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Environmental Assessment of Heavy Metals in New and Used Engine Oils: A Case Study from Benghazi, Libya

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Abstract

The presence of heavy metals in lubricating engine oils is a critical factor in assessing engine performance, lubricant degradation, and potential environmental impacts. This study investigated the concentrations of selected heavy metals (Pb, Cr, Ni, Cu, and Fe) in both new and used engine oils using Atomic Absorption Spectrophotometry (AAS) Engine oil samples of different brands were collected from vehicles in Benghazi, Libya, and analyzed to determine the concentrations of selected heavy metals and assess changes in physicochemical properties, including viscosity, flash point, density, and total base number.

The results showed that heavy metal concentrations were substantially higher in used oils than in new oils. Lead (Pb) concentrations increased from nearly undetectable levels in new oils to over 70 mg/kg in used oils. Similarly, chromium (Cr), nickel (Ni), copper (Cu), and iron (Fe) showed increases of more than 90% in used samples compared to new ones. These increases reflect mechanical wear, additive degradation, and contamination during engine operation. The study also highlighted marked changes in physicochemical properties between new and used oils, including decreased viscosity index, reduced flash point, and reduced sulfated ash content. Such findings confirm the diagnostic value of oil analysis for preventive maintenance, while also underlining the environmental hazards posed by improper disposal of used lubricants. This work emphasizes the urgent need for strict regulations and sustainable waste management practices in Libya and globally. Furthermore, the integration of more advanced analytical techniques, such as ICP-OES and ICP-MS, is recommended for enhanced detection accuracy in future research.

Keywords: Engine Oils, Heavy Metals, AAS, Used Oil, Environmental Impact, Preventive Maintenance.

Introduction

Lubricating oils constitute an essential element in the operation of internal combustion engines, where they minimize friction, transfer heat, and protect metallic surfaces against corrosion and wear (Cassap, 2008; Sharma et al., 2025). Despite these indispensable roles, oils undergo significant physicochemical transformations during service, progressively degrading into hazardous wastes that may pollute soil, water, and air (Madanhire & Mbohwa, 2016; Zając et al., 2013). Improper disposal of used oils has been identified as a major environmental issue, with contamination levels often surpassing those from accidental oil tanker spills, while their persistence and toxicity pose long-term ecological and health threats (Prasannakumar et al., 2025). One of the most critical concerns is the accumulation of heavy metals in used lubricants. These elements are non-biodegradable, capable of bioaccumulation through the food chain, and highly toxic even.

at trace levels (Zając et al., 2013). Metallic contaminants in oils originate primarily from two pathways: the deliberate addition of performance-enhancing additives to new oils and the mechanical wear of engine components such as pistons, bearings, and cylinder walls, which can release Fe, Cr, Cu, Pb, and Ni particles into the lubricant. (Madanhire & Mbohwa, 2016; Sáez et al., 2024). Additional contamination may arise from incomplete combustion processes, ingress of dust particles, and environmental exposure (Vinić et al., 2020).

The classification of lubricants by the American Petroleum Institute (API) is based on saturate content, sulfur concentration, and viscosity index, categorizing oils into Groups I–V, ranging from conventional mineral oils to synthetic formulations (Pirro et al., 2016). Additives such as detergents, dispersants, and antioxidants are incorporated to enhance performance; however, many contain metallic compounds, including zinc dialkyldithiophosphates (ZDDP), which introduce Zn and P into fresh oils and must therefore be distinguished from wear-derived metals during analysis (Li et al., 2017). The lubrication circuit of the engine and the role of additives in reducing wear are schematically represented in Fig. (1), which illustrates the oil flow cycle.

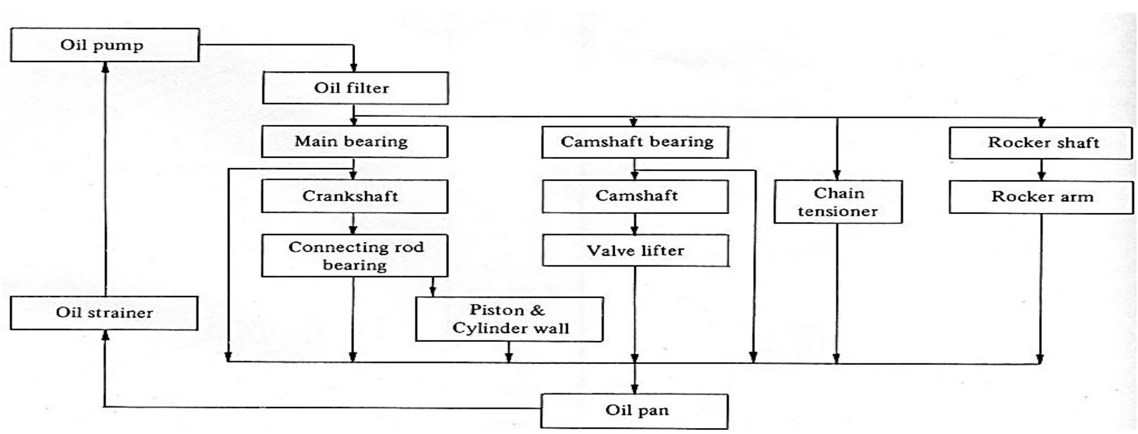

Fig. (1) Schematic representation of the engine oil circulation cycle (Li et al., 2017).

From an environmental perspective, used lubricants represent one of the most widespread sources of contamination. They contain carcinogenic polycyclic aromatic hydrocarbons (PAHs) and toxic metals such as Pb, Cr, Ni, Cu, and Fe (Das & Chandran, 2011). Even small volumes of discharged oil can have catastrophic consequences; according to the U.S. EPA (2001), a single gallon of used oil can contaminate up to one million gallons of freshwater. Soil and water bodies near urban roads accumulate hydrocarbons and metals transported by runoff, leading to elevated pollutant concentrations in sediments and disruption of biological activity (Raymond et al., 1976; Wakeham, 1977). For instance, runoff from high-traffic areas contains significantly higher levels of Pb and PAHs compared to residential areas. The pathways of environmental pollution and bioaccumulation are well summarized in Fig. (2), which demonstrates the fate of lubricants in the environment, while Fig. (3) illustrates the routes of human exposure through the food chain (Sonone et al., 2020).

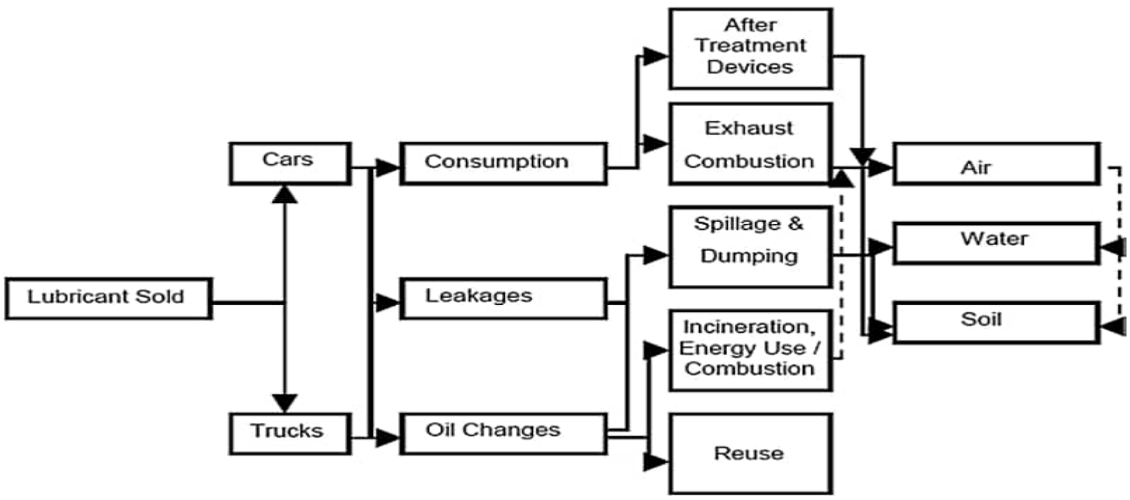

Fig. (2) Flow Diagram on Fate of Lubricants (adanhire & Mbohwa, 2016)

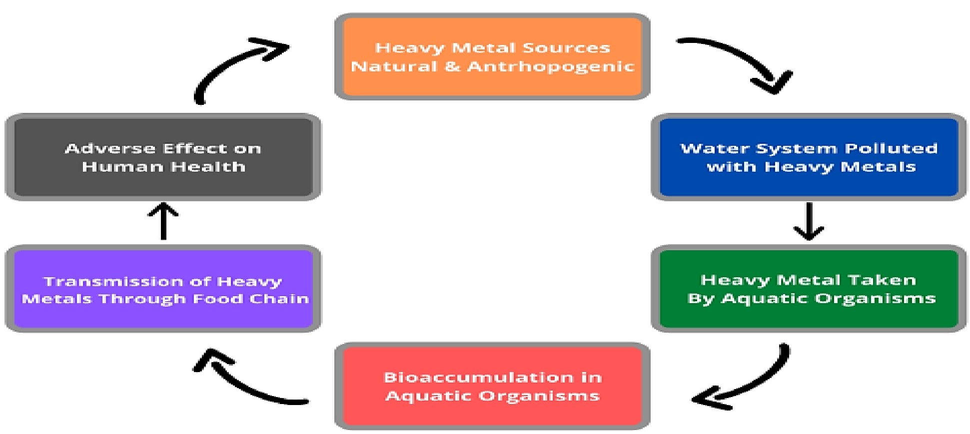

Fig. (3) Routes of human exposure to heavy metals through the food chain (Sonone et al., 2020).

The persistence of these contaminants has severe implications for human health. Chronic exposure to heavy metals can cause neurological, cardiovascular, renal, and developmental disorders (Nordberg et al., 2005). The combustion of used oils adds further risks, as burning releases airborne particulates rich in Pb, Zn, Cr, and Cu, in addition to gaseous pollutants such as SO_2 and NO_x (Mumford et al., 1986). Studies have shown that up to 70% of Pb present in used oils can be emitted to the atmosphere upon combustion, making the practice a significant source of toxic air pollution (EPA, 1972).

In terms of regulations, different international frameworks have attempted to limit the impacts of heavy metals in lubricants. For example, the European Commission (EC No. 1907/2006, REACH) restricts hazardous substances in oils, while the American Petroleum Institute (API) defines standards that indirectly limit metallic contaminants through performance specifications (API, 2021). UNEP also promotes sustainable practices for lubricant waste management (UNEP, 2021). At the national level, Libyan regulations, such as Law No. 15 of 2003, provide general guidelines for environmental protection but lack specific limits for heavy metals in lubricants, leaving a regulatory gap that hinders effective management (FAO, 2021).

Overall, while extensive studies have been conducted globally on the behavior of heavy metals in lubricants, research in Libya remains limited. Considering the country’s growing automotive fleet and weak enforcement of disposal practices, the risks posed by heavy metals in used engine oils are of increasing concern. This study addresses this gap by determining the concentrations of Pb, Cr, Ni, Cu, and Fe in new and used engine oils available in Benghazi using Atomic Absorption Spectrophotometry (AAS). The results provide not only diagnostic insights into engine wear but also essential data for the development of waste management policies and environmental protection strategies in Libya.

Methodology

This study was designed to determine the concentrations of selected heavy metals (Pb, Cr, Ni, Cu, and Fe) in new and used lubricating oils collected from vehicles in Benghazi, Libya. The methodology involved systematic sampling, preparation, analysis by Atomic Absorption Spectrophotometry (AAS), and determination of key physicochemical properties.

1. Sample Collection:

Samples of new engine oil were purchased directly from commercial suppliers to represent unused reference conditions, while used oil was collected from service stations and vehicle workshops. Used samples were taken immediately after an oil change to avoid secondary contamination. A total of 20 oil samples were collected, including four fresh engine oil samples and 16 used engine oil samples. The four fresh oil samples, representing commonly used brands in Benghazi, are listed in Table (1). The 16 used oil samples were collected from service stations and vehicle workshops across different districts of Benghazi. Each used-oil sample represented a composite sample collected from multiple vehicles operating in the corresponding district. The sampling locations included Ganfouda, Al-

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Hawari, Sidi Faraj, Al-Qawarsha, Vanessa Street, Tablino, Balaoun, Majory, Sabri, Salmani, Deqadosta, Shebna, Hayy Al-Salam, Kuwaifiya, Sidi Khalifa, and Bouatni, as shown in Fig. (4).

Table (1): Brands of new Engine Oil Samples

Sample No	Brand
17	Canmore
18	Bizol
19	Gazprom
20	Lukoil

Each sample was stored in acid-washed polyethylene bottles, labeled with detailed information (oil type and collection date) as shown Fig. (5), and preserved under ambient conditions until analysis.

Fig. (4) geographical distribution of sampling points in Benghazi and No. of Sample.

2. Sample Preparation:

Prior to analysis, all containers and glassware were soaked in 10% nitric acid (HNO_3) and rinsed with deionized water to prevent contamination (EPA, 1996). Oil samples were homogenized by thorough mixing, and aliquots of approximately 5 mL were taken for digestion. The digestion procedure was performed using concentrated nitric acid on a hot plate at controlled temperature until the solutions became clear. The digested samples were cooled, diluted with deionized water, and quantitatively transferred into 50 mL volumetric flasks. This procedure ensured complete breakdown of the oil matrix and release of metallic species for subsequent spectroscopic determination.

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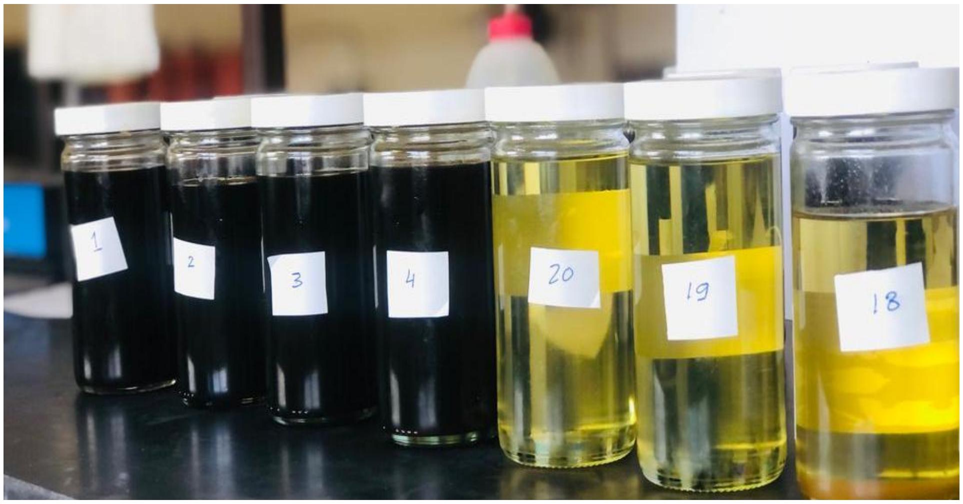

Fig. (5) collected samples from the analyzed engine oils.

3. Analytical Procedure:

3.1 Atomic Absorption Spectrophotometry (AAS):

Heavy metal concentrations were determined using an Atomic Absorption Spectrophotometer (Perkin Elmer Analyst series). Calibration standards for Pb, Cr, Ni, Cu, and Fe were prepared from certified stock solutions. Calibration curves exhibited strong linearity ($R^2 > 0.995$) across the studied concentration ranges, confirming the reliability of the method. The experimental setup and instrumentation are illustrated in Fig. 6, which shows the AAS unit with sample introduction system. Operating conditions (wavelength, lamp current, and slit width) were adjusted according to manufacturer specifications to optimize detection sensitivity (Kashif et al., 2018).

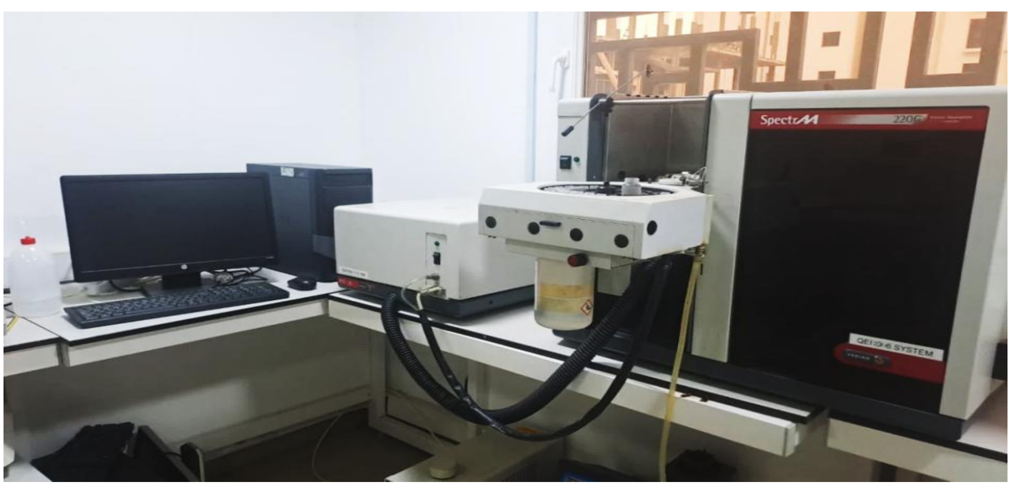

Fig. (6) Atomic Absorption Spectrophotometer setup used for heavy metal determination.

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3.2 Quality Control and Validation:

Quality assurance was achieved through the use of blanks, duplicate measurements, and spiked recovery tests. Recovery percentages ranged consistent with values reported in similar studies (Kashif et al., 2018; Vinić et al., 2020). The method detection limits (MDLs) were also established for each metal, ensuring accuracy and repeatability of results.

4. Determination of Physicochemical Properties:

In parallel with heavy metal analysis, physicochemical characteristics of the oil samples were measured to provide insights into degradation processes during engine operation. The parameters included:

- Viscosity determined according to ASTM D445 using a capillary viscometer.
- Flash Point, measured using the Cleveland open cup apparatus following ASTM D92.
- Density, determined using a hydrometer in accordance with ASTM D1298.
- Total Base Number (TBN), analyzed by potentiometric titration.
- Sulfated Ash Content, determined by ASTM D874.

5. Data Analysis:

Data obtained from AAS and physicochemical measurements were statistically processed. Mean values, standard deviations, and relative standard deviations (RSD%) were calculated. Comparative analysis was performed between new and used oils to evaluate the degree of metal accumulation and property deterioration.

Results and Discussion

The analysis of new and used engine oils revealed significant differences in both heavy metal concentrations and physicochemical properties. These variations reflect the processes of engine wear, additive degradation, and contamination during service.

1. Heavy Metal Concentrations:

The concentrations of Pb, Cr, Ni, Cu, and Fe in new oils are presented in Table. (2), while the corresponding values for used oils are shown in Table. (3). Results indicate that new oils contained either very low or undetectable levels of these metals, whereas used oils exhibited significantly elevated concentrations, reflecting the accumulation of wear particles during service.

Lead (Pb):

As illustrated in Fig. (7), Pb concentrations increased sharply in used oils compared to new samples. This rise is attributed mainly to bearing wear and, in some cases, residual contamination from fuel additives. The near absence of Pb in fresh oils and its marked presence in used ones align with earlier reports by Zali et al. (2015) and Kashif et al. (2018). The environmental and health risks of Pb are well documented, particularly its neurotoxicity and persistence in soils.

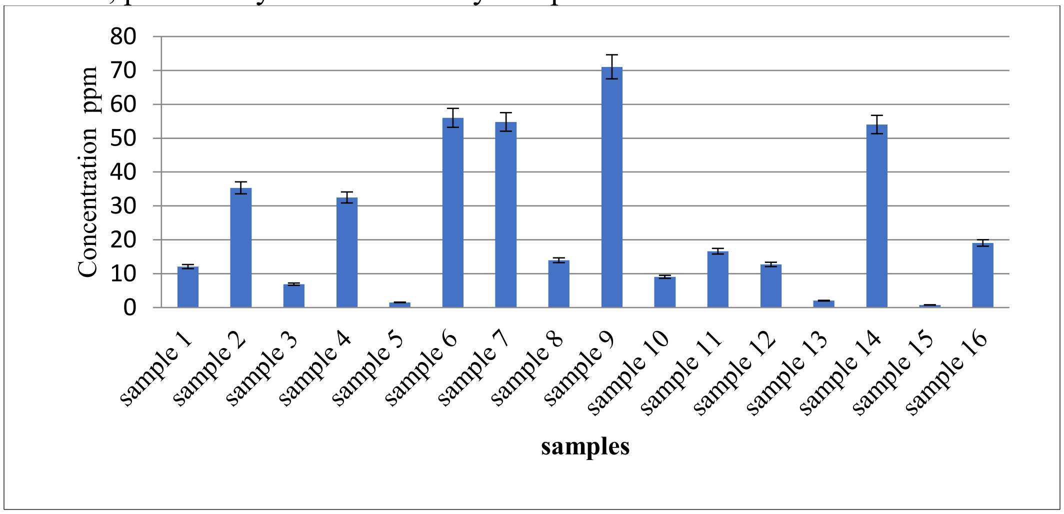

Fig. (7) Lead (Pb) concentrations in used oils

Chromium (Cr):

The data in Fig. (8) reveal higher Cr levels in used oils, which can be linked to the wear of alloyed steel components such as piston rings and cylinder liners. Comparable findings were documented by Vinić et al. (2020). The detection of Cr is a strong indication of high-friction wear processes in engine operation.

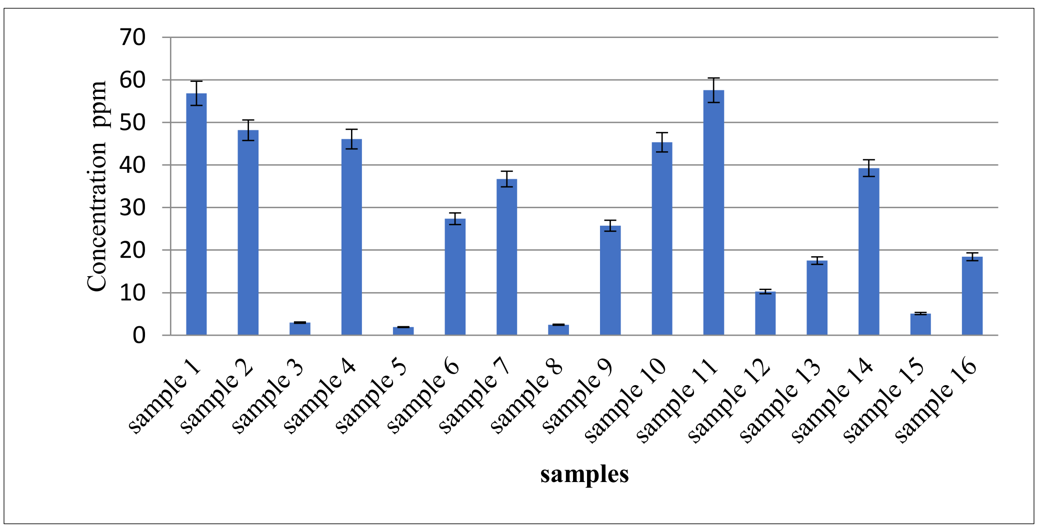

Fig. (8) Chromium (Cr) concentrations in used oils

Nickel (Ni):

As shown in Fig. (9), Ni concentrations also increased in used oils. Ni typically originates from alloy steels and exhaust valve materials. Its accumulation in waste oils is of concern due to its recognized carcinogenic properties (Nordberg et al., 2005).

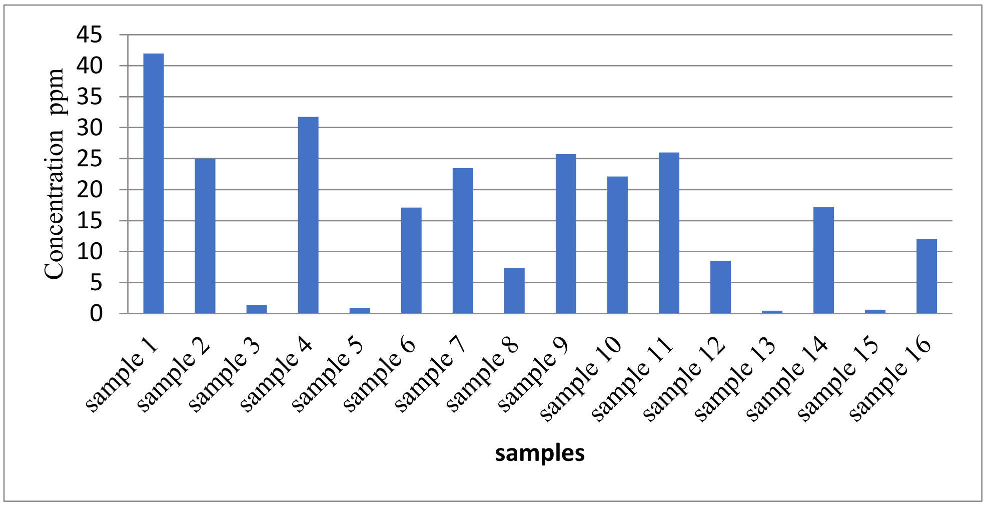

Fig. (9) Nickel (Ni) concentrations in used oils

Copper (Cu):

Fig. (10) demonstrates a distinct rise in Cu levels in used oils. Cu is derived mainly from bronze and brass bearings, reflecting bearing wear and possible corrosion within the lubrication system. Aguirre et al. (2020) identified Cu as one of the most sensitive markers of bearing health in used oil analysis.

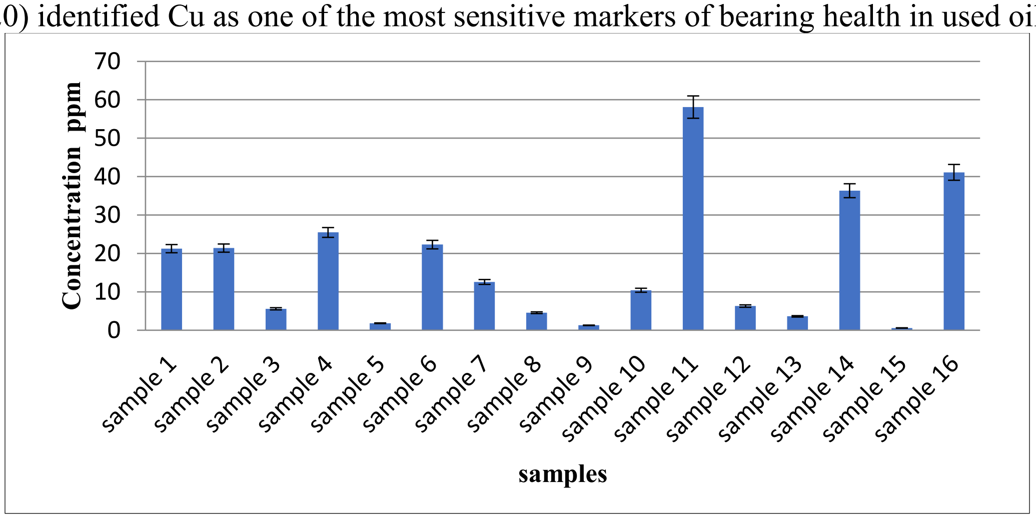

Fig. (10) Copper (Cu) concentrations in used oils

Iron (Fe):

Among all analyzed metals, Fe showed the most dramatic increase in concentration, as illustrated in Fig. (11). This dominance reflects the abundance of Fe in engine components such as cylinder liners, piston rings, and crankshafts. The sharp rise in Fe agrees with Zając et al. (2013) and highlights its diagnostic value as the primary indicator of mechanical wear.

The comparative overview in Fig. (12) further reinforces these trends, clearly showing that all metals (Pb, Cr, Ni, Cu, and Fe) increase substantially after engine operation, with Fe as the dominant element. Collectively, these results confirm that used oils serve both as diagnostic media for engine condition monitoring and as carriers of toxic metals, posing environmental risks when improperly discarded.

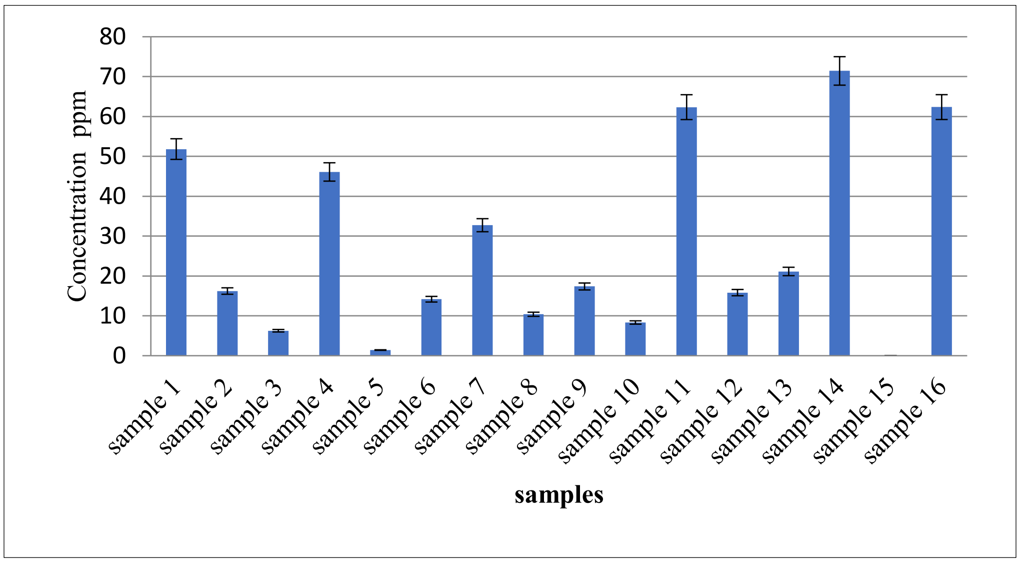

Fig. (11) Iron (Fe) concentrations in used oils

2. Comparison with Previous Studies:

When compared to earlier works, the results of this study are consistent with global findings. Kashif et al. (2018) reported similar increases in Pb and Cu in Nigerian oils, while Zając et al. (2013) and Chin et al. (2012) confirmed the presence of high concentrations of Fe and Ni in used lubricants. The magnitude of metal accumulation observed in Benghazi oils is within the range reported internationally, but the lack of effective waste oil management in Libya makes these findings particularly critical.

Table. (2): Heavy metal concentrations in new oil (mg/kg)

Sample.No	Pb	Cr	Ni	Cu	Fe
17	0.00	0.00	0.00	0.00	0.02
18	0.00	0.00	0.00	0.00	1.23
19	3.57	0.70	0.62	1.4	0.14
20	0.00	0.00	0.00	1.29	1.15

Table. (3): Heavy metal concentrations in used engine oil (mg/kg)

Sample.No	Pb	Cr	Ni	Cu	Fe
1	12.09	56.83	41.97	21.24	51.82
2	35.33	48.17	24.99	21.39	16.22
3	6.90	2.97	1.37	5.58	6.27
4	32.50	46.08	31.75	25.46	46.09
5	1.53	1.91	0.93	1.82	1.42
6	56.00	27.37	17.10	22.30	14.17
7	54.80	36.70	23.46	12.57	32.73
8	13.97	2.47	7.34	4.56	10.39
9	71.07	25.73	25.73	1.28	17.37
10	9.07	45.33	22.10	10.41	8.33
11	16.63	57.57	26.01	58.10	62.34
12	12.73	10.27	8.53	6.30	15.83
13	2.03	17.53	0.44	3.62	21.13
14	54.03	39.27	17.13	36.33	71.42
15	0.77	5.10	0.60	0.60	0.05
16	19.07	18.43	12.03	41.11	62.35

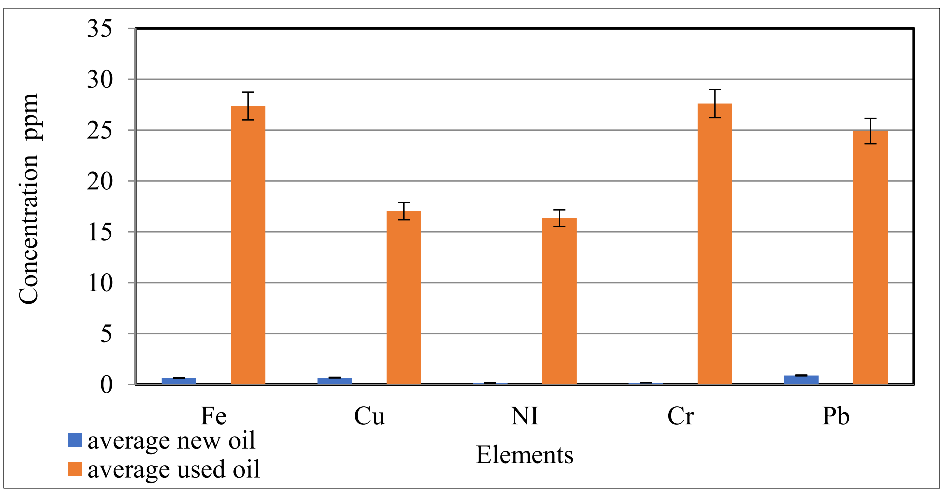

Fig. (12) Comparative concentrations of Pb, Cr, Ni, Cu, and Fe in new vs. used oils)

3. Physicochemical Properties:

The physicochemical characteristics of the lubricating oils showed significant changes after use, reflecting degradation processes and contamination during engine operation.

The viscosity of the used oils increased compared to the new oils, mainly due to oxidation reactions, thermal degradation products, and soot accumulation. This behavior is illustrated in Fig. (13), where the rise in viscosity highlights the thickening effect of prolonged engine service.

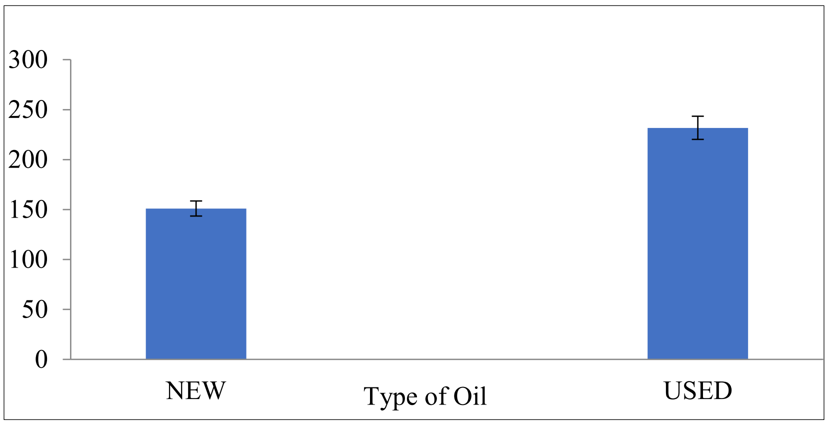

Fig. (13) comparison of viscosity index between used and new oils

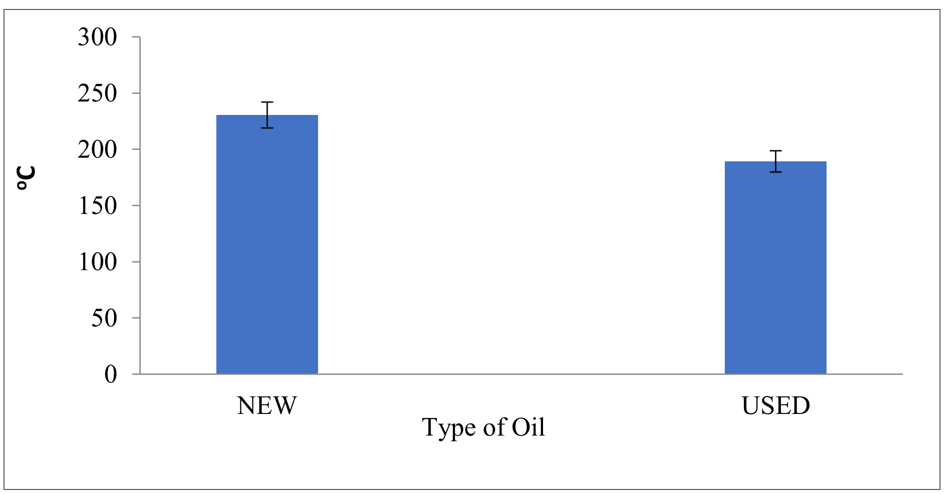

Fig. (14) comparison of flash point between used and new oils

In contrast, the flash point of the used oils decreased markedly Fig. (14), indicating the presence of volatile contaminants and possible fuel dilution during operation.

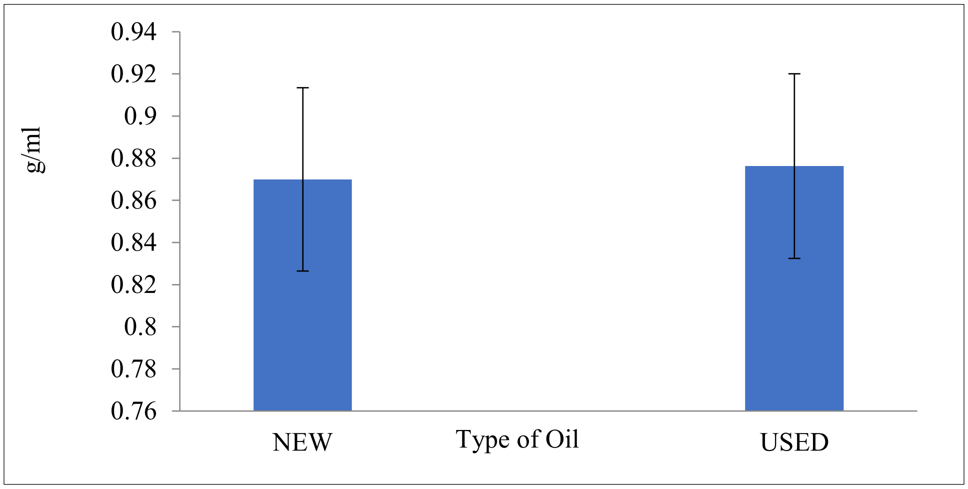

Fig. (15) comparison of density between used and new oils

The density of the used oils also increased slightly relative to the fresh samples Fig. (15), consistent with the buildup of oxidation products and particulate matter.

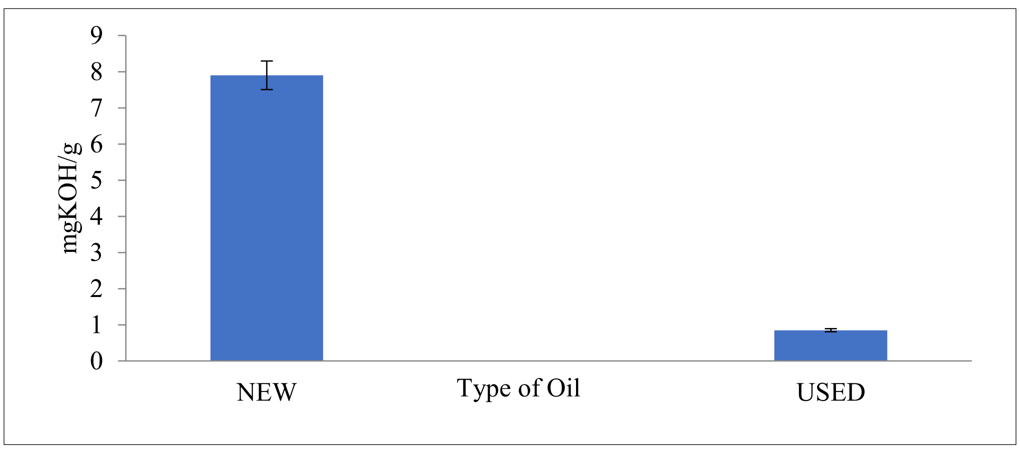

Fig. (16) comparison of TBN between used and new oils

A pronounced reduction in the TBN was observed Fig. (16), confirming the depletion of alkaline additives responsible for neutralizing acidic combustion byproducts. This loss of neutralizing capacity marks a critical indicator of oil end-of-life.

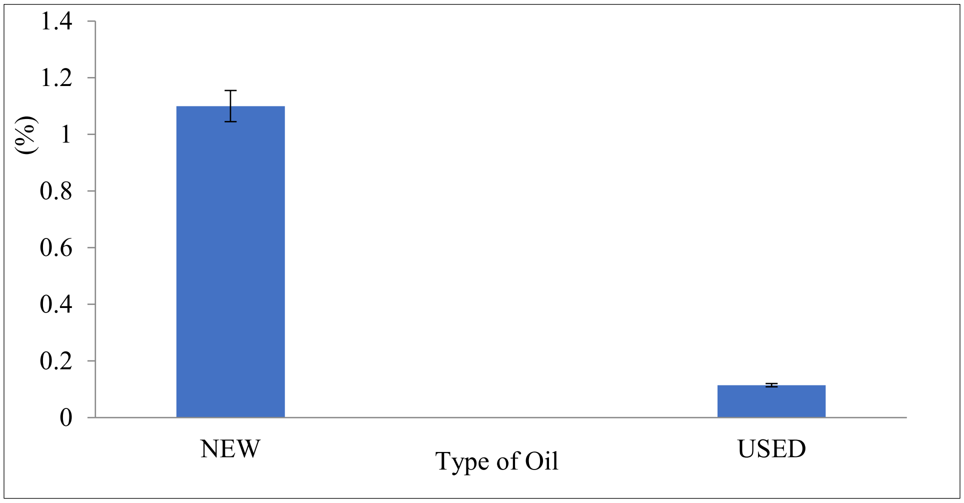

Fig. (17) comparison of sulfate ash between used and new oils

Meanwhile, the sulfated ash content decreased markedly in the used oils compared with the new oils, as shown in Fig. (17). This reduction may reflect changes in the inorganic additive fraction during engine operation. Further investigation is required to determine the specific mechanisms responsible for this change.

4. Environmental and Technical Implications:

The presence of high concentrations of heavy metals in used oils has both technical and environmental consequences. Technically, the accumulation of wear metals can accelerate degradation of engine parts, increasing the risk of mechanical failure. Environmentally, the disposal of metal-rich oils without treatment poses serious risks to soil and water quality, as Pb, Cr, and Ni are highly toxic and persistent. These findings reinforce the need for regular monitoring of lubricants as a diagnostic tool for preventive maintenance, as well as the establishment of stricter regulations for the collection and recycling of used oils in Libya.

Conclusions

This study investigated the concentrations of selected heavy metals (Pb, Cr, Ni, Cu, and Fe) and the physicochemical properties of new and used engine oils collected in Benghazi, Libya, using Atomic Absorption Spectrophotometry (AAS) and standard ASTM methods. The results clearly demonstrated that used lubricants exhibit significantly higher levels of heavy metals compared to new oils, confirming that wear of engine components and degradation of additives are the primary sources of contamination. Iron (Fe) was found to be the dominant wear metal, reflecting the erosion of cylinder liners and piston rings, while Pb, Cr, Ni, and Cu accumulation indicated contributions from bearings, alloyed steels, and external contamination.

In parallel, the physicochemical analysis revealed substantial deterioration in oil quality during service. Used oils displayed increased viscosity and flash point, alongside increased density and ash content. These changes reflect oxidation, thermal breakdown, and additive depletion, emphasizing the diagnostic value of routine oil analysis for preventive maintenance. The depletion of the TBN in particular highlights the loss of the oil's neutralizing capacity, a key indicator of lubricant end-of-life. From an environmental perspective, the accumulation of toxic and persistent heavy metals in used oils poses significant hazards. In the absence of proper disposal and recycling practices, these wastes threaten soil fertility, groundwater quality, and human health through bioaccumulation pathways. Compared with international studies, the results obtained in Libya fall within similar ranges, yet the lack of strict waste oil regulations makes the problem more acute at the national level.

Future work should address several aspects to extend the scope of this research. First, a larger sample size covering more oil brands and vehicle types should be analyzed to strengthen the representativeness of the findings. Second, advanced analytical techniques such as Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) should be employed to enhance detection sensitivity and accuracy. Third, long-term monitoring of heavy metal accumulation in lubricants under different driving conditions would provide valuable insights into the relationship between mileages, oil degradation, and wear mechanisms. Finally, environmental impact assessments of used oil disposal practices in Libya should be undertaken, with a view to developing sustainable recycling strategies and informing national regulatory frameworks.

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