
Oral Presentation:

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ABSTRACT

Soil-vapour sampling protocols associated with petroleum-hydrocarbon release sites often ignore the value that an evidence-based assessment of natural attenuation can provide to data evaluation and interpretation. The author’s experience is that minimalistic approaches, whereby soil-vapour is collected only for quantification against standardized volatile organic compounds (VOC) analytical spectrums, is typical of industry practice. This approach, whilst allowing interpretation of human-health exposures associated with vapour inhalation, significantly limits interpretation of naturally occurring biologically-driven attenuation processes. Where monitored natural attenuation (MNA) forms part of the long term remedial strategy for a contaminated site, an understanding of the degradative processes occurring can be particularly valuable. General gas data can assist in the determination of areas where naturally occurring biodegradation is occurring, and the specific breakdown mechanisms favoured within areas under investigation. The authors have come across specific instances where the sub-surface concentration of methane and oxygen have been such that mixing of this soil-vapour with ambient air may potentially lead to explosive gaseous mixtures. As the risk associated with methane in the presence of other flammable gases is unknown, inclusion of general gas analysis in soil vapour sampling assessment offers dual value, by identifying potential risk, and providing data for interpretation of natural attenuation processes occurring.

A review of general gas data across 24 sites has identified that the maximum methane concentration detected in soil vapour samples exceeded the Lower Explosive Limit (LEL, 5%vol) at over a third of the sites. A review was undertaken to identify whether parameters typically assessed at contaminated petroleum sites may be useful for identifying problematic sites. The review included the comparison of methane concentrations with; presence of light non-aqueous phase liquid (LNAPL), the inferred groundwater velocity, surface covering, vadose zone lithology and air porosity, and the depth to groundwater.

INTRODUCTION

As mirrored in North America and Europe, the collection and interpretation of soil-vapour samples in Australia to assess potential human-health risks associated with volatile organic compounds (VOCs) by means of vapour inhalation exposure pathways, is shifting from a niche area of expertise to mainstream site assessment practice. This progression has been
propelled by increasing acceptance by clients, regulators and auditors, and consequently in Australia there has been a growth in practitioners collecting and interpreting soil-vapour samples. In the absence of Australian regulatory guidance, the result of increased soil-vapour assessments has been greater disparity in the breadth of work scopes, the quality of fieldworks and data interpretation amongst practitioners.

The contaminated-land assessment industry in Australia is a highly competitive, cost sensitive marketplace, and as such, it is typical of consultants to scope works which are minimalistic at best to win work. Given the relative expensiveness of soil-vapour assessments, when compared to soil and groundwater assessments, and the infancy of soil-vapour assessment in Australia, the minimalist approach exacerbates the data quality. Typically, samples collected at single depth and broad-spectrum VOC analysis are the extent of the assessment scopes, whilst ‘practitioners’ routinely ignore quality assurance (QA) protocols (such as tracer testing), and bioattenuation markers such as methane, carbon dioxide and oxygen at petroleum-release sites, and ethane and ethylene where contaminants of potential concern (COPC) are chlorinated compounds.

**Natural Attenuation of Petroleum Hydrocarbons**

Natural attenuation refers to any naturally-occurring process in soil and/or groundwater environments that acts without human intervention to reduce the mass, toxicity, mobility, volume or concentration of contaminants in those media. These in-situ processes include biodegradation, dispersion, dilution, sorption, volatilisation, and chemical or biological stabilisation or destruction of contaminants.\(^\text{20}\)

Primary lines of evidence for natural attenuation (i.e. observed reductions in impact geometry and contaminant concentrations) can be determined through periodic sampling of soil-vapour analyte concentrations over time. This approach is considered to be more conclusive than secondary lines of evidence, as assessment objectives are generally framed around health risks arising from exposure to COPCs. However, an assessment based solely on primary line of evidence requires successive rounds of sampling. Multiple sampling events are costly, and this data cannot be used to interpret which, if any, sub-surface biological processes are driving the reduction in contaminant mass, and the extent to which the processes are occurring.

Secondary lines of evidence for natural attenuation can be established through evaluation of geochemical indicators of the biodegradation processes. These techniques are useful for evaluating the occurrence and extent of biodegradation of petroleum hydrocarbons, one of the primary mass removal processes contributing to natural attenuation. In general, biodegradation follows an order of favourable electron acceptor availability (\(\text{O}_2 > \text{NO}_3^- > \text{Mn}^{4+} > \text{Fe}^{3+} > \text{SO}_4^{2-} > \text{CO}_2\)), due to the decreasing amount of energy gained by the micro-organism through the reduction of these compounds.

Manganese (\(\text{Mn}^{4+}\)), nitrate (\(\text{NO}_3^-\)), ferric iron (\(\text{Fe}^{3+}\)) and sulphate (\(\text{SO}_4^{2-}\)) are non-volatile, and thereby cannot be measured in soil-vapour. However, oxygen (\(\text{O}_2\)), carbon dioxide (\(\text{CO}_2\)) and methane (\(\text{CH}_4\)) can be measured as these analytes are gaseous at standard temperatures and pressures. Although intermediate steps form the progression from aerobic to anaerobic
conditions, via the reduction of nitrate, manganese, ferric iron and/or sulphate, an assessment of biodegradative process can be conducted through comparison of oxygen and carbon dioxide concentrations in soil-vapour sample. Furthermore, a comparison of carbon dioxide and methane concentrations can also be used to determine whether the biodegradation of petroleum is producing electron acceptors (carbon dioxide) and electron donors (acetate and hydrogen) required for methanogenesis. Although methanogens do not directly utilise the majority of compounds that constitute petroleum hydrocarbon, the production of methane indicates that biodegradation via other micro-organisms, predominantly bacteria, is occurring in the vicinity of petroleum hydrocarbon impacts at the site.

General gas samples collected from co-located sample points installed at a site in Northern Queensland demonstrate the information which can be sourced from the collection of natural attenuation indicators (Figure 1).

Figure 1. General gas data from 3 depths

Particular attention should be paid to changes in carbon dioxide concentration with depth, especially the increased evidence of degradation shown by carbon dioxide in the sub-slab sample point. When taken in conjunction with the increased oxygen concentration, assumed to be associated with the operation of an air conditioning system within the building, this data suggests that significant aerobic degradation is occurring beneath the slab.

A confounder to the interpretation of bioattenuation at petroleum-hydrocarbon release sites is the potential microbiological interaction of oxygen and methane, especially in near-surface environs. In the presence of oxygen, methane can be an energy source for methane utilising bacteria, known as methanotrophic bacteria. However, as shown in Figure 1 above, elevated carbon dioxide concentrations may serve as a marker for biodegradation. As higher concentrations of methane were detected deeper within the sub-surface profile, and concentrations decrease closer to the ground surface, the biological processes occurring are likely to include both the degradation of residual petroleum hydrocarbons, and also oxidation of methane via methanotrophic bacteria.

The authors stress that identification of methane in the sub-surface coexisting with volatile petroleum hydrocarbons is not indisputable evidence for methanogenesis associated with the secondary source. Lundegard et al. demonstrated using carbon isotopes that the significant majority of methane measured at a site in Seattle, Washington, was associated with the natural breakdown of lake sediments and wood debris. The authors have used analysis for mercaptans and ethane/methane ratios in soil-vapour to establish that elevated methane
reported at a petroleum release site in Melbourne, Victoria, was associated with a leaking gas main immediately adjacent to the site, and not as a result of petroleum hydrocarbon degradation. This case study presented in Table 1.

**Potential Explosibility**

Whilst the presence of methanotrophic bacteria may introduce complexity into the interpretation of secondary lines of evidence, the concurrence of oxygen and methane in the sub-surface at certain ratios can prove problematic. Methane-oxygen mixtures with methane concentrations as low as 5% vol (lower explosive limit (LEL)) can produce explosive, or potentially explosive (where mixed with ambient air) environments under particular conditions. A graphical presentation of this relationship is presented in Figure 13-1 of Kissell which incorporates the potential explosibility of oxygen-methane mixtures when diluted with atmosphere. However, the relationship is an exclusive prediction of explosibility of oxygen and methane mixtures, and does not take into account potential enrichment associated with the other volatile chemicals such as a petroleum hydrocarbon source.

Whilst potential explosive risks are generally incorporated into site occupational health and safety (OH&S) protocols at petroleum-release sites (e.g. use of LEL field meters), where the primary source is combustible (e.g. distillate) rather than flammable (e.g. gasoline), the likelihood of potentially explosive gas/vapour mixtures may be underrepresented as the potential additivity of methane from bioattenuation is not considered.

This article considers soil-vapour secondary lines of evidence for bioattenuation (general gases) collected from 24 separate petroleum-release sites across Australia. The sample point construction at each site was specific to the data quality objectives (DQOs) for the specific assessment however all sample points were permanent constructs so as to permit confirmatory sampling rounds where needed. Sample investigation points range from discrete or nested configurations within soil-bores to sub-slab sample points.

**EXPERIMENTAL METHODS**

**Sample Point Construction**

Installation protocols described by API, NJDEP, and NYSDOH were adopted for the installation of permanent discrete or nested soil-vapour sample points, while for permanent sub-slab soil-vapour sample points, installation protocols described by DiGiulio et al. and DTSC were adopted.

**Minimum Soil-vapour Sample Depths**

Where technically feasible soil-vapour sample points were installed at a minimum depth of 1.5m below ground surface (mbgs) in accordance with USEPA guidance. Exceptions to the minimum sample depth of 1.5mbgs occurred as a result of site-specific limitations including shallow groundwater and auger refusal on bedrock.

Where the minimum sample depth of 1.5mbgs could not be achieved, additional sample collection protocols were adopted to minimise the potential for atmospheric drawdown. NYSDOH provides guidance for sampling soil-vapour from shallow sample depths provided
that appropriate construction and sampling procedures are undertaken. As such, further to helium tracer shroud testing at each sample location (see below) which tests sample point integrity, sample volume limits described by ITRC were also incorporated into the sampling methodology.

Based on protocols described in ITRC for near-surface sampling of soil-vapour, a limit of 1L of soil-vapour was permitted to be extracted from the sample point during sample collection on any one day. To achieve this sampling requirement, the collection of soil-vapour was typically split across two days where general gases samples were collected on the first day of sampling at each sample point, while VOCs were collected from each sample point on the following day.

**General Gas Sampling Procedures**

**Collection of General Gas Soil-vapour Samples**

General gas soil-vapour samples collected at all sample points within this assessment were collected into a 3L Tedlar bag using a vacuum chamber. Note that at least two days was permitted between sample point installations (which is the equilibrium time described by DTSC & CRWQCB for augured locations) and sample collection.

Sample flowrates during the collection of soil-vapour samples did not exceed 200mL/min which is in accordance with NJDEP. Furthermore, vacuum pressure during sample collection within the sample increment did not exceed 100-inches-of-water as vacuum pressures greater than this limit can upset partitioning to soil-vapour (API) and there is the potential that moisture may be entrained through the Teflon tubing.

The purpose of using a vacuum chamber, also known as a lung-box, was so that field pumps would not come into contact with the samples and thereby reducing the potential for sample cross contamination during sample collection.

Duplicates were collected at a ratio of at least 1-per-10 to assessment the sample reproducibility. The significant majority of relative percent differences (RPDs) were within the range considered acceptable by the American Public Health Association for VOCs.

Upon collection of the general gas sample, the Tedlar bag was stored out of direct sunlight and submitted to the analysing laboratory for analysis within 48-hours. The analysing laboratory utilised for all samples within this assessment was Leeder Consulting Pty Ltd. Samples were analysed using gas chromatography (GC) coupled with thermal conductivity detectors in accordance with laboratory method MA-1105.

General gas concentrations were reported in %vol ranges. The level of reporting (LOR) for the petroleum-hydrocarbon natural attenuation indicators are listed below.

- Carbon dioxide – 0.01%vol.
- Methane – 0.1%vol.
- Oxygen – 0.1%vol.
**Helium Tracer Shroud Testing (Quality Control)**

Helium tracer shroud quality control testing was undertaken at all sample points during the collection of general gas samples. This testing involves establishing a helium-rich atmosphere above each sample point prior to collection of a soil-vapour sample. The soil-vapour sample was then extracted whilst the helium tracer was continually being injected beneath the shroud at the surface. Helium was included as an analyte in the laboratory analytical analysis to quantify the level of surficial leakage (atmospheric drawdown) during sample collection. All sample points used within this assessment reported leakage levels below the trigger levels recommended by NYSDOH.

**RESULTS**

A statistical analysis of the dataset, which comprises information from all 24 petroleum hydrocarbon release sites, was undertaken to identify relationships between parameters typically recorded during site assessment and elevated methane concentrations. Sites where the source of methane was shown to not be related to a petroleum hydrocarbon release, such as the case study presented in Table 1, were not included in the dataset.

All statistical analysis was done using Minitab 16. For data sets including non-detect values, analysis was undertaken using publicly available macros specifically written for environmental data (www.practicalstats.com/nada).

In total, data from 203 sampling points across 24 sites was used in the analysis. Where noted, analysis was subsequently limited to the 142 sampling points where detectable concentrations of petroleum hydrocarbons were also reported. Methane was detected in 3 sampling points (0.02%, 0.03% and 3.9%) where petroleum hydrocarbons were below the level of detection. As impact was noted in adjacent or deeper sampling points at the same location, it has been assumed that the methane detected at all sites included in the dataset is due to the presence of petroleum hydrocarbon impact rather than degradation of organic material endogenous to the site.

**Ground Cover**

A statistically significant relationship was found between the presence/absence of hardstand surface coverage and methane concentrations, Figure 2 (P value of 0.02, non-parametric Mann-Whitney Test). Where samples have been collected beneath open ground, the likelihood of methane concentrations in excess of the LEL, is significantly reduced. Conversely, where soil-vapour samples have been collected beneath hardstand, there appears to be an increased probability of elevated methane concentrations. Interestingly, the average methane concentration beneath paved surfaces (concrete) was between that for sub-slab and open ground, and was not statistically different to either of the other ground covers.
Vadose Zone Lithology

To investigate whether there was a relationship between vadose zone soil-type and methane concentrations, the maximum methane concentration for each site for different lithologies was compared, Figure 3. Whilst the dataset is not sufficiently broad enough to capture all soil-types, the analysis identified that the likelihood for methane concentrations in excess of the LEL is increased in highly porous soil-types typically classified as sand compared to porous fractured rock (P=0.04, 2-sample t-test). Four of the seven sites classified as sand recorded methane concentrations above LEL, compared to none of the seven sites classified as porous fractured rock. The average methane concentration in clay was less than half that reported in sand, however there was insufficient evidence to confirm that the difference was statistically significantly.
Petroleum Hydrocarbon Soil Vapour Concentrations

Regression analysis was undertaken to identify whether the maximum petroleum vapour concentrations at each site were a predictor of maximum soil vapour methane concentrations (Figure 4a). Although not statistically significant ($P = 0.056$), as logic dictates, the results suggest that the presence of petroleum hydrocarbons in soil vapour may be indicative of methane concentrations under certain, yet to be defined, circumstances.

When methane concentrations from individual samples were compared to petroleum hydrocarbon concentrations (Figure 4b), a statistically significant correlation was found ($P<0.001$). The low coefficient of determination (R-Squared) however indicates that actual petroleum hydrocarbon concentrations are unlikely to be able to be used to accurately predict methane concentrations.

![Figure 4a. Maximum Petroleum Hydrocarbon vapour concentrations vs Methane](image)

![Figure 4b. Petroleum Hydrocarbon vapour vs methane - all sampling points](image)

Depth to Groundwater

The authors also investigated via regression analysis whether a relationship could be found between methane concentrations and depth to groundwater (Figure 5).

![Figure 5. Distance to Water vs Maximum Methane Concentration](image)
A statistically significant correlation was found ($P = 0.007$), between depth to water and methane concentrations, however, as for petroleum hydrocarbon concentration data, the poor coefficient of determination suggests that actual value is a poor predictor of exact methane concentrations.

The potential relationship between methane concentrations, seepage velocity and vadose zone air porosity was also investigated; however no statistically significant relationships could be confirmed. It is noted that the data for these two parameters relied heavily on literature values rather than field derived data. With site-specific data, the significance of these potential associations may become more relevant.

Interestingly, the presence of LNAPL also showed no significant correlation with methane concentrations, with the average methane concentration very similar for sites with LNAPL and dissolved phase impact (Figure 6).

Methane and oxygen concentrations for the sites investigated in this assessment were overlain on Figure 13.1 of Kissell, ‘relation between quantitative composition and explosibility of mixtures of methane and air’ (Figure 7).
The graphical relationship confirms that a number of sample locations potentially have methane-oxygen concentrations which lie within the ‘capable of forming explosive mixtures with air’ range and at least one sample point (which was from a shallow soil-vapour sample) potentially lies within the ‘explosive’ range.

DISCUSSION

The data from 24 petroleum release sites around Australia has identified at least four potential site-specific relationships which may contribute to an increased likelihood of elevated methane concentrations due to biodegradation of petroleum hydrocarbon impact. The four site-specific factors identified were petroleum soil lithology, surface covering, hydrocarbon vapour and depth to groundwater. Other elements, including seepage velocity and vadose zone air porosity, which logically may also be expected to affect the generation of methane generation, were not statistically significantly correlated with methane concentrations. The use of predominantly literature based values for these parameters in the current analysis may potentially be obscuring any relationship (only 8 of the seepage velocities values were based on field derived data, and two of the vadose zone air porosities). Future in depth characterisation of the sites involved may assist in clarifying the importance of these parameters in methane generation.

The observation that increased methane concentrations are associated with the presence of hardstand over petroleum hydrocarbon impacted areas is interpreted by the authors to most likely be associated with that lack of recharge of oxygen into the sub-surface. When compared to open ground, a hardstand covering over an impacted area has the potential to substantially reduce infiltration of oxygen thereby potentially favouring anaerobic biological activity. In addition to possibly providing an environment favourable to methanogenesis, assuming moisture is also present, the lack of oxygen would also be expected to limit the oxidation of methane by methanotrophs. In the absence of oxygen, attenuation of methane would therefore be limited to advection and diffusion. Predictive modelling of sub-surface oxygen concentrations by Abreu & Johnson, along with oxygen and carbon dioxide field measurements published by Patterson & Davis, and Lundegard, support this potential mechanism.¹,¹⁸,¹¹

The observation that methane concentrations correlated with particle size, and that sandy lithologies correlated with the highest methane concentrations, initially appears counter-intuitive. We hypothesise that the association of heightened soil permeability with elevated methane concentrations may be due to the ratio of vertical migration to lateral migration of vapours. In a highly permeable substrate, the vertical migration rate may be such that the residence time of methane in the oxygenated section of the vadose zone, where methane oxidation can occur, may be limited. This hypothesis, based on decreased residence time in an aerobic zone, would also to an extent be consistent with the observed inverse correlation between depth to water and methane.

The finding that increased methane concentrations correlated with petroleum hydrocarbon vapours is not unexpected. The larger the hydrocarbon mass present, the greater the demand
for electron acceptors, and the more likely that strongly reducing anaerobic conditions where methanogenic substrates; CO₂ and hydrogen, are being produced are present.

The poor coefficient of determination (r²) noted in all regression analysis, suggests that a simple numeric equation to estimate the likelihood of significant methane concentrations (>5%vol) is unlikely to exist. The lack of quantitative certainty is not unexpected given the variable nature of environmental sampling. However, the identification of statistically significant correlations between four commonly measured parameters and methane concentrations, indicates that it may be possible to develop a risk matrix to identify sites were sampling for methane may be warranted.

The methane-oxygen concentration plot of the collated soil-vapour dataset identifies the potential hazard associated with biologically sourced methane. Methane was reported in excess of the LEL (5%vol methane) at over a third of the sites included in the assessment (9 out of 24). A higher percentage of sites may be considered potentially hazardous by some Australian regulatory agencies who adopt screening concentrations lower than the LEL; such as 5% of the LEL

The conservatism of some of these guidelines have justifiably been questioned as flux rates are unknown and dilution in air is likely to be significant in most situations. However, based on the precautionary principle, as risks associated with potential explosive methane-oxygen sub-surface vapour mixtures and the resultant associated liabilities are unknown, we suggest that further investigation is warranted.

**Case Study – Non-site Sourced Methane Concentration at a Petroleum Hydrocarbon Release Site**

The case study presented below is a site investigated by Coffey Environments whereby concentration of methane, which correlated to elevated petroleum hydrocarbon VOC concentrations, was confirmed not to be site sourced. Unlike the former petroleum service station investigated by Lundegard in Seattle, Washington, the methane source was thermogenic in origin. Additional forensic investigative steps were therefore necessary to confirm the off-site source.

<table>
<thead>
<tr>
<th>Site Setting and Analytical Results Summary</th>
<th>Methods Used to Identify Methane Source</th>
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<tbody>
<tr>
<td><strong>Melbourne, Victoria – active service station.</strong></td>
<td>The methane concentrations reported in soil-vapour were at a level unlikely to be the result of biological breakdown of petroleum hydrocarbons. Coffey Environments contacted the metropolitan gas supplier to advise the potential for a leaking gas main in the vicinity of the site. The metropolitan gas supplier ‘investigated’ and advised that their infrastructure was not leaking. Following this advice, soil-vapour samples and a sample from the metropolitan gas supply were targeted for carbon and hydrogen isotopic analysis. The analysis confirmed that all samples were from thermogenic sources. The major source of methane at the site was most likely petroleum based (i.e from the metropolitan gas supply or petroleum impact).</td>
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<td>The site is an active service station in metropolitan Melbourne. Historical environmental investigations have identified LNAPL impact and given the operational status of the petroleum-related infrastructure, a petroleum hydrocarbon soil source is likely at the site. Clayey sand. Standing water level ~4mbgs. Groundwater seepage velocity &lt;10m/year. Groundwater VOCs.</td>
<td></td>
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<tr>
<td>• BTEX: &lt;0.002mg/L – 14.1mg/L.</td>
<td></td>
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<tr>
<td>• Naphthalene: &lt;0.001mg/L – 0.38mg/L.</td>
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<tr>
<td>• TPH C₆₋₉: &lt;0.02mg/L – 40.3mg/L.</td>
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<tr>
<td>• TPH C₁₀₋₁₄: &lt;0.05mg/L – 6.3mg/L.</td>
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Groundwater natural attenuation indicators.

- Oxygen: 0.25mg/L – 0.88mg/L.
- Methane: <0.01mg/L – 4.8mg/L.
- Sulphate: 55mg/L – 419mg/L.

Soil-vapour VOCs (3.5mbgs).

- BTEX: <0.01mg/m³ – 1,794mg/m³.
- Naphthalene: <0.01mg/m³ – 10.3mg/m³.
- Aromatic EC>6-16: <0.1mg/m³ – 3,495mg/m³.
- Aliphatic EC>6-16: <0.1mg/m³ – 2,633mg/m³.

Soil-vapour general gases (3.5mbgs).

- Oxygen: 0.5%vol – 19%vol.
- Carbon dioxide: 1.8%vol – 13%vol.
- Methane: 0.02%vol – 91%vol.
- Ethane: <0.01%vol – 5.1%vol.

Targeted sampling of soil-vapour for mercaptans also confirmed the presence of tetrahydrothiophene ranging from <0.1ppm to 1.5ppm. Tetrahydrothiophene is an odorant commonly added to metropolitan gas supplies. The addition of this odorant to the locally provided gas was subsequently confirmed by the gas supplier.

Following this forensic investigation by Coffey Environments, the metropolitan gas supplier investigated their infrastructure with greater care, and confirmed a leaking gas main immediately adjacent to the site, which was subsequently repaired.

Subsequent advice from the metropolitan gas supplier for another site confirmed that the ethane concentration in mains gas supplies are typically <10% of the methane concentration whilst alkenes, ethene and propene are typically absent or in sub-percent concentrations.

SUMMARY

Statistically significant relationships were identified linking an increased likelihood of methane concentration at petroleum hydrocarbon release sites to soil type, surface covering, depth to groundwater and the presence of petroleum hydrocarbon impact in the vadose zone. Other factors, such as seepage velocity and vadose zone air porosity may also be relevant, however no conclusions could be made, possibly due to the reliance on literature values for the majority of the sites. Increased collection of site-specific data for use in vapour intrusion modelling, and refinement of conceptual site models, is likely to elucidate relationships between other parameters and soil vapour methane concentrations.

The inclusion of natural attenuation indicators within the scope of works for a soil-vapour investigation can bring a number of benefits to an assessment of health risks. Whilst the biological mechanistic processes are important from a conceptual standpoint, the dataset identified that methane concentration can be a contamination-related hazard. Future investigation and potential mitigation appears to be warranted.

ACKNOWLEDGEMENTS

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**KEY WORDS**

Soil-vapour, petroleum, methanogenesis, biodegradation, natural attenuation.