Advances in the characterisation of sites contaminated with petroleum hydrocarbons: insights from a collaborative effort

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ABSTRACT

Petroleum hydrocarbons (PHCs) such as gasoline and diesel are among the most common and widespread contaminants in urban and industrial environments. The authors were engaged by the imprint Springer to complete a book giving visibility to technologies overcoming limitations associated with conventional characterisation approaches, as well as pertinent concepts and methods that may still be underutilised by the industry internationally. The open access book entitled 'Advances in the characterisation and remediation of sites contaminated with petroleum hydrocarbons' was prepared as a contributed volume involving the participation of more than 100 global experts from academia, government agencies, and the private sector. An analysis of the book contents yielded general insights into the state of the art regarding the investigation of PHC-impacted sites. As highlighted in several chapters, fate and transport of fuel products are controlled by multiphase flow mechanics and constitutive relations intrinsically linked to biological phenomena and the spatial and temporal variability of multiple subsurface properties. Most site characterization methods presented in the book (from direct-push vertical profiling and biogeophysics to sequence stratigraphy or molecular biological tools) address aspects often overlooked in conventional site investigation projects, including: (i) the entrapment of fuel products due to capillary forces, (ii) the essential role played by microbial activity, and (iii) subsurface heterogeneity effects. Further research and adoption of up-to-date concepts and methods are encouraged to ensure best practices are implemented and PHC risks are managed sustainably and responsibly.

Keywords: biogeophysics; contaminated site characterization; laser-induced fluorescence logging; spatial variability.

1. Introduction

Petroleum hydrocarbons (PHCs) such as petrol (gasoline) and diesel are among the most common and widespread contaminants in urban and industrial environments (Johnston 2010). PHCs commonly reach soil and groundwater systems following accidental spills and leaks from storage tanks and pipelines that sometimes go unnoticed for years.

Crude oil and most refined PHC products are complex mixtures of predominantly non-polar organic chemicals (Alden et al. 2023). Due to their toxicity and, in the case of some compounds, carcinogenicity, PHCs can pose risks to the environment and exposed populations (e.g., chronic human health risks associated to frequent inhalation of vapours or drinking contaminated water) as well as potential damage to a business' reputation or real estate development opportunities, among others. Natural attenuation mechanisms like biodegradation often contribute substantially to mitigate these risks (Verginelli 2023), but costly remediation and management strategies are still required in many sites.

Hydrocarbon fuels are relatively immiscible with water and typically remain as non-aqueous phase liquids (NAPLs) in the subsurface, where they can persist as a source of contamination for decades. Most fuels are lighter-than-water NAPLs (LNAPLs). Partitioning mechanisms such as dissolution and volatilisation can increase the mobility of these contaminants and facilitate the creation of complete exposure pathways or the migration of PHC mass beyond a site's boundaries.

In soil and groundwater systems, NAPLs coexist with water and soil gas (Lenhard and García-Rincón 2023). The distribution of NAPL mass in this multiphase system is complex due to the heterogeneous nature of these environments and the multiple processes involved in NAPL fate and transport, some of which are depicted in Fig. 1. Since NAPL architecture may vary radically between sites and across geological settings (CL:AIRE 2014), detailed site characterisation is paramount for making informed management decisions and for the design of effective remediation plans.

Nevertheless, conventional site investigations have commonly consisted of collecting a limited number of physical samples for subsequent laboratory analysis, which generally does not suffice to capture the

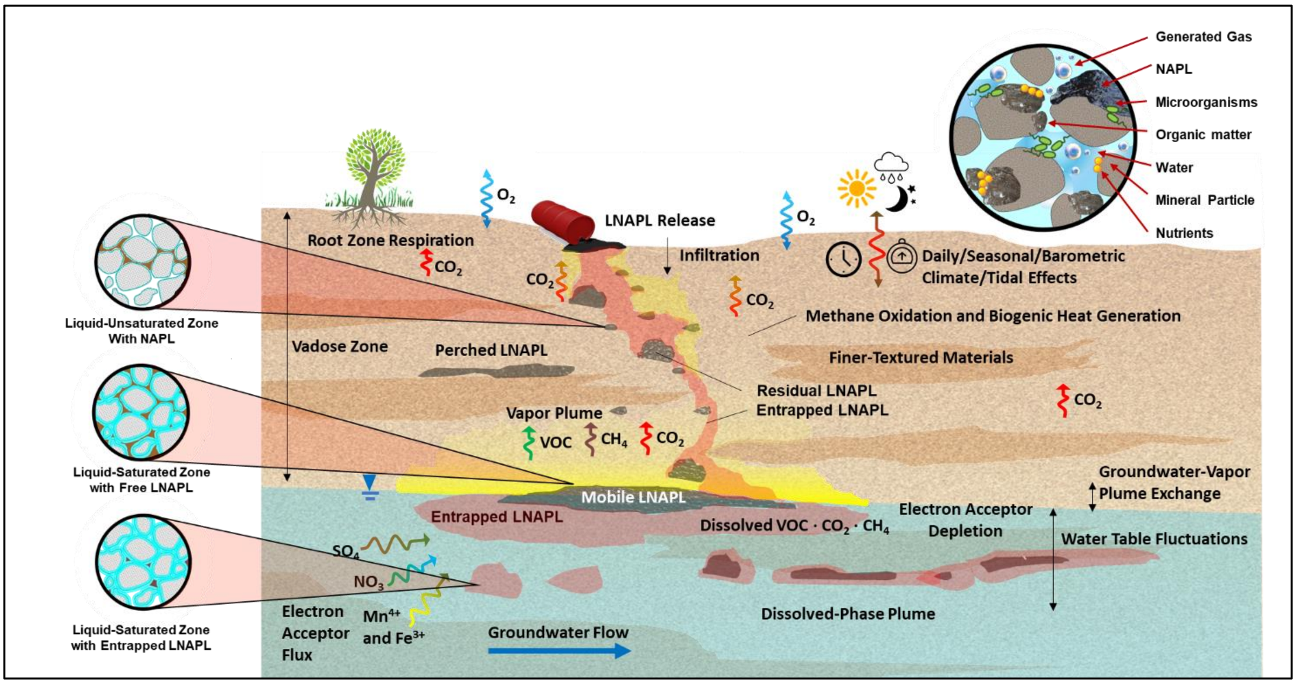

Figure 1. Conceptualisation of LNAPL distribution, fate, and transport processes following a point release (Alden et al. 2023).

subsurface heterogeneous conditions (Sadeque and Samuels 2023) and often leads to poor conceptual site models and ineffective remediation designs. As a result, multiple advances have been done in the field of contaminated site characterisation to better address these challenges.

In this context, the authors were engaged by the imprint Springer to complete a book giving visibility to technologies overcoming limitations associated with conventional characterisation approaches, as well as pertinent concepts and methods that may remain underutilised by the contaminated land industry internationally. The objective of this paper is to summarise some of the key findings from this collaborative effort.

2. Advances in the characterisation and remediation of sites contaminated with petroleum hydrocarbons

The open access book entitled ‘Advances in the characterisation and remediation of sites contaminated with petroleum hydrocarbons’ (García-Rincón et al. 2024) was completed as a contributed volume consisting of 18 chapters written by authors from industry and academia. It complements other works presenting the fundamentals of PHC and/or NAPL fate and transport (e.g., Corey 1994; Johnston 2010; CL:AIRE 2014; ITRC 2018) or characterisation and remediation methods for other contaminants like chlorinated solvents (Kueper et al. 2014).

The book chapters can be roughly divided in three sections: chapters 1–6 primarily addressed understanding and analysing the subsurface behaviour of PHCs; chapters 7–11 were dedicated to site investigation technologies; and chapters 12–18 focused on site management strategies. Future lines of research and best practices were suggested throughout the book.

The site investigation methods presented in the book included improved stratigraphic interpretation methods based on sequence stratigraphy (Sadeque and Samuels 2023), field technologies providing high-resolution data like direct-push profiling tools (Liu et al. 2023; St. Germain 2023) or biogeophysics (Atekwana et al. 2023), and techniques useful in the assessment of biodegradation processes such as natural source zone depletion (NSZD) methods (Karimi Askarani, Sale, and Palaia 2023), molecular biological tools (Taggart and Key 2023), and compound-specific isotope analysis (Bouchard, Sueker, and Höhener 2023).

An analysis of the book contents yielded insights into the state of the art regarding the investigation of sites contaminated with PHCs. More specifically, the site characterisation methods presented in the book addressed aspects frequently overlooked in conventional site investigations, including: (i) the entrapment of NAPL mass occluded by water due to capillary forces, (ii) the importance of NSZD and other biodegradation processes, and (iii) the spatial variability of subsurface and contaminant properties.

3. Key findings

3.1. Delineating entrapped and residual LNAPL

As depicted in Fig. 1, following a release of LNAPL into the subsurface, the LNAPL migrates downwards in the unsaturated zone or laterally as it encounters capillary barriers. If sufficient LNAPL volume is released, it can reach the water saturated zone and laterally spread with limited invasion below the water table due to buoyant forces.

LNAPL redistribution occurs due to factors like water table fluctuations inducing LNAPL mass to migrate vertically or to become practically immobile. In the case of a decreasing water table, part of the LNAPL mass moves downward while some residual LNAPL may be retained in the form of films or wedges. In the case of a rising water table, some LNAPL migrates upward while other LNAPL mass becomes entrapped (occluded by water and disconnected from the rest of the LNAPL body because of the action of capillary forces). Consequently, LNAPL may exist trapped metres below current water table elevation levels and will not enter monitoring wells. Mobile LNAPL may also become confined and remain located metres below the potentiometric surface. However, collecting samples only in the vadose zone and using monitoring wells screened at the top of the saturated zone is a common practice in many conventional investigations at sites contaminated with PHCs.

As illustrated in Fig. 2, direct-push profiling technologies like laser-induced fluorescence (LIF) logging as well as traditional geophysical methods can take advantage of PHC properties (for instance, the fluorescence of certain PHC molecules contained in petroleum LNAPLs in the case of LIF) to find and delineate LNAPL in either free, residual or entrapped forms even if in a qualitative/semi-quantitative fashion.

By collecting in-situ data, direct-push profiling methods may also overcome limitations of conventional soil sampling methods like contaminant loss, redistribution during sample retrieval or poor core recovery (depicted at the 'E' depth interval in Fig. 2). Adequate interpretation of LIF data must rely not just on fluorescence intensity measurements, but also on the analysis of the multi-wavelength waveforms and lifetime data recorded by the system. This enables differentiation between LNAPL and materials naturally fluorescent (e.g., calcite) as shown in Fig. 2 at the 'D' depth interval.

As discussed by Lenhard and García-Rincón (2023), an analytical model has also been developed to predict free (mobile), residual, and entrapped LNAPL saturation values based on historical and current in-well water and LNAPL levels, porous medium properties, fluid properties, and retention parameters, although the later are often not measured in field investigations despite controlling the resulting LNAPL distribution to a great extent.

3.2. Investigating microbial activity effects

Microbial activity plays a crucial role in PHC-contaminated sites by degrading PHC compounds to less toxic substances and reducing risks. By changing the contaminant composition and by depleting PHCs, biodegradation may also influence the contaminant physical properties controlling its transport and behaviour. Furthermore, microbial activity may change properties in the porous medium and its byproducts can influence certain field measurements.

Biodegradation may occur under aerobic and anaerobic conditions ranging from nitrate reducing to methanogenic. In particular, the significance of methanogenesis has been increasingly recognised over the years and now it is typically accepted that NSZD mechanisms like methanogenesis and direct outgassing from the LNAPL body may substantially exceed the depletion rates corresponding to natural attenuation

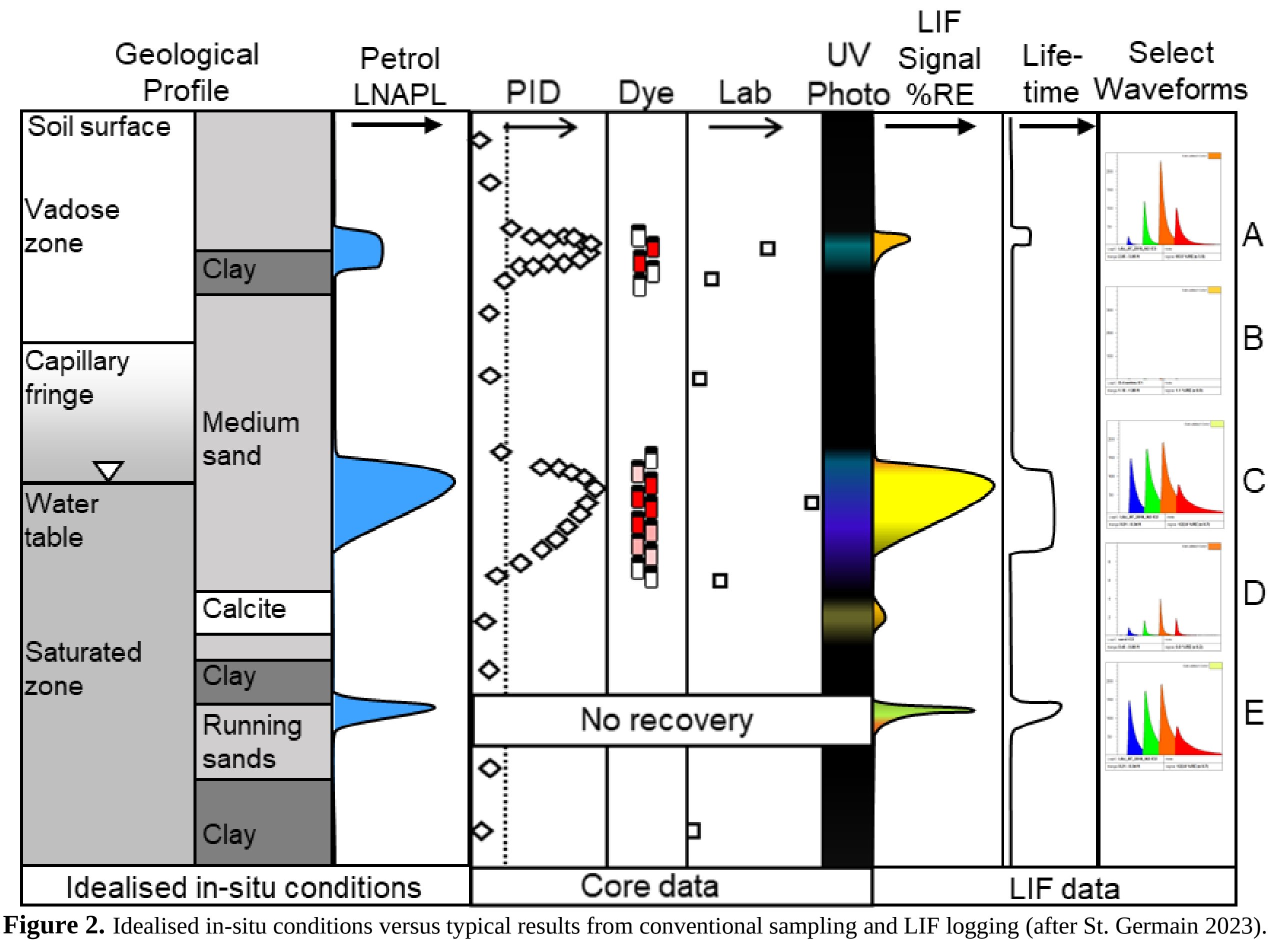

Figure 2. Idealised in-situ conditions versus typical results from conventional sampling and LIF logging (after St. Germain 2023). PID: photoionisation detector; UV: ultraviolet; LIF: laser-induced fluorescence; RE: reference emitter.

phenomena in the aqueous phase and sometimes also exceed the depletion rates achieved with active remediation systems. In a few sites, NSZD estimates recorded during decades suggested that NSZD rates are variable in space and time, revealing the need for more long-term monitoring studies.

Multiple methods have been specifically designed to estimate NSZD rates, including soil gas methods (e.g., passive CO_2 flux traps or dynamic closed chambers) and temperature-based methods. The popularity of molecular biological tools and compound-specific isotope analysis for the purposes of demonstrating the occurrence of biodegradation and assessing remediation performance has also growth over the years.

Furthermore, the influence of biodegradation processes in geophysical signatures (by changing the pore fluid chemistry via enhanced dissolution, altering the properties of solids via mineral precipitation or influencing the overall microbial activity) has led to the development of the field of biogeophysics. An example of this influence is the conductive response sometimes observed in sites contaminated with weathered LNAPL instead of the resistive response that could be expected given the LNAPL properties. The impact of NSZD phenomena can also be seen in measurements from other methods like LIF, where the LNAPL fluorescence characteristics may dramatically change depending on the LNAPL type and weathering degree.

3.3. Addressing spatial variability

The importance of subsurface heterogeneity in contaminant fate and transport cannot be overstated. Addressing the spatial variability of all the relevant parameters influencing LNAPL behaviour in a site must start with a good understanding of the geological environment, with facies analysis and sequence stratigraphy rising as improved methodologies (in contrast to layer-cake model simplifications) for predicting the large-scale distribution of preferential pathways and fine-textured areas potentially acting as capillary barriers or confining layers. At smaller scales, heterogeneity governs LNAPL behaviour too as shown by Alfaro Soto et al. (2023) for multimodal scenarios.

Collecting data at appropriate scales through high-resolution site characterisation (HRSC) techniques can also improve the development of conceptual site models and site management strategies while avoiding pitfalls frequently encountered during conventional site investigations. As shown Fig. 2, the number of soil samples collected for laboratory analysis is typically low, which complicates the detection of contamination hotspots and the accurate calculation of risk values. This issue can be mitigated by obtaining multiple lines of evidence and by embracing high-density sampling designs, although at a lower productivity than using direct sensing technologies like LIF.

As in the case of cone penetration testing and other direct-push profiling methods, the LIF system provide real-time results, enabling adaptive field plans to be developed. This may contribute to better determine the logging locations depending on the variability of the subsurface properties of interest observed on site.

4. Conclusions

Despite the numerous advances observed in the field of contaminated site characterisation, many practitioners still rely on conventional methods that cannot adequately delineate subsurface contaminant distributions nor capture the spatial variability of hydrogeological and contaminant properties. Improved understanding of aspects like multiphase flow mechanics, microbiological processes, and subsurface heterogeneity effects have contributed to more confidently assess and manage PHC-impacted sites, but methodologies often recognised as best practice by government agencies (e.g., sequence stratigraphy or HRSC) are still seldom implemented in the field compared to the ubiquitous installation of monitoring wells and the collection of sparse soil samples in the vadose zone.

Future needs include the development of methods improving the quantification of subsurface properties at appropriate scales in the vertical and horizontal planes, the adoption of remote systems to enhance the monitoring of site dynamics, and the integration of non-deterministic and data-driven methods to honour site investigation uncertainties.

Further research and adoption of up-to-date concepts and methods are encouraged to ensure best practices are implemented and PHC risks are managed sustainably and responsibly.

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