

## Investigation on metals (V, Ni, and Fe) accumulation in the collection site of oil sludge

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**ABSTRACT:** The present study investigates the accumulation of vanadium, iron, and nickel in different depths of soil in collection sites of oil sludge, in Masjed Soleyman Oil and Gas Exploitation Company, located in Choob Sorkh Region. To conduct the research, four sampling points have been selected at the mentioned site, with one sampling point chosen outside the site, as the clean area. Soil sampling has been carried out at depths of 50 and 100 cm, using an auger. All samples are measured to evaluate heavy metals, according to the standard method of Inductive Coupled Plasma (ICP) spectroscopy. The parameters of pH, EC, density, and organic compounds have also been measured. Results have shown that EC, TOM, and density of the soil in the collection site of oil sludge were relatively higher than the reference site. In addition, statistical analysis has shown that electrical conductivity and organic compounds were influenced by the discharge of oil sludge. The mean concentrations of Ni, V, and Fe in both depths (50 cm and 100 cm) of the four studied plots were 68.8 mg/kg, 46.3 mg/kg, and 53565 mg/kg, respectively, indicating that Ni concentration is more than the acceptable limits in the soil. Although, the amounts of V (36.3 mg/kg), Ni (62 mg/kg), and Fe (19416 mg/kg) in the reference site were lower than the studied oil sludge accumulation site. Thus the study area is a place for the accumulation of oil sludge, since the high concentration of heavy metals can be attributed to human interference.

**Keywords:** Choob Sorkh Region, heavy metals, Masjed Soleyman City, oil contamination, sludge accumulation.

## INTRODUCTION

The ever-increasing development of human communities and world nations have always been accompanied by the exploitation of natural reserves and resources; however, during the exploitation of oil and gas reserves, some waste materials are produced, whose unprincipled discharge adversely influences the surrounding environment (Adamo et al., 2002).

Heavy metals are naturally found in stones and soils abundantly; however, the amount of these elements in soils is increasing due to agricultural and industrial activities of human beings (Hoveidi et al. 2013; Shams Fallah et al., 2012; Karbassi & Pazoki, 2015). They enter the environment through atmospheric deposition, erosion of the geological matrix, and from anthropogenic sources arising from both stationary and mobile sources (Moaref et al., 2014; Ghadaksaz zadeh et al., 2014;

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Hosseini Alhashemi et al., 2012; Taghinia Hejabi et al., 2010). Evaluation of the concentration of heavy metals in soil-water-plant system is of great importance, owing to the impact of these substances on food cycle as well as animals and plants' wellbeing (Hosseini Alhashemi et al. 2011; Janadeleh et al., 2016). This type of industrial and human pollutants can be absorbed by plant roots and agricultural crops, then to enter the cycle and eventually into the human body. This type of toxic elements, while moving through the pores of different layers of soil, enters aquifers, contaminating drinking water sources in different societies (Misra & Chaturvedi, 2007). Accordingly, numerous studies have been conducted in this regard. Alonsohernández et al. (2011) investigated the soil contamination of the northern regions of Serbia, the Noway region, and parts of the Bosnia and Herzegovina. They reported that soil contamination with nickel and chromium is caused by agricultural and human activities. Soil contamination has become a global problem, since mid-1980s. A group of soil-contaminating sources is related to oil exploration, production, storage, transportation, distribution, and final discharge of these compounds' wastes. These industries can jeopardize the environment if they are contaminant (Yeung et al., 1997). It is estimated that over 60 million tons of sludge are produced every year (Hu et al., 2013). Petrochemical industries and oil refinery plants introduce toxic compounds such heavy metals or generally mutagenic and carcinogenic compounds into the environment (Karbassi et al., 2015; Pazoki & Hasanidarabadi 2017). The sewage or wastewater of oil industries contains elements such as cadmium, mercury, lead, vanadium, arsenic, and other dangerous metals and compounds (Alonsohernández et al., 2011). The accumulation sites of oil sludge are among places that gradually introduce a large volume of metals into the deep soil, owing to constant aggregation of oil materials.

Accordingly, this research focuses on the extent of oil contamination, influenced by traditional and nonstandard discharge of oil sludge in Unit Number 9, Masjid Suleiman Oil and Gas Exploitation Company, located in Choob Sorkh Region along with the emission of heavy metals present in the mentioned oil wastes within the depths of 50 and 100 cm of the contaminated soil.

## **MATERIALS AND METHODS**

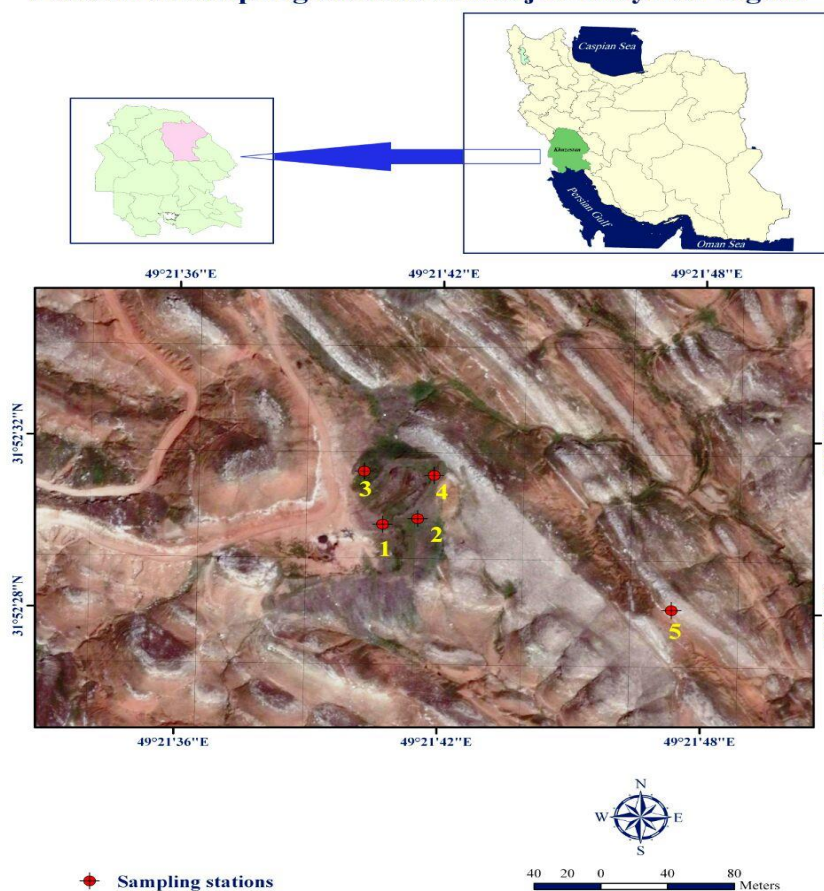
### **Study area**

Choob Sorkh Region is located 5.5 km away Unit 9 Oil and Gas Production Plant in Masjed Soleyman City (north east of Khouzestan Province). The area, about 65 m in 57 m, is the site of oil sludge accumulation from oil production units in Masjed Soleyman City. Figure 1 illustrates the situation of the area of the study along with the soil sampling points.

### **Sampling and analytical procedure**

Soil samples were collected, using an auger from four points of the site of accumulation of oil sludges in Choob Sorkh Region at three different time intervals at two depths of 50 and 100 cm from March to June 2015. Moreover, one sampling point was chosen in a clean area, outside the oil sludge accumulation area. All soil samples were sealed in polyethylene bags and transferred to the laboratory. They were air dried for 24 h and then passed through a 63  $\mu$ m mesh sieve to separate large fractions. The sieved samples were used for physicochemical parameters of soils (pH, EC, and total organic carbon), according to ROPME 1999. For trace metal analysis, 0.5 g of soil was treated using 5 ml of aqua regia and heated until most of the liquid got evaporated and was allowed to cool before adding 3 ml of concentrated perchloric acid. The temperature was maintained at 100°C until the liquor was clear. Finally, samples were cooled down to room temperature, in flasks, the volume of which was equal to 1 N HCl (Chester & Hughes, 1967; Tessier et al., 1979).

**Position of sampling stations in Masjed-soleyman region**



**Fig. 1. Geographic situation of the sampling points in Choob Sorkh sludge site, Masjed Soleyman City**

**Statistical analysis**

To quantify the degree of elemental accumulation in soil,  $I_{geo}$  was calculated, according to Muller (Eq. 1; Karbassi et al., 2008).

$$I_{geo} = \log_2 \frac{C_n}{B_n \cdot 1.5} \quad (1)$$

where  $C_n$  is the total elemental content in sediments;  $B_n$ , the concentration of metals in the shale; and 1.5 is a factor for normalization of background metal concentrations in the shale.

To understand the relation amongst studied metals and physic-chemical parameters, Multi Variable Statistical Program (MVSP) was used. Moreover, to understand the relationship among various metals in the three matrices, SPSS was used for the purpose of comparing the mean concentration of the evaluated

elements across time intervals; moreover, one-way analysis of variance (Duncan test) was employed to determine the relation among the elements. All tests were regarded as statistically significant when  $P < 0.05$ .

**RESULTS AND DISCUSSIONS**

Table 1 provides the analysis results of physicochemical parameters. As Table 1 indicates, there is not any significant difference between pH content in all studied points and depths; while, EC and organic compounds, showed significantly lower values in reference site than other points in the oil sludge collection site.

Table 2 provides the concentration of studied metals in the soil in depths of 50 cm and 100 cm.

**Table 1. Physiochemical parameters of the soil in Choob Sorkh sludge site**

Parameter	Reference site	Sampling points				
		1	2	3	4	
pH	Depth 50 cm	7.6±0.1 <sup>a</sup>	7.5±0.2 <sup>a</sup>	7.6±0.06 <sup>a</sup>	7.7±0.1 <sup>a</sup>	7.4±0.1 <sup>a</sup>
	Depth 100 cm	7.6±0.1 <sup>a</sup>	7.4±0.15 <sup>a</sup>	7.6±0.2 <sup>a</sup>	7.8±0.2 <sup>a</sup>	7.5±0.2 <sup>a</sup>
EC (ms/cm)	Depth 50 cm	4.7±0.05 <sup>a</sup>	19.5±3.8 <sup>b</sup>	10±3.8 <sup>c</sup>	10.9±3.5 <sup>c</sup>	6.1±1.5 <sup>d</sup>
	Depth 100 cm	4.7±0.05 <sup>a</sup>	12.7±0.8 <sup>b</sup>	14.5±0.8 <sup>b</sup>	11.7±0.4 <sup>b</sup>	4.4±0.1 <sup>d</sup>
Organic compounds (%)	Depth 50 cm	0.7±0.2 <sup>a</sup>	5.6±1.7 <sup>b</sup>	4.6±1.3 <sup>c</sup>	3.7±0.8 <sup>b</sup>	3.1±1.6 <sup>b</sup>
	Depth 100 cm	0.7±0.2 <sup>a</sup>	4.5±0.9 <sup>b</sup>	4.5±0.7 <sup>b</sup>	3.8±0.1 <sup>c</sup>	2.8±1.8 <sup>c</sup>

<sup>a</sup>The different letters mean significant difference (P<0.05)

**Table 2 Mean concentration of metals in soil of Choob Sorkh sludge site (mg/kg)**

Metals	Reference site	Sampling points				
		1	2	3	4	
V	Depth 50 cm	9.7±2.1 <sup>a</sup>	34.1±8.5 <sup>d</sup>	89.3±2.9 <sup>c</sup>	50.9±3.6 <sup>b</sup>	62.8±7.8 <sup>b</sup>
	Depth 100 cm	9.6±3.5 <sup>a</sup>	49±5 <sup>b</sup>	60.6±6.3 <sup>b</sup>	51.6±2.8 <sup>b</sup>	25.2±1.8 <sup>c</sup>
Ni	Depth 50 cm	54±4.7 <sup>a</sup>	60.2±6.8 <sup>c</sup>	71.8±7.3 <sup>bc</sup>	79.3±8.6 <sup>b</sup>	70±8.3 <sup>bc</sup>
	Depth 100 cm	45±4.7 <sup>a</sup>	69.6±7.9 <sup>b</sup>	56.6±8.7 <sup>c</sup>	86.3±4.9 <sup>d</sup>	73±7.8 <sup>b</sup>
Fe	Depth 50 cm	14483±3962 <sup>a</sup>	43600±470 <sup>b</sup>	69000±3362 <sup>c</sup>	40966±1642 <sup>d</sup>	24350±3976 <sup>e</sup>
	Depth 100 cm	14591±962 <sup>a</sup>	41526±928 <sup>b</sup>	70933±1680 <sup>c</sup>	16260±81 <sup>d</sup>	25416±5918 <sup>e</sup>

<sup>a</sup>The different letters mean significant difference (P<0.05)

**Table 3. I<sub>geo</sub> classification for metals in soil/sediment (Muller, 1979)**

Degree of soil contamination	I <sub>geo</sub>
Unpolluted	0
Unpolluted to slightly polluted	0-1
Slightly polluted	1-2
Slightly polluted to highly polluted	2-3
Highly polluted	3-4
Highly polluted to severely polluted	4-5
Severely polluted	<5

As it is clear in the two studied depths of soil, iron had the highest concentration, due to its abundance in the crust. The concentrations of vanadium and nickel were relatively high, which can be justified by the oil fields in the study area. Concentrations of studied metals were a bit higher at the depth of 50 cm as well; though, there were no significant difference for the studied metals in two studied depths, except for vanadium in plot 4. The geochemical accumulation of metals

was calculated based on I<sub>geo</sub> formulae (Muller, 1979). It should be noted that the mean values of both depths were used for the computation of I<sub>geo</sub>. Results of I<sub>geo</sub> computation for all data were equal to zero, showing that based on this index, the soil was unpolluted (Table 3).

Cluster analysis was conducted to understand the relation between metals and physicochemical parameters in depths of 50 cm and 100 cm of soil in Choob Sorkh sludge site (Fig. 2).

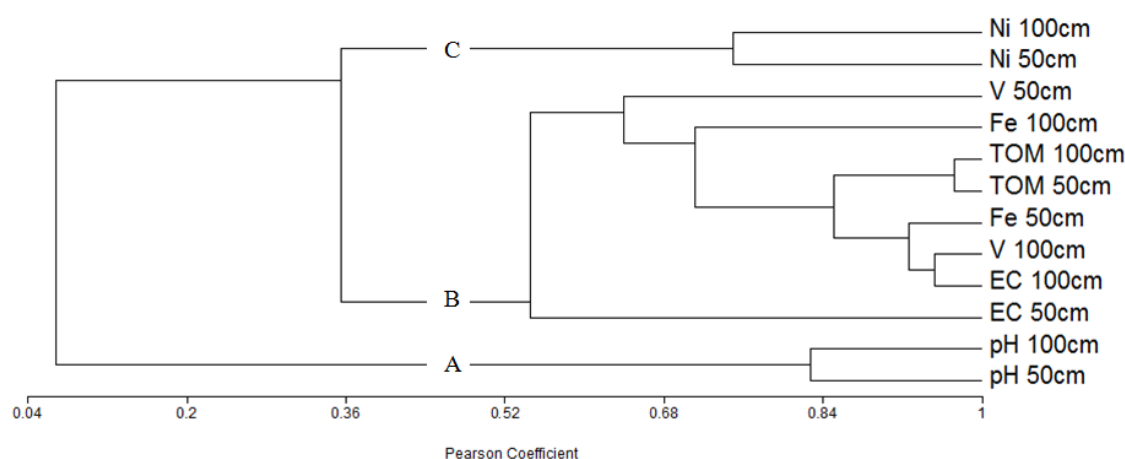


Fig. 2 Dendrogram of cluster analysis among metals and physicochemical parameters in two depths of soil in Choob Sorkh Sludge site

Table 4. Comparison of mean concentration of metals in Choob Sorkh oil sludge's soil and some worldwide limits (mg/kg)

Sampling points	Ni	V	Fe
Reference site	62	36.3	19416
1	64.9	41.5	22563
2	64.2	74.9	69966
3	82.8	51.2	101783
4	63.5	17.6	19949
Earth's crust <sup>a</sup>	80	160	-
Shale	68	130	-
Acceptable values in soil <sup>b</sup>	50	50	-

<sup>a</sup>Bowen (1979)

<sup>b</sup>Fabis (1987)

The pH in both depths shows a significant similarity coefficient and similar behavior in cluster "A". In cluster "B" EC, TOM, Fe, and V have positive meaningful relation together. This can represent the issue that oil and lithogenous materials have a controlling role in their contents in the soil of the study area. Although Ni in depths of 50 cm and 100 cm has a strong positive relation to one another in cluster "C". Finally, all clusters show that physicochemical parameters (except pH) control Fe and V accumulation in the study area.

Comparison of the concentration of studied metals in the soil of Choob Sorkh sludge site with the mean crust, shale values, and acceptable values of heavy metals in soil (Table 4) shows that Ni exceeds shale in sampling point 3, higher in all studied

sampling points than acceptable values in soil; however, concentrations of V in plots No. 2 and 3 are higher than acceptable values in soil but meet two other mentioned worldwide limits.

### CONCLUSION

Masjed Soleyman is an important place for oil activities in Khuzestan Province, having serious consequences on its surrounding environment. In this study, a collection site of oil sludge in Choob Sorkh Region near Masjed Soleyman City was selected and the soil from two depths (50 cm and 100 cm) was chemically analyzed in order to determine the concentration of Fe, Ni, and V. Results show that concentrations of all three metals in the collection site are higher than the studied reference site. Moreover,

concentration of Ni is higher than shale and acceptable values of heavy metals in soil, since nickel and vanadium are undoubtedly indices of oil pollution. Comparing the results with other similar researches approves our findings in oil destructed areas. Further investigation is needed to investigate other metals in oil fields of Masjed Soleyman City and chemical partitioning to determine anthropogenic and natural share of metals in this sector; hence, calculating  $I_{POLL}$ , which uses lithogenous portion of metals, would prove more useful.

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