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# Comparative Investigation of Wear Metals in Virgin and Used Lubricant Oils

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## ABSTRACT

Four samples of virgin lubricating oils were categorized as A1, B1, C1 and D1 while their used oil counterparts were designated as A2, B2, C2 and D2 respectively. A dry ash method was adopted for digestion of the samples in a 1:1 ratio (w/v) of oil: concentrated $H_2SO_4$ followed by dissolution with 2 M $HNO_3$ acid. The digested samples were separately subjected to flame atomic photometry analysis for alkali and alkaline earth metals while other metals were subjected to atomic absorption spectrometric analysis. The specific densities of the virgin oils fell within the range of 0.941–0.952 while their corresponding used oil values ranged between 0.923 and 0.932. The viscosity value ranges obtained were 72.77–79.27 cp for virgin oil and 64.27–79.27 cp for used oil. The wear metal concentrations determined for virgin oil were in the range of 110–150, 17–1957, 5.0–53.3, 1.1–1.7, 3.2–14.1, 2.7–5.2, 1.5–5.4, 45.13–106.8, 46.1–61.0 mg/kg for Na, Mg, Pb, Cd, Cr, Cu, Fe, Zn and Mn, respectively. Their corresponding used oil metal concentrations were in the range of 99–193, 72–2567, 150–810, 1.1–20.3, 5.1–754, 2.4–5.13, 3.2–6.2, 13.0–73.6 and 30.6–50.7 mg/kg respectively for the same metal ions. Among the investigated metal ions of C2, Pb made up 20.63% while Cr made up 56.53% of B2. The information about these metal concentrations will be helpful in monitoring and maintaining vehicles and machine engines while also indicating which metals could be quantitatively recovered and thereby being used to solve environmental problems.

**Keywords:** atomic absorption spectroscopy, new and old oil, index ratio, vehicle engine oil

## INTRODUCTION

Global economic recessions are much felt in Africa and third world countries. Often these lead to the influx of used vehicles, machineries, engines and heavy duty trucks into third world countries as "second hand machines and vehicles" and it has become a thing of great concern. These vehicles and machineries need lubricants especially lubricating oils for proper functioning of engine parts and reduction in its wear (Aucelio 2007). The newly manufactured vehicles and machines of various categories also need lubricating oils.

Nadkarni (1991) defined a lubricant as a liquid introduced between two surfaces to reduce friction thereby leading to decrease in wear. More than 50 million tones of lubricants are consumed annually and 30% of lubricants by volume of hydraulic and transmission fluids are consumed (Nadkarni 1991). In developed nations, lubricants constitute 25% of total pollution released into the environment. Lubricants are basically 90% base oil and less than 10% additives. Vegetable oils and synthetic oils are sometimes used as base oils.

Lubricating oil from petroleum fractions are mainly composed of paraffinic, naphthenic, and small amount of aromatic hydrocarbons while metalo-organic compounds are usually added as additives (Aucelio 2007). Additives reduce friction and wear, increase viscosity, provide resistance to corrosion and aging of engine parts. Additives also serve as automotive greases to stabilize the grease against high temperature. Greases are used to pack wheel bearings and disc breaking system where much heat are generated.

It has been noted that the effectiveness of lubricating oil contributes to the life span of an engine (Maten 2008). Thus, lubricating oil functions by preventing friction between sliding or rolling engine parts; protection of surfaces from corrosion, transportation of wear metal particles and contaminants as well as transfer of heat through the engine parts.

Cassap (2008) classified metals in lubricating oils into three categories, namely wear metals, contaminants and addictive elements. He reported that analysis of lubricating oils in motor cars and motor cycles utilized in sports during 24 hours endurance championship races help in reduction of number of stops and improve the extent of time on the track. This is because analysis of the oil samples taken along the way would have indicated which component of the vehicle or motor cycle to be replaced before a total break down of the engine component is experienced. The first application of analysis of engine oil of rail road companies in 1940 was first used for detection of engine component failure of train (Eisentraut 1984).

The spectroscopy oil analysis programme (SOAP) of the United States Air Force monitors the extent of wear metals in lubricating oil by indicating trouble areas within the engine parts (Mckenzie 1981). This programme was implemented by the United States Armed Forces, commercial airlines, railways, tractor manufacturers and large trucking firms as a predictive maintenance of engine wear before physically dismantling of the engine. The Canadian Air Force authorities also adopted the programme for maintenance of their engines (Aucelio 2007).

Anderau *et al.* (1999) analyzed samples of new and old lubricating oils obtained from a customer using ICP–OES (inductive coupled plasma optical emission spectrometry). They diluted the oil in 1:100 ratio (w/v) using deodorized kerosene and found that the values of wear metals in used oil are higher than those of new oil. They also indicated that some wear metals that were not in the new oil were found in the used oil after use.

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The GBC Scientific Application note (2008) points out that periodical analysis of lubricating oil predicts damage within the engine parts and could be corrected before major break down or need for physical visual of the engine parts. The note showed that oil sample preparation involves dilution in the ratio of 1:10 or 1:5 or 1:1 with kerosene depending on the level of metals in the oil. The note also highlighted that wear metals may be present as metallic particles rather than dissolved. The particle size usually $< 1$ nm as well as the dissolved metal concentration of individual wear metals in oil vary from one element to another and are dependent on engine type, age of oils and efficiency of oil filters. Saba *et al.* (1985) prepared oil samples by diluting in 1:4 ratio with kerosene and aspirated directly into the flame of atomic absorption spectroscopy (AAS) as they proved that AAS equipped with a graphite furnace atomizer is effective for determination of Fe, Cu, Al, Mg and other critical wear metals in lubricating oils.

Aucelio (2007) studied the analysis of wear metals in engines and turbine components and found that the extent of wear is reduced by using lubricating oils. He reported that the wear could be physical generating metallic particles of varying sizes or chemicals that produce both metallic particles as well as soluble metallo-organic species. He noted that sometimes metallic debris passes through the filters and collectors into the engine ports and cause more wear.

Since used lubricating oils might contain metallic particle sizes as well as various concentrations of dissolved metals, total wear metal concentration of the oils could be carried out using flame AAS after a pre-digestion of the oil samples.

Thus, the main objective of this study was to compare the concentration of these wear metals in virgin and used lubricating oils. It will also indicate the efficiency of engines of various vehicles from which the used oils were obtained. Comparisons among the lubricating oil types of virgin lubricating oils are also be presented. The results in this study also indicated high concentration of heavy metals which are injurious to human, aquatic and terrestrial life if used oils are not properly disposed or recycled to isolate the heavy metals.

## MATERIALS AND METHODS

### Material

Four samples of known used lubricating oils were collected from vehicles in a mechanic workshop, Ibadan, Western Nigeria and stored in 5 L plastic containers. The samples were designated as used lubricant oil samples. Their corresponding virgin lubricant oils were purchased from three petrol filling stations in Ibadan. The names of manufacturing companies of these lubricant oil samples are Lubcon Oil Co., Ltd., Nigeria; A-Z Oil Co. Ltd., Nigeria; Total Lubricants Co., Nigeria while the names of the oil types are Lubcon Performa XV 50 premium quality motor oil SAE 50 API SF/CC, Lubcon oil Natta, A-Z Crown super high performance engine oil SAE 20W/50 API SG/CD and Total quartz 5000 ultra high performance multigrade engine oil 20W50 API SL/CF representing A1, B1, C1 and D1 virgin oil types respectively. The letters A2, B2, C2 and D2 represent their corresponding used oil types.

Four virgin lubricant oil samples from three manufacturers were investigated. One manufacturer produced two of the oil samples while each of the other two manufacturers produced one oil sample each.

Thus, our nomenclature for the virgin oil samples are $A_1$, $B_1$, $C_1$ and $D_1$ while $A_2$, $B_2$, $C_2$ and $D_2$ represent their corresponding used oil sample. The lubricant oil samples $A_2$ and $D_2$ are from same manufacturer but of different brand. The used oil ($A_2$) was obtained from Toyota car (1987) while $B_2$ used oil from Nissan car (1980). The $C_2$ used oil sample was obtained from Mercedes Benz 200 car (1982) model series and $D_2$ used oil obtained from Toyota car (1987), the manufacturer of virgin oils $A_1$ and $D_1$.

### Methods

The ash method of metal analysis was adopted (Mckenzie 1981). A known weight of the eight lubricating oil samples (virgin and used) were separately mixed with concentrated $H_2SO_4$ acid in a 1:1 ratio w/v and heated gently on a hot plate to dryness in an evaporating dish. It was then carefully transferred into a Galen kamp furnace and ashed at 550°C for 1 hour. Each of the ashed samples were then diluted in a little quantity of 2 M $HNO_3$ acid and made up to 50 mL mark in a standard volumetric flask. Each of the prepared samples was then subjected to analysis for alkali and alkaline earth metals using flame photometry. The designated heavy metals, addictives and other critical wear metals were analyzed using atomic absorption spectroscopy Buck 205 model with the aid of fuel rich air acetylene flame at their individual $\lambda$max wavelengths. A blank study was also carried out.

The data obtained were subjected to ANOVA statistical analysis as well as using multiple comparisons with Harmonic mean at 95% confidence level to obtain Duncan multiple range homogeneous sub sets.

**Table 1** Brief history of vehicles.

| Source of Lubrication oil | Table | Vehicle | Year | Period of oil contact with engine |
|---|---|---|---|---|
| Virgin oil | $A_1$ | Toyota | 1987 | NA |
| | $B_1$ | Nissan | 1980 | NA |
| | $C_1$ | Mercedes 200 | 1982 | NA |
| | $D_1$ | Toyota | 1987 | NA |
| Used oil | $A_2$ | Toyota | 1987 | 2 months |
| | $B_2$ | Nissan | 1980 | 2 months |
| | $C_2$ | Mercedes 200 | 1982 | 2 months |
| | $D_2$ | Toyota | 1987 | 2 months |

NA means not available

**Table 3** Heavy wear metals contaminants in lubricant oils.

| Commercial Lubricant oil types | Wear Metal Concentration (mg/kg) | | | |
|---|---|---|---|---|
| | Pb | Cd | Cr | Cu |
| A1 | 34.4 | 1.1 | 3.20 | 4.2 |
| B1 | 53.3 | 1.29 | 14.1 | 2.7 |
| C1 | 5.24 | 1.72 | 6.3 | 5.2 |
| D1 | 5.01 | 1.43 | 4.14 | 3.18 |
| A2 | 15.0 | 2.11 | 6.17 | 5.13 |
| B2 | 125.63 | 1.09 | 753.96 | 2.4 |
| C2 | 810.4 | 1.1 | 5.1 | 3.2 |
| D2 | 61.9 | 20.3 | 21.6 | 3.3 |

$A_1$, $B_1$, $C_1$, $D_1$ are virgin lubricant oil samples and $A_2$, $B_2$, $C_2$ and $D_2$ are used lubricant oil samples, concentration of wear metals are in mg/Kg.

**Table 2** Alkali and alkaline earth metals as addictives in lubricant oil.

| Commercial lubricant oil types | Wear metal concentration | | | | |
|---|---|---|---|---|---|
| | Na | K | Ca | Mg | Description of oil sample |
| $A_1$ | 133.6 | 14.7 | 43.7 | 1956.6 | Virgin |
| $B_1$ | 110.7 | 11.9 | 49.8 | 1347.3 | Virgin |
| $C_1$ | 123.4 | 241.2 | 1057.6 | 437.3 | Virgin |
| $D_1$ | 150.1 | 9.6 | 41.4 | 17.32 | Virgin |
| $A_2$ | 193.4 | 371.1 | 1104.2 | 541.1 | Used oil |
| $B_2$ | 118.2 | 17.8 | 129.2 | 127.9 | Used oil |
| $C_2$ | 172.6 | 36.2 | 199.2 | 256.7 | Used oil |
| $D_2$ | 98.7 | 12.8 | 936.96 | 71.7 | Used oil |

$A_1$, $B_1$, $C_1$, $D_1$ are virgin lubricant oil samples and $A_2$, $B_2$, $C_2$ and $D_2$ are used lubricant oil samples, concentration of wear metals are in mg/Kg.

## RESULTS AND DISCUSSION

The brief history of vehicles from which used oils were obtained is presented in **Table 1**.

The concentration of 8 wear metals (Na, K, Ca, Mg, Pb, Cd Cr and Cu) in each of the four lubricating oil of used and virgin oil samples are presented in **Tables 2** and **3**. The ratio of wear metals in virgin oils to used oils are also presented in **Table 4**. The statistics of the result are shown in **Tables 5, 6** and **7** while **Table 8** compares values obtained in the literature with those obtained in this study. **Figs. 1** and **2** describe some of the wear metal concentration distribution in the virgin and used oils respectively.

From **Table 2**, the concentration of Mg in the virgin oil decreased from 1956.6 to 541.1 mg/kg in type A lubricating oil while type B decreased from 1347 to 127.9 mg/kg. However an increase in concentration was observed for C and D types lubricating oil. The high concentration of Mg in the virgin oils of A1 and B1 makes them better than C1 and D1 virgin oils because the oils are more viscous by virtue of high concentration of Mg and thus prevents wear or corrosion which is exhibited effectively in the Nissan and Toyota cars. The decreases in Mg concentration also indicate that Mg is consumed as suggested in literature (Casap 2008; Maten 2008). Furthermore, a coolant leak is identified with the Toyota car that made use of D1 lubricating oil as a result of reduction in Na metal in the used oil (McKenzie 1981).

**Table 7** Statistical comparison of wear metals in virgin lubricating oil types.

| Metal types | Lubricating oil types wear metal concentration (mg/Kg) | | | |
|---|---|---|---|---|
| | **A1** | **B1** | **C1** | **D1** |
| Fe | 1.50 a | 2.70 b | 5.40 d | 4.70 c |
| Zn | 106.8 d | 61.4 b | 68.2 c | 45.13 a |
| Sn | 0.40 b | 0.20 a | 0.56 c | 0.47 bc |
| Mn | 61.0 d | 46.20 a | 51.2 c | 48.54 b |
| Co | 0.80 a | 0.90 a | 0.98 a | 0.86 a |
| Ni | 2.2 a | 6.0 d | 4.01 c | 3.15 b |
| Si | 1.523 a | 2.70 b | 2.59 c | 2.21 b |
| Ti | 2.20 a | 1.90 a | 1.72 a | 1.41 a |
| Pb | 34.40 b | 53.30 c | 5.24 a | 5.01 a |
| Cd | 1.1 a | 1.29 b | 1.72 c | 1.43 b |
| Cr | 3.20 a | 14.1 d | 6.30 c | 4.14 b |
| Cu | 4.2 c | 2.7 a | 5.2 d | 3.18 b |
| Na | 133.60 c | 110.7 a | 123.4 b | 150.1 d |
| K | 14.70 c | 11.90 b | 241.2 d | 9.6 a |
| Ca | 43.7 b | 49.8 c | 1057.6 d | 41.4 a |
| Mg | 1956.60 d | 1347.3 c | 437.3 b | 17.32 a |

Values with the same superscript letters along the rows are not significantly different while those with different letters are significantly different.

**Table 5** ANOVA data for lubricating oil types.

| Wear metals types | Lubricating Oil Types[a] | | | | Virgin oil types |
|---|---|---|---|---|---|
| | **A** | **B** | **C** | **D** | |
| Fe | 0.000 | 0.000 | 0.000 | 0.000 | 0.000* |
| Zn | 0.000 | 0.000 | 0.008 | 0.000 | 0.193 |
| Sn | 0.006 | $0.110^{+}$ | 0.012 | 0.009 | 0.992 |
| Mn | 0.000 | 0.000 | 0.000 | 0.000 | 0.000* |
| Co | $0.387^{+}$ | $1.000^{+}$ | 0.000 | 0.000 | 0.030* |
| Ni | 0.000 | 0.000 | 0.000 | 0.000 | 0.023* |
| Si | 0.001 | 0.000 | 0.001 | 0.000 | 0.795 |
| Ti | $0.700^{+}$ | $0.679^{+}$ | 0.000 | $0.791^{+}$ | 0.064 |
| Pb | 0.000 | 0.000 | 0.000 | 0.000 | 0.020* |
| Cd | 0.000 | $0.078^{+}$ | 0.000 | 0.000 | 0.073 |
| Cr | 0.000 | 0.000 | 0.000 | 0.000 | 0.068 |
| Cu | 0.000 | 0.017 | 0.000 | $0.441^{+}$ | 0.777 |
| Na | 0.000 | 0.000 | 0.000 | 0.000 | 0.343 |
| K | 0.000 | 0.000 | 0.000 | 0.000 | 0.783 |
| Ca | 0.000 | 0.000 | 0.000 | 0.000 | 0.187 |
| Mg | 0.000 | 0.000 | 0.000 | 0.000 | 0.982 |

$^{+}$ indicates where there is no significance difference between the virgin and used oil types at P ≤ 0.05; while *means values are significantly different among virgin oil types at P ≤ 0.05.

From **Table 3**, the presence of wear heavy metals in both the virgin and used oils, though in varying concentrations are observed. The highest value of Pb (810.4 mg/kg) and Cr (753.96 mg/kg) were obtained for C2 used lubricating oil and B2 used oil, respectively. The comparison of **Tables 1** and **3** indicates that the Mercedes Benz 200 that utilized virgin oil type C1 has experienced critical wear in a bearing whereas the Nissan car with high wear of Pb and Cr concentration indicated that wear in bearings, piston and rings and coolant liners has occurred. Among all the metal ions investigated in C2 used lubricating oil, Pb constitutes 20.63% while Cr makes up 56.53% among all the B2 used oil studied. $B_2$ contained 9.42 % of Pb. The engines of the Mercedes Benz and Nissan cars need to be dismantled and their damaged parts like bearing, piston, rings and cylinder

**Table 4** Ratio of wear metals concentration difference in used oil to virgin oil (Wear Index value).

| Oil types | Fe | Zn | Sn | Mn | Co | Ni | Si | Ti | Pb | Cd | Cr | Cu |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Type A (Toyota) | 2.44 | -0.37 | 0.45 | -0.17 | 0.19 | 16.0 | 0.45 | -0.26 | -0.56 | 0.92 | 0.93 | 0.22 |
| Type B (Toyota) | 1.30 | -0.79 | 0.50 | -0.34 | 0.00 | -0.62 | -0.26 | 0.32 | 1.36 | -0.16 | 52.47 | -0.13 |
| Type C (Mercedes Benz) | 18.11 | -0.05 | -0.29 | -0.06 | 1.04 | 0.5 | -0.19 | 2.66 | 153.7 | -0.36 | -0.19 | -0.38 |
| Type D (Nissan) | 29.55 | 0.63 | -0.36 | -0.27 | 11.67 | 1.67 | 0.36 | 0.35 | 11.36 | 13.20 | 4.22 | 0.12 |

**Table 6** Statistical comparison of wear metals in virgin and used lubricating oil types.

| Metal types | Lubricating oil types wear metal concentration (mg/Kg) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **A1 virgin** | **A2 Used** | **B1 virgin** | **B2 Used** | **C1 virgin** | **C2 Used** | **D1 virgin** | **D2 Used** |
| Fe | 1.50 a | 5.16 b | 2.70 a | 6.20 b | 5.40 a | 103.2 b | 4.7 a | 143.6 b |
| Zn | 106.80 b | 67.43 a | 61.4 b | 13.00 a | 68.20 b | 64.6 a | 45.13 a | 73.6 b |
| Sn | 0.40 a | 0.58 b | 0.20 a | 0.30 a | 0.56 b | 0.40 a | 0.47 b | 0.30 a |
| Mn | 61.0 b | 50.72 a | 46.2 a | 30.60 b | 51.20 b | 48.10 a | 48.54 b | 35.5 a |
| Co | 0.80 a | 0.95 a | 0.90 a | 0.90 a | 0.98 a | 2.0 b | 0.86 a | 10.9 b |
| Ni | 2.20 a | 37.40 b | 6.0 b | 2.30 a | 4.01 a | 6.0 b | 3.15 a | 8.40 b |
| Si | 1.52 a | 2.47 b | 2.7 b | 2.0 a | 2.59 b | 2.1 a | 2.21 a | 3.0 b |
| Ti | 2.20 a | 1.62 a | 1.90 a | 2.5 a | 1.72 a | 6.30 b | 1.41 a | 1.90 a |
| Pb | 34.4 b | 15.0 a | 53.30 a | 125.63 b | 5.24 a | 810.4 b | 5.01 a | 61.90 b |
| Cd | 1.10 a | 2.11 b | 1.29 a | 1.09 a | 1.72 b | 1.10 a | 1.43 a | 20.34 b |
| Cr | 3.20 a | 6.17 b | 14.10 a | 753.96 b | 6.30 b | 5.10 a | 4.14 a | 21.60 b |
| Cu | 4.20 a | 5.13 b | 2.70 b | 2.40 a | 5.20 b | 3.20 a | 3.18 a | 3.30 a |
| Na | 133.60 a | 193.4 b | 110.70 a | 118.20 b | 123.40 a | 172.60 b | 150.1 b | 98.7 a |
| K | 14.70 a | 371.1 b | 11.90 a | 17.50 b | 241.20 b | 36.20 a | 9.6 a | 12.8 b |
| Ca | 43.70 a | 1104.2 b | 49.80 a | 129.20 b | 1057.60 b | 199.20 a | 41.4 a | 936.92 b |
| Mg | 1956.6 b | 541.1 a | 1347.3 b | 127.90 a | 437.30 a | 2566.70 b | 17.32 a | 71.70 b |

Values with the same superscript letters along the rows are not significantly different while those with different letters are significantly different.

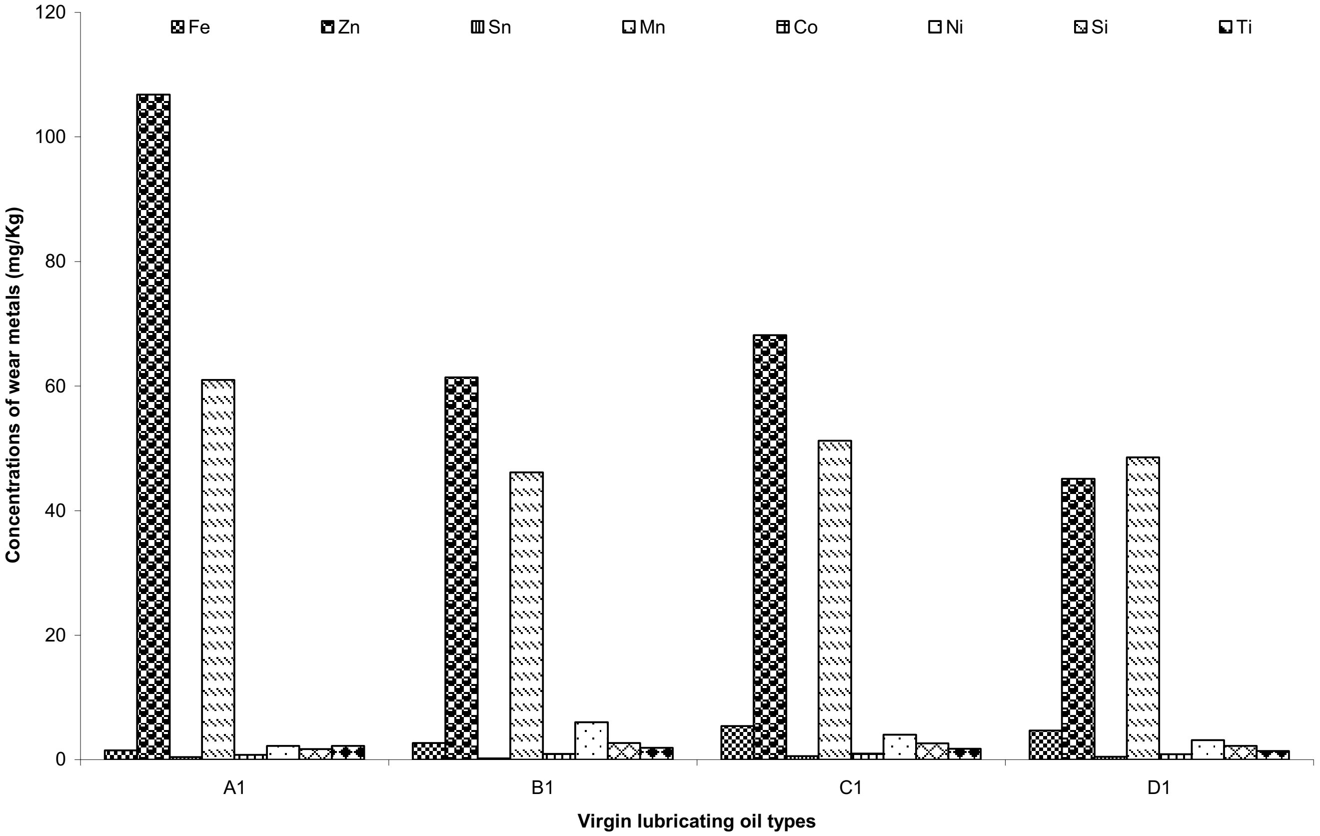

**Fig. 1 Wear metal concentrations of lubricating virgin oil types.**

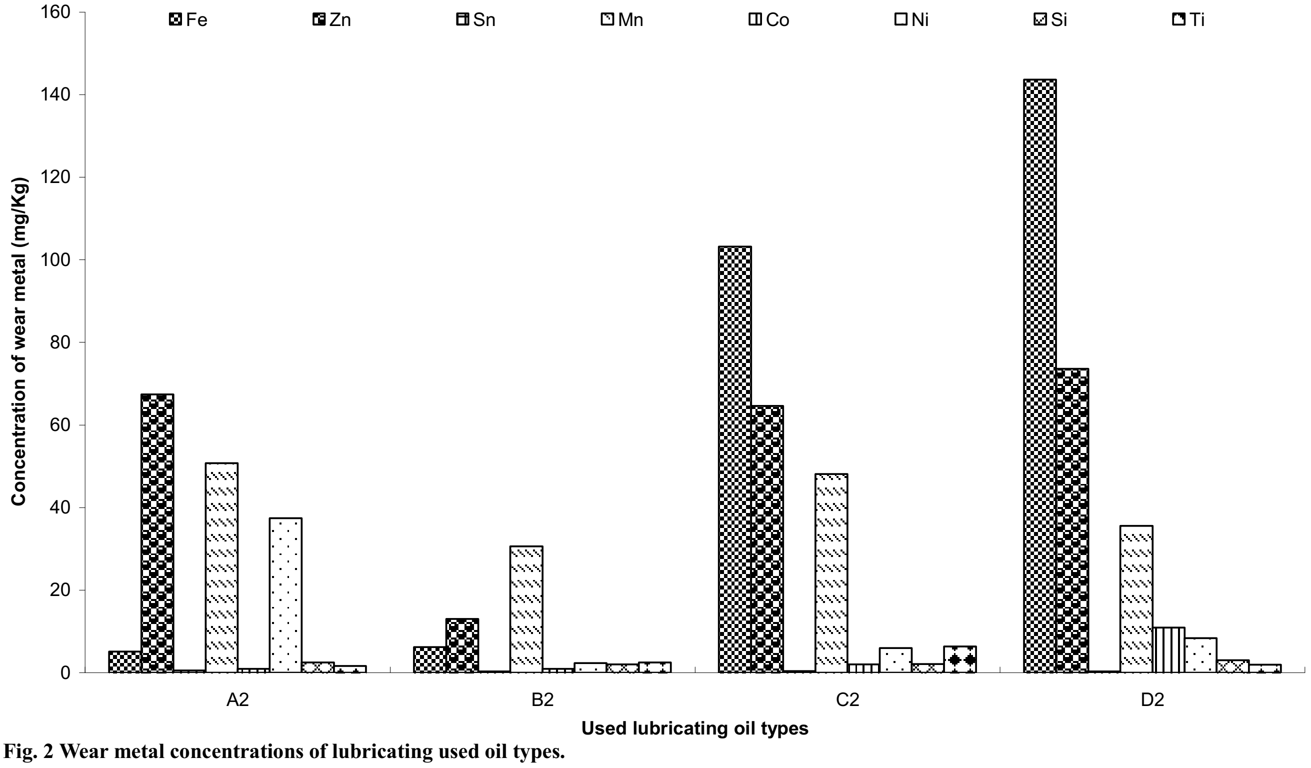

**Fig. 2 Wear metal concentrations of lubricating used oil types.**

liners replaced else their used oil if not properly disposed will cause great environmental problem. In fact, Cd has been reported to be injurious to kidney while lead causes adverse damage to nervous system, kidney and red blood cells. It has also been found that high exposure of Cr (VI) eventually result in death due to its acute poisoning effect (Viessman and Hammer 1993).

The value of Pb content for all the virgin lubricating oil types are in the 5.01-53.3 mg/kg range which is in line with that reported by Casap (2008) (16.0 mg/kg) and Andrew *et al.* 1999 (< 86 mg/kg).

However, the Cr content ranged between 3.2 and 14.1 mg/kg, a bit higher than those reported by Casap 2008 (< 3 mg/kg). Thus the four lubricants products from three manufacturers seem to be similar with other manufacturers in their lubricating oil formulation when quantities of these Cr, Pb, Cu and Cd in virgin oils are considered with those reported in literature.

From **Fig. 1**, the values of some other wear metals in virgin oil investigated are in the range (mg/kg) given below:

**Table 8** Summarized values of virgin and used oil types.

| **Wear metals** | **Casap (2008)** | | **Anderau *et al*. (1999)** | | **Concentration of wear metals (mg/kg)** | | | | **Concentration of wear metals (mg/kg)** | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **New oil** | **Old oil (mg/kg)** | **New oil (mg/kg)** | **Old oil (mg/kg)** | **$A_1$** | **$B_1$** | **$C_1$** | **$D_1$** | **$A_2$** | **$B_2$** | **$C_2$** | **$D_2$** |
| Ca | 1103 | 3014 | 1472 | - | 43.7 | 49.8 | 1057.6 | 41.41 | 1104.2 | 129.2 | 199.2 | 936.9 |
| Cd | 0.15 | 0.27 | - | - | 1.1 | 1.29 | 1.72 | 1.43 | 2.11 | 1.09 | 1.1 | 20.3 |
| Cr | 0.12 | 2.54 | < 3 | 104,000 | 3.2 | 14.1 | 6.3 | 4.14 | 6.17 | 753.96 | 5.1 | 21.6 |
| Cu | 0.58 | 3.49 | < 2.1 | 100,000 | 4.2 | 2.7 | 5.2 | 3.18 | 5.13 | 2.4 | 3.2 | 3.3 |
| Fe | 2.76 | 30.8 | < 18 | 394,000 | 1.5 | 2.7 | 5.41 | 4.7 | 5.16 | 6.2 | 3.2 | 3.6 |
| Mg | 870.8 | 323.4 | 315 | - | 1956.6 | 1347.3 | 437.3 | 17.32 | 541.13 | 127.9 | 2566.7 | 717 |
| Mn | 0.21 | 0.89 | < 2 | 97,000 | 61.0 | 46.1 | 51.2 | 48.54 | 50.72 | 30.6 | 48.1 | 35.5 |
| Na | 5.71 | 3.71 | - | - | 133.6 | 110.7 | 123.4 | 150.13 | 193.44 | 118.2 | 172.6 | 98.7 |
| Ni | 0.73 | 0.48 | < 70 | 84,000 | 2.2 | 6.0 | 4.01 | 3.15 | 3.74 | 2.3 | 6.0 | 8.4 |
| Pb | 16.0 | 8.0 | , 86 | $1.45 \times 10^7$ | 34.4 | 53.3 | 5.24 | 5.01 | 15.0 | 125.63 | 810.4 | 61.9 |
| Si | 7.15 | 10.8 | - | - | 1.7 | 2.7 | 2.59 | 2.21 | 2.47 | 2.0 | 2.1 | 3.0 |
| Sn | 7.70 | 2.53 | < 40 | 131,000 | 0.4 | 0.2 | 0.56 | 0.47 | 0.58 | 0.3 | 0.4 | 0.3 |
| Ti | 0.40 | 0.51 | - | - | 2.2 | 1.9 | 1.72 | 1.41 | 1.62 | 2.5 | 6.3 | 1.9 |
| Zn | 1038 | 1106 | $1.098 \times 10^6$ | - | 106.8 | 61.4 | 68.2 | 45.13 | 67.43 | 13.0 | 64.6 | 73.6 |
| | ICP method | | ICP – OES method | | AAS | | | | | | | |

Fe (1.5-5.4), Zn (45.13-106.8), Sn (0.2-0.56), Mn (46.1-61.0), Co (0.8-0.98), Ni (2.2-6.0), Si (17-2.7) and Ti (1.41-2.2). These values are lower than Zn (1038), Si (7.15), Sn (7.70) mg/kg values reported by Casap (2008) (**Table 8**). The Zn concentration is 20 times more than the value obtained for the virgin oils studied while Sn is 15 times higher. The value of Fe (2.76 mg/kg) in the literature is comparable to that obtained in our investigated virgin lubricating oil (1.5-5.4 mg/kg). However, the value of 0.73 and 0.40 mg/kg for Ni and Ti, respectively (Casap 2008) is lower than 2.2-6.0 and 1.41-2.2 mg/kg, respectively obtained for the virgin oils we investigated.

There is increase in the wear metal Fe in the used oil (**Figs. 1, 2**) which indicates cylinder liners, piston, rings, ball roller bearing or gears wear in all the cars (Aucelio 2007). It is not surprising as all the cars from where the used lubricating oils are obtained are more than 20 years old since the date of manufacture. More so, the values of 0.4 mg/kg for Sn in virgin oil for A1 type are lower than their corresponding value in used lubricating oil (0.58 mg/kg) which indicates that there is slight wear in bearing cages and retainers for the Toyota car that utilized A1 oil type whereas bearing cages and retainers for Mercedes Benz 200 and Nissan cars indicated that they are still relatively in good condition. The same discussion also holds for Ni metal which showed wear in the plating and the engine valve of the Toyota car. The reduction in the value of Mn metal from 46.1-61.0 to 30.6-50.72 mg/kg suggests that Mn as an addictive was consumed and an appropriate portion must be added in the lubricating oil so that the engine will last long. As such the servicing of the cars in terms of draining the oil and refilling with new one should be regular. The oil filters of the Mercedeze Benz 200 and Nissan cars are in good condition as the Si metal content in virgin and used lubricating oils are relatively constant, but the condition of the oil filter for the Toyota car suggest dirt or sand intrusion and that air cleaner need to be cleaned or changed (McKenzie 1981; Aucelio 2007).

The ratio of wear metal concentration to the same metal in virgin oil values are presented in **Table 4** as Wear Index Value (WI). WI could be defined as the ratio of concentration of leached or consumed metal ion in the used oil to the concentration of their values in the virgin oil. Thus, WI could be expressed as:

$$WI = [M^{n+}]_{\text{used}} – [M^{n+}]_{\text{virgin}} / [M^{n+}]_{\text{virgin}}$$

where $[M^{n+}]_{\text{used}}$ indicates concentration of metal ion in used lubricating oil and $[M^{n+}]_{\text{virgin}}$ symbolizes concentration of wear metal in virgin oil type.

The negative values obtained for some of the wear metals in **Table 4** indicate that the metals were consumed during the period of usage before next servicing time. The larger the negative value, the greater the quantity of wear metals (addictives) consumed and the more the effectiveness of the lubricating oil in protecting the engine parts. If WI > 1 for a particular wear metal, then the engine parts of that automobile or machinery has indicated damage. It also implies that the wear metal must have leached from a particular part of the engine into the oil and that the greater the value of the ratio, the more the wear of the engine parts. Similarly, if WI < 1, it depicts that some of the wear metals might have been consumed and thus show that those wear metals functioned well as antioxidant as well as anti- wear for that particular engine (Cassap 2008). If WI = 0, then the engine parts that are constructed with such metals are assumed to be in good condition. It also suggests that the oil lubricated the engine parts well. Furthermore, if WI = 1, then the engine parts from where the metals leached are in 50% state of good condition. Among all the wear metals, the highest WI value of 153.66 was exhibited by Pb metal and was obtained for the Mercedes Benz 200 engine that made use of type C lubricating oil. It was followed by Cr metal with ratio value of 52.47 obtained for Toyota car that made use of type B lubricant oil. The Wear Index values of 29.55 and 18.11 for Fe metal are obtained for Nissan and Mercedes Benz 200 cars that utilized type D and type C lubricant oil respectively. Since the same Toyota car utilized both type A and type B lubricant oil types, the Wear Index for all the metals, suggest that the Toyota car engine might be protected better from wear and last longer, especially from parts that are constructed with Cr metal such as gear, piston and rings (Mackezie 1981). In general, it is possible to predict the state of an engine part or a vehicle via analysis of their lubricating oil sampled from their used oil and the particular erring engine part identified.

From **Table 5**, ANOVA data indicates that all the wear metals in the lubricating oil types for comparison between virgin and used oil types are lower than 0.05 probability value with exception of Co and Ti for ‘A oil type’; Co, Sn and Ti for ‘B oil type’; Ti and Cu for ‘D oil type’ as their probability values are greater than 0.05. Futhermore, the variability of significant values of the various wear metal concentration among the different virgin oil types depicts that the wear metals are not significantly different with exception of Fe, Mn, Co, Ni and Pb.

**Table 6** shows the Duncan subset grouping of multiple comparisons of 16wear metals at 95% confidence level between virgin and used lubricating oil types. It is proved from **Table 5** that the concentration of all the wear metals in virgin lubricating oil type A are significantly different from their corresponding wear metal concentration in the used oil with exception of Sn, Co, and Ti. Similarly, concentrations of all wear metals in virgin oil type B are significantly different with exception of Sn, Co, Ti and Cd while all the wear metals concentration in virgin oil type C are also significantly different with their corresponding ones in the used oil without any exception. The implication is that the

Mercedes Benz 200 engine parts from which the used oil was obtained are in real bad condition and need to be dismantled and erring parts replaced. The type D virgin oil contained wear metals that are significantly different from those of their corresponding used oil type D with exception of Ti and Cu that showed no significant difference. The comparison of all the virgin lubricating oil types indicate that they are all significantly different in terms of metal content with exception of Co and Ti since they carry the same super script letter along the row where there is no significant different among all the virgin oils (**Table 7**). However, there is also no significant difference in Sn concentration between Virgin oil type D and those of A and C oil types. There is also no significance difference for Si between virgin oil types B and D while for Pb metal no significance difference between virgin oil type C and D is observed (**Table 5**).

**Table 8** presents a summarized form of the concentration of our investigated virgin and used oils as well as values of new and old oils reported in literature (Anderau *et al.* 1999; Casap 2008).

## CONCLUSION

It has been found that there is generally an increase in concentration of most wear metals (that are not used as addictive) in used oil when compared to their virgin corresponding lubricating oil. It has also been shown that high concentration of heavy metals like Pb, and Cr which are injurious to living things and human are contained in the used oils disposed. Thus, the high concentration of heavy metals is a signal of danger to life in areas where the used oil is not properly disposed. The study has also been able to predict which components parts of the four cars need attention of mechanics for physical dismantling of the engine and replacement of the damaged engine parts

This study suggests that the virgin oils produced by manufacturers investigated contain additives required for good lubricating oils.

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