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Qualitative and Quantitative comparison of field-based analytical technologies for petroleum hydrocarbons determination in soils

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Qualitative and Quantitative comparison of field-based analytical technologies for petroleum hydrocarbons determination in soils

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ABSTRACT

The performance of seven field-based technologies including 3 portable solvent-based technologies and 4 handheld solvent free technologies were evaluated for petroleum hydrocarbons determination in soil and soil-gas samples from a range of gasoline and diesel spiked soils as well as soils from field sites contaminated with hydrocarbons. Performance of the field technologies were compared to an established reference gas chromatography coupled to mass spectrometry (GC-MS) analytical method for petroleum hydrocarbons. Further to this, the recovery and performance of the solvent-based technologies were assessed using a certified soil reference material and benchmarked against commercial accredited laboratory analysis for the field contaminated samples.

KEYWORDS

Total petroleum hydrocarbons; hydrocarbon speciation, field techniques, rapid measurement tools

INTERNET

CONTENTS

SUMMARY

Over the past decade, a range of commercial and R&D field-based analytical technologies have been made available for soil analysis. This has allowed the determination of hydrocarbons in soil to be expedited, increase the number of soil samples that can be processed at lower cost and enhance spatial resolution of soil data at contaminated sites. There are to date, however, aspects that have not been fully studied such as the performance and the accuracy of the analytical field technologies for different soil types, levels of contamination and fuel type contamination (e.g. gasoline and diesel). Furthermore, information on their ability to speciate and quantify hydrocarbon groups for risk assessment purpose is still limited. In this study, the performance of seven field-based analytical technologies covering gas chromatography (GC), infra-red (IR) and ultraviolet fluorescence (UVF) spectroscopy, and photoionization were evaluated for a range of gasoline and diesel spiked soils and soils contaminated with hydrocarbons from field sites (**Table 1**). Performance of the field technologies were compared to established reference gas chromatography coupled to mass spectrometry (GC-MS) method for the spiked soils and accredited commercial laboratory analysis for the real soils. Overall, the portable GC-MS performed well and close to the benchtop GC-MS. While the headspace analysis of the portable GC-MS was easy to use and allowed time to be saved compared to the benchtop GC-MS, extra analysis time was required for the soil extraction and analysis due to manual injection. The non-destructive and solvent free Fourier-Transform IR (FTIR) and visible and near-infrared reflectance IR (vis-NIR) spectroscopic technologies performed well with diesel and demonstrated to be versatile, fast, and easy to use approach, but the accuracy was lower than for other technologies when total petroleum hydrocarbons (TPH) levels were <1000 mg kg^{-1}. The procedures for soil calibration and validation may further limit the FTIR and vis-NIR applicability for diverse soil type and fuel type. In comparison, the non-dispersive IR (NDIR) and UVF spectroscopy technologies showed better performance, typically ±15% precision and ±30% bias for quantifying TPH in soil, which meet regulatory requirements. The UVF technology also provided additional quantitative information into hydrocarbons groups which can inform swiftly remediation monitoring and validation. Analysis of soil-gas samples by photoionization detector (PID) showed that PID underestimated concentrations compared to both portable and benchtop GC-MS which was expected as PID only provides an indirect and approximate indication of concentration of volatile compounds (VOC) in soil. It is however worthwhile to consider using PID along other field technologies given its simplicity to use, and low cost. Finally, comparison with the accredited GC-MS based methods for remediated soils that require validation data showed that most of the field technologies may not been able to achieve performance requirements of ±30% bias for low petroleum hydrocarbons level (<50 mg kg^{-1})

Table 1: Summary of the selected field-based analytical technologies for petroleum hydrocarbon analysis

Analytical technology	Field instrument		Method type[1]		Media[2]		Fuel type[3]		Analytes[4]				Level 1		Level 2		Level 3		Analysis time	Skill level
			SB	SF	S	SG	G	D	VOCs	BTEX	TPH	HC Spec.	P ≤15%	B ≤30%	P ≤15%	B ≤30%	P ≤15%	B ≤30%		
Gas chromatography coupled to mass spectrometry (GC-MS)	Person portable FLIR Griffin™ G510	FT1	√		√	√	√	√	√	√	√	√	√	√	√	√	√	√	15-40 min	Medium-High
Nondispersive infrared spectroscopy (NDIRS)	InfraCal 2 ATR-SP TOG/TPH analyser	FT2	√		√		√	√	√		√		√	√	√	√	√	√	5-10 min	Low-Medium
Ultraviolet fluorescence spectroscopy (UVFS)	QED hydrocarbon analyser	FT3	√		√		√	√	√	√	√	√	√	√	√	√	√	√	5-10 min	Medium
Visible near infrared spectroscopy (Vis-NIRS)	ASD Field Spec 4 High resolution spectroradiometer	FT4		√	√			√			√				√	√	√	√	<5 min	Medium-high
Fourier transform infrared spectroscopy (FTIRS)	Agilent 4300 handheld FITR spectrometer	FT5		√	√			√			√				√	√	√	√	<5 min	Medium-High
Fourier transform infrared spectroscopy (FTIRS)	RemScan® handheld FITR Spectrometer	FT6		√	√			√			√				√	√	√	√	<5 min	Medium
Photoionization detection (PID)	MiniRAE 3000 PID	FT7		√		√	√	√	√		√		√	n.a.	√	n.a.	√	n.a.	<5 min	Low

[1] **SB**: Solvent based extraction method; **SF**: Solvent free, non-intrusive method; [2] **S**: soil sample; **SG**: soil-gas sample; [3] **G**: Gasoline; **D**: Diesel; [4] **VOC**: Volatiles Organic Compounds that include a range of selected low molecular weight aliphatic and aromatic hydrocarbons up to $EC_{12;}$ **BTEX**: benzene, toluene, ethylbenzene and xylenes; **TPH**; Total petroleum hydrocarbons; **HC Spec**. Hydrocarbon group speciation; **P**; precision; **B**: bias; Level 1 = 100 mg kg^{-1}; Level 2 = 1000 mg kg^{-1}; level 3 = 10,000 mg kg^{-1}; **n.a.** not applied.

1. INTRODUCTION

Determination of petroleum hydrocarbons in soil has long been an area of active investigation and is still attracting significant interest as they are the most frequently encountered contaminants on site which are toxic to human and environmental receptors (Concawe, 2021). Petroleum hydrocarbons include a wide range of chemical compounds that can be grouped according to their chemical structure into aliphatic and aromatic hydrocarbons. When analysing petroleum hydrocarbons in soil, the difference between the term petroleum hydrocarbons (PHC) as such and the term total petroleum hydrocarbons (TPH) should be noted. PHC typically refers to the hydrogen and carbon containing compounds that originate from crude oil, while TPH pertains to the measurable amount of petroleum-based hydrocarbons in an environmental matrix and thus to the actual results obtained by sampling and chemical analysis (Coulon and Wu, 2017). TPH is thus an analytical method-defined term and therefore estimates of TPH concentrations will vary depending on the analytical method and technique used to measure it (Concawe, 2021).

The analysis of contaminated soils during site investigation and remediation often involves a range of non-specific screening techniques carried out on site and specific fingerprint techniques completed off-site by commercial laboratories that use certified analytical methods (Horta et al., 2015; Wang et al., 2019). The non-specific techniques such as field-screening gas chromatography with flame ionisation (GC-FID) or photo-ionisation detection, infra-red (IR) spectrophotometry, turbidimetry, and ultraviolet fluorescence (UVF) spectroscopy are typically used to screen TPH, quantify aliphatic and aromatic hydrocarbons during site investigation, identify potential hydrocarbon concentration hotspots and compare TPH concentrations in environmental media (Concawe, 2021). Similarly, the lab-based fingerprint techniques such as gas chromatography coupled to mass spectrometry (GC-MS) or high-performance liquid chromatography-mass spectrometry (HPLC-MS) provide detailed high-quality data into aliphatic and aromatic hydrocarbons speciation, qualitative and quantitative hydrocarbon degradation due to weathering or engineered remediation, as well as high sensitivity and accuracy for risk indicator compounds which is required to meet regulatory requirements. While the analytical methods associated with the lab-based fingerprint techniques provide a very high level of accuracy and precision, the laboratory procedures involved are often pointed out as time-consuming and expensive and therefore do not always provide cost effective approaches for decision making needed during site investigation, remediation monitoring and validation (Wijewardane et al., 2020; Wang et al., 2020).

Over the past decade, a range of commercial and R&D field-based analytical technologies have been developed, expediting hydrocarbon determination on site, and increasing the number of soil samples that can be analysed at lower cost, and hence enhancing the spatial resolution of site investigation and remediation phases (Concawe, 2021). To date, there are however aspects that have not been fully studied such as the performance and the accuracy of field analytical technologies for different soil types, different levels of contamination and different fuel types (e.g., gasoline and diesel). Furthermore, comparison of their ability to speciate and quantify different hydrocarbon groups for risk assessment purposes and evaluation of whether they could offer a good alternative to lab-based technologies for remediation monitoring and validation is still limited.

In this study, the performance of seven field-based technologies for petroleum hydrocarbons determination in soil and soil-gas samples for different soil types and fuel types was evaluated (**Table 2**). The selection of the technologies was based on the previous work of Concawe (2021). The field-based technologies performance was further compared with lab-based GC-MS and standard TPH analytical methods. Further to this, performance of the field technologies and the reference lab-based GC-MS were evaluated for real contaminated and remediated soil samples and benchmarked against commercial accredited laboratory analysis.

Table 2: Overview of the field and reference technologies evaluated for petroleum hydrocarbons determination in soil-gas and soil samples

N.	Field instrument name	Instrument	Technology	Hydrocarbons targets	Media	LOD and range
FT1	Person portable FLIR Griffin^{TM} G510 GC-MS		Gas chromatography coupled to mass spectrometry (GC-MS)	VOC, BTEX and SVOC and PAH	Soil-gas and soil solid	0.001 mg kg^{-1} (ppb) to ppt (headspace analysis) 1-10 ppm (full scan) 1-10 ppt (SIM)
FT2	InfraCal 2 ATR-SP TOG/TPH analyser		Nondispersive Infra-red spectroscopy (NDRIS)	TPH C_6-C_{26}	Soil solid	3 mg kg^{-1} 1 - 2000 mg/kg
FT3	QED hydrocarbon analyser		Ultra-violet Fluorescence spectroscopy (UVFS)	Total BTEX, GRO, DRO, TPH	Soil solid	GRO, DRO, TPH: <1 mg kg^{-1} PAH: 0.005 mg/kg
FT4	Analytical Spectral Devices (ASD) Field Spec 4 Hi-Resolution spectroradiometer		vis-NIR spectroscopy (vis-NIRS)	TPH C_{10}-C_{40}	Soil solid	- 0.1 - 50,000 mg kg^{-1}
FT5	Agilent 4300 handheld FITR spectrometer		FTIR spectroscopy (FTIRS)	TPH C_{10}-C_{40}	Soil solid	- 0.1 - 50,000 mg kg^{-1}
FT6	RemScan® handheld FITR Spectrometer		FTIR spectroscopy (FTIRS)	TPH C_{10}-C_{40}	Soil solid	68 mg kg^{-1} 0.1 - 100,000 mg kg^{-1}
FT7	MiniRAE 3000 PID		Photo-ionization detector (PID)	Total VOC	Soil-gas	0.1 ppm 0 to 15,000 ppm
RT	Shidmazu GCMS-TQ8040N and AOC 6000		Benchtop GC-MS reference technology	VOC, BTEX and SVOC and PAH	Soil-gas and soil solid	0.001 mg kg^{-1} (ppb) to ppt (headspace analysis) 1-10 ppm (full scan) 1-10 ppt (SIM)

BTEX: benzene, toluene, ethylbenzene and xylenes; **DRO**: Diesel Range Organic hydrocarbons (C_{10}-C_{40}); **FT**: Field technology; **GRO**: Gasoline Range Organic hydrocarbons(C_5-C_9); **LOD**: limit of detection; **PAH**: Polycyclic aromatic hydrocarbons usually comprised of the 16 PAHs listed by the US Environmental Protection Agency; **RT**: reference technology **SVOC**: Semi-volatiles Organic Compounds including aliphatic and aromatic hydrocarbons in the range of C_{12}-C_{40}; **SIM**: Selected ion monitoring; **TPH**; Total petroleum hydrocarbons; **VOC**: Volatiles Organic Compounds that include a range of selected low molecular weight aliphatic and aromatic hydrocarbons up to EC_{12}.

2. MATERIALS AND METHODS

2.1. CHEMICAL AND REAGENTS

All reagents were purchased from Merck-Sigma-Aldrich (UK) and all solvents were HPLC grade. A C8 to C40 alkanes calibration standard and the EPA 525 PAH Mix A were purchased from Sigma Aldrich (UK). The standards were used to verify chromatographic separation quality, quantification, and calibration for the lab-based GC-MS reference method (Risdon et al., 2008). The internal standards used were comprised of deuterated alkanes mix (C10 ^{d22}, C19 ^{d40} and C30 ^{d62}) and deuterated polycyclic aromatic hydrocarbons (PAH) mix (naphthalene ^{d8}, anthracene ^{d10}, chrysene ^{d12} and perylene ^{d12}) at 10 μg mL^{-1} each for the solvent phase extraction method as previously described in Coulon and Wu (2014). Toluene d^{8} (2 μg mL^{-1}) was used as internal standard for the volatile organic compounds (VOC) determination. A certified reference material RTC-SQC026 (TPH in soil, Supelco) was also acquired from MERCK (UK) to determine the accuracy of the results provided by the GC-MS reference method used and the field technologies. Gasoline and diesel fuels were purchased from a local petrol station near Cranfield University (UK).

2.2. SOILS CHARACTERISTICS

Three commercial soils were used for this study and defined according to the USDA and UK-ADAS textural key to soil taxonomy as sandy loam, silty clay loam, and clay loam (**Table 3**). Moisture and organic carbon were determined by loss on evaporation (105°C for 17 h) and loss on ignition (450°C for 4 h) following the British Standard BS EN 13039:2000.

Table 3: Overview of the three commercial soils

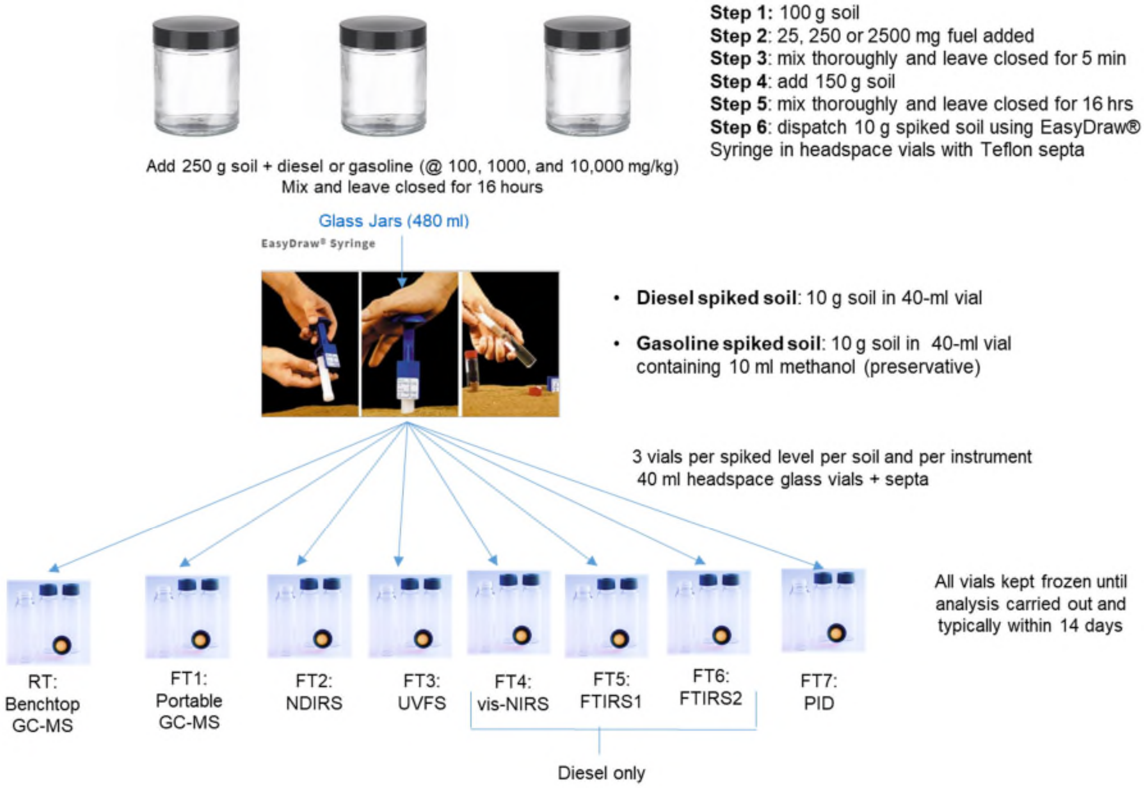
Textural classification	Commercial name	Organic carbon (%)	Moisture (%)	Clay (%)	Sand (%)	Silt (%)
Sandy loam	Suregreen Melcourt Topsoil Blended loam [a]	5	7	18	55	30
Silty clay loam	Super Surrey Loam [b]	6	16	28	15	57
Clay loam	Country loam [b]	17	3	32	30	38

a) https://www.sure-green.com/; b) https://www.agrigem.co.uk/.

2.3. SOILS SPIKING PROCEDURE

All purchased soils were then air-dried for 11 days at 17°C. The soils were then homogenised and sieved through a 1-mm gauge sieve to remove larger aggregates. The soil samples were stored in sealed polytetrafluoroethylene (PTFE) containers until spiking as summarised in **Figure 1**. Briefly, 100 g of soil was spiked with gasoline or diesel fuel on weight/weight basis to achieve the desired spike level (100, 1000 and 10,000 mg kg^{-1}) before closing the lid and mixing thoroughly for 1 min. The jars were then left closed for 5 min before adding and mixing with the remaining 150 g of soil (**Figure 1**). The jars were then closed for an additional 24-h period at room temperature before commencing the subsampling to allow the spike to interact and equilibrate with the soils.

Figure 1: Overview of the soil spiking procedure and analytical technologies



Aliquot samples (10 g triplicate) for each analytical technology were collected with the EasyDraw Syringe® and Power Stop Handle Soil Sampler® as described in EPA SW-846 Method 5035A and transferred to a 40 ml glass headspace vial for diesel spiked soils. For gasoline spiked soils, pre-tared headspace vials containing 10 ml methanol as a preservative were used. Vials were then stored at -4°C until the analysis was carried out (typically within 14 days).

2.4. FIELD SOIL SAMPLES

In total, eight field samples contaminated with PHC from petrol stations were collected from three different sites based in the UK. The soil samples were either collected during site investigation (GS1 and 2) or after remediation happened and requiring hydrocarbon verification measurements (GS3 to 8). Approximately about 2-3 kg of soil sample was collected at each sampling point from the upper layer of soil of 0–20 cm with a spade. All samples were stored at -4°C until analysis.

2.5. FIELD ANALYTICAL TECHNOLOGIES AND BENCHTOP GC-MS TECHNOLOGY

The seven field-based technologies (FT) selected for this study include one portable GC-MS (FT1), one portable nondispersive infrared (NDIR) spectrophotometer (FT2), one portable ultraviolet fluorescence (UVF) spectrometer (FT3), one handheld visible and near-infrared reflectance (vis-NIR) spectrometer (FT4), two handheld Fourier-transform infra-red (FTIR) spectrometers (FT5 and 6), and one handheld photoionization detector (PID; FT7). The field-based technologies were evaluated against a benchtop GC-MS equipped with a multifunctional autosampler allowing to run both liquid and headspace samples (**Table 2**).

The performance of the PID and the headspace of both portable and bench GC-MS were compared for all gas-soil samples from the spiked soils. Similarly, the spiked soil samples were evaluated with all field technologies, with exception of the FTIR and vis-NIR spectroscopy for gasoline spiked soils as it was not possible to use methanol as preservative as it would interfere with the analysis. It has also been reported that non preserved samples contaminated with gasoline are subject to volatilisation losses that occur during the analytical process which result in poor performance for such technique (Concawe, 2021).

2.6. VOLATILE ORGANIC COMPOUNDS EXTRACTION AND MEASUREMENT METHODS

The general methodology used for the extraction and determination of volatile organic compounds from the spiked soils followed the EPA Method 5021A and the EPA Method 8260D (SW-846). Briefly, the headspace analysis was performed with a Shidmazu AOC 6000 multifunctional autosampler. The optimal parameters of the headspace were as follows: thermostatting time 10 min, thermostatting temperature 45°C, agitator bloc speed 250 rpm, syringe temperature 60°C. The chromatographic analysis was then performed using a Shidmazu GCMS-TQ8040N (Benchtop GC-MS reference) operated at 70 eV in positive ion mode. The column was a Restek® fused silica capillary column (30 x 0.25 mm internal diameter) coated with RTX®-5MS (0.25 µm film thickness). Split ratio injection of 30 and 200 with headspace sample volume of 500 µL was applied for diesel and gasoline, respectively. The oven temperature was with an initial hold at 40°C for 2.5 min, and then ramped to 210°C at a rate of 35°C min^{-1} and held at this temperature for 3.5 min. The ion source temperature of the mass spectrometer was 200°C, the interface temperature 230°C and solvent cut time set at 2 min. MS was operated at full scan mode (range m/z 50-250) for quantitative analysis of target volatile aliphatic and aromatic hydrocarbons. For quality control, duplicate blank controls were analysed every 20 samples. No carry-over contamination was observed between runs.

Regarding portable headspace GC-MS analysis (FT1), vapour emissions were extracted and heated from the headspace of the sample vials with a heated sample probe; the operational parameters were membrane introduction mass spectrometry inlet temperature 130°C, trap temperature 40°C hold for 0.50 min, and desorb temperature 250°C hold for 2 min. The inlet temperature was 225°C and was operated in split mode as follows: 40% hold for 0.1 min, then 10% hold for 0.88 min and 10% thereafter. The carrier gas was ultra-high purity helium. The chromatography column was a ValcoBond® capillary VB-5 column (15 m x 0.18 mm x 0.18 µm, VICI Metronics). The GC oven temperature was maintained at 40°C for 0.98 min, then ramped to 250°C at 30°C min^{-1}. Detection and data acquisition were performed at full scan mode between 45 and 400 m/z. Same blank controls were used for the portable GC-MS headspace analysis.

In addition to the GC-MS headspace analysis, soil-gas samples were analysed by using a MiniRAE 3000 PID (FT7) equipped with a standard UV lamp with a photon energy of 10.6 eV. Prior to measurements and calibration, the PID was allowed to stabilise in the laboratory for at least 30 min. The PID was calibrated by the rental company with 100 mg L^{-1} isobutylene immediately prior to despatch. Drift over the period of use was expected to be negligible. Samples were placed in glass vials closed by a cap bearing septa through which headspace was drawn by piercing them with a hypodermic needle. The needle attached to a PtFE transfer line was connected to the PID inlet probe with silicone gaskets. The air withdrawn from the sample was replenished via a second needle inserted through the septum to avoid any change in pressure over the sample. Once the PID was connected to the sampling line the sample was allowed to equilibrate for 5 min before recording a reading. The reading in ambient air was regularly recorded, both by drawing it through the needle and sample line and directly through the PID probe.

2.7. SOLVENT BASED TPH EXTRACTION AND MEASUREMENT METHODS

Sequential ultrasonic solvent extraction was used as previously described by Risdon et al (2008) with some modifications. Briefly, 10 g of soil sample was mixed with 20 mL of hexane (HEX):dichloromethane (DCM) solution (1:1, v/v), shaken for 16 h at 150 oscillations per min over 16 h, and finally sonicated for 30 min at 20°C. After centrifugation, extracts were cleaned on 12 mL Discovery® Silica solid phase extraction (DSC-Si SPE) tube by elution with 1:1 HEX:DCM. The final extracts were diluted (1:10) for GC-MS analysis. Deuterated alkanes (C10d22, C19d40 and C30d62) and deuterated PAH (naphthalene d8, anthracene d10, chrysene d12 and perylene d12) were added as internal standards to the extracts at 0.5 µg mL^{-1} each, respectively. Aliphatic hydrocarbons and PAHs were identified and quantified with a Shidmazu GCMS-TQ8040N (Benchtop GC-MS reference) operated at 70 eV in positive ion mode. The inlet temperature was 250°C. The column used was the same as mentioned above. Splitless injection with a sample volume of 1 µL was applied. The GC oven temperature was maintained at 50°C for two minutes, and then ramped to 220°C at 20°C min^{-1} and then to 310°C at 6°C min^{-1} and held at this temperature for 15 min. The mass spectrometer was operated using the full scan mode (range m/z 50-500) for quantitative analysis of target alkanes and PAHs. For each compound, quantification was performed by integrating the peak at specific m/z and retention times. External multilevel calibrations were carried out using alkane (standard C8-C40 solution) and PAH (EPA 525 PAH Mix A) standards, the concentration of which ranged from 2.5 to 50 µg mL^{-1}, respectively. Prior to measurements, the portable GCMS (FT1) was allowed to stabilise in the laboratory for 30 min. Briefly, 1 µL of the extract was manually injected in split mode (10% after 5 min). The inlet temperature was 225°C. The chromatography column was the same as described above. The GC oven temperature was maintained at 50°C for two minutes, then ramped to 300°C at 30°C min^{-1} and kept at 300°C for 5 min. Detection and data acquisition were performed in full scan mode between 45 and 425 m/z . For quality control, blank controls and a 500 µg mL^{-1} diesel standard solution (ASTM C12-C60 quantitative, Supelco) were run every 20 samples on both GC-MS. When analysed, if the blank concentration exceeded the method reporting limit of 10 mg kg^{-1} for TPH, the samples were re-analysed.

For the portable NDIRS (FT2), the instrument was allowed to stabilise in the laboratory for at least 30 min as recommended by the manufacturer (Spectro Scientific®). Soil TPH programme was used and the Infracal 2 ATR-SP user guide for measuring oil and grease from water and soil was followed (Spectro Scientific, 2019). Briefly, soil samples were extracted by adding 1 v/w of hexane to soil and shaken for 2 min. The extract was then cleaned using activated silica gel and Whatman no. 40 filter paper. For level 3 spiked soils, the extracts were further diluted 5 times to be within the detection range of the Infracal (**Table 2**). Before each measurement, the attenuated total reflectance (ATR) crystal was cleaned with isopropanol (99.9% fisher, UK) and zeroed every hour. To measure a sample, 60 µL was deposited into the ATR crystal, and the solvent was given time to evaporate before the measurement was taken.

For the UVFS (FT3), the instrument was allowed to warmup for 10 min before carrying out the calibration procedure as per the manufacturer's operating instructions (version 4.0, QROS, UK). For the calibration and quality control check, a 5 mL methanol calibration Scan Set solution containing less than 0.00001% of fluorescent compound provided by the manufacturer was used. Four checks were automatically run to confirm the solvent, cuvette and cover holder were clean and the cuvette holder foil, excitation source and sensor systems were in good condition. Calibration was carried out just before analysing the samples. If more than 2 hours elapsed between running the calibration and running a sample, a re-run of the calibration procedure was required to ensure best accuracy. Sample extraction was carried out by adding 20 mL HPLC grade methanol (>99.9% purity, Fisher, UK) and vigorously shaken for more than one minute. The methanol extract was then allowed to settle before the supernatant was added to a clean cuvette and diluted in 3 mL HPLC grade methanol. After measurement using the soil sample default selection, a serial dilution would be provided by the FT6 if necessary. The correct hydrocarbon match was carried out using the QED App Library software. The background subtraction procedure from non-petroleum hydrocarbons from the soils was also used as per manufacturer's operating instructions.

2.8. NON-INVASIVE AND SOLVENT FREE TPH MEASUREMENT METHODS

Calibration data for both the vis-NIR spectrometer (FT4) and 4300 Handheld FTIR spectrometer (FT5) were created by serial dilution of diesel spiked soils providing a working range of ten TPH concentrations from 0 to 12,500 mg kg^{-1} measured 10 times. For the Remscan® spectrometer (FT6), the TPH calibration procedure of 15 TPH concentrations ranging from 0 to 100,000 mg kg^{-1} was followed as per the supplier's instruction (Ziltek Pty Ltd, 2021). For measurement with all IR spectrometers, samples were stirred and compacted to smooth the surface. Each sample was then measured three times and averaged to provide the final spectrum and TPH results. TPH determination with FT6 was carried out using Ziltek's proprietary Python code to develop partial least square regression (PLSR) chemometric prediction model for each soil type. The Remscan was operated as per the operation manual Z048-09 (Ziltek Pty Ltd, 2021). No further processing was needed to obtain TPH results for the soil samples.

Spectral measurements with FT4 and FT5 was carried out as described by Douglas et al. (2018) and Douglas et al. (2019), respectively. Briefly, FT4 was powered on 20 min before use and had its background set by using a Spectralon (Labsphear, UK) reference every 20 min. Spectral measurements of all samples were recorded by placing the sample in direct contact with the high intensity probe. For each sample, 30 successive spectrum measurements were acquired and further averaged in one representative spectrum of a soil sample to produce the final spectrum. For FT5, the instrument was powered on 30 min before using a silver cap reference (Agilent Technologies, USA) which was measured every 10 min. Samples were measured under the Diffuse Reflectance mode and the deuterated triglycine sulfate (DTGS) detector was set at a gain of 249. For each spectrum measurement, soil samples were scanned 64 times with a resolution of 8 cm^{-1} and averaged to produce the final spectrum. The spectral data were collected using the Microlab software V5.0 supplied with the spectrometer. The collected raw spectra in reflectance (R) format were converted into absorbance by calculating log (1/R).

Pre-processing and predicting modelling for FT4 and FT5 measurements were performed in Unscrambler (Camo, Norway) as previously described by Okparanma and Mouazen (2013) and Douglas et al (2019). The raw average spectra of the background and spiked soils were subjected to pre-processing including successively, noise cut, maximum normalization, first derivative and smoothing with R software (R Core Team, 2013). Maximum normalization was then implemented to align all spectra to the same scale or to obtain even distribution of the variances and average values. Spectra were then subjected to first derivation using Gap-segment derivative (gapDer) algorithms (Norris, 2001), with a second-order polynomial approximation. Finally, the Savitzky-Golay smoothing with polynomial of 2 and window size of 21 was adopted to remove noise from spectra (Okparanma and Mouazen, 2013). Separate models were generated for each soil, and contaminant using partial least squares regression (PLSR) on the calibration data with 25% of the data for each concentration being excluded from the model for further validation. The TPH was then predicted using these models for comparison with other instruments in the study.

2.9. INTRA AND INTER SPIKING PROCEDURE AND VALIDATION PROCEDURE

Soil spiking for each level (0, 100, 1000 and 10,000 mg kg^{-1}) and fuel type (gasoline or diesel) were done in triplicate (**Figure 1**) resulting in a total of 72 samples for each soil type and fuel type (**Table 4**). Further to this, the spiking procedure for the silty clay loam soil with diesel was repeated three times for inter spiking procedure comparison (**Table 4**).

Table 4: Overview of spiked soil samples replicates for the intra and inter-spiked comparison

Fuel type	**Soil type**	**Spiked samples (mg kg^{-1}) and replicates**				**Total samples number**	
		0	**100**	**1000**	**10,000**		
Gasoline	Clay loam	triplicate	triplicate	triplicate	triplicate	72	
	Silty clay loam	triplicate	triplicate	triplicate	triplicate	72	
	Sandy loam	triplicate	triplicate	triplicate	triplicate	72	
Diesel	Clay loam	triplicate	triplicate	triplicate	triplicate	72	
	Silty clay loam	triplicate	triplicate	triplicate	triplicate	72	216
		triplicate	triplicate	triplicate	triplicate	72	
		triplicate	triplicate	triplicate	triplicate	72	
	Sandy loam	triplicate	triplicate	triplicate	triplicate	72	

The intra and inter spikes consistency were evaluated by determining (1) precision which is the distribution of the repeated TPH measurement from the triplicates expressed as the percentage of relative standard deviation (%RSD) and (2) bias which is the difference expressed as a percentage between the mean of the replicate measurements and the spiked theoretical concentration level. Similarly, performance comparison of the field technologies against the benchtop GC-MS technology was carried out by determining the difference (%) between the mean measurements determined by the benchtop GC-MS and the field technologies evaluated. Additionally, performance characteristics of the GC-MS were determined by analysing the certified reference material RTC-SQC026 in triplicate.

3. RESULTS AND DISCUSSION

3.1. COMPARISON OF THE FIELD TECHNOLOGIES PERFORMANCE FOR GASOLINE SPIKED SOILS

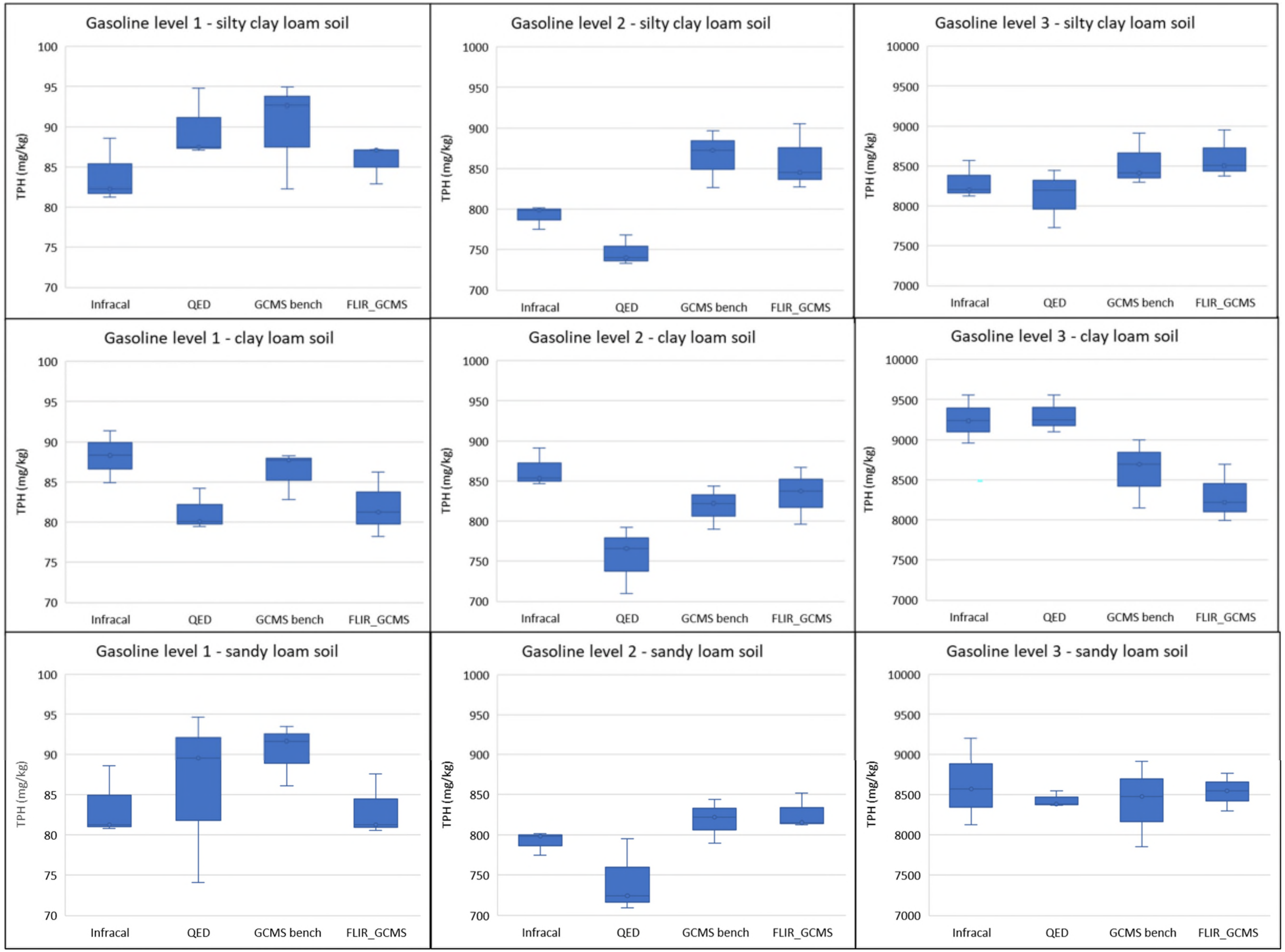
Comparison of the TPH determination from the benchtop GC-MS technology (reference) against each solvent extraction-based FT showed that TPH measurements were within -14% and 6% of those of the reference technology independently of soil type (**Table 5**).

Table 5: Comparison of the TPH determination of the field technologies against the benchtop GCMS reference technology for gasoline spiked soils (n = 3)

Gasoline spiked soils		Level 1	Level 2	Level 3	Level 1	Level 2	Level 3
		TPH 100 mg kg^{-1}	TPH 1000 mg kg^{-1}	TPH 10,000 mg kg^{-1}	% Diff with RT	% Diff with RT	% Diff with RT
silty clay loam	**GC-MS bench (RT)**	**90**	**865**	**8537**	-	-	-
	FLIR GC-MS (FT1)	85	829	8608	-5	-4	1
	Infracal (FT2)	84	792	8297	-7	-8	-3
	QED (FT3)	84	747	8223	-7	-14	-4
clay loam	**GC-MS bench (RT)**	**86**	**819**	**8611**	-	-	-
	FLIR GC-MS (FT1)	82	767	8299	-5	-6	-4
	Infracal (FT2)	88	864	8384	2	6	-3
	QED (FT3)	81	756	9299	-6	-8	8
sandy loam	**GC-MS bench (RT)**	**90**	**754**	**8413**	-	-	-
	FLIR GC-MS (FT1)	83	820	8503	-8	9	1
	Infracal (FT2)	84	792	8631	-8	5	3
	QED (FT3)	86	743	8365	-5	-2	-1

The mean TPH concentration for each concentration level and precision for each technology are shown in **Figure 2.** The results confirmed that the field technologies are performing well independently of soil type with relative standard deviation (RSD) values within 15% and bias within 30% for all spiked soils.

Figure 2: Performance overview of the technologies for gasoline spiked soils (n = 3)



3.2. COMPARISON OF THE FIELD TECHNOLOGIES PERFORMANCE FOR DIESEL SPIKED SOILS

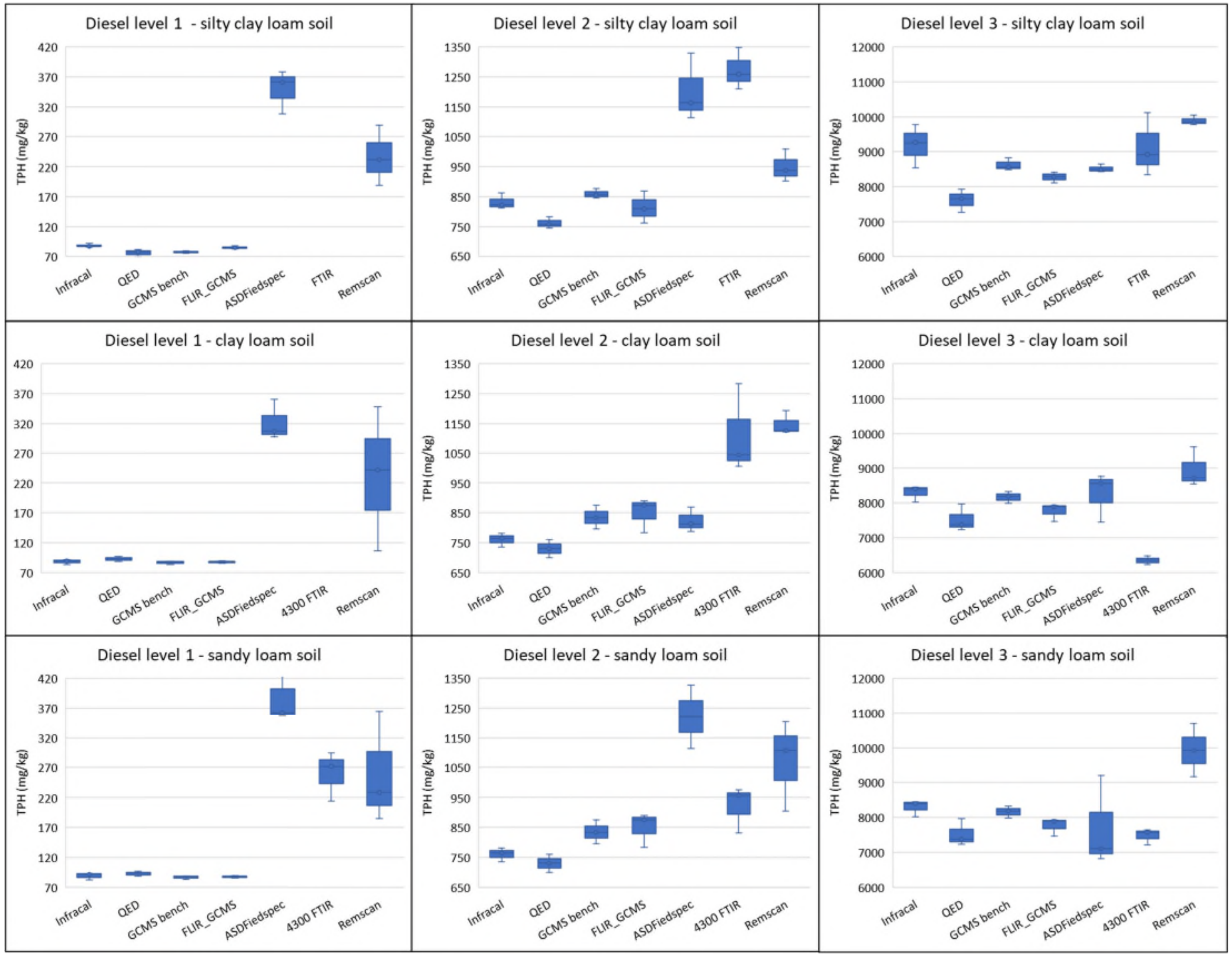
As for gasoline spiked soils, the comparison between the TPH determination from the benchtop GC-MS reference technology and FT determination showed that all TPH solvent extraction-based FT (FT1-FT3) were within -13% and 6% determination independently of soil type and diesel spiked level (**Table 6**). The mean TPH concentration achieved for each diesel spiked soil, concentration levels, and precision for each technology are shown in **Figure 3**. The results showed that all solvent extraction-based FT are performing consistently and independently of soil type with RSD values within 15% for all spiked soils and measurement bias within 30%. Additionally, the inter spikes comparison for the silty clay loam soil showed TPH determination for each technology was within 10% variability across the three spike levels and batches.

Table 6: Comparison of the TPH determination of the field technologies against the GC-MS bench reference technology for diesel spiked soils (n = 3)

Diesel spiked soils		**Level 1**	**Level 2**	**Level 3**	**Level 1**	**Level 2**	**Level 3**
		TPH 100 mg kg^{-1}	**TPH 1000 mg kg^{-1}**	**TPH 10,000 mg kg^{-1}**	**% Diff with RT**	**% Diff with RT**	**% Diff with RT**
fromsilty clay loam	**GC-MS bench (RT)**	**79**	**832**	**8602**	-	-	-
	FLIR GC-MS (FT1)	82	781	8051	4	-6	-6
	Infracal (FT2)	81	839	8419	3	1	-2
	QED (FT3)	78	812	7890	-2	-2	-8
	ASD FieldSpec (FT4)	348	1202	8522	341	44	-1
	4300 FTIR (FT5)	648	1348	8347	721	62	-3
	Remscan FTIR (FT6)	291	1021	10023	269	23	17
clay loam	**GC-MS bench (RT)**	**86**	**834**	**8166**	-	-	-
	FLIR GC-MS (FT1)	88	850	7766	2	2	-5
	Infracal (FT2)	88	760	8293	2	-9	2
	QED (FT3)	93	758	7327	8	-9	-10
	ASD FieldSpec (FT4)	354	824	9517	310	-1	17
	4300 FTIR (FT5)	600	1045	5489	596	25	-33
	Remscan FTIR (FT6)	358	946	9456	315	13	16
sandy loam	**GC-MS bench (RT)**	**86**	**825**	**8079**	-	-	-
	FLIR GC-MS (FT1)	88	741	7966	3	-10	-1
	Infracal (FT2)	91	845	8150	6	2	1
	QED (FT3)	90	752	7753	4	-9	-4
	ASD FieldSpec (FT4)	386	792	7707	347	-4	-5
	4300 FTIR (FT5)	295	957	7574	242	16	-6
	Remscan FTIR (FT6)	225	1124	10119	161	36	25

All solvent free, non-invasive FT (FT4-FT6) showed higher variability and low accuracy for the level I spikes (**Table 4** and **Figure 3**). Analysis of the three uncontaminated soils with different levels of organic carbon showed that the sandy loam soil with 5% of organic carbon produced a TPH reading of 206, 222 and 129 mg kg^{-1} when using FT4 (vis-NIR), FT5 and FT6 (FTIR) spectrometers, respectively.

Figure 3: Performance overview of the technologies for diesel spiked soils (4300 FTIR (FT5) data for Level 1 silty clay and clay loam soils not shown as out of range due to poor prediction) (n = 3)



Similarly, the silty clay loam soil containing 6% organic carbon returned TPH values of 296, 571, 192 mg kg^{-1} and the clay soil with 17% of organic carbon returned TPH reading of 910, 551 and 1258 mg kg^{-1} and with FT4, FT5 and FT6, respectively. These suggest that IR FTs were influenced by the different soil types. Previous studies indicated that both NIR and FTIR spectra are sensitive to alkyl functional chemical group in organic matters (Chakraborty et al., 2010; Forrester et al., 2013). Thus TPH-sensitive IR peaks may overlap with natural organic matter such as an alkyl-CH_2 group.

Previous studies reported that contaminated soils with high organic matter content can interfere with IR measurement due to surface reflection and interference by soil organic matter which can cause error leading to TPH overestimation (Wijewardane et al., 2020; Chen and Tien, 2020). Typically for soil samples with high organic matter or clay content, detection by IR spectrometers may become difficult for TPH below 300 mg kg^{-1} (Wijewardane et al., 2020). In our study this was observed for low level spikes and especially for the silty clay and clay loam soils for which samples showed high variation thought to be partly due to the soil properties and to some extent to poor regression and high bias especially for FT5, where outliers were omitted for regression analysis. In comparison, FT6 (Remscan® FTIRS) prediction and regression performed much better likely due to the fact the instrument gain was set to maximum (255) using a silicon carbide reference cap to obtain sufficient signal from the soil samples. This was not possible for FT5 (4300 Agilent FTIRS), as the instrument uses gold and silver reference caps which are too reflective for a maximum gain and the associated software for FT5 (Microlab) is calibrated to work only with the gold and silver caps. Overall, the IR technologies can be useful to classify accurately field samples into low, medium, and high concentrations applying a threshold of 1000 mg kg^{-1}, however for TPH determination below 500 mg kg^{-1} an alternative technology should be considered.

3.3. PERFORMANCE OF THE SOLVENT-EXTRACTION BASED TECHNOLOGIES

The performance of solvent-extraction based technologies was further assessed by using a certified reference material (RTC-SQC026) as the recoveries obtained with spiked soils may not be representative of those obtained with native hydrocarbon compounds (Risdon et al., 2008). At the same time, it is expected that the technologies and associated methods would yield different TPH recoveries since TPH is a defined analytical term based on the method used which rely on different solvent extraction and clean up procedures as well as detection methods (Concawe, 2021). In this study, the certified concentration of the total extractable petroleum hydrocarbons (TEPH) ranging between C10 and C34 of the RTC-SQC026 was 812.1 ± 4.1 mg kg^{-1}. As shown in **Table 7**, the recovery (bias) and precision were within 5% with the ultrasonic HEX:DCM extraction method for the GC-MS technologies, 19% with the hexane extraction method for the NDIR technology and 27% following the methanol extraction method for the UVF technology (FT3). It can be deducted that the three solvent-based extraction FT can provide GC comparable TEPH recoveries and meet the performance requirements for regulatory standards Environment Agency, 2018). The use of certified reference material can be a suitable alternative to confirm and demonstrate the performance of the selected FT when comparison with GC-MS technology is not possible. It can further help in establishing comparability and accuracy of the analytical results between different locations and over time.

Table 7: Replicates, mean concentration, precision, and bias for each technology

Technology	TEPH R1 (mg kg^{-1})	TEPH R2 (mg kg^{-1})	TEPH R3 (mg kg^{-1})	TEPH Mean (mg kg^{-1})	Bias %	Precision %RSD
Reference Technology	815.2	780.2	810.3	801.9	-1.3	2.4
FLIR GC-MS (FT1)	810.6	761.5	745.3	772.5	-5	4.4
Infracal (FT2)	626.88	661.79	682.14	656.9	-19	4.2
QED (FT3)	573.7	610.5	586.7	590.2	-27	3.1

3.4. HYDROCARBON SPECIATION AND QUANTIFICATION

From a risk assessment point of view, compositional analysis of TPH in soil can provide valuable information such as differentiating between aliphatic and aromatic hydrocarbon fractions, or light and heavy hydrocarbons fractions [i.e., Gasoline Range Organic (GRO) vs Diesel Range Organic (DRO)] or hydrocarbon groups such as BTEX, VOC and SVOC. Such information is typically obtained applying GC-fingerprint techniques (Concawe, 2021). However, the laboratory procedures involved are often pointed out as time-consuming and expensive and therefore do not always provide cost effective approaches for decision making.

Among the FT evaluated in this study, the UFV field technology (FT3) can provide simultaneously determination for total BTEX, GRO C5-C9, DRO C10-C40, TPH C5-C40, and total aromatics C10-C35 within roughly 5 min (QROS, 2020). This offers advantageous time saving for individual soil sample analysis compared to GC-MS methods typically ranging between 20 and 25 min for headspace analysis (BTEX and GRO) and 36-40 min run for DRO and TPH C10-C35 analysis (Concawe 2021). Therefore, one of the motivations of this study was to compare the hydrocarbon group speciation performance of FT1 (portable GC-MS) and FT3 (QED analyser) versus the benchtop GC-MS reference for both gasoline and diesel spiked soils (**Table 8** and **9**, respectively). Overall, the hydrocarbon group quantifications with the portable GCMS (FT1) were within ±10% and ±15% of those of the benchtop GC-MS reference (RT) for gasoline (**Table 8**) and diesel spiked soils (**Table 9**), respectively.

Regarding FT3, BTEX determinations were between 20 and 29% lower than those of the benchtop GC-MS reference for the low and medium level gasoline and diesel spikes, possibly due to volatile losses or thermal decomposition of compounds. Differences were less than 20% for the high spike levels and this was consistent for each soil and fuel type investigated in this study. GRO concentrations of the gasoline spiked soils determined with FT3 were within 9 and 14% of those of the GC-MS (**Table 8**) and between 15 and 25% for the diesel spiked soils (**Table 9**). Similarly, DRO determination of the FT3 for the gasoline spiked soils varied between 3 and 16% of those determined by GC-MS and between 2 and 22% for the diesel spiked soils. Differentiation between total aromatics, which is directly obtained from the FT3 measurement, and total aliphatics, which was determined by subtracting TPH C5-C40 to total aromatics, showed good correspondence (within 17% for gasoline spiked soils and 20% diesel spiked soils) with the GC-MS data. Greatest variability was observed for the determination of the aromatic concentrations of both gasoline and diesel spiked silty clay loam soil (up to 17% difference) and in diesel spiked sandy loam soil; this suggests that the aromatic hydrocarbons can strongly bind to the soil matrix and increase variability.

Table 8: Comparison of the hydrocarbon speciation of the UVF spectrometer against the benchtop GC-MS technology for gasoline spiked soils

Gasoline spiked soils	Benchtop GC-MS (RT)			Portable GC-MS (FT1)			QED (FT3)		
	Level 1	Level 2	Level 3	Level 1	Level 2	Level 3	Level 1	Level 2	Level 3
	TPH 100 mg kg^{-1}	TPH 1000 mg kg^{-1}	TPH 10,000 mg kg^{-1}	% Diff with RT	% Diff with RT	% Diff with RT	% Diff with RT	% Diff with RT	% Diff with RT
Silty clay loam									
BTEX (mg kg^{-1})	1.5	404.2	2793.1	7	-3	-7	-27	-25	-11
GRO C5-C9 (mg kg^{-1})	46.8	692.0	8244.7	-3	-4	1	-6	-14	-3
DRO C10 - C40 (mg kg^{-1})	43.2	173.0	291.7	-9	-3	-6	-6	-13	-17
Total Aliphatics (mg kg^{-1})	67.0	780.6	8421.4	-6	-4	1	-7	-13	-4
Total Aromatics (mg kg^{-1})	22.9	84.3	115.0	-5	-5	-1	-6	-17	-7
TPH C5 - C40 (mg kg^{-1})	**90**	**865.0**	**8536**	**-5**	**-4**	**1**	**-7**	**-14**	**-4**
Clay loam									
BTEX (mg kg^{-1})	3.53	266.03	2960.94	-6	-4	-11	-29	-24	-5
GRO C5-C9 (mg kg^{-1})	53.7	717.4	8298.1	-4	-6	-3	-13	-8	9
DRO C10 - C40 (mg kg^{-1})	32.5	101.2	313.3	-7	-10	-11	7	-4	-6
Total Aliphatics (mg kg^{-1})	56.35	742.95	8482.35	-2	-6	-4	-10	-8	8
Total Aromatics (mg kg^{-1})	29.89	75.69	128.76	-10	-10	2	2	-3	-4
TPH C5 - C40 (mg kg^{-1})	**86.2**	**818.6**	**8611.4**	**-5**	**-6**	**-4**	**-6**	**-8**	**8**
Sandy loam									
BTEX (mg kg^{-1})	1.81	5.28	2608.0	-7	-6	-1	-26	-22	-13
GRO C5-C9 (mg kg^{-1})	23.1	542.9	7408.7	-4	6	1	-2	-7	-2
DRO C10 - C40 (mg kg^{-1})	67.3	211.1	1004.3	-10	-3	5	-6	11	10
Total Aliphatics (mg kg^{-1})	41.6	569.6	7992.4	-4	13	1	-7	-2	-1
Total Aromatics (mg kg^{-1})	48.8	184.4	420.6	-12	-9	-4	-3	-1	-2
TPH C5 - C40 (mg kg^{-1})	**90.4**	**754.0**	**8413.0**	**-8**	**9**	**1**	**-5**	**-2**	**-1**

Table 9: Comparison of the hydrocarbon speciation of the UVF spectrometer against the benchtop GC-MS reference technology for diesel spiked soils

Diesel spiked soils	Benchtop GC-MS (RT)			Portable GC-MS (FT1)			QED (FT3)		
	Level 1	Level 2	Level 3	Level 1	Level 2	Level 3	Level 1	Level 2	Level 3
	TPH 100 mg kg^{-1}	TPH 1000 mg kg^{-1}	TPH 10,000 mg kg^{-1}	% Diff with RT	% Diff with RT	% Diff with RT	% Diff with RT	% Diff with RT	% Diff with RT
Silty clay loam									
BTEX (mg kg-^{1})	0.95	1.89	36.79	7	-6	-11	-21	-11	-12
GRO C5-C9 (mg kg-^{1})	15.8	249.7	2494.5	-13	4	-9	-14	2	-8
DRO C10 - C40 (mg kg-^{1})	63.1	582.7	6107.3	8	-10	-5	1	-4	-8
Total Aliphatics (mg kg-^{1})	52.9	541.0	7311.6	4	-13	-9	-3	-4	-13
Total Aromatics (mg kg-^{1})	26.0	291.3	1290.3	5	7	11	1	0	16
TPH C5 - C40 (mg kg^{-1})	**78.9**	**832.4**	**8601.9**	**4**	**-6**	**-6**	**-2**	**-2**	**-8**
Clay loam									
BTEX (mg kg-^{1})	1.04	3.48	23.47	-6	-8	3	-20	-13	-9
GRO C5-C9 (mg kg-^{1})	17.3	292.0	1633.1	-10	4	-9	2	-13	-13
DRO C10 - C40 (mg kg-^{1})	69.0	542.3	6532.5	5	1	-4	9	-7	-10
Total Aliphatics (mg kg-^{1})	57.8	542.3	5715.9	-1	-5	-3	7	-4	-12
Total Aromatics (mg kg-^{1})	28.5	292.0	2449.7	8	14	4	9	-29	2
TPH C5 - C40 (mg kg^{-1})	**86.3**	**834.3**	**8165.6**	**2**	**2**	**-5**	**8**	**-9**	**-10**
Sandy loam									
BTEX (mg kg-^{1})	1.41	6.70	26.36	-15	-4	-8	-12	-22	-19
GRO C5-C9 (mg kg-^{1})	7.71	237.4	2342.9	-13	-3	-2	-5	15	-19
DRO C10 - C40 (mg kg-^{1})	78.0	587.2	5736.0	4	-13	-1	6	-19	2
Total Aliphatics (mg kg-^{1})	34.9	536.0	6463.1	-13	-11	-1	-5	-5	-11
Total Aromatics (mg kg-^{1})	50.9	288.6	1615.8	13	-9	-3	13	-24	-6
TPH C5 - C40 (mg kg^{-1})	**85.8**	**824.6**	**8078.9**	**3**	**-10**	**-1**	**5**	**-9**	**-4**

Overall, the hydrocarbon speciation measurements obtained with FT3 give comparable concentrations (within +/-25%) to those of the benchtop GC-MS technology. The main advantage is however faster time determination with FT3 (< 5 min) compared to typical GC-MS determination (within 1- or 3-days comprising sample extraction and analysis).

3.5. COMPARISON OF THE FIELD TECHNOLOGIES FOR GAS-SOIL VOC QUANTIFICATION

Detection and quantification of gasoline or diesel vapours on site can assist with a rapid evaluation of soil contamination (Bocos-Bintintan et al., 2019). Most of the methods applied for soil contamination are based on extraction of VOC from soil and further quantification with GC-based techniques hyphened with either headspace analysis, purge and trap analysis or thermal desorption or solvent extraction (Concawe 2021). For all methods, the sampling step is the critical factor for VOC analysis as it can lead to volatilisation and therefore to the loss of compounds of interest. A good alternative is a direct, fast detection of the gas-soil vapours using PID detectors which are known to be very sensitive, non-expensive, compact, and robust instrument for real time detection of total VOCs (Concawe, 2021). Comparison of the soil-gas vapours concentrations from the gasoline and diesel spiked soils using a portable PID (FT7), headspace analysis of the handheld portable GC-MS (FT1) and headspace analysis of the reference lab-based GCMS is provided in **Table 10**. Results showed the total VOC of the gas-soil vapours of the spiked soils were systematically underestimated with the PID compared to both GC-MS headspace analyses. This was expected as the PID only returned the total amount of photo-ionizable components and cannot detect many aliphatic compounds while the headspace analysis allowed the selective detection of aliphatic and aromatic hydrocarbon compounds (Concawe, 2021). Further to this, it has been previously reported that soil concentration can in some instances provide poor indication of soil vapour concentration due to many reasons including equilibrium which is dependent on moisture of the soil, temperature, type of soil, and compaction of soil (Concawe, 2021). Such limitations are overcome when using headspace analysis. The comparison of the headspace analysis from the GC-MS systems also showed that the portable GC-MS returned lower VOC concentration (between 15% and 68% lower) for gasoline spiked soils and between 8 and 73% lower for the diesel spiked soils (data not shown). This can be due to the different heating programme and set-up of the two headspace systems. It is known that the temperature is a very important parameter in headspace analysis because of its significant effect on the partition coefficient of the analyte (Anyakudo et al., 2018). Also, for the portable headspace GC-MS analysis, the headspace vials with PTFE lined caps were opened to allow the heated sample probe to collect the soil-gas vapours while the benchtop headspace GC-MS analysis was carried out in closed headspace vials during the whole process and by inserting the solid phase microextraction (SPME) needle into the GC-MS, which further explained the difference observed. Nevertheless, comparison of the portable and benchtop headspace analyses along the PID showed they can be used in a complementary fashion for screening and increased understanding of the soil-gas vapours on-site. Even if the total VOC values obtained with the PID are only moderately comparable with the GC-MS headspace analyses, it remains a valuable instrument for site risk screening considering is low cost and ease to use.

Table 10: Comparison of the field technologies for gas-soil VOC quantification in gasoline and diesel spiked soils

Soil	Fuel type	Spiked level	PID		Headspace portable GCMS		Headspace benchtop GCMS	
			Total VOC (ppm)	%RSD	Total VOC (ppm)	%RSD	Total VOC (ppm)	%RSD
Silty clay loam soil	Gasoline	1	17.6	2	18.1	9	21.3	4
		2	26.9	5	53.2	8	98.2	21
		3	110.3	1	351.1	2	1104.8	2
	Diesel	1	1.5	7	2.4	6	3.9	4
		2	9.7	6	27.6	14	32.9	4
		3	62.1	3	108.9	2	149.8	4
Clay loam soil	Gasoline	1	16.9	0.3	15.2	11	18.1	1
		2	24.7	5	46.3	13	86.0	7
		3	98.8	7	347.1	8	1180.2	3
	Diesel	1	1.2	13	2.6	9	5.6	14
		2	8.2	8	15.9	13	58.0	11
		3	62.7	11	182.5	12	210.5	5
Sandy loam soil	Gasoline	1	13.1	5	14.0	13	21.2	15
		2	24.6	2	50.5	11	84.5	4
		3	96.7	2	330.2	10	931.4	7
	Diesel	1	1.0	6	6.6	13	13.5	8
		2	9.0	15	40.2	14	73.2	13
		3	55.0	8	130.2	11	160.5	12

*Total VOC include benzene, toluene, o-xylene, p-xylene and m-xylene, and alkanes ranging between C7 to C9.

3.6. APPLICATION TO FIELD SOIL SAMPLES

The TPH concentrations of 8 field site soil samples were analysed with the three solvent based technologies for comparison purpose with the GC-MS analysis from accredited commercial laboratories. The vis-NIR or FTIR technologies were not evaluated as the spectroscopic calibrations of the spike soils are only valid for samples with similar characteristics which was not the case for the field soil samples (Wijewardane et al. 2020). GS1 and GS2 were collected during site investigation and GS3 to GS8 were collected after remediation was completed. The benchtop reference technology and method used in this study showed comparable results for the soil samples while higher variability was observed for the low concentrations typically for <10 mg kg^{-1} (**Table 11**). This was expected as the method used in this study followed the one reported by Risdon et al. (2008), while commercial laboratories used certified in-house method with silica gel split/clean-up for GS3 to GS8.

Table 11: TPH determination comparison from accredited GC-MS analysis with the field technologies and benchtop GCMS analyses for the field soil samples

	TPH	GS1	GS2	GS3	GS4	GS5	GS6	GS7	GS8
Accredited GCMS analysis	mg kg^{-1}	**86.5**	**2222**	**<10**	**<10**	**22**	**32**	**27**	**231**
RT (benchtop GCMS)	mg kg^{-1}	108	2871	<4	<6	23	32	35	270
	%Bias	25	29	-58	-37	6.4	-0.2	28	17
FT1 (portable GCMS)	mg kg^{-1}	105	2707	<4	<6	23	31	33	248
	%Bias	21	22	-59	-39	3	-5	21	7
FT2 (NDIRS)	mg kg^{-1}	103	1909	17	14	20	23	25	213
	%Bias	20	-14	71	39	-11	-29	-8	-8
FT3 (UFVS)	mg kg^{-1}	111	2593	5	6	16	23	24	214
	%Bias	29	17	-49	-37	-29	-27	-10	-8

Overall, the field technologies provided comparable values to the benchtop GC-MS technology as observed with the spiked soils and at the exception of samples with TPH <10 mg kg^{-1}, all TPH values were within ±30% of those from the commercial analysis indicating the ability of these technologies to provide onsite, rapid and relatively accurate TPH determination. Further to this, hydrocarbon speciation performance of the benchtop and portable GC-MS systems and UVFS against the commercial laboratory analyses confirmed that the portable GC-MS and portable UVFS can provide quantitative and comparable values for aliphatic and aromatic hydrocarbon fractions determination (within ± 30%) when TPH concentrations are > 50 mg kg^{-1} (**Table 12**).

Table 12: Comparison of hydrocarbons speciation of the field samples

Samples	Speciated hydrocarbons	mg kg^{-1}	% diff accredited lab GCMS /benchtop GCMS	% diff accredited lab GCMS /portable GCMS	% diff accredited lab GCMS /UVFS
GS1	GRO (>EC5-EC10)	1.71	-3	-9	-30
	Total Aliphatic (>EC10 - EC44)	62.2	24	19	26
	Total Aromatic (>EC10 - EC44)	24.3	30	25	36
	TPH (Ali & Aro >C10-C44)	86.5	25	21	29
GS2	GRO (>EC5-EC10)	7.32	7	2	-11
	Total Aliphatic (>EC10 - EC44)	2146	30	23	16
	Total Aromatic (>EC10 - EC44)	76	2	-21	24
	TPH (Ali & Aro >C10-C44)	2222	29	22	17
GS3	Sum BTEX	<0.01	n.d.	n.d.	n.d.
	TPH CWG Aliphatics (>EC5 - EC35)	<1	n.d.	n.d.	n.d.
	TPH CWG Aromatic (>EC5 - EC35)	<10	-58	-59	-49
	TPH (Ali & Aro >C5-C35)	<10	-58	-59	-49
GS4	Sum BTEX	<0.01	n.d.	n.d.	n.d.
	TPH CWG Aliphatics (>EC5 - EC35)	<10	n.d.	n.d.	n.d.
	TPH CWG Aromatic (>EC5 - EC35)	<10	-38	-39	-37
	TPH (Ali & Aro >C5-C35)	<10	-38	-39	-37
GS5	Sum BTEX	0.15	20	-20	-33
	TPH CWG Aliphatics (>EC5 - EC35)	10	22	20	-23
	TPH CWG Aromatic (>EC5 - EC35)	10	12	5	-21
	TPH (Ali & Aro >C5-C35)	22	6	3	-29
GS6	Sum BTEX	0.06	-17	-17	67
	TPH CWG Aliphatics (>EC5 - EC35)	24	-11	-12	-42
	TPH CWG Aromatic (>EC5 - EC35)	14	-25	-33	-32
	TPH (Ali & Aro >C5-C35)	32	-0.2	-5	-27
GS7	Sum BTEX	<0.01	n.d.	n.d.	n.d.
	TPH CWG Aliphatics (>EC5 - EC35)	< 10	-26	-36	-76
	TPH CWG Aromatic (>EC5 - EC35)	27	1	-3	-16
	TPH (Ali & Aro >C5-C35)	27	28	21	-10
GS8	Sum BTEX	<0.01	n.d.	n.d.	n.d.
	TPH CWG Aliphatics (>EC5 - EC35)	150	16	8	-14
	TPH CWG Aromatic (>EC5 - EC35)	81	29	25	-25
	TPH (Ali & Aro >C5-C35)	231	17	7	-7
	TPH CWG Aliphatics (>EC5 - EC35)	<0.01	n.d.	n.d.	n.d.

n.d. not determined

4. CONCLUSIONS

The present work demonstrates that the solvent-based extraction field technologies, including person portable GC-MS (FT1), portable NDIRS (FT2), and portable UVFS (FT3) performed well for the detection and quantification of TPH ranging between 100 and 10,000 mg kg^{-1}, independently of soil type and fuel type. TPH determinations were comparable and within +/- 30% of those obtained with benchtop GCMS technology. Similarly, the non-invasive, solvent free infra-red technologies (FT4, 5 and 6) performed well between 1,000 and 10,000 mg kg^{-1}, but they were not advisable for soil contaminated with low hydrocarbon levels (<100 mg kg^{-1}). They may further be influenced by soil properties such as high organic matter or clay content. Similarly, gasoline contaminated soils are not suitable for IR analysis due to volatilisation losses that can occur during the analytical process. The portable UVF technology provides added advantage compared to the other field technologies (FT1 to FT7) as quantitative discrimination of aliphatic and aromatic hydrocarbons comparable to GC-MS systems can be obtained within 5-10 min. The portable GC-MS can also provide higher hydrocarbons resolution which are comparable to the benchtop GC-MS system, and therefore providing a rapid quantitative tool for hydrocarbons on site. One of the drawbacks is however the manual injection of the samples which can limits its use for large number of samples to be analysed. Finally, the PID (FT7) remains a valuable instrument for site risk screening of soil-gas vapours considering is low cost and ease to use.

5. GLOSSARY

ATR	Attenuated total reflectance
BTEX:	Benzene, toluene, ethylbenzene and xylenes
DTGS	Deuterated triglycine sulfate
DRO	Diesel Range Organic hydrocarbons (C_{10}-C_{40})
FT	Field technology
LOD	Limit of detection
FTIRS	Fourier-transform infrared spectroscopy
GCMS	Gas chromatography coupled to mass spectrometry
NDIRS	Nondispersive Infra-red spectroscopy
PAH	Polycyclic aromatic hydrocarbons usually comprised of the 16 PAHs listed by the US Environmental Protection Agency
PID	Photo-ionization detector
PLSR	Partial least square regression
RT	Reference technology
SPME	Solid phase microextraction
SIM	Selected ion monitoring
SVOC	Semi-volatiles Organic Compounds including aliphatic and aromatic hydrocarbons in the range of C_{12}-C_{40}
TPH	Total petroleum hydrocarbons
VOC	Volatiles Organic Compounds that include a range of selected low molecular weight aliphatic and aromatic hydrocarbons up to EC_{12}
UVFS	Ultra-violet Fluorescence spectroscopy
Vis-NIRS	Visible and near-infrared reflectance spectroscopy

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