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Assessment of heavy metal pollution in the soil of Ahwaz oilfield by using the five-stage process of chemical dissociation and Dendrogram interpretation and pollution severity index

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Abstract

The aim of this study is to evaluate heavy metal pollution in the soil of Ahwaz oil field which is the biggest oil field in Iran, by using chemical dissociation process and Dendrogram interpretation and pollution severity index. The 20 stations were selected on the soil surface. Parameters of nickel, vanadium, cobalt, iron, chromium, barium, arsenic and total petroleum hydrocarbons concentrations were determined. Five-step process of chemical dissociation method was used to identify and determine human-made and natural heavy metals concentration, and also MVSP software was used to draw the cluster analysis dendrogram. The results of chemical dissociation show that the origin of the nickel, vanadium and cobalt elements and also of iron, chromium and arsenic in new wells is higher in the human-made and the natural phase, respectively. The results of pollution severity index for nickel showed that 25% of the stations in clean class, 50% in low pollution class and 25% are in middle pollution class. 40% of the stations in terms of vanadium pollution in clean class, 40% in low pollution class and 20% are in middle pollution class. In terms of cobalt pollution, 35% of the stations in the clean class, 40% in low pollution class, 20% in the middle pollution class and 5% are in the high pollution class. In terms of chromium pollution, 75% of the stations in the clean class, 25% are in low pollution class and also for iron and arsenic all the stations are in the clean class.

Keywords

Ahwaz oilfield, five-stage chemical dissociation, heavy metals

1. Introduction

The oil exploration and production processes have always been associated with environmental risks [1,2]. Soil pollution and accumulation of heavy metals in soils contaminated with oil especially drilling fluids is one of the most important environmental issues which is a serious threat for plants, animals and human[3,4]. Heavy metals are considered important because of irresolvable features, toxicity, less movement, complex chemical behavior, cumulative and carcinogenic

effects [5,6]. The oil industry as our main industry has over a hundred years history in Iran [7]. Drilling mud and logs are inevitable toxic byproducts in drilling oil and gas wells. Drilling logs is formed about 10% of total drilling wastes. During drilling process, dangerous fluid and drilling logs combine with oil, water and other chemicals materials which provide a toxic mixture including toxic chemicals such as oil, grease, suspension solids phenols, arsenic, chromium, lead, mercury, natural radioactive materials and

barium [1,8,9]. In addition to salt, many produced waters contain large amounts of calcium, magnesium, potassium and some aluminum, antimony, arsenic, mercury, barium, boron, chromium, cobalt, copper, gold, iron, lead, manganese, nickel, phosphorus, platinum, radon, vanadium, etc [10]. Crude oil naturally contains very different concentrations of various metals in which nickel and vanadium have the highest concentrations among them [11]. Heavy metals from the exploration, drilling and production of oil may be beneficial or harmful depending on the type and concentration of metals; some of these metals at too low concentrations are essential for cell activities that including chromium, iron, manganese, vanadium, zinc, molybdenum while same metals at high concentrations have devastating and irreparable effects on biological systems. The metals attached to vivo proteins and would stop their activities as soon as enter the body so they causing damage to kidneys, liver, nervous system and other vital organs of living creatures [6,9]. In the Ahwaz oil field, drilling mud with complex compounds was used for drilling operations due to certain geological conditions [12]. Drilling wastes is discharged into the specific layer around tower during the operations or after the end of it which may lead to environmental pollution. In the Ahwaz oil field, a pit for each well is designed to discharge all drilling wastes of the well. Water and drilling fluids have no intended physical and chemical properties for all drilling mud needs [7,13]. The biggest environmental concern in terms of contaminants of oil and gas wells drilling waste is their heavy metals, salts, oil hydrocarbons and grease which at the end all of them were discharged into the specific layer around well that called Pit; Each pit has 100 meters length and width, and also 5.1 meters height [7, 8]. After discharging drilling wastes into pits, they left without any care, and any maintenance or advantage does not take happened [14,1]. The main objective of this research is evaluating heavy metals in the Ahwaz oilfield soil by using five-stage process of chemical dissociation and also assessment of soil contamination by pollution severity index. In previous studies, several challenges have been studied, such as heavy metals concentration and ecological risk assessment of drilling fluid [2,9,15,16,17], environmental impacts assessment of drilling fluid process [18], drilling wastes management, and limiting the amount of waste pollution [1,13] as well as the effects of pollution due to industrial

activities in oil fields on human health [6]. The present study was conducted in Iran in 2016. The researches on the challenge of heavy metals in drilling fluid in the oil industry have often exploited geochemical indicators. [8,13,15,16,17], Nevertheless, in the present study and geochemical indicators, we will also apply a five-phase chemical dissociation methodology.

Study Area

Khuzestan province is located in southwestern of Iran (Figure 1), southwest of Zagros structural-sedimentary zone. One of the most important geological features of Khuzestan is multiple oil fields in both mountainous and lowland region. Large number of oil reserves causes particular attention to pollution studies in addition to geologic studies.

The study area is the Folded Zagros with spectral range from the Cambrian to Recent, and major outcropping formations in oil fields and related to the groundwater can be classified in calcareous formations (Asmari), formations of gypsum - marl (Gachsaran), Bakhtiari conglomerate formation and recent sediments.

2. Materials and Methods

2.1. Soils samples

20 wells were selected to determine sampling sites in the soil surface of Ahwaz oilfield due to limitations, the UGC map, and data related to type of wells, construction time of wells, drilling date and duration in the Ahwaz oilfield. Out of 20 stations, 4 new stations, 7 relatively new stations, 7 old stations and 2 relatively old stations are selected. Old wells related to the years from 1350 to 1370, relatively old wells related to the years from 1370 to 1380, relatively new wells related to the years from 1380 to 1390 and new wells are related to the years from 1390 to 1394. The five-stage chemical dissociation method was used to determine the phase's share of man-made and natural elements and the percentage of each element in the chemical bonds. A large percentage of the study area is barren lands, agricultural lands and residential areas so the depth of 0 to 30 cm were considered for soil sampling because roots of plants are shallow and on the other hand the depth of achieving groundwater static surface is low, and also according to the similar conducted studies.

Table 3.4: Selected stations in the soil surface of Ahwaz oil field for chemical dissociation analysis

Station Number	Station Class	X (length)	Y (Width)	Number of wells
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3	New	2699678	348.930	497
21		2937761	3463263	488
22		2948832	3464844	489
35		3.8818	340.310	493
2	Relatively new	268140	348430.	365
6		270719	3477821	396
7		277.77	3477412	371
18		288878	3466233	354
29		3.18876	3406171	375
36		3.8483	34487.1	385
39		311728	344610.	349
10	Relatively old	281276	3470342	335
123		283884	347237.	301
14		286870	3468721	224
17		288874	3467828	293
23		2973.2	3467764	218
26		3.0788	3409.19	262
33	3.0292	3401798	216	
1	Old	260103	3489129	51
40		312014	3443963	52

2.2. Chemicals

Complete dissolution method was used to analyze soil samples. In the first stage, about 5 ml HF (Hydrofluoric acid) is added to the sample and heated by sand bath at the temperature of 125 °C. Second solution is the composition of 1:3 hydrochloric acid and nitric acid (aqua regia). About 7 ml of aqua regia is added to the sample and then heated on a sand bath under 125 °C, the sample was picked up from the sand bath when about 6.5 cc evaporated out of 7 cc of acid. Here the sample is transferred into a volumetric flask and ultimately the volume of volumetric flask is implemented to its line.

2.3. Soil Contamination

Generally elements are linked to the soil with 5 types of bonds:

1. Loosely Bonded Ions
2. Sulphide Bonded Ions
3. Organic-Metallic Bond
4. Resistant Bond
5. Within Lattice Bond

Elements may be present by every 5 links in an uncontaminated environment; in other words, 10% of the total concentration of each element is allowed to link naturally with three loosely, sulfides and organic -metallic bonds, but this amount is not taken into account since the whole area in this study was suspected to be contaminated; the total concentration of elements in loosely, sulfides and organic -metallic bonds, and in resistant and within lattice bonds was determined as the human-made phase and the natural phase respectively [19].

- Karbasi pollution index 2008

Muller geochemical is one of the earliest indicators of pollution severity, that was adopted in 1979. The formula is as follows[20].

Equation (1):

$$I_{geo} = \log_2 \left(\frac{C_n}{1/5B_n} \right)$$

- I_{geo} = Accumulation Severity Index of elements in soil
- C_n = Heavy metal concentrations in this study
- B_n = The concentration of heavy metals in the shale
- 1.5 = Shale correction factor

If chemical dissociation statistics will available, Mueller's formula would be optimized or modified. Because the chemical dissociation technique separates the human-made from the natural phase, so the exact B_n rate is obtained. Muller formula was changed by Karbasi in 2008 which is as follows[21].

$$I_{poll} = \log_2 [C_n / B_n] \quad (2)$$

The I_{geo} and I_{poll} ruler, that was used to determine the extent of contamination, has been modified and shown in Table 1.

Table 1: soil classification based on Muller geochemical and pollution index

Geoaccumulation index	The degree of pollution
0.42>	Clean
0.42 to 1.42	Low pollution
1.42 to 3.42	Middle pollution
3.42 to 4.42	High pollution
4.42<	Very high pollution

3. Results and Discussion

The results of chemical dissociation of heavy metals bonds in Station 3 shows that the percentage of nickel in each of the five phases was 65%, 15%, 9%, 10% and 1% for loosely bond, sulphide, organic-metallic, resistant and within lattice respectively. The percentage of vanadium in five phases was 71%, 9%, 9%, 10%, % 1 respectively. The percentage of cobalt in each of, sulphide, organic - metallic, resistant and within lattice bonds was determined 50%, 17%, 24%, 8% and 1% respectively. The percentage of barium in each bond or phase was 40%, 25%, 22%, 11% and 2% respectively; the highest amount of nickel, vanadium, cobalt and barium was in loosely bond. Loosely bond is the most dangerous elements bonds with the soil particles and also serious danger to the environment. The percentage of iron in each of the bonds was 2%, 4%, 1%, 90% and 3% respectively. The concentration of chromium

in each of the bonds was 3%, 5%, 16%, 74%, % 2 respectively. The greatest amount of iron, chromium and arsenic was in resistant bond with the soil particles. The percentage of arsenic in each of the phases was 15%, 83% and 2% respectively. The percentage of the elements in each of these phases at the station 21 for nickel (loosely, sulphide, organic - metallic, resistant and within lattice) was equal to 60%, 13%, 5%, 21% and 1%. The percentage of vanadium in each of the bonds was 51%, 4%, 18%, 26% and 1% respectively. The concentration of cobalt in each of these phases was recorded 47%, 10%, 15%, 27% and 1% respectively. The highest amount of nickel, vanadium and cobalt was in loosely bond which is the most dangerous elements bonds with the soil particles. The percentage of chromium in each of the bonds was 5%, 13%, 13%, 67% and 2% respectively. The percentage of barium in each of the bonds was determined 61%, 18%, 10%, 10% and 1% respectively. We could not determine the concentrations of arsenic in each of the bonds at the station 21 by using chemical dissociation method. By using the results of chemical dissociation of heavy metals at the station 22, the percentage of elements concentrations in each of the bonds for nickel was determined 52%, 9%, 14%, 23% and 2% respectively; for vanadium was 49%, 18%, 6%, 25% and 2% respectively; for cobalt was recorded 47%, 22%, 0%, 29% and 2% respectively. The highest percentage for nickel, vanadium and cobalt is in loosely bond. The concentration percentage of iron in each of these phases 9%, 12%, 10%, 66% and 3%, for chromium 5%, 15%, 4% 74% and 2%, and for barium was determined 45%, 21%, 15%, 18 % and 1% respectively; and for arsenic could not be determined. The results of chemical dissociation of metals in each of these phases at Station 35 showed that the percentage of the elements in each of these phases for nickel equal to 49%, 16%, 9%, 24% and 2%, for vanadium equal to % 38,% 17, 15%, 28% and 2%, for cobalt equal to 50%, 12%, 6%, 31% and 1%, for iron equal to 4%, 14%, 8%, 71% and 3%, for chrome equal to 8% ,% 0,% 21,% 69 and% 2, for barium equal to 49%, 15%, 14%, 20% and 2%, and for arsenic was equal to 6%, 10%, 81% and 3% respectively. The highest percentage of nickel, vanadium, cobalt and barium is in loosely bond as the most dangerous type of elements bond with the soil in the environment. The largest percentage of iron, chromium and arsenic were determined in the resistant phase. The elements are less in relation to the within lattice bond. The results of

chemical dissociation of metals in each of these phases at the station 2 which is the relatively old station, showed that the percentage of the elements in each of loosely, sulphide, organic-metallic, resistant and within lattice bonds for nickel equal to %12 ,%0 ,%28 ,%5 and ,%3, for vanadium equal to %16 ,%12 ,%19 ,%5 and ,%2, for cobalt equal to 14%, 19%, 24%, 42% and 1%, for iron equal to 0%, 18%, 4%, 75% and 3%, for chrome equal to 0% ,% 0,% 25,% 72 and% 3, and for barium was equal to 12%, 26%, 8%, 52% and 2%, respectively. The highest percentage of nickel, vanadium, cobalt, iron, chromium and arsenic was reported in resistant phase. The percentage of nickel, vanadium and cobalt in the organic-metallic phase was higher than the rest metal from man-made bonds. The percentage of any parameters in each phase at the station 5 for nickel equal to 26%, 13%, 24%, 36% and 1%, for vanadium equal to 31%,% 0,% 28,% 39 and% 2, for cobalt equal to % 16,% 41,% 12,% 30 and 1%, for iron equal to 10%, 33%, 16%, 40% and 1%, for chromium equal to 14%, 8%, 12%, 63% and 3%, for barium equal to 48%, 12%, 9%, 30% and 1%, and at the end for arsenic was equal to 0%, 0%, 24% 72% and 4% respectively. The highest percentage of nickel and vanadium is in resistant phase while for cobalt is in sulfide phase which in fact is an alarm for the environment. The highest percentage of iron, chrome and arsenic is in resistant phase and for barium is in loosely phase. Station 6 is relatively new and located at the city of Ahvaz where is highly affected by Khuzestan Steel Industries. High concentration of iron in the human-made phase is related to the case. The results of elements chemical dissociation at the station 7 showed that in order to the elements percentage in each of these phases for nickel equal to 16%, 19%, 15%, 48% and 2%, for vanadium equal to % 17,% 19,% 23, 39% and 2%, for cobalt equal to % 13,% 20,% 20,% 44 and% 3, for iron equal to 0%, 11%, 9%, 78% and 2%, for chrome equal to % 0,% 16,% 14,% 67 and% 3, for barium equal to 10%, 28%, 19%, 41% and 2%, and for arsenic was equal to 0%, 19%, 12%, 65% and 4% respectively. The highest percentage of all elements is in resistant phase and the lowest percentage of all elements is related to the within lattice phase. The percentage of elements in each of the five bonds at Station 18, for nickel equal to 6%, 17%, 19%, 56% and 2%, for vanadium equal to 9%, 15%, 21% 53 and 2%, for cobalt equal to 8%, 24%, 26%, 40% and 2%, for iron equal to % 0,% 4,% 0,% 93 and% 3, for Chrome equal to 0%, 6%, 23%, 69% and 2%, and

for barium was equal to 0%, 0%, 0%, 98 and 2 respectively, and also the percentage of arsenic was not determined. The highest percentage of the elements was recorded in resistant phase. The percentage of the elements in each phases or bonds at the station 29 for nickel equal to 19%, 23%, 7%, 49% and 2%, for vanadium equal to 25%, 6%, 26%, 42% and 1, for cobalt equal to 18%, 17%, 20%, 43 and 2, for iron equal to 0%, 14, 6%, 78% and 2%, for Chrome equal to 0%, 15%, 10, 71% and 4%, and for barium was equal to 19%, 12%, 30%, 37 and 2 respectively, and no result was obtained for arsenic at this station. The results of elements chemical dissociation at the station 36 showed that the concentration percentage of elements for nickel equal to 25%, 0%, 27%, 46% and 2%, for vanadium equal to 15%, 19% 21, 43% and 2%, for cobalt equal to 6%, 29%, 27%, 36% and 2%, for iron equal to 0%, 0%, 10%, 87 and 3, for Chrome equal to 0, 0%, 24%, 73 and 3, for barium equal to 33%, 21%, 7%, 37% and 2%, and for arsenic was equal to 0%, 19%, 78% and 3% respectively. The highest concentration percentage for all elements was determined in the resistant phase. The concentration percentage of elements in each of the bonds at the station 39 for nickel equal to 0%, 0%, 9%, 88% and 3%, for vanadium equal to 0%, 0%, 9%, 88% and 3%, for cobalt equal to 0%, 0%, 14%, 84 and 2, for iron equal to 0%, 0%, 0%, 96% and 4%, for Chrome equal to 0%, 0%, 0%, 99 and 1, for barium equal to 0%, 0%, 95% and 5%, and for arsenic was equal to 0%, 0%, 7%, 89% and 4% respectively. The concentration of all elements was determined higher than 80% in the resistant phase. Station 39 is relatively new station but also is the oldest one of the relatively new stations. Station 10 is the first relatively old station which chemical dissociation process was conducted to its soil samples. The results of elements chemical dissociation in this station showed that the concentration percentage of the elements in each of the bonds for nickel equal to 17%, 21%, 9%, 50% and 3%, for vanadium equal to 12%, 6%, 37%, 44% and 1%, for cobalt equal to 0%, 16, 26%, 55% and 3%, for iron equal to 0%, 0%, 7%, 89% and 4%, for Chrome equal to 0%, 0%, 0%, 96% and 4%, for barium equal to 0% , 0%, 0% 98 and 2, and for arsenic was equal to 0%, 13%, 9%, 75% and 3% respectively. The highest percentage of elements was reported in the resistance phase. The percentage of elements in each of the bonds at the station 12 for nickel equal to 20%, 13%, 24%, 41 and 2, for

vanadium equal to 0%, 3%, 20%, 76% and 1%, for cobalt equal to 0%, 0%, 17%, 80% and 3, for iron equal to 0%, 8%, 7%, 81% and 4%, for Chrome equal to 0%, 0%, 0%, 98% and 2%, for barium equal to 0%, 0%, 0%, 96% and 4%, and for arsenic was equal to 0%, 20%, 0%, 77% and 3% respectively. The results of elements chemical dissociation at the station 14 showed that the percentage of elements in each of the bonds for nickel equal to 0%, 15%, 19%, 62% and 4%, for vanadium equal to 0%, 8%, 22% , 67 and 3, for cobalt equal to 0%, 0%, 35%, 62% and 3%, for iron equal to 0%, 4%, 9%, 84% and 3%, for Chrome equal to 0, 0%, 0%, 96% and 4%, for barium equal to 0%, 0%, 0%, 99 and 1, and for arsenic was equal to 0%, 6%, 0%, 90 and 4 respectively. The percentage concentration of metals in each of the bonds at the station 17 for nickel equal to 0%, 9%, 27%, 62% and 2%, for vanadium equal to 4%, 17%, 12%, 64 and 3, for cobalt equal to 0%, 0%, 28%, 69 and 3, for iron equal to 0%, 9%, 6%, 82% and 3%, for Chrome equal to 0%, 0%, 0, 96% and 4%, for barium equal to 0%, 0%, 0%, 99 and 1, and for arsenic was equal to 0%, 0%, 15%, 81% and 4% respectively. The results of chemical dissociation at the station 23 showed that the percentage of elements in each of the bonds for nickel equal to 0%, 0%, 5/4% 6/92 and 9/2, for vanadium equal to 0%, 0%, 7/6, 0,3% / 89% and 4%, for cobalt equal to 0%, 0%, 0%, 97% and 3%, for iron equal to 0%, 0%, 7%, 89% and 4%, for chromium equal to 0%, 0%, 0%, 99 and 1, for barium equal to 0%, 0%, 0%, 99% and 1%, and for arsenic was equal to 0%, 0%, 0, 97% and 3% respectively. The percentage of the elements in each of the bonds at the station 26 for nickel equal to 0%, 0%, 3% 8% and 88%, for vanadium equal to 0%, 0, 6%, 90% and 4%, for cobalt equal to 0%, 0%, 2% 96% and 2%, for iron equal to 0%, 0%, 0%, 96% and 4%, for Chrome equal to 0%, 0%, 0%, 96 and 4%, for barium equal to 0%, 0%, 0.97% and 3, and for arsenic was equal to 0%, 6%, 90% and 4% respectively. The results of elements chemical dissociation at Station 33 showed that the elements percentage in each of the bonds for nickel equal to 0%, 0%, 11%, 86% and 4%, for vanadium equal to 0%, 0%, 9%, 89% and 2%, for cobalt equal to 0%, 0%, 0%, 96 and 4%, for iron equal to 0%, 0%, 0%, 96% and 4%, for Chrome equal to 0%, 0%, 0.98% and 2%, for barium equal to 0%, 0%, 0, 98% and 2%, and for arsenic was determined equal to 0%, 0%, 0%, 96% and 4% respectively. The percentage of the elements in

each of the bonds or phases in the old station 1 for nickel equal to 0%, 0%, 0%, 96% and 4%, for vanadium equal to 0%, 0%, 0%, 96 and 4, for cobalt equal to 0%, 0%, 0%, 96% and 4%, for iron equal to 0%, 0%, 0%, 96 and 4%, and for Chrome equal to 0%, 0%, 0%, 96 and 4%, and for barium was equal to 0%, 0%, 0%, 99 and 1, also the percentage of arsenic was not evaluated. The percentage of the elements in each of the phases at the old station 40 for nickel equal to 0%, 0%, 0%, 96% and 4%, for vanadium equal to 0%, 0%, 0%, 97% and 3%, for cobalt equal to 0%, 0%, 0%, 96 and 4%, for iron equal to 0%, 0%, 0%, 98 and 2%, for chrome equal to 0%, 0%, 0%, 97% and 3%, for barium was equal to 0%, 0%, 0%, 96 and 4, also for arsenic was not determined.

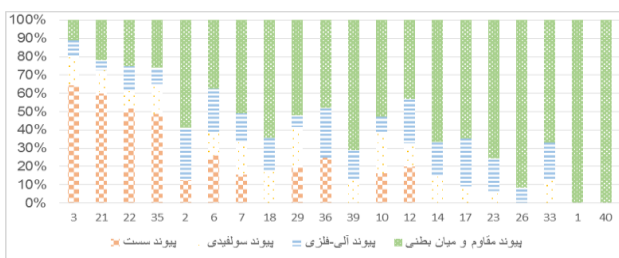


Diagram 1: The results of chemical dissociation for nickel in the Ahvaz oilfield soil (percentage)

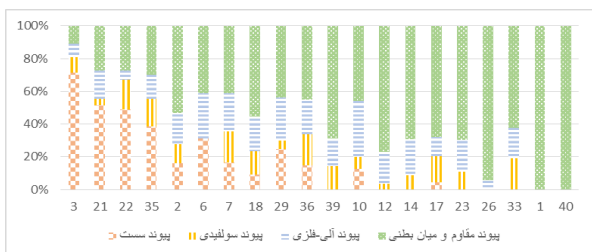


Diagram 2: The results of chemical dissociation for vanadium in the Ahvaz oilfield soil (percentage)

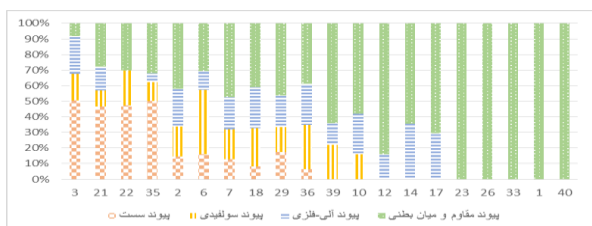


Diagram 3: The results of chemical dissociation for cobalt in the Ahvaz oilfield soil (percentage)

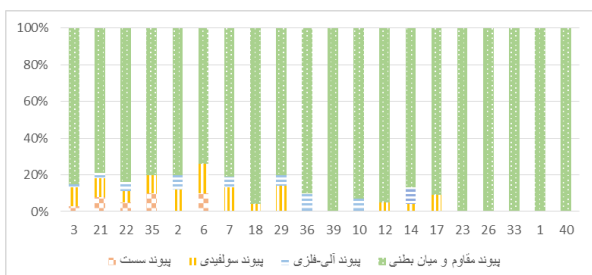


Diagram 4: The results of chemical dissociation for iron in the Ahvaz oilfield soil (percentage)

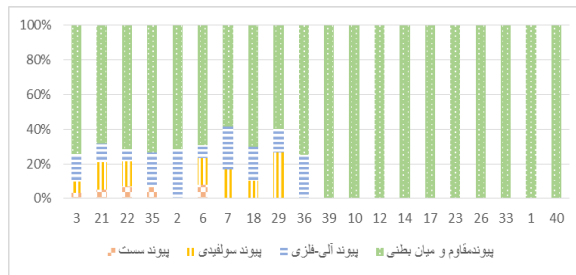


Diagram 5: The results of chemical dissociation for chrome in the Ahvaz oilfield soil (percentage)

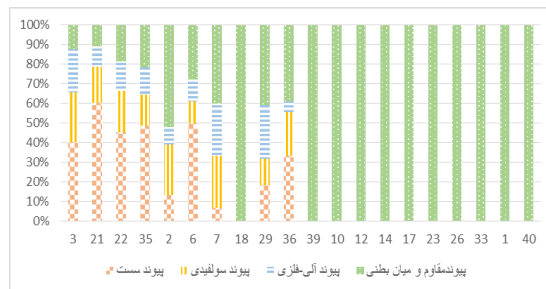
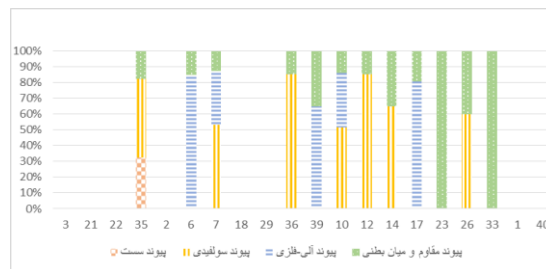


Diagram 6: The results of chemical dissociation for barium in the Ahvaz oilfield soil (percentage)



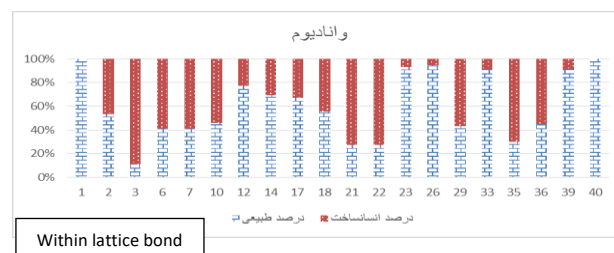
Within lattice bond

Diagram 7: The results of chemical dissociation for arsenic in the Ahvaz oilfield soil (percentage)



Within lattice bond

Figure 8: The concentration percentage of natural and man-made for nickel in Ahvaz oilfield soil



Within lattice bond

Figure 9: The concentration percentage of natural and man-made for vanadium in Ahvaz oilfield soil

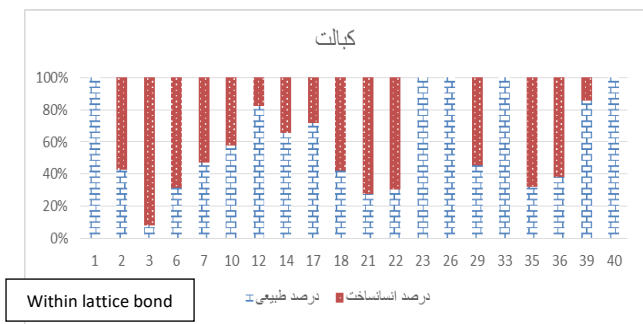


Figure 10: The concentration percentage of natural and man-made for cobalt in Ahvaz oilfield soil

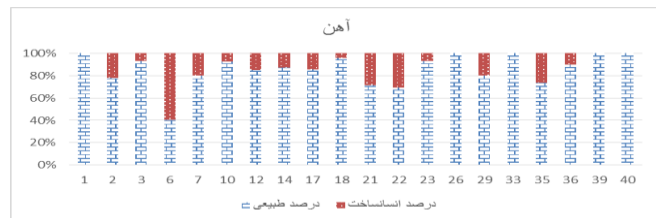


Figure 11: The concentration percentage of natural and man-made for iron in Ahvaz oilfield soil



Figure 12: The concentration percentage of natural and man-made for chrome in Ahvaz oilfield soil

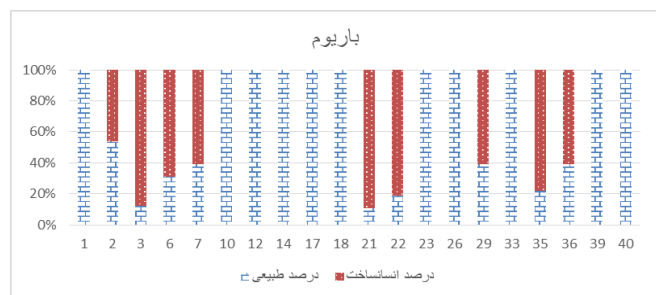


Figure 13: The concentration percentage of natural and man-made for barium in Ahvaz oilfield soil

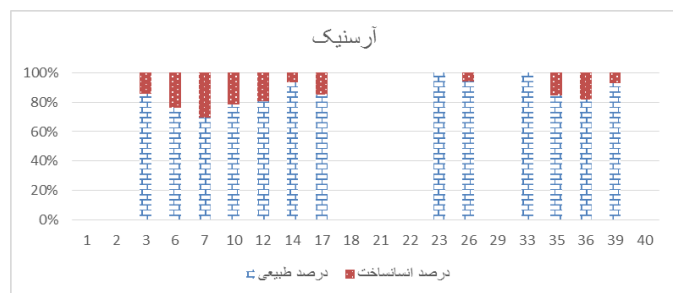
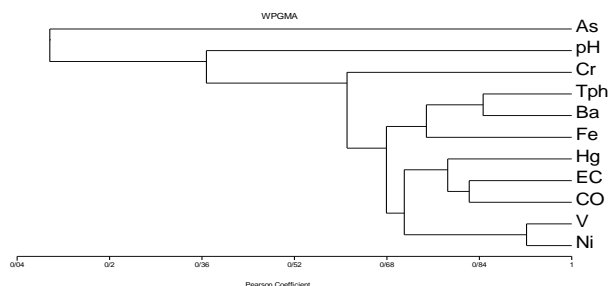


Figure 14: The concentration percentage of natural and man-made for arsenic in Ahvaz oilfield soil

Dendrogram interpretation of cluster analysis of heavy metals and other parameters in Ahvaz oilfield soils

According to the Dendrogram, five branches are recognized: branches A, B, C, D and E. branch A included arsenic, pH and the elements of the branch B. Arsenic is connected Ph and elements of branch B by the similarity coefficient of about 0.05, and this shows that there is no significant relationship between them. On the other hand, the pH is connected to the elements of the branches B by similarity coefficient of 0.36, and this means that pH is not highly affected by heavy metals concentrations of branch B. Branch B contained of chrome and elements of the branch C. Branch C includes both D and E branches. In the branch B, chrome is connected to the elements of branch C by the positive similarity coefficient of about 0.06. Due to the presence of nickel, vanadium, cobalt and total petroleum hydrocarbons in this branch, we can say that Chrome is under the effect of oil pollution index. Iron as a natural indicator is present in branch D, but the dominance and correlation of oil pollution index is more. Vanadium and nickel are connected to each other by similarity coefficient of 0.9 which shows the high correlation of these two elements. In addition to that nickel and vanadium have naturally high concentrations in Iran crude oil; they are oil pollution index as well. High similarity coefficient indicates that they also affected on each other. Cobalt and the EC are connected under significant similarity coefficient of about 0.8, and it shows they are affected from each other. Mercury is connected to the EC and cobalt by the similarity coefficient of about 0.75, and this shows that the mercury is affected form concentration of salt and cobalt. Mercury, cobalt and EC are connected to nickel and vanadium by similarity coefficient of about 0.7. Due to the high concentration of nickel and vanadium which are oil pollution index, it shows that mercury, cobalt and salt are affected by the oil pollution and have oil origin as well. Total oil hydrocarbons are connected to barium under positive and significant similarity coefficient of 0.84. This shows that they affected each other. Iron is connected to barium and total petroleum hydrocarbons under similarity coefficient of about 0.72, and it shows that the concentration of barium and total petroleum hydrocarbons is affected by iron concentration in the soil; and according to iron natural origin, we can say that total petroleum hydrocarbons and barium have natural origin but also they are under oil pollution as well. The elements of D and E

branches are connected to each other by positive and significant similarity coefficient of about 0.68. Finally it can be said that total petroleum hydrocarbons, barium, mercury, salt, chromium, cobalt, nickel, iron and vanadium have the natural origin, are under the influence of oil pollution, and also have petroleum origin. (Figure 15).



Results of pollution severity index

According to the ruler, pollution severity index of the soil are placed in 5 levels in terms of the degree of contamination. The results of pollution severity index for nickel showed that 25% of the stations in clean class, 50% in low pollution class and 25% are in middle pollution class. 40% of the stations in terms of vanadium pollution in clean class, 40% in low pollution class and 20% are in middle pollution class. In terms of cobalt pollution, 35% of the stations in the clean class, 40% in low pollution class, 20% in the middle pollution class and 5% are in the high pollution class. In terms of iron pollution, 100% of the stations are in the clean class. In terms of chromium pollution, 75% of the stations in the clean class, 25% are in low pollution class. Also results for barium showed that 65% of the stations in clean class, 15% in low pollution class and 20% are in middle pollution class. All stations are in clean class in terms of arsenic pollution.

4. Conclusion

Normal and standard level of metals is achieved by chemical dissociation process and there is no longer need to use the correction factor in the formula of geoaccumulation index. Given that the 5-stage chemical dissociation process was conducted, the pollution estimation is more accurate and closer to reality. Due to the weather conditions and pollution in recent years at the southern regions, Inter-basin water transfer projects from Karun River to Zayande Roud, severe shortage of drinking water, reducing rainfall and frequent droughts, big dilemma of dust, sand storms and also the establishment of more than 75% of the country's industry in Khuzestan province, make the attention necessity

of soil and ground water pollution as reliable source of drinking water much more higher. Since the Ministry of Petroleum has privacy for the all oil and gas wells in which has oil and gas or without, other utilities will not be allowed around the oil wells. Usually oil wells adjacent to each other and often other industry does not establish in oil fields except in special cases. The soil generated pollution is spotty and located around the oil wells and drilling activities space which affected by the drilling mud type, user type wells (oil or gas), type of oil and gas, drilling waste management system and the time of drilling that is the most important variable. Since the heavy metals concentrations were different in the wells by various ages and the concentrations of most elements were as a function of well age, it can be concluded that several processes can be the cause of this incident. Including the phenomenon of dust from the old age (oldest wells) until recent years has increased, and on the other hand the processes of leaching and increased drought and wind erosion of soil is also can be responsible for the emergence of this phenomenon. In the reference [8], the drilling wastes in one of the wells of oil field Ahvaz have been studied. The results of this study represented that the concentration of lead, copper, arsenic, zinc, molybdenum, antimony, mercury, and strontium in wastes is higher than the region's standard and soils. Also, calculating the correlation coefficient between the elements in the waste represented that the mineral phases in the form of impurities with drilling barite are quite evident. Environmental studies represent that these wastes are more polluted than metals such as mercury and antimony, arsenic, copper, and lead. The utilization of high purity barite can reduce the concentration of many contaminants. In the reference [17], the soil contamination due to heavy metals such as cadmium, lead, and copper in the oil industry lands of West Karun region, Khuzestan province, Iran, was investigated. The results represent that the average cadmium, lead, and copper concentrations in oil field soils are 40 ± 1.00 , 8.89 ± 5.91 , and 55.83 ± 52.81 mg/kg, respectively. The average amount of heavy metals such as cadmium and copper is higher than the world average, but the average amount of lead is lower than the world average. The highest risk of soil contamination is due to the high level of toxic substances in cadmium. Lajmiri Orak et al., 2021a and Lajmiri Orak et al., 2021b studied drilling wastes in the oil field Ahvaz. In these studies, the concentrations of strontium, barium, zinc, copper, lead, and cadmium were calculated [15,16]. The

results represented that the average values of the ecological risk factor of these elements are in the range of very high ecological potential risk. Also, enrichment and pollution coefficients represented that the source of pollution of this metal is human-centered activities such as oil drilling activities in the region. Therefore, continuous monitoring of the concentration of metal contaminants in the drilling fluid and the performing of heavy metal stabilization methods in the drilled areas is critical.

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