



Application of portable gas chromatography–mass spectrometer for rapid field based determination of TCE in soil vapour and groundwater

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ABSTRACT

The application of portable chromatography–mass spectrometer (GC–MS) is restrained by its detection limits without the development of proper sample pre-concentration methods. The primary focus of this paper is to introduce a practical field measurement methodology for the analysis of volatile organic compounds (VOCs) in soil vapour and groundwater using a portable gas (GC–MS) system for application to *in situ* assessment of vapour intrusion from VOC contamination. A solid-phase micro-extraction (SPME) technique was applied for sample pre-concentration before the GC–MS measurement. Practical in-field soil gas SPME sampling methods have been developed to optimise the SPME extraction efficiency to then ultimately improve the detection limits of portable GC–MS. An Australian site impacted by a chlorinated VOC, trichloroethylene (TCE), was the subject of the case study. To rapidly assess soil vapour samples in subsurface soil, in-house-developed retractable soil vapour sampling probes (SVSPs) were installed at the site in clusters at depths of 1 m, 2 m and 3 m below ground level at each sampling location. Use of the SVSPs for sampling enabled the generation of a three-dimensional map and distribution contours for TCE concentrations using the *in situ* measurement results of a portable GC–MS analysis for vapour intrusion investigation. The results of the portable GC–MS analysis were compared with the results from conventional USEPA methods, such as TO-15 and Method 8265 for soil vapour and groundwater samples, respectively. This work demonstrates that the developed methodology of using a portable GC–MS system has the capability for in-field quantitative analysis of VOCs for rapid contaminated site vapour intrusion assessment.

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1. Introduction

Long-term exposure to volatile organic compounds (VOCs) such as trichloroethylene (TCE) potentially increases the risk of developing cancers in humans, including non-Hodgkin lymphoma, kidney or liver cancer (Dechellis and Yee, 2018; Kleinfelder Australia Pty Ltd, 2017). In some cases, TCE-impacted groundwater and vapour in the soil have migrated

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off-site and have been detected beneath residential properties. Using current standard laboratory analytical methods for determination of VOCs, such as USEPA Methods TO-14 and TO-15 (Method TO-17, 1999; Compendium Method TO-15, 1997), requires collection of the samples with specified containers and their transport to a laboratory for analysis. Alternatively, soil gas sampling was finished by purging soil gas to sorbent tube to absorb target VOCs, then the sealed sorbent tubes were sent back to the laboratory to desorption with solvent and test with GC-MS (Zhang et al., 2019). These laboratories are typically equipped with the most sensitive equipment and the analysis for VOCs carries with it high costs and lengthy timeframes. However, targeting molecules may be lost through vaporisation or degradation, while samples are being stored or transported to an analytical laboratory (Hewitt et al., 1992). On-site, rapid chemical analysis of VOCs would minimise the risks of losing target analytes and can be applied to rapid health risk assessments. Safeguarding sample integrity may be achieved by performing the sample collection, extraction, and analysis on-site using portable GC-MS technology. As well as a reduction in the time to obtain results, in-field analysis provides a significant reduction in labour and commercial laboratory costs.

Recently, the portable GC-MS has been used widely in different applications for VOCs/SVOCs detections, including analysing VOCs/SVOCs in indoor air samples (Hopler, 2012; Leary et al., 2016; Barnes et al., 2004; Shakoor et al., 1997; Fair et al., 2010; Gorder and Dettenmaier, 2011). Unlike conventional benchtop GC-MS systems, which are normally coupled with sample concentrating equipment using thermal desorption. Without proper rapid in-field sample preparation and pre-concentration procedures, in-field measurement using portable GC-MS is usually not able to reach the detection limits to satisfy the requirements of environmental protection authorities (EPA). The solid-phase micro-extraction (SPME) technique has been widely applied for sampling molecules (Pawliszyn, 1997; Haddadi and Pawliszyn, 2009; Jia et al., 2000; Dean, 2009; Hook et al., 2002; Zhao et al., 2011). Sample molecules are pre-concentrated to SPME fibres to improve the detection limit of portable GC-MS. The suitability of headspace SPME-GC-MS combining method has been proved to detect PCE, TCE and other VOCs at trace levels for the quantitative analysis of real samples (Zhang and Harrington, 2015; Fabbri et al., 2007; Zhou et al., 2011; George et al., 2015). Unlike thermal desorption sample pre-concentration techniques, when using SPME as a sampling technique, there are many causative factors, such as extraction time, temperature and solvent, which impact the extraction efficiency (Jia et al., 2000; Zhao et al., 2011; Zhang and Harrington, 2015). These factors include extraction time, temperature, solvent etc. Without considering these causative factors, the GC-MS system will be inaccurately calibrated, with an SPME as the sampling method. Therefore, in this study the impacts of the causative factors have been investigated to improve the extraction efficiency of SPME. Importantly, improving the extraction efficiency of SPME can consequently enhance the sensitivity of the detection.

As a case study, an Australian site with both groundwater and soil impacted by TCE was evaluated using a portable GC-MS in the field. For the assessment of vapour intrusion in the subsurface, a soil vapour bore is essential for sampling soil gas. However, the installation of a conventional sampling bore is time-consuming and is technically demanding. To rapidly and comprehensively detect VOCs in soil vapour, an 'easy to install' and retractable soil vapour sampling probe (SVSP), has been designed and developed. The SVSP performs faultlessly after placement into a pre-drilled borehole which has been back-filled with soil. At the case study site, the SVSPs were installed at different locations with different depths. By collecting the soil gas samples and analysing them using a portable GC-MS, a three-dimensional map and distribution contours with different depths for TCE concentrations were developed from the results for the vapour intrusion assessment.

2. Materials and methods

2.1. Portable GC-MS

The portable GC-MS (Torion T9) uses an MXT-5 stainless steel column of 5 m length and 100 μm inner diameter. The inner surface is coated with 0.4 μm thickness of diphenyl dimethylpolysiloxane as a low polarity stationary phase. This column is suitable for the gas separation of pesticides, hydrocarbons, and semi-volatiles. The resolution of GC separation was improved using the temperature programming mode. The temperature sequence was programmed using CHROMION 1.2 software in a personal computer and transferred to the portable GC-MS using an Ethernet cable connection. The temperature was set initially at 50 $^{\circ}\text{C}$ and held for 10 s before it was increased 2 $^{\circ}\text{C}$ per second to 200 $^{\circ}\text{C}$. The temperature programme finished by holding the temperature at 200 $^{\circ}\text{C}$ for 10 s. The portable GC-MS can be powered either by its battery or external power supplies with its power adapter. The portable instrument contains a 90 mL stainless steel helium cylinder at 170 kPa GC column head pressure. One helium gas cylinder was able to supply around 8 h of field measurement. Alternatively, a standard helium cylinder can be applied through an external connection.

Data were saved in comma-separated value (CSV) format, which is editable using Excel 2016. The contour maps of TCE concentrations in soil vapour were generated using the Krig interpolation algorithm in ArcGIS with the sampling locations. The three-dimensional contour was generated using MATLAB R2018b. The OpenChrom software was employed to analyse the gas chromatograph and mass spectrum. Theoretically, with the same temperature sequence, a particular VOC reaches the GC detector and creates a chromatographic peak at a specific time of retention. TCE was the main pollutant at the test site. The retention time for TCE was approximately at 25.5 s, and the identical mass was 131. For calibration, firstly, standard TCE solutions were prepared with ethanol. The standard solutions were then injected into a 2 L empty glass bottle sealed with layers of Parafilm, to generate standard vapour calibration samples. The vapour was then collected and transferred to the portable GC-MS using the SPME (65 μm polydimethylsiloxane (PDMS)/divinylbenzene (DVB)) for equipment standardisation.

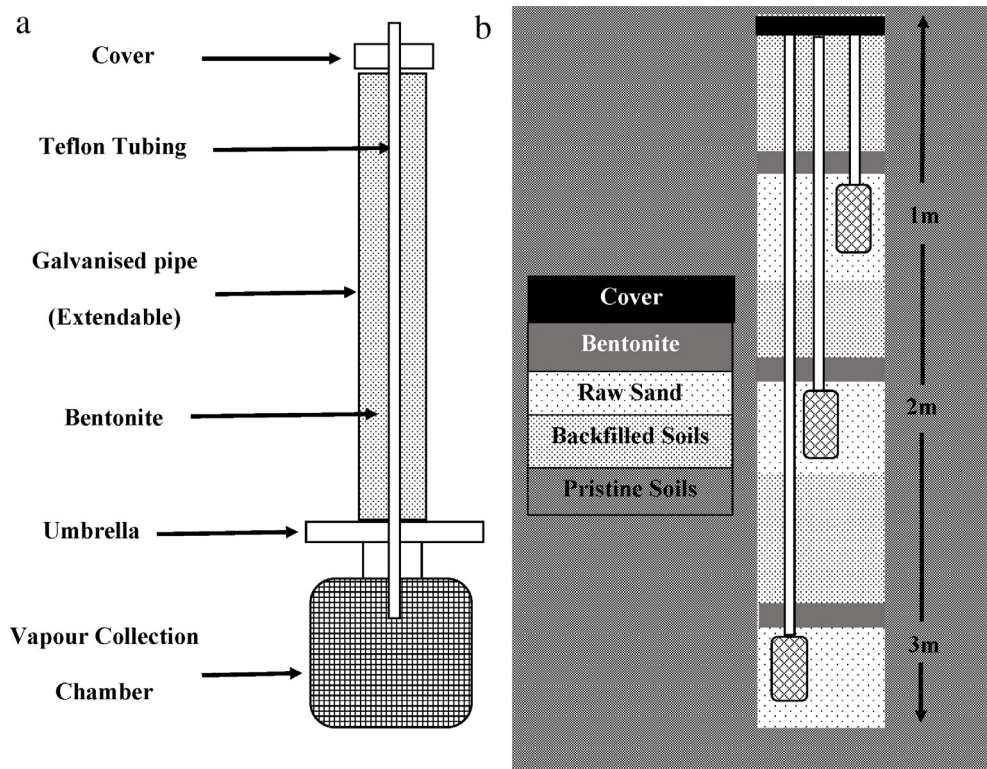


Fig. 1. The retractable soil vapour probe and installation.

2.2. Soil vapour sampling probe (SVSP) and installation

To rapidly and comprehensively detect VOCs in soil vapour, an 'easy to install' and retractable (SVSP), has been designed and developed. The design of the SVSP is shown in Fig. 1a. The SVSP consists of a meshed stainless steel cylindrical vapour chamber, of 100 mm length and 80 mm diameter attached to a rigid metal tube through which a non-absorbent Teflon sampling tube passes to connect the vapour chamber to ground level, from which samples can be taken. The chamber allows the collection of soil vapour from the surrounding subsurface soil by preventing soil particles from blocking the sampling tube. Brass fittings were used on the SVSP and the depth of the SVSP in the subsoil was adjusted to a particular sampling requirement by the use of different lengths of galvanised pipe. A Teflon sampling tube of 6 mm inner diameter connects the vapour chamber at the base of the SVSP in the soil to the sample collection point. The sampler tubing protrudes above the soil surface and is protected in a 20 mm diameter rigid galvanised pipe fitted to the chamber. To ensure that vapour is only sampled through the soil surrounding the chamber, the pipe is sealed internally with bentonite. Either Tedlar bags or vapour canisters are then used to collect the sample at the soil surface.

As shown in Fig. 1b, after placement of an SVSP into a pre-drilled borehole, clean sand was poured into the hole until the SVSP chamber was immersed. This was followed by a thin layer of bentonite to seal the borehole to prevent air intrusion from above the chamber. Soil was then back-filled into the hole until the depth for installing the next SVSP was reached. Three SVSPs were installed at each location at 1 m, 2 m and 3 m depths. Sixteen locations were selected in a four by four (120 m by 120 m) grid approximately 40 m apart. A total of 48 SVSP units were installed at the site – 3 at each location.

2.3. Soil vapour sampling

1L volume airbags (Tedlar), made of non-absorbent DuPont film, were used to collect the soil vapour samples. An airbag was placed in a sealed air sample box and, under negative pressure provided by an air pump, the air sample bags were filled directly from the SVSP sample tube. As depicted in Fig. 2, the airbag was connected to Teflon tubing that extends from the vacuum box to the sample point of an SVSP. The flow rate of the air pump was set to 150 ml/min and, before sample collection, the SVSPs were purged for one minute to eliminate any residual air/vapour existing in the SVSPs. Then 750 mL of soil vapour sample was collected into the airbag over a 5-minute period. The airbag was then disconnected from the vacuum box, and an SPME syringe needle was then pierced through the airbag's septum. The syringe's internal

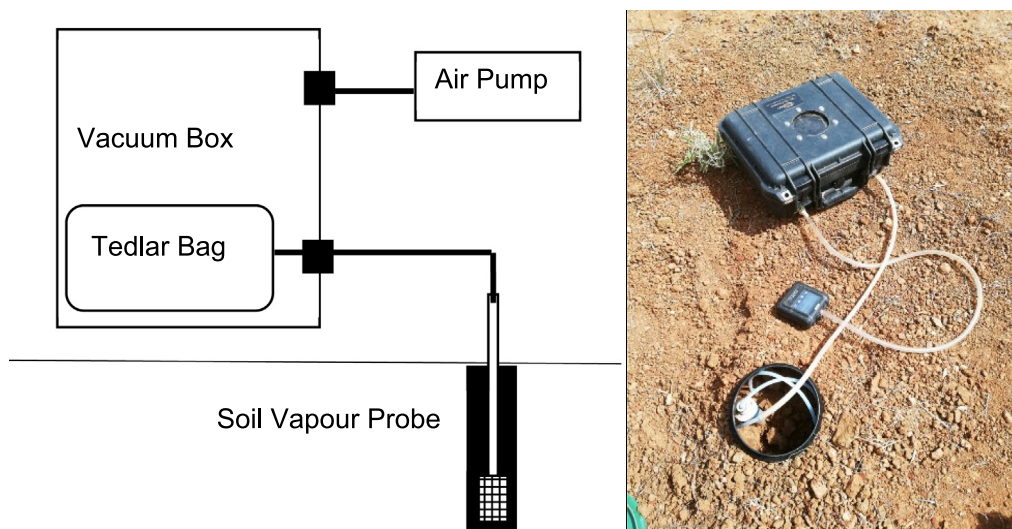


Fig. 2. A diagram of the air bag sampling system.

fibre was then exposed for 8 min to the vapour sample for extraction of the analytes. During the extraction, the airbag was placed over ice in a cooler box to maintain the samples close to 4 °C. Following the extraction onto the fibre, the SPME fibre was inserted directly into the portable GC–MS for VOC analysis.

For the validation of results obtained from the portable GC–MS analysis of soil vapour phase obtained by the SVSPs, the conventional soil vapour sampling method was also employed. Duplicate vapour samples (1.5 L volume) were collected in Siltek treated SUMMA canisters, with 150 mL/min flow controller or critical orifice. The initial pressure of the canisters was approximately –200 kPa and following sample collection, the pressure in the canisters was approximately –20 kPa. The canister samples were submitted to a NATA-certified laboratory for analysis using a conventional GC–MS with US EPA Method TO-15.

2.4. Groundwater sampling

Groundwater was collected using a submersible pump with braided Teflon tubing. The pumping rate was set at 150 mL/min, and three groundwater bore volumes of water were purged from each well before sampling. The measurement of VOCs in groundwater by the T9 was based on the headspace method. Firstly, 10 mL of groundwater was sampled into a 40 mL vial and mixed with 3 g of sodium chloride. The vial was then securely capped with a polypropylene screw-top hold cap and a 3 mm thick polytetrafluoroethylene septum, purchased from Agilent. A vortex mixer was used to vigorously mix the salt and groundwater sample in order to release the solute VOCs into the vial's headspace by increasing the water salinity (Zhou et al., 2011). SPME syringe needle was pierced into the vial through the septum and the fibre exposed to the headspace for extraction for 10 min at ambient temperature. After collection of the sample onto the fibre, the SPME was inserted directly into a portable GC–MS for VOC analysis.

A traditional groundwater sampling method with acid preservation was also applied for comparison. Each groundwater sample was filled into two 40 mL volatile organic analysis vials with no headspace. 40 µL of 200 mg/L sulphuric acid was added as the preservative to prevent biodegradation. The groundwater samples were stored at 4 °C then analysed with conventional GC–MS using US EPA method 8265.

2.5. SPME extraction study

To study the efficiency impact of extraction solvents (ethanol, hexane and acetone), 1–10 µL of pure chlorinated hydrocarbons, 1, 2 dichloroethylene (DCE), TCE and tetrachloroethylene (PCE) solutions were prepared in 1 mL each of ethanol, hexane, and acetone. In this study, all chemicals were analytical reagent grade and purchased from Sigma-Aldrich. 2 µL of the standard calibration solutions were injected into three containers with three different volumes (200 mL, 2 L, and 20 L) to create 1 to 100 mg/m³ standard vapour samples with nitrogen. After injection, the inlet of the containers was properly sealed with multi-layer Parafilm. An SPME syringe was pierced into the multi-layer Parafilm and the fibre was exposed to the vapour sample. The temperature study was carried out in constant temperature rooms (CTRs) with standard proportional–integral–derivative (PID) temperature controllers (TCs).

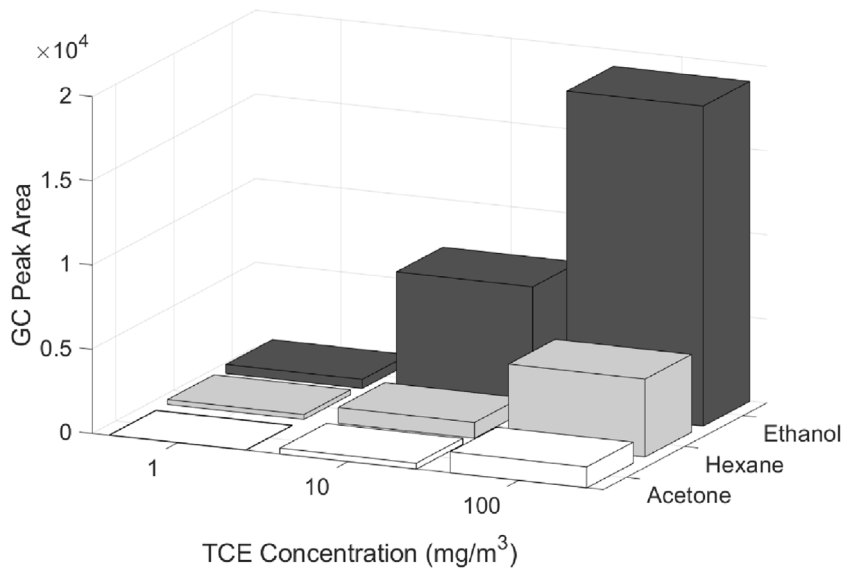


Fig. 3. The comparison of three extraction solvents spiked into TCE samples.

Legend:

x-axis – three TCE concentration levels: 1, 10 and 100 mg/m³;

y-axis – chromatographic peak area response to TCE by using the portable GC-MS;

z-axis – three different extraction solvents: acetone, hexane, ethanol.

3. Results and discussion

3.1. SPME extraction efficiency optimisation

For the TCE measurements using the portable GC-MS, the detection limit by coupling with the SPME extraction method is currently around 1000 $\mu\text{g}/\text{m}^3$. To satisfy the requirements of EPAs, the detection limit needs to be improved to reach below 100 $\mu\text{g}/\text{m}^3$. Optimising the extraction efficiency of SPME by sample pre-processing can consequently improve the sensitivity of the detection. Therefore, laboratory benchtop studies were undertaken to investigate the causative factors which will impact the extraction efficiency of SPME, including extraction time, temperature and solvent.

3.1.1. Extraction solvent

Additional organic solvents are usually avoided when applying SPME, because the SPME fibre may become saturated with the solvent instead of the desired analyte. However, it was found that adding water-immiscible solvents can dramatically enhance the extraction efficiency of SPME (Zhao et al., 2011). The immiscible solvents probably serve to extract and concentrate the analytes in the organic phase and isolate vapour moisture (George et al., 2015). Also, the organic solvents can act as surfactants to decrease interfacial tension, hence increase the extraction yield. Furthermore, it was found that the lower density of the solvent the better enhancement of the extraction efficiency. Zhang et al. also found that the extraction efficiency of SPME can be significantly improved with the addition of minute amounts of organic solvents (Zhang and Harrington, 2015). Six different solvents were compared, and hexane was found to be the most efficient solvent in their study. However, they did not compare hexane with acetone and ethanol, which are two commonly used solvents used in analytical chemistry for dilution. To study the efficiency impact of these three extraction solvents, 1~10 μL of pure TCE solutions were prepared in 1 mL each of ethanol, hexane, and acetone.

After injection, the inlet of the containers was properly sealed with multi-layer Parafilm. After a 5 min vaporisation time in room temperature at 20 °C, an SPME syringe was pierced into the multi-layer Parafilm and the fibre was exposed to the vapour sample for 10 min. The 3-D bar graph in Fig. 3 illustrates the results by using the three different extraction solvents. It was found that ethanol was the most efficient solvent to improve the extraction, compared to acetone and hexane. Either comparing the GC peak area or MS mass integration, the values were improved more than ten times by comparing ethanol with acetone.

3.1.2. Extraction time

SPME is an equilibrium based technique, and extraction efficiency improves with the increase of the extraction time, before the extraction reaches equilibrium (Zhao et al., 2011). Jia et al. (2000) and other studies mentioned that the exposure time of SPME to the samples impacts on the extraction efficiency. In this study, the SPME fibre was exposed to the single vapour sample of chlorinated hydrocarbons (DCE, TCE and PCE) for three different times: 5, 10 and 20 min,

respectively. The extraction solvent was ethanol. There was no significant improvement for extraction by increasing the adsorption time, which means the equilibrium is reached. On the contrary, the extraction efficiency decreased significantly after a five-minute extraction for low concentration, 1 mg/m^3 . For the medium concentration level 10 mg/m^3 , the best adsorption was 10 min. There was no improvement by extending the extraction time after 10 min. Furthermore, it is evident that the extraction efficiency for these three chlorinated hydrocarbons was different. From 1 to 100 mg/m^3 , the best extraction was for PCE. Nevertheless, there was no significant difference for extracting TCE and PCE at the high concentration of 100 mg/m^3 . The SPME has the weakest extraction efficiency for DCE. For TCE, the highest GC response was at 5 min rather than 10 and 20 min.

3.1.3. Mixture standards

When measuring a mixture of multi-compounds, the competition between different compounds might affect the extraction efficiency. To study this impact, mixture standards of DCE, TCE and PCE were used to create the three concentration vapour samples. There were three different mixtures: (1) TCE mixed with PCE and DCE; (2) TCE mixed with PCE; (3) TCE only. There were two SPME extraction times (5 min and 10 min) for each sample. By comparison, the mixture of other compounds did affect the extraction of TCE. The more compounds in the mixture, the more significant is the effect. The impact was more significant from the mixture with PCE and DCE than the mixture with PCE only. Furthermore, by comparing the two extraction times of all the three mixtures, a 5 min extraction time still provided better signals than 10 min for TCE.

3.1.4. Extraction temperature

The temperature study was carried out at three temperatures 4, 20 and 36 degrees Celsius ($^{\circ}\text{C}$), in CTRs. $0.6 \mu\text{L}$ of the standard solutions was injected into the 1L Tedlar bags with 600 mL nitrogen to create $100 \mu\text{g/m}^3$ to 100 mg/m^3 standard vapour samples in air bags. SPME extraction time was 10 min. The SPME extraction efficiency for the three chlorinated hydrocarbons was significantly improved at the decreased temperature. TCE and DCE improved more significantly than PCE. TCE was detected at a lower level, at $100 \mu\text{g/m}^3$ level at 4°C , while this low-level of TCE was not detected when the temperature was 20°C or above. According to Zhao et al. (2011), the high temperature normally increases the diffusion rate of the analytes, which leads to faster extraction. However, because adsorption is an exothermic process, the amount of analytes adsorbed on the SPME fibre decreases when the temperature is increased.

3.2. TCE in situ measurement

3.2.1. Soil vapour

Conditioning the vapour samples by spiking with a minute amount of ethanol and by decreasing the exposure temperature to around 4°C , the extraction efficiency of SPME was improved significantly. Therefore, for the field sampling and measurement in this study, after filling up an airbag with soil vapour sample, $1 \mu\text{L}$ of ethanol was injected with a syringe ($5 \mu\text{L}$, SGS). To reduce the SPME extraction temperature, the airbags were placed into a 20 L insulated portable storage container filled with 3 L of ice. An SPME syringe needle was pierced into the airbags through the septum and to expose the fibre to the vapour sample for extraction for 10 min at around 4°C . After collecting a sample on the fibre, the SPME was inserted directly into the portable GC-MS for VOC analysis.

Fig. 4 shows the correlations between the GC peak area values and TCE concentrations determined by conventional GC-MS (USEPA method TO15). The data with the symbols 'o' and '□', represent the GC-MS signal response to the sample with and without conditioning, respectively. The GC-MS system had higher sensitivity when responding to the samples with ethanol conditioning. The SPME was saturated by TCE when the concentration was higher than 10 mg/m^3 , or when the GC peak area was greater than twenty thousand. Therefore separate calibration curves were applied to the samples containing TCE under or above $10,000 \mu\text{g/m}^3$. In contrast, saturation did not occur with the unconditioned samples since the GC peak area values were all under the saturation threshold, and a single calibration curve could be applied. For detection sensitivity comparison, clear GC-MS signals were recorded by a conditioned sample, with TCE higher than $200 \mu\text{g/m}^3$, whereas GC-MS could only provide notable signals for the unconditioned samples with TCE above $500 \mu\text{g/m}^3$. This was a significant outcome regarding improving the detection sensitivity of the GC-MS.

By using the regression lines demonstrated in Fig. 4, the mean of relative errors (MRE) between the predicted results from the portable GC-MS and the measurement results from canister (TO15) method, were approx. 9% and 12% for the measurement of conditioned samples and unconditioned samples, respectively. However, due to the SPME fibre saturation, the linear range of the detection was reduced. This result evidenced sample conditioning method can improve both the detection sensitivity and prediction accuracy. The feasibility and robustness of this method have also been proved for rapid in field VOC measurements.

3.2.2. Groundwater

The GC-MS measurements of groundwater were based on the headspace method and the results were compared with the analyses by conventional GC-MS using US EPA Method TO15. Fig. 5a summarises the comparison between the GC peak area values of GC-MS and TCE concentrations provided by the conventional GC-MS analysis for all the groundwater samples. The MRE was approx. 8% between the portable GC and the conventional method. A highly significant

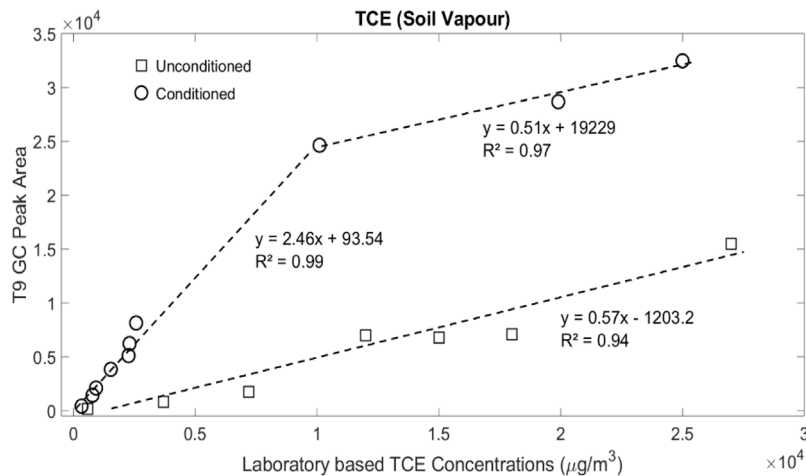


Fig. 4. T9 GC peak area against TCE concentrations provided by external laboratory service. The data with the symbols 'o' and '□', represent the T9 signal response to the sample with and without conditioning, respectively.

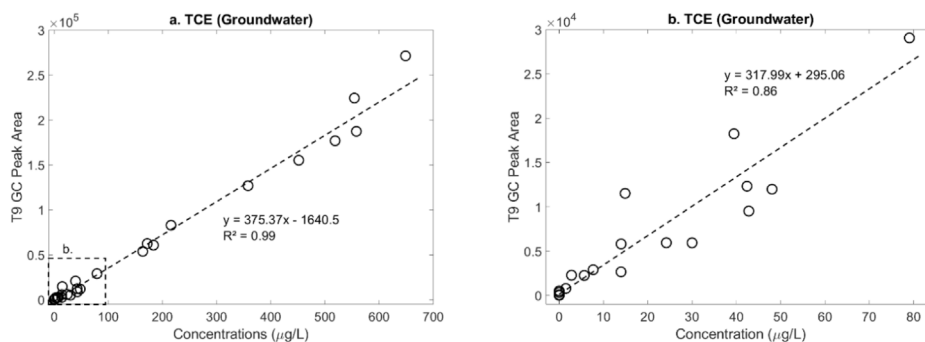


Fig. 5. T9 GC peak area against TCE concentrations for groundwater samples. (a) Calibration range including concentrations up to 1000 µg/L and (b) calibration range from 0 to 100 µg/L.

linear relationship was observed between the GC peak area values and TCE concentrations provided by the conventional laboratory using US EPA method 8265. However, the linear relationship was not as durable over the concentration range below 10 µg/L (Fig. 5b). Significant signals from the T9 were still recorded for the measurement of TCE in groundwater, which the concentrations were lower than 1 µg/L.

By comparing the calibration curves between soil vapour (conditioned) and groundwater methods, the groundwater headspace method provided GC signals that were less sensitive than the Tedlar bag method. One of the main reasons for differences in sensitivity is that the headspace method only measured the VOCs vaporised from the solutions. Adding salt and shaking the solution released only a portion of the VOCs from the solution, and significant amounts of VOCs remained in solution. A secondary reason is due to the sample extraction temperatures. The Tedlar bag method was temperature-controlled to just above zero degrees Celsius by placing the soil vapour samples into an ice-filled cooler container, whereas the groundwater headspace method was conducted at ambient air temperature without sample conditioning, which was around twenty degrees Celsius. As mentioned in the previous SPME conditioning study, reducing the extraction temperature can significantly improve SPME extraction efficiency. In our groundwater study, TCE concentrations in the groundwater samples were much higher than in the soil vapour samples. Sample conditioning method can improve the detection sensitivity but reduce the linear detection range by causing SPME fibre saturation. Hence the sample conditioning method was not applied to the groundwater study.

3.3. Vapour intrusion assessment (3D mapping)

The site assessment contour maps of TCE concentrations in soil vapour were generated using the Krig interpolation algorithm in ArcGIS and the results are shown in Fig. 6. The contour maps show that there was a hotspot of TCE at the south corner, SVSP N4W4, where the concentrations were above 5, 9 and 10 mg/m³ from one-, two- and three-metre depths of SVSP, respectively. There was a relatively small difference between the measurements from the 2 m and 3 m

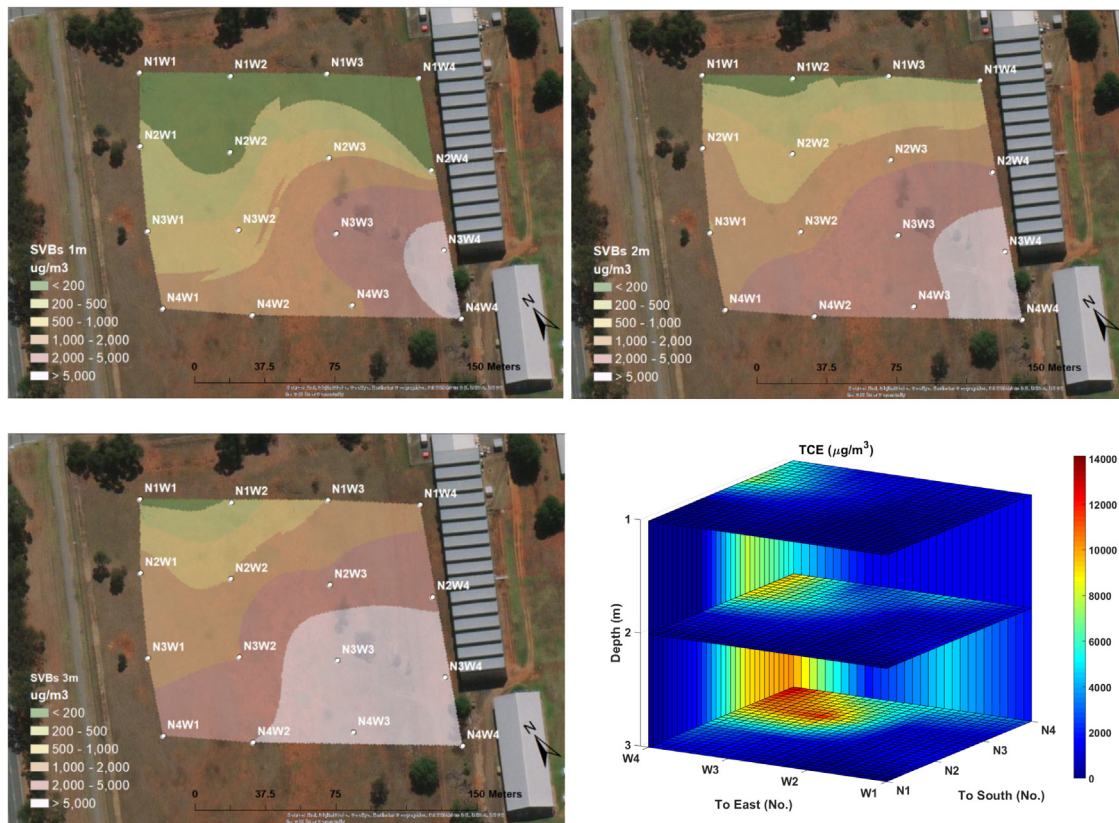


Fig. 6. The contour and 3D maps of the test site TCE concentrations from the SVSPs at 1, 2, 3 m depths.

SVSPs at location N4W4, which were both significantly higher than the 1 m SVSP. The concentration of TCE at the 1 m SVSP was just over 50% of the 3 m SVSP. Overall, comparing all the samples in the sixteen locations with three different depths, 1, 2 and 3 m, TCE concentrations measured in the vapour samples increased with increasing depth of the SVSPs. The TCE vapour intrusion was lower in the northern side of the contour area. TCE was lower than the detection limit at the north corner N1W1. A three-dimensional map was obtained by combining the contour data (Fig. 6). The soil type distribution (Fig. 7) indicates clay-rich soils towards the north-east corner (N1W3, N1W4 and N2W4), and sandier soils towards the south and southeast (N4W4). Soil texture plays a significant role in the migration of subsurface volatile chemicals (Waitz et al., 1996; Fitzpatrick and Fitzgerald, 1997). According to 6, soil with finer particles has lower soil vapour permeability. Soil composed of finer particles has less pore space between the soil particles that serve either to transport vapour to form connecting pores or to store vapours. Hence, on the north-east side of the site, the clay-rich soils demonstrated more resistance to TCE vapour intrusion compared with the southeast corner. The TCE concentrations were relatively high at the southeast corner of the grid but this could be due to the higher porosity of the soil in that area which allows TCE vapour to diffuse more readily.

Considered in conjunction with the groundwater TCE distribution contour (Krig interpolation) illustrated in Fig. 8, the results showed a hotspot containing the highest TCE concentration of more than 5000 $\mu\text{g/L}$, at groundwater bore GW2171. This groundwater hotspot overlapped a hotspot of the soil vapour measurement. The SVSP N3W3 was installed adjacent to the groundwater monitoring well GW2171, which is about 12 m deep, where the TCE concentration was 6448 $\mu\text{g/L}$. Under the assumption of TCE in soil vapour at 12 m is equivalent to the groundwater concentration, then a logarithmic linear relationship was generated between the depth of soil and TCE concentrations, which is demonstrated in Fig. 9. With further information, including soil moisture, organic matter, etc, vapour intrusion models, such as Johnson and Ettinger (J&E) Model, can be applied for validation (Fitzpatrick and Fitzgerald, 1997). Nevertheless, vapour intrusion modelling is beyond the aim of this study.

4. Conclusion

Without proper and rapid in-field sample preparation and pre-concentration procedures, in-field measurement using portable GC-MS to reach the detection limits which satisfy the requirements of environmental protection authorities

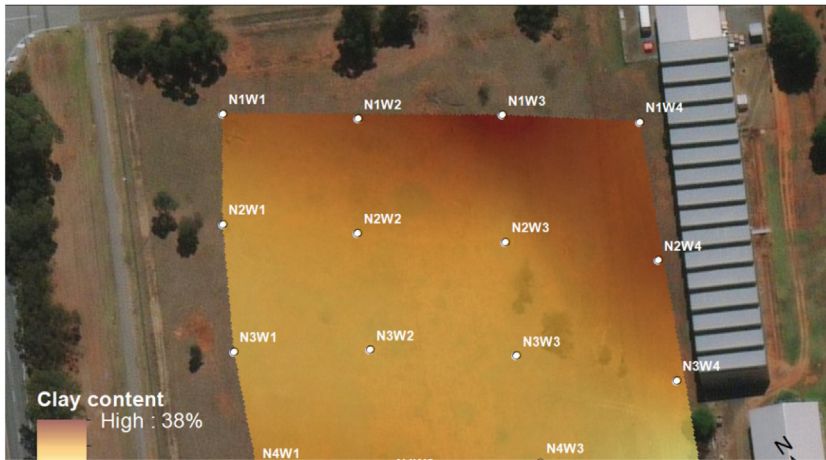


Fig. 7. The contour of clay content.

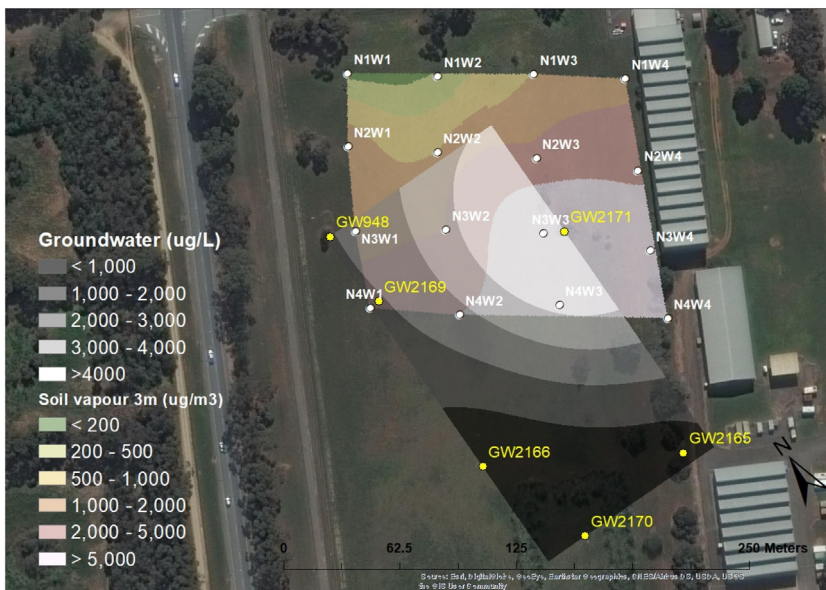


Fig. 8. Overlapping the groundwater contour map with 3 m SVSP contour map.

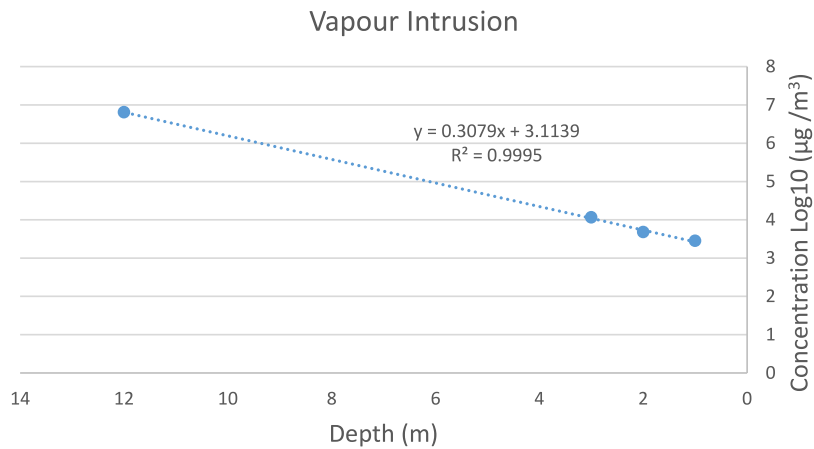


Fig. 9. Vapour intrusion at the location N3W3.

(EPA) is challenging. An infield soil gas sample preparation method has been developed through this study. Based on our benchtop investigation, using our sample preparation method to optimise the SPME extraction efficiency, the detection limit of the portable GC–MS is improved from 1000 to nearly 100 $\mu\text{g}/\text{m}^3$, for TCE vapour determination. However, sampling conditioning caused the SPME to become saturated more rapidly than for unconditioned samples, and thus required separate calibration curves for concentrations above saturation.

To rapidly access soil vapour samples in subsurface soil, in-house-developed retractable SVSPs were installed in clusters with three different depths at the site. A three-dimensional map and distribution contours for TCE concentrations were generated using the *in situ* measurement results of a portable GC–MS analysis, which can be used for vapour intrusion investigation. Based on the results of this study, the portable GC–MS was shown to be able to detect and provide a linear response to the targeted VOCs for rapid in-field contaminated site assessment. This work is a demonstration that the portable GC–MS system has the capability for in-field quantitative analysis of VOCs for rapid contaminated site assessment.

CRediT authorship contribution statement

Liang Wang: Public responsibility for the content, Including participation in the concept, design, analysis, writing, or revision of the manuscript. **Ying Cheng:** Public responsibility for the content, Including participation in the concept, design, analysis, writing, or revision of the manuscript. **Ravi Naidu:** Public responsibility for the content, Including participation in the concept, design, analysis, writing, or revision of the manuscript. **Sreenivasulu Chadalavada:** Public responsibility for the content, Including participation in the concept, design, analysis, writing, or revision of the manuscript. **Dawit Bekele:** Public responsibility for the content, Including participation in the concept, design, analysis, writing, or revision of the manuscript. **Peter Gell:** Public responsibility for the content, Including participation in the concept, design, analysis, writing, or revision of the manuscript. **Mark Donaghey:** Public responsibility for the content, Including participation in the concept, design, analysis, writing, or revision of the manuscript. **Mark Bowman:** Public responsibility for the content, Including participation in the concept, design, analysis, writing, or revision of the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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