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Comparative Study Of The Levels Of Heavy Metals In Fresh And Used Lubricating Engine Oils Distributed In Nairobi, Kenya

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Abstract: ***Engine Lubricating oils are essential products and the quality of used lubricating oils is of great importance. It calls for careful examination of the quality of spent engine oils before disposal because they are usually loaded with heavy metals which pose a threat to the environment. The determination of heavy metals in used lubricating engine oil is essential for the assessment of environmental acceptability. The research established a comparison of heavy metals (Pb, Fe, Cu, Cr, Sn, V, Ni and Ag) concentration in fresh engine oils and progressive increase in concentration during its usage in the engine until it was drained. The study revealed the correlation of the heavy metals concentration with the oil brand and type as well as a progressive increase in the concentration of heavy metals over distance travelled. This was achieved by sampling and analysing the samples collected at regular intervals of approximately 2500 km travelled so that a continuous set of data was generated during the study. Vehicles in regular maintenance service from reputed vehicle service companies in Nairobi were considered for the study. The sampling of vehicles used in the study used a quota sampling where all medium and heavy engine vehicles in a particular maintenance service station was given equal chances of selection with restriction on the maximum mileage of 210,000 km. ASTM D6595-16 standard method was employed in which trace quantities of elements dissolved and suspended as fine particles in the lubricant were measured using the rotating disc electrode (RDE) AES and the results compared with the NEMA, EPA and Idaho administrative code maximum allowable limits.***

Keywords: Heavy metals; Used lubricating engine oils; Fresh lubricating engine oils; Medium engine vehicles; Heavy engine vehicles; Rotating disc electrode; Total base number; Soot; Kinematic viscosity.

I. INTRODUCTION

Engine lubricating oil is one of the most used product in our everyday life in industries and automobiles and because of its widespread usage it poses a great danger as an environmental pollutant and other associated health hazards or risks such as threat to aquatic life. Since it is a mandatory commodity to use, studies on the levels of hazardous components such as heavy metals that have been identified as the potential environmental pollutants has to be done. It is worth noting that due to growing Kenyan economy, new industries are coming up, more and more people are acquiring motor vehicles hence the upsurge in the demand of engine oils and consequently, large volumes of lubricating oils are consumed. Statistics has shown that lubricating oil has recorded increased consumption as a proof of the growth of transport vehicles and machinery for use in agriculture and manufacturing industries. Figure 1 shows consumption of total petroleum products in million metric tonnes and in thousand metric tonnes of lubricating oils according to the Petroleum Institute of East Africa (PIEA, 2016).

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Noting that these lubricants once used are rarely treated to remove toxic heavy metals, they eventually find their way into the ecosystem and hence polluting soil, water points and food. More importantly, it poses health risks on the people handling the used oils as the oils are known to be carcinogenic and carries heavy metals which are detrimental to health. Toxicological studies of these heavy metals have established that used lubricating oil is toxic to humans [Tamada *et al.*, 2012]

The removal of Lead and Barium using Kaolinite (Aluminium-silicate) sorbent from the used lubricating oils has been studied [Mathew, 2004] in which an inorganic sorbent to adsorb heavy metals emission from incinerated metal containing waste lubricating oil has been done.

Other related study on distribution of heavy metals and hydrocarbon contents in an alfisol contaminated with waste-lubricating oil ammended with organic wastes has been done [Adesodun and Mbagwu]. The results indicated higher accumulation of Cr and Ni in twelve months, while Pb and Zn diminished with time. The results further showed higher accumulation of Cr followed by Zn, relative to other metals, with oil pollution.

In the article entitled the feasibility studies on sonochemical processes for treating used oil, a chemical-aided ultrasonic irradiation method was used to remove the heavy metals from used oil [Chia, 2008].

Cleaning of heavy metals from spent lubrication oil by adsorption process using acid modified clay [Atsar *et al.*, 2013] proved very effective in the removal of heavy metals from spent lubricating oil. In this study, spent lubrication oil was treated with naturally sourced clay materials modified with three different mineral acids. 1.0 M of nitric, sulphuric and phosphoric acids were used to modify the natural clay. Analysis of the spent lubricating oil showed the presence of Pb, Zn, Fe, Cu, Cr, Mn and Ni. Fe and Zn had the highest concentration of 73.4 mg/L and 24.1 mg/L respectively while Cu had the lowest amount of 0.02 mg/L [Atsar *et al.*, 2013].

It is generally believed that 3,000-mile oil change is suitable and various customers hold on to it only because they are basically ignorant of advances in automotive technology. The majority of OEMs call for oil changes between 7,500 to 10,000 miles which is more than twice the conventional 3,000-mile interval. Oil change intervals using synthetic oil is normally much longer than mineral based engine oils [Edmunds, 2015].

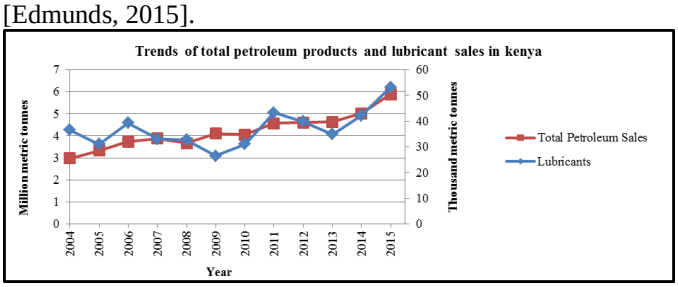

Figure 1: Trends of total petroleum products and lubricant sales in Kenya, PIEA

Levels of contamination in waste oils vary extensively, depending on different types of uses or oil change interval of the virgin lube oil and hence EPA has established a set of used oil specifications to control the potential hazards posed by used oil when burned for energy recovery. Table 2 provides these allowable parameters for the waste oil to be used as fuel as applied by EPA and Idaho administrative code [EPA, 1993 and Idaho, 2005]

Comparison between heavy metals (Cd, Co, Cr, Cu, Fe, Ni, Pb) concentration in fresh and used lubricating oils using flame atomic absorption spectroscopy have been examined in Yemen [Nozil *et al.*, 2014]. The study established an elevated concentration of heavy metals in all the used lubricating oils. The dry-ashing method adopted depicts the presence of various metals in varying levels in all the investigated metals. Fresh oils from shell reported higher concentrations of the heavy metals, whereas Fuchs oil had the lowest. Using a new filter was found to reduce the Pb concentration even with long mileage.

Investigation to compare the heavy metals content against mileage for two different engines using different lubricating oil brands has been done [Nozil *et al.*, 2014]. Fuchs Titan super GT brand was used on Toyota TownAce engine and Petromin super was used in Suzuki VIP engine. The results demonstrated a consistent increase in heavy metals concentration against the distance travelled. From their results they concluded that heavy metals present in all lubricating oils sample increases with mileage and that copper and iron were below the limits. In a related study the same authors determined the changes in the properties of the lubricating oil with respect to travelled distance. In the study the changes in total base number, kinematic viscosity, flash point, viscosity index, foaming tendency and pour point of two lubricating oil samples were evaluated with respect to mileage in order to assess the deterioration and the optimal oil drain interval. Using the heavy metals content, FTIR spectral analysis and the physicochemical test properties of the oils, the combination of all the results suggested that the oil samples can possibly be used up to 3000 km, however, the flash point and foaming tendencies increases sharply beyond this point.

The trace elements from used lubricating oils usually find their way into water bodies such as rivers, lakes, oceans or seas. Extracts from trend analysis performed over a given period in the Total ANAC database depicts the trends in the accumulation of wear elements over a period of time or distance travelled for various elements in engine oils. There is a general increase in concentration in all the wear elements analysed against distance covered.

Some oil brands exhibit higher value of wear elements in parts per million. This is a fact that has been demonstrated by previous comparative studies of used engine and fresh engine oils based on property analysis. The Pb concentration exhibited higher concentration in Castrol Magnatec oil SAE 5W30 multigrade [Syarifa *et al.*, 2013]. The mild cluster elements category (Sn, Cu and Ag) shows decreasing value of wear compared to its unused oil. The wear elements for both the Perodua Genuine and Castrol Magnatec oils were similar, which consisted of Sn, Cu, Ag, and Pb. The difference on the severity of wear was on Lead observed in both Perodua Genuine and Castrol Magnatec oil in which CM presented higher wear values.

All the trend curves showed a sudden elevation of the heavy metals towards the end of the period studied. This is because as the lubricant gradually deteriorates, its ability to protect the engine from wear is compromised and hence the

observed rise in the concentration of the heavy metal concentration.

Environmental degradation has become a major societal issue due to uncontrolled anthropogenic activity and natural factors. Entry of toxic heavy metals into human system is mainly through contaminated water, food and air. This leads to dangerous health problems. At times expensive modern corrective measures (e.g. refining of used engine oils) are not easy for a third world country like Kenya and hence emphasis has to be on preventing the used engine oils from getting into environment before prior treatment. The major hazardous metals of concern in Kenya in terms of their environmental and health effects are lead, chromium, vanadium and nickel. Human activities and vehicle emissions are the most common airborne routes through which these heavy metals find their way into the environment. Natural processes like leaching from rocks, volcanicity and forest fires can also contribute minerals like arsenic salts of natural origin. Motor vehicle emissions are a major source of airborne contaminants including cadmium, cobalt, nickel, lead, antimony, vanadium, zinc, platinum, palladium and rhodium [Balasubramanian and Wang, 2009]

Hazardous heavy metals are crucial global problem in that they pollute the environment to a great extent. These elements are chemically stable, bio-accumulative and hard to establish their safe limits. The oxidation state for these metals determines toxicity of these elements. Elements like Fe, Zn, Cu, Co, Mn and Ni are essential minerals for human metabolism but may be toxic at higher levels. Others like Hg, Pb, and Cd and As have no beneficial role at all.

Although some heavy metals are essential trace elements, majority can be toxic to all forms of life at higher concentrations due to complex compounds formed in the cells. Biodegradation is not possible in heavy metals once introduced into the environment unlike in the organic waste which can be degraded by microorganisms. They persist indefinitely and cause air, water and soil pollution. Thus, the main strategy of pollution control is to reduce the bioavailability and mobility of metals.

Remediation methods of heavy metal-contaminated environments include physical removal, detoxification, bioleaching, and phytoremediation [Seid *et al.*, 2011]. Microorganisms have evolved several intolerance mechanisms e.g. adsorption, complexation and reduction of metal ions by using them as terminal electron acceptors in anaerobic respiration.

Lead acid battery manufacturing plants are the main source of lead in the environment. Recycling of old batteries also pose a great risk to the environment as it releases lead into the environment in the ionic form Pb2+. Smelting plants of scrap metals in addition introduces As, Ni, Cr and Cd into environment since these metals are used in various metal alloys. Moreover, metals which are electroplated with copper, zinc and silver releases these elements to the environment during smelting operations in the recycling plants of scrap metals [Bahadurshah, 2011].

The sources of various heavy metals are also well defined in the oil analysis reports of many oil-testing laboratories. Total ANAC specifically states the sources of each wear element in the engine lubricating oil as shown in Table 1 [ANAC, 2015].

Management of used oil is primarily done using three methods; refining into base oil for reuse, distillation into marine diesel oil fuel and using it as untreated fuel oil [Boughton, 2004]. The third method is the most undesirable as it pollutes the environment significantly. When utilized as fuel oil, emission of lead and zinc goes up 150 and 5 folds respectively than when refined or distilled. It has been established that Zinc and lead from used oil are the major contributors to the earth surface and toxicity to terrestrial life [Boughton, 2004].

Since it is quite expensive to refine or distil used oil into base oil or marine diesel oil fuel, majority of used oil management methods adopts combustion method as a way of disposing used oil. However, this method is of high concern to environmentalist because of the high concentration of heavy metals it releases into the environment. This study highlighted the heavy metals in used engine oils especially at the time it is drained from the engines.

Before the ban on the use of leaded gasoline fuel, environmental lead pollutant originated mainly from gasoline engine exhaust fumes. Likewise, Zinc in the environment largely emanates from motor oils, tire wear, corrosion of galvanized parts and greases.

Metals	Sources
Fe	Cylinder liners, shafts, piston rings and timing gears
Pb	Connecting rod and crankshaft bearings.
Cu	Connecting rod and crankshaft bearings (in combination with lead), rocker bushings, turbo bearing and oil cooler
Cr	Piston rings, cylinder liners and valve lifters.
Al	Pistons and bearings.
Ni	Piston pin, crankshaft, camshaft, rockers, valves and hardened components.

Table 1: Sources of heavy metals in engine parts

Each heavy metal has associated toxicity effects in humans and animals alike. Clinical data detailing the toxicological impact of each of heavy metals found in fresh and used engine oils have been documented. In Kenya, no study has been done to determine at what point and how much heavy metals are introduced into the lubricant from the time the fresh oil is applied into the engine oil sump up to the time it is drained. These heavy metals negatively affect used-oil handlers e.g. vehicle mechanics who are exposed to the oil. Furthermore, lubricants containing heavy metals contaminate soils in places where there is severe spillage such as garages, water bodies when runoff water emanating from such contaminated soils finds its way to rivers, springs and other water points.

Oil change interval is determined by changes in physicochemical parameters such as viscosity, viscosity index, water contamination, fuel dilution, drop in total base number, sharp increase in soot content and not necessarily the amount of heavy metals load accumulating over time. This implies that if the lubricating oil is robust enough to maintain the above mentioned physicochemical properties for a long time frequent oil change is not recommended and as a result a point

is reached when the oil heavy metal load goes beyond the allowable limits.

The present study established a point at which the lubricating oil usage becomes heavily loaded with toxic heavy metals for the lubricants widely distributed in Kenya. The oil running hours, engine type and make, determine the kind of toxic heavy metal present in the lubricant since various metal parts have different metal alloys or coating with lead, chromium, nickel, silver and vanadium which wear out during operations and thus release these metals into the lubricant used.

II. MATERIALS AND METHODOLOGY

A. SPECTROCHEMICAL ANALYSIS

The choice of vehicles where the samples were collected from was done carefully with the following criteria strictly considered:

- ✓ The vehicles were under regular operating schedules.
- ✓ The vehicles were in regular service and maintenance schedules; this allowed the sampling of all the five intermediate samples until the oil was exhausted and discarded (drained).
- ✓ The highest total mileage of the vehicles was not greater than 210,000 km to avoid using a vehicle which was too old.

The use of vehicles which met the above criteria justified the assumption that vehicles with longer mileage which do not operate on regular service maintenance have a tendency to produce used engine oils richer in wear metals (heavy metals) than new vehicles with lower mileage.

Fresh oil samples were collected before topping the oil sump of the sampled vehicles whose registration numbers, sump capacity, fuel capacity, make, model and type are known and the initial tachometer reading recorded. The oil analysis results of the fresh oil were used as the point of reference or the benchmark against which intermediate samples were measured. The used oil samples were collected from sampled vehicles every time at approximately 2500 km interval until the oil was drained and a fresh one added. Table 3 shows the details of the vehicles, brand names of the lubricants used and sample identification information.

Two important criteria for achieving representative used oil samples were strictly followed. First, the sample was extracted from a moving volume of lubricant. The samples were only extracted when the lubricant was in circulation and thus a very homogenous and representative sample of the sump volume was collected every time the sample was drawn [Yuegang, 2014].

Secondly, the oil sample was extracted when the machine had been running for several hours before the time of sampling [Bosch, 2014]. About 120 ml of sample sufficient for complete analysis was tapped. The bottles were then sealed to avoid contamination en route to the lab for analysis.

ASTM D6595-16 for determination of wear metals and contaminants in used lubricating oils and used hydraulic fluids by rotating disc electrode atomic emission spectroscopy (RDE-AES) was used. This method provided a quick indication for abnormal wear and the presence of contamination in new or used engine lubricants. Conostan certified oil analysis standards were used for calibration. The test method detects and quantifies elements resulting from wear and contamination ranging from dissolved materials to particles approximately 10 µm in size and this explains why Spectroil M rotrode atomic emission spectrophotometer was preferred to inductively coupled plasma AES in analysing the samples collected.

B. QUALITY CONTROL

The multi-element certified oil analysis calibration standard solutions (Conostan oil-soluble organometalic complexes) were used. A quality control check sample was analysed after 25 samples during intermittent operation to confirm that the instrument was still within the required ±10 % accuracy guidelines for each element of interest. [ASTM, 2016]

III. RESULTS AND DISCUSSION

All the wear elements analyzed from 100 samples collected from the 20 vehicles were tabulated in tables 4 to 8. From the data obtained, elements with minute concentrations, moderate concentrations and the most predominant elements in the used oil are clearly illustrated which is in agreement with what previous studies has shown [Syarifa *et al.*, 2013]. In addition, comparison of the concentration of all the heavy metals in fresh oil with the used oil shows a gradual increase in the metals concentrations right from the first sample (fresh oil) all through the three intermediate samples up to the last sample (5th sample) before drainage. This trend was observed in all the twenty vehicles sampled. All the results were plotted in a bar graph (Fig. 2 and 3) so as to give a clear representation of gradual increase in heavy metals from the first to the fifth sample.

The results of the fifth samples collected were labelled as HINO/05, HINO/10, HINO/15, HINO/20, MITS/05, MITS/10, MITS/15, MITS/20, ISUZ/05, ISUZ/10, ISUZ/15, ISUZ/20, ACTR/05, ACTR/10, ACTR/15, ACTR/20, SCAN/05, SCAN/10, SCAN/15 and SCAN/20. These were the last samples collected when the exhausted oil was being discarded and pose a great danger to the environment as they are greatly contaminated with heavy metals. They are usually discarded into the environment without the necessary precaution to prevent environmental pollution - this is usually the case in many urban centres in Kenya. The concentration of the heavy metals for these samples were compared with the three standards namely NEMA (National environmental Management authority, Kenya), EPA (Environmental Protection Agency of USA) and Idaho administrative code and they were found to be way above the set limits and hence cannot be discharged into the environment without first treating the used oils to remove the excess heavy metals. The data (Table 4 to 8) revealed that beginning from the 3rd sample the heavy metals concentrations remarkably increase and when these elements are compared with the EPA, NEMA

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and Idaho administrative code, most of them exceeds the upper limits.

After examining all the results for the fresh oil before use in all the lubricant brands, it was observed that the concentration of their wear metals were generally lower than the used oils. The data from all the samples indicated that iron was the most prevalent heavy metal in the used oil. This was followed closely with copper, vanadium, chromium, tin, nickel and silver respectively.

From the data, it was also noted that with increasing distance covered there was a consistent increase in silicon concentration and this was evidenced in all samples analysed. This phenomenon is attributed to dust which finds its way through the air filter. The entry of dust containing abrasive dust into an engine accelerates wear and hence the increase in the concentration of the various elements in the intermediate samples.

The three physicochemical parameters (Viscosity, total base number and soot) also displayed expected pattern for engine oils in use as shown in Table 4 to 8. The average viscosity at 100°C for all the lubricants throughout the study period was 13.99 mm2/s which actually fall within the SAE (Society of automotive engineers)limits for 15w40 grade engine lubricating oils. Increasing soot content results in thickening of the lubricant and consequently increasing the viscosity of the oil which consequently increase wear of the engine.

Increased wear of the piston, liners and rings explains the increasing concentration iron, aluminium and chromium. Chromium is a constituent element of metal used in manufacturing piston rings, cylinder liners and valve lifters. On the other hand, iron forms about 96% w/w of the whole engine in most iron based engine blocks and connecting rods - that's why its concentration is higher compared to the other elements.

Similarly, the simultaneous decrease in Total Base Number and the increasing soot content has a direct relationship with increased wear and hence increased concentrations of the wear elements as tabulated in Table 4 to 8. Low TBN (Total base number) and high soot content compromise the ability of the oil to protect the engine hence accelerates wear and consequently increases the heavy metals concentrations.

It was observed that the iron concentrations from the 2nd to the 5th sample do not conform to the NEMA standards for effluent discharge into the environment which is set at 10 ppm. However, EPA and Idaho administrative code has not set any maximum on iron concentration for used oil.

All the samples collected had less than 10 ppm concentration of chromium and hence complied with EPA standards on this particular heavy metal. However, Idaho administrative code and NEMA sets the maximum limits at 0.33 ppm and 2.00 ppm respectively and based on this all the 5th samples reported values more than 2 ppm and hence they do not conform to these standards.

Since the maximum limit set for Lead according to EPA standards is very high, it is clear from the data that all the used oils are permissible to be used as fuel oil. The highest value reported was 10.757 ppm taken from sample identity ISUZ/05 which used Rubia Tir 7400. On the other hand, both NEMA and Idaho administrative code limits are stringent on this parameter and thus none of the 5th used oil sample could have been permitted to be discharged into the environment without prior treatment to remove lead. Similarly, copper according to NEMA standards disqualifies all the used engine oils since the 5th sample of all the lubricants had copper concentration greater than 1 ppm. Limited data is available on the toxicological consequences of tin and hence all the three standards did not mention the maximum limits. However, it is reported that over 200 mg/kg daily intake can develop short-term effects in some people [EFSA, 2005].

NEMA sets nickel concentration at 3.00 ppm and apparently none of the used oil samples tested had concentration of nickel above 3 ppm. In fact the highest value reported was 2.996 ppm which was slightly below the set limit. The delisted level for silver concentration is 0.3 ppm according to Idaho administrative code. This value is relatively stringent and thus disqualifies all the twenty samples drawn on the 5th round of sampling. This was also the case with vanadium which as per Idaho standards none of the samples could have pass the compliance limits of 2 ppm.

	Concentration of metals in ppm							
Standards	Fe	Cr	Pb	Cu	Sn	Ni	Ag	V
NEMA: Standards for effluent discharge into the environment (3rd schedule)	10.0	2.0	0.1	1.0	x	0.3	x	x
NEMA: Standards for effluent discharge into public sewers (5th schedule)	x	2.0	1.0	1.0	x	3.0	x	x
Idaho administration code	x	0.33	0.15	x	x	x	0.30	2.00
EPA Maximum allowable limits for waste oil	x	10.0	100.0	x	x	x	x	x

X stands for no data available.

Table 2: Metal concentration set by NEMA, EPA and Idaho administartive code

Vehicle Make and swept volume.	Oil brand	Sample identity
HINO RANGER JO7C 6634 cm^3	DeoMax HP	HINO/05
	DX Super	HINO/10
	Rubia Tir 7400	HINO/15
	Rimula R4 X	HINO/20
MITSUBISHI FH 6D34-0AT2 5867 cm^3	DX Super	MITS/05
	DeoMax HP	MITS/10
	Rimula R4 X	MITS/15
	Rubia Tir 7400	MITS/20
ISUZU FRR6HH1 8226 cm^3	Rubia Tir 7400	ISUZ/05
	Rimula R4 X	ISUZ/10
	DeoMax HP	ISUZ/15
	DX Super	ISUZ/20
ACTROS 3340 OM 501 LA 11946 cm^3	Rubia Tir 7400	ACTR/05
	Rimula R4 X	ACTR/10
	DX Super	ACTR/15
	DeoMax HP	ACTR/20
Scania P380 DC12-17 11705 cm^3	Rubia Tir 7400	SCAN/05
	Rimula R4 X	SCAN/10
	DeoMax HP	SCAN/15
	DX Super	SCAN/20

Table 3: Specifications of vehicles from which samples were collected

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Vehicles No.	Mileage (km)	Oil mileage (km)	Oil Sample ID		TBN (mg KOH/g)	Viscosity (mm^2/s)	Soot (%w/w)	Fe (ppm)	Cr (ppm)	Pb (ppm)	Cu (ppm)	Sn (ppm)	Ni (ppm)	Ag (ppm)	V (ppm)	Si (ppm)
1	162,741	0	HINO/01	1st	8.231	13	0.0	3.869	0.298	0.104	0.623	ND	ND	ND	ND	0.861
	165,422	2681	HINO/02	2nd	6.35	13.02	0.7	13.937	1.385	0.827	9.21	0.55	0.06	0.322	0.066	4.981
	167,986	5245	HINO/03	3rd	5.192	13.08	0.8	29.205	2.675	1.469	19.09	1.89	0.76	0.618	1.091	5.234
	170,477	7736	HINO/04	4th	4.956	13.13	0.8	68.302	4.257	2.948	29.04	2.97	2.41	0.912	2.132	15.043
	173,507	10766	HINO/05	5th	4.328	13.33	1	173.49	5.785	7.067	30.42	4.08	2.72	1.449	2.803	29.537
2	178,545	0	HINO/06	1st	10.418	13.34	0.0	2.755	0.178	0.245	0.572	ND	ND	ND	ND	0.487
	181,227	2682	HINO/07	2nd	7.421	13.47	0.4	18.102	0.662	0.994	7.595	0.94	0.43	0.388	0.012	4.475
	183,835	5290	HINO/08	3rd	6.144	13.51	0.5	38.568	2.864	4.774	17.97	2.52	1.25	0.577	1.389	5.575
	186,263	7718	HINO/09	4th	4.686	13.55	0.7	56.149	3.805	6.487	21.4	3.39	1.76	1.041	2.3	15.724
	189,203	10658	HINO/10	5th	4.22	13.57	1.2	186.013	5.919	7.394	38.03	3.43	2.55	1.732	2.56	26.203
3	151,616	0	HINO/11	1st	10.618	13.88	0.0	4.534	0.462	0.245	1.343	ND	ND	ND	ND	0.691
	154,170	2554	HINO/12	2nd	8.451	13.92	0.4	19.277	1.436	1.389	7.3	1.23	0.26	0.314	0.493	3.696
	156,877	5261	HINO/13	3rd	5.373	13.94	0.8	37.08	2.566	3.783	19.06	2.03	0.65	0.458	0.697	8.733
	159,265	7649	HINO/14	4th	4.688	14.50	0.8	47.379	4.066	7.615	27.78	3.08	2.46	0.904	1.594	11.001
	162,251	10635	HINO/15	5th	4.632	14.87	1.2	182.139	5.105	9.13	44.02	4.38	2.54	1.718	2.791	36.116
4	191,585	0	HINO/16	1st	10.88	13.88	0.0	3.73	0.482	0.48	0.757	ND	ND	ND	ND	0.24
	194,181	2596	HINO/17	2nd	9.637	14.15	0.5	7.83	0.608	1.063	8.929	0.45	0.39	0.145	0.472	3.813
	196,687	5102	HINO/18	3rd	6.959	14.24	0.8	27.552	2.033	2.854	10.48	2.1	1.28	0.521	0.881	5.805
	199,368	7783	HINO/19	4th	4.442	14.47	0.8	62.919	4.685	6.637	27.55	2.97	2.22	0.883	2.094	10.287
	202,101	10516	HINO/20	5th	4.244	14.82	0.9	187.769	5.943	8.185	45.55	3.7	2.97	1.656	2.866	25.101

Table 4: Change in wear elements concentration, total base number, viscosity and soot content against distance

Vehicles No.	Mileage (km)	Oil mileage (km)	Oil Sample ID		TBN (mg KOH/g)	Viscosity (mm^2/s)	Soot (% w/w)	Fe (ppm)	Cr (ppm)	Pb (ppm)	Cu (ppm)	Sn (ppm)	Ni (ppm)	Ag (ppm)	V (ppm)	Si (ppm)
5	156,780	0	MITS/01	1st	10.683	14.84	0.0	4.398	0.184	0.404	0.52	ND	ND	ND	ND	1.812
	159,285	2,505	MITS/02	2nd	7.875	14.86	0.4	7.847	0.768	1.08	7.385	1.05	0	0.083	0.168	4.212
	161,809	5,029	MITS/03	3rd	5.147	14.94	0.9	35.488	3.399	3.653	10.1	1.36	1.47	0.663	1.307	8.468
	164,445	7,665	MITS/04	4th	4.54	15.00	0.8	40.608	3.769	5.415	20.55	2.98	2.08	1.045	1.712	14.144
	16,7018	10,238	MITS/05	5th	4.259	13.75	1.2	106.277	5.147	8.203	32.31	4.56	2.88	1.325	2.763	31.974
6	175,298	0	MITS/06	1st	7.875	13.51	0.0	2.611	0.243	0.367	0.002	ND	ND	ND	ND	0.093
	177,876	2,578	MITS/07	2nd	6.132	13.27	0.4	18.451	0.565	1.577	6.352	0.55	0.22	0.123	0.418	3.818
	180,521	5,223	MITS/08	3rd	5.346	13.43	0.8	22.875	2.529	1.657	12.46	1.94	1.08	0.592	1.145	7.074
	182,952	7,654	MITS/09	4th	4.874	14.06	0.8	41.341	3.932	6.163	29.97	3.39	1.84	1.018	1.715	16.845
	185501	10,203	MITS/10	5th	4.577	14.69	1.0	131.954	5.276	10.113	45.71	4.51	2.52	1.363	2.534	20.163
7	155,514	0	MITS/11	1st	10.008	13.75	0.0	4.321	0.402	0.224	0.233	ND	ND	ND	ND	1.655
	158,129	2,615	MITS/12	2nd	7.554	14.98	0.5	10.064	1.234	1.537	5.481	1.33	0.3	0.357	0.111	4.441
	160,738	5,224	MITS/13	3rd	5.15	13.52	0.9	34.675	2.935	4.494	17.09	1.98	1.15	0.688	0.935	9.345
	163,159	7,645	MITS/14	4th	4.305	14.70	0.8	52.835	4.554	5.977	27.23	2.59	2.08	1.129	1.849	15.744
	165,678	10,164	MITS/15	5th	4.058	14.65	1.2	171.792	5.069	7.557	38.44	4.49	2.7	1.326	2.931	29.854
8	197,278	0	MITS/16	1st	10.598	13.51	0.0	2.272	0.065	0.404	0.532	ND	ND	ND	ND	0.259
	199,840	2,562	MITS/17	2nd	7.547	14.36	0.4	13.699	1.728	1.67	6.782	0.71	0.2	0.259	0.407	3.336
	202,562	5,284	MITS/18	3rd	5.328	13.19	0.7	32.828	3.214	1.922	13.54	2.08	0.88	0.598	1.119	9.766
	204,955	7,677	MITS/19	4th	4.248	14.81	0.9	46.205	3.86	6.756	27.14	2.51	1.68	0.894	2.373	10.173
	209,971	12,693	MITS/20	5th	4.007	14.01	1.1	154.238	5.626	8.075	33.82	3.68	2.72	1.673	2.767	28.051

Table 5: Change in wear elements concentration, total base number, viscosity and soot content against distance

Vehicles No.	Mileage (km)	Oil mileage (km)	Oil Sample ID		TBN (mg KOH/g)	Viscosity (mm^2/s)	Soot (% w/w)	Fe (ppm)	Cr (ppm)	Pb (ppm)	Cu (ppm)	Sn (ppm)	Ni (ppm)	Ag (ppm)	V (ppm)	Si (ppm)
9	153,813	0	ISUZ/01	1st	10.9	14.71	0.0	3.628	0.009	0.309	0.481	ND	ND	ND	ND	0.335
	156,450	2,637	ISUZ/02	2nd	8.57	13.94	0.5	8.307	0.616	1.87	6.035	0.96	0.14	0.315	0.301	4.345
	159,003	5,190	ISUZ/03	3rd	6.89	13.66	0.9	34.321	2.592	2.442	15.02	1.84	0.61	0.658	0.729	6.693
	161,476	7,663	ISUZ/04	4th	4.27	13.71	0.9	51.521	4.618	5.761	28.75	3.19	1.56	0.924	1.849	17.644
	163998	10,185	ISUZ/05	5th	4.011	13.77	1.1	81.688	6.92	10.757	41.23	3.56	2.94	1.302	2.886	26.629
10	172,166	0	ISUZ/06	1st	10.7	14.25	0.0	3.235	0.115	0.468	0.121	ND	ND	ND	ND	1.258
	174,692	2,526	ISUZ/07	2nd	7.43	14.09	0.4	12.204	0.872	1.078	8.619	1.17	0.08	0.012	0.323	3.025
	177,339	5,173	ISUZ/08	3rd	6.92	14.15	0.8	26.51	2.309	2.475	17.59	1.91	1.05	0.496	1.361	6.582
	179,748	7,582	ISUZ/09	4th	4.69	13.15	0.8	59.039	4.365	7.316	23.96	2.7	2.22	1.136	1.864	13.593
	182,264	10,098	ISUZ/10	5th	4.036	13.69	1.0	93.9	5.711	8.525	43.91	4.01	2.8	1.653	2.912	36.046
11	170,776	0	ISUZ/11	1st	7.985	14.67	0.0	3.454	0.157	0.28	0.158	ND	ND	ND	ND	1.057
	173,402	2,626	ISUZ/12	2nd	7.985	14.67	0.0	12.009	0.664	0.64	6.546	0.54	0.41	0.296	0.226	3.32
	175,804	5,028	ISUZ/13	3rd	6.148	13.34	0.4	32.096	3.232	3.054	12.72	2.39	1.06	0.42	0.972	7.574
	178,362	7,586	ISUZ/14	4th	5.237	13.74	0.9	69.048	3.779	4.693	26.36	2.69	2.34	1.156	2.149	11.957
	180,876	10,100	ISUZ/15	5th	4.618	14.19	0.8	168.766	5.653	6.368	33.23	4.31	2.72	1.319	2.947	40.388
12	172,485	0	ISUZ/16	1st	10.3	13.10	0.0	6.216	0.343	0.327	0.388	ND	ND	ND	ND	1.361
	175,129	2,644	ISUZ/17	2nd	9.22	13.40	0.4	16.838	1.494	0.71	8.205	1.07	0.49	0.178	0.487	4.561
	177,588	5,103	ISUZ/18	3rd	5.63	14.88	0.9	28.367	3.237	3.593	17.65	2.23	0.51	0.554	1.479	5.13
	179,997	7,512	ISUZ/19	4th	4.95	13.78	0.9	55.493	4.289	4.482	27.73	2.47	1.94	0.847	1.916	14.944
	185,118	12,633	ISUZ/20	5th	4.023	14.51	1.1	171.071	5.056	7.385	33.34	3.49	2.96	1.6	2.833	41.592

Table 6: Change in wear elements concentration, total base number, viscosity and soot content against distance

Vehicles No.	Mileage (km)	Oil mileage (km)	Oil Sample ID		TBN (mg KOH/g)	Viscosity (mm^2/s)	Soot (% w/w)	Fe (ppm)	Cr (ppm)	Pb (ppm)	Cu (ppm)	Sn (ppm)	Ni (ppm)	Ag (ppm)	V (ppm)	Si (ppm)
13	177,831	0	SCAN/01	1st	10.664	14.79	0.0	4.594	ND	ND	0.243	ND	ND	ND	ND	1.834
	180,365	2,534	SCAN/02	2nd	9.774	13.90	0.3	17.423	1.85	1.349	6.452	0.72	0.29	0.268	0.211	3.937
	182,967	5,136	SCAN/03	3rd	6.815	13.86	0.8	26.955	3.051	3.871	12.58	2.52	1.21	0.691	0.595	6.913
	185,420	7,589	SCAN/04	4th	4.404	13.76	0.7	44.34	4.523	4.739	26.24	3.2	2.09	0.852	1.897	10.019
	187,927	10,096	SCAN/05	5th	4.026	14.79	1.1	144.895	6.129	5.288	45.5	4.24	2.68	1.385	2.708	47.684
14	193,878	0	SCAN/06	1st	10.905	14.56	0.0	2.851	ND	ND	0.647	ND	ND	ND	ND	0.018
	196,510	2,632	SCAN/07	2nd	8.017	13.34	0.3	7.803	1.236	1.366	9.943	1.2	0.43	0.391	0.002	4.003
	198,959	5,081	SCAN/08	3rd	6.133	14.43	0.7	22.096	3.242	4.413	19.03	2.24	1	0.665	0.972	6.659
	201,640	7,762	SCAN/09	4th	4.954	13.39	0.8	59.643	4.661	5.748	28.16	3.13	1.84	1.143	2.117	18.976
	204,182	10,304	SCAN/10	5th	4.283	14.09	1.1	113.998	5.916	9.894	38.61	4.6	2.72	1.407	2.615	21.884
15	189,848	0	SCAN/11	1st	8.048	13.23	0.0	6.814	ND	ND	1.483	ND	ND	ND	ND	1.382
	192,410	2,562	SCAN/12	2nd	6.305	13.64	0.4	15.225	1.929	1.81	7.785	1.39	0.04	0.253	0.147	3.218
	195,061	5,213	SCAN/13	3rd	5.285	14.17	0.9	27.63	2.435	4.008	17.72	1.9	0.67	0.735	0.51	5.443
	197,417	7,569	SCAN/14	4th	4.564	14.99	0.9	54.242	4.697	4.924	22.91	3.46	2.29	0.848	1.594	11.898
	199,926	10,078	SCAN/15	5th	4.339	13.33	1.0	117.935	6.279	10.607	43.56	3.97	2.51	1.439	2.596	37.489
16	188,427	0	SCAN/16	1st	10.836	14.42	0.0	6.124	ND	ND	0.772	ND	ND	ND	ND	1.356
	190,982	2,555	SCAN/17	2nd	8.98	13.15	0.3	10.591	1.29	0.479	8.357	1.31	0.14	0.373	0.433	3.6
	193,428	5,001	SCAN/18	3rd	6.638	14.17	0.9	32.066	3.141	3.438	14.61	1.92	1.08	0.564	0.943	9.182
	196,033	7,606	SCAN/19	4th	4.989	13.33	0.8	56.391	4.319	7.616	21.83	3.44	1.98	0.919	2.414	10.095
	198,599	10,172	SCAN/20	5th	4.651	14.42	1.2	116.513	6.567	9.675	33.63	3.63	2.81	1.681	2.593	40.337

Table 7: Change in wear elements concentration, total base number, viscosity and soot content against distance

Vehicles No.	Mileage (km)	Oil mileage (km)	Oil Sample ID		TBN (mg KOH/g)	Viscosity (mm^2/s)	Soot (% w/w)	Fe (ppm)	Cr (ppm)	Pb (ppm)	Cu (ppm)	Sn (ppm)	Ni (ppm)	Ag (ppm)	V (ppm)	Si (ppm)
17	151,606	0	ACTR/01	1st	14.351	13.13	0.0	5.592	0.024	0.242	0.014	ND	ND	ND	ND	0.487
	154,155	2,549	ACTR/02	2nd	12.358	14.76	0.5	13.373	1.265	0.518	8.176	1.51	0.24	0.372	0.435	4.826
	156,857	5,251	ACTR/03	3rd	10.269	13.23	0.7	31.153	2.907	4.679	11.86	1.63	1.38	0.487	0.535	7.064
	159,239	7,633	ACTR/04	4th	8.28	13.70	0.7	49.965	4.93	6.625	22.5	3.22	2.03	1.107	1.633	15.59
	161,810	10,204	ACTR/05	5th	7.354	14.04	1.0	85.235	5.792	7.47	48.93	4.51	2.77	1.764	2.683	47.186
18	162,731	0	ACTR/06	1st	10.8	14.24	0.0	2.261	0.012	0.281	0.371	ND	ND	ND	ND	1.97
	165,407	2,676	ACTR/07	2nd	9.36	14.31	0.3	19.061	1.659	0.59	9.582	1.48	0.5	0.277	0.213	4.719
	167,966	5,235	ACTR/08	3rd	5.92	14.78	0.9	28.096	2.634	1.66	19.91	2.51	0.88	0.506	0.661	6.831
	170,451	7,720	ACTR/09	4th	4.48	14.18	0.7	65.261	4.88	4.465	22.89	3.4	2.07	1.099	2.068	14.051
	172,999	10,268	ACTR/10	5th	4.36	14.03	0.9	127.795	5.075	7.012	48.29	3.57	2.92	1.357	2.709	35.333
19	191,575	0	ACTR/11	1st	10	14.34	0.0	4.876	0.025	0.386	0.996	ND	ND	ND	ND	0.607
	194,166	2,591	ACTR/12	2nd	8.02	14.01	0.4	18.452	0.945	0.727	8.617	1.19	0.35	0.261	0.07	3.138
	196,667	5,092	ACTR/13	3rd	6.12	14.15	0.9	32.072	2.975	3.992	10.67	1.86	0.78	0.686	0.893	8.793
	199,342	7,767	ACTR/14	4th	4.56	14.02	0.7	54.184	4.78	7.474	26.53	3.13	1.66	0.955	1.788	16.942
	201,885	10,310	ACTR/15	5th	4.05	14.52	1.0	70.433	5.703	10.139	38.32	3.81	2.68	1.263	2.578	24.047
20	178,535	0	ACTR/16	1st	7.866	13.81	0.0	3.668	0.076	0.109	1.191	ND	ND	ND	ND	0.219
	181,212	2,677	ACTR/17	2nd	6.295	14.17	0.5	12.108	1.952	1.694	7.541	1.09	0.12	0.359	0.399	4.869
	183,815	5,280	ACTR/18	3rd	5.443	14.45	0.9	22.009	2.042	2.798	10.13	2.33	1	0.448	1.407	6.498
	186,237	7,702	ACTR/19	4th	4.889	14.02	0.7	66.877	4.023	7.241	21.31	2.53	2.29	1.137	1.562	12.963
	188,810	10,275	ACTR/20	5th	4.382	14.00	1.1	97.028	6.141	9.286	34.34	4.22	2.61	1.702	2.504	28.94

Table 8: Change in wear elements concentration, total base number, viscosity and soot content against distance

Accuracy, bias and Precision of the data was determined directly by 10 replicate analyses with the test method on a 100 ppm certified reference standard for all the test elements. Accuracy = $\frac{\bar{x}}{u}$ x 100, Bias = $\frac{\bar{x}-u}{u}$ x 100 which gave (90%-110%). Precision was determined by expressing the standard deviation as a percentage of the mean of the 10 test values. Precision = $\frac{s}{\bar{x}}$ x 100 which gave (2% - 8%). Where $\bar{x}$ = mean of the 10 test values, u = true value given for the 100 ppm standard and s is the standard deviation. Method Detection Limit (ppm): MDL for Fe, Ag, Cr, Cu, Ni, Sn, Pb and V were 0.21, 0.02, 0.36, 0.09, 0.66, 0.88, 0.2 and 1ppm respectively. ND stands for not detected.

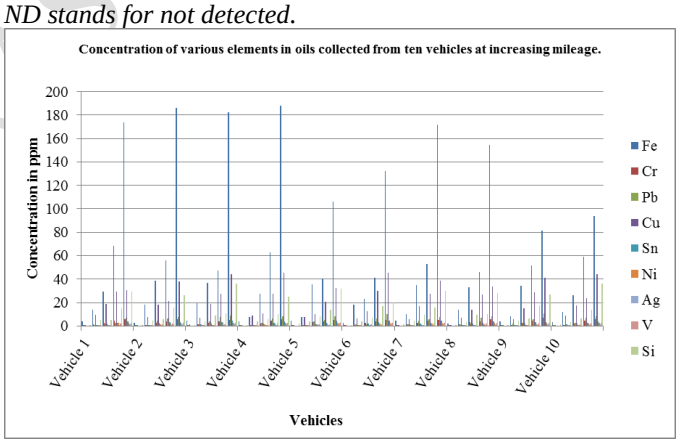

Figure 2: Chart showing gradual increase in concentration of metals against distance travelled from 1st to 5th sample.

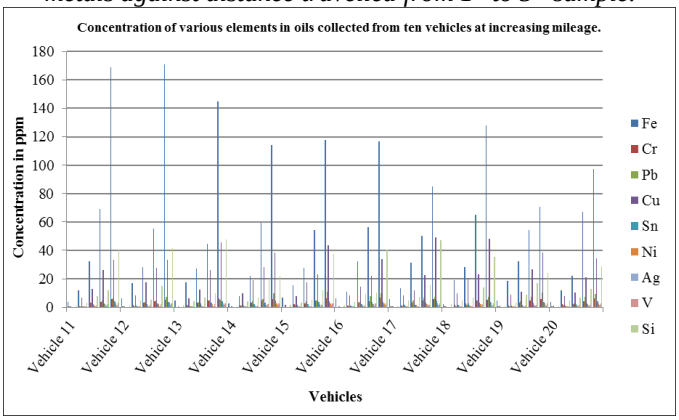

Figure 3: Chart showing gradual increase in concentration of metals against distance travelled from 1st to 5th sample

IV. CONCLUSION

The Kenya gazette supplement No. 68 (Legal notice No. 120) of 2006 gives the standards for effluent discharge into the environment. The 3rd and 5th schedule enumerates both the organic and inorganic compounds of the effluent and the maximum allowable limits for effluent discharge into the environment.

It is evident from the data obtained that most of the heavy metal concentrations exceeds the maximum limits set by NEMA and Idaho administrative code and hence it was concluded that none of the used oil meet the specification of the two standards and consequently declared unfit to be discharged into the environment as ordinary effluent. However, according to EPA all the used oil samples could have been permitted to be used as fuel oil as they meet the standards. All the used oil sampled and tested had one or more of the eight heavy metals concentrations going beyond the set limits as per NEMA and Idaho administrative code rules and standards. This study suggested that any used oil drained beyond this point should be treated by refining into base oil or distilled for use as fuel oil. This conclusion was arrived at after comparing the maximum values stated in table 2 with the final heavy metals results tabulated in table 4 to 8. In addition the study established the relationship between the lubricant running hours or mileage and the progressive accumulation of heavy metals over time. From this relationship wear profile trends was established as shown in Fig. 2 and 3. Based on these results a policy can be formulated which governs the extent of engine oil drain interval. The study concluded that there is a marked difference between fresh oil and used oil in that the later is laden with toxic heavy metals.

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