

Vertical Distribution of Typical Petroleum Pollutants in an Oilfield of Gudao, china

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Keywords: oil pollution, total petroleum hydrocarbons, PAHs, vertical distribution.

Abstract. In oilfields, crude oil exploiting process led to heavy soil contamination with petroleum pollutants. In this work, ten soil profile samples were collected and analyzed with GC-MS method to investigate the vertical distribution of typical petroleum pollutants in an oilfield of Gudao Region. The results showed that the highest concentrations of the five typical petroleum pollutants appeared in the range of 0-40 cm depth, and then the concentrations of these pollutants gradually decreased with increasing soil depth below 40 cm. The peak concentrations of total petroleum hydrocarbons (TPHs), polycyclic aromatic hydrocarbons (PAHs) and sulfur were 33.84 g/kg, 4624.58 µg/kg and 1298.50 mg/kg, respectively, all found in the 0-10 cm soil layer of the profile. The n-alkanes content of 88.10 mg/kg was highest at the 10-20 cm depth of the soil profile. The highest content of 3293.68 µg/kg for BETX (Benzene, Toluene, Ethylbenzene and Xylenes) appeared at the 30-40 cm soil layer. The soil size and organic matter content were the probable factors affecting the vertical distribution of the pollutants. The results could provide basic data for pollution monitoring and soil remediation.

1. Introduction

Economic development caused a significant enhancement of crude oil extraction and utilization. Similar to various other mining activities, the crude oil exploration process inevitably induced serious environmental pollution. As an example, total petroleum hydrocarbons (TPHs) and polycyclic aromatic hydrocarbons (PAHs), being important petroleum pollutants, have drawn the attention of the related researchers due to their mutagenic and carcinogenic potential [1, 2]. However, in the Yellow River Delta, most studies focused on the distributions of heavy metals, N and P [3, 4]; A few studies on the distributions of hydrocarbon pollutants [5-7] have been undertaken, but rarely on aliphatic hydrocarbons such as TPHs, PAHs and n-alkanes in the oilfield [8], which have great significance to pollution control and soil remediation.

The paper aims to elucidate the vertical distribution characteristics of the typical petroleum pollutants in the oilfield soil through analyzing the concentrations in different soil profile layers, and to find out the possible reasons affecting the distributions of these pollutants.

2. Materials and Methods

2.1 Study Area.

The study area was located in Gudao Region of Shengli Oilfield (the second biggest oilfield in China), north of the Yellow River Delta (Fig. 1). Gudao town is a new developing oil-industry town based on oil exploitation, which has a long oil exploitation history of more than 40 years and a short urbanization history of about 20 years. The average annual temperature of the study area is 12.1 °C, and the annual precipitation is approximate 580 mm. The soils in the study area are mostly fluvo-aquic and coastal solonchaks (World Reference Base for Soil Resources).



Fig.1 Location of the study area

2.2 Sampling Procedure.

Ten profile soil samples were collected in July, 2013 near oil wells where the soils were contaminated by crude oil to investigate the vertical distribution of typical petroleum pollutants. A pit was dug with dimensions of 1.5 m length, 0.8 m width and 1.0 m depth, and then the soil samples were collected with 10 cm intervals from bottom to surface. For each sample, firstly, at least three subsamples of similar weights with about 1 kg were collected with a plastic scoop and a stainless steel shovel. Secondly, the subsamples were mixed together homogeneously. Finally, the weight of the mixed sample was decreased to be about 1 kg with the quarter method to improve the sample representativeness [9]. The soil samples were stored in plastic bags.

2.3 Sample Analysis.

The soil samples were dried at room temperature and then purified by discarding the plant roots and stones. The soil sample (15 g, dry weight) were Soxhlet extracted using 300 ml dichloromethane for 24 h. Activated copper and zeolite were added to remove the elemental sulfur. After extraction, the extract was concentrated to a volume of about 2-3 ml. Then, the extract was evaporated and weighed, and n-hexane was added to the extract to precipitate the asphaltene. Finally, the extract was evaporated and weighed again. The total petroleum hydrocarbons (TPHs) content was the difference between the two weights. The extract was solvent-exchanged into 20 ml n-hexane to reduce the volume to about 1-2 ml with a rotary vacuum evaporator. PAHs and n-alkanes were fractionated by 40 ml dichloromethane/n-hexane (v/v 1/1) and 25 ml n-hexane using a 2:1 silica gel/alumina column, respectively. The PAHs fraction and n-alkanes fraction were then condensed to 1 ml by rotary vacuum evaporator and finally to 0.2 ml under a gentle gas stream of high purity nitrogen, respectively.

The PAHs were analyzed by gas chromatography coupled to mass spectrometry (GC-MS) (Agilent/6890N-5973N, Agilent Co., USA) with helium as carry gas. The n-alkanes were analyzed with gas chromatography (GC-2014, Shimadzu Co., Japan). The BTEX components were determined with a purge-and-trap sample concentrator (Eclipse 4660, OI analysis instrument Co., USA) in combination with gas chromatography. The sulfur was determined using high frequency IR carbon-sulfur spectrometer (CS-878A, Sichuan JingKe Instrument Manufacturing Co., Ltd., China).

2.4 Quality Assurance and Quality Control (QA/QC).

Method blanks (solvent) and spiked blanks (standards spiked into solvent) were applied as quality assurance and quality control methods. The relative standard deviations and recoveries of PAHs, n-alkanes and BTEX ranged from 1.8-12.5% and 75.8-98.5%, 2.5-14.1% and 76.5-102.3%, and 4.6-14.3% and 83.2-99.7%, respectively. The detection limits of PAHs, n-alkanes and BTEX were in range of 2.3-23.7, 3.2-19.5 and 0.132-0.679 $\mu\text{g}/\text{kg}$, respectively. Additionally, the relative standard deviation and detection limit for sulfur was 4.9% and 0.013 g/kg, respectively.

3. Results and Discussion

Five typical petroleum pollutants, total petroleum hydrocarbons (TPHs), polycyclic aromatic hydrocarbons (PAHs), n-alkanes, BTEX (Benzene, Toluene, Ethylbenzene and Xylenes) and sulfur,

were chosen as the representatives to investigate the vertical distribution for their toxicity, persistence and representativeness in the study.

Fig. 2 illustrated the vertical concentration distribution of petroleum pollutants along the soil profile of the oilfield.

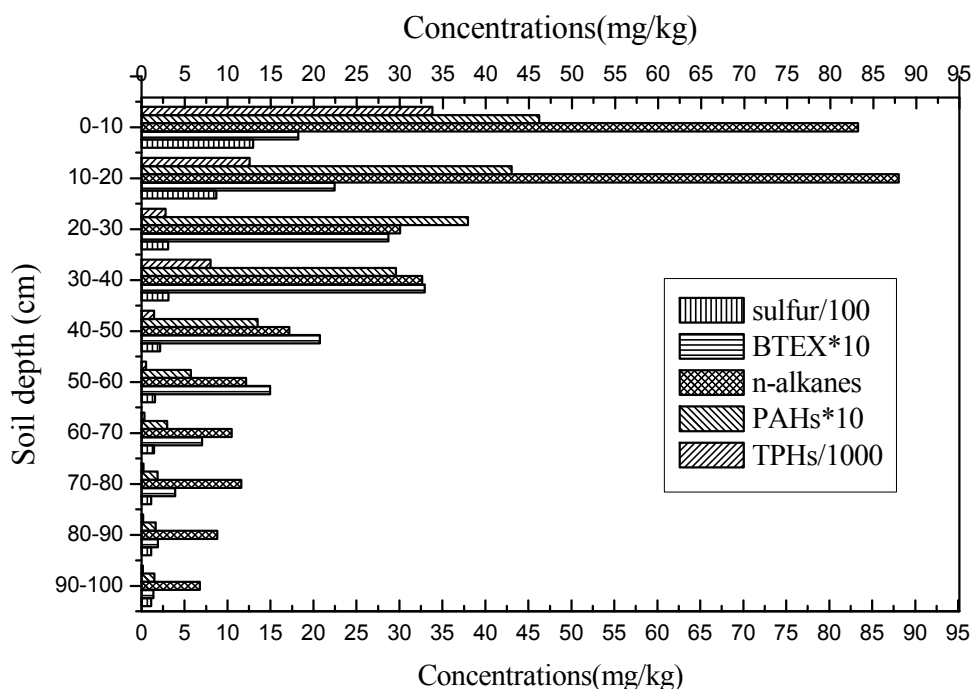


Fig. 2 Vertical distribution of petroleum pollutants in the oil-polluted soil profile

As seen in Fig. 2, from the top to the bottom of the profile, the highest concentrations of the five typical petroleum pollutants appeared in the range of 0-40 cm, and then the concentrations of these pollutants generally decreased with the increase depth below 40 cm.

For TPHs, the concentrations in the soil from the surface to the depth of 60 cm were all above the national pollutant control standard (500 mg/kg) [10], suggesting that these layers were all polluted by petroleum. First, the TPHs contents were reduced significantly from 33.84 g/kg to 2.80 g/kg from the surface to the 20-30 cm depth. Second, the TPHs content was slightly increased to 8.02 g/kg at the depth of 30-40 cm. Finally, the concentrations of TPHs were decreased gradually from the 30-40 cm depth to the bottom of 90-100cm. The possible reasons were as follows: the upper soil is mostly sandy, which has strong permeability, weak retention, multi-porosity and low organic carbon content, leading to increasing the infiltration rate and depth of TPHs in the soil profile; On the other hand, the thick property of the oil in Gudao Region results in that the TPHs concentration in the upper layer is several times higher than in the lower layer; The small peak at the depth of 30-40 cm is probably ascribed to the accumulation of petroleum pollutants for many years; Below 60 cm depth, it is difficult for TPHs to migrate to next layer because of the weak permeability and strong retention of the clay.

As illustrated in Fig. 2, the concentrations of PAHs decreased gradually with increasing the depth from the soil surface. The highest PAHs content was 4624.58 $\mu\text{g}/\text{kg}$ in the surface soil of 0-10 cm. Maliszewska-Kordybach [11] classified the soil contaminated by PAHs to four levels, which was shown in Table 1. The three classification thresholds were 200, 600 and 1000 $\mu\text{g}/\text{kg}$, obtained from the monitored concentrations in European soils and from an estimation of human exposure risks [12]. It can be seen from Fig. 2 and Table 1 that the soils from surface to the 40-50 cm depth were all classified as "Heavily contaminated", the soil layers of 50-60 cm and 60-70 cm were fallen under "Weakly contaminated" classification, and the soils from 70-80 cm to 90-100 cm depth were under the class "Not contaminated". Moreover, It can be noticed from Fig. 2 that the decrease rate of PAHs in the depth of 0-40 cm was slower than in the depth of 40-100 cm. In 0-40 cm soil layers, the light

PAHs components were volatile and easily degraded, leading to no significant differences of PAHs concentrations among upper layers of the soil profile. In 40-100 cm soil layers, the organic matter content decreased and the clay content increased, resulting in the gradual decrease of PAHs in bottom layers of the soil profile.

Table 1 Classification of soil contamination by PAHs [11]

Class of soil contamination	PAHs ($\mu\text{g}/\text{kg}$ d. w.)
Not contaminated	<200
Weakly contaminated	200-600
Contaminated	600-1000
Heavily contaminated	>1000

The highest concentration of 88.10 mg/kg for n-alkanes was found in 10-20 cm depth of the soil profile. The n-alkanes content in 0-10 cm soil layer was 83.35 mg/kg, slightly lower than that in 10-20 cm soil layer. The concentration of n-alkanes was sharply decreased from 88.10 mg/kg in 10-20 cm soil layer to 30.08 mg/kg in 20-30 cm soil layer. Then the n-alkanes content gradually decreased with the increase depth below 30 cm.

The vertical distribution of BTEX showed that the concentration increased gradually from the surface to the 30-40 cm depth and then decreased rapidly from 30-40 cm depth to 90-100 cm depth of the soil profile. The highest concentration of BTEX was 3293.68 $\mu\text{g}/\text{kg}$ at 30-40 depth of the soil profile. The BTEX components were easier to be dissolved in water than PAHs and n-alkanes, which led to that BTEX components could move to underlying layers from the surface soil with rainfall infiltration and leaching. Consequently, the BTEX content reached the peak at 30-40 cm depth of the soil profile. In the bottom layers, the increase of soil viscosity resulted in that BTEX was difficult to move to the next layers.

In addition, the vertical distribution of sulfur was similar to that of TPHs. The sulfur concentration decreased rapidly from 1298.50 mg/kg in the soil of 0-10 cm depth to 307.67 mg/kg in the soil of 20-30 cm depth. Then, the sulfur concentration increased slightly to 314.13 mg/kg at 30-40 cm soil layer. At last, the sulfur content decreased slowly from the 30-40 cm depth to 90-100 cm depth of the soil profile. The sulfur mostly exists in the asphaltene component of oil, which was hardly soluble in water, resulting in that the sulfur was difficult to migrate to the underlying layers.

4. Summary

The vertical distribution of typical petroleum pollutants in oil-polluted soil of Gudao Region were studied. The methods of GC, GC-MS and purge-and trap-GC were applied to analyze the petroleum pollutants. The results showed that the highest concentrations of the five petroleum pollutants were all found in the range of 0-40 cm soil layers. The concentrations of these pollutants decreased with increasing the soil depth from 40-50 cm to 90-100 cm. The peak concentrations of TPHs, PAHs and sulfur were 33.84 g/kg, 4624.58 $\mu\text{g}/\text{kg}$ and 1298.50 mg/kg, respectively, all appeared in the 0-10 cm soil layer of the profile. The highest content of n-alkanes was 88.10 mg/kg, finding in the 10-20 cm depth of the soil profile. Additionally, for BTEX, the content of 3293.68 $\mu\text{g}/\text{kg}$ was highest, which was found at the 30-40 cm soil layer. The soil size and organic matter content affected the vertical distribution of the petroleum pollutants. In conclusion, the study results could provide important data for pollution monitoring and oil-polluted soil remediation.

Acknowledgements

The study was supported by ministry of environment production's special funds for scientific research on public causes No. 201109022 and the Scientific Research Funds for Yong Scholars of Weifang University of Science and Technology (No sdlg2013w003).

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