Mobility of total petroleum hydrocarbons in Shambat soil in Sudan

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Abstract

Purpose – A laboratory experiment was conducted in the soil laboratory in the Department of Environment and Environmental Pollution, Environment and Natural Resources Research Institute, National Centre for Research. The purpose of this paper is to study the movement of crude oil through soil column.

Design/methodology/approach – Polyvinyl chloride columns were filled with Shambat soil, amended with three concentrations of light crude oil (0.16, 0.32, and 1.28 ppm), obtained from Petrodar Oil Company. Soil samples were taken from 5 and 10 cm depths after two, 14 and 28 days from crude oil addition. At each sampling date, the recovery of petroleum hydrocarbons measured.

Findings – The results obtained indicated that high by significant differences among the different concentrations, different depths and different sampling durations. Moreover, the downward mobility of petroleum hydrocarbons decreased with increasing crude oil concentration.

Originality/value – Results of the experiment revealed the importance of studying the fate and mobility of total petroleum hydrocarbons (TPH) in soils in order to facilitate a proper reclamation practice specially in oil polluted sites.

Keywords Sustainable environment, Crude oil, Research institutions, Downward mobility, Hydrocarbons, Oil contaminated soil

Paper type Research paper

1. Introduction

Petroleum is a complex mixture of hydrocarbons with a characteristic chemical composition and specific physical properties, depending on the geological and geographical origin of the crude oil and the nature of the cracking process used during refining. The problem of petroleum hydrocarbons in the environment is that they have serious health effects on humans and animals.

In Sudan, the new expansion of petroleum industries caused some environmental problems these may include, mainly polluting the soils with the polychlorinated

hydrocarbons. Unfortunately there are no plans of waste management for the produced water from industries and refineries. Most of the produced water is disposed of the nearby areas without monitoring the change in soil characteristics and assessing the fate of such pollutants in soils.

Mobility of organic chemicals through the different media depends on the unique physical and chemical properties of the chemicals themselves and of the media with which they come into contact. The mobility of TPHs through soil column is dependent on three main factors, these are:

(1) crude oil properties and soil properties (Adam *et al.*, 2002);

(2) distribution coefficient (Ehlers *et al.*, 2010); and

(3) climatic conditions (Daly *et al.*, 2007).

The higher concentration of aromatics in diesel may prevent the downward migration of the contaminant due to their low solubility and increased adsorption on soil components (Adam and Duncan, 2001). Adam *et al.* (2002) studied diesel fuel mobility through soil profile. It was followed in a 1-m soil column and the effect of ethanol addition to diesel fuel on this mobility was determined. The addition of 5 percent ethanol to diesel fuel was found to enhance the downward migration of the diesel fuel components. At 25 percent aqueous ethanol, the majority of hydrocarbons were mobilized and the retention behavior of the soil column lessened. At 50 percent aqueous ethanol, all the hydrocarbons were found to move unimpeded through the columns.

The concentrations of 16 petroleum hydrocarbon pollutants for the contaminated soil were analyzed in four size fractions (<62, 62-125, 125-250, and 250 μm). The total concentrations of pollutants ranged from 7.3 to 358 $\mu g\,g^{-1}$, the highest concentrations were associated with the large size (>250 μm) fractions while the fine silt and clay fractions (<62 μm) contained relatively low petroleum hydrocarbons (Wang *et al.*, 2001). O'Reilly *et al.* (2001) reported that the concentration of an organic chemical has 100 times the affinity for the organic phase than for the water phase.

The concentration of total petroleum hydrocarbons (TPH) decreases with depth in all sites. This implies that most of the petroleum hydrocarbons accumulate at the topsoil compared to the other depths. The accumulation pattern of petroleum hydrocarbon depends on the textural and physical soil properties, contaminant supplies, amount that are water soluble and the hydrology of the area.

Coulon *et al.* (2009) found the K-value decreased with the increase in molecular weight of the considered petroleum hydrocarbon compounds. Once released into the environment, most of the lower molecular weight petroleum hydrocarbon compounds are subject to volatilization, oxidation, dissolution and biotransformation processes (Howard *et al.*, 2005). In contrast, the heavier compounds (boiling points ca. $300°C > 600°C$ and carbon number ranges $>C_{20}$) are desorbed slowly into the aqueous phase of the oil-soil matrix due to their low water solubility, low vapor pressure and high octanol-water partition coefficients (K_{ow}) (Huesemann *et al.*, 2004).

Several different factors may account for the seasonal changes in soil petroleum hydrocarbon concentrations including annual temperature cycle, which results in greater deposition during the colder months and greater volatilization during the summer; the uptake of contaminants into newly growing biomass; the release of contaminants from organic litter; the degradation, redistribution and dilution of contaminants through the soil profile by soil mixing during the summer (Daly *et al.*, 2007).

The general objectives of this study are to study the mobility of crude oil vertically through soil with hydrodynamic dispersion process and to identify the petroleum hydrocarbons in soils and the mode of action of petroleum hydrocarbons.

2. Materials and methods

2.1 Materials

The soil used in laboratory studies was collected from the Faculty of Agriculture, University of Khartoum, demonstration farm, Shambat, Khartoum North, Sudan. It classifies as Fine, loam mixed isohyperthermic, Typic, Torrifluvent and it is reported by Mohammed (2011). The crude oil used in the experiment was delivered by Petrodar Oil Company/Khartoum, Sudan. It is light and its bulk density was $0.81 \, g \, cm^{-3}$. The seven petroleum hydrocarbon components were found in crude oil. These include Decane, Undecane, Tridecane, Tetradecane, Pentadecane, Nonadecane and Heneicosane. These findings were supported by the results of the previous studies (Gustafson, 1997) who found hydrocarbon fractions containing a number of carbons ranged between C_8 and C_{22}.

2.2 TPH mobility experiment

This experiment was used to estimate the mobility rate for the TPHs. Discharge sampling method was used to achieve the experiment.

In total, 27 columns of polyvinyl chloride (PVC) with of length 15 cm and internal diameter of 10.16 cm were used. Each column was filled up to 10 cm with 1.27 kg air-dried soil. The bottom of the column had a fine Nylon mesh covering the lower end to prevent the soil from escaping, but allowing the leachate to freely drain away. The experiment was done at a room temperature approximately 30°C.

The calculated and suggested concentrations namely: 0.4953 ml (0.16 ppm), 0.9906 ml (0.32 ppm), 3.9624 ml (1.28 ppm) of crude oil were diluted in 10 ml of n-hexane to ease distribution of crude oil on the soil surface (n-hexane was evaporated at room temperature) using a 10 ml syringe, to the top of each soil column. The crude oil was allowed to penetrate into the soil for approximately 30 min. After this time, 253 ml of distilled water were poured to fill the pore volume of the soil column. The flow rate depended entirely on gravity flow and the density of the soil packed column. Distilled water was added to fill the pore volume each day. This process was continued for two, 14 and 28 days. In total, 40 g subsamples were taken from the depths of 5, and 10 cm. The samples were then extracted separately to determine the amount of TPH present in each depth.

To determine the TPH 40 g fresh soil (sieved $<2 \, mm$) was extracted for 30 min in 100 ml 1:1 acetone: dichloromethane in a shaker ($200 \, rev \, min^{-1}$). The extract was filtered with (Whatman No. 42) into a 100 ml volumetric flask and the volume was made up to 100 ml with 1:1 acetone: dichloromethane. This extract was analyzed by GC-FID using the conditions described below and the TPH value was calculated. The method for TPH analysis by capillary GC-FID was modified from the US EPA method 8,100 for the analysis of ploy nuclear aromatic hydrocarbons (US EPA, 1986).

2.3 Statistical analyses

Data collected from the experiment were analyzed as factorial complete randomized design. Analysis of variance was performed according to the method described by Gomez and Gomez (1984). Means were separated by using Duncun's Multiple Range Test. Ten assigned peaks were used for verification of acceptable replicate analysis. The average total peak area from the three replicates was calculated and used to work out the total TPH content of that section.

3. Results and discussion

From the general investigation of the ten hydrocarbons in the studied soil, three components of such hydrocarbons, namely, Octane, Nonane, and Decosane were not detected; therefore, the mobility of only seven petroleum hydrocarbons was studied.

Figures 1 and 2 illustrate the results of distribution of Decane and Undecane hydrocarbon fractions in different soil depths, under different crude oil treatments during different intervals of time. It was observed that Decane was detected in 10 cm depth for 0.32 ppm crude oil treatment after 28 days from oil addition and Undecane was detected 0.16 ppm crude oil treatment after two days from oil addition. At the depth of 5 cm, Decane was detected after two days and in 10 cm after 28 days under 0.32 ppm crude oil treatment. These findings agreed with that reported by Coulon *et al.* (2010) who concluded that the mobility of hydrocarbons fractions in the soil was governed by its leaching factors (special parameters of hydrocarbons) which were very high in Decane and Undecane hydrocarbon fractions.

Figure 3 shows the percent recovery of Tridecane at different soil depths under different crude oil treatments and different intervals of time. The results showed that the recovery of Tridecane at the depth of 5 cm was 17.09 percent, which was higher than that at the depth of 10 cm (1.0 percent), under 0.16 ppm crude oil treatment. Under the treatment of 0.32 ppm crude oil at the depth of 5 cm and the depth of 10 cm the recovery levels were 1.72 and 1.16 percent, respectively and with higher recovery in 28 days samples at the depth of 5 cm. While, for 1.28 ppm crude oil treatment, the concentration of Tridecane at the depth of 5 cm was higher than the depth of 10 cm. This may be attributed to the effect of some soil properties such as total organic carbon (TOC) and clay particles that can retard the high molecular compounds to move down. Similar conclusions were reported by Broholm *et al.* (1999b).

For Tetradecane distribution results in different soil depths, under different treatments, as shown in Figure 4, it was observed that this fraction was detected under few treatments and had low recovery perenctages, as compared to the other
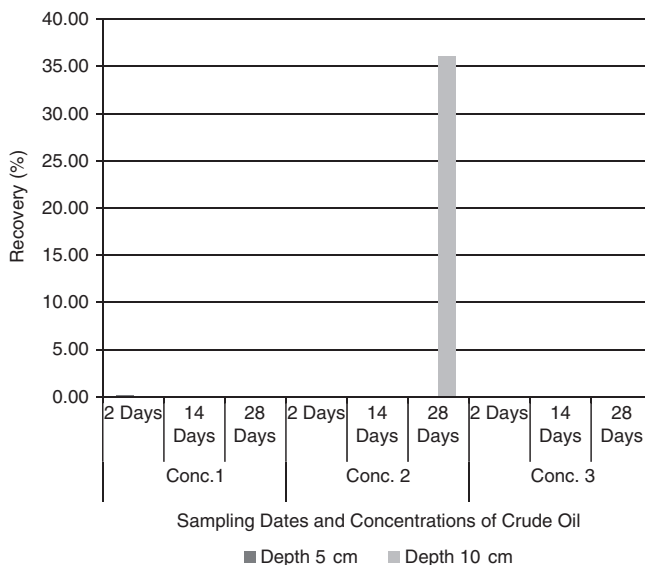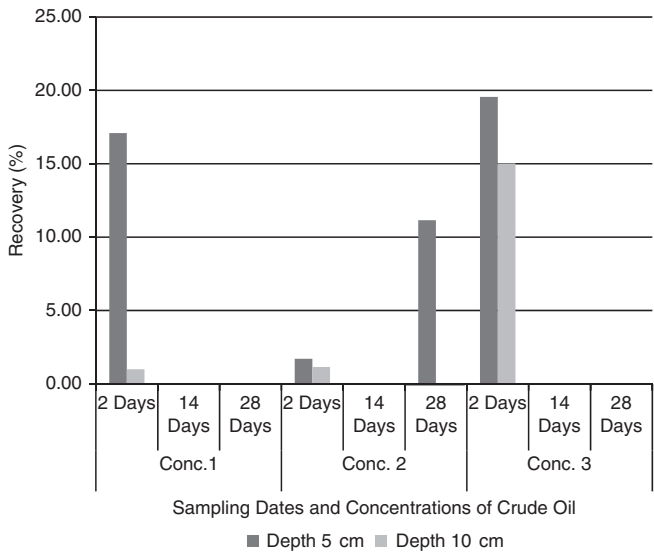

Figure 1.
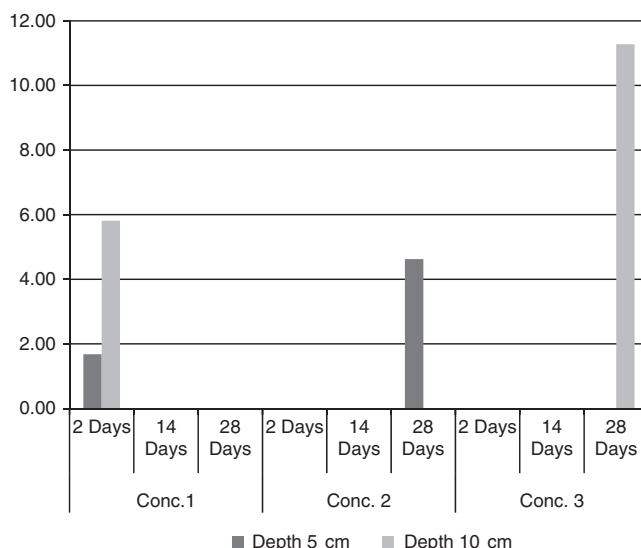Recovery percentage of Decane at different sampling dates and different concentrations of crude oil

Figure 2.
Recovery percentage of
Undecane at different
sampling dates and
different concentrations
of crude oil
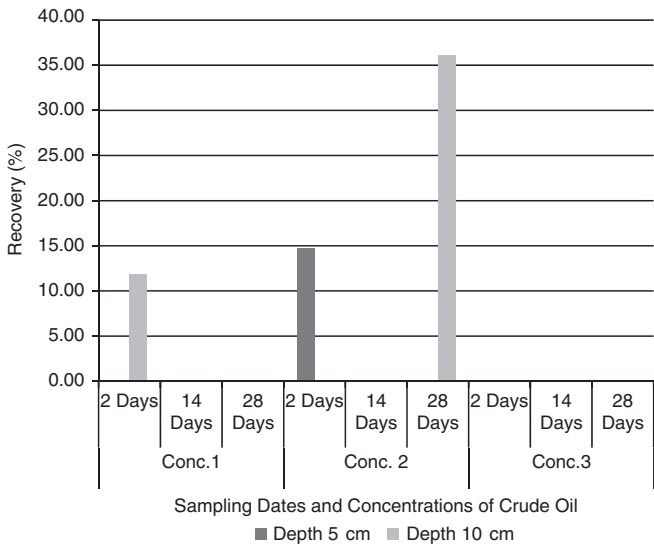
Figure 3.
Recovery percentage of
Tridecane at different
sampling dates and
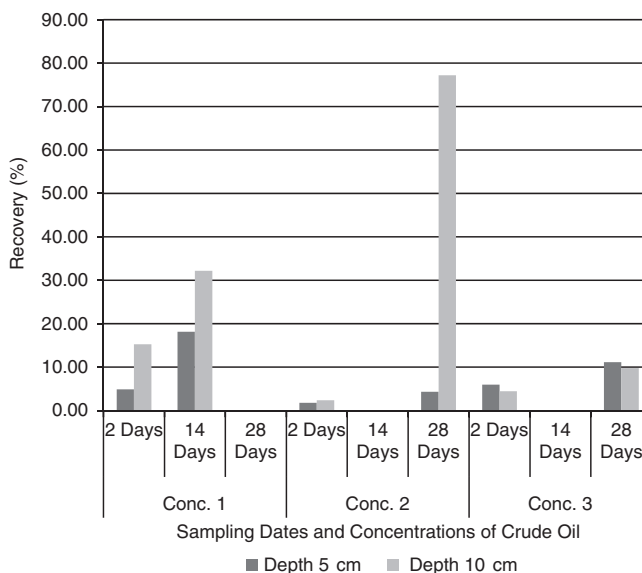different concentrations
of crude oil

components. For 0.16 ppm crude oil treatment, the data revealed that the recovery at the depth of 5 cm was lower than at the depth of 10 cm. However, for 0.32 ppm crude oil treatment, this fraction was detected only at the depth of 5 cm after 28 days (4.63 percent). For 1.28 ppm crude oil treatment, the concentration of Tetradecane was 11.28 percent at the depth of 10 cm after 28 days. The observed decrease in the recovery percentage of this fraction might be attributed to the ability of organic amendments in soil, that immobilized such organic compounds as described by Arias *et al.* (2002) who reported that humic acid, a component of soil organic matter, can enhance the adsorption capacity of mineral surfaces.

Figure 4.
Recovery percentage of
Tetradecane at different
sampling dates and
different concentrations
of crude oil

Figure 5 illustrates the data concerning the distribution of Pentadecane hydrocarbon fraction in different soil depths under different crude oil treatments, during different intervals of time. The results indicated that for 0.16 ppm crude oil treatment this fraction has higher recovery at the depth of 10 cm than that detected at the depth of 5 cm after two days and 14 days, however, this fraction was not detected after 28 days. On the other hand, for 0.32 ppm crude oil treatment, this fraction showed different mobility behaviour through the soil column, since its recovery at the depth of 5 cm was lower than at that of the depth of 10 cm after two days and after 28 days. The highest recovery (80 percent) was detected at the depth of 10 cm after 28 days.
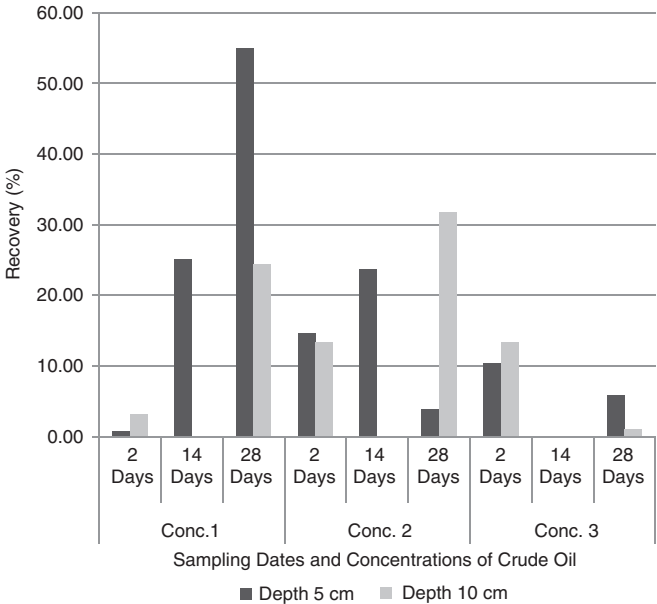

Figure 5.
Recovery percentage of
Pentadecane at different
sampling dates and
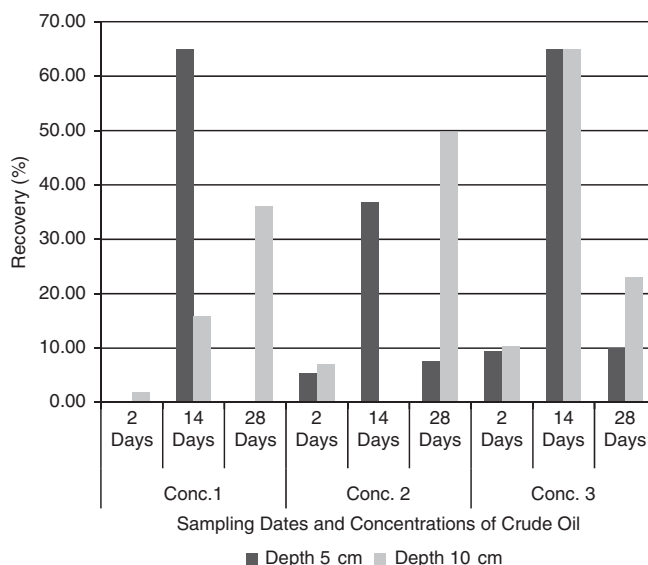different concentrations
of crude oil

For 1.28 ppm crude oil treatment, the recovery at the depth of 5 cm was higher than that at the depth of 10 cm after two days and 28 days. These results revealed that Pentadecane has high rate of mobility through Shambat soil under lower concentrations. This may be attributed to the fact that higher concentrations of oil can strongly be absorbed by clay soil. Similar findings were obtained by Broholm *et al.* (1999a), who reported that hydrocarbons can move in soils with the action of runoff and infiltration, but they concluded that these processes are affected by different types of soils and compounds.

Figure 6 shows the recovery percentage of Nonadecane under 0.16 ppm crude oil treatment. The recovery percentage at the depth of 5 cm increased gradually with increasing time. However, at the depth of 10 cm the recovery percentage decreased after two days, till 0 percent after 14 days and increased after 28 days. For 0.32 ppm crude oil treatment, Nonadecane recovery percentage at the depth of 5 cm increased from the first two to 14 days and decreased in 28 days. At the depth of 10 cm, the recovery increased from the first (two days) to third sampling (28 days). For 1.28 ppm crude oil treatment, the recovery was higher in the first sampling (two days) than in the third (28 days), while after 14 days there was no Nonadecane at the depths of 5 and 10 cm. These observations are supported by the findings of Zhihuan *et al.* (2008) who reported that the concentrations of parent sulfur and oxygen heterocyclic aromatic hydrocarbons (SOHAHs) decreased with depth in soil profiles, and changed markedly in the upper horizons and maintained constant at deep part (>40 cm). When compared with the TOC proles, the same trend between concentration and TOC was observed, and this characteristic does not changed with different environmental domains, suggesting that SOHAHs concentrations in soils were affected by TOC, which likely indicated that the pollutant sources were clearly different between the top soil and the deep part.

As shown in Figure 7, the recovery percentage of Heneicosane under 0.16 ppm crude oil treatment increased gradually at the depth of 10 cm within the period of the

Figure 6.
Recovery percentage of Nonadecane at different sampling dates and different concentrations of crude oil

Figure 7.
Recovery percentage of
Heneicosane at different
sampling dates and
different concentrations of
crude oil

experiment (28 days), and at the depth of 5 cm this fraction was detected after 14 days. Also, for 0.32 ppm crude oil treatment, the recovery percentage increased gradually within the 28 days, while at the depth of 5 cm, it increased and then decreased. For 1.28 ppm crude oil treatment, the recovery decreased after two days, then increased after 14 days and decreased again after 28 days. This result showed high recovery percent, which reflected the presence of Heneicosane and that demonstrated the high rate of mobility of Heneicosane hydrocarbon fraction through soil profile.

4. Conclusion

It is concluded that, studying the mobility of total petroleum hydrocarbon in soils is very important as it depends on the concentration of oil in soils and the characteristics of soils. Further research experiments are recommended to study the mobility in different soil types under different climatic conditions, e.g. temperature.

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