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Impact of oil waste discharge from Al-Nassiriya oil refinery upon physical chemical properties and heavy elements content of vicinity soil

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***Abstract*— The present study attempt to know the impact of oil waste discharge from Al-Nassiriya oil refinery upon some physical chemical properties and heavy elements (HEs) concentration in the vicinity soil , during the period from January until August 2020 . Some physical and chemical factors were measured also selected HEs (Co , Ni , Pb and V) concentration in the soil were measured by using Flam Atomic Absorption Spectrometry (FAAS) , in addition to soil texture and total organic carbon content were measured as percentage . The results revealed that the range of the soil parameters were , Temp.(16.3 – 44.3) ◦c , pH (6.0 - 8.7) , electrical conductivity E.C. (119.2-312.10) µs/cm , salinity (0.02 - 1.63) gm/kg , porosity (29 – 58) % , NO3 (7.91 - 97.5) mg /kg , PO4 (5.4 - 24.7) mg/ kg , SO4 (480 - 1739) mg/kg , while soil texture was silty clay at st.1 and st.2 , sandy loam at st.3 and silty loam at st.4 . Total organic carbon (TOC %) content and organic matter (OM%) were ranged from (3.89 - 17.52) % and (2.26 – 10.16) % respectively . HEs content in the soil of study were ranged from Pb (5.9 - 63.7) , Co (4.7 - 51.77) , V (36 - 181) and Ni (5.57 - 222) mg/kg dry weight respectively . It concluded from the study that discharge oil waste from the oil refinery of Al-Nassiriya was affected upon the characteristics of some physicochemical factors and increase the concentration of some HEs in the soil of the study area .**

***Keywords*— Heavy elements , Soil , oil , physical chemical properties ,Oil refinery , AL-Nassiriya .**

I. INTRODUCTION

Soil is fundamental to human life on the earth , soil pollution is the reduction in the productivity of soil due to the presence of soil pollutants (Rajesh, et.al.2016) . Pollution of soil by oil spill which creat from oil waste discharge from oil facilities is wide spread environmental problem, that often requires cleaning up of the polluted sites (Oyem and Oyem , 2013) . A large number of studies has been carried out to determine the effect of this type of pollution on the environment , soils , plants , animals and humans (Amine, et. al. 2016) . Iraqi is a major world producer of crude oil , so soil exposed to many pollutants among which is oil hydrocarbons and HEs (Al-Khafaji , 2017) . HE refer to any element has atomic number more than twenty , also it is any element has specific density more than 5 gm/cm3 called HE (Adesine and Adelasoya, 2014) . The demand of crude oil as a source of energy and primary raw material for industries has increased , and these lead to an increase in production , transportation and refinery which have therefor resulted in grossing pollution of environment (Rowell ,2017). Few studies have been done about oil pollution in Al-Nassiriya city such as (Karkush and Altaher ,2017 ; Al-obaidy and shaia, 2018) about remediation of contaminated soil with petroleum , and about evolution Geotechnical properties of oil pollutants respectively . There is no any previous study deal with study the impact of the oil waste discharge from Al-Nassiriya oil refinery upon the vicinity soil , so the aim of study is investigate the effects of oil refinery discharge upon the nearby soil , through some physical and chemical properties and HEs (Pb , Co , Ni and V) content in the soil vicinity from the refinery , and this study designed to provide baseline information on the effecst of oil waste discharge upon the nearby soil . This information used to compear with other studies in future about this subject .

II. THE STUDY AREA

Al-Nassiriya oil refinery is an important oil production facilite in Al-Nassiriya city south of Iraq . It was founded in 1980 , it is situated in the east region of the city . Because of no efficient treatment unit for treat it is waste , the waste discharge out of the refinery directly on the vicinity soil opposite of the refinery from 1980 until now . This process creat oil spill opposite of refinery , the spill is about (120 , 70 and 50) meter in length , wide and depth respectively . This spill composed of 75% water mixed with oil waste , and the heavy waste is about 25% from this spill (personal communication with director general of the refinery) . Four stations were elected to execute this study , these were as follow . Station 1 (st.1) was represent the oil spill , st.2 was in the west of st.1, and st.3 was in the east side of st.1 . Whereas st.4 reference station (control) , it was about 500 meter far from the mentioned stations north of st.1 , the distance between st.1 (oil spill) and st.2 , st.3 was about 20 meter (Fig.1) .

Fig. (1) Map of the study area showing the study stations . (by Google)

III. Material and Methods

Samples were collected from the study stations during the period January up to December 2020. Samples from st.1 (sediment) were collected by using grape sampler, soil samples from st.2 , st.3 and st.4 were collected from (0-20) cm depth by using a stainless steel tube auger. The representation soil samples were transferred into tight polythene bags brought into laboratory for proper processing , triplicate samples was collected from each station .

Soil temperature was measured by using simple thermometer gratuated from (0-100) ◦c after set the thermometer about (3-5) manut in the soil . In the laboratory pH was measured by using pH meter type HANNA Model (H18424) , conductivity of the soil measured by E.C. meter type HANNA Model (E.C.215) , soil salinity calculated according to the equation salinity ‰ = E.C. *640*106 (Mackereth et al., 1978) . Nitrate (No3) , phosphate (Po4) , Sulfate (So4) were measured according to (APHA,2005) . Soil porosity was measured according to (Kadhim and Sabar , 2012) procedure . Soil texture was measured according to (Bashour and Sayegh , 2007) . Total organic carbon (Toc%) was measured according to (Guadette et al., 1974) , while organic matter (OM) was calculated according to the equation % OM = % Toc * 1.742 (Onojake and Osuji , 2012) . Heavy elements (HEs) soil were extracted according to (APHA.2005) , while their concentration measured by using Flam Atomic Absorption Spectrophotometer (FAAS) pyuniem sp9. The standard solutions were prepare from a stock solution of 1000 mg/L to make the calibration curve . Blanks were processed through all digestion and filtration steps , and blank results were evaluated relation to according samples results . Statistical analysis ,The data obtained were subjected to both description and interferential statistics . Analysis of variance (ANOVA) was used to compere means and significant different , mean was separated using LSD person moment correlation analysis was also done to relate soil properties and the HEs content in the soil using SAS package 9.2 (SAS,2007) .

IV. Results and Discussion

The results (Table, 1) show the seasonal variation in physical and chemical parameters . Soil pollutants have advers effects on the physical , chemical and biological properties of the soil and reduce it is productivity (Rajesh, et.al. 2016). Soil temperature values lower and higher were 16.3± 0.2 ◦c and 44.3± 1.6 ◦c recorded at st.2 and st.3 during winter and summer season respectively , this due to that Iraq country is situated in semitropical region , it is hot in summer and cold in winter . pH value determine to what degree the soil environment is acidic or alkaline (Oyem and Oyem, 2013). Higher and lower values of pH were 8.7 ± 0.5 and 6 ± 0.2 were recorded at st.4 and st.1 in summer and autumn respectively , higher value of pH at st.4 due to the normal case that the soil tend to alkaline value in pH , also this station is far from the pollution source , while the lower value was at st.1 this due to that this station was exposed to intensity pollution by oil waste , so existans and fluctuation in OH- and H+ ion were presence in the mentioned station .Non significant differences in pH value were observed at P ≤0.05 during the study seasons between st.4 and the rest stations except st.1 . E.C. and salinity are important soil parameters , their value across the study stations were significantly different from to another . The higher and lower E.C. values were 312.68 µs/cm at st.2 and 119.2 µs/cm at st.4 in summer season respectively , also significantly differences were observed in salinity values among the study stations .Lower values of salinity were recorded at st.4 compere with the other stations . The high values of E.C.in waste oil polluted soil may refer to high presence of high ions cations and anions in the soil (Oyem and Oyem, 2013) . The higher and lower values in different stations compere with lower values at st.4 (control station) , this due to the effect of refinery waste discharge upon soil of these stations . Soil porosity posses agreet important in agricultural production , because of it is effects upon the quality and mobile of water and gases in the soil (Kadhim and Saber, 2012) . Higher mean of soil porosity was 58% recorded at st.4 in summer season (Table,1) , also significant differences were observed between porosity means at st.4 and other stations . The higher of soil porosity at st.4 in summer due to that the mentioned station was far from the source of oil pollution , while the lower percentage of it was at st.1 in winter refer to that the mentioned station was exposed to the heavy oil waste pollutants . Nitrate , phosphate and sulfate were recorded high values (97.5 , 24.7 and 1739) mg/Kg at st.1 , st.3 and st.2 during Autumn , spring season respectively , while the lower values for the mentioned compounds were recorded at st.4 during the study season . The values of No3 , Po4 and So4 at st.4 were observed significant differences P≤0.05 with their values at another stations (1,2 and 3) , this refer to the effect of oil waste upon the stations soil (Essieft, et.al. 2010) . The changes in the mentioned physical and chemical characters in the soil of the study area , this mean the oil waste effect on these parameters (Mishra, et.al. 2016) .The results (Fig. 2) recorded that the soil texture description at the study stations were silty clay at st.1 ,2 and sandy loam at st.3 , while it was silty loam at st.4 . Higher percentage of sand observed at st.3 during summer and winter season , this due to that this station previously was oil spill before this time

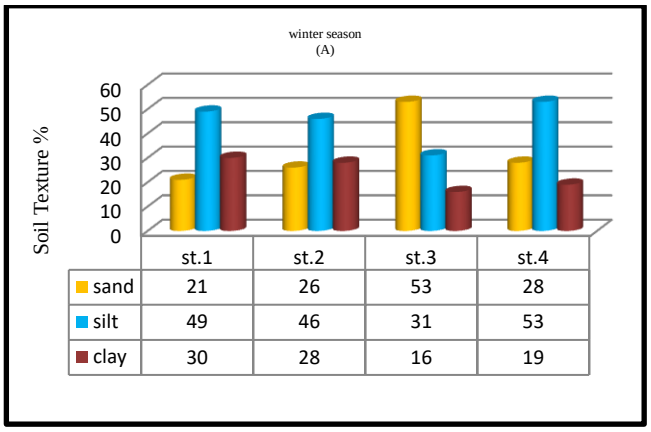
and treated by covered with thick layer from the sand to prevent the pollution by oil spill (personal communication with the director general of refinery) , where is the high percentage 49% of silt of study this due to the sludge content at this station. Soil with finer loamy texture predominate in the reference station st.4, while in the other stations the prevailing soil texture was loamy sand .

Table (1) Mean values ± SD. of soil physical and chemical factors in the study area during study season .

parameter / Station	Season	Temp. °C	pH	E.C. µs/cm	salinity %	Porosity %	No_3 Mg/Kg	Po_4 mg/Kg	So_4 Mg/Kg
st.1	Winter	/	6.3±0.02 a	217.5±6.01a	1.26±0.01a	29.0±0.2 a	23.5±2.1 b	22.8±0.1 a	591±6.6a
	Spring		6.5±0.1a	176.5±8.01b	1.33±0.01	39.1±0.5b	31.8±0.6a	21.1±0.1 a	636±4.5a
	summer		6.7±0.2a	210.5±8.02a	0.88±1.01	32.0±1.2a	47.9±3.5c	9.9±0.2b	940±6.7b
	Autumn		6.0±0.2a	212.1±8.03a	1.33±0.02	33.0±1.1a	97.5±3.2 d	19.3±0.5 c	750±3.1a
St.2	Winter	16.3±0.2 b	6.5±1.2b	229.65±9.01a	0.11±0.01c	33.0±1.2b	21.9±0.6a	16.2±0.1 c	810±10.6a
	Spring	31.5±2.1 c	7.2±1.5a	218.84±5.01a	0.23±0.01a	38.0±0.6a	22.48±0.5a	22.8±0.1 a	1739±9.5b
	summer	40.1±2.5 a	7.1±0.3a	212.68±6.01b	0.54±0.03b	35.0±2.1b	41.6±1.3 b	9.46±1.2 b	1344±11.5c
	Autumn	24.6±2.1 c	7.5±0.02 a	312.10±8.1b	0.21±0.01a	39.0±1.3a	68.5±2.2c	15.1±1.5 c	1275±7.9c
St.3	Winter	16.8±0.5 b	7.0±1.1a	218.52±6.05a	1.34±0.02a	28.1±1.5b	22.9±0.1a	14.7±0.2 a	701±10.7a
	Spring	30.1±0.7 c	7.1±1.7a	216.5±8.4a	1.62±0.01a	39.5±1.1a	30.4±0.6 b	24.7±0.3 b	704±12.1a
	summer	44.3±1.6 a	6.9±1.1b	193.84±9.01b	1.21±0.02a	32.0±1.6b	45.6±3.1c	10.3±0.5 a	810±11.5b
	Autumn	28.6±1.8 c	6.5±0.7b	184.37±8.05b	1.4±0.01a	34.0±1.5b	83.0±2.5 d	17.2±0.3 c	873±10.2b
St.4	Winter	17.5±1.1 b	8.5±1.3a	150.11±0.5a	0.013±0.01 a	52.0±1.3a	11.2±0.0 1a	7.4±0.1a	503±7.5a
	Spring	28.5±2.1 b	8.2±1.2b	186.6±0.02b	0.04±0.02a	57.0±1.5b	9.91±0.2a	7.41±0.1 a	593±16.1a
	summer	42.5±1.2 a	8.7±0.5a	119.2±0.01b	0.02±0.0a	58.0±2.5b	21.6±0.2 b	5.4±0.01 a	598±11.5a
	Autumn	25.7±0.9	8.3±1.2a	126.2±0.1a	0.23±0.01a	55.0±2.5a	25.1±0.2 b	9.3±0.1b	480±13.1a

/ = No measure in the station

The same latter refer there is no significant differences between the mean values , while the different letter mean significant differences at P≤0.05 .



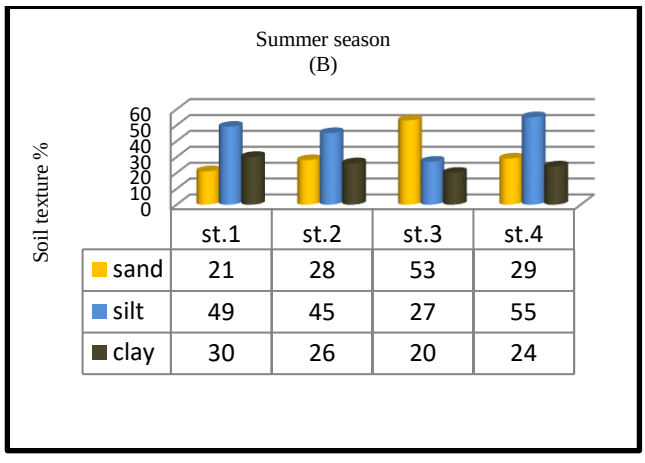


Fig : (2) Soil texture % of the study stations during winter A and summer B .

The result (Table 2) showed that the higher mean of Toc % content was 10.16 recorded in the soil at st.1 , it was higher this the mean of the rest stations (2,3 and 4) , and this creat higher OM at the same stations . Significant correlation were revealed between the Toc % mean values and OM values in all stations (1-4) were r=0.92 , r=0.842,r=0.875 and r=0.726 P≤0.05 respectively . Higher content of Toc % in the soil refer to organic pollution and an increase in Toc% in the soil this mean an increase in OM content (Al-Asadi,*et.al.*2011) . The higher content of Toc and OM in the soil at st.1 this due to the high level of organic hydrocarbons , which resulted from discharge of oil waste from Al-Nassiriya refinery , in addition to degradation process by microorganisms at soil stations , this was confirmed by significant correlation between Toc and OM at all study stations during season , this may be due to the mineralization and high biodegradation to organic matter in the mentiond season , because of increasing in the temperature degree in the summer season which effected upon the activity of microorganisms in the soil (Onojak and Osuji, 2012) . Higher content of Toc and OM revealed in the winter season , this due to high concentration of oil hydrocarbons which discharge from oil refinery in the study area , in addition to reducing in activity of microorganisms , these factors lead to revealed high content of Toc and OM in the mentiond season (Kotrozo,*et.al.*2014) . Heavy elements (HEs) are presented in industrial waste and reach the soil either directly with water or indirectly through the air (Al-Khafaji, 2017) .

Table (2) Total organic carbon content % (Mean ± SD.) and the range in the soil of the study area during the season .

TOC %				
Station \ Season	Summer	Spring	Winter	Autumn
st.1	8.44 ± 0.05 (6.3 - 9.5)	9.87 ± 0.22 (5.8 - 10.1)	11.53 ± 0.6 (6.9 - 12.6)	10.89 ± 0.3 (9.5 - 11.3)
st.2	6.01 ± 0.11 (3.1 - 7.4)	6.24 ± 0.08 (5.2 - 7.3)	8.03 ± 0.3 (7.4 - 9.6)	7.12 ± 0.6 (6.7 - 8.6)
st.3	5.4 ± 0.4 (4.5 - 6.1)	6.71 ± 0.5 (4.5 - 7.2)	6.98 ± 0.11 (4.2 - 7.1)	5.54 ± 0.2 (5.1 - 6.4)
st.4	1.29 ± 0.01 (0.8 - 1.8)	2.43 ± 0.21 (1.7 - 2.9)	2.8 ± 0.4 (2.5 - 2.9)	2.51 ± 0.4 (1.9 - 2.81)

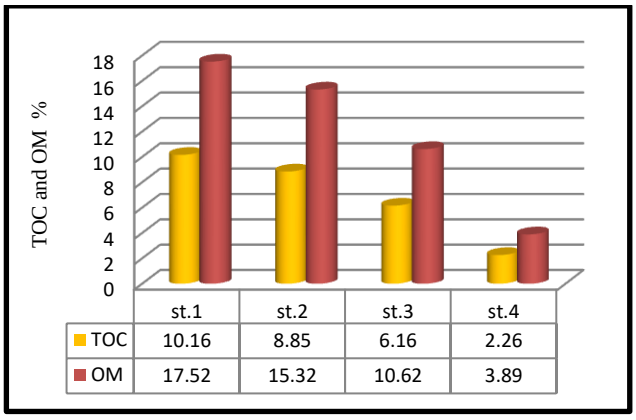


Fig: (3) Mean percentage of Toc content and organic matter in the stations of the study during the study period .

The results (Table 3) showed that Ni and V recorded higher concentration 222 and 181 mg/ Kg in the soil at st.1 in the summer season respectively , this may be due to the high concentration of the mentiond HEs in oil waste discharge from Al-Nassiriya refinery. (Al-Saad, 1995) , Indicated that because of the high content of Ni and V in the structure of crude oil , they can be used as indicator for oil pollution in aquatic environmental .Also the low concentration 5.57 and 36.0 mg/ Kg of the mentiond HEs at st.4 in the summer season , this may be due to that this

station was far from the effect of pollution source . Co and Pb recorded different values during the study season in the all stations soil , this mean that the study stations are exposure to the oil pollutants , which discharge from Al-Nassiriya oil refinery . Mohammed , (2007) indicated that Ni , Co , Pb and V are HEs which enter in the structure of crude oil . The higher means concentration of HEs at st.1 , st.2 and st.3 (Fig 4) were recorded with the high organic carbon content in the soil of the mentiond station. Significant correlation were observed between mean of Toc and mean of Co , Ni Pb and V concentration in the soil of the study area , were r=0.865 , r=0.921 , r=0.823 and r=0.864 P≤0.05 for mentiond elements respectively , also significant correlation observed between mean concentration of HEs in the soil and clay % for all stations , this due to that the clay fine grain size accumulate high concentration from the mentiond HEs, because the fine grain size pocess large surface area this lead to accumulate high concentration from HEs (Al-Khafaji, 1996). In our finding with the exception of soil in st.4 , the studied HEs in all the soil of the rest stations showed higher concentration values greater than permissible limit for all HEs, compare with their values which site by (WHO) for oil polluted soils.

Table (4) concentration mg/Kg dry weigh of heavy elements Mean ±SD. In the soil of the study stations .

Station	Season	Heavy elements con. mg/kg dry wt.			
		Co	Ni	Pb	V
St.1	Autumn	44.3±2.5a	203±7.5a	55.4±1.2	177±6.1
	Winter	38.5±3.7b	198±2.8a	60.1±3.3	163±5.3
	Spring	57.77±3.4c	177±5.4b	63.7±2.8	170±2.7
	Summer	50.5±5.4c	222±6.5b	59.4±1.2	181±7.1
St.2	Autumn	22.7±1.3a	120±6.1a	44.7±3.1a	123.5±3.3
	Winter	33.5±2.2b	135±5.5b	38.6±2.3b	135.4±1.2
	Spring	28.4±1.6c	129±1.6a	22.4±3.7c	126±3.4
	Summer	30.7±2.1c	145±2.2c	35.3±0.8b	137±3.4
St.3	Autumn	45.6±2.5a	170±4.5	50.4±2.6a	155.1±3.9a
	Winter	40.5±3.2a	183±5.7	48.2±3.7a	163.4±6.5b
	Spring	49.7±2.9b	172±4.2	45.6±2.5b	150.7±2.7a
	Summer	50.3±3.3b	166±3.3	48.5±1.2a	155.3±5.1a
St.4	Autumn	6.5±0.05a	7.5±1.2a	8.7±2.2a	54.5±2.2a
	Winter	4.7±0.61b	8,2±0,8a	5.9±0.6b	49.8±1.6b
	Spring	7.5±0.55a	10.39±0.05b	6.2±0.22b	40.5±3.1a
	Summer	10.13±0.61c	5.57±1.33a	10.45±0.71a	36.0±1.7a

The same letters mean no significant differences P≤0.05 between the means, while the different letters refer to significant differences .

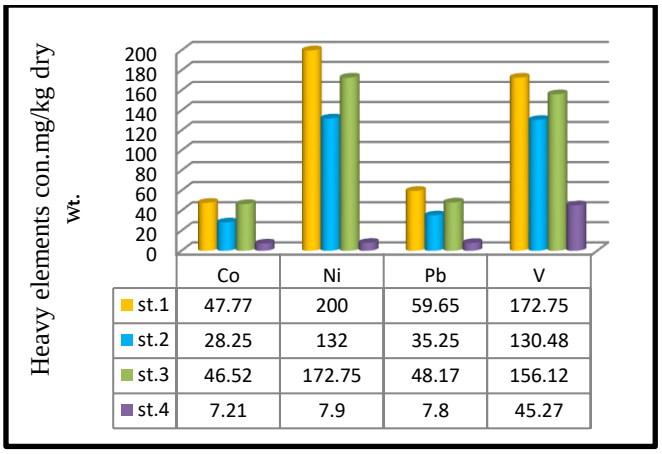


Fig : (4) Mean concentration (mg/kg) dry weight of heavy elements in the soil of the study area during the study period .

It concluded from the present study that the discharge of oil waste from Al-Nassiriya refinery affected upon the studied parameters (physical and chemical parameters) which represent the soil characteristics and increase the content of Toc and OM , also increase the concentration of the studied HEs in the stations soil with the exception of st.4 (control station) .

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