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# Evaluating the Stages of Environmental Pollution and Vital Indicators in the Qayyarah Refinery Area, Mosul, Iraq

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## **Key Words:**

Toxic chemicals

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## **ABSTRACT**

Oil spills can have varying degrees of impact on the aquatic environment depending on factors such as the type of oil spilled, the volume released, and the ecosystem affected because crude oil and refined petroleum contain harmful substances such as hydrocarbons, heavy metals, and toxic chemicals. When released into the water, these substances can have immediate and long-term effects on marine life. This research aims to find the factors affecting the degree of pollution from oil spills on the aquatic environment and the areas adjacent to the Qayyarah refinery in northern Iraq. Combines the fuzzy comprehensive evaluation method and the analytical hierarchy process to evaluate the degree of pollution from oil spill incidents in the areas adjacent to the refinery. The statistical analysis showed that there were statistically significant differences and that the value of the correlation coefficient was positive between exchanged cadmium, residual cadmium, exchanged lead, where the lead exchange rate ranged correlation coefficient at a minimum R2 0.674 and a clear increase in the number of bacteria indicating contamination the total number of bacteria coli, fecal coliform bacteria, and fecal strep bacteria (where the numbers of coliform bacteria ranged 102 × 102- (cells/011 mL, and fecal coliform bacteria were between 160 × 102 cells/011 mL. These rates are environmental and vital indicators of the presence of significant levels of organic pollution and evidence of the presence of microorganisms dangerous to the health of residents and living organisms.

## INTRODUCTION

The topic of oil pollution emerged due to the swift technological advancements in the oil industry, resulting in heightened production and irregular utilization. However, oil refineries are considered important sources of water pollution because the refineries use water during the process and dispose of it (Cuong & Hong-Xiang 2019).

Oil contaminants stand out as significant water pollutants, known for their swift dispersion, reaching distances up to 110 km from the spill site, manifest in diverse forms originating from various petroleum activities such as extraction, refining, manufacturing, transportation, and more. Hydrocarbons represent the primary components of petroleum pollutants the most important of which are aliphatic compounds, aromatic compounds, aromatic compounds, asphaltenes, and mineral compounds (Jie et al. 2013). These pollutants enter the aquatic environment in several ways, the most important of which are spills as a result of accidents and during the unloading and loading of tankers, which causes cases of pollution (Ajmi et al. 2018).

Pollution of seawater, rivers, and soil with petroleum derivatives is considered one of the most dangerous pollutants in the world, because of its harmful impact on human health, the marine and terrestrial environment, as well as the economy, so companies and entities working in the field of oil, oil wealth, and maritime transport must develop plans to prevent it due to its high toxicity owing to the toxic gases that are released upon evaporation such as hydrogen sulfide and other gases that prevent sunlight to reach plants (Li et al. 2017). Insufficient light for plant organisms causes an imbalance in the food chain, which in turn leads to a sharp decline in fish stocks. Oil flow leads to groundwater pollution, especially when the water formations have high permeability, which facilitates oil leakage. The multiple forms of interaction and diffusion of oil in nature are: diffusion Natural decomposition, Evaporation

and Dispersion, Precipitation, oxidation, dissolution, Biodegradation, and bacterial decomposition (Wang et al. 2020).

The oil refining industry is spread across large parts of Iraq, as large and small refineries are spread over a wide area from north to south, and the waste that is discharged from these refineries varies according to the nature and type of processing units available in the refineries that affect the surrounding environment and throws its waste into the river without a treatment process, and if the treatment processes exist, they are weak and irregular, including the Qayyarah refinery (Do Carmo et al. 2010). This refinery is located in this area, in the southeastern direction of the city of Mosul, 91 km south of the city of Nineveh in northern Iraq. Many special operations are conducted there with the refining of crude oil, which uses large amounts of water; most of this water ends up as waste in the Tigris River, which is one of the most important water resources in the Iraqi environment (Aghajanloo & Pirooz 2011).

The current study aims to evaluate the quality of waste resulting from the Qayyarah refinery treatment station before being treated.

#### **MATERIALS AND METHODS**

Different methods have been to evaluate the degree of pollution due to oil spills in the Qayyarah refinery, the comprehensive evaluation method was adopted in the paper because it takes into account the multiple effects of crude oil, based on the history of the area and accumulative level of pollution resulting from oil spills was based on factors such as oil characteristics, spill location, weather, and hydrological conditions, in addition to emergency measures according to the data source in the refinery to determine pollution factors in the study area and determine standard weights using the subjective method described by (Lang et al. 2011, Han et al. 2018).

The current study was conducted near the Qayyarah refinery located south of the city of Mosul, samples were collected in the period August to September 2023 on the basis of (APHA 2017) to conduct biological and heavy metal tests. Laboratory tests were conducted in the laboratories of the Department of Environment and Quality Control of the Iraqi Ministry of Commerce and were as follows:

#### **Extraction of Heavy Elements in Water**

In the current study, the distribution of heavy metals in the water of the study area was monitored at several levels

# **Dissolved Heavy Elements**

Water samples were taken from the study sites, and 2 liters

of water for each sample was filtered through a type of filter paper and dried at a temperature of  $60^{\circ}\text{C}$  for 12 hours. Add 1.5 mL of concentrated nitric acid for every liter of filtered water samples to preserve the elements in their shape ionic water, and then 1000 mL of filtered water is taken at a temperature of  $70^{\circ}\text{C}$  before drying. The concentrate contains 10 mL of ion-free water, HNO, and 1 mL of acid is added to it. We leave the solution until the dissolution is complete, and then complete the final volume to 25 mL with distilled water. The ions are stored in polyethylene bottles until the concentrations of the element ions are measured using Atomic absorption spectrophotometry, expressed as a result of  $\mu g.L^{-1}$  (200).

# **Particulate Heavy Elements**

The filter papers used to filter the water samples were dried at 20°C for 22 hr and weighed to extract the amount of plankton present in it and then element ions from it with a weight of 0.6 g as for the dry sample, it was placed in special Teflon containers for this purpose and treated with 5 mL of the mixture and heated, concentrated nitric acid, HNO<sub>3</sub>, and concentrated HCl, heat a plate at a temperature of 20°C and evaporate until almost dry, then add 2 mL of the mixture to it. The two concentrations were mixed in a ratio of 10 to 5. Next, the HF and HClO<sub>3</sub> solutions were evaporated. Perchloric acid and leave it until it almost dries, and then the precipitate is dissolved with 30 mL of hydrochloric acid. Ten minutes later, the sample was separated in a centrifuge for 30 min at 2000 rpm, the solution was taken and placed in a 36 mL volumetric bottle, while the precipitate was washed with deionized distilled water. Wash water was added to the volumetric bottle after separating the sediment and the volume was completed to 36 mL, the samples were kept in clean, labeled 36 mL plastic containers to be examined with the flame atomic absorption spectrum, and the result is expressed in µg.g<sup>-1</sup> dry weight according to (Fingas 2011).

# **Extraction of Heavy Elements from Sediments**

The sediment samples were mixed well after removing the solid and foreign parts, and then dried, it was ground with ceramic mortar and then passed through and stored in special polyethylene containers that are marked exchangeable. The element ions in the exchangeable fraction of the sediment were then extracted as follows: Residual fraction and the remaining fraction according to (Lu & You 2014).

## **Extraction of Exchangeable Heavy Elements**

Heavy metal ions were extracted from the exchangeable portion of the sediment, and 10 grams of ions were weighed the dried sample was placed in a 60 mL Teflon container

with a tight lid. 30 mL was added to 0.5 mL carefully and carefully, placed in a vibrating device for 50 hr. hours of hydrochloric acid. It was separated by centrifuge at 2000 rpm for 30 min, then the solution was transferred to special plastic bottles were stored until measured using a flame atomic absorption spectrometer according to (Mil'Shtein 2014).

## **Extraction of Residual Heavy Elements**

After the exchanged portion of the sediment was extracted, the remaining sediment portion was taken and tested the digestion process to extract the remaining element ions in the sediment was added 20 mL of distilled water free of ions was to the precipitate to eliminate traces of exchanged elements and from used acid was then centrifuged on the samples to quickly get rid of the wash water 2000 rpm for 20 min, then transfer the precipitate quantitatively to a Teflon baker, avoiding any loss of the precipitate. Then the test tube was rinsed several times with deionized distilled water to remove any residue from the sediment stuck to the walls of the tube, and then the washing water was added to the beaker containing the sample evaporated.

The sample was dried until it was nearly dry at 20°C. Then add 5 mL of the mixture to the sediment concentrated nitric and hydrochloric acids in a ratio of (10%) and evaporated at a temperature of 20°C until approximately at the rate of HClO and perchloric acid, 4 HF, then add 2 mL of the hydrofluoric acid mixture, after that, the solution was evaporated until it was almost dry. The precipitate was dissolved with 30 mL of acid 0.5, the solution was left for 10 min, then it was separated by a centrifuge for (N) hydrochloric acid for 30 min at a speed of 2000 rpm, and the solution was placed in a volumetric bottle 36 mL. The sediment was washed. Twice with deionized water, and the rinse water was added to the volumetric bottle after separating the precipitate, then complete the volume to 36 mL and place the solution in clean, marked plastic bottles for examination with Flame atomic absorption spectrum according to (Zhao et al. 2016).

#### **RESULTS AND DISCUSSION**

According to an initial appearance examination by volume

and weight, the results of the extraction of elements compounds in the oil residues in the refinery water and sediments including paraffin, naphthenate, precipitated, exchanged, and residual heavy elements, and aromatic hydrocarbons were obtained, this is an indication that the compounds produced during the refining and extraction stage are stable and can remain in water without being decomposed, and this applies to (Sahoo et al. 2016), the greater the intensity and continuity of oil spills, the greater their stability and the longer their retention period increases, with the greater damage to their surroundings. According to (APHA 2017) crude oil levels can be divided into light (>10), medium (10~20), heavy (20~34), and extra thick crude oil (<40).

Compared to our results in Table 1, we note that it is almost dangerous depending on the level of toxicity, persistence, flammability, viscosity, depending on the toxicity and flammability of oil spills resulting from flash depending for the extraction station according to (Zhang & Wang 2015). Through observational evaluation, the flash point level was reached, as the lower the flash point, the greater the risk of oil spillage, through orbital evaluation of the quality of the extracts, petroleum products were divided into lubricating oils and greases (> 125°C), diesel and heavy oil (45~125°C), kerosene (°45~28C), solvent oils and gasoline (< 28°C). The focus was on the level of viscosity, which represents the fluidity of oil spills in the study area, as the higher the viscosity, the greater the value of organic matter assigned to a higher level of oil pollution. This applies to (Wang & Xiao 2010) and this is shown in the distribution form in Fig. 1.

The results of the dissolved, particulate, and residual heavy metals showed that the concentration of dissolved non-sensitized lead and cadmium was 63 mg.L<sup>-1</sup> in general, and the percentage of cadmium particles ranged from 4.95 to 2.45 ppm in dry weight as a minimum.

The results of the statistical analysis showed that there were no statistically significant differences between the study categories, with a significant positive relationship between dissolved cadmium particles and lead particles,

Table 1: Level sub-indexes of oil properties on site.

Elements	Dissolved heavy elements in water	Particulate heavy elements in water	Exchangeable heavy elements in water	Residual heavy elements in water
Pb	0.046	0.342	0.46	4.95
Cd	0.394	0.084	0.63	2.45
Elements	Dissolved heavy elements in Sediments	Particulate heavy elements in Sediments	Exchangeable heavy elements in Sediments	Residual heavy elements in Sediments
Pb	0.901	0.984	0.054	0.122
Cd	0.999	0.768	0.074	0.046

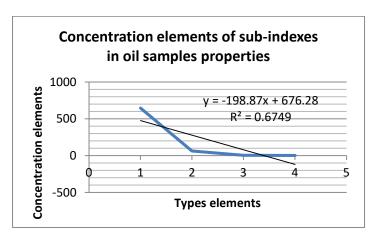


Fig. 1: Concentration elements of sub-indexes of oil properties between elements.

from the water and sediments were also recorded. Given that oil extraction affects the topography and geology of the region and the social conditions and climatic conditions are in their nature, the exploration process and their extraction often leave significant effects that may cause significant damage to it or may cause permanent or temporary changes in it, and it also leaves clear effects on the natural resources and environmental components on the surface of the earth. High concentrations of these two elements were recorded, exceeding the permissible limits internationally and in the Arab world, according to what was mentioned in (Wang & Xiao 2010), that's shown in Fig. 1.

The results of the statistical analysis showed that there were statistically significant differences and that the value of the correlation coefficient was positive between exchanged cadmium, residual cadmium, exchanged lead, and residual lead in Fig. 2, where the lead exchange rate ranged correlation coefficient at a minimum R<sup>2</sup> 0.674, and this is consistent with a previous study (Lang et al. 2011). Therefore, studies monitoring oil spill pollution must rely in large part on measuring the concentration of heavy metals in the sediment, especially concerning the remaining quantity, because some factors may affect the re-dissolution of these elements and their return to the water again, and one of the most important of these factors is decomposition during the process. Elements between water and sediments (Lancellotti et al. 2023).

Compared to other studies, the concentration of lead and cadmium was much higher. This may be due to the entry of rainwater laden with clay, silt, and organic materials causing an increase in the concentrations of these elements in the water used to bury oil pollutants, as well as the accumulation of organic biological materials, and this applies according to what he mentioned (Lang et al. 2011).

It was also noted that the concentrations of the remaining elements in the sediments were higher than the exchangeable and short elements in cadmium and lead elements were higher in the exchangeable case. This can be attributed to the introduction of high concentrations resulting from human sources and oxides caused by nearby means of transportation or through wastewater surrounding the area, which contain organic materials that form complexes as a result of dust storms, polluted water and rain, and high concentrations of this element that are carried into river water or any nearby body of water, according to what was mentioned in (Rahmatullah & Ajmi 2022).

This discrepancy in element concentrations between the current studies can be explained by the fact that the final fate of heavy metals in water is their release on plankton or in the form of sediments in water sediments and water sources. Therefore, there are studies on monitoring the pollution of the aquatic environment with heavy metals, and a large part of them must depend on measuring the concentration of heavy metals in sediments, but some factors may influence it. To re-dissolve these elements and return them to the water again, and among these factors is the acidity index and Iraqi studies on different areas of the Euphrates River, relying on sedimentary analytical methods to extract heavy metals from sediments, as well as the degree of sensitivity of the devices used, such as the atomic analysis spectrometer, where they found a variation in the concentrations of the elements. Heavy metals are extracted from soil particles, sediments, dust, and various biological tissues using different mixtures of acids and organic materials (Ajmi et al. 2018).

## **Membership Evaluation Indicators**

The AHPA references to compare our results are used to

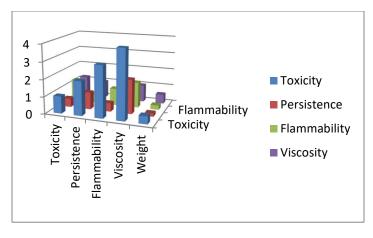


Fig. 2: Membership evaluation indicators elements Level 1.

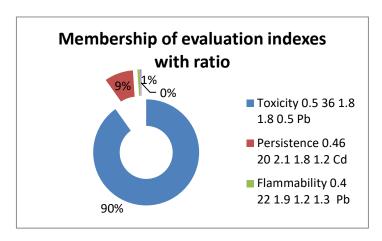


Fig. 3: Membership evaluation indicators elements Level 2.

determine the weight of each indicator and the weights of oil properties and oil spill location respectively in Figs. 2 and 3, levels 1 and 2. It is a level II oil spill pollution classification system, taking oil properties as an example to illustrate the fuzzy comprehensive evaluation process of the first or second level which can be obtained from the membership matrix in the subgroups of toxicity, stability, flammability, and viscosity along with the remaining exchangeable and residual heavy metal concentrations. As an example to illustrate the process level, the overall rating of the membership level R2 can be obtained from the subgroup. Therefore, the overall classification matrix was 90% of toxicity of the study area according to the comprehensive assessment level.

Through the evaluation matrix of pollution levels based on the subgroups of toxicity, stability, flammability, viscosity, and element accumulations, it is considered a second level. Taking the characteristics of the oil as an example to illustrate the level of the process, which amounts

to 90 %, which is the result of a comprehensive assessment of the degree of pollution resulting from oil spills on the surface of the sea at the natural level without human influences, according to what was mentioned in (Zhou et al. 2016), to the nature of the bottom, the sediments, the distance it travels, the nature of human activities, and the waste that reaches the river. Therefore, the next step was to detect organic materials, which caused an increase in the evaluation of the level from the first to the second, which is the biological elements, as the presence of coliform bacteria, fecal coliforms, and fecal streptococci that were detected is considered Vital evidence of pollution resulting from drainage water and its ability to persist in areas where petroleum oil is available, as mentioned in (Han et al. 2018).

The actual treatment operations were not carried out in the station except for the process of skimming large oils on the surface of the tanks, and no chemical substance was added to treat the water leaving the refinery. There is no type of treatment operation on the water leaving the refinery, causing the growth of bacterial colonies that appear in this wastewater is consistent with (Zhao et al. 2016). Therefore, the results of the bacteriological tests were an estimate of the total number of coliform bacteria and fecal coliform bacteria at high levels according to Iraqi specifications and World Health Organization specifications. The presence of this level of bacterial contamination indicates that the Qayyarah refinery environment is vulnerable to organic pollution resulting from water spills, even from conveyor pipes, during pipe leakage incidents, such as corrosion of pipes due to their aging, failure to establish systems to protect against corrosion, and the theft of oil liquids by creating holes in the pipelines.

#### CONCLUSION

The process of exploration and extraction often leaves a permanent change in the surrounding environment and is in the form of accumulations resulting from deposition unless preliminary treatment is carried out before discharge. It is in the form of levels according to natural matrices of factors binding to residual and alternative elements and organic materials. The effects related to oil leaks and spills, such as the presence of large quantities of oil ponds and large containers containing crude oil or water with a high percentage of oil spills and leaks lead to significant pollution targeting soil, surface, or groundwater and affect biological and microbiological diversity. Oil is considered one of the most dangerous sources of soil pollution, as it turns it into sterile soil that is unfit for plant and animal life and all living organisms, especially since its accumulations exceed a high level of toxicity, as in our current study, which exceeded 90%, which may lead to complete disruption of the ecosystem. Therefore, it was a process Evaluation of the levels used to set research priorities to determine the permeability of residual and exchangeable elements to learn prevention, response, and mitigation techniques for these organic and microbial contaminants in the future.

## **RECOMMENDATIONS**

The study can recommend focusing on managing waste resulting from oil pollution and arranging it according to priority, including reducing the amount of oil-contaminated waste, reusing the resources used during the cleaning process, and recycling bulk oil by introducing it into refining streams or stabilizing oil-contaminated materials used in land reclamation projects. or in road construction and restoration, as well as the calorific value of waste materials as fuel for power generation

or heating, which is important for getting rid of waste that can only be treated by burning it, burying it in landfills, or converting it into fertilizers to reduce the problems of oil spills.

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