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Determination of Pollution Levels of Hydrocarbons and Heavy Metals (Cobalt - Cadmium - Nickel) in The Soils of Farms Near the Southern Refineries - Basrah City - Southern Iraq

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***Abstract*- The research included studying the concentrations of total petroleum hydrocarbons and some heavy elements (cobalt - cadmium - nickel) for ten samples of which soils, the sample (S1-S8) close to the South Refinery, and two samples of soils (S9-S10) for agricultural lands far from the source of pollution represented by the South Refinery. Where they were considered as comparative samples that collected samples for the two seasons in the winter and summer of 2019, the results of the study showed that the highest average concentration of total petroleum hydrocarbons was 13.21 µg / g in the S1 model in the winter season and the lowest rate was 3.96 µg / g in the S10 model in the summer season and the highest rate of concentration. Cobalt was 24.82 µg / g in the S1 a sample in the summer season, and the lowest value was 9.73 µg / g in the S10 a sample in the winter season, and the highest cadmium rate in the summer season was 1.93 µg / g in the S2 a sample and the lowest value in the S9 model, and its value was 0.10 µg / g. As for the nickel element, the highest rate was in the S1 model and it was 26.88 µg / g in the summer season and the lowest value was 13.10 µg / g in the S9 model in the winter season. It was concluded from the current study that the total hydrocarbon values are high in the soils of farms close to the source of pollution represented by the South Refinery and their decrease in soils of comparison farms far from the source of pollution, as well as heavy metals (cobalt, cadmium and nickel)we notice that their values have increased, but they did not exceed the maximum permissible limits, and this indicates the effect of the refinery pollutants on the soils of nearby agricultural lands.**

***Keywords*- total petroleum hydrocarbons, heavy elements, and agricultural soils.**

I. INTRODUCTION

Basra governorate is one of the governorates that owns an oil refinery represented by the Shuaiba Refinery of the Southern Refineries Company, and it is one of the 16 companies affiliated with the Iraqi Oil Ministry. The refinery is located 20 km to the west of the city of Basra, which is not without disadvantages and an expensive tax represented by the emission of various pollutants to soil and converting it into sterile soil from here it became necessary to study soils in general. The problem of soil pollution with hydrocarbons is a common problem facing most of the industrial establishments and centers that deal with petroleum products, such as refineries, factories, storage and distribution centers, and public and private fuel stations. (Melhem and Kayal ,2004). The organic matter is naturally present in the soil, but it rarely reaches toxic levels, but its danger lies in the presence of factors that help to exacerbate it in the soil, including the remnants of oil refineries that lead to a change in soil properties (Al-Qarghouli,2019). Often the cause of the spread of oil waste (gaseous, liquid and solid) is road accidents, neglect, leakage, flow, seepage, or emptying from underground tanks flowing over agricultural lands in addition to accidental accidents and pouring waste in the open without treatment. The spread of waste depends horizontally and vertically in the soil On basic factors that are multiplied by the rate and volume of flow, the density of hydrocarbons, pores of soil and rocks, and the forces of attraction in water and hydrocarbons (Module ,1999) Solid waste is more dangerous and its danger lies in its containment of hydrocarbons, which include volatile organic compounds, as well as heavy elements found in crude oil such as cadmium, nickel, cobalt and others (Kemper and chepil, 1965). As for heavy metals, they are among the most important and dangerous organic pollutants that have spread in the environment in a form Its gradual accumulation leads to its transformation into more toxic mineral compounds that remain for a long period of time in the environment, causing an imbalance in the natural balance of the ecosystem, as it affects soil properties and destroys biodiversity and may lead to rendering the soil useless as a medium for plantgrowt (Lasat,1999) Because of the importance of large soils, it became necessary to study high concentrations of total hydrocarbons and heavy metals, which in turn became the focus of researchers when advanced detection techniques showed the transfer of pollutant sources to groundwater and crops and then their direct and indirect impact on humans. Soil is exposed to all kinds of pollution in Iraq, especially oil pollution, which is part of environmental pollution, and because most oil derivatives have a slight degree of solubility in water because their density is less than it, and this determines their spread to a large degree in the soils of the region to which the water saturated with these oil derivatives penetrates through the first two forces Gravity and the second force of capillary pressure and any effect, no matter how weak, but with continued exposure for a long time, it causes cumulative effects They turn into more toxic compounds and remain for a long period of time in the environment, causing an imbalance in the natural balance of the soil

and rendering it useless as a medium for plant growth (Al-sadi and Sami, 2002), and in a study similar to (Hammouda, *et al*., 2018), he noted the presence of high concentrations of hydrocarbon. The reason for this increase in the soils of the beaches extending from the Ras Lanuf area to the Derianah region is due to heavy oil depots, refineries and oil tanker shipping operations. Petroleum hydrocarbon compounds,especially aromatic compounds, are considered dangerous environmental pollutants through their transport in the food chain (Muhammad and Shoaib ,2017)as well as Its toxicity to other organisms, its mutagenic and carcinogenic action, and its complex physical and chemical characteristics that make it difficult to decompose (Al-Taie *et al*., 2016) In other studies, it has been indicated that plants are negatively affected when the soil is contaminated with crude oil, as pollution causes a delay and a significant reduction in the rate of germination. It has also been shown that the rapid reclamation of oil-contaminated soil is carried out by the process of activating microorganisms that use hydrocarbon as a source of carbon and energy (Abu al-Ghaith, *et al*., 2020). The present study aims to determine the values of total hydrocarbons and some heavy elements (cobalt - cadmium - nickel) in the soils of some agricultural lands close to the Basrah Refinery (Al-Shuaiba) and the extent to which they are affected by the source of pollution.

II. MATERIALS AND METHODS

A.Site and nature of the study area

Al-Zubayr district is located in the southwestern part of Basrah governorate and has an area of 10318 km2 with 54% of the total area of Basrah, the valley Al-Batin is one of the largest valleys in the study area, where large quantities of the Dabdabah formations which consist of sand, calcareous and gravel deposits were transported and Sand, which is characterized by its high porosity(Al-issawi,2014) Fig. 1 also shows the locations of the study samples.

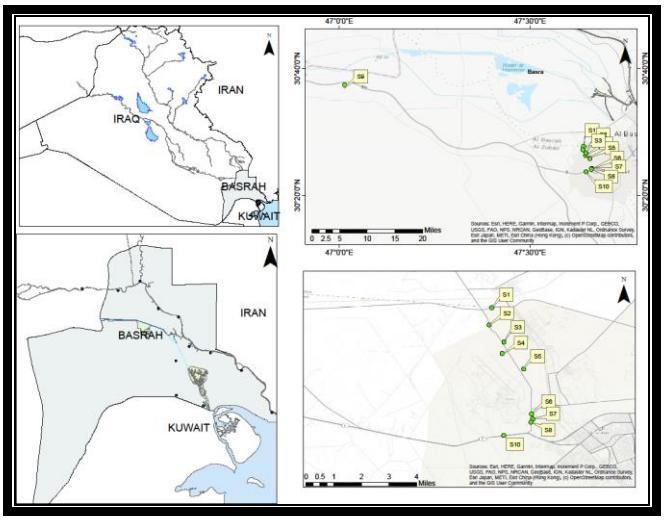

Figure .1. Location map shows the study area (Department of Marine Environmental Chemistry- Marine Sciences Center- University of Basra).

B. Sample collection

The fieldwork included the process of collecting 10 soil samples for the selected sites of agricultural land, eight of which are near the Basrah refinery and two farther from the refinery represented as control models, for both the winter season and the summer season of 2019, and a GPS device determined the areas. The samples were taken manually with the auger leg probe device. And the Samples were placed in polyethylene plastic bags and sent to the laboratories of the Marine Sciences Center, Basrah University, where the samples were dried and then crushed in a ceramic mortar mechanically for the purpose of conducting the necessary analyzes to calculate the total hydrocarbon concentrations and the elemental concentrations of nickel, cadmium and cobalt in the study soils. Then, it was crushed in ceramic mortar mechanically for the purpose of preparing it to carry out the necessary analyzes to calculate the total hydrocarbon concentrations and the initial concentrations of nickel, cadmium and cobalt in the study soil.

C. Total Petroleum Hydrocarbons

Petroleum hydrocarbons were extracted in the soil according to the method (Goutx and Saliot, 1980)., and they were subjected to a Soxhlet Extraction Noncontionuos using a mixture of methanol-benzene at a ratio of (1:1) and the extraction process was carried out for a period of 36-24 hours in the extraction device Then the soaping process is carried out for two hours by adding 20 ml of the solution to methanolic potassium hydroxide after the expiration of the period. The extract is left to cool down, then 50 ml of n-hexane is added to the separation funnel and shaken well and then left to form, the upper two layers are the layer containing hydrocarbons and the lower layer containing Fatty acids are eliminated.The layer is taken which contains the hydrocarbon dissolved in the hexane and pass over a chromatographic separation column that contains at the bottom a piece of glass wool topped by 2 grams of anhydrous sodium sulfate to absorb water if any and 2 grams of alumina to get rid of the fatty acid residues and evaporate to the point of dehydration so that the sample is ready for analysis by a fluorination device type RF540 From Shimadzu corporation Japanese after calibrating the device with standard solutions the emission intensity was measured at the wavelength of 360 nm and the excited wavelength of 310 nm.

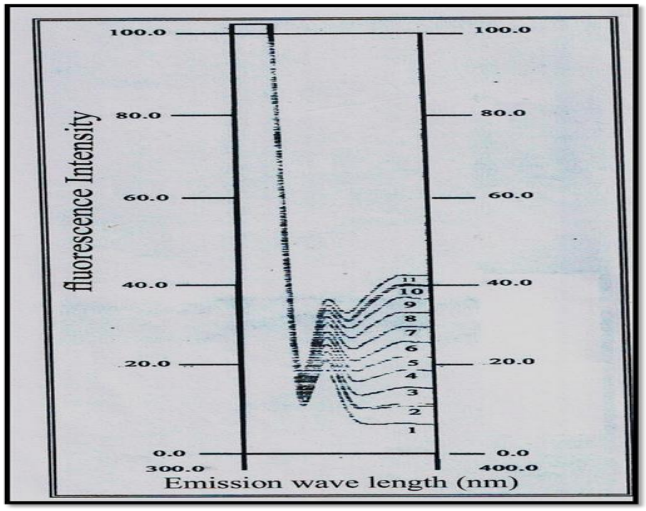

Figure .2. Standard spectra of a standard oil sample

D. Extraction of heavy elements from the soil

I followed the method of(Yi, *et al.*, 2007), where the samples were dried after removing the solid parts and dirt and grinded with a ceramic mortar, then passed through a sieve,then a weight of 5 g was taken from the sample and 6 ml of a mixture of hydrochloric and nitric acid tion in a ratio of 1: 1 and then placed on a hot plate At a temperature of 80 °C and before drying, 4 ml of a concentrated hydrochloric acid mixture in a ratio of 1: 1 was added to it and placed on a hot plate and before drying the sample was dissolved by adding 20 ml of 0.5 standard hydrochloric acid after which the sample was filtered and placed in clean polyethylene plastic bottles and measured using an atomic absorption device Phoenix986 type.

III. STATISTICS ANALYSIS

The results were analyzed statistically by using the ready-made statistical program Special Package for Social Science (SPSS) in analyzing the data and testing the least significant difference (LSD) at a probability level $P < 0.05$ and the values of the standard deviation (SD) were extracted.

IV. RESULTS AND DISCUSSION

A. Total hydrocarbons

From the results of the study, Table (1) shows that the highest rate of total hydrocarbon values was in the S1 site, which was the closest to Basra Refinery, where it recorded to 13.21 g / µg in the winter season, while the lowest value was at S10, which is one of the comparison sites far from the impact of the refinery and the residues. Where the average total hydrocarbon concentration, µg / g, reached to 3.96 in the summer season ,due to high temperatures and the oxidative bacterial activity of hydrocarbons. Fig.3, showed that the concentrations of total petroleum hydrocarbons in the soils of the study area varied spatially and temporally as their concentration rates exceeded the permissible limits of 10 µg / g, as shown in Table (2) Since we notice the high values of cauterizing

hydrocarbon in the models taken from farms near the refinery, where we notice that they exceed the permissible rate in most models and decrease in models far from the pollution area and the comparison models that were within the permissible limits. The results also show the high values in the winter season and their decrease in the summer season The reason for this is due to weather factors, in the summer season and as a result of high temperatures, it leads to the evaporation of hydrocarbons, as well as an increase in the concentration of the growth of bacteria that are responsible for breaking down hydrocarbons in contrast to the winter, in which the temperatures are low, which leads to slow evaporation of liquids (Bruno,*et al.* ,1996).

TABLE .1. Average total hydrocarbon concentrations µg / g for the winter and summer seasons of the study area for the year 2019.

Sample	Winter season	Summer season	Average
S1	13.21	11.95	12.58
S2	13.11	12.01	12.56
S3	11.24	10.92	11.08
S4	12.35	11.02	11.68
S5	10.57	10.04	10.30
S6	11.07	10.71	10.89
S7	10.35	9.97	10.16
S8	9.44	9.12	9.28
S9	4.96	4.05	4.50
S10	4.19	3.96	4.46
Average	10.04	9.37	10.24

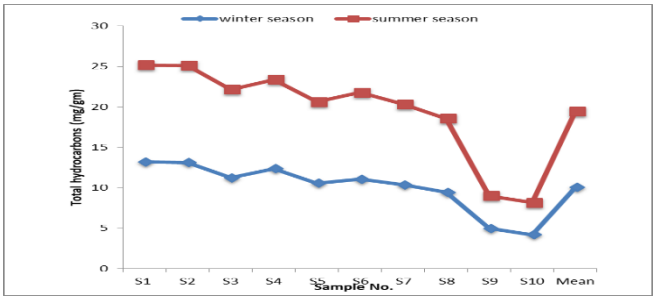

Figure .3. The total hydrocarbon concentrations for the winter and summer seasons for the year 2019 for the study sites

TABLE.2. Natural abundance, natural content and maximum permissible concentration of hydrocarbons and heavy elements µg / g.

Element/ Composite	Code	The element natural abundance (Moon, et al. 2006)	The normal content is mg / kg (UNEP), 2003	Maximum permissible concentration mg / g UNEP, (2003)
Hydrocarbons	HC	-	-	10
Cobalt	Co	10	50-30	50
Cadmium	Cd	0.1-0.5	0.1-1	3
Nickel	Ni	17	2-5	75

B. Heavy metals

Cobalt Co is a rare element, as its average concentration in the rocks of the earth's crust reaches 30 parts per million and the soil content ranges from (0.05-300) parts per million. Research and studies have indicated that the oxidation and reduction effort has an effect on increasing the concentration of Co, as the base soil is rich in cobalt compared to acidity due to the increased mobility (Al-Sultani and 2006) and it is among the (heavy) nutrients that the plant needs in very small quantities that do not exceed a millionth of the main and secondary elements. The Other (Al-Saad, 2006) Table .3 showed that the highest concentration of cobalt was in the S1 model, as it reached to 24.82 µg / g in the summer season and the lowest value was in the S10 model, which reached to 9.73 µg / g in the winter season, and many local and international studies have proven that the highest levels of heavy elements are near From the industrial area and sanitation outlets and the concentration decreases the further we move away from these areas, as (Khuwaidem and his group, 2009) indicated in a study to determine the level of heavy elements in the soil of the city of Basrah - Iraq that most of the studied elements increased in the areas west of Basra, where the oil installations. According to Table .2 , the cobalt values were within the permissible limits, but they were high values compared to the natural abundance of cobalt, and this shows the effect of pollutants resulting from refinery waste on those lands.

TABLE.3. Cobalt Co concentrations of the study soil samples µg / g for the winter and summer seasons 2019

Sample	Winter season	Summer season	Average
S1	24.34	24.82	24.58
S2	22.26	24.77	23.51
S3	18.81	21.56	20.18
S4	16.34	17.11	16.72
S5	19.55	21.81	20.68
S6	15.21	19.94	17.57
S7	13.33	17.11	15.22
S8	15.01	17.60	16.30
S9	10.01	11.21	10.61
S10	9.73	9.98	9.85
average	16.459	18.591	17.52

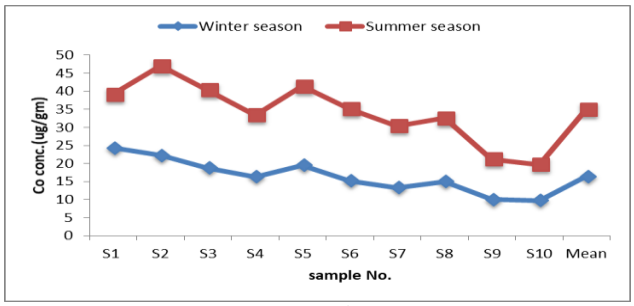

Figure.4. Cobalt element concentrations for the winter and summer seasons of 2019 for the study sites

Cadmium Cd Cadmium is found in soils and sandstones, and in petroleum and kerosene ores. It is also found in all soils at very low concentrations that do not exceed (0.1-0.5) µg / g in their maximum limits (Faust and Aly, 1991). Because of its high toxicity, its entry into soils and water can lead to the creation of environmental problems if it is allowed to enter the food chain, as it is one of the unnecessary elements whose increase leads to plant toxicity and on the other hand it does not perish in the environment but rather changes from one form to another (Elkhatib ,*et al.*, 2001) and Table .4, shows that the highest concentration was in S2, reaching 1.93 µg / g in the summer season, and the lowest value was in S9, where it was 0.10 µg / g in the winter season, and it is one of the comparison sites as shown in Fig. 5. The Cadmium did not exceed the maximum permissible limits in the soil.

TABLE.4. Average cadmium concentrations (Cd) µg / g for the study soil samples for the winter and summer seasons 2019

Sample	Winter season	Summer season	average
S1	1.06	1.22	1.14
S2	1.67	1.93	1.80
S3	0.83	0.88	0.85
S4	0.66	0.79	0.72
S5	0.45	0.52	0.97
S6	0.39	0.41	0.40

S7	0.44	0.50	0.47
S8	0.19	0.23	0.21
S9	0.10	0.15	0.12
S10	0.12	0.13	0.12
average	0.591	0.676	0.68

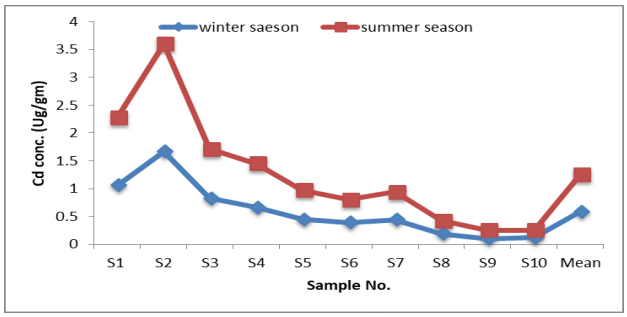

Figure .5. Cadmium element concentrations for the winter and summer seasons of 2019 for the study sites

Nickel is among the minerals whose ores nickel take different formulas, including niclite, millerite, and balandite Nickel is characterized as being among the toxic elements, especially if it is in the form of powder, and nickel is among the metals that move easily in air and water, and the values of its concentrations in the soil range between (10-70) mg / kg. (Al-Sabunaji, 2005) Table .5, shows that the highest value of nickel was 26.88 µg / g at site S1 in the summer season and the lowest value was 13.10 µg / g at S9 in the winter season. And the natural content of it, where we notice the high values in the models close to the source of pollution. As for the comparison models, the concentration in them decreased to below the maximum permissible limits as shown in Fig .6 .

TABLE .5. Average Ni-nickel concentrations of soil samples in the study µg / g for the winter and summer seasons 2019

Sample	Winter season	Summer season	Average
S1	25.93	26.88	26.40
S2	26.01	26.54	26.27
S3	24.07	25.20	24.63
S4	21.11	22.49	21.80
S5	21.24	24.48	22.86
S6	19.87	20.71	20.29
S7	19.93	22.04	20.98
S8	18.79	19.67	19.23
S9	13.10	13.55	13.32
S10	13.22	14.17	13.69
average	20.327	21.573	20.94

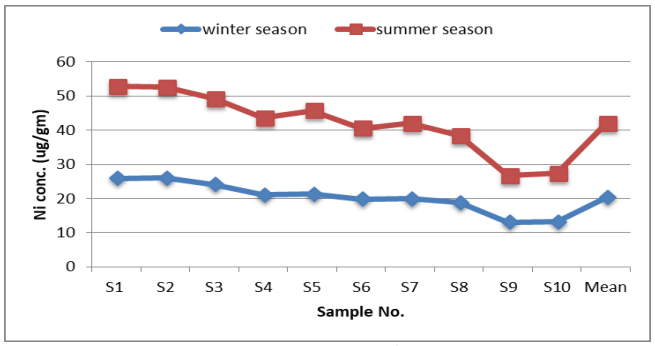

Figure .6. Nickel element concentrations for the winter and summer seasons of 2019 for sites to study.

When comparing the previous rates of concentrations of heavy elements in the study models with their rates in Basra soil and some international soils, and as shown in Table .6, it is noticed that the general rate of cobalt for soils of the studied models was close to Basra soils and less than the average of Wasit and Maysan soils and less than the United States, but it is higher than The global average was twice as high as the cadmium element was higher than the global general average and the United States and less than Basra, Maysan, Wasit, Brazil, and the nickel element was less than the world average, Hungary, Brazil, Maysan, and close to the soils of Basra, Wasit and the United States (Khwaidem and his group, 2009).

TABLE.6. Comparison of elemental concentrations in Al-Zubayr soils and some of their rates in Basra, some governorates of Iraq and soils of other countries in the world µg / g

Soils	Co	Cd	Ni
Study area soil	17.52	0.68	20.94
Basra	18.8	5.5	20.9
Maysan	42.33	3.00	108.15
Wasit	23.54	0.73	22.28
United State	27.5	0.16	18.3
Brazil	-	3	30
Hungary	9	-	25
World average	8	0.06	40

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