Vertical screening distances for total petroleum hydrocarbon for vapour intrusion risk assessment at petroleum underground storage tank sites

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Abstract: The US Environmental Protection Agency Office of Underground Storage Tanks (US EPA OUST) and Interstate Technology and Regulatory Council (ITRC) have recently published guidance indicating that buildings separated from light non-aqueous phase liquid (LNAPL) sources by more than 15 ft (4.6 m) are not a concern for vapour intrusion at petroleum underground storage tank (UST) sites. At this distance, there is a greater than 95% probability that soil gas concentrations for all key constituents of potential concern are below risk-based screening levels (RBSLs) between the LNAPL source and building foundation. Vertical screening distances for bulk Total Petroleum Hydrocarbon (TPH), common TPH fractions (C5–C8 aliphatics, C9–C12 aliphatics, and C17–C19 aromatics), and indicator compounds (n-hexane and naphthalene) are less certain, however, because of a general lack of empirical data and highly variable soil-gas RBSLs. This study addresses these gaps through a statistical analysis of hundreds of soil-gas samples collected above LNAPL sources at more than 30 petroleum UST release sites. Resulting vertical screening distances for the various TPH fractions range between 0 and 7 ft (2.1 m) depending primarily on soil-gas RBSLs, which vary by over 5 orders of magnitude. Vertical screening distances for naphthalene are generally <3 ft (0.91 m). Vertical screening distances for n-hexane range from 12 (3.7) to 16 ft (4.9 m) and vary geographically. Vertical screening distances for total (bulk) TPH generally exceed 15 ft (4.6 m). Petroleum vapour intrusion risk assessments involving total (bulk) TPH are not recommended, however, because of uncertainties in quantifying soil-gas and indoor-air concentrations and defining RBSLs for fuel mixtures with variable source composition, toxicity, and fate and transport properties. Overall, the findings of this study validate the 15-ft screening distance recommended by ITRC and US EPA for application at petroleum UST sites with LNAPL sources.

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Evaluating petroleum vapour intrusion (PVI) risks from total (bulk) Total Petroleum Hydrocarbon (TPH) and TPH fractions is challenging because of several factors including method of analysis, background sources of both petroleum and non-petroleum hydrocarbons, uncertainties in quantifying chemical fate and transport and toxicity, and subsurface weathering and biodegradation. In addition, fuel composition can be highly variable, even for similar fuel types, like gasoline. Fuels, such as gasoline, are manufactured to meet performance specifications, which differ depending on where and how they are manufactured and local regulatory requirements. PVI risks are generally greater for gasoline fuels, including aviation gas and JP-4 jet fuel, because they contain the highest percentage of TPH compounds that are sufficiently volatile (i.e. vapour pressure >1 mm Hg, Henry’s Law constant >10^{-5} atm·m^3/mol), soluble (i.e. have the potential to form off-site groundwater plumes) and toxic (i.e. have high risk-based screening levels – RBSLs) (US EPA 2015a; ITRC 2014). The vapour composition above fresh gasoline sources is mainly dominated by C5–C8 aliphatics, based on their relative abundance and volatility in the parent fuel (ITRC 2014). Individual C5–C8 aliphatic hydrocarbons, with the potential exception of n-hexane, are generally less toxic, however, than corresponding aromatic hydrocarbons (e.g. benzene, toluene, ethylbenzene, xylenes – BTEX, etc.) within the same carbon range and thus less of a concern for PVI. Over time, preferential volatilization of C5–C8 aliphatics from a gasoline source will cause the composition of vapour in equilibrium with the light non-aqueous phase liquid (LNAPL) to become increasing enriched in BTEX and other aromatics (Baehr 1987). The straight-chain C5–C8 aliphatics are highly susceptible to aerobic biodegradation in the unsaturated zone (DeVaull 2007); however, these compounds partition less into the pore water (aqueous phase) where biodegradation occurs. The branched/cyclic C9–C12 aliphatics (e.g. methycyclohexane, isopentane) are generally less biodegradable (Suthersan 1999) and can exhibit little decrease in concentration with distance above an LNAPL source (US EPA 2013).

Diesel and other middle distillate fuels (e.g. kerosene, #2 fuel oil, JP-8 jet fuel, heating oil) contain larger percentages of C9+ aliphatics and aromatics than gasoline. These compounds are semi-volatile, but can dominate the TPH composition of soil-gas above an LNAPL source (Brewer et al. 2013). Lower overall volatility generally of the TPH contained in diesel and middle distillate fuels generally equates to a lower overall PVI risk compared to gasoline. C9+ aliphatics and aromatics do, however, have lower overall odour thresholds compared to <C9 compounds and thus can represent an aesthetic risk for PVI. For example, PVI commonly occurs with heating oil releases which occur near or within building foundations and are sources for preferential vapour migration into buildings through utility conduits, sumps or floor drains (ITRC 2014). Residual fuels (such as fuel oil Nos 4, 5 and 6, lubricating oils, waste oils and asphalts) contain very few volatile compounds and generally pose little PVI risk other than potential generation of biogenic methane during degradation (ITRC 2014). Methane can pose an acute safety (flammability) hazard if present at percent-level concentrations in soil-gas adjacent buildings or other confined spaces (ASTM 2016). Such vapour concentrations have also been observed during biodegradation of gasoline containing >10% vol/vol ethanol (Ma...
et al. 2012; Morgan et al 2014) and biodiesel containing fatty acid methyl esters (FAME) (Thomas et al. 2017). Percent-level concentrations of methane in soil gas are a rare occurrence at petroleum underground storage tank (UST) sites, however (US EPA 2013). PVI is also not often observed at petroleum UST sites relative to the large number of documented fuel releases (Lahvis et al. 2013). PVI is more commonly associated with large-volume petroleum releases at terminal, pipeline and manufacturing sites (McHugh et al. 2010).

Although methods for evaluating TPH risks in soil and groundwater are relatively routine, TPH is not generally addressed in PVI risk assessments (Bowers & Smith 2014). Only the US Environmental Protection Agency (US EPA 2015b), a few US states (HI, LA, MA, MO, OR and WA) and Australia have vapour intrusion screening criteria (soil-gas RBSLs) for TPH fractions or total (bulk) TPH (see Table 1). Analytical methods for quantifying TPH in air are also quite variable. One of the more commonly referenced and researched TPH methods used in PVI risk

|                  | C₃ - C₄ ALIPHATICS | C₅ - C₁₂ ALIPHATICS | C₃ - C₁₆ AROMATICS | TPH | n - HEXANE | NAPHTHALENE |
|------------------|--------------------|----------------------|--------------------|-----|------------|-------------|
| Alaska           |                    |                      |                    | 7300|            | 7.2         |
| California²      |                    |                      |                    | 50,000|            | 31.9        |
| Colorado         |                    |                      |                    | 24000|            | 2.8         |
| Delaware         |                    |                      |                    | 2400 |            | 2.7         |
| Florida          |                    |                      |                    |      |            | 30          |
| Hawaii           |                    |                      |                    | 630,000|            | 72          |
| Idaho            |                    |                      |                    |      |            | 7           |
| Illinois         |                    |                      |                    |      |            | 110         |
| Indiana          |                    |                      |                    | 7300 |            | 8.3         |
| Kansas           |                    |                      |                    | 24300|            | 23.9        |
| Louisiana        |                    |                      |                    | 1900000³ | 11,000 | 22,000 | 22,000 | 31 |
| Maine            |                    |                      |                    |      |            | 36          |
| Maryland         |                    |                      |                    |      |            | 14600       |
| Massachusetts    |                    |                      |                    | 4,100 | 4,800 | 700 |      | 42 |
| Michigan         |                    |                      |                    |      |            | 24000       |
| Minnesota        |                    |                      |                    |      |            | 20000       |
| Missouri         |                    |                      |                    | 372000000³ | 20400000⁴ | 20400000⁵ | 3.97E+08 | 42600 |
| New Hampshire    |                    |                      |                    |      |            | 130         |
| New Jersey       |                    |                      |                    |      |            | 36000       |
| North Carolina   |                    |                      |                    | 4870 |            | 26          |
| Oregon           |                    |                      |                    |      |            | 79,000      |
| Pennsylvania     |                    |                      |                    | 28000 |            | 28          |
| Tennessee        |                    |                      |                    |      |            | 34857       |
| Vermont          |                    |                      |                    | 70000 |            | 3           |
| Virginia         |                    |                      |                    |      |            | 2430        |
| Washington       | 90,000             | 4,700                | 6,000              |      |            | 10700       |
| Wisconsin        |                    |                      |                    |      |            | 28          |
| Wyoming          |                    |                      |                    | 24000 |            | 2.8         |
| US EPA RSLs⁶     |                    |                      |                    | 21,000 | 3,300 | 100 | 22,000 | 2,400 | 2.45 |
| **MINIMUM**      | 4,100              | 3,300                | 100                | 22,000 | 2,400 | 2.8         |
| **MAXIMUM**      | 3.72E+08           | 2.04E+07             | 2.04E+07           | 3.97E+08 | 70,000 | 42,600    |
| **MEDIAN**       | 90,000             | 4,800                | 6,000              | 79,000 | 22,000 | 26.0       |

³ Default (Tier 1) values assuming a Carcinogenic Target Risk of 10⁻⁶ or a Hazard Index of 1.0.
² Values reported by Office of Environmental Health Hazard Assessment (OEHHA) for volatile chemicals below buildings constructed without engineered fill below sub-slab gravel.
⁴ Value reported for C₃ - C₄ aliphatics.
⁵ Value represents equivalent risk-based target levels reported for C₃ - C₁₅ and C₃ - C₁₂ aliphatics.
⁶ Calculated from Regional Screening Levels (RSLs) for indoor air reported in US EPA (2017) assuming a foundation (slab) attenuation factor of 0.03. Values cited in table for C₃ - C₄ Aliphatics, C₅ - C₁₂ Aliphatics, and C₅ - C₁₆ Aromatics represent US EPA values reported for Aliphatic Low (C₃ - C₄ aliphatics); Aliphatic Medium (C₅ - C₁₄ aliphatics); and Aromatic Medium (C₅ - C₁₄ aromatics) carbon ranges, respectively. 0.1 - naphthalene; 0.01 - various TPH fractions.
assessment is the Massachusetts Department of Environmental Protection’s (MADEP) air-phase petroleum hydrocarbon (APH) gas-chromatography/mass spectrometry (GCMS) method (MADEP 2009). In the APH method, volatile aliphatic and aromatic hydrocarbons are grouped into three carbon ranges: C₅–C₈ aliphatics, C₉–C₁₂ aliphatics and C₁₀ aromatics. Positive bias resulting from background sources of non-petroleum hydrocarbons cannot be eliminated from the method, however, which greatly affects the analysis of indoor-air samples and quantitative risk determinations. Slightly different TPH carbon ranges (Aliphatic Low (C₅–C₈ aliphatics), Aliphatic Medium (C₉–C₁₈ aliphatics) and Aromatic Medium (C₁₀–C₁₆ aromatics)) have been defined by the US EPA (2017) and used to establish indoor-air RBSLs. The difference in methods is not likely to be significant in most cases, given that the additional C₁₂⁺ constituents included in the Aliphatic Medium and Aromatic Medium fractions are semi-volatile. Of note, the soil-gas RBSLs reported in Table 1 were determined by dividing the indoor-air RBSLs by the building (slab) attenuation factor of 0.03 recommended by US EPA (2012). In Australia, soil-gas RBSLs (Health Screening Levels for PVI risk assessment) are grouped within singular aliphatic and aromatic carbon ranges for F₁=₆–₄ and TPEX and F₁=₆–₄ minus naphthalene hydrocarbons (Friebel & Nadebaum 2011). Similar carbon-range fractions are applied in Canada (Health Canada 2010); however, RBSLs are only published for soil and groundwater. The UK recommends use of the more discrete carbon-range fractions defined by the TPH Criteria Working Group (1997) (e.g. C₅–C₈ aliphatics, C₉–C₁₀ aromatics, C₁₀–C₁₂ aliphatics, C₁₂–C₁₄ aromatics). The approach affirms that PVI risks at petroleum UST sites are negligible for buildings located more than 5–6 ft (1.5–2 m) from dissolved-phase sources and 15 ft (4.6 m) from LNAPL sources. At these distances, petroleum vapour concentrations for all constituents of potential concern are below a level of concern or RBSL in soil gas or indoor air. The vertical screening distance roughly coincides with the location above a petroleum source in soil or groundwater where hydrocarbon and oxygen (O₂) concentrations are sufficient to support aerobic biodegradation (i.e. the aerobic/anaerobic interface). The interface is marked by hydrocarbon concentrations that decrease by several orders of magnitude and O₂ concentrations that increase by several percent within a relatively short (e.g. 1 – 3 ft or 0.5 – 1 m) vertical distance (DeVaul 2007). The interface develops because rates of aerobic biodegradation for most petroleum hydrocarbons are rapid (e.g. half-lives on the order of hours or days) and generally exceed rates of physical transport in the unsaturated zone by gaseous-phase diffusion and advection (Davis et al. 2009). The location of the aerobic/anaerobic interface (or vertical screening distance) above a hydrocarbon source differs primarily on hydrocarbon type and whether the source is dissolved or LNAPL. Studies of empirical soil-gas data collected at hundreds of petroleum UST sites with predominantly gasoline releases showed that vertical screening distances were longer for benzene than other hydrocarbons (US EPA 2013). Reasons for this result include benzene’s relatively high source mass, volatility, toxicity (i.e. low soil-gas RBSL), and low biodegradability in the unsaturated zone relative to other hydrocarbons. Benzene was thus used to define the 5–6 ft (1.5–2 m) and 15 ft (4.6 m) vertical screening distances for dissolved-phase and LNAPL sources, respectively.

Vertical screening distances for C₅–C₈ aliphatics, C₉–C₁₂ aliphatics, C₁₀–C₁₂ aromatics, n-hexane and naphthalene are assumed to be much less than the 15 ft (4.6 m) recommended for LNAPL sources. This assumption is based on the US EPA (2013) finding that TPH fraction, n-hexane and naphthalene concentrations in soil gas decreased below soil-gas RBSLs at LNAPL source–separation distances >4 ft (1.2 m). Actual screening distances for the TPH fractions remain somewhat uncertain, however, because these distances were derived from a relatively small dataset (e.g. total of 53 soil-gas samples from 11 petroleum UST sites) and using soil-gas RBSLs that are up to 1.5 – 7× higher than those recently published for relatively similar TPH carbon ranges defined by US EPA (2017). In addition, the US EPA (2013) analysis did not consider bulk TPH, which was found to ‘drive’ PVI risk over individual compounds (e.g. benzene) in 24% of the soil-gas samples reported in US EPA’s database (Brewer et al. 2013). The purpose of this study is to address these gaps by evaluating a larger population of empirical soil-gas data and a more complete range of soil-gas RBSLs. Vertical screening distances are calculated specifically for C₅–C₈ aliphatics, C₉–C₁₂ aliphatics, C₁₀–C₁₀ aromatics, n-hexane, naphthalene and total (bulk) TPH and intended for application at petroleum UST sites with LNAPL sources. Vertical screening distances associated with dissolved-phase (groundwater) sources are not considered because the TPH fractions and indicator compounds (n-hexane and naphthalene) have relatively limited aqueous solubility and thus pose little PVI risk.

### Table 2. Summary of empirical soil-gas database

| Analyte          | Sites | Locations | Soil-gas samples |
|------------------|------|-----------|------------------|
| C₅–C₈ aliphatics | 33   | 88        | 193              |
| C₉–C₁₂ aliphatics| 31   | 82        | 152              |
| C₁₀–C₁₀ aromatics| 31   | 94        | 204              |
| n-hexane         | 33   | 114       | 175              |
| Naphthalene      | 31   | 79        | 180              |
| total (bulk) TPH | 35   | 118       | 180              |

TPH, Total Petroleum Hydrocarbon.
Methodology

Vertical screening distances were calculated using the ‘vertical distance’ method employed by Lahvis et al. (2013) and US EPA (2013) based on a statistical analysis of empirical soil-gas data collected at numerous petroleum UST sites with LNAPL sources. The database included C5–C8 aliphatics, C9–C12 aliphatics, C9–C10 aromatics, n-hexane, naphthalene and total (bulk) TPH soil-gas data previously compiled by the US EPA (2013), Wright (2011), as well as TPH fraction and naphthalene soil-gas data from 28 additional petroleum UST sites in Massachusetts. The additional data were extracted from electronic PVI reports submitted to MADEP and maintained by Shell Oil Company. In total, the soil-gas database was composed of 35 sites from the US and 33 sites from Australia. The database was reviewed to ensure data quality objectives for interpretation and assessment, which involved examining: soil-gas, groundwater monitoring and borehole log data; site plans; soil-gas sampling locations relative to current and former petroleum UST equipment (tanks and dispensers); sampling methods and analyses; data quality (e.g. pneumatic and tracer testing, purging procedures, sample breakthrough results); and overall consistency with the conceptual model for aerobic and anaerobic hydrocarbon biodegradation (i.e. reviews of general relations between hydrocarbon, O2, CO2 and CH4 concentrations in the unsaturated zone). The database

![Fig. 1. Plot of (a) C5–C8 aliphatic, (b) C9–C12 aliphatic, (c) C9–C10 aromatic, (d) n-hexane, (e) naphthalene and (f) TPH (Total Petroleum Hydrocarbon) concentrations in soil gas v. distance above a LNAPL hydrocarbon source. Non-detect values are plotted at the reporting limit.](http://qjegh.lyellcollection.org/Downloaded from)
comprised information on soil type, soil-gas probe location, depth to groundwater, reported presence of free product, soil and groundwater concentrations, sampling date, land surface condition (building foundation, open ground, pavement) and QA/QC measures (e.g. tracer testing, field blanks, etc.).

Gasoline was the primary source of TPH. The gasoline likely contained methyl tert-butyl ether (MTBE) or ethanol given the 16-year time-span (from 1995 to 2011) over which the data were collected and the vast geographical regions (North America and Australia) where the fuels were marketed. The predominance of gasoline sources introduces some bias to the vertical screening distances derived in this study. In particular, vertical screening distances of C_5–C_8 aliphatics and n-hexane are exaggerated (conservative) where there was a larger occurrence of diesel sources because diesel contains a very small percentage and much lower source vapour concentrations of these compounds. Conversely, vertical screening distances of C_9–C_12 aliphatics, C_9–C_10 aromatics and naphthalene are less than predicted based on a larger occurrence of diesel sources and higher overall source vapour concentrations of these compounds. The underestimates in screening distances are not likely to be significant, however, because source vapour concentrations for C_9–C_12 aliphatics, C_9–C_10 aromatics and naphthalene are only 2–3× higher in diesel than gasoline (ITRC 2014) and these compounds have been shown to decrease in concentration by several orders of magnitude within short vertical distances (e.g. <3 ft or 1 m) above LNAPL sources (US EPA 2013).

The soil-gas data were filtered to eliminate data collected above dissolved-phase sources and sites with fractured rock located between the LNAPL source and building foundation. Source-type

Fig. 2. Probability of (a) C_5–C_8 aliphatics, (b) C_9–C_12 aliphatics, (c) C_9–C_10 aromatics, (d) n-hexane, (e) naphthalene and (f) TPH (Total Petroleum Hydrocarbon) concentrations in soil gas ≤ minimum, median and maximum soil-gas RBSLs (risk-based screening levels) at specified vertical distances above a LNAPL source, for the soil-gas data reported in Figure 1.
determinations (dissolved v. LNAPL) were based on the LNAPL indicator criteria published by ITRC (2014). LNAPL sources were primarily identified by concentrations of benzene >1000 µg l\(^{-1}\) and BTEX >20 000 µg l\(^{-1}\) in groundwater measured at any time prior to soil-gas sampling in ‘paired’ monitoring wells located within 30 ft (10 m) of soil-gas probe locations. The top of the vapour (residual-phase LNAPL) source was defined as the top of the LNAPL smear zone. This datum is unknown but assumed to coincide with the maximum water-table elevation recorded in the ‘paired’ monitoring wells prior to soil-gas sampling. Soil-gas samples collected below this horizon are plotted in figures at negative distances above the source. The selection of the top of the LNAPL smear zone as the top of the vapour source is assumed to yield conservative estimates of the vertical screening distance (i.e. a longer screening distance than actual) given that LNAPL tends to distribute above the water table, which would include the maximum reported water-table elevation.

The resultant soil-gas database associated with LNAPL sources is summarized in Table 2. The percentage of soil-gas samples collected below building foundations, open ground and pavement is c. 22, 22 and 56%, respectively. The percentage of soil-gas samples collected in coarser (e.g. sand, loam, gravel, fill) and finer (e.g. clay, silt) soils is c. 61 and 39%, respectively.

Vertical screening distances were evaluated for the TPH fractions, \(n\)-hexane, naphthalene and total (bulk) TPH using non-parametric, Kaplan–Meier statistics (Kaplan & Meier 1958). The Kaplan–Meier method is recommended for statistical analyses of censored data with multiple reporting limits and numerous non-detects (Helsel 2005). Vertical screening distances were defined at locations above the LNAPL source where >95% of soil-gas concentrations fell below the minimum, median and maximum RBSLs reported in Table 1. Probabilities were calculated at discrete 2-ft source–separation intervals (e.g. \(2 \times 4 \times 4 \times \ldots \times 16 \) ft), which required apportioning the soil-gas data into corresponding sample populations. As noted in the next section, probabilities generally increased with increasing source–separation distance and decreasing soil-gas concentration; however, this trend could be reversed in certain cases depending on population size.

### Results and discussion

The TPH fraction, \(n\)-hexane, naphthalene and total (bulk) TPH, soil-gas data associated with LNAPL sources at petroleum UST sites are shown in Figure 1. The resultant vertical screening distances calculated from these data, assuming the minimum, median and maximum RBSLs, are reported in Table 1, illustrated in Figure 2 and summarized in Tables 3 and 4.

As shown in Figure 1, TPH fraction (C₅–C₈ aliphatics, C₉–C₁₂ aliphatics and C₉–C₁₀ aromatics) concentrations in soil gas rapidly decrease with increasing source–separation distance. More specifically, soil-gas concentrations decrease by about four orders of magnitude within 5 ft (1.5 m) of the LNAPL source. The soil-gas concentration gradients are most pronounced for C₉–C₁₀ aromatics and C₉–C₁₂ aliphatics, which both exhibit a greater percentage of non-detects (C₉–C₁₀ aromatics ~ 58%; C₉–C₁₂ aliphatics ~ 37%) than C₅–C₈ aliphatics (8%). These results are consistent with lower overall source vapour concentrations and higher sorption of C₉–C₁₀ aromatics and C₉–C₁₂ aliphatics relative to C₅–C₈ aliphatics.

Biodegradation may also contribute to the more rapid decrease in C₉–C₁₂ aliphatics v. C₅–C₈ aliphatics concentrations with distance above the LNAPL source (Suthersan 1999).

The vertical screening distances for C₅–C₈ and C₉–C₁₂ aliphatics are similar (0 – 4 ft or 0 – 1.2 m) for a range of soil-gas RBSLs that span over four orders of magnitude (see Fig. 2a and b). Vertical screening distances for C₉–C₁₀ aromatics (see Fig. 2c) are roughly \(2 \times \) longer (7 ft or 2.1 m) than the distances derived for the TPH aliphatics. This result is largely driven by the minimum soil-gas

| Analyte | Vertical screening distance in ft (m) | Minimum (RBSL) | Median (RBSL) | Maximum (RBSL) |
|---------|-------------------------------------|---------------|---------------|---------------|
| C₅–C₈ aliphatics | 4 (1.2) | (4000 µg m\(^{-3}\)) | (4000 µg m\(^{-3}\)) | (70 000 µg m\(^{-3}\)) |
| C₉–C₁₀ aromatics | 4 (1.2) | (4000 µg m\(^{-3}\)) | (4000 µg m\(^{-3}\)) | (70 000 µg m\(^{-3}\)) |
| C₉–C₁₂ aliphatics | 2 (0.61) | (70 000 µg m\(^{-3}\)) | (70 000 µg m\(^{-3}\)) | (70 000 µg m\(^{-3}\)) |

*Note: on-gas concentrations are below the RBSL in <95% of cases at a vertical screening distance of 15 ft (4.6 m).*
RBSL for C₅–C₁₀ aromatics (100 µg m⁻³), which is over an order of magnitude less than the minimum soil-gas RBSL values reported for C₅–C₈ (4100 µg m⁻³) and C₉–C₁₂ aliphatics (3300 µg m⁻³). Collectively, these results confirm the applicability of the 15-ft (4.6-m) screening distance recommended for use at petroleum UST sites with LNAPL sources to TPH fractions. Relatively good agreement between C₅–C₈ aliphatic, C₉–C₁₂ aliphatic and C₉–C₁₀ aromatic and benzene concentrations in soil gas (see Fig. 3a–c) implies that TPH fractions are only likely to be a concern for PVI when benzene concentrations are elevated. The agreement is best between benzene and the C₉ and C₁₀ aromatics, which is expected given similarities in molecular structure.

N-hexane concentrations in soil gas decrease less rapidly with distance above LNAPL (see Fig. 1d) than TPH fractions or naphthalene (see Fig. 1e). Closer examination of the n-hexane soil-gas concentrations does, however, reveal some disparity with the C₅–C₈ aliphatic concentrations shown in Figure 1a. In particular, soil-gas concentrations are generally higher for n-hexane (a C₆ aliphatic) than the entire C₅–C₈ aliphatic fraction at source–separation distances >5 ft (1.5 m). The reason for this ambiguity is unknown but may somehow be linked to regional differences in laboratories used for soil-gas analysis given that the anomalous data were largely collected in Australia (see Fig. 4a and b). The n-hexane soil-gas concentrations are, however, reasonably well correlated with benzene (see Fig. 3d), which implies that vapour transport in the unsaturated zone is analogous for these compounds, even though their physiochemical properties (e.g. vapour pressure, Henry’s Law constants) vary significantly.

The vertical screening distances derived from n-hexane concentration data range from 12 ft (3.7 m) to 16 ft (4.9 m) for the range of soil-gas RBSLs (2400–70 000 µg m⁻³) reported in Table 1 (see Fig. 2d). Although roughly equivalent to the 15 ft (4.6 m) vertical screening distance recommended by ITRC (2014) and US EPA (2015b), the distances are assumed to be conservative given the high volatility of the compound and potential for source concentrations to decrease substantially over the 30-year exposure duration typically assumed in PVI risk assessment (Baehr 1987). Vertical screening distances derived from the US data range from 5 ft (1.5 m) to 11 ft (3.4 m) and are significantly less than those derived from the Australia data (12 to c. 16 ft or 3.7 m to c. 4.9 m) (see Fig. 5a and b).
Naphthalene soil-gas concentrations decrease by over four orders of magnitude within 1–2 ft (0.2–0.6 m) of the LNAPL source and are non-detect (i.e. below ∼0.2 µg m$^{-3}$) in nearly 80% of samples (see Fig. 1e). This distribution is like the one observed for the broader C$_9$–C$_{10}$ aromatic carbon range (see Fig. 1c) and the potential for naphthalene to undergo relatively rapid biodegradation in the unsaturated-zone soils (Andersen et al. 2008). Naphthalene and benzene concentrations in soil gas also show quite good agreement (see Fig. 3e), which is consistent with the good agreement observed between the broader C$_9$–C$_{10}$ aromatic carbon range and benzene. Vertical screening distances derived for naphthalene, assuming median (26 µg m$^{-3}$) and maximum (42 600 µg m$^{-3}$) soil-gas RBSLs, are <3 ft (0.9 m) (see Fig. 2e). Vertical screening distances for the minimum soil-gas RBSL (2.45 µg m$^{-3}$) could not be calculated at source–separation distances >12 ft (3.7 m) because of insufficient data (17 total soil-gas samples). Naphthalene concentrations in soil gas are, however, non-detect (∼0.2 µg m$^{-3}$) in all 6 samples collected at source–separation distances >13.6 ft (4 m). Overall, the results indicate that naphthalene is not likely to be a PVI concern unless the LNAPL source is located relatively close (<3 ft or 0.91 m) to a building foundation.

Concentrations of total (bulk) TPH decrease less rapidly with distance from LNAPL sources than the individual TPH fractions (see Fig. 1f). The discrepancy between total (bulk) TPH and TPH
fraction transport is uncertain but may be related to issues with quantifying total (bulk) TPH concentrations and defining RBSLs in soil gas. Approximately 79 – 90% of the total (bulk) TPH concentrations in soil gas fall below the minimum (22 000 µg m⁻³) and median (79 000 µg m⁻³) RBSL, respectively, at source–separation distances of 15 ft (4.6 m) (see Fig. 2f). Again, the 15 ft (4.6 m) vertical screening distance recommended by ITRC (2014) and US EPA (2015b) would not apply in situations where this soil-gas RBSL was invoked. Application of vertical screening distances for bulk TPH is not recommended, however, given uncertainties from background sources in indoor-air and soil-gas RBSLs for fuel mixtures composed of hydrocarbons with highly disparate fate and transport characteristics and toxicity (TPH Criteria Working Group 1997). Field instruments (e.g. photo-ionization and flame-ionization detectors) used to quantify total (bulk) TPH concentrations may, however, be useful as a PVI screening tool for soil-gas sampling given the relatively good agreement between total (bulk) TPH and benzene soil-gas concentrations (see Fig. 3f).

Summary
Vertical screening distances for LNAPL sources were derived for C₂–C₈ aliphatics, C₉–C₁₂ aliphatics, C₉–C₁₀ aromatic fractions, n-hexane, naphthalene and total (bulk) TPH based on an empirical soil-gas, groundwater and soil data collected at more than 30 petroleum UST sites in the US and Australia. Results show that vertical screening distances for the various TPH fractions range between 0 and 7 ft (2.1 m) depending on the soil-gas RBSL used in the analysis. The variability is primarily attributed to regulatory soil-gas RBSLs which can differ by over five orders of magnitude. Vertical screening distances based on median soil-gas RBSLs are roughly equivalent for the various TPH fractions (differ by 3 ft or 0.91 m), even though the fate and transport properties and toxicity of these fractions vary substantially. Vertical screening distances for n-hexane are roughly equal to 15 ft (4.6 m), but assumed to be conservative given the high relative volatility of the compound and potential for source concentrations to decrease (weather) considerably from LNAPL sources at petroleum UST sites over the 30-year exposure duration typically assumed in PVI risk assessments. Vertical screening distances for naphthalene are generally short (<3 ft or 0.91 m); hence, this compound is not expected to be a concern for PVI unless the LNAPL source was located relatively close to a building foundation. There may be certain regulatory jurisdictions where very conservative naphthalene soil-gas RBSLs (2.45 µg m⁻³) are invoked for where the 15-ft (4.6 m) screening distance would not apply, however. The 15-ft (4.6 m) screening distance may also not be applicable for total (bulk) TPH in the few regulatory jurisdictions where such PVI risks are considered. Total (bulk) TPH is not recommended for PVI risk assessment, however, because of uncertainties in estimating soil-gas RBSLs and quantifying vapour concentrations, most notably in indoor air, where measurements are likely to be affected by background

Fig. 4. Plots of n-hexane concentrations in soil gas v. distance above a LNAPL source for data collected in (a) the US and (b) Australia. Non-detect values are plotted at the reporting limit.

Fig. 5. Probability n-hexane concentrations in soil gas are ≤ minimum, median and maximum soil-gas RBSLs (risk-based screening levels) at specified vertical distances above a LNAPL source, for (a) the US and (b) Australia soil-gas data reported in Figure 4.
(including non-petroleum) sources. PVI risks for total (bulk) TPH would be better defined and bounded by the vertical screening distances derived for various TPH fractions. It is important to note, however, that total (bulk) TPH can drive PVI risk in certain cases where benzene is not the primary petroleum constituent in LNAPL (e.g. some crude oils, middle distillate fuels) (Brewer et al. 2013). Analysis of total (bulk) TPH soil-gas concentrations may be warranted in such cases. Total (bulk) TPH concentration measurements can also be useful in helping identify LNAPL sources, acute health and safety (flammability) risks, petroleum vapour source type (dissolved v. LNAPL) and potential instances of benzene vapour intrusion. Overall, the results generally support the 15-ft (4.6 m) screening distance for LNAPL sources at petroleum UST sites.

Additional information

The Kaplan-Meier statistics were calculated using the Microsoft Excel® spreadsheet ‘KMStats V 1.4’ provided by Dr Dennis Helsel, at http://www.practicalstats.com/resources/NADA-resources/KMStats16.xls. The US EPA (2013) and Wright (2011) petroleum vapour intrusion databases are available at https://www.epa.gov/ust/petroleum-vapour-intrusion-database.

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