon vapours and soil gas is more limited in finer grained or competent cohesive formations and soils with a higher moisture content. Limitation of oxygen influx to the subsurface, such as due to hardstanding, will limit NSZD rates. Bedrock presence does not preclude NSZD monitoring, but affects method selection.
Methane concentration in shallow soil gas	Presence of elevated methane at or near ground surface indicates soil gas exchange is limited and methane oxidation is incomplete. In the absence of elevated carbon dioxide and biogenic heat, method selection will potentially include calculation and/or measurement of methane flux.
LNAPL distribution and hydrostratigraphy	LNAPL can occur in the subsurface under unconfined, confined, or perched conditions. Each of these conditions could affect the NSZD rates.
LNAPL in fractured bedrock	NSZD has been demonstrated in many environments, including fractured bedrock (e.g. McHugh *et al*., 2020). LNAPL distribution, soil gas/vapour and solute transport in fractured rock are specific considerations affecting how NSZD at these sites is investigated and monitored, and how NSZD rates are estimated.

Table A2.2: Summary of key attributes of NSZD monitoring methods (modified from API, 2017 and crcCARE, 2018). Reproduced courtesy of the American Petroleum Institute and crcCARE.

Attribute	Aqueous	Gradient	Passive flux trap	Dynamic closed chamber	Biogenic heat	LNAPL compositional change
Data objective	COPC-specific or bulk NSZD occurrence or rate estimation for aqueous expression only (typically <10% total NSZD)	Bulk NSZD occurrence or rate estimation for gaseous expression only (typically >90% total NSZD)	Bulk NSZD occurrence or rate estimation for gaseous expression only (typically >90% total NSZD)	Bulk NSZD occurrence or rate estimation for gaseous expression only (typically >90% total NSZD)	Bulk NSZD occurrence or rate estimation for gaseous expression only (typically >90% total NSZD)	COPC-specific or bulk NSZD occurrence for overall rate estimation
Snapshot or time-averaged rate estimate	Snapshot	Snapshot	Time-averaged	Snapshot or time-averaged	Snapshot or time-averaged	Not applicable
Sample media	Groundwater	Soil gas and vapour	Soil gas	Soil gas	Not applicable	LNAPL and soil/rock
Measurement type	Solute concentration and volumetric discharge	Gas and vapour concentration vertical profile	Near surface carbon dioxide mass/flux	Near surface soil gas concentration/flux	Subsurface temperature vertical profile	Constituent mass/concentration Physical properties
Transport process quantified	Groundwater advection	Gaseous diffusion	Gaseous diffusion and advection [A]	Gaseous diffusion and advection [A]	Gaseous diffusion and advection [A]	Not applicable

Attribute	**Aqueous**	**Gradient**	**Passive flux trap**	**Dynamic closed chamber**	**Biogenic heat**	**LNAPL compositional change**
Method of background correction (i.e. non-NSZD related processes)	Monitoring upgradient/ background wells	^{14}C analysis Monitoring in unimpacted location(s)	^{14}C analysis Monitoring in unimpacted location(s)	^{14}C analysis Monitoring in unimpacted location(s)	Mathematical procedures Monitoring in unimpacted location(s)	Conservative marker constituent analysis
Site suitability (ideal site conditions)	Unsaturated zone <1.5 m thick Site with existing groundwater monitoring network (e.g. for MNA)	Unsaturated zone >1.5 m thick Site with pre-existing multi-level soil gas/vapour sampling network	Carbon dioxide dominant in soil gas vertical profile Variable effects of natural soil respiration on oxygen and carbon dioxide flux	Uniform background gas flux	Aerobic biodegradation-dominant Long-term monitoring requirement	Other methods unsuitable Mobile LNAPL accumulated in monitoring wells
Intrusiveness	High, monitoring well network installation (Low if using existing network) Ongoing access required for repeat sampling	High, multi-level monitoring network installation (Low if using existing network) Ongoing access required for repeat sampling	Low, surface/shallow and temporary installation Ongoing access required for repeat sampling	Low, surface/shallow and temporary installation Ongoing access required for repeat sampling	Moderate, new probe installations (Low if using in-well measurements in existing network) Access not required for repeat monitoring if using telemetry	Moderate, if borings required for sampling (Low if sampling existing well network) Ongoing access required for repeat sampling

Attribute	Aqueous	Gradient	Passive flux trap	Dynamic closed chamber	Biogenic heat	LNAPL compositional change
Spatial coverage/data density	Low	Low	Moderate	High	Low	Low
Real-time data	No	Yes, with on-site measurement	No	Yes	Yes	No
Laboratory requirements	Commercial, UKAS accredited	Optional Commercial, UKAS accredited	Specialist	Not required	Not required	Specialist
Fieldwork intensity	High	High	Low	Moderate	High, initially Low, long-term	Low
Relative one-time implementation cost [B]	£££	£££ (cost reductions possible if using existing network and/or on-site measurements)	££	£	££ (favourable cost-benefit if used long-term)	£££ (cost reductions possible if sampling existing wells)

[A] Methods quantify the combined effects of diffusion and advection. The method does not allow for the quantification of the individual contributions from each gas transport process.

[B] Indicative costs include accounting of the labour, materials and analytical expenses required to perform a one-time round of NSZD measurements.

crcCARE (2018) provides guidance on the deployment of surface and subsurface methods for monitoring gaseous expressions of NSZD in various geological settings. Examples from this guidance are presented in Figure A2.7. In relatively homogeneous conditions, uniform soil gas flux is expected such that subsurface methods (gradient, biogenic heat) and/or surface methods (passive flux trap, dynamic closed chamber) could be deployed subject to other technical and practical constraints. In more complex systems, consideration to the effects of heterogeneity (anthropogenic and natural) and the number and distribution of LNAPL sources is required to meet data quality objectives. For example in Figure A2.7 (B), the apparent physical heterogeneity above the LNAPL may cause stratification of soil gases (and soil properties). The simplest way to address this complexity might be to measure gaseous flux at the surface (passive flux trap or dynamic closed chamber). However, if subsurface layers are relatively wet, this could limit soil gas diffusivity to the surface resulting in underestimation of NSZD. If subsurface methods are used (gradient or biogenic heat), the differences in soil properties (effective diffusion coefficient or thermal conductivity) between sand and silt/clay should be accounted for, along with measurements of soil gas or temperature in each layer.

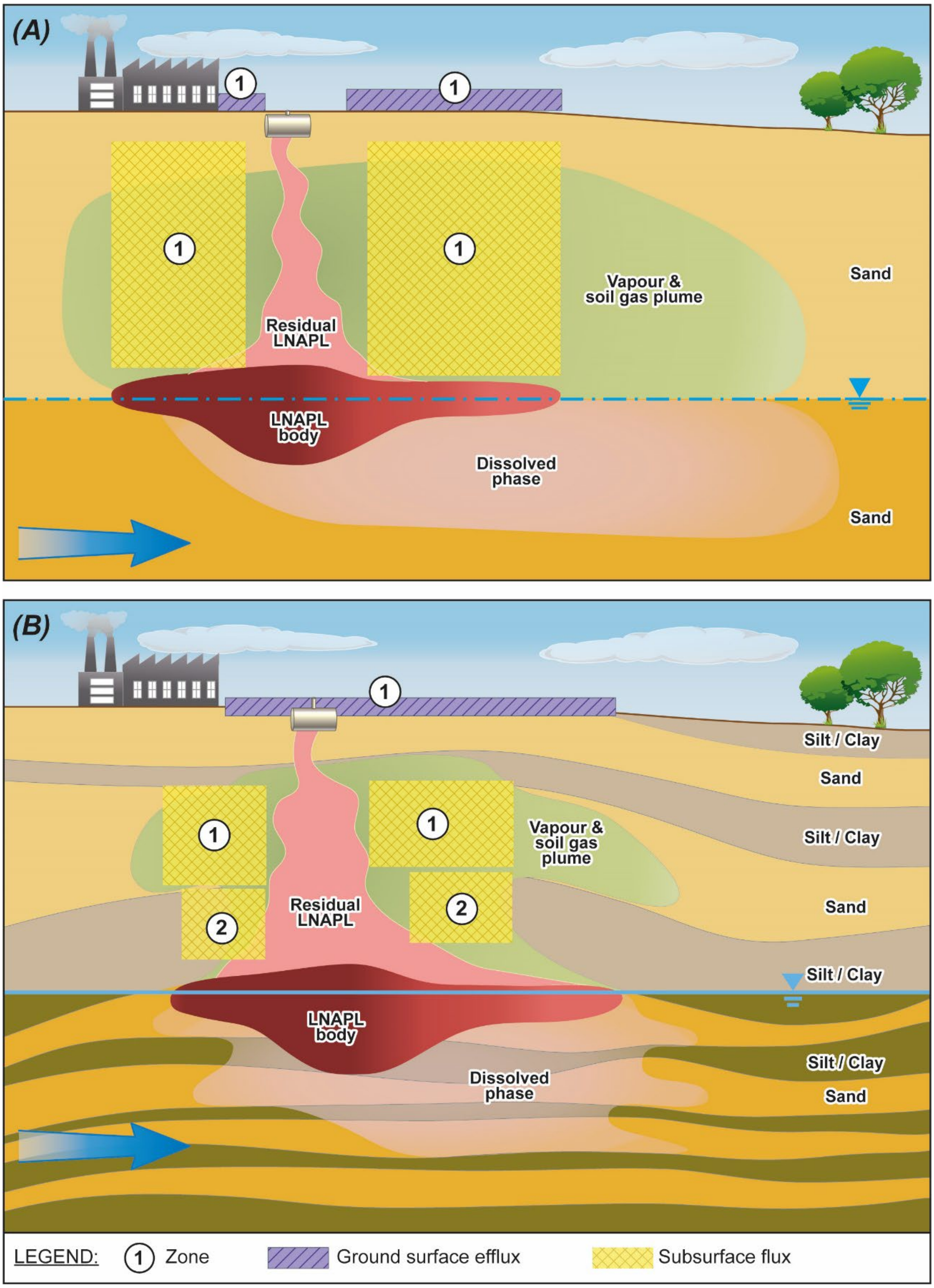


Figure A2.7: NSZD monitoring locations at sites with LNAPL release into (A) relatively homogeneous sand (B) interbedded sand and silt/clay (layered heterogeneity). Yellow shading indicates where subsurface methods could be deployed; purple shading denotes where surface methods could be deployed. Numbered zones indicate where additional measurements will be required to address complexity introduced by heterogeneity (crcCARE, 2018).

Appendix 3: LNAPL Conceptual Site Model for NSZD

A3.1 Overview

An advanced CSM for LNAPL, supported by good quality data collection and analysis, is required to understand NSZD and demonstrate its effectiveness as a long-term risk-management strategy. The CSM incorporates key attributes of the LNAPL, site conditions at the surface and within the subsurface and associated risks to receptors (CL:AIRE, 2014), to support assessment and decision-making within the framework described in this guidance document (Section 2).

The CSM will evolve as LNAPL management and actions move through stages of the remediation site lifecycle, as outlined in the Land Contamination Risk Management guidance (Environment Agency, 2023); namely Stage 1 Risk Assessment, Stage 2 Options Appraisal and Stage 3 Remediation and Verification. Each stage of the remediation site lifecycle requires different information but the need to characterise and understand the LNAPL and associated risks is a consistent thread.

Three evolutions of the LNAPL CSM are envisaged to support decision-making for NSZD, aligned with the framework presented in this document:

1. The Screening CSM concerns the nature and extent of LNAPL, and the potential effects of LNAPL and/or NSZD on receptors;
2. The Demonstration CSM underpins detailed evaluation of NSZD as a preferred risk-management option for NSZD; and
3. The Implementation CSM supports verification of the long-term effectiveness of NSZD.

The Screening CSM will integrate understanding of the physical-chemical state and distribution of the LNAPL, groundwater and vapour plumes with potential contaminant linkages, assessed by detailed quantitative risk assessment of LNAPL, soil gas, vapour and groundwater plumes (required at Stage 1 Step 3 of LCRM; Environment Agency, 2023). Theoretical or qualitative understanding of the potential effectiveness of NSZD may be sufficient at this stage. However, to advance the CSM to the Demonstration and Implementation stages requires more quantitative spatially- and temporally-integrated, process-specific understanding of NSZD and its effects on the LNAPL.

A3.2 LNAPL Site Characterisation for NSZD

Information typically required to develop a CSM for a LNAPL-impacted site is described by CL:AIRE (2014), crcCARE (2015) and ITRC (2018):

- Site setting (historical and current): land use, LNAPL use/storage (volumes and periods) and release mechanisms, groundwater classification and use, receptor presence and proximity;
- Geological and hydrogeological information;

- LNAPL physical properties (density, viscosity and interfacial tension) and chemical properties (constituent chemistry, constituent solubilities, vapour pressures and mole fractions);
- Spatial distribution of LNAPL saturations, horizontally and vertically;
- LNAPL mobility and migration potential;
- LNAPL recoverability information;
- Dissolved-phase and vapour-phase hydrocarbon plume information;
- NSZD process information (soil gas, soil temperature, unsaturated zone and saturated zone TEAPs etc.).

Evolution of the CSM requires data collection and detailed analysis that meets data quality objectives. Data should be relevant, sufficient, reliable and transparent. Setting data quality objectives is a logical process that informs planning for data acquisition (e.g. USEPA, 2006). The data quality objective process includes:

1. Prioritising data gaps and developing hypotheses;
2. Defining data collection objectives;
3. Establishing what types of data are required, how data will be used and the means to assess whether the collected data are acceptable (e.g. thresholds for PARCCS); and finally
4. Designing the data collection plan.

The amount and complexity of data required to adequately characterise LNAPL and NSZD is proportional to the scale and complexity of site conditions, and the level of confidence required to inform decision-making. Figure A3.2 illustrates how the required understanding and data needs increase as the scale and complexity of the problem increases (ITRC, 2018).

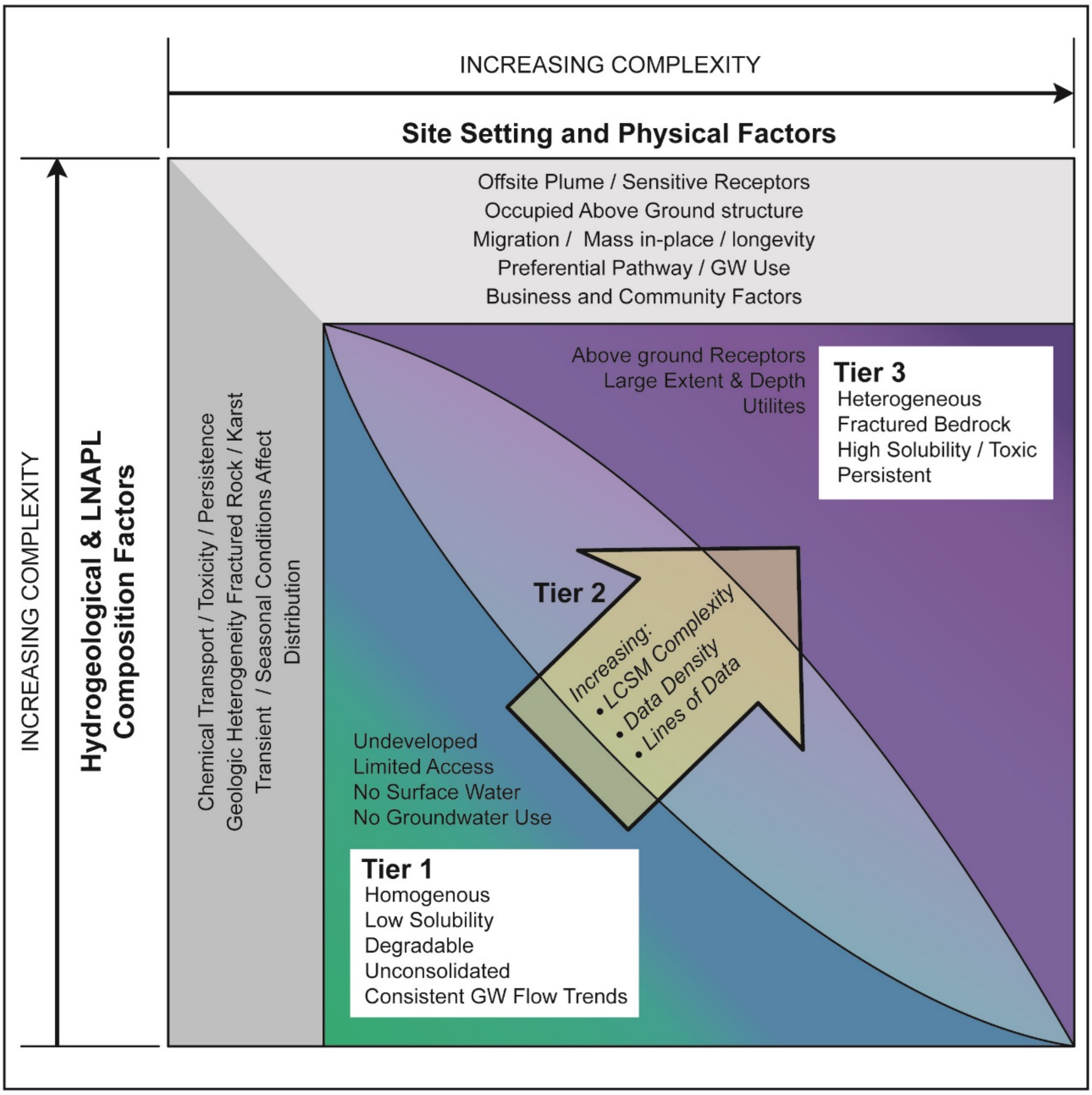


Figure A3.1. Illustration of factors affecting the amount and complexity of data collection for LNAPL site characterisation (ITRC, 2018). Tier 1, 2 and 3 refer to increasing levels of LNAPL conceptual site model complexity.

The CSM provides a framework where the uncertainty in site understanding can be identified and explored, and the need for additional information against the improvement in certainty and cost can be evaluated. Ultimately, environmental professionals must assess whether sufficient information has been gathered to make appropriate decisions regarding risks and remediation (Gormley *et al*, 2011; CL:AIRE, 2014).

It is now widely recognised that monitoring well observations alone are expected to be a poor basis for conceptualising the distribution of LNAPL. Rather, understanding the processes controlling the transport and fate of LNAPL in porous or fractured hydrogeological domains of interest is key to producing representative CSMs (CL:AIRE, 2014; ITRC, 2018). The fundamental concepts controlling the subsurface behaviour of LNAPLs are presented in various guidance documents (e.g. ITRC, 2009; CL:AIRE, 2014; crcCARE, 2018; ITRC, 2018). Further illustration of common behaviours of LNAPL in exemplar hydrogeological environments, with varying formation heterogeneity and flow characteristics, is provided by CL:AIRE (2014).

Developing process understanding of LNAPL typically requires an iterative approach. Various remote, indirect and direct LNAPL site characterisation tools can be used in combination to develop multiple convergent lines of evidence of the extent and behaviour of LNAPL. Descriptions of LNAPL site characterisation tools are provided by CL:AIRE (2014) and ITRC (2018). Indirect sensing tools, such as laser-induced fluorescence, can be used to acquire high-resolution, qualitative or semi-quantitative information to indicate where more detailed investigation using quantitative direct measurement tools might be applied. Examples of the type of LNAPL information acquired in vertical profiles by two laser-induced fluorescence tools deployed with direct push technologies are provided in Figure A3.2.

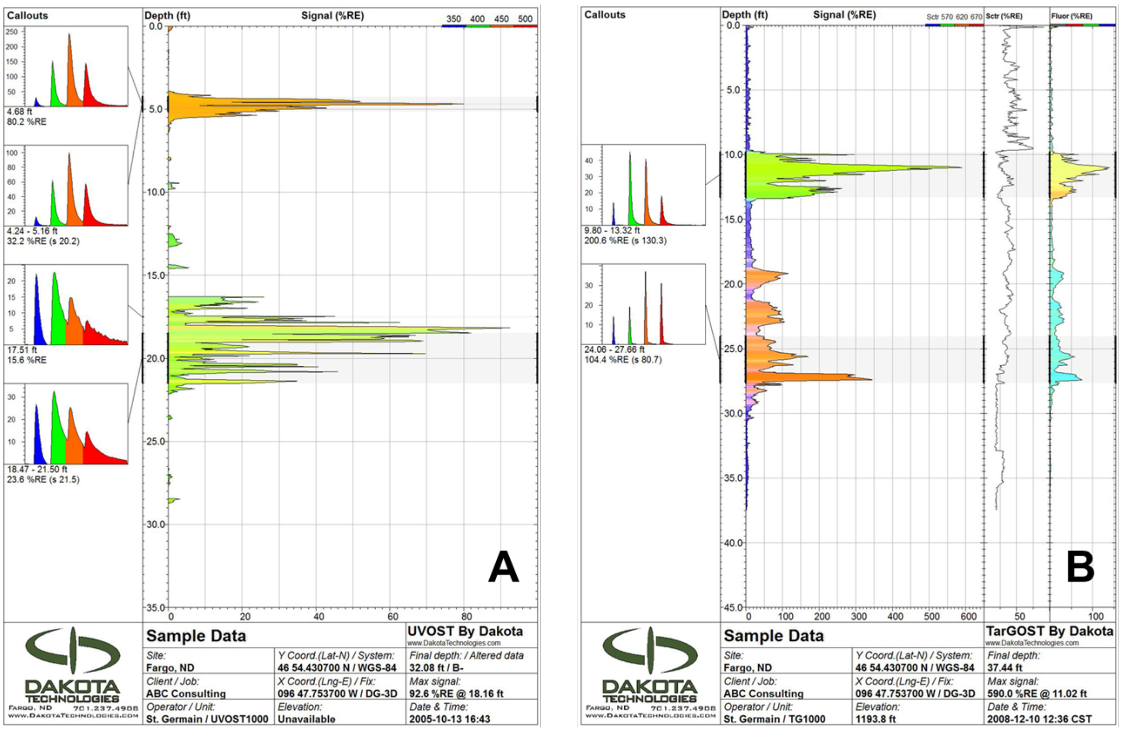


Figure A3.2: Example laser-induced fluorescence data for delineation of (A) petrol, diesel, jet fuel and hydraulic oils and (B) coal tars, creosotes, heavy crudes and tank bottoms (Source: Dakota Technologies, Inc). The fluorescence signal is proportional to NAPL saturation and the colour shading denotes different NAPL types.

Direct measurement tools, such as gauging groundwater monitoring wells and sampling and analysing physical and chemical properties of soil and LNAPL, are often used to provide higher value information albeit at lower resolution. Physical properties include parameters that inform understanding of multi-phase flow, such as LNAPL saturation, density, viscosity, interfacial tension, wettability, mobility, capillarity and relative permeability. Chemical properties include LNAPL constituent chemistry, groundwater and vapour plume biogeochemistry.

Integration of different LNAPL site characterisation tools and data analysis provide a means to develop more robust CSMs and assess uncertainty. While application of multiple remote, indirect sensing and direct measurement tools will not be required for every LNAPL site, characterisation of larger or more complex sites may require combinations of these methods to enable efficient decision-making.

For Screening (Stage 1), the initial LNAPL CSM is required to assess whether NSZD is occurring and measurable, and has potential to be effective, as indicated by estimated rates on a theoretical or semi-quantitative basis. For example, initial characterisation may be able to rely upon data from single monitoring/sampling events in existing environmental monitoring networks to verify NSZD is occurring (ITRC, 2018):

- Field screening of soil gas concentrations and/or fluxes;
- Concentrations of vapour-phase hydrocarbons;
- Concentrations of dissolved-phase hydrocarbons and TEAPs indicating parameters; and/or
- Vertical profiles of soil temperature.

Rapid screening methods (e.g. Ririe and Sweeney, 2022) may provide critical information to assist the development of an initial CSM considering NSZD processes, and aid the selection of appropriate investigation and monitoring techniques.

At sites with historical investigation and monitoring data, suitable information to appraise LNAPL and NSZD may already be available or can be supplemented relatively easily and quickly. However, when more quantitative NSZD understanding is required to demonstrate NSZD effectiveness (Stage 2) or monitor long-term performance (Stage 3), alternative measurement strategies are required. A higher density and frequency of monitoring may be needed to understand spatial and/or temporal variability of NSZD (Stage 2). Subsequently, it may be feasible to optimise the monitoring strategy to a reduced number of key locations and times of year to assess long-term performance (Stage 3). Typical durations and scopes of work needed to inform the CSM at the different stages of the decision-making process are provided in Table A3.2.

Table A3.2: Typical NSZD monitoring scopes of work (adapted from API [2017] and crcCARE [2018]). Reproduced courtesy of the American Petroleum Institute and crcCARE.

Decision-making stage	Data use objective	Scope of work	Duration of site work
1. Screening	Affirmation of NSZD occurrence, measurability and effectiveness	Theoretical/semi-quantitative analysis using historical or newly acquired site data	Up to ≈1 week
2. Demonstration	Snapshot NSZD rate estimate	Single event, multiple locations (early Winter preferable [Sihota *et al.*, 2016])	Up to ≈1 month
	Estimated range of NSZD rates	Two events, multiple locations coinciding with extremes in seasonal changes and water table elevation	≈6 to 8 months
	Estimated annual NSZD rate	Three or more events, multiple locations capturing extremes and averages in seasonal variations	≈1 year

Decision-making stage	Data use objective	Scope of work	Duration of site work
3. Implementation	Verification of long-term performance of NSZD	Variable, potentially reduced, scope depending on existing CSM and NSZD rates. Long-term monitoring may only be required in a few key locations at annual to multiple year intervals, depending on NSZD performance and potential risks to receptors.	Duration of risk-management strategy

A3.3 Risk Assessment for LNAPL Sites

Direct and indirect risks from LNAPL need to be effectively managed (e.g. Environment Agency, 2017). The risks posed by LNAPL to human health or the environment could include (CL:AIRE, 2014):

- Accumulation of flammable gases and hydrocarbon vapours in subsurface and surface structures;
- Chronic risk to human health via long-term exposure to hazardous substances (primarily consumption of polluted drinking water or vapour intrusion);
- Acute risk to human health via short-term exposure to (higher concentrations of, or more) hazardous substances (primarily direct contact with LNAPL);
- Pollution of groundwater or groundwater-dependent receptors by migrating LNAPL and/or dissolved-phase constituents, including metals mobilised in the presence of degrading hydrocarbons;
- Impairment of aesthetic qualities of potable supplies (taste, odour and discolouration);
- Detrimental effects on ecosystem structure and function; and
- Asphyxiation risk due to confined-space accumulation of vapours and anoxic conditions (although this is unlikely compared to, for example, landfill gas and mine gas scenarios).

The COPCs to be considered in risk assessment include soil gas (carbon dioxide, methane), hydrocarbon vapours, dissolved-phase hydrocarbons and the LNAPL itself. Risks should be evaluated at the detailed quantitative risk assessment level, such as including pathway-specific information that is not adequately represented by generic/screening level procedures.

If a LNAPL body is present within 1 m of the ground surface (Section 2.2), the potential risks to human health alone may preclude NSZD as a viable strategy for risk management. For LNAPL present at depths >1 m below the ground surface, the considerations for risk assessment introduced below are intended to support decision-making for sustainable management of LNAPL impacts in the subsurface:

LNAPL migration

ASTM (2021) provides a tiered framework to assess mobility and migration potential for LNAPL in porous media. The framework aims to identify whether LNAPL is mobile at pore scale (a "NAPL body"). If movement of mobile LNAPL is demonstrated to be only within the NAPL body extent, the LNAPL is "stable" and does not pose direct risk to receptors. If LNAPL movement includes entry into pore space beyond the NAPL body extent, this indicates the LNAPL is migrating. The probable extent of migration can be further evaluated to assess the potential for LNAPL to directly impact a receptor (Figure A3.3).

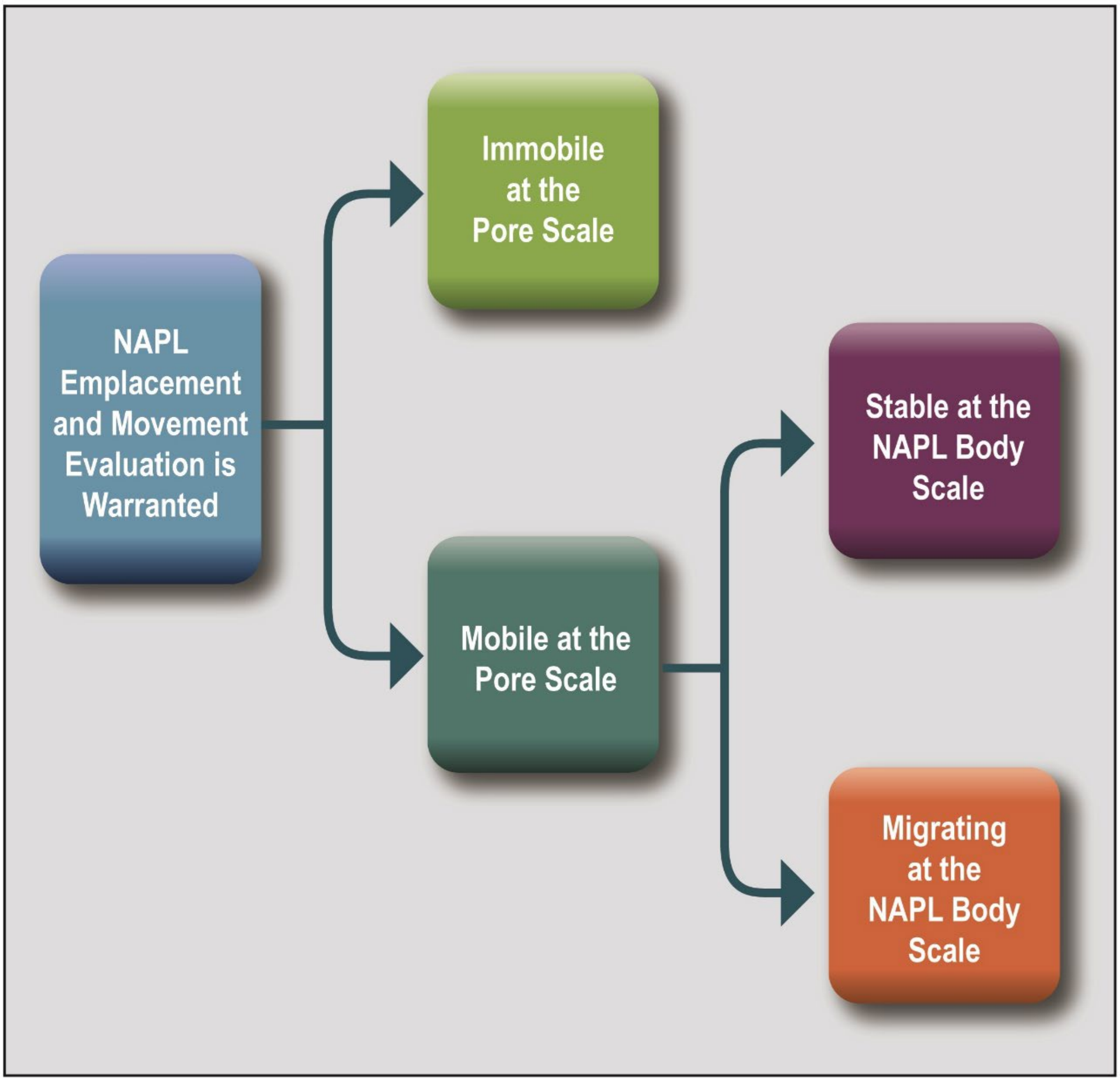


Figure A3.3: General NAPL movement evaluation framework (Gefell, 2022). Reproduced with permission from Applied NAPL Science Review.

LNAPL mobility and migration potential are controlled by saturation and multiple other factors (CL:AIRE, 2014; ITRC, 2018). A multiple lines of evidence approach is therefore suggested by ASTM (2021) to understand the weight of evidence for LNAPL mobility at pore scale and migration at the NAPL body scale.

Assessment of LNAPL mobility and migration potential requires an understanding of the physical properties of LNAPL. Laboratory analysis of LNAPL saturation and mobility, as well as soil hydraulic properties, are beneficial to risk assessment as well as assessment of NSZD rates (Appendix 2). A range of laboratory and data analysis methods are outlined in ASTM (2021) and Gefell (2021), that could also be supplemented with analysis of other gauging data collected at many LNAPL sites (e.g. Appendix 1 [CL:AIRE, 2014]).

Groundwater plume

The dissolution and migration of hydrocarbon solutes in groundwater is an indirect effect of LNAPL in the subsurface, with potential to impact current or planned water resources, sensitive ecosystems and chemical status of surface waters.

Procedures for assessment of the groundwater plume are provided by Environment Agency (2006), and updated by CL:AIRE (2017). Considerations for assessment of the potential impacts of the aqueous expressions of NSZD are introduced below:

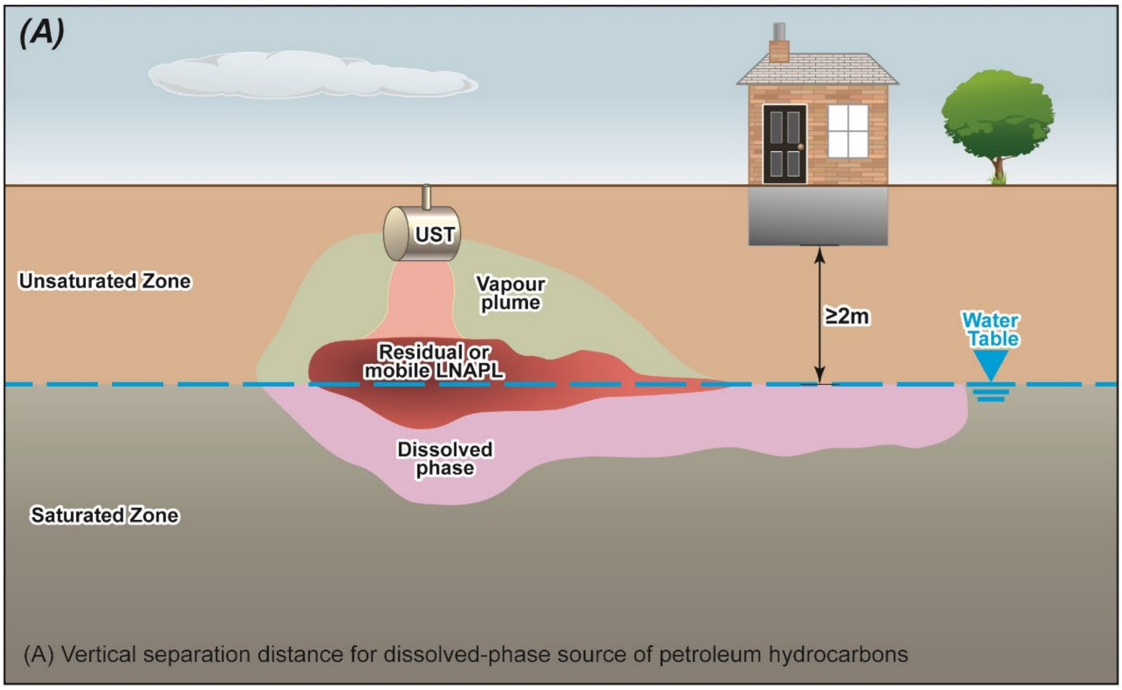
- LNAPL has often been considered to represent a constant source of impacts to groundwater. However, the dissolution of LNAPL is a mass depletion process and the long-term effects on source mass discharge should therefore be incorporated into risk assessments for NSZD. Field and simulation studies of the source mass/source mass discharge response suggest that NAPL source dynamics are predictable, based on the source zone heterogeneity and NAPL saturation (e.g. Falta *et al.*, 2005a; Falta *et al.*, 2005b).
- The rates of dissolution of LNAPL constituents are controlled by their mole fraction and Raoult's Law. The mole fractions of constituents change with time, altering their effective solubility and potential for long-term impacts to groundwater.
- Extensive biodegradation of dissolved-phase hydrocarbons can occur near to the LNAPL. The extent of biodegradation is subject to multiple site-specific factors, including the type and availability of electron acceptors. Literature values for biodegradation of COPC and petroleum hydrocarbon fractions should not be relied upon at this level of assessment. Rather, development of site-specific estimates is recommended, based on observed concentration data and other lines of evidence (e.g. data indicating TEAPs, compound specific isotope analysis [CSIA]; CL:AIRE, 2024).
- Relatively simple reduced order solute transport models are frequently used to support quantitative risk assessment in groundwater. While these models can provide screening-level information quickly, easily and with limited site data, these tools may not adequately represent complex processes indicated by LNAPL site characterisation data. Analytical or numerical groundwater models that integrate solute transport with multicomponent NAPL source dynamics and/or advanced hydrocarbon biodegradation models (kinetic or geochemical [electron balance]) may offer advantages over simpler screening models (e.g. Wilson *et al.*, 2005; Falta *et al.*, 2012).

Vapour plume and vapour intrusion

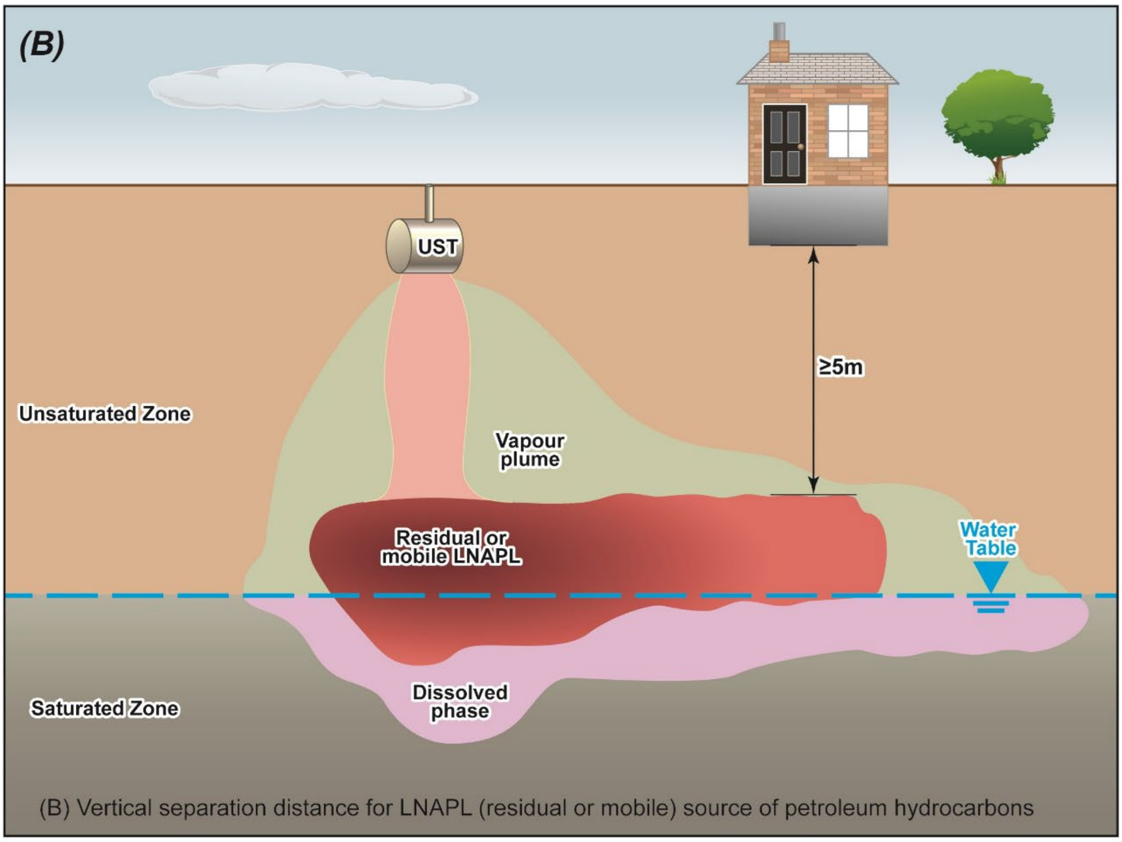
LNAPL constituent partitioning to the vapour-phase from LNAPL and pore water has potential to impact human health and/or the built environment. The risks to human health are typically increased where vapours can intrude enclosed spaces occupied or used by people – “vapour intrusion”. UK guidance on risk assessment of vapour intrusion is limited and not specific to hydrocarbons (Environment Agency, 2009; CIRIA, 2009). However, guidance developed in other parts of the World provides both relevant and pragmatic advice for detailed quantitative risk assessment of gaseous expression of NSZD (e.g. crcCARE, 2013; USEPA, 2015).

Considerations for assessment of the potential impacts of hydrocarbon vapours from NSZD are introduced below:

- Lateral inclusion zone and vertical separation distance are alternative risk screening concepts for hydrocarbon vapours introduced by USEPA (2015), and developed for the UK by the Energy Institute (2023). The lateral inclusion zone is the area around LNAPL through which vapours are transported and may intrude buildings. The vertical separation distance is the thickness of uncontaminated, biologically active soil between the highest extent of the source and the lowest point of a building (including cellars/basements). Further assessment of the potential risks posed by vapour intrusion are likely unnecessary for buildings (existing or theoretical) that are located outside the inclusion zone or separation distance. USEPA (2015) and the Energy Institute (2023) proposes a vertical separation distance ≥5 m from LNAPL and ≥2 m from dissolved-phase hydrocarbons (Figure A3.4); the lateral inclusion zone is assumed to be a similar distance horizontally from LNAPL or other hydrocarbon sources.
- Soil and groundwater concentration data provide a poor, overly conservative indication of soil vapour concentrations (e.g. McAlary *et al.*, 2011; Lahvis *et al.*, 2013). Soil vapour concentrations predicted from soil or groundwater may be over-predicted by more than 2- to 3-orders of magnitude (SoBRA, 2017). Sampling and measurement of hydrocarbon vapour concentrations is suggested, which may better serve sustainable decision-making by directly addressing uncertainties compared with simple analytical modelling approaches.
- Generic, modelled sub-slab to indoor air attenuation factors that do not consider biodegradation of hydrocarbon vapours are conservative and likely overestimate the transfer of hydrocarbons from sub-slab to indoor air in most buildings (e.g. calculated by Contaminated Land Exposure Assessment [CLEA] [Environment Agency, 2009; SoBRA, 2017]). Collection of paired sub-slab and indoor air vapour concentration data is suggested to enable determination of building-specific vapour intrusion attenuation factors. Where collection of paired samples is not possible, attenuation factors can be derived from vapour intrusion models that account for biodegradation (USEPA, 2015).



(A) Vertical separation distance for dissolved-phase source of petroleum hydrocarbons



(B) Vertical separation distance for LNAPL (residual or mobile) source of petroleum hydrocarbons

Figure A3.4: Vertical separation distances between sources of hydrocarbon contamination and buildings (A) dissolved source, (B) LNAPL (after USEPA, 2015; Energy Institute, 2023).

Soil gas (carbon dioxide and methane)

Efflux of carbon dioxide and methane from LNAPL, dissolved-phase and vapour-phase hydrocarbons undergoing biodegradation has potential to pose risk to human health and the built environment. Soil gas that is depleted of oxygen, with elevated concentrations of carbon dioxide and methane, diffuses through the unsaturated zone towards the underside of a building and is then drawn up through cracks and gaps in the floor (if present) by negative pressure inside the building, known as the “stack effect” (Card *et al*., 2019). Additionally, expansion of soil gas due to falls in atmospheric pressure may further promote ingress of buildings.

Currently, it is common practice to assess risks for methane and carbon dioxide by simple reference to Gas Screening Values (GSVs) (Wilson *et al*., 2020), as described in BS 8485:2015+A1:2019 (British Standards Institution, 2019). This approach disregards the CSM and is unlikely to be appropriate for LNAPL and NSZD sites, except as one strand in a multiple lines of evidence approach such as the process of detailed quantitative risk assessment outlined by CL:AIRE (2021).

Considerations for assessment of the potential risks associated with carbon dioxide and methane from NSZD are introduced below:

- Although carbon dioxide and methane can diffusively intrude a building via cracks and gaps in the floor, concentrations in indoor air are unlikely to achieve concentrations that pose risk to human health or explosion (CL:AIRE, 2018; Card *et al*., 2019). For example, Figure A3.5 indicates that methane diffusing from >1 m depth below a building will not result in indoor air concentrations >10% lower explosive limit (LEL). The absence of risk is further illustrated by a case study of diffusive gas flow into a building located over a landfill (Appendix 1, Card *et al*., 2019).
- Guidance on gas monitoring is provided in BS 8576 (British Standards Institution, 2013) and other ground gas guidance referred to in this document. Gaseous efflux is likely to fluctuate over long time periods and this needs to be taken account of in the gas monitoring programme. If spot monitoring is completed it requires data on weather conditions and barometric pressure variations prior to and during the monitoring period, along with enough closely spaced visits, so the relationship between the gas concentrations and flows and changes in pressure can be assessed (CL:AIRE, 2021). Continuous monitoring may allow a more robust risk assessment in many cases. In both cases (spot and continuous) the monitoring should cover a number of periods within the worst-case zone described by CL:AIRE Technical Bulletin 17 (CL:AIRE, 2018) – this approach covers advection dominated flow and is therefore conservative for the assessment of risks from diffusion-dominated soil gas transport.

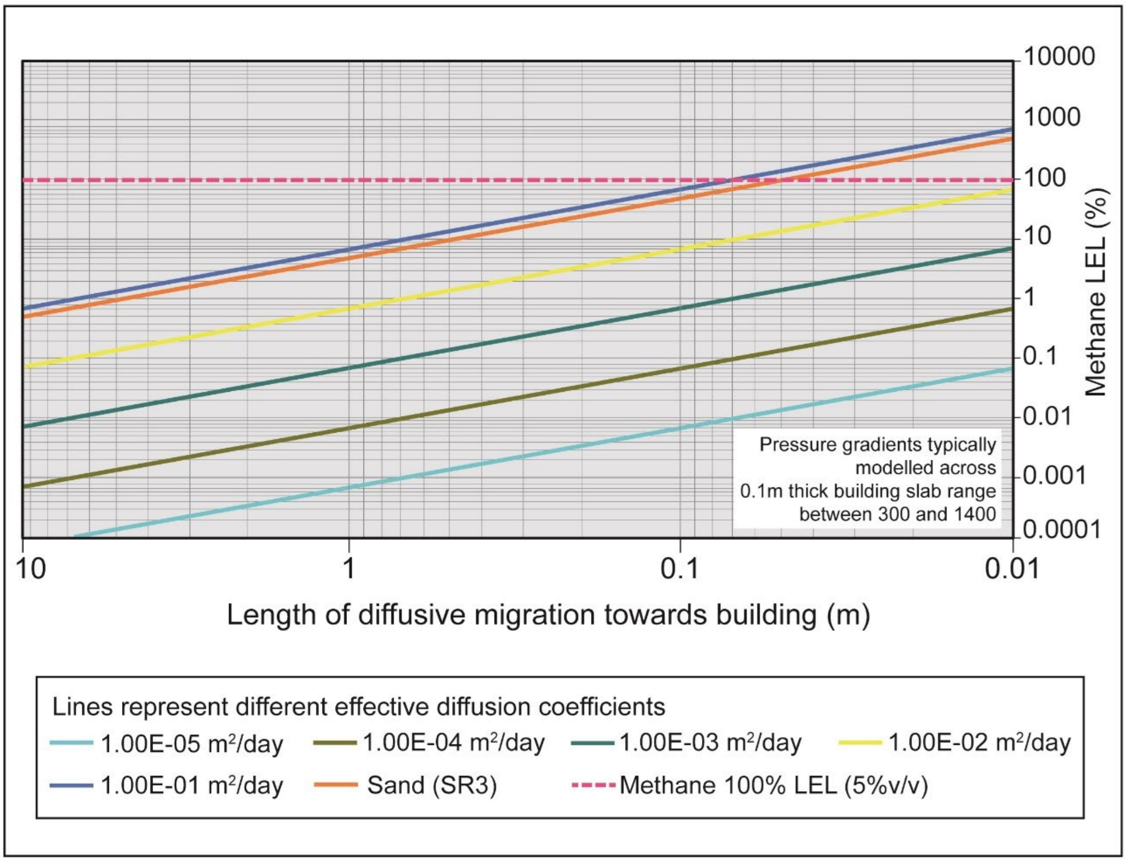


Figure A3.5: Methane indoor air concentration for diffusive dominated transport (Card *et al.*, 2019). SR3 refers to Contaminated Land Exposure Assessment (Environment Agency, 2009).

- The gas monitoring protocol for spot monitoring is particularly important. Peak flow rates and gas concentrations should be recorded at the start of monitoring and then at 1 minute intervals until steady values are achieved. Gas spot monitoring should be completed for 10 minutes for flow rates and a further 10 minutes for gas concentrations (or until steady flows or concentrations are recorded for more than 2 minutes). Gas monitoring instruments must measure all the principal permanent gases – methane, carbon dioxide and oxygen (CL:AIRE, 2021).
- Lines of evidence to appraise the risk from carbon dioxide and methane can be developed by performing various analyses on soil gas data (CL:AIRE, 2018; CL:AIRE, 2021). For example:
    - Assessing the vertical distance for diffusive transport between LNAPL and buildings and predicted indoor air concentrations (Figure A3.5).
    - Comparing soil gas flow rates and concentrations with weather data (in particular, air temperature and barometric pressure). Poor correlations indicate low potential for soil gas emission (i.e. diffusion dominated for which risks are unlikely to be realised).
    - Use of ternary plots to support characterisation of the ground gas regime and risk, in particular where only low concentrations of carbon dioxide and/or methane (compared to high-risk sources – landfill and mine workings etc.) have been recorded without elevated flow rates (i.e. diffusion dominated) (Wilson *et al.*, 2018).

  - Modelling and assessing gas migration rates through the ground using approaches in the Ground Gas Handbook (Wilson *et al*., 2009).

Potential effects of climate change

NSZD may be utilised as a risk-management strategy over periods of years to decades, rendering its resiliency susceptible to the potential effects of climate change. The Intergovernmental Panel on Climate Change (IPCC) predicts multiple environmental stressors that could impact NSZD processes, and therefore risks associated with LNAPL undergoing NSZD (IPCC, 2018; IPCC, 2021). Consideration of potential effects of climate change on the direct and indirect risks from LNAPL is therefore recommended.

Based on predicted global averages reported in IPCC (2018) and IPCC (2021), Cavelan *et al*. (2022) describes the critical effects on LNAPL mobility, partitioning and biodegradation of decreased summer precipitation (-23%), increased winter precipitation (+12%), greater extreme precipitation (+25% frequency, duration and intensity) and temperature rise (between 1.5°C and 5.4°C, +9°C locally). Rather than temperature, the most critical factor could be the development of more dynamic water table conditions in response to changing precipitation and recharge. While this may serve to smear and immobilise LNAPL in the unsaturated zone, high water table conditions may temporarily reduce the separation distance between LNAPL and receptors and increase dissolved-phase mass discharge through groundwater. Low water table conditions could temporarily increase vapour partitioning and biodegradation but onset of drought conditions may result in a reduction in biodegradation (e.g. Yadav and Hassanizadeh, 2011).

The potential effects of climate change on LNAPL risks are non-trivial and likely to be temporally variable. Ultimately, local factors will dictate outcomes of climate change, that will need to be assessed by qualitative judgement through to numerical modelling to support decision-making, depending on site conditions and the level of confidence sought by stakeholders for the long-term protection of receptors.

A3.4 Predicting NSZD Rates

NSZD rate prediction is valuable at various stages of the LNAPL CSM development to support decision-making regarding the feasibility, viability and long-term performance of NSZD, as well as helping design NSZD investigation and monitoring and establishing expectations for field measurements (API, 2017; crcCARE, 2018).

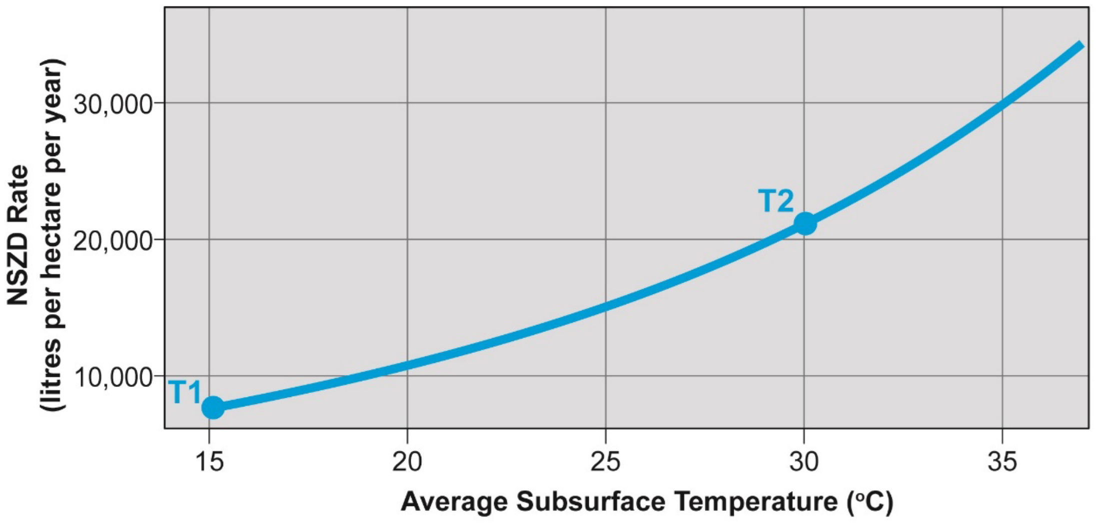
Quantitative assessment of NSZD can be performed using the following options, listed in increasing order of complexity:

- Screening-level assessment;
- Mass balance models;
- Analytical calculations; and
- Advanced modelling.

Depending on the level of confidence sought, a screening-level assessment could be performed based upon:

- Empirical data from multiple study sites or reviews cited in this document (e.g. Garg *et al*., 2017);

- Estimates from existing field measurements of relevant parameters, such as carbon dioxide flux or soil temperature (Figure A3.6), using available tools, such as the Concawe LNAPL Toolbox (Concawe, 2022); and/or
- Nomograms developed using parameter values that may be representative of ranges of site conditions with established theoretical analytical equations and assumptions. Examples of NSZD rate nomograms are provided by API (2017), Garg *et al*. (2017) and Ririe and Sweeney (2018) (Figure A3.7).



Answer:
NSZD Rate at Enhanced Temperature (T2):
21,210 (L/Ha/a)

Figure A3.6: Example application of the Concawe LNAPL Toolbox NSZD Temperature Enhancement Calculator to predict NSZD rate at a given temperature (T2) from a reference NSZD rate and temperature (T1) (Concawe, 2022). In this example, the NSZD rate at T1 (15°C) is 7,500 L/Ha/a and temperature at T2 is 30°C.

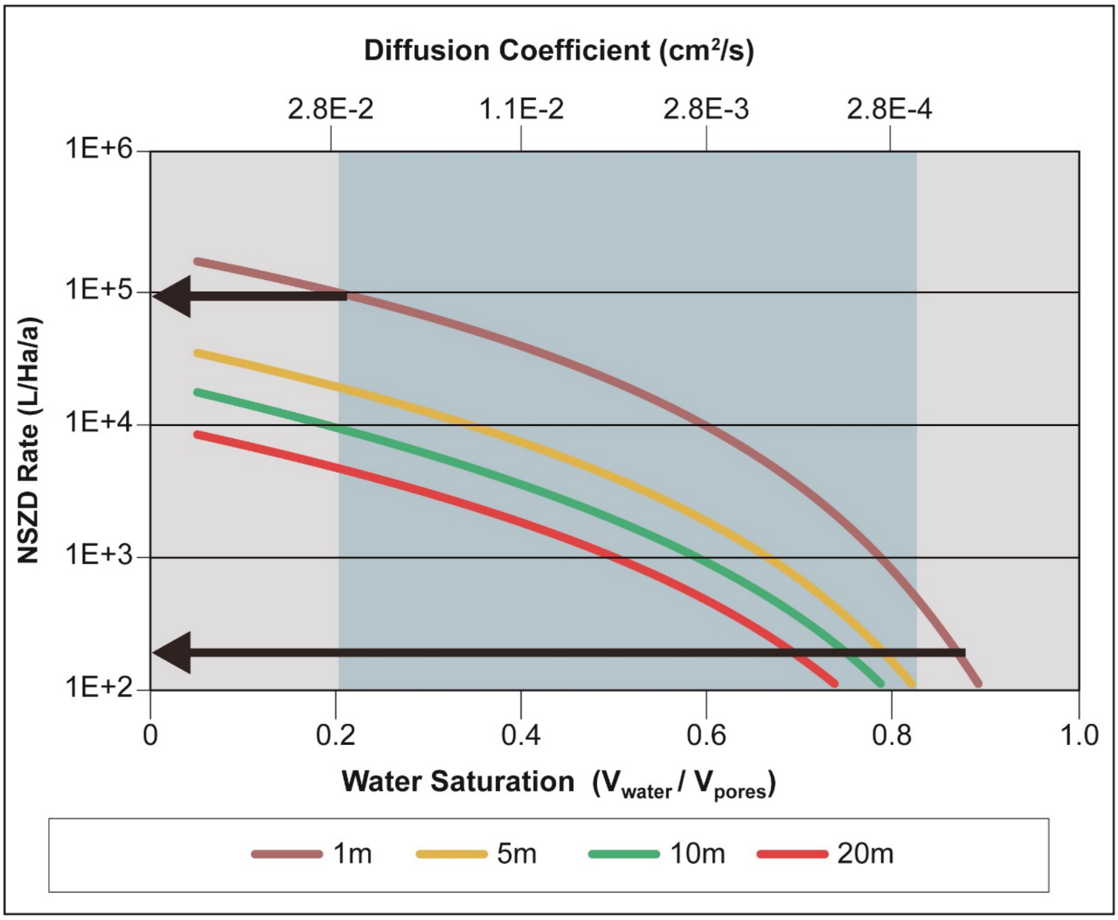


Figure A3.7: Example nomogram illustrating the maximum NSZD rate that can be measured without oxygen diffusion limitation, as function of soil moisture (after Garg *et al*., 2017). Typical water saturations for seven soil types ranging from sand to sandy clay are shown in light blue (0.2 to 0.82), and the resulting maximum NSZD rate shown by the black arrows (ranging from 200 to 100,000 L/Ha/a).

Quantitative interpretation of NSZD rates from site measurements of expressions of NSZD processes requires application of mass balance models and/or analytical models, such as those summarised by Sookhak Lari *et al.* (2019) and in Appendix 2:

- Mass balance models are site-specific 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, to give preliminary estimates of process rates (Johnson *et al*., 2006; Verginelli and Baciocchi, 2021) or to provide estimates of the longevity of LNAPL (Concawe, 2022).
- Analytical models are constrained by assumptions, such as homogeneity, isotropy, spontaneous reactions etc. While the subsurface rarely exhibits these assumptions, analytical models can still be relied upon to estimate NSZD rates where their limitations are acknowledged and the analysis is performed in a transparent and justified manner. The outcomes of analytical modelling may be sensitive to parameters that are inherently variable in the subsurface. Familiarity with the influence of these parameters and appropriate characterisation are pre-requisites to using analytical models to appraise uncertainties in estimated NSZD rates.

A principal objective of advanced modelling (e.g. Ng *et al*., 2015; Sookhak Lari *et al*., 2022) is to enable the future behaviour and performance of NSZD to be forecast with sufficient confidence to enhance understanding of the viability of NSZD as a long-term risk-management strategy. Prediction of long-term NSZD trends requires linking physicochemical partitioning and transport processes with bioprocesses at multiple scales within a modelling framework (Sookhak Lari *et al*., 2019). Such a framework should allow constraints on the future performance of NSZD to be assessed, similar to the application of groundwater and solute transport models to assess MNA (CL:AIRE, 2024). Advanced modelling requires considerably more data collection and site characterisation and should only be performed by practitioners experienced in the simulation of LNAPL transport and NSZD-type processes.

Currently available commercial models are inadequate to represent NSZD holistically (crcCARE, 2018). Sookhak Lari *et al*. (2019) reviewed critical processes that should be included in conceptual and mathematical models of NSZD. Amongst the 36 models evaluated, multi-phase multicomponent models had the strongest basis for future NSZD modelling but had rarely been used to study NSZD. A significant gap exists in upscaling micro-scale biological processes to the macro scale at which decisions concerning LNAPL sites are made. While it has been possible to link relevant microbial, geochemical and biodegradation processes within frameworks utilising multi-phase multicomponent models, potentially transient subsurface conditions remain challenging for long-term estimation of NSZD and LNAPL longevity (Sookhak Lari *et al*., 2019).

The emergence of digital twin approaches is promising for the simulation of NSZD for LNAPL sites. Digital twin refers to a comprehensive (physical and functional) description of a system, from which a digital representation of the system under study is developed. Sookhak Lari *et al*. (2022) used a multi-phase multicomponent multi-microbe non-isothermal approach to simulate NSZD at field scale. This approach successfully matched field data for soil gas and aqueous phase concentrations and soil temperature from the extensively studied LNAPL release at the Bemidji site (Essaid *et al*., 2011; Baedecker *et al*., 2018), enabling prediction of future NSZD performance. Advanced modelling has potential to enhance understanding of current and future expressions of NSZD (Figure A3.8) and provide critical information supporting decision-making for NSZD-based risk-management programmes at LNAPL sites.

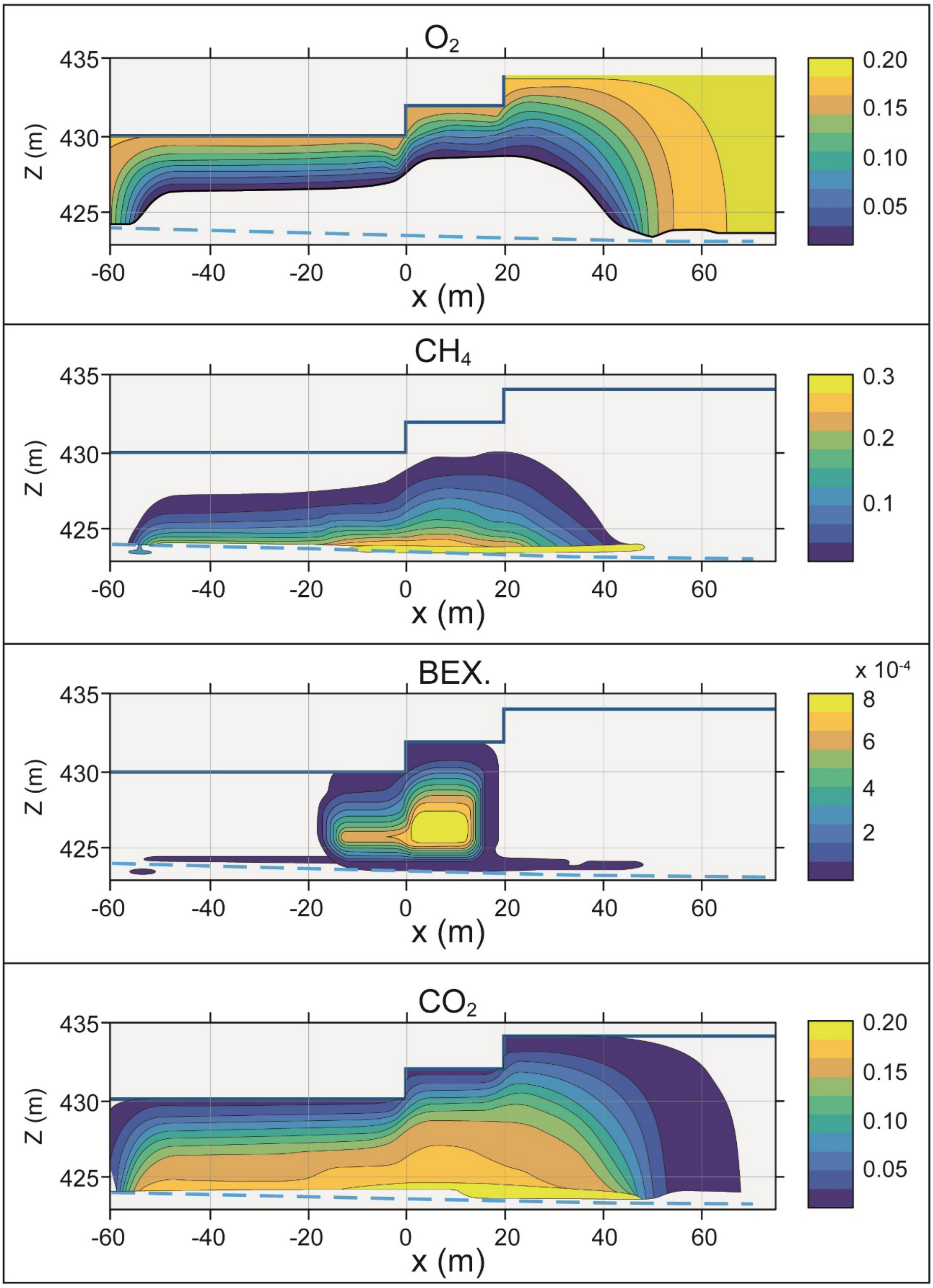


Figure A3.8: Depth section of the mole fractions of oxygen (O_2), methane (CH_4), carbon dioxide (CO_2) and BEX (benzene, ethylbenzene and xylene) in the gaseous phase at 27 years of simulation (Sookhak Lari *et al*., 2022). The upper blue solid line is the ground surface, and the blue dashed line is the water table.

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