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Strategies for cost-effective remediation of widespread oil-contaminated soils in Kuwait, an environmental legacy of the first Gulf War

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ABSTRACT

The Kuwaiti oil fire during the first Gulf War resulted in the formation of approximately 300 "oil lakes" of varying sizes that covered over 110 km² of the desert land. This threatens the fragile desert ecosystems and human health. Following the award of over US\$2 billion to the State of Kuwait by the United Nations, large-scale remediation of the oil-contaminated soils has now been on the agenda. However, how to implement the remediation program in a cost-effective way represents a major challenge. In this study, cost-effective remediation strategies were developed based on field and laboratory investigations in a typical oil lake area. Overall, most of the lighter petroleum hydrocarbons (PHCs) were lost due to evaporation. Long-chain aliphatic PHCs dominated the PHCs in the investigated oil lake area. This has implications for developing remediation strategies. Toxicity assessment results showed that the majority of soils pose a low environmental risk with a hazard index <1. Therefore, intensive treatment of these PHCs may not be necessary for these soils. Although active treatment methods are needed to remove the contaminants as soon as practical for the relatively small areas of high contaminated soils, it may not be necessary to remove the soils from the contaminated sites. A low-cost capping method should be sufficient to minimize human exposure to the PHC-contaminated soils.

1. Introduction

Petroleum hydrocarbons (PHCs) are common environmental pollutants that have adverse impacts on human health and ecosystems (Park and Park, 2011; Hentati et al., 2013; Khan et al., 2018). The Kuwaiti oil fire during the first Gulf War from August 1990 to February 1991 is an unprecedented environmental disaster in human history (Browning et al., 1991). Fires were set by the retreating Iraqi army on approximately 700 oil wells (Al-Sawari, 1998), resulting in emission of toxic gases and particulates into atmosphere (Husain, 1998), discharge of crude oil into marine environments (Massoud et al., 1998) and formation of approximately 300 "oil lakes" of varying sizes that covered over 110 km² of the desert lands within the State of Kuwait (Salam, 1996). This caused severe damage to the environment, threatening the fragile ecosystems and health of the residents (Kelsey et al., 1994; Price, 1998). The oil lakes, in combination with the construction of oil trenches by the Iraqi military force and the soil bunds built by the rescue team to contain the spilled oil, led to widespread contamination of soils by the petroleum hydrocarbons. At some locations where seawater was used to put out the oil fire, the light components of the crude oil penetrated to reach shallow aquifers, threatening the precious groundwater resources (Al-Sulaimi et al., 1993; Al-Awadi et al., 2009; Mukhopadhyay et al., 2017).

While the air pollution had a relative short-term impact on the local ecosystems and human health, and the contaminated ocean environments have been largely recovered over time, the widespread soil contamination by PHCs remains a significant problem to be resolved. Following the award of over US\$2 billion to the State of Kuwait by the United Nations Compensation Commission for oil lake remediation project, large-scale remediation of the oil-contaminated soils has now

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been on the agenda (Al-Gharabally and Al-Barood, 2015). However, how to implement the remediation program in a cost-effective way represents a major challenge. Although various methods and techniques for treatment of petroleum hydrocarbon-contaminated soils have been developed globally (e.g. Lu et al., 2010; Liu et al., 2012; Thapa et al., 2012; Madadian et al., 2014; Huguenot et al., 2015; Karthick et al., 2019; Priyadarshini et al., 2023), there are limitations for their direct uses in the area of concern. First, many of the available treatment methods focus on the soils contaminated by petroleum products such as gasoline that contains predominantly the volatile short-chain hydrocarbons, which is quite different from the weathered crude oil that consists mainly of long-chain hydrocarbons in the Kuwaiti oil lake areas. Second, the cost-effectiveness of some methods is evaluated based on the research work conducted in the areas where natural environmental conditions are favourable and therefore no extra costs will incur for environmental manipulation; for example, bioremediation is highly cost-effective for fertile soils in humid regions but its application to desert soils may be challenging due to low levels of moisture and nutrients, high salinity and extreme temperatures. Third, treatment design is frequently based on small-scale contamination caused by accidental spills. Its applicability to widespread soil contamination by crude oil such as in Kuwait needs to be carefully evaluated.

Crude oil is a mixture of organic molecules with varying number of hydrogen and carbon (collectively known as petroleum hydrocarbons) plus other elements such as oxygen, sulfur, and nitrogen as impurities. Petroleum hydrocarbons can be divided into different categories based on chemical structure and size of the molecules. In terms of chemical structure, petroleum hydrocarbons can be classified into aromatic PHCs and non-aromatic PHCs. Aromatic PHCs are compounds that contain at least one aromatic ring i.e. cyclic hydrocarbons with alternating double and single bonds. Non-aromatic PHCs are also called aliphatic PHCs, which include alkanes, alkenes, alkynes and cycloalkanes that contain carbon and hydrogen arranged in straight chains, branched chains or non-aromatic rings (Rudzinski and Aminabhavi, 2000). The toxicity of PHCs to a given receptor varies from species to species, and the toxicity of each PHC varies from receptor to receptor. In general, aromatic PHCs tend to be more toxic, as compared to their aliphatic counterparts (on a carbon number basis); short-chain hydrocarbons tend to be more toxic than long-chain hydrocarbons for the same type of PHCs (Kuppusamy et al., 2020).

Traditionally, the total amount of PHCs i.e. total petroleum hydrocarbon (TPH) was used to set clean-up target for remediation of PHCcontaminated soils (Pinedo et al., 2013). However, TPH does not distinguish between petroleum hydrocarbon species of different toxicological characteristics contained in a contaminated soil for accurate hazard assessment (Park and Park, 2011; Pinedo et al., 2014). Consequently, understanding the chemical composition of the contaminated soils is an important step for more reliably evaluating the potential harmful effects of soil-borne PHCs in the environments. Despite that several monitoring programs were conducted for air quality and marine contamination (Husain, 1998; Massoud et al., 1998), investigation into the PHC-contaminated soils in the Kuwaiti oil lake areas has been limited except for some work on estimating the extent of soil contamination (Omar et al., 2006) and physical and geotechnical characteristics of the oil-contaminated soils (Al-Sanad et al., 1995; Al-Sarawi et al., 1998). There is currently a lack of information on the detailed chemical composition of soil-borne PHCs in the oil lake soils for sound environmental risk assessment, which is essential for developing cost-effective strategies to remediate the PHC-contaminated soils.

From an environmental remediation perspective, PHC-contaminated soils should only be treated when they pose a threat to the receptors. It has been increasingly accepted that environmental risk assessment of petroleum hydrocarbon-contaminated soils needs to focus on specific hydrocarbons of high toxicity rather than the bulk concentration (Weisman and Gustafson, 1999; Park and Park, 2010; Pinedo et al., 2013). Park and Park (2011) proposed a scheme for human health risk assessment of PHC-contaminated soils based on 13 aliphatic and aromatic fractions while Pinedo et al. (2013) used polycyclic aromatic hydrocarbon species (PAHs) and volatile aromatic hydrocarbon species such as benzene, toluene, ethylbenzene and xylenes (BTEX) as key assessment criteria. So far, site specific applications of these assessment systems were limited to contaminated sites of small sizes (Park and Park, 2011; Pinedo et al., 2012).

The aim of this work was to develop strategies for cost-effective remediation of the broad-acre oil-contaminated soils in the Kuwaiti oil lake areas. Three specific research objectives were set to achieve the overall research aim: (a) understanding of the pedogenesis of the investigated area; (b) understanding of the contamination status of the investigated area; and (c) provision of recommendations for remediation strategy formulation based on the assessment of environmental risks posed by the existing contaminated soils.

2. Research methods

2.1. Regional settings

Kuwait is part of the Arabian plate and is located at the northwestern end of the Arabian Peninsula between latitudes 28°30'and 30°5' North and longitudes 46°33' and 48°30' East. It covers approximately 17,800 km² of desert land with no river and natural lake (STATE OF KUWAIT Environment Public Authority, 2012). The topography is characteristic of low to moderate relief. The geological materials exposed on the land surfaces are of early Miocene to Recent origins (Milton, 1967). Kuwait has a hyper arid desert climate with an average annual rainfall of 116 mm. In summer months, average daily high temperatures range from 42 °C to 46 °C, with the highest ever recorded temperature of 53.5 °C (STATE OF KUWAIT Environment Public Authority, 2012).

The surface materials of the desert lands are dominated by gravel lag that stabilizes the surface of the desert floor and playa deposits that occur in areas of depressions (Khalaf and Al-Ajmi, 1993). Kuwait's desert soils are characteristic of arid soil, with poorly developed profiles and sandy texture. The calcareous hardpan (gatch) occurs at varying depths and locations. These hardpan layers consist predominantly of calcium carbonates and quartz. The desert soils only contain a limited amount of organic matter and nitrogen. Although the concentration of total phosphorus is relatively high. its bioavailability is low due to formation of practically insoluble Ca and Mg carbonates.

2.2. Selection of study site

There are two major oil lake areas within Kuwait; Rawdhatain oilfield located in northern Kuwait and Burgan oilfield in southern Kuwait. There have been concerns about the possible contamination of groundwater by petroleum hydrocarbons in the Rawdhatain oil lake area (Viswanathan et al., 1997). The study area is an exclusion zone containing unexploded ordnance (UXO) from the First Gulf War. Strict approval procedures needed to be followed in order to get access to the study area. This posed some limitations to the development of the research plan, including but not limited to selection of the sampling sites and preparation of sampling schedule. For this study, only the central part of the oil lake (B Section of the Raudhatain Area) was selected for sample collection (Fig. 1).

2.3. Field methods

Samples were collected from 17 soil locations (Fig. 1) using a random grid sampling method. At each location, the soils samples were taken at set depths to account for vertical variation of petroleum hydrocarbons along the soil profile to enable easy comparison of results between the soil profiles. Soil samples were collected at 10 cm intervals for the soil profile with a depth of contamination less than 50 cm, and at 20 cm intervals for the soils with a depth of contamination between 50 and



Fig. 1. Map showing the soil sampling locations in the study area.

100 cm. For each soil profile at these 17 locations, the sampling location (Universal Transverse Mercator (UTM) coordinates 34 N World Geodetic System 1984 (WGS84)) was determined with a Garmin GPS unit (Model GPSMAP® 66st, manufactured by Garmin Australasia Pty Ltd, Marsden Park, NSW, Australia) and then 5 soil samples at different depths were collected. The soil samples were taken using a trowel wrapped with a plastic cover, which was changed after each sample was collected to avoid cross contamination. Each sampling location was assigned a location ID, which was composed by the last 4 digits of northern UTM and the last 4 digits of eastern UTM.

The soil samples were taken from the lower layer up and the description and labelling were the opposite to this (in order from top to bottom of the pit). In addition, a photograph of each soil profile was taken with a measuring tape being placed in the sampling pit for depth reference. Soil attributes described in the field included horizon thickness and sequence, colour, texture, structure, consistence, presence of salt crystals, coarse fragments, mottles, and roots.

Composite sampling was used for the sample collection. This involved thoroughly mixing discrete samples from the same soil layer at the same location to obtain a representative soil sample for that location. Composite sampling is widely used for large-scale soil investigation to achieve a cost-efficient goal. This was deemed appropriate for this study given that the accuracy of soil data from the composite samples was sufficient for this project while the costs can be minimized, which is the primary goal for any technologies to be used for soil remediation under the United Nations Kuwait Environmental Remediation Program (KERP). After collection, each composite soil sample was split into 2 subsamples and contained in two separate 170 mL glass jars that were packed into a plastic cooler with ice. The packed samples were then shipped from Kuwait to the Manchester laboratory (UK).

2.4. .4 laboratory methods

1:5 (soil:water) extracts were prepared by shaking 5 g of the air-dried soil in 25 mL of deionized water in a rotary shaker for 1 h pH and electrical conductivity (EC) in the soil extracts were then measured by a calibrated pH (HI-2020 edge) meter and a Mettler Toledo EC meter, respectively.

Since no or only a trace amount of soil particles with a diameter less than 0.063 mm was present in the soil samples, particle size distribution was determined by sieving only. 50 g of the soil was passed through a series of sieves with mesh sizes of 2 mm, 0.6 mm, 0.355 mm, 0.125 mm and 0.063 mm. The weight of various particle size fractions (>2 mm, 0.6–2 mm, 0.355–0.6 mm, 0.125–0.355 mm and 0.063–0.125 mm) was determined by weighing. The sieving was conducted by a mechanical sieve shaker.

Various elements in the soils, including potassium, sodium, aluminium, arsenic, barium, beryllium, calcium, cadmium, cobalt, chromium, copper, iron, mercury, magnesium, manganese, molybdenum, nickel, phosphorous, lead, antimony, selenium, silica, tin, sulfur, tellurium, thallium, vanadium, zinc were determined by inductively coupled plasma-optical emission spectrometry (Agilent Varian 720-ES manufactured by Alilent Technologies, Inc., 5301 Stevens Creek Blvd Santa Clara, CA 95051, USA) after aqua regia digestion in a microwave digester (MARS 5 Digestion Microwave System manufactured by CEM Corporation, 3100 Smith Farm Road, Matthews, NC 28104, USA).

A modified CWG (Criteria Working Group) TPH method was used to determine the petroleum hydrocarbon fractions in the soils. Various petroleum hydrocarbons contained in the soils were extracted by dichloromethane. Sodium sulfate and silica were used for solution cleanup. The aliphatic and aromatic fractions are separated using solid-phase extraction techniques. Additional clean-up for the extract was performed by passing the solution through a membrane filter. The filtrate was treated with 15 g of acid silica in a clean round bottom flask placed on a rotary evaporator with no heat for 30 min. The aliphatic fractions in the solution were then determined using a capillary gas chromatography with flame ionization detection (GC/FID) method.

BTEX in the soil samples was determined by headspace gas chromatography mass spectrometry (GC/MS). The sample is heated and shaken vigorously. This carries the volatile components into the headspace of the extraction vessels. A volume of the headspace is sampled and passed onto the head of gas chromatography (GC) column which separates the different components. The eluent from the GC column passes into the ion source of a mass spectrometer, which, records mass spectra continually at a regular interval and with unit mass resolution. A series of aqueous standards are analyzed by this method and the data are used for reference and calibration. Deuterated internal standards are added to all samples, spikes and blanks prior to analysis. In instances where a compound is not present in the calibration material, a tentative identification and result is produced based upon a comparison of the mass spectra obtained with those found in the National Institute of Standards and Technology (NIST) mass spectral databases. 16 common polycyclic aromatic hydrocarbon species were also determined by headspace gas chromatography-mass spectrometry. Soluble potassium, sodium, calcium and magnesium in water extracts were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES).

2.5. Quality assurance and quality control

The sample analysis was performed in an accredited commercial analytical laboratory (Concept Life Sciences Analytical & Development Services Limited, Hadfield House, 9 Hadfield St, Old Trafford, Stretford, Manchester M16 9FE, United Kingdom). Analytical quality control is maintained by a number of measures, including (a) multi-point calibration with authentic standards (with defined minimum performance characteristics), (b) analysis of control samples within each analytical batch, such as independent standards, matrix spikes or reference materials, (c) analysis of reagent/method blanks within each analytical batch, (d) ongoing quality assured by the use of control charts in conjunction with warning and action limits for the quality control (QC) sample data, and (e) participation in external proficiency testing and inter laboratory schemes such as LGC Standards CONTEST and AQUA-CHECK, the two key proficiency testing schemes designed for quality assurance and quality control of contaminated soil analysis under the UK Environment Agency's Monitoring Certification Scheme (MCERTS).

3. Results and discussion

3.1. Pedogenesis in the investigated area

The Arabian Peninsula experienced a humid period during the early to mid-Holocene (Engel et al., 2012), followed by the late-Holocene dry period (Woronko, 2012). The soils in this region were developed from the sediments deposited under humid climate. The reworking of these sediments under desert conditions could lead to the removal of fine soil particles by winds, making the soils become coarse texture, as observed in this study. Fig. 2 shows the soil particle size distribution of Soil Profiles 10 and 19. It can be seen that the soils consisted mainly of coarse fraction (>0.6 mm). As expected, the soils also had alkaline pH (Table S1), which is common in desert areas (Wiesman, 2009).

The oil lakes are located in the low-lying areas. These topographic positions acted as sink for sediments and soluble salts being brought from the surrounding highlands during the Holocene humid period. Evaporation drove the precipitation of salts. Depending on the location, the chemical composition of the soils could be very different. Table 1 gives a comparison of the soil chemical composition between the soil profile in the norther part (Profile 10) and the southern part (Profile 19) of the study area. It can be seen that the concentration of potassium and magnesium was very similar at the two locations. However, the concentration of sodium, calcium and sulfur was much higher in the Profile 10 that in the Profile 19.

Calcium in desert soils is usually present as chemical compounds of



Fig. 2. Soil grain size distribution patterns for the different soil layers in (a) Soil Profile 10 (representing the soils with contamination depth <50 cm) and (b) Soil Profile 19 (representing the soils with contamination depth >50 cm).

low water solubility such as calcium carbonates and gypsum. In Profile 10, the soil contained a substantial amount of sulfur, suggesting that gypsum was present in the soil. The molar ratio of calcium to sulfur was about 2.56, indicating over half of the calcium was associated with other ligands, most likely carbonate to form practically insoluble calcium carbonate. In contrast, the mean concentration of sulfur in Profile 19 was very low (460 mg/kg), suggesting that gypsum might be present, if any, at a small amount. Sulfate in geological formations is derived from acid sulfate weathering e.g. oxidation of pyrite, as described by the following chemical equation:

$$4\text{FeS}_2 + 15\text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{SO}_4 \tag{1}$$

Acid sulfate weathering generates sulfuric acid, which can react with calcium ion to form sparsely insoluble calcium sulfate (gypsum):

$$Ca^{2+} + H_2SO_4 \rightarrow CaSO_4 + 2H^+$$
⁽²⁾

There was a perfect relationship between the total sulfur and sulfatesulfur with a slope nearly 1 (Fig. 3) for Soil profile 10, indicating that the sulfur contained in the soil was almost in the form of sulfate. The hydrogen ion (H⁺) can consume hydroxy ion (OH⁻) and lower soil pH.

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Table 1

A comparison of major soil properties (profile average) between Profile 10 (representing the soils in the northern part of the investigated area) and Profile 19 (representing the soils in the southern part of the investigated area).

Soil parameter	Profile 10	Profile 19
Potassium (mg/kg)	1090	1254
Sodium (mg/kg)	7780	656
Calcium (mg/kg)	100,400	81,600
Magnesium (mg/kg)	8200	9640
Sulfur (mg/kg)	31,280	460
рН	7.93	8.36
EC (mS/m)	1855	844



Fig. 3. Relationship between the total sulfur and the sulfate-sulfur for a representative soil profile (Profile 19).

This explains the relatively lower pH in Profile 10, as compared to Profile 19.

Acid sulfate weathering accelerates decomposition of silicate minerals, leading to release of soluble salts and increase electrical conductivity. This may be responsible for the observed relationship between the pH and EC in the investigated soils where soil pH was inversely related to soil EC (Fig. 4).

3.2. Soil contamination by petroleum hydrocarbons

For the majority of the investigated soils, the contamination by PHCs was limited to a depth of 50 cm. Contamination beyond 50 cm depth was only observed in 4 soil profiles at Locations 11, 18, 19 and 20, which are all located in the southmost part of the investigated area (Fig. 1). A relatively thicker layer of oil sludge overlying the soil was present in the shallower-contaminated soil profiles than in the deeper-contaminated soil profiles (Fig. 5).

The total petroleum hydrocarbon (TPH) in the contaminated soils was highly variable both horizontally and vertically (Table S2). The lowest profile average of TPH (76 mg/kg) was recorded in Location 8 while the highest profile average of TPH (20604 mg/kg) was found in Location 11. The soils with a TPH concentration of over 10,000 mg/kg (>1%) were only found at 9 out of 17 sampling locations (i.e. Locations 5, 7, 10, 11, 13, 15, 18, 19 and 20) and limited to the topsoil layer (0–10 cm) except for Soil Profiles 11, 18, 19 and 20, where a high level of TPH was detected to a depth of 60 cm. There is a clear trend that TPH decreased with increasing depth along the profile and on average, the top 20 cm of soil profile accounted for 81% and 57% of the profile TPH



Fig. 4. Relationship between pH and EC for the investigated soils.



Fig. 5. Photographs showing (a) a shallower-contaminated soil profile (<50 cm) at Location 10 and (b) a deeper-contaminated soil profile (>50 cm) at Location 19.

for the shallower-contaminated soils and the deeper-contaminated soil profile, respectively (Fig. 6)

No or only a small amount (<50 mg/kg) of aromatic hydrocarbons was detected in most of the investigated soil profiles (data not shown) except for Locations 5, 9, 11, 15, 18, 19 and 20. In most situations, Fraction C8–C16 dominated the aromatic hydrocarbons (Table S3).

For the soil profiles with shallower contamination depth (Profiles 5, 9 and 15), the level of aromatic hydrocarbons was lower and limited to a thinner surface soil layer, as compared to the soil profiles with deeper contamination depth (Profiles 11, 18, 19 and 20). Soil profile 11 had the highest level of total aromatic hydrocarbon in the top 10 cm of the soil profile. Different soil profiles had different dominant fraction; Soil Profile had Fraction C10–C12 being the most important fraction while Fraction C12–C16 was more important than C10–C12 in Soil Profile 20 (Table S3).

Aliphatic hydrocarbons dominated the petroleum hydrocarbons in the investigated soils. Like TPH, the sum of aliphatic hydrocarbons (total aliphatic hydrocarbon) was highly variable both horizontally and vertically. The soils with higher concentration of aliphatic hydrocarbons were found at Locations 5, 7, 10, 11, 13, 15, 18, 19 and 20 and limited to the topsoil layer (0–10 cm) for some soil profiles. Soil Profiles 11, 18, 19 and 20 tended to have thicker contamination layer, as compared to the others. In most situations, Fraction C16–C35 dominated the aliphatic hydrocarbons and in general, the following decreasing order was observed: C21-35 > C16-21 > C12-16 > C35-40 > C10 -12. Fraction < C10 was only at trace amount or non-detectable (Fig. 7).

BTEX were not detected for most of the locations except in the southmost portion of the investigated area (Locations 11, 18, 19 and 20). The sum of BTEX in these 4 locations ranged from 0 to 14,350 mg/kg with a mean value of 686 mg/kg. No benzene was detected in any samples collected. Xylene (o-xylene and m/p-xylene) dominated BTEX (83%). BTEX tended to decrease with increasing depth within the soil profile but different vertical variation patterns were observed. However,



Fig. 6. TPH (mg/kg) in different soil layers for (a) the shallower-contaminated soils (<50 cm) and (b) the deeper-contaminated soil profile (>50 cm).



Fig. 7. Distribution patterns of different aliphatic hydrocarbon fractions for (a) Profiles 7 (representing soil with shallow contamination depth) and (b) Profile 19 (representing soil with deep contamination depth). The aliphatic PHCs with carbon number ranging from 5 to 40 determined by the CWG TPH method were divided into 8 fractions. For example, the C12–C16 fraction stands for the sum of PHCs with carbon number range of 12–16.

for Profile 11, the concentration of toluene, ethylbenzene and xylenes was lower in the surface layer (0–20 cm) than in the subsoil layer (20–60 cm). The distribution of BTEX in different soil layers more or less maintained the same patterns with Soil Profile 11 showing the following decreasing order: m/p xylene > o xylene > ethylbenzene > toluene while other soil profiles showing the trend of m/p xylene > o xylene > ethylbenzene > toluene (Table S4).

Polycyclic aromatic hydrocarbons in the surface soils were only detected from 9 out of the 17 sampling locations. The sum of the 16 investigated PAHs was less than 16 mg/kg with the total PAH greater than 10 mg/kg only being found at Locations 10, 13 and 20. The total PAH in the surface soils of various sampling locations was in the following decreasing order: Location 20 > Location 13 > Location 10 > Location 18 > Location 11 > Location 7 > Location 19 > Location 5 (Table S5). Major PAH species included naphthalene, phenanthrene and anthracene, depending on the sampling locations. Phenanthrene was found in all the soil profiles listed in (Table S5). Other more common PAH species included benzo(a)anthracene and chrysene. Soil Profile 20 contained 13 out of the 16 investigated PAH species.

The absence of short-chain hydrocarbons in most of the investigated locations suggests that emission of volatile hydrocarbons dominated transport processes in the investigated area. This can be attributed to the desert climate conditions which, on one hand, favour (due to low relative humidity and high temperature) volatilization of these lighter hydrocarbon species with low vapor pressure and, on the other, disfavor their downward migration (due to a lack of rainfall). Under such conditions, the heavier component (after partitioning of the volatile portion) migrated through the soil column under the force of gravity. Because of their low mobility and large molecular size that could be easily trapped in soil pores, the downward moment of these long-chain hydrocarbons tended to be slower, as compared to the low-molecularweight petroleum hydrocarbons. After the oil lake completely dried out, it is unlikely that any further downward migration of hydrocarbons by force of gravity will take place.

The extremely variable TPH among the different sampling location is probably attributable to the thickness of the overlying crude oil layer that was controlled by the surface elevation. Although the soils were generally of coarse texture, the connectivity of soil pores was likely to be poor due to the presence of secondary minerals such as gypsum and carbonates, which could block soil pores. This may be another reason for the impeded vertical migration of the spilled oil. The relatively deeper penetration of the downwardly moving PHCs at Locations 11, 18, 19 and 20 may be attributed by the lack of gypsum present within the soil profiles, as demonstrated from Profile 19, which favoured the infiltration of the spilled crude oil at the earlier stage. This allowed some of the short-chain PHCs being transported downwards and stored with the soil profiles, as observed at Locations 11, 18, 19 and 20 in the southern part of the study area, which represents a hot spot that poses high level of environmental risk.

In-situ biodegradation is likely to be very limited due to the harsh environmental conditions encountered in the investigated area, oil lake dried out. Rainwater is the only possible driver for future downward migration of the soil-borne hydrocarbons. However, since the hydrocarbons retained in the soils are almost completely composed of long-chain aliphatic hydrocarbons that have very low solubility in water and rainfall in the investigated area is rare in the predictable future, it is most unlikely that these soil-borne petroleum hydrocarbons pose any risk to groundwater in the investigated area.

3.3. Assessment of human health risk from exposure to soil-borne petroleum hydrocarbons

The human health risk from exposure to a toxic substance can be evaluated by hazard quotient (HQ), which is calculated by the following formula (Qin et al., 2021):

$$HQ = ADD (mg / kg body weight / day) / RfD (mg / kg body weight / day)$$
(3)

where ADD is the average daily dose of a toxic substance while RfD is the reference dose that is operationally defined as the maximum amount of the toxic substance that a person can take within a day without causing harmful effects.

By setting the human weight at 60 kg, ADD can be calculated by the following formula:

ADD
$$(mg/kg body weight/day) = I_s (kg/day) \times C (mg/kg) / 60$$
 (4)

where I_s denotes daily soil ingestion rate by the exposed person and C stands for the concentration of the soil-borne toxic substance.

For a soil containing multiple contaminants, the combined toxicity of the contaminated soil can be assessed by hazard index (HI), which is the sum of HQs for all the soil-borne toxic substances:

$$HI = \sum_{i=1}^{n} HQ_i$$
(5)

In theory, a value of HI less than 1 indicates that no harmful effect from the intake of the soil-borne petroleum hydrocarbons is expected.

Except for the locations where there were still short-chain petroleum hydrocarbons, the inhalation of volatile petroleum hydrocarbons is unlikely. The only exposure pathways will be ingestion and dermal contacts though inhalation of petroleum hydrocarbon-containing dusts may be possible.

The contaminated soils in the investigated area contained various petroleum hydrocarbon fractions with different toxicities. Adopting the RfD value of 0.1, 2, 0.04 and 0.03 (mg/kg/day) for aliphatic fraction C8–C16 (F1), aliphatic fraction C16–C40 (F2), aromatic fraction C8–C16 (F3) and aromatic fraction 16–40 (F4) (Park and Park, 2011), the HI for each petroleum hydrocarbon-contaminated soil can be calculated as follows:

$$HI = HQ_{F1} + HQ_{F2} + HQ_{F3} + HQ_{F4}$$

 $= (C_{F1} \; x \; I_s \; / \; 60) \; / \; 0.1 + (C_{F2} \; x \; I_s \; / \; 60) \; / \; 2 + (C_{F3} \; x \; I_s \; / \; 60) \; / \; 0.04 + (C_{F4} \; x \; I_s \; / \; 60) \; / \; 0.03$

including extreme soil temperatures, low moisture content and high salinity etc. In addition, the supply of nutrients especially nitrogen may not be sufficient to sustain the microbes that mediate the biodegradation of the petroleum hydrocarbons.

There is no evidence to show that groundwater has been contaminated in the investigated area. As mentioned above, any further downward migration of hydrocarbons by force of gravity is unlikely after the

$$= C_{F1} x I_{s} / 6 + C_{F2} x I_{s} / 120 + C_{F3} x I_{s} / 2.4 + C_{F4} x I_{s} / 1.8$$

= I_s (C_{F1} / 6 + C_{F2} / 120 + C_{F3} / 2.4 + C_{F4} / 1.8) (6)

where I_s (mg/kg/day) represents the daily soil ingestion rate. C_{F1} , C_{F2} , C_{F3} and C_{F4} (mg/kg) stand for the concentration of F1, F2, F3 and F4 in



Fig. 8. Required daily soil ingestion rate to make the HI value reach 1 for each of the sampling locations.

the contaminated soil. When HI = 1, the I_s can be calculated by the following formula:

$$I_{s} = 1 / (C_{F1} / 6 + C_{F2} / 120 + C_{F3} / 2.4 + C_{F4} / 1.8)$$
(7)

I_s at HI = 1 can therefore be used to indicate the maximum allowable daily ingestion rate of the contaminated soil from a human health risk assessment perspective. Fig. 8 shows the daily soil ingestion rates required to make the HI value reach 1 for all the sampling locations except for Locations 6, 8 and 16 where the soils only contained trace amounts of petroleum hydrocarbons. It can be seen from the figure that the required daily soil ingestion rate exceeded 1.5 g/day for most locations with some locations having the required I_s value greater than 5 g/day, which is much greater than what is likely to be encountered by children in playground (224 mg/day, Özkaynak et al., 2011) or adults in e-waste dismantling area (383 mg/day, Yang et al., 2022).

The oil lakes are far away from any residential areas. Therefore, human exposure to these contaminated soils is limited in terms of number of exposed people and exposure duration. Even for the highly contaminated locations e.g. Locations 11 and 20, the required Is to cause harm is 250 and 781 mg/kg, which is still unlikely to be reached under most circumstances. Clearly, despite the high levels of TPH at many locations, the pre-dominant presence of less toxic long-chain aliphatic hydrocarbons means that the hazardousness of the contaminated soils is likely to be much lower than what was thought during development of the KERP program. The oil lake areas are unlikely to be used for agricultural purposes. The most likely land uses will be for industrial purposes because it is within the major oil field. Therefore, human exposure to the petroleum hydrocarbons will be limited to the oilfield workers and the contractors who will carry out soil remediation work. For the majority of oilfield workers who are not involved in activities related to land disturbance, the health risk from exposure to soil-borne petroleum hydrocarbons is low. However, contractors working on soil remediation involving soil excavation could be increasingly exposed to soil-borne petroleum hydrocarbons by dermal contact, ingestion and inhalation. Therefore, workplace health and safety measures must be implemented to reduce the exposure of the contractors to soil-borne petroleum hydrocarbons.

For the small areas of contaminated hot spots such as those at Locations 11, 18, 19 and 20, inhalation of volatile petroleum hydrocarbons is likely due to the presence of xylenes, ethylbenzene and toluene. The concentration of xylenes, ethylbenzene and toluene in the soils was below the unacceptable levels for industrial/commercial uses or for excavation workers (New Zealand Ministry for Environment, 2011). Therefore, the human health risk from inhalation of xylenes, ethylbenene and toluene alone is low. However, the soils at these locations also contained PAHs especially the highly toxic naphthalene (El-Masri, 2005). The combined effect of BTEX inhalation and ingestion of various

PHC fractions plus naphthalene could pose a significant risk to the excavation workers.

3.4. Recommendations for soil remediation strategies

From an environmental remediation perspective, removal of the PHCs from the soils may be challenging. This is due to the fact that longchain PHC fractions dominated the soil-borne PHCs. Long-chain PHCs are resistant to either chemical or biological decomposition, especially for biodegradation, which can also be adversely affected by the high soil salinity apart from the harsh climatic conditions such as strong solar radiation, high temperature and low moisture content. Although the soils contained a certain level of phosphorus, the majority of soil-borne phosphorus may not be bioavailable due to the immobilization by calcium to form practically insoluble calcium phosphate.

Given that the composition and quantity of PHCs varies markedly from location to location within the investigated area, different strategies are required to meet the specific needs in various parts of the investigated area. For the contamination hotspots that contain high concentrations of BTEX, aromatics and PAHs, more active treatment methods should be used to remove the contaminants as soon as practical to minimize their adverse impacts on the environment and human health. For the larger area of the non-hotspots, more cost-effective passive methods should be considered to minimize the remedial costs.

Soil washing is a possible method for clean-up of hydrocarboncontaminated soils. However, this method is unlikely to be effective for the contaminated soils containing predominantly long-chain aliphatic hydrocarbons that are practically insoluble in water. In addition, intensive soil washing operations could enhance the volatilization of BTEX, causing air pollution and possibly harms to the operators.

The presence of phosphorus is also a beneficial factor for microbially mediated degradation of hydrocarbons. However, the high soil salinity at many locations, as indicated by high electrical conductivity, will affect microbial activities. Therefore, desalinization of these soils may be required for bioremediation of the contaminated soils.

Chemical treatment using advanced oxidation technologies may be a more cost-effective method for treating the mobile fractions of hydrocarbons. The advanced oxidation method is rapid with no release of harmful substances. It is also possible to develop in-situ oxidation method to reduce the costs associated with translocation of the PHCcontaminated soils to purpose-built facilities for ex-situ treatment.

For the soils containing no or small amounts of BTEX, aromatics and PAHs, containment may be more appropriate. However, ex-situ containment such as landfilling may be only appropriate for hydrocarbon-rich sludge but not the soils with dominant presence of aliphatic hydrocarbons. Given the extremely low risk in terms of groundwater contamination by the contaminated soils, it is not necessary to remove the soils from the contaminated sites. A low-cost capping method should be sufficient to minimize human exposure to the PHCcontaminated soils.

4. Conclusion

The soils in the investigated oil lake area were of coarse texture and had alkaline pH. They contained large amounts of calcium compounds. Depending on the location, large amounts of gypsum might be present, causing blockage of soil pores and impeding infiltration of the spilled crude oil. The soils without significant amounts of gypsum appeared to allow better penetration of the PHCs. This also enabled storage of some short-chain PHCs within the soil profile that was absence in the other soil profiles. Overall, most of the lighter PHCs was lost due to evaporation under the desert climatic conditions. Long-chain aliphatic PHCs dominated the PHCs in the investigated oil lake area. This has implications for developing remediation strategies. The dominance of longchain PHCs in the contaminated soils means that it will be difficult to treat these soils because the heavier PHCs are resistant to decomposition. The majority of soils had a hazard index <1, indicating low environmental risk. Therefore, intensive treatment of these PHCs may not be necessary for these soils. Different methods need to be adopted to deal with different types of contaminated soils. For the contamination hotspots that contain high concentrations of BTEX, aromatics and PAHs, more active treatment methods should be used to remove the contaminants as soon as practical to minimize their adverse impacts on the environment and human health. For the larger area of the non-hotspots, more cost-effective passive methods should be considered to minimize the remedial costs. For the soils containing no or small amounts of BTEX, aromatics and PAHs, containment may be more appropriate. Given the extremely low risk in terms of groundwater contamination by the contaminated soils, it is not necessary to remove the soils from the contaminated sites. A low-cost capping method should be sufficient to minimize human exposure to the PHC-contaminated soils.

Credit author statement

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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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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