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Evaluation of Heavy Metals Concentration in Petroleum Derivatives in Al- Anbar Governorate

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Abstract
This research aims at evaluating heavy metals concentrations in petroleum products. The heavy metals, present in petroleum products sold in Anbar Governorate specifically Ramadi, were analyzed. Motor Oil and diesel were obtained from the Anbar branch of the Petroleum Products Distribution Company, while Gasoline and Kerosene were obtained from the old Ramadi Gas Station. The samples were digested by using a mixture of sulfuric acid as well as nitric acid and analyzed using an Atomic Absorption Spectrometer(AAS). The results showed that the lead concentration values in all the petroleum products were higher than the permissible value, with the highest value in kerosene reaching 2.6 mg/L and the lowest value in diesel fuel reaching 1.153 mg/L. The zinc concentration values in motor fuel also exceeds the permissible limits, reaching 6.585 mg/L. The nickel concentration values also slightly exceeds the permissible limits, reaching 1.010 mg/L. In addition, the high levels of lead can be attributed to two sources: anthropogenic like additives used during refining, absorption of metals from storage tanks as well as supply vessels and natural like the existence of metals in the rocks of the crude oil. In addition, such high level of pollution poses a serious environmental threat in the vicinity where these products are used.
Keywords: Petroleum Products, Heavy Metals, Motor Oil, Diesel, Gasoline, Kerosene, Pollution

1-**Introduction**

Heavy metals cause environmental pollution which occurs primarily through two main pathways: the release of hydrocarbons into the atmosphere during combustion processes, and direct spills of hydrocarbons into the environment. Crude oil contains various potentially harmful substances, including heavy metals, its toxicity (1). In the modern context of advanced and developing industrialization, petroleum products and their derivatives constitute one of the major sources of environmental pollution. During the extraction, transport, distribution and storage of crude oil and its products, these may be released into the environment in an uncontrolled manner, causing pollution of the atmosphere, lithosphere, hydrosphere and biosphere (2). Heavy metals are a group of metals and metalloids with an atomic density higher than the 4000 kg/m3. The heavy metals are toxic in nature which cause serious health illness to human beings and animals, even at very low concentration (3). Various sources contribute to heavy-metal emissions from vehicles, including fuel combustion, lubricating oil consumption, tire wear, brake wear, and road abrasion. The consumption of lubricating oil and tire wear are the primary sources of Cd emissions, while tire wear and galvanized parts, such as fuel tanks, contribute to Zn emissions. Cu and Pb emissions primarily come from brake wear, although Pb emissions can also come from exhaust gas and worn metal alloys in the engine (4). Petroleum hydrocarbons play a significant role in environmental pollution. This

pollution primarily occurs through two main pathways: the release of hydrocarbons into the atmosphere during combustion processes, and direct spills. Petroleum derivatives are gaining increasing popularity. Crude oil is the primary raw material in the petrochemical industry, used to produce diesel and fuel oils, gasoline, kerosene, lubricants, and asphalts. It is also utilized in the manufacture of explosives, dyes, cosmetics, and insecticides (5). Significant crude oil spills have had a negative impact on soil inorganic levels. The presence of heavy metals in petroleum is contingent upon the geological setting in which the crude is being generated. Crude oil contains several elements because of the kind of metals found in the rock's source. These metals separate in the rocks' pore water, which is then absorbed by the crude oil. These heavy metals might be crucial catalysts in the transformation of organic materials into petroleum. The presence of various trace metals in crude oil is primarily attributed to the migration of these metals from the source rock to the reservoir rock during the geological process (6). The addition of drilling mud fluids to the oil well during the extraction of crude oil is another potential source of heavy metals in crude oil. These substances are introduced straight to the crude oil, and they always end up contaminating the earth (7). This clarifies why heavy metals detected in oil-producing nations may originate from the fuels used in drilling rigs (8). When petroleum fractions are fractionated and refined, the heavy metals in the crude oil disperse among them, which explains why petroleum products contain heavy metals. Thus, this study focuses on examining the distribution and presence of heavy metals in kerosene, diesel and petrol in order to assess how these metals' concentration levels compare and determine if they match desired requirements or not (9). Because the topic of heavy metals is broad in scope no one can cover all its aspects; therefore, it has been dealt with from various perspectives. (Razan (2019), Jaccob (2020), Sikakwe, Tyopine and Eyong (2022), Wadi, Pasha, Abojassim(2022), Sikakwe, Tyopine and Eyong (2022), Konstantinova, Minkina, Antonenko, Sherstnev, Mandzhieva, Sushkova, Rajput and Konstantinov (2023), , Kareem and Abdulla (2023), Anthony, Hannah and Samuel (2024). For instance, Razan (2019) showed an estimation of the concentrations of some trace heavy metal elements (Cd, Pb, Cu, Zn and Ni) in the hair of some donors in several areas in the Latakia city. The study showed that the content of elements is high in mining, plastics and battery workers compared to administrative employees, which gives a clear indication and a close link between the concentrations of these elements and the amount of environmental pollution (10). The researcher Jaccob (2020) evaluated the lead and copper content in the hair of workers in petroleum products distribution companies in Iraq The results showed that lead and copper concentrations in the hair increased significantly among workers at oil stations compared to ordinary individuals who live in the city of Basra, far from dangerous pollutants.(11) . For Sikakwe, Tyopine and Eyong (2022) study, they showed another way to evaluate the health risks of heavy metals, including zinc (Zn), iron (Fe), lead (Pb), copper (Cu), and cadmium (Cd), for selected samples of gasoline. The results showed that the majority of kerosene samples are safe to use.(12). Wadi, Pasha, Abojassim (2022) also evaluated inhalation health risk assessment of some of heavy metals for locally Kerosene samples in Iraqi market. They studied the concentrations of five elements (Zn, Fe, Pb, Cu, and Cd) collected from different of warehouses oils in Iraq. The measurements have been done using Atomic Absorption Spectrophotometer. The results showed that most of the kerosene samples were safe. (13). In addition, Konstantinova et al. (2023) evaluated polycyclic aromatic hydrocarbons and heavy metals pollutants in soil around peri-urban gas stations and

automobiles Mechanical. They found that the soil was polluted and the reason for this was that heavy metals were generated from car exhausts and parent rocks, as well as that polycyclic aromatic hydrocarbons in the soil were produced through the internal combustion of gasoline and kerosene (14). As for the study conducted by, Kareem and Abdulla (2023), its purpose was to measure the content of eight heavy metals in plant leaves and soil. These samples were collected twice during the study period from the area surrounding the refineries along Erbil-Gwer Road. The researchers evaluate concentrations of total petroleum hydrocarbons (TPH) in local soil samples. They also evaluate the concentrations of total petroleum hydrocarbons (TPH) in local soil samples. The results showed that the amounts of lead, nickel, cadmium, chromium, zinc and manganese in the soil samples varied significantly ($P < 0.05$). With reference to Cu and Zn, no appreciable variations were seen between dry and wet seasons. The sequence of metal levels for both times was as follows: Mn > Cr > Zn > Ni > Cu > Pb > As > Cd (15).. As for a study conducted by Anthony, Hannah and Samuel (2024), it aims to evaluate the concentration of heavy metals chromium, lead, mercury, and arsenic in mechanical people compared to non-mechanical people. The results showed an increase in the values of lead and mercury concentrations in the blood of people who work as mechanics and who are in daily contact with petroleum products compared to people who are not mechanics (16). To this end, the present study attempts to answer the following question: What are the current levels of heavy metals concentration in petroleum derivatives within Al-Anbar Governorate?

Objective

Determine the current levels of heavy metals concentration in different types of petroleum derivatives within Al- Anbar Governorate.

Preparation of Samples

Ten ml of each product from (kerosene, gasoline, and diesel) and one ml from motor oil product were digested by using a mixture of 20 ml of nitric acid and sulfuric acid in a ratio of 4:1. The digestion process involved gently heating the samples in a water bath at 80°C for four hours daily, over a period of nine days. 15 ml of distilled water and chloroform were gradually added to the organic material to ensure that all ions precipitated. The aqueous solution was separated from the organic solution using a separating funnel. The organic matter was discarded and the aqueous extract was taken to measure the percentage of ions. To ensure complete digestion, samples were measured in science laboratories, Anbar University. A Buck Scientific Model VGP-210 Atomic Absorption Spectrophotometer was used to determine the metal content of each fermented sample. Copper (Cu), lead (Pb), nickel (Ni), zinc (Zn) and cadmium (Cd) are analyzed depending on the following wavelengths:324.7 nm, 283.3 nm, 232.0 nm, 213.9 nm, and 228.8 nm (17)(18). This method was adopted to prevent inflammation. The digested samples were recorded and analyzed, respectively. The concentrations of the metals were obtained from the absorbance that were measured. To ensure quality control and assurance, replicate analyses were conducted on the samples. This involved performing multiple analyses on each sample to calculate the mean concentration, which was used to establish trueness. The standard deviation of the mean was also calculated to assess precision. Procedural blanks and standard solutions were included as part of the analytical quality control measures.

Results and Discussion

The current study was concerned with estimating the levels of heavy metals in different manufactured petroleum products. Table (1) shows the levels of lead, cadmium, copper, zinc,

and nickel in petroleum products (diesel, gasoline, kerosene, and motor oil). In this part, the most important results were discussed and compared with the permissible values of aforementioned metals in petroleum products. An increase in these elements above standard values may cause many problems for people who are in direct and daily contact with these products, especially station workers, mechanics, and people who work in crowded places, as previous studies have shown.

Table 1:Mean concentration of heavy metals in petroleum product (mg/l)

Sample	Pb	Cd	Cu	Zn	Ni
Diesel	1.153	1.527	0.707	0.210	0.507
Gasoline	2.562	3.097	0.430	0.122	0.562
Kerosene	2.694	0.403	0.530	0130	1.010
Motor oil	2.677	0.315	0.850	6.585	0.887
Permission limit	0.075	5	1	5	1

1-Lead concentration

As can be seen in figure (1) below, the results show high lead concentration values in all petroleum product samples, where the values were (1.153 , 2.562, 2.694 and 2.677) mg/l for Diesel , Gasoline, Kerosene and Motor oil respectively while the allowed value is (0.075 mg/l).The high percentage of lead in all samples may be due to several reasons. First, human factors such as the use of refining additives, second, absorption of metals from storage tanks as well as supply vessels, and third the inherent presence of these metals in the source rock from which the ore was extracted. The results show that lead concentration values are high in all petroleum product samples

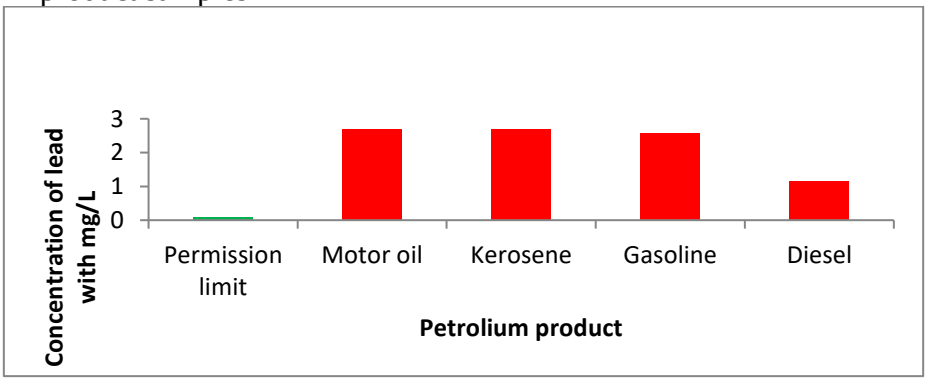

Figure 1: shows the contamination of lead contamination in petroleum derivatives.

2-Cadmium concentration

The values of cadmium concentrations did not exceed the permissible levels in all types of petroleum products, as they ranged from (0.315 mg/l in Motor oil product to 3.097 mg/l in Gasoline) while the permissible value was (5 mg/l). Figure (2) shows the percentage of cadmium contamination in petroleum derivatives.

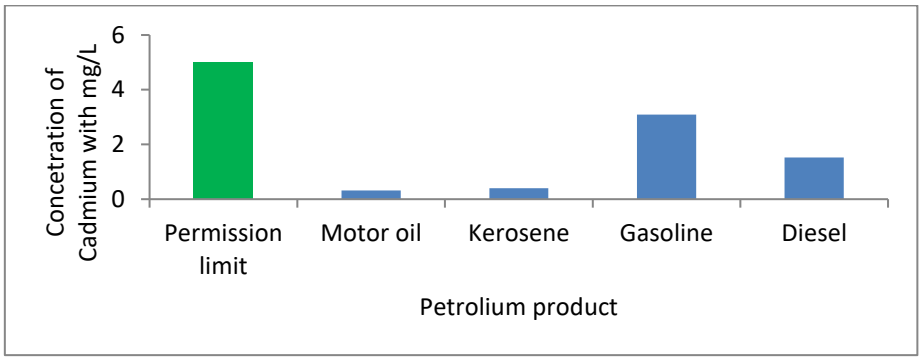

Figure 2: shows the contamination of cadmium in petroleum derivatives.

3-Copper concentration

The copper concentration values in the motor oil (0.85 mg/l) and diesel (0.707 mg/l) samples approached the permissible values of (1 mg/l), while the copper metal concentration values in the kerosene and gasoline models were 0.530 mg/l and 0.430 mg/l respectively. Figure (3) shows the percentage of copper contamination.

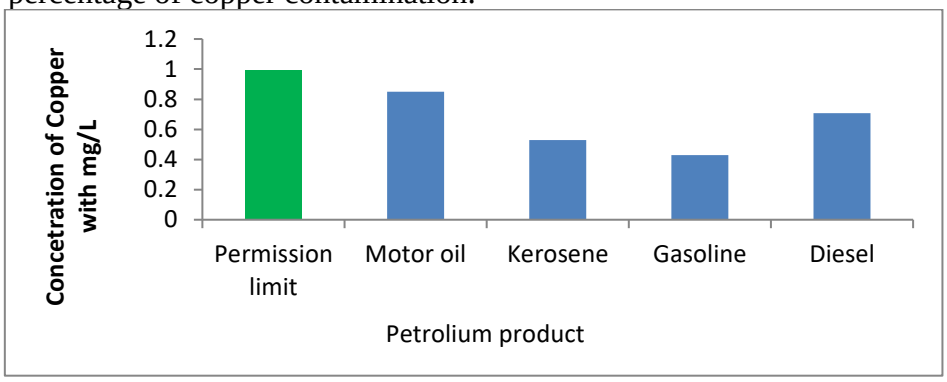

Figure 3: shows the concentration of copper petroleum derivatives

4-Zinc concentration

From the figure (4), It can be seen that the motor oil sample recorded a clear increase in the value of zinc concentration, reaching 6.585 mg/L, thus exceeding the permissible value of 5 mg/L. While the values of the kerosene, gasoline, and diesel samples were (0.210, 0.122 and 0.130) mg/L, respectively, they did not exceed the permissible values.The danger of these metals causes health problems to humans.

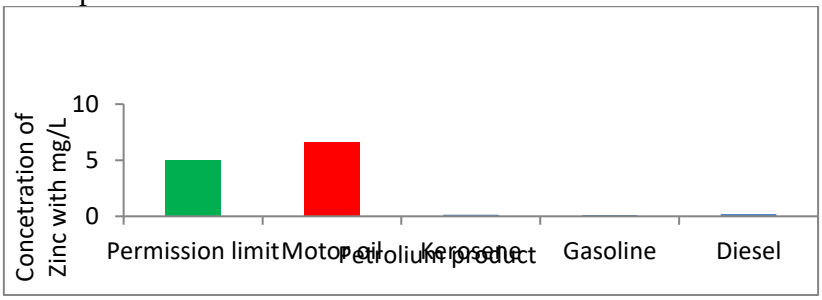

Figure 4 : shows the concentration of zinc in petroleum derivatives

5-Nickel concentration

As can be seen in figure (5), a slight increase in the concentration of nickel metals above the permissible values, as the nickel concentration was 1.01 mg/L, while the rest values of the petroleum products were less than the permissible value. When these metals burn, oxides are discharged into the atmosphere and surrounding environment. This might endanger the lives of those who live there.

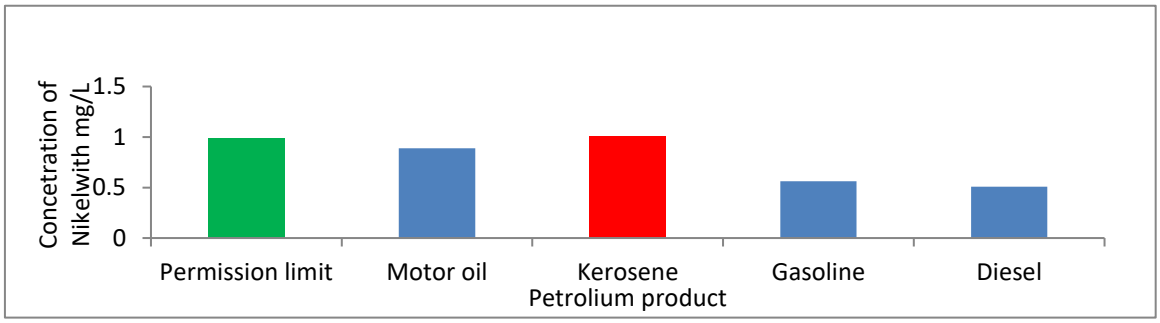

Figure 5: shows the concentration of nickel in petroleum derivatives

Conclusions and Recommendations

The study's findings demonstrated that an analysis was done on the amount of heavy metals present in petroleum products. It revealed that the levels of lead in petroleum products were shockingly high, far above available limits. Thus, the researchers provoked and suggested that petroleum products should be under government control. To prevent additional environmental pollution, first, the government should check that the Petroleum Products, which were refined internally and externally, meet the regulatory norms. Second, Workers at gas stations and production refineries should submit periodically to heath tests. Third, providing capabilities and logistical support for researchers and specialists in the field.

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