Real-world uncertainties during a site assessment of vapour migration into a residential house from soil and groundwater

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Abstract: Assessing the relationship between hydrocarbon groundwater concentrations and overlying vapour concentrations is fraught with uncertainties resulting from effects of moisture and biodegradation in the capillary fringe above the water table, the combined effects of solubility and Raoult's law associated with free phase hydrocarbon and, not least, the subsequent potential vapour transport mechanisms. This paper reports on a UK site containing an uninhabited house adjacent to soil and groundwater source zones. Hydrocarbon concentrations within shallow groundwater, soil, soil vapour and indoor air have been measured over several sampling events. Potential for biodegradation has been assessed using biotrap samples. Recent publications and this site's data suggest that models are conservative and may overestimate potential indoor air concentrations. Attenuation from the subsurface into the house may be less than predicted if preferential pathways exist, but preferential pathways limit modelling applicability. As always, a robust and full understanding of the conceptual model is critical. At this site, and most real-world sites, this understanding is often full of expensive to obtain. Notwithstanding this caveat, the results at this site suggest that both modelling algorithms and source-separation distance approaches are valid screening tools in the UK provided that a robust understanding of the conceptual model is developed.

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Assessment of potential vapour migration into UK houses from subsurface contamination has historically relied upon US models such as that of Johnson & Ettinger (1991) with modifications to account for suspended timber floors typical of older UK housing stock, such as those in the study by Ferguson et al. (1998). These algorithms have been noted by Environment Agency (2009) and Provost et al. (2009) to have relatively high uncertainty owing to poorly understood spatial and temporal variability in subsurface concentrations, and at real sites there is an ambition to verify them by field measurements. Although verification work on vapour intrusion has been done under the auspices of the UK’s Contaminated Land regulatory regime (Defra 2012), much of this work remains unpublished. A lack of published field data documenting spatial–temporal variability in soil vapour concentrations at sites with timber floors is a data gap that this paper seeks to begin to address, by comparing theoretical vapour intrusion estimations with measurements from an older residential property with both suspended and solid floors, where petroleum or coal-tar derived contamination is present in the adjacent subsurface.

Conceptual site model

The site is a small, compact, former coal gas manufacturing plant with a nineteenth century residential property, forming part of a terrace, immediately adjacent to the former gas processing area. The construction of both the gasworks and the original residential property are believed to be roughly contemporaneous. Rear extensions to the residential property appear to have been added at a later date. Within 3 m of the residential boundary (Fig. 1), an underground tank is believed from historical maps to be present but is currently overlain by operational gas pipelines that cannot be disturbed. Schematic cross-sections are presented in Figure 2a and b. From ground investigation works, the tank area appears to be the largest potential source of organic compounds leaking into soil, groundwater and soil vapour in the vicinity. There appears to be a separate source of chlorinated solvents to the north and west of the residence. There is also evidence of another hydrocarbon soil source to the south of the house around investigation location VP4, potentially from the in situ made ground of probable gasworks origin.

Contamination may subsequently migrate via diffusion and advection towards the residence in the vapour phase because the site is underlain predominantly by granular made ground (Fig. 3) with underlying glacial silty sand and gravel, either of which provides a viable vapour migration pathway. The front (north) of the c. 100-year-old residential property is constructed on both a suspended floor (no air bricks) and a concrete ground slab, with the back (south) constructed sometime later with a suspended timber floor that is ventilated by air bricks. There is a further small solid floored lean-to extension at the rear of the property. The apron around the house comprises concrete pathways that will restrict venting of vapour to the atmosphere. Although double glazed and structurally sound, the property has been vacant for several years, which has allowed investigation of the subsurface conditions in the vicinity.

A series of shallow groundwater and vapour wells have been installed around the property and sampled. In conjunction with both sub-floor and ambient indoor air samples, this sampling programme has allowed the vapour migration pathway to be assessed as shown in schematic cross-sections in Figure 2a and b. The groundwater flow direction, ascertained by monitoring groundwater elevations in wells completed in the glacial silty sand and gravel, is from BH4 to BH5 in Figure 1.

Sampling method

The most pertinent investigations for this paper are summarized below.
Soil

Borehole soil samples were recovered from the shallow made ground and from the underlying natural strata, if encountered, from five locations close to the house up to a maximum depth of 1.5 m below ground level (mbgl).

Groundwater

Wells were constructed with a high-density polyethylene (HDPE) casing, screened at the water table, with a filter sand pack around the screened interval and a bentonite seal to surface. An example groundwater well construction is shown in Figure 4b. Groundwater sampling was undertaken from the five groundwater wells shown in Figure 1 on four occasions over 18 months. Depth to groundwater is shown in Table 1. As an indication of groundwater contamination, well BH5, completed in the sandy gravel c. 15 m directly down groundwater flow gradient from the presumed tar tank, contained a 1 mm thickness of light non-aqueous phase liquid (LNAPL) on one occasion at a depth of c. 1.9 mbgl.

The groundwater sampling was undertaken using a low-flow method comprising the use of a peristaltic pump and flow cell. The sample depth was chosen so as to be within the installed response zone, with the flow rate of the pump set such that the well was not de-watered during sampling and did not exceed 1 l min$^{-1}$. Prior to sampling, the well was purged through the flow cell while recording physicochemical parameters. Readings were recorded every minute for the first 5 min and every 5 min thereafter and continued for at least 25 min and until all parameters had stabilized to within 10% over at least two monitoring periods (i.e. 10 min). On completion of purging, the flow cell was disconnected and samples were decanted directly from the tubing into laboratory-supplied sterile glass jars and vials suitable for the analysis to be undertaken. Vials were filled so as to ensure no headspace remained. The samples were transported under chain of custody protocols and analysed for volatile organic compounds (VOC) in waters by headspace gas chromatography mass spectrometry at a UK Accreditation Service (UKAS) accredited laboratory.

Soil vapour

During the soils investigation, vapour monitoring wells VP1–VP5 were excavated by hand to a depth of c. 1 mbgl close to the house and were installed with a narrow diameter (2 mm external diameter) HDPE vapour monitoring tube from c. 0.9 mbgl to surface to allow subsequent collection of soil vapour samples. The wells were completed with coarse sand in the response zone (typically 0.9 – 1.0 mbgl to provide an indication of vapour concentrations in the unsaturated zone pathway) and sealed above and below the response zone with bentonite. A three-way plastic stopcock was installed at the top of each installation and the well was closed to air. An indication of ground conditions in which vapour wells were

![Fig. 1. Site plan, investigation and cross-section locations.](image-url)
installed is shown in Figure 4a. Soil vapour from VP1–VP5 was sampled on five occasions over a period of 18 months (generally concurrent with groundwater sampling). Prior to sampling, the external soil vapour wells were purged. Purging was carried out using a disposable 60 ml plastic syringe attached to the three-way stopcock using a screw fitting. The stopcock was opened so as to link the tubing with the syringe and prevent ingress of ambient air to the well. A total of 180 ml of air was purged from the system by
extracting three syringe volumes; the well was closed to air and syringe pathways using the stopcock between each 60 ml purge. On completion of purging, vapour samples were collected using 450 ml pressurized vacuum canisters connected to the well pathway of the stopcock. The vacuum canisters were set to fill at a rate of 200 ml min\(^{-1}\) by connecting flow valves. Stopcocks were closed on completion of sampling. New syringes were used for each sample location and monitoring period. The samples were analysed by a UKAS accredited off-site laboratory using a Compendium Method TO-15 ‘Determination Of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS) for Volatile Organic Compounds in gas’ USEPA 1999.

Sub-floor vapour

Sub-floor monitoring points designated VPIS-1 and VPIS-2 beneath the suspended floor of the property and VPIG-1 beneath the ground bearing slab in the front half of the property (Fig. 1) were installed. The sub-floor monitoring well VPIG-1 installed within the concrete ground floor slab in the kitchen area of the property was facilitated by drilling a narrow 10 mm external diameter hole through the concrete slab; the thickness of the slab was c. 10 cm. A length of 2 mm external diameter HDPE tubing was lowered through the slab and sealed with bentonite at the surface. A three-way plastic stopcock was placed at the top of this installation. The suspended floor monitoring locations VPIS-1 and VPIS-2 were sampled using 2 mm external diameter HDPE temporarily lowered through gaps in the floor boards into the void space between the floor boards and underlying soil. Considering the temporary installation of these locations, and potential for mixing of sub-floor air with ambient air through the floorboards, a sealed monitoring system was not possible and therefore stopcocks were not used. VPIS-1, VPIS-2 and VPIG-1 were sampled using the same vacuum canister method concurrently with other vapour and groundwater samples with VPIG-1 also being purged according to the method described for soil vapour wells above.

Indoor air

Ambient air samples were recovered from both within and externally to the residential property using the above-mentioned vacuum canister method. Indoor ambient samples from above the ground bearing slab at c. 1.2 m above ground level next to the...
chimney were designated VPIG-A, and those above the suspended floor in the kitchen on the work surface were designated VPIS-A. The house was empty apart from built-in cupboards. Ambient samples recovered from external ambient air were denoted VPB, and were taken on the outside windowsill next to the rear patio at c. 1.2 m above ground level at the same time as other vapour sampling events.

**Biotraps**

Screening level algorithms have been suggested by Provoost et al. (2009) to overestimate the soil vapour concentrations, but not necessarily the predicted indoor air concentrations. It is not clear what causes overestimation of soil vapour concentrations derived from soil or groundwater sources, but Picone et al. (2012) demonstrated that the distribution of water in the unsaturated soil layer, which controls the oxygen supply and hence degradation mechanisms, affected the resultant indoor air concentrations of hydrocarbon compounds by up to three orders of magnitude. Increased saturation reduced degradation by reducing the oxygen supply. Biodegradation removing contaminants in a predominantly dry soil vapour phase beneath the house or surrounding concrete apron could therefore result in over-predictions by the models. The UK regulatory assessment model ‘Contaminated Land Exposure Assessment’ (CLEA) does not explicitly allow for biodegradation and highlights a lack of published evidence of biodegradation in the unsaturated zone in the UK (Environment Agency 2009). To address this data gap, biotrap samples were left in the unsaturated zone adjacent to the VP3 and VP4 soil vapour monitoring well response zones at c. 0.9 mbgl in the patio area of the residential property. Biotraps were left in situ for 1–2 months on one occasion to see whether there was evidence of biological activity.

**Results**

**Soil source term**

In terms of the soil next to the house, the sample results presented in Table 2 were obtained during vapour well installation. Whereas naphthalene, toluene, ethylbenzene and xylenes were elevated above the detection limit in soil from VP4, it is notable that benzene was below the detection limit in all soil samples. The elevated concentrations in VP4 are believed to be associated with the made ground at this location, with spare material from the adjacent gasworks possibly being used to build up this ground prior to the addition of the last rear extension and patio. It is noted that the presence of soil with elevated hydrocarbon concentrations in the unsaturated zone at VP4 made it difficult to extrapolate soil vapour results modelled from adjacent groundwater concentrations (the top of the soil source zone appears to be as shallow as 0.15 mbgl, as shown in the log in Fig. 4a).

**Groundwater source term**

By interpretation of the groundwater flow direction, the primary groundwater plume was believed to be offset from the building foundation (i.e. not below the building foundation), although the plume edge has not been constrained and may be closer to the house than BH4. As with many petroleum vapour intrusion investigations, 1D (D&E) vapour transport modelling is applied assuming a worst-case scenario that the house overlies the plume. This may not reflect real-world conditions that could require lateral migration before vertical migration into the house if the plume does not extend beneath the house.

As seen from Table 3, concentrations in groundwater varied through time. The average groundwater benzene concentration in BH4 was above the 1% of solubility rule of thumb (benzene solubility 1780 mg l\(^{-1}\) (Eugris, http://www.eugris.info/index.asp), indicating free phase hydrocarbon (Kresic 2006). This was one line of evidence that there was free phase hydrocarbon c. 2 m to the SW of the house near the likely tar tank source across groundwater flow gradient. Other lines of evidence from USEPA (2015) and ITRC (2014), such as concentrations of benzene \(>1 \sim 5 \text{ mg l}^{-1}\) and Benzene, Toluene, Ethylbenzene, and Xylene (BTEX) >20 mg l\(^{-1}\) in groundwater, and being within 20 feet of a suspected release area meant that BH2, BH3, BH4 and BH5 could have had residual LNAPL present. As such, groundwater was a potential source of vapours to proximal vapour wells and the house. Chemicals with a high aqueous solubility will partition readily and rapidly into the aqueous phase and will often remain in solution and be available for degradation. Chemicals that are sparingly soluble in water will often dissolve slowly into solution and partition more readily into other phases including air and adhere to the surface of solid particles including soil (Environment Agency 2008). Phenol was present in groundwater in the highest concentrations of all contaminants, but was not in the vapour sample analytical suite, which is a potential future research area. In declining order of mean groundwater concentrations, the compounds present were benzene, then toluene followed by naphthalene, m,p,x-xylenes, then ethylbenzene. These concentrations reflect the differing relative solubility of these compounds, and are close to the 1% of solubility line of evidence for free phase hydrocarbon in BH4 and BH5 as well as exceeding the USEPA (2015) and ITRC

| Soil | VP1 | VP2 | VP3 | VP4 | VP5 |
|------|-----|-----|-----|-----|-----|
| Depth (mbgl) | 0.95 | 0.85 | 0.9 | 0.85 | 0.9 |
| Organic matter (%) | 0.9 | 2.8 | 2.8 | 11* | 4.8 |
| Phenol (µg kg\(^{-1}\)) | <0.1 | <0.1 | <0.1 | 730 | <0.1 |
| Naphthalene (µg kg\(^{-1}\)) | 0.13 | 2.3 | 1.9 | 840 | 0.13 |
| Benzene (µg kg\(^{-1}\)) | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| Toluene (µg kg\(^{-1}\)) | <1.0 | <1.0 | <1.0 | 11 | <1.0 |
| Ethylbenzene (µg kg\(^{-1}\)) | <1.0 | <1.0 | <1.0 | 6.7 | <1.0 |
| m,p,x-xylenes (µg kg\(^{-1}\)) | <1.0 | <1.0 | <1.0 | 130 | <1.0 |

*Potentially artificially elevated because of organic contaminants.

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**Table 1. Groundwater depth (mbgl)**

| Date       | VP3     | VP4     | VP5     | VP6     | VP7     | VP8     |
|------------|---------|---------|---------|---------|---------|---------|
| 20 August 2013 | 1.649   | 1.708   | 1.644   | Slight hydrocarbon odour |
| 2 September 2013 | 1.645   | 1.668   | 1.673   | Slight hydrocarbon odour |
| 10 July 2014   | 1.88    | 1.811   | 1.756   | Slight hydrocarbon odour |
|              | 2.244   | 2.327   | 2.215   | Slight hydrocarbon odour |
|              | 1.917   | 1.903   | 1.784   | Hydrocarbon odour; 1 mm NAPL in August 2013 |

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**Table 2. Soil concentrations within 2 m of house**

| Soil      | VP1 | VP2 | VP3 | VP4 | VP5 |
|-----------|-----|-----|-----|-----|-----|
| Depth (mbgl) | 0.95 | 0.85 | 0.9 | 0.85 | 0.9 |
| Organic matter (%) | 0.9 | 2.8 | 2.8 | 11* | 4.8 |
| Phenol (µg kg\(^{-1}\)) | <0.1 | <0.1 | <0.1 | 730 | <0.1 |
| Naphthalene (µg kg\(^{-1}\)) | 0.13 | 2.3 | 1.9 | 840 | 0.13 |
| Benzene (µg kg\(^{-1}\)) | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| Toluene (µg kg\(^{-1}\)) | <1.0 | <1.0 | <1.0 | 11 | <1.0 |
| Ethylbenzene (µg kg\(^{-1}\)) | <1.0 | <1.0 | <1.0 | 6.7 | <1.0 |
| m,p,x-xylenes (µg kg\(^{-1}\)) | <1.0 | <1.0 | <1.0 | 130 | <1.0 |

*Potentially artificially elevated because of organic contaminants.
indicative limits. Concentrations of these hydrocarbons in the other wells were two to >10 times lower.

The average depth to groundwater in the area over the 18 month monitoring period was between 1.65 and 2.04 mbgl, indicating the thickness of the unsaturated zone. BH1 is up-hydraulic (groundwater flow) gradient from the suspected tar tank source and this was generally reflected in the contaminant concentrations being at or below the detection limit. Naphthalene concentrations in groundwater were just above detection limit at BH1, suggesting some limited background contamination in this area. Wells BH2 and BH3 were also up-hydraulic gradient of the tar tank position indicated on historical plans and confirmed there were other potential gasworks sources of contamination, likely to be associated with the gasworks retort house based on old plans. BH4 is across groundwater flow gradient c. 2 m from the interpreted tar tank, whereas BH5 is c. 15 m down-hydraulic gradient of the tar tank. The variation between depth to groundwater and groundwater concentration in BH4 as well as vapour concentrations in VP4 are shown in Figure 5. With a variation of only 10 cm over the year groundwater depth readings were taken, groundwater fluctuations do not appear to have had a large influence on groundwater concentrations or vapour concentrations at this site.

Vapour pathway

Oxygen, carbon dioxide, methane and nitrogen concentrations were recorded from the bulk samples recovered from the vapour wells on three occasions in June 2015 and January 2016, with the results

table 3: groundwater concentrations (µg l−1) within 2 m of house August 2013 to March 2015

| August 2013          | BH1    | BH2    | BH3    | BH4    | BH5    |
|----------------------|--------|--------|--------|--------|--------|
| Phenol               | <0.5   | <0.5   | <0.5   | 67000  | 43000  |
| Naphthalene          | <0.01  | 87     | 65     | 1600   | 2600   |
| Benzene              | <1.0   | 1920   | 1050   | 17800  | 19200  |
| Toluene              | <1.0   | 12.7   | 2.4    | 4360   | 4880   |
| Ethylbenzene         | <1.0   | 7.9    | <1.0   | 66.2   | 76.6   |
| m&p-xylene          | <1.0   | 27.6   | 89.7   | 930    | 1030   |
| Trichloroethene      | na     | na     | na     | na     | na     |
| Tetrachloroethene    | na     | na     | na     | na     | na     |
| September 2013       |         |        |        |        |        |
| Phenol               | <0.5   | <0.5   | <0.5   | 150000 | 120000 |
| Naphthalene          | <0.01  | 340    | 1500   | 2500   | 2700   |
| Benzene              | <1.0   | <1.0   | 930    | 31000  | 27900  |
| Toluene              | <1.0   | <1.0   | 268    | 6790   | 6470   |
| Ethylbenzene         | <1.0   | 1.8    | 15.1   | 61.1   | 69     |
| m&p-xylene          | <1.0   | 12.2   | 176    | 813    | 894    |
| Trichloroethene      | <1.0   | <1.0   | <1.0   | <1.0   | <1.0   |
| Tetrachloroethene    | <1.0   | <1.0   | <1.0   | <1.0   | <1.0   |
| July 2014            |         |        |        |        |        |
| Phenol               | <0.5   | 890    | 1900   | 160000 | 7700   |
| Naphthalene          | <0.01  | 260    | 900    | 580    | 250    |
| Benzene              | <1.0   | 3900   | 4900   | 40900  | 19000  |
| Toluene              | <1.0   | 15.4   | 801    | 9480   | 2220   |
| Ethylbenzene         | <1.0   | 15.8   | 52.1   | 144    | 81.5   |
| m&p-xylene          | <1.0   | 55.5   | 394    | 1650   | 826    |
| Trichloroethene      | <1.0   | <1.0   | <1.0   | <1.0   | <1.0   |
| Tetrachloroethene    | <1.0   | <1.0   | <1.0   | <1.0   | <1.0   |
| March 2015           |         |        |        |        |        |
| Phenol               | <0.5   | 53     | 130    | 37000  | 3800   |
| Naphthalene          | 0.19   | 220    | 1800   | 1200   | 1300   |
| Benzene              | <1.0   | 443    | 2130   | 6340   | 6420   |
| Toluene              | <1.0   | 902    | 391    | 1420   | 978    |
| Ethylbenzene         | <1.0   | 13.8   | 53.7   | 38.7   | 91     |
| m&p-xylene          | <1.0   | 43.4   | 430    | 452    | 991    |
| Trichloroethene      | <1.0   | <1.0   | <1.0   | <1.0   | <1.0   |
| Tetrachloroethene    | <1.0   | <1.0   | <1.0   | <1.0   | <1.0   |
| Average*             |         |        |        |        |        |
| Phenol               | 0.5*   | 240    | 510    | 100000 | 44000  |
| Naphthalene          | 0.06   | 230    | 1100   | 1500   | 1700   |
| Benzene              | 1.0*   | 1600   | 2300   | 24000  | 18000  |
| Toluene              | 1.0*   | 230    | 370    | 5500   | 3600   |
| Ethylbenzene         | 1.0*   | 10     | 30     | 78     | 80     |
| m&p-xylene          | 1.0*   | 35     | 270    | 960    | 940    |
| Trichloroethene      | 1.0*   | 1.0*   | 1.0*   | 1.0*   | 1.0*   |
| Tetrachloroethene    | 1.0*   | 1.0*   | 1.0*   | 1.0*   | 1.0*   |
| Average groundwater depth (mbgl) | 1.7 | 1.7 | 1.7 | 1.8 | 1.8 |

*Mean calculation includes detection limit values; values with an asterisk indicate detection limit. Mean used for illustrative purposes. Values to two significant figures. na, not available.
shown in Table 4. These indicate that aerobic conditions existed at all locations at all times. There was evidence of oxygen consumption at wells VP3, VP4 and VP5, and occasional oxygen consumption beneath the suspended floor VPIS-1 in June 2015. All vapour samples had slightly more carbon dioxide than ambient samples, suggesting that short-circuiting to atmosphere was not occurring.

There were multiple detections of hydrocarbon vapour in VP1, which is up-hydraulic gradient from the other wells and sources. Given naphthalene was the only contaminant detected in soil and groundwater at this location, the presence of other volatile components in the vapour sample(s) was evidence of a source other than the tar tank. No proximal soil or groundwater sources have been identified nearby for vapour in VP1 although the historical gasworks retort house was c. 15 m away. The soil vapour results are shown in Tables 5 – 7.

The distribution of contaminants in the vapour phase more closely correlated with groundwater as opposed to soil concentrations, with toluene having the highest of the contaminant vapour concentrations. However, a further distinction could be made in that unless the vapour monitoring points are within a few metres of a proven groundwater source, the correlation between soil vapour and groundwater was also limited. McAlary et al. (2011) suggested that using a soil concentration as starting point, instead of groundwater concentration, is generally not recommended for assessing subsurface vapour intrusion to indoor air because there are no published studies that clearly show a direct relationship between measured soil concentrations and measured soil vapour concentrations. Apart from the soil concentrations at VP4, soils at this site provided a poor indication of vapour concentrations. Lahvis et al. (2013) went further and suggested that neither soil nor groundwater concentrations correlate well with soil vapour concentrations at petroleum vapour intrusion sites. Although the presence or absence of compounds in the vapour phase correlated roughly with the presence or absence in groundwater for BTEX compounds, the Lahvis et al. (2013) supposition was also generally supported at this site. For example, the vapour phase benzene concentrations were lower than toluene concentrations in all vapour wells in all sampling rounds where there were groundwater data (except VP3 in March 2015), despite benzene exceeding toluene concentrations within groundwater in all groundwater wells in all sampling rounds (except BH2 in

| Table 4. Bulk gas readings during purging prior to vapour sampling |
|---------------------------------------------------------------|
| | External soil vapour | Sub-floor vapour | Indoor air samples | Background ambient |
| | VP1 | VP2 | VP3 | VP4 | VP5 | VP1G-1 | VP1G-2 | VP1S-1 | VP1S-2 | VP1G-A | VP1S-A | VPA |
| 22 June 2015 | | | | | | | | | | | | |
| Carbon dioxide | 0.63 | 0.15 | 2.08 | 1.53 | 6.57 | 0.08 | 1.42 | <0.05 | na | na | <0.05 | |
| Carbon monoxide | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | na | na | <0.05 | |
| Methane | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | na | na | <0.05 | |
| Nitrogen | 79.8 | 79.2 | 80.2 | 79.7 | 87 | 79.4 | 81 | 79.3 | na | na | 79.1 | |
| Oxygen | 19.5 | 20.7 | 17.7 | 18.8 | 6.4 | 20.5 | 17.6 | 20.6 | na | na | 20.9 | |
| 27 January 2016 | | | | | | | | | | | | |
| Carbon dioxide | 0.32 | 0.43 | 0.38 | 0.85 | 1.09 | 0.11 | 0.08 | 0.09 | 0.08 | 0.1 | 0.06 | |
| Carbon monoxide | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | |
| Methane | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | |
| Nitrogen | 78.9 | 79.6 | 78.9 | 79.3 | 84.7 | 79.1 | 79.1 | 79.1 | 79.1 | 79.1 | 79.1 | |
| Oxygen | 20.8 | 20 | 20.8 | 19.9 | 14.2 | 20.8 | 20.8 | 20.9 | 20.8 | 20.8 | 20.8 | |
| 28 January 2016 | | | | | | | | | | | | |
| Carbon dioxide | 0.36 | 0.26 | 0.66 | 0.93 | 0.89 | 0.16 | 0.1 | 0.08 | 0.09 | 0.12 | <0.05 | |
| Carbon monoxide | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | |
| Methane | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | |
| Nitrogen | 78.9 | 78.8 | 79 | 79.1 | 81.3 | 79 | 79.1 | 79.1 | 79.2 | 79.1 | 79.1 | |
| Oxygen | 20.7 | 20.9 | 20.4 | 20 | 17.9 | 20.8 | 20.8 | 20.8 | 20.7 | 20.8 | 20.8 | |

na, not available.
March 2015). The Henry’s Law constants for these two contaminants are relatively similar (benzene 557 Pa m³ mol⁻¹ (25°C), toluene 660 Pa m³ mol⁻¹ (25°C); Environment Agency 2008; Mackay et al. 1979) so the fact that dissolved benzene concentrations were over five times greater than those of toluene should have meant that vapour concentrations were similarly elevated. In addition, groundwater elevation fluctuation means that a smear zone can be created, where the higher vapour pressure of benzene might have been expected to increase the benzene vapour concentration relative to toluene. This may not be a large factor at this site because the smear zone is likely to be limited as a result of small groundwater fluctuations over the monitoring period (Table 1). The interpretation for benzene concentrations in vapour being consistently lower than the toluene concentrations in all vapour wells when toluene was detected was that either (1) there was another localized unsaturated zone source of toluene, but this was not seen in soil concentrations, or (2) the benzene was being rapidly degraded in the unsaturated zone. Degradation was further supported by the consistent absence of benzene in the vapour phase both up groundwater flow gradient in VP1 (excluding June 2015) and c. 15 m down groundwater gradient in VP5.

The presence of trichloroethene and tetrachloroethene in soil vapour was unexpected because they are not typical gasworks contaminants. The most likely source was the adjacent former gasworks where solvents and degreasers may have been used. The absence of these compounds in groundwater suggested an unsaturated zone vapour source, but further investigation of the potential source was constrained by the site size and access constraints.

Naphthalene was never detected beneath the house nor in indoor air, suggesting that it was attenuated in the vapour pathway or was too strongly sorbed to the soil sediments to volatilize. Hayes et al. (2006) suggested that polyethylene tubing can be subject to absorption of chemicals of potential concern such as naphthalene, resulting in negative bias in results, which is another potential reason why naphthalene was not detected in the vapour phase.

### Table 5. Vapour pathway concentrations (µg m⁻³) outside the house

| Date                        | VP1  | VP2  | VP3  | VP4  | VP5  |
|-----------------------------|------|------|------|------|------|
| 10 July 2014                |      |      |      |      |      |
| Trichloroethene (TCE)       | <8.1 | <8.1 | 237  | 36.5 | na   |
| Toluene                     | <5.7 | <5.7 | <5.7 | 6.4  | na   |
| Tetrachloroethene (PCE)     | <10.2| <10.2| 421.9| 295.1| na   |
| m&p-xylenes                | <6.5 | <6.5 | <6.5 | 11.7 | na   |
| o-xylene                    | <6.5 | <6.5 | <6.5 | 6.9  | na   |
| 27 March 2015               |      |      |      |      |      |
| Benzene                     | <4.8 | <4.8 | <4.8 | 11.5 | <4.8 |
| Toluene                     | <5.7 | <5.7 | 9    | 69.3 | <5.7 |
| Ethylbenzene                | 7.4  | <6.5 | <6.5 | 13   | <6.5 |
| m&p-xylenes                | 25.6 | <6.5 | <6.5 | 46.9 | <6.5 |
| o-xylene                    | 9.1  | <6.5 | <6.5 | 16.9 | <6.5 |
| 16 May 2015                 |      |      |      |      |      |
| Benzene                     | <4.8 | 6.1  | 6.4  | <4.8 | <4.8 |
| Toluene                     | <5.7 | 13.9 | <5.7 | <5.7 | <5.7 |
| Trichloroethene (TCE)       | <8.1 | <8.1 | 175.2| 24.2 | <8.1 |
| Tetrachloroethene (PCE)     | <10.2| <10.2| 278.8| 192  | <10.2|
| 23 June 2015                |      |      |      |      |      |
| Benzene                     | 617.2| <4.8 | 5.4  | <4.8 | na   |
| Trichloroethene (TCE)       | <8.1 | <8.1 | 295.6| 41.9 | na   |
| Toluene                     | 211  | 8.3  | <5.7 | 9.8  | na   |
| Tetrachloroethene (PCE)     | <10.2| 17.6 | 614.5| 421.9| na   |
| Ethylbenzene                | 323.9| <6.5 | <6.5 | <6.5 | na   |
| m&p-xylenes                | 865  | <6.5 | <6.5 | 32.6 | na   |
| o-xylene                    | 263.1| <6.5 | <6.5 | 19.1 | na   |
| 27 January 2016, cold property |    |      |      |      |      |
| Benzene                     | <4.8 | <4.8 | 21.7 | 33.9 | 9.9  |
| Trichloroethene (TCE)       | <8.1 | <8.1 | <8.1 | <8.1 | <8.1 |
| Toluene                     | <5.7 | <5.7 | 13.2 | <5.7 | 9.4  |
| Tetrachloroethene (PCE)     | <10.2| <10.2| <10.2| <10.2| <10.2|
| Ethylbenzene                | <6.5 | <6.5 | <6.5 | <6.5 | 19.1 |
| m&p-xylenes                | <6.5 | <6.5 | 14.8 | <6.5 | 80.3 |
| o-xylene                    | <6.5 | <6.5 | <6.5 | <6.5 | 35.2 |
| 28 January 2016, after heating property |    |      |      |      |      |
| Benzene                     | <4.8 | <4.8 | <4.8 | <4.8 | <4.8 |
| Trichloroethene (TCE)       | <8.1 | <8.1 | <8.1 | <8.1 | <8.1 |
| Toluene                     | <5.7 | <5.7 | <5.7 | <5.7 | 7.5  |
| Tetrachloroethene (PCE)     | <10.2| <10.2| <10.2| <10.2| <10.2|
| Ethylbenzene                | <6.5 | <6.5 | <6.5 | <6.5 | 18.2 |
| m&p-xylenes                | <6.5 | <6.5 | <6.5 | <6.5 | 161.1|
| o-xylene                    | <6.5 | <6.5 | <6.5 | <6.5 | 47.8 |

na, not available.
Although Tables 5–8 provide an overview of average contaminant distribution, they do not show the variation over time. Figure 5 shows the variation of selected contaminant concentrations in the soil vapour and groundwater for BH4 and VP4 in conjunction with depth to groundwater in BH4 (secondary axis). These wells are c. 3 m apart and contained the highest contaminant groundwater and vapour concentrations. The vapour in VP4 could have been derived from either in situ soil made ground contaminants or groundwater contamination emanating from the groundwater plume. The presence of chlorinated solvents in soil vapour but not in groundwater in VP2, VP3 and VP4 suggested there was an additional unsaturated zone soil vapour source that could not be investigated at this site owing to size and access constraints.

The continuous lines in Figure 5 show that vapour concentrations varied dramatically between monitoring rounds, from orders of magnitude above to below the detection limit. The dashed lines show that groundwater contaminant concentrations also changed with time, but in a less pronounced manner. Even though the distribution of BTEX vapour appeared to be related to the presence of groundwater contamination, the temporal trends in the two phases did not correlate closely. This suggested that the processes taking place in the vapour phase caused greater variability in vapour concentrations than relatively minor variations observed in the groundwater phase concentrations. One possibility that has not been investigated in this paper is whether contaminant mass transfer to the unsaturated zone has taken place owing to groundwater fluctuations (McAlary et al. 2011), but there is likely to be a limited smear zone at this site owing to small groundwater elevation fluctuations (Table 1).

Recent research (Guo et al. 2015) has identified preferential pathways (e.g. sewers, land drains and other underground piping) as critical factors in vapour intrusion assessments. Such pathways are difficult to identify through conventional sampling. Controlled pressure method (CPM) testing can be used to identify alternative vapour intrusion pathways that may go undetected using conventional sampling methods. At the Guo et al. (2015) study site, measured emission rates of volatile organic compounds were two orders of magnitude greater than screening model estimates owing to

| Date               | VAPIS-1, suspended floor | VAPIS-2, suspended floor | VPIG-1, solid floor |
|--------------------|--------------------------|--------------------------|---------------------|
| 10 July 2014       | Trichloroethene (TCE)    | na                       | na                  |
|                    | Toluene                  | na                       | na                  |
|                    | Tetrachloroethene (PCE)  | na                       | na                  |
|                    | m&p-xlenes              | na                       | na                  |
|                    | o-xylene                 | na                       | na                  |
| 27 March 2015      | Benzene                  | <4.8                     | 8.6                 |
|                    | Toluene                  | <5.7                     | 7.5                 |
|                    | Ethylbenzene             | 6.9                      | <6.5                |
|                    | m&p-xlenes              | 26.5                     | <6.5                |
|                    | o-xylene                 | 7.8                      | <6.5                |
| 16 May 2015        | Benzene                  | 6.7                      | 5.4                 |
|                    | Trichloroethene (TCE)    | 13.4                     | <8.1                |
| 23 June 2015       | Tetrachloroethene (PCE)  | <10.2                    | <10.2               |
|                    | Benzene                  | <4.8                     | <4.8                |
|                    | Toluene                  | <5.7                     | <5.7                |
|                    | Ethylbenzene             | <6.5                     | <6.5                |
|                    | m&p-xlenes              | <6.5                     | <6.5                |
|                    | o-xylene                 | <6.5                     | <6.5                |
| 27 January 2016, cold property | Benzene      | 76                       | <4.8                |
|                    | Trichloroethene (TCE)    | <8.1                     | <8.1                |
|                    | Toluene                  | <5.7                     | <5.7                |
|                    | Tetrachloroethene (PCE)  | <10.2                    | <10.2               |
|                    | Ethylbenzene             | 13                       | <6.5                |
|                    | m&p-xlenes              | 19.5                     | <6.5                |
|                    | o-xylene                 | <6.5                     | <6.5                |
| 28 January 2016, warm property | Benzene      | <4.8                     | <4.8                |
|                    | Trichloroethene (TCE)    | <8.1                     | <8.1                |
|                    | Toluene                  | <5.7                     | <5.7                |
|                    | Tetrachloroethene (PCE)  | <10.2                    | <10.2               |
|                    | Ethylbenzene             | <6.5                     | <6.5                |
|                    | m&p-xlenes              | <6.5                     | <6.5                |
|                    | o-xylene                 | <6.5                     | <6.5                |

na, not available.
alternative pathways (sewers). CPM testing was beyond the scope of this investigation and in many other real-world assessments especially when the houses are inhabited, but preferential pathway flow may have played an important role in vapour intrusion at this site.

The above provides an overview of the subsurface conceptual model and how contaminant concentrations varied with time. A key focus of a human health risk assessment is how much contaminant can pass from the source (soil, vapour or groundwater) to a receptor. Contaminant concentrations in the various pathway stages at specific dates are shown in Tables 5 and 6, and at the receptor in Table 7. A summary of the data trends in Tables 5 – 7 is presented below.

(1) In July 2014 hydrocarbon vapours were detected in the wells outside the house, but there were no detections in the ambient air within the house.

(2) In March 2015, benzene and toluene were detected in VP4, and these detections were mirrored beneath the suspended floor (VPIS-2) and the ground slab (VPIG-1), further away from the tar tank interpreted source. The benzene and toluene concentrations in both subfloor samples were similar to each other despite one being beneath a solid floor and the other being under a ventilated timber floor. This may have indicated that there was little difference in vapour migration beneath floor types. Oxygen and carbon dioxide readings

### Table 7. Ambient air receptor point concentrations (µg m⁻³) inside and outside the house

| Date         | Indoor VPIS-A | Indoor VPIG-A | Outdoor VPB |
|--------------|---------------|---------------|-------------|
| 10 July 2014 | <8.1          | <8.1          | <8.1        |
| Trichloroethane (TCE) | <8.1          | <8.1          | <8.1        |
| Toluene     | <5.7          | <5.7          | <5.7        |
| Tetrachloroethane (PCE) | <10.2     | <10.2         | <10.2       |
| m&p-xylenes | <6.5          | <6.5          | <6.5        |
| o-xylene    | <6.5          | <6.5          | <6.5        |
| 27 March 2015| <4.8          | <4.8          | <4.8        |
| Benzene     | <4.8          | 24.3          | na          |
| Toluene     | <5.7          | 21.1          | na          |
| Tetrachloroethane (PCE) | <10.2     | <10.2         | <10.2       |
| Ethylbenzene| <6.5          | 43.4          | na          |
| m&p-xylenes | <6.5          | 123.3         | na          |
| o-xylene    | <6.5          | 35.6          | na          |
| 16 May 2015 | 5.1           | 6.7           | na          |
| Benzene     | <4.8          | <4.8          | <4.8        |
| Tetrachloroethane (PCE) | <10.2     | <10.2         | <10.2       |
| 23 June 2015| <8.1          | <8.1          | <8.1        |
| Benzene     | <4.8          | 24.3          | na          |
| Toluene     | <5.7          | 21.1          | na          |
| Tetrachloroethane (PCE) | <10.2     | <10.2         | <10.2       |
| Ethylbenzene| <6.5          | 43.4          | na          |
| m&p-xylenes | <6.5          | 123.3         | na          |
| o-xylene    | <6.5          | 35.6          | na          |
| 27 January 2016, cold property | 5.1           | 6.7           | na          |
| Benzene     | <4.8          | <4.8          | <4.8        |
| Tetrachloroethane (TCE) | <8.1          | <8.1          | <8.1        |
| Toluene     | <5.7          | <5.7          | <5.7        |
| Tetrachloroethane (PCE) | <10.2     | <10.2         | <10.2       |
| Ethylbenzene| <6.5          | 6.5           | <6.5        |
| m&p-xylenes | <6.5          | <6.5          | <6.5        |
| o-xylene    | <6.5          | <6.5          | <6.5        |
| 28 January, after heating | <4.8          | <4.8          | <4.8        |
| Benzene     | <4.8          | <4.8          | <4.8        |
| Trichloroethane (TCE) | <8.1          | <8.1          | <8.1        |
| Toluene     | <5.7          | <5.7          | <5.7        |
| Tetrachloroethane (PCE) | <10.2     | <10.2         | <10.2       |
| Ethylbenzene| <6.5          | <6.5          | <6.5        |
| m&p-xylenes | <6.5          | <6.5          | <6.5        |
| o-xylene    | <6.5          | <6.5          | <6.5        |

na, not available.

### Table 8. Mean* vapour concentrations (µg m⁻³) within 2 m of house, August 2013 to March 2015

| Vapour          | VP1     | VP2     | VP3     | VP4     | VP5     |
|-----------------|---------|---------|---------|---------|---------|
| Naphthalene     | 1.7*    | 1.7*    | 2.8     | 23      | 2.9     |
| Benzene         | 4.8*    | 5.1     | 5.1     | 8.1     | 4.8*    |
| Toluene         | 24      | 25      | 33      | 42      | 52      |
| Ethylbenzene    | 6.7     | 6.5*    | 6.8     | 11      | 6.5*    |
| m&p-xylenes     | 10      | 6.5*    | 11      | 52      | 6.5*    |
| 1,2,4-trimethylbenzene | 7.5     | 7.4*    | 9.3     | 27      | 7.4*    |
| Trichloroethene | 8.1*    | 9.0     | 72      | 32      | 11      |
| Tetrachloroethene | 12      | 33      | 140     | 150     | 28      |

*Mean calculation includes detection limit values; values with an asterisk indicate detection limit. Mean from four monitoring rounds used for illustrative purposes. Values to two significant figures.
beneath the floor types would have been useful in assessing whether there was a difference in aerobic conditions and biological activity beneath each floor type (as was available for the June 2015 monitoring; Table 4). Ethylbenzene and xylenes were detected in VP1 at the northern end of the house, and this was mirrored beneath the ventilated suspended floor sample VPIS-1 (most southerly subfloor sample), rather than the beneath the ground slab VPIG-1, which is closer to VP1. There were no indoor air detections of the identified contaminants of concern in March 2015.

(3) In May 2015 benzene was detected in soil vapour, sub-slab vapour and indoor air at similar concentrations, just above the respective detection limits. This indicates that there was no attenuation along the pathway or at the receptor, which is not logical when considering literature-documented fate and transport behaviour. The trace (detection limit × 5) benzene detections in the May 2015 sampling should therefore be viewed with caution and may have been due to sampling or analytical interference. Trichloroethene was detected in soil vapour outside the house and beneath the suspended floor but not in indoor air, which was more logical because soil vapour should have become diluted as it entered indoor air owing to the regular air exchange rates expected in the house.

(4) Measured concentrations of BTEX compounds in soil vapour outside the house in VP1 were highest in June 2015. Vapour concentrations of BTEX compounds in VP1 were higher in general than in VP4, which in other monitoring rounds contained the highest concentrations. However, none of the BTEX compounds were detected beneath the house in soil vapour. In June 2015, the highest indoor air concentrations (BTEX only detected) were detected above the solid floor slab, but only in sample VPIG-A, closest to VP1. This suggested a short-circuiting pathway to the source of soil vapour in VP1 (BTEX only detected), or a compromised adjacent sub-slab sample not showing the active pathway. Sample VPIG-A was taken on a kitchen work surface, with the wall behind forming a chimney. There were no obvious utilities or utility corridors entering the house at this location, so the chimney in conjunction with a permeable lateral feature beneath the house was the likely potential preferential pathway. Tracer testing would need to be done to test this hypothesis. Well VP4 is nearer the better diluted wooden floor, which would encourage aerobic degradation and which may have explained the lack of vapour phase contaminants in the subfloor or ambient space in these locations, even though soil vapour outside the house was elevated in June 2015. The ventilated sub-floor sample VPIS-1 showed evidence of localized oxygen consumption in June 15, because, in contrast, the sub-slab sample VPIG-1 and the other suspended floor sample VPIS-2 had oxygen concentrations similar to atmospheric, as seen in Table 4. In June 2015 tetrachloroethene was detected in VP2, VP3 and VP4 outside the house and trichloroethene in VP3 and VP4, but neither compound was detected beneath the house nor in indoor or ambient air.

(5) In January 2016 two rounds of sampling were undertaken with a gap of c. 19 h to allow the house to be heated, to determine whether heating alone could cause vapours to be sucked into the house via the stack effect. From Table 5, BTEX compounds were detected in VP3, VP4 and VP5 in the first round of sampling. These perhaps represented steady-state conditions, as there had been a long period before these samples were taken when the well was undisturbed. The concentrations beneath the suspended floor in VPIS-1 were the highest recorded with 76 µg m⁻³ benzene, 13 µg m⁻³ and 19.5 µg m⁻³ m&p-xylenes. Oxygen and carbon dioxide data indicated that the vapour beneath the suspended floor and solid floor was similar to ambient concentrations even after a long period with the house closed up. No hydrocarbon vapour was detected in the house or ambient air. During the second round of sampling, the following day, only toluene, ethylbenzene and xylenes were detected in VP5, with xylenes detected in higher concentrations than on the previous day. As noted in the previous section, the groundwater well adjacent to VP5 occasionally contains free phase hydrocarbon and these concentrations may have resulted from Raoult’s Law partitioning of the relative composition of the free phase (not known) in the vicinity. There were no detections below the house in sub-floor samples after heating the house. After heating the house, no hydrocarbon compounds were detected in the house or ambient air. The effect of heating the house overnight did not appear to induce vapour flow to beneath the house or into the house.

Ambient air in the house and to a lesser extent shallow vapour concentrations beneath the house could have also varied in time depending on wind, barometric pressure and temperature. These factors are presented in Table 9 and further work could be done to determine whether there are pressure gradients from inside to outside the building or under-pressurization within the house during indoor air sampling. Summer temperatures (average over 10°C) produced the highest soil vapour concentrations outside the house. Winter 2016 sampling produced the highest sub-floor concentrations under the suspended floor. There are insufficient data on atmospheric pressure, trend and wind speed to draw definitive conclusions on these factors.

**Biotrap samples**

To assess the potential for microbial activity (and hence biodegradation of contaminants) in unsaturated zone soils, biotaps were placed at two locations where contamination was evident around the house. A picture of a biotrap is shown in Figure 6.

The biotrap worked on the principle of micro-organisms migrating to the sorption beads in the biotrap over the period of 1–2 months. The biotrap was then retrieved and quantification of

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**Table 9. Weather conditions**

| Monitoring visit | Barometric pressure (mbars) | Trend      | Temperature (°C) | Average wind speed (km h⁻¹) |
|------------------|----------------------------|------------|------------------|-----------------------------|
| 10 July 2014     | 1015                       | Rising     | c. 15            | 18                          |
| 27 March 2015    | 1017                       | Rising     | c. 7             | 16                          |
| 16 May 2015      | 1021                       | Rising     | c. 12            | 18                          |
| 23 June 2015     | 1016                       | Rising     | c. 10            | 12                          |
| 26 January 2016  | 1012                       | Falling    | c. 8             | 21                          |
| 27 January 2016  | 1005                       | Falling    | c. 10            | 29                          |

*According to [www.wunderground.com](http://www.wunderground.com) (Norwich station, c. 10 km NE).
the specific functional genes responsible for both aerobic and anaerobic biodegradation of BTEX, polycyclic aromatic hydrocarbons (PAHs) and a variety of short- and long-chain alkanes was performed. The QuantArray® included a suite of assays targeting the initial oxygenase genes of the known pathways for aerobic BTEX biodegradation. Aerobic biodegradation of aromatic hydrocarbons has been intensively studied and multiple catabolic pathways have been characterized. The range of compounds biodegraded via each pathway is largely determined by the specificity of the initial oxygenase enzyme. For example, the enzyme toluene/benzene dioxygenase (TOD) incorporates both atoms of molecular oxygen directly into the aromatic ring. Although commonly called toluene dioxygenase, the substrate specificity of this enzyme is relaxed, allowing growth on toluene and benzene along with co-oxidation of a variety of compounds including ethylbenzene, o-xylene, m-xylene and trichloroethene (TCE). Another example is naphthalene dioxygenase (NAH), which incorporates both atoms of molecular oxygen into naphthalene to initiate aerobic metabolism of the compound. However, the broad substrate specificity of naphthalene dioxygenase has also been widely noted. When expressed, naphthalene dioxygenase is capable of catalysing the oxidation of larger PAHs such as anthracene, phenanthrene, acenaphthylene, fluorene and acenaphthene.

**Discussion**

This section looks at the discrete phases (groundwater, soil and soil vapour) and how they related to one another and indoor air. Tables 5 – 7 data indicate that the source–pathway–receptor ‘system’ never reached a ‘steady state’ or equilibrium whereby there was a constant relationship between soil vapour outside the house, vapour beneath the house and indoor air. This may have been due to a system that incorporated a short-circuiting mechanism (June 2015) whereby soil vapour was drawn up outside the chimney, or due to a combination of factors such as soil moisture content, atmospheric conditions, the capillary fringe and/or biodegradation that could have affected this contaminant linkage to varying degrees at different times. Models such as BioVapor, a steady-state 1D analytical model, can be used to improve understanding of the potential effect of unsaturated zone aerobic biodegradation on the vapour intrusion pathway. Studying the ratio of BTEX compounds to chlorinated compounds did not help the assessment because they appeared to be from two different source zones and did not appear together beneath the house. Of note is that although no contaminants were detected in indoor air in most sampling rounds, when they were detected in May and June 2015 they were present at similar concentrations to soil vapour, with limited attenuation. Although the double glazed and unoccupied nature of the house limited air exchange, some dilution as the soil vapour migrated into ambient air would have been expected.

**Measured v. predicted vapour concentrations using groundwater concentrations**

Standard UK industry models CLEA and P20 do not directly include the ‘volatilization from groundwater to indoor air’ pathway, so Risk-Based Corrective Action (RBCA) v2.5 software was used instead to derive water screening values (WSV), with exposure scenarios modified according to the Environment Agency Science Report SC050021/SR3 residential conceptual exposure model (Environment Agency 2009). Use of WSV allows identification of contaminants that may pose an unacceptable risk to on-site residents through inhalation of vapours from groundwater. A comparison of WSV with maximum groundwater concentrations in BH4 is presented in Table 10. Groundwater concentrations from BH4 were chosen because it was the closest well to the house and was the well containing greatest dissolved concentrations.

The naphthalene concentrations in groundwater were typically just above the WSV, whereas the benzene concentrations were typically orders of magnitude above the screening value. If the model accurately models migration from dissolved phase to indoor air for this site scenario, then there would have been elevated concentrations of both naphthalene and more especially benzene in the indoor air near BH4, where the maximum naphthalene and benzene concentrations in groundwater were measured. However, these contaminants were not observed in indoor air except for benzene in May 2015 (noting that data readings should be used with caution in this round), when vapour well concentrations in VP4 did not contain benzene. Noting also that the highest indoor air concentrations (in June 2015) appeared to be linked to vapour in VP1 where groundwater samples from adjacent BH1 in previous sampling rounds had been below detection limits, the groundwater to vapour model appeared to be over-conservative, as has been suggested by researchers such as Provoost et al. (2009) and Lahvis et al. (2013). Biodegradation was likely to be the main factor influencing these results, with the biotrap results in Table 11 providing evidence of aerobic BTEX degradation with some aerobic naphthalene degradation in the unsaturated zone.

**Measured v. predicted vapour concentrations using soil concentrations**

The current UK regulatory tool (CLEA 1.071) software (Environment Agency 2015), which includes the Johnson & Ettinger (1991) model to predict vapour concentrations, has been used to provide context to the soil results. Selecting a residential scenario for a female child receptor aged 0 – 6 years in a small terraced house on sand geology, using the highest contaminant soil concentrations from VP4, and using default CLEA values (which include a depth to contamination of 65 cm and a soil organic matter content of 6%), the results in Table 12 have been predicted. Table 12 also includes a comparison with the maximum soil vapour and ambient air values measured in Tables 5 and 7.

Although for the half of the house underlain by a ground bearing slab the site conceptual model was similar to the Johnson & Ettinger (1991) model, the measured soil vapour concentrations in vapour wells immediately outside the house were much lower than those

| Table 10. Exceedances of groundwater screening values (µg L⁻¹) for vapour pathway |
|------------------------------|-------|-------|-------|-------|-------|
| WSV  | BH4, August 2013 | BH4, September 2013 | BH4, July 2014 | BH4, March 2015 |
|-------|-----------------|--------------------|----------------|-----------------|
| Naphthalene | 952             | 1600               | 2500            | 580             | 1200        |
| Benzene    | 88.8            | 17800              | 31000           | 40900           | 6340        |
predicted by the CLEA model. Beneath the house (both the section on a ground bearing slab and the section underlain by a suspended timber floor), measured contaminant concentrations were generally even lower. The results suggest that the soil vapour concentrations were over-predicted at this site if soil concentrations were used and this agrees with McAlary et al. (2011), who suggested that using a soil concentration as starting point, instead of groundwater concentration, is not recommended for assessing subsurface vapour intrusion into a building. However, the maximum observed indoor air concentrations of BTEX compounds on one occasion were higher than those predicted by almost an order of magnitude. Therefore, the modelling for vapour ingress into buildings may have been under-predicting potential maximum indoor air concentrations if preferential pathways exist.

**Measured v. predicted indoor air concentrations using soil vapour concentrations**

Using the current UK regulatory tool (CLEA 1.071) software but entering soil vapour concentrations from close to the house (excluding VP5, which is c. 15 m from the house) directly into the model provided the predictions shown in Table 13. Using soil vapour concentrations close to the house is the approach likely to be taken by many risk assessment practitioners in the UK, because going into a house and taking subfloor samples has the potential to cause blight.

Use of CLEA in this way combines several processes, but in simple terms represented an estimation of the dilution between near-building soil vapour and the house itself. Although most of the monitoring round results agreed with the predictions in Table 13 (i.e. no contaminants were routinely detected in indoor air, even when concentrations were detected beneath the house), the maximum observed indoor values exceeded those predicted on one occasion (two for benzene). The results confirmed the soil concentration modelling that suggested that the model under-predicted the worst-case transport of vapour from the subsurface into this particular house, although at this house there may have been a short-circuiting mechanism via the chimney flue above the concrete floor that meant that modelling was not appropriate.

For an alternative approach to modelling, the USEPA has assembled a database of empirical sub-slab-to-indoor vapour attenuation factors (USEPA 2012a,b). Although most of the data in this EPA database are for chlorinated solvents, the sub-slab attenuation factors can be applied to petroleum hydrocarbons because little bio-attenuation is expected between sub-slab and indoor air. Sub-slab attenuation factors in the USEPA (2012b) database vary over several orders of magnitude because of spatial and temporal variability in both indoor air and sub-slab vapour concentrations and background sources of chemicals in indoor air. In the USEPA (2012b) database, the 50th and 95th percentiles of the sub-slab attenuation factor are 5.0 × 10⁻³ and 1.8 × 10⁻¹ respectively, when the data are limited to indoor air concentrations above a 90th percentile background concentration found in the literature. When the data are limited to sub-slab vapour concentrations greater than 100 times the literature background, the 50th and 95th percentiles of the sub-slab attenuation factor are 2.5 × 10⁻³ and 2.0 × 10⁻² respectively (USEPA 2012b). Therefore, a shallow soil vapour-to-indoor air attenuation factor of 0.01 is considered a reasonably conservative attenuation factor for hydrocarbon and chlorinated contaminants.

At this site the sub-slab vapour concentrations were either accompanied by an absence in the indoor air samples, or a similar concentration in the indoor air samples (May 2015, but data should be treated with caution). The soil vapour concentrations therefore varied from more than 100 times higher than the indoor air concentration to less than 10 times the indoor air concentration. In summary, although the 0.01 attenuation factor was valid for most of the time, in June 2015 the attenuation factor was closer to 0.1.

As noted by Provoost et al. (2009), the inclusion or exclusion of a capillary fringe or temperature correction for the Henry constant in the mathematical concept could be significant. Volatilization from the groundwater could be limited by the diffusion rate through the capillary fringe, which, besides soil air, also contains porewater. Diffusion coefficients in water are two to four orders of magnitude lower than in air, and some models, like the Johnson & Ettinger.
been generated in VP1, where no evidence of NAPL was available above LNAPL sources because of weathering. At this site in June below a risk-based screening level in soil gas >60% of the time who noted that benzene concentrations in soil gas are likely to be elevated soil vapour concentrations. However, the potential NAPL the time the presence of NAPL at this site would have produced developed using the database, the results suggested that for most of shallower than the depth range (3.4-4.6 m lateral or vertical) when the conditions in the underlying groundwater were relatively stable.

The Hers & Truesdale (2013) report developed an inclusion distance approach for screening petroleum release sites based on evidence that in the presence of oxygen, petroleum hydrocarbon vapours can rapidly biodegrade. A resulting inclusion distance, defined in that report as the contamination source-separation distance beyond which the potential for petroleum vapour intrusion may be insignificant, was calculated. An inclusion distance approach is potentially more efficient than current modelling approaches for investigating petroleum vapour intrusion sites.

At this site, applying the Hers & Truesdale (2013) 1.6 m vertical distance from the contaminated groundwater to the house would have effectively meant that there was no unacceptable risk if the benzene concentration in soil vapour was 100 µg m$^{-3}$ and the attenuation factor of 0.01 soil vapour-to-indoor air was applied. In the same report, Hers & Truesdale (2013) published findings from analysis of LNAPL sources at underground storage tank sites in the USA. The groundwater concentrations from BH4 were one line of evidence for the presence of non-aqueous phase liquid. The average depth to groundwater in BH4 was 2.3 mgbgl. Because this was shallower than the depth range (3.4-4.6 m lateral or vertical) developed using the database, the results suggested that for most of the time the presence of NAPL at this site would have produced elevated soil vapour concentrations. However, the potential NAPL at BH4 did not produce benzene or toluene soil vapour concentrations above 100 µg m$^{-3}$. This may have indicated an old NAPL plume, with many of the volatile compounds already released or degraded, and is consistent with the findings of Lahvis et al. (2013), who noted that benzene concentrations in soil gas are likely to be below a risk-based screening level in soil gas >60% of the time above LNAPL sources because of weathering. At this site in June 2015, the elevated indoor vapour concentrations appear to have been generated in VP1, where no evidence of NAPL was available (and groundwater contaminants were not detected in the adjacent groundwater well in previous monitoring events).

Conclusions

(1) At this site, for most of the time, the results were consistent with recent research and guidance. However, on one occasion the results were consistent with other recent findings that investigated preferential pathways. Documentation and validation of preferential pathways and comparative assessment of vapour intrusion across slabs v. suspended timber floors has been highlighted by this work as an area that needs more understanding in the UK.

(2) At this site, processes taking place in the vapour phase were more variable than in the groundwater phase, with conditions changing rapidly in the vapour phase even when the conditions in the underlying groundwater were relatively stable.

(3) Recent publications and database predictions suggest that models may overestimate potential indoor air concentrations. Part of this comes from overestimating the soil vapour concentrations, or underestimating the attenuation that occurs. The data from this site support the theory that models such as that of Johnson & Ettinger (1991) overestimate the soil vapour generated. At this site, there was evidence of aerobic biodegradation, which may be the reason for the lower than expected soil vapour concentrations from soil and groundwater. This leads to the conclusion that a site will be better conceptualized by obtaining vapour samples close to the building at the site investigation stage, rather than by trying to model the soil- or groundwater-to-soil vapour transport mechanism. However, it should be noted that there was a poor correlation between sub-slab vapour concentrations and indoor air concentrations at this site in some monitoring events.

(4) The data from this site indicated that most of the time there was sufficient attenuation such that soil vapour outside the house did not transfer to sub-floor vapour concentrations and so indoor air did not contain detectable concentrations of the BTEX, naphthalene or the chlorinated compounds found in vapour outside the house. On the occasions when sub-slab vapour was detected, indoor air concentrations were not detected. However, there were two occasions when contaminant concentrations were detected inside the house. In the first instance (May 2015) the indoor air benzene concentration was the same as the sub-slab concentration, indicating no attenuation, although these results need to be viewed with caution and highlight the requirement for thorough Quality Assurance/Quality Control (QA/QC) sampling during these investigations. In the second instance (June 2015) the indoor air concentrations were c. 0.1 times the soil vapour concentrations outside the house, even though no contaminants were detected beneath the floor. A short-circuiting mechanism, possibly involving the chimney above the concrete solid floor close to the ambient air sampling location, is suggested. Smoke and/or tracer testing could potentially be used to investigate this pathway. In addition, controlled pressure method monitoring to ascertain vapour flow direction may help to develop the conceptual site model further.

(5) The models might give a reasonable long-term average picture, with confirmatory measurements provided by a majority of indoor air sampling results showing no detectable contaminants. However, observed site concentrations may occasionally exceed the modelled assessment criteria if there are short-circuiting mechanisms (which negate the effectiveness of any modelling). The evidence from this site was that models generally over-predict the soil vapour concentrations. With this conclusion in mind, groundwater concentrations provided a better indication of the source term.
than soil concentrations, and soil vapour concentrations outside the house were better than groundwater concentrations. However, if short-circuiting mechanisms exist, then they should be investigated thoroughly because the transfer efficiency of vapour into the house may be underpredicted. The importance of a detailed site conceptual model cannot be overestimated. Although no contaminants were detected in indoor air in most sampling rounds, when they were detected in May and June 2015, they were present at similar concentrations to soil vapour, with limited attenuation. Although the double glazed and unoccupied nature of the house limited the air exchange and provided another uncertainty, some dilution as the soil vapour migrated into ambient air would have been expected.

(6) One of the possible reasons for models over-predicting potential indoor air concentrations is that they do not take biodegradation into account. At this site Biotrap provided a line of evidence for BTEX and naphthalene aerobic degradation. Oxygen and carbon dioxide readings were another line of evidence for biological activity. In particular, the benzene concentration in soil vapour was much lower than expected based on its physical properties and lines of evidence that there was free phase hydrocarbon present overlying groundwater.

(7) Recently developed inclusion zone techniques from the USA including the presence of free phase hydrocarbon on groundwater, which are an alternative method of assessing the risks from vapour intrusion, appear to be valid in the UK if short-circuiting mechanisms are absent.

(8) Although modelling and source separation methods based on soil or groundwater concentrations are insufficient to assess the risk from vapour migration accurately, they are viable screening tools at suitable sites because of their conservatism. Monitoring soil vapour outside or underneath a building can offer a relatively robust picture of likely long-term internal conditions assuming an absence of short-circuiting mechanisms, because an incomplete pathway can be demonstrated. For this house with two areas of suspended floor and two of concrete slab, and because there is a potential short-circuiting mechanism, there were considerable uncertainties in vapour transport mechanisms into the house. Coupled with its situation within 2 m of a non-aqueous phase liquid plume at 2 m below ground level and an uninvestigated in situ tar tank source within 3 m, the only robust method of accurately assessing risk would be regular indoor air monitoring in ‘lived-in’ conditions over a prolonged period. This interpretation should be taken in the context that the contamination adjacent to this house was elevated in comparison with most sites subject to vapour assessments.

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