

**KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY
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**LEVELS OF CONTAMINANTS IN USED MOTOR OIL AND THEIR
POTENTIAL EFFECT ON THE ENVIRONMENT**

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THE MASTER OF SCIENCE DEGREE IN ENVIRONMENTAL SCIENCE**

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DECLARATION

I hereby declare that this thesis represents my own work towards the Degree of Master of Science programme undertaken. And to the best of my knowledge and belief, it contains no material which has been previously included in a thesis or dissertation submitted to this or any other institution for diploma, degree or any other qualification, except where due reference has been made in the text.

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ABSTRACT

Motor oil used by internal combustion engines requires replacement over a period due to contamination that affects its lubricating functions. The used motor oil finally ends up in the environment, whose physicochemical compositions are unknown to determine the impact. This thesis contains information concerning the environmental impact associated with used motor oil. Some of the various ways by which it enters the environment were reviewed. The physicochemical properties (heavy metals, volatile aromatic hydrocarbons, total petroleum hydrocarbons, H_2S , density, specific gravity, water content, viscosity, pour point, flash point, soot content, and colour), determined by collecting ten used motor oil samples each from private and commercial vehicles and two samples of fresh motor oil for petrol and diesel engines using the American Standard for Testing Measurement (ASTM) are as described. The results showed that the used oils recorded high levels of contaminants above the EPA maximum permissible limit for waste oils. Again the commercial vehicles recorded high levels of contaminants in the used oils than the private vehicles. It can be concluded that motor oils have significant amount of harmful substances and metals, and therefore must be treated to reduce these contaminants levels before they are reused or final disposal into the environment.

DEDICATION

I dedicate this Thesis to my Lord and Saviour Jesus Christ.

To Him be all the glory; World without end.

Amen!



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I thank the Lord God Almighty in the name of my Lord and Saviour Jesus Christ for inspiring me by the power of the Holy Spirit to make this programme a success. Glory, Honour, Praise and Power be unto the Lord Jesus Christ for His Lordship over my life and my entire family.

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LIST OF ABBREVIATIONS



ACS	American Chemical Society
API	American Petroleum Institute
As	Arsenic
ATSDR	Agency for Toxic substances and Disease Registry
BTEX	(Benzene, Toluene, Ethyl benzene, and Xylene)
Ba	Barium
Cd	Cadmium
Cr	Chromium
CMS	Chip Mess System
cSt	Centi Stroke
Cu	Copper
EPA	Environmental Protection Agency
Fe	Iron
IPCS	International Programme on Chemical Safety
LPG	Liquefied Petroleum Gas
Mn	Manganese
Ni	Nickel

PAH Polycyclic Aromatic Hydrocarbon

Pb Lead

PC Personal Computer

PCB Polychlorinated Biphenyl

SAE Society of Automobile Engineers

STDEV Standard Deviation

TOR Tema Oil Refinery

TPH Total Petroleum Hydrocarbon

V Vanadium

VI Viscosity Index

VII Viscosity Index Improver

"W" Winter

Zn Zinc

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CHAPTER ONE

1.0 INTRODUCTION

1.1 Background Information

Motor oil is suitable for use in engine crankcase. It can also be used to lubricate electric motors. It is used to lubricate various parts of internal combustion engines as well as the moving parts (Klamman, 1984) to reduce friction, prevent corrosion, dissipate heat, and hold in suspension the micrometer-sized by-products of engine wear, combustion (soot) and oil degradation products (Ritter, 2013).

Motor oil is about 90% paraffinic hydrocarbon base stock distilled from crude oil, with the remainder constituting the "additives package" (Bachelder, 2006). The additives package may differ depending on the manufacturer, but they are mostly detergent inhibitor package and viscosity index improvers (Nehal, 2011). There are two major categories of base oils and these are mineral base oil and synthetic base oil (Magnante, 2002). The mineral base oils are made from crude oil (IARC, 1984) while the synthetic base oils are chemically synthesized (Magnante, 2002; Randles, *et al.*, 2007). The mixture of these two base oils in certain proportions produces semi-synthetic motor oil (Jackson, 1987; Mobile 1, 2005). There are standards for motor oil set by the Society of Automobile Engineers (SAE) based on viscosity (SAE, 1999); which allows motor oil to be graded as single-grade (i.e. cannot use Polymeric Viscosity Index Improvers), and multi-grade (i.e. can use Polymeric Viscosity Index Improvers).

There are various brands of motor oils, and the basic differences are the base oils and the additives used by the manufacturers (Klamann, 1984) which determine the quality.

The quality of mineral base oils depends on the composition of the original crude oil and the refining processes while that of synthetic base oil is based on the ability of the formulator (synthetic chemist) to chemically synthesize selected molecular structures at targeted specifications to obtain the desired properties (Jackson, *et al.*, 1987). Specific additives, depending on the brand and the application are also selected based on the molecular structure of the base oil and other properties such as thermal and oxidation stability, traction, volatility, viscosity, pressure, shear strength, flash point and pour point (Hentschel, 1985). Additives such as rust and corrosion inhibitors, anti-wear and extreme pressure (anti-seize or antiscaffing), antioxidants, dispersants, detergents are meant to serve various purposes in the motor oil but their compositions may differ with respect to the brand. For instance, rust inhibitors are designed to reduce oxidation and neutralize acids (Nehal, 2011). They have high polar attraction toward metal surfaces (Rizvi, 2009; Leslie, 2003) and interact with the metal surface to form obstinate, continuous film that prevents water from reaching the metal surface. Organosulfur and organo-phosphorus compounds are usually used as anti-wear and extreme pressure (anti-seize or anti-scaffing) additives (Leslie, 2003). The type and number of chemicals used as additives also comes with cost (Jackson, *et al.*, 1987), which could influence the quality of the brands.

However, synthetic motor oils are meant to meet needs that mineral motor oils cannot. They do not have undesirable weak links inherent in conventional mineral oils that break down in extreme heat and congeal in extreme cold (Mobil, 2005), and are therefore meant for high performance engines with extreme operating temperatures.

In the process of normal use, motor oil gets contaminated with impurities such as dirt, products of combustion, wear metals from engine parts, fuel, and toxic chemicals (based on chemical composition of additives as well as molecular structure of base stock) (Roy, 1997).

These contaminants usually darken the motor oil (Scott, 2005). The additives breakdown and the oil become deteriorated losing its lubricity (Livingstone, *et al.*, 2009). However, the used oil finally ends up in soil, air and water by escape and loss of oil during engine operation, application on rural roads for dust suppression, asphaltting with asphalt containing oil, and indiscriminate disposal or landfill (Rafael, 1988) and cause pollution.

1.2 Statement of the Problem

Motor oil used by internal combustion engines requires replacement over a period due to contamination (Elena and Pichtel, 2004), which affects its lubricating functions (Livingstone, *et al.*, 2009). Some of these contaminants include products of combustion, engine wear, dirt, and fuel (Roy, 1997). The used motor oil removed from vehicles is finally released into the environment, whose physicochemical composition is unknown. Studies have shown that used motor oil is a source of oil contamination of waterways (USEPA, 2003; Sander, 2009). It has the potential to contaminate soil (Abdulsalam, *et al.*, 2012), and also release volatile organic compounds as well as combustion products into the atmosphere and cause undesirable conditions (Hopmans, 1974; Rafael, 1988).

1.3 Main Objective

To assess the physicochemical properties of used crankcase lubricating oil from private and commercial vehicles in Tema, Ghana.

1.4 Specific Objectives

- i. To measure the physical properties such as density, specific gravity, water content, viscosity, pour point, flash point, soot content, and colour of used motor oil.
- ii. To measure levels of heavy metals (Pb, Ba, Cr, Cd, Zn, Fe, Cu, Ni, V, As and Mn), volatile aromatic hydrocarbons (benzene, ethyl benzene, toluene and xylene - BTEX), total petroleum hydrocarbons (TPH), and hydrogen sulfide.

1.5 Justification

The rampant indiscriminate disposal and re-use of used motor oil across the country has necessitated a study on the physicochemical characters of used motor oil in order to assess its potential impact on the environment; to enable stakeholders and policymakers to make informed decisions to address the problem which could be harmful to biota.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Nature of Motor Oil

The colour of fresh motor oil is amber. However, the oil gets dirty in the process of its normal use as a result of contamination and become darker (Scott, 2005). It is slippery, and often appears out of the exhaust pipe as blue/gray (Goering and Fry, 1984).

2.2 Origin of Motor Oil

After the invention of car wheel it was discovered that a smear of cooked animal fat on the axle made pushing easier (Scott, 2005). This brought about the birth of lubrication technology. Vegetable oils were also used in early times for lubrication (Johnson, *et al.*, 2002) as well as by-products of crude oil (Kramer, *et al.*, 2001) to protect the sliding and rotating metal parts of the early internal combustion engines. Originally, each new vehicle designer had its own type of lubrication oil products. However, as automobile numbers grew standardization set in, and by the early nineteen thirties, vehicle manufacturers had recognized the need to fixed standards of performance of lubricants and fuel so that vehicles could be sold anywhere world-wide without major modifications (Scott, 2005). They made the decision to compare and define lubricating oils by viscosity which reflects on the internal shear strength of the liquid. The Society of Automobile Engineers (SAE) decided to compare the viscosity of oils at 100 °C, which is the approximate engine operating temperature (SAE, 1999). Viscosity decrease as temperature increase (Troyer, 2002), and mineral oils become very thin at about 100 °C (Scott, 2005).

The SAE then set down numbers to define ranges of viscosities as shown in the table below:
(SAE, 1999).

Table 2.2.1 SAE Kinematic Viscosity Rating for Engine Oil

Viscosity at 100	
Centi Stoke (cSt)	SAE Rating
16.3 - 21.9	50
12.5 - 16.3	40
9.3 - 12.5	30
5.6 - 9.3	20
less than 5.6	10

SAE 30 became accepted as the standard for engine oil, giving reasonable film strength for metal bearings. This weight oil is usable to around -10 °C before it become too thick to move round the engine. Lighter and heavier weight oils were available for extreme climate use. Racing engines which need greater film strength due to higher bearing loads generally called for the 40 and 50 weight oils. However, Engine oils needed to be changed from summer to winter due to variable weather conditions. Therefore straight SAE 30 and SAE 50 oils were transformed to SAE 20w30 and 20w50 respectively by the addition of viscosity modifiers to address the need. To differentiate between 'straight' oils and those which had viscosity modifiers added winter rating test was introduced, leading to oils being classified for cold temperature use as shown in Table 2.2.2: (SAE, 1999).

Table 2.2.2 SAE Winter Rating for Engine Oil

Low Temperature	
Temperature at which oil is usable	SAE Rating
-5°C	25w
-10°C	20w
-15°C	15w
-20°C	10w
-25°C	5w
-30°C and below	0w

Mineral oil was found to deteriorate quickly, especially when mixed with fuel residues; losing its lubrication and protective properties (Mark, 2003). Advances in the petrochemical industry led to the introduction of synthetic detergent packages, anti-wear and antiscaff additives (Scott, 2005). However, with metallurgy and engine manufacturing technology advances, mineral oil still had some challenges, especially in the Aircraft industry. Gas turbine engines fry mineral oil on contact due to the high pressures and temperatures involved. This brought about the introduction of synthetic lubricants using Poly Alfa Olefins (PAO) (LePera, 2000).

.3 Types of Motor Oil

2.3.1 Mineral Motor Oil

Mineral motor oil is the term used to describe motor oils manufactured with base oil derived from crude oil (IARC, 1984; Magnante, 2002). These type of oil include mineral engine oil 200 5w30 11, GB 5000 mineral engine oil, Classic light 20w-65 mineral oil, Classic medium 25w-70 mineral oil, Classic heavy 40-70 mineral oil, MC4ST 20w-50 SAE 30 mineral oil, MC4ST HD50 SAE 50 mineral oil etc.

2.3.2 Synthetic Motor Oils

Synthetic motor oil refers to motor oils manufactured from chemically synthesized base oil at targeted specification to obtain desired properties (Magnante, 2002) ideally suited for high performance engines with extreme operating temperatures (Randles, *et al.*, 2007). These include Series 3000 SAE 5W-30 synthetic heavy duty diesel oil, XL-7500 synthetic motor oils, SAE 10W- 30 synthetic motor oil, SAE 60 synthetic heavy racing oil, synthetic natural gas engine oil, SAE 20W-50 synthetic high performance motor oil etc.

2.3.3 Semi-synthetic Motor Oil

Semi-synthetic motor oils are manufactured from a blend of mineral base oil and about 30% synthetic base oils (Jackson, 1987; Mobile 1, 2005). Semi- synthetic oils are better suited to emissions controls and offers enhanced resistance to high operating temperatures (LePera, 2000). These include XP5 20W-50 semi-synthetic racing oil, SAE 5W-20 semi-synthetic oil, 5W30 semi -synthetic oil, 10W40 semi -synthetic oil etc.

.4 Grades of Motor Oil

2.4.1 Single-grade

Single-grade motor oils are defined by Society of Automobile Engineers (SAE) J300 classification system as oil that cover a single requirement and cannot use a polymeric viscosity index improver. SAE has established eleven viscosity grades; six winter-grades with the designation “W” and five non-winter grades. These are 0W, 5W, 10W, 15W, 20W, 25W, 20, 30, 40, 50, and 60 (SAE, 1999). Motor oil grade for winter is based on the coldest temperature at which the oil flows; and the viscosity grade is directly proportional to the temperature at which the oil can flow. The higher the viscosity of motor oil the higher the SAE viscosity grade. However, the kinematic viscosity of single non-winter grade oils is measured at a temperature of 100 °C (cSt) (SAE, 1999).

2.4.2 Multi-grade

Engines are exposed to wide range of temperatures such that specific motor oil can have high viscosity when cold and low viscosity when hot. The differences in viscosities between the temperature extremes for most single-grade oils are very wide and to bridge these gaps viscosity index improvers are added to the oil. The oil then becomes multi-grade. The SAE designation for multi-grade oils includes two viscosity grades; for example, *10W-30* designates common multi-grade oil. The first number '10W' is the viscosity of the oil at cold temperature and the second number is the viscosity at 100 °C. The two numbers used are individually defined by SAE J300 for single-grade oils. Therefore oil labeled as 10W-30 must pass the SAE J300 viscosity grade requirement for both 10W and 30. However, motor oil can be labeled as

2

either single or multi grade if it does not contain any viscosity index improvers, but meets the requirement for multi-grade (SAE J300, 1999).

.5 Brands of Motor Oil

There are various brands of motor oils on the market which includes AMSOIL, Royal Purple, Castrol, Chevron, Cosworth, Innotec, Kendall Motor Oil, Mobil 1, Neo Synthetic Oil, Pennzoil, Quaker State, Pure Power Lubricants, Rotella T, Valvoline, peak, Mobile super, Chalet, 76 Lubricants Company, Bel-Ray Company, Inc., Innotec, Kendall Motor Oil Lubrication Engineers, Maxima Racing Lubricants, Neo Synthetic Oil, RedLine Synthetic Oil Corp., Quartz, and Motorcraft. These are mineral, synthetic or semi-synthetic motor oil, and the basic differences are the base oils and the additives used by the manufacturers (Klamann, 1984); which determines the quality. The quality of the mineral base oils depends on the composition of the original crude oil and the refining processes while that of synthetic base oil is the ability of the formulator to chemically synthesize selected molecular structures at targeted specifications (Jackson, 1987). These synthesized molecular structures include hydrocarbons (e.g. polyalphaolefins, polyisobutenes, cycloaliphatics, alkylated aromatics etc.), esters, polyethers, halogenated fluid and silicones (Gunderson and Hart, 1962). Specific additives, depending on the brand and the application (Jackson, 1987) are also selected based on the molecular structure of the base oil and other properties such as thermal and oxidation stability, traction, volatility, viscosity, pressure, shear strength, flash point and pour point (Hentschel, 1985).

2.6 Components and Characteristics of Fresh Motor Oil

Motor Oil is about 90% paraffinic (heavy) hydrocarbon base stock distilled from crude oil, with the remainder constituting the "additives package," (Bachelder, 2006). The additives package may differ depending on the manufacturer but they are mostly detergent inhibitor package and viscosity index improvers (Nehal, 2011).



2.6.1 Base Oil

Base oil is defined by the American Petroleum Institute (API) as oil with a boiling point range between 287.8 and 565.6 °C; consist of hydrocarbons with 18 to 40 carbon atoms. This can be either paraffinic or naphthenic in nature depending on the chemical structure of the molecules (Global, 2010). There are two major categories of base oils and these are mineral base oil and synthetic base oil (Magnante, 2002). Base oils are divided into five groups. Groups I-III are mineral oil, with little extra refining done to Group I and some cracking done to Group III. Groups IV and V are synthetic oils (Noria, 2012).

Mineral Base oils

Mineral base oils are made from crude oil (IARC, 1984). The hydrocarbon composition and physical characteristics of the oil depend on both the composition of the original crude oil and the processes used during refining (Concawe, 1997). Mineral base oils break down in extreme heat and congeal in extreme cold due to impurities such as sulfur, trace metals and carbon residues, which can limit its performance (Mobil, 2005). They are further subdivided into three subgroups such as Group I, Group II, and Group III as follows: (Noria, 2012).

Group I

Group I base oils are classified as less than 90% saturates and has about 0.03% sulfur with a viscosity-index range of 80 to 120. The temperature range for these oils is from 0 to 65.5 °C, and is solvent-refined.

Group II

Group II base oils are defined as being more than 90% saturates with less than 0.03% sulfur and a viscosity index of 80 to 120. They are often manufactured by hydrocracking.

Since the entire hydrocarbon molecules of these oils are saturated, Group II base oils have better anti-oxidation properties.

Group III

Group III base oils are greater than 90% saturates with less than 0.03% sulfur and have a viscosity index above 120. These oils are refined even more than Group II base oils and generally are severely hydrocracked. This longer process is designed to achieve purer base oil. Although made from crude oil, Group III base oils are sometimes described as synthesized hydrocarbons.

Synthetic Base Oil

Synthetic base oils are artificially formulated by polymerizing short chain hydrocarbons into longer chain hydrocarbon polymers (Randles, *et al.*, 2007). The degree of variation in molecular size, chain length and branching is much less than occurs in base stocks extracted from crude oil (OECD, 2004). The synthetic oils do not contain undesirable weak links such as waxes inherent in conventional mineral oils (Randles, *et al.*, 2007) because the process is designed to build specific molecules in combination with additives necessary to achieve the desired properties of the finished product. These oils are characterized by higher oxidative and thermal stability, lower pour points, lower volatility, higher viscosity index, higher flash points and higher lubricity (Kroschwitz, 2004). Synthetic base oils are often blended with mineral oil in order to provide desired combinations of properties (Boyde, 2002). There are many types of synthetic base oils which include polyalphaolefins (PAOs), esters, alkylated naphthenes (Gunderson and Hart, 1962) under group IV and V. However, the widely used are the PAOs (Randles, *et al.*, 2007).

Group IV

Group IV base oils are PAOs. They have much broader temperature range and are great for use in extreme cold conditions and high heat applications (Noria, 2012).

Group V

Group V base oils are classified as all other base oils, including silicone, phosphate ester, polyalkylene glycol (PAG), polyolester, biolubes, etc. (Gunderson and Hart, 1962). These base oils are at times mixed with other base stocks to enhance the properties. An example is PAO-based compressor oil that is mixed with a polyolester.

2.6.2 Additives

Additives are chemical compounds added to motor oil to obtain targeted specifications (Nehal, 2011). They impact positively by improving the original properties, add new and useful properties and also reduce the rate at which undesirable changes occur in the life span of the product (Ludema, 1996; Leslie, 2003). These additives are detergent inhibitor packages and viscosity index improvers.

2.6.2.1 Detergent Inhibitor Packages

Detergent inhibitor packages are made up of dispersants, detergents, friction modifiers, seal conditioners, anti-wear and extreme-pressure additives, anti-oxidants, rust & corrosion inhibitors, pour point depressants, anti-foams, and diluents oil (Nehal, 2011).

2.6.2.2 Viscosity Index Improvers

Viscosity index is a scale to compare the rate of viscosity change with temperature among different fluids (Margareth, *et. al.*, 2010). Organic liquids thin out when heated and thicken up when cooled but differs in the rate at which it occurs.

A fluid that thins more when heated and therefore thickens more when cooled has a lower viscosity index than the one that thins less and thickens less (SAE, 1999).

Viscosity index improvers, also known as viscosity modifiers are chain high molecular weight polymers (Obasi, 2014) which can cause the relative viscosity of an oil to increase at high temperatures and decrease at low temperatures (SAE, 1999). This occurs as a result of change in the polymer's physical configuration with increasing temperature of the mixture. The huge molecules coil up when cold and uncoil when hot (Rizvi, 2009; Leslie, 2003; Margareth, *et. al.*, 2010).

2.7 Characteristics of Used Motor Oil

The chemical composition of motor oil varies with the crude oil type, refining process, and the additives used in the formulation (Rafael, 1988). However, motor oil is altered during normal use (Roy, 1997), and do not have the same components and characteristics due to chemical transformations as a result of high temperatures and mechanical constraints that the oil undergo during engine operation, breakdown of additives, the presence of contaminants (products of combustion, metals from engine wear and tear, fuel, dirt, water etc.) (Rafael, 1988). However, the major components may consist of aliphatic and aromatic hydrocarbons such as Phenol, Naphthalene, Benz anthracene, Benzo, Pyrene, and Fluoranthene (Upshall, 1993).

2.7.1 Aromatic Hydrocarbons

The presence of aromatic hydrocarbons in used motor oil is as a result of the basestock as well as contamination from fuel (Rafael, 1988). Motor oil breaks down in the process of its use to give a wide variety of oxygenated and aromatic hydrocarbons (Upshall, 1993).

Aromatics are often distinguished by the number of rings they possess, which may range from one to five. Lighter, mono-aromatics (one ring) compounds include benzene, toluene, ethylbenzene, and xylenes. Aromatics with two or more rings are referred to as polyaromatic hydrocarbons (PAHs), which may be present in used motor oil in high concentrations (Grimmer, 1981). Studies have shown that some of these PAHs are mutagenic (Peake and Parketer, 1980) and carcinogenic (Grimmer, 1982; Rafael, 1988), and are therefore very dangerous to human health.

2.7.2 Heavy Metals

Heavy metals content of used motor oil originate from engine wear, additives and fuel (Rafael, 1988). These metals include Pb, Ba, Cr, Cd, Zn, Fe, Cu, Ni, V and Mn. Some of the sources of these metals in used motor oil are as follows (MTS, 2011):

2.7.2.1 Lead

Lead is a wear metal. It is used on surfaces such as bearings; Pb based babbitt alloys, main crankshaft journal bearings, and sealing gaskets (MTS, 2011).

2.7.2.2 Iron

Iron is a wear metal. It is the main component of steel. Sources in motor oil include cylinder liners, camshaft lobes, crankshaft journals, engine blocks, differential and transmission housings, gearboxes, bearing, gears, valves, rocker arms, and oil pumps (MTS, 2011).

2.7.2.3 Chromium

Chromium is a wear metal mostly associated with the piston rings. It is also use to make steel harder and can be an indicator of gear wear, roller bearing and shaft wear. Anti-freeze additive also contain Chromium (MTS, 2011).

2.7.2.4 Copper

Copper is a wear metal. It is widely used due to its high ductility and thermal conductivity and mainly utilized in bushings and bearings such as crankshaft journal bearings, camshaft bushings, piston wrist pin bushings etc. Another source is additives (MTS, 2011).

2.7.2.5 Cadmium

The presence of cadmium in used motor oil is as a result of engine wear and tear (MTS, 2011).

2.7.2.6 Zinc

Zinc is used as anti-wear, anti-oxidant, and corrosion inhibitor additive in motor oil. It is also commonly found in bearing alloys (MTS, 2011).

2.7.2.7 Manganese

Manganese is sometimes used in certain steel alloys. It is also used as additive in unleaded gasoline (MTS, 2011).

2.7.2.8 Vanadium

Vanadium is a wear metal. It can be found in certain types of hard steels. The element is a contaminant in crude oil (MTS, 2011).

2.7.2.9 Barium

Barium is used as oil additive in certain brands of motor oil as well as fuel. It is also used as detergent against corrosion and rust in some synthetic oils. Some types of greases contain barium (MTS, 2011).

2.8.2.10 Arsenic

Arsenic is a wear metal. It is used in the hardness of lead and copper alloys (MTS, 2011).

2.7.2.11 Nickel

Nickel can be found in certain alloys of steel for internal engine parts. It is also used as a coat on bearings. Its presence is therefore an indication of shaft wear, gear wear and roller or ball bearing wear (MTS, 2011).

2.8 Sources of Used Motor Oil into the Environment

2.8.1 Release to Land/Soil

There are many ways by which used motor oils are released into soil. However, these include escape and loss of oil during engine operation, application on untarred roads for dust suppression, asphaltting with asphalt containing oil, and indiscriminate disposal, especially at landfill site (Rafael, 1988). During engine operation some of the oil is lost on pavement surfaces, roads, car parks, garages, and also through the activities of automobile service centers as well as individuals who change oil and filter at home. The oil migrates downward by gravity through soil and spread laterally due to capillary forces and soil heterogeneity (Mahaney, 1993). The soil quality is affected due to the presence of hydrocarbons, heavy metals and other constituents of the oil (Harrison, 1974).

2.8.2 Release to Air

Volatile aromatic hydrocarbons, heavy metals and other volatile organic compounds find their way into the atmosphere when used motor oil is released (Hopmans, 1974; Fahlahi-Ardakani, 1984).

The volatile compounds in the oil escape into the atmosphere during engine operation (Mumford, 1986). Oil used for dust suppression has its constituents volatilized into air, carrying along particulate matter by adsorption (Mahaney, 1993). Used motor oil used as combustion fuel emit oxides of heavy metals such as Pb, Cr, Cd, Zn, Cu etc. (Rafael, 1988), and polychlorinated dibenzofur, dibenzodioxin compounds as well as inorganic substances like sulphur, nitrogen, phosphorus, and halogens compounds (Mahaney, 1993).

2.8.3 Release to Water

Used motor oil spilled on land eventually ends up in the aquatic ecosystem due to rain and runoff waters (Rafael, 1988; Mahaney, 1993). Polycyclic aromatic hydrocarbons (PAHs), heavy metals, additives and antioxidants, trace levels of chlorinated solvents and Polychlorinated biphenyl (PCBs) detected in used motor oil (Mahaney, 1993) are released into water; which can bioaccumulate in the bodies of organisms. According to the U.S. Environmental Protection Agency, 1 gallon of used motor oil can contaminate 1 million gallons of fresh water (USEPA, 2003).

2.9. Effects of Components of Used Motor Oil on Human and the Environment

2.9.1 Effects of Heavy Metals

Studies have shown that used motor oil contain heavy metals and have various effects on human health and the environment (Mahaney, 1993; Roberts, 1999; MTS, 2011; Schaumberg, *et al.*, 2004). Some of these metals are as follows:

2.9.1.1 Lead

Pb has serious effects on human health (Schaumberg, *et al.*, 2004). It can enter the human body through food, water, and air. Some of the health effects include disruption of the biosynthesis

of haemoglobin and anaemia, rise in blood pressure, kidney damage (IOSH, 1999), miscarriages and subtle abortions, disruption of nervous systems, brain damage, declined fertility of men through sperm damage (Schaumberg, *et al*, 2004), diminished learning abilities of children, behavioural disruptions of children (Roberts, 1999, and Dietrich, 2004), damage to the nervous system and the brains of unborn babies (Jennings, *et al.*, 1996).

Pb accumulates in the bodies of aquatic (Demayo, 1982; Baby, *et al.*, 2010) and soil organisms (Demayo, 1982) causing Pb poisoning. It can accumulate in individual organisms and move through the food chains unto higher organisms. Phytoplankton is an important source of oxygen production in seas and also food for many larger sea-animals. However, the body functions can be affected as a result of lead interferes (Crist, *et al.*, 1992). Soil functions can also be affected as a result of lead interventions (ATSDR, 1992).

2.9.1.2 Iron

Fe is an essential part of hemoglobin (Baby, *et al.*, 2010) and it is responsible for oxygen transport in the body. Excess exposure can cause damage to the liver, cardiovascular system, and kidneys (Roberts, 1999). However, deficiency in Fe causes anaemia (Gary and Lucier, 1998). Fe is a naturally occurring element but can persist in the environment at high concentrations.

2.9.1.3 Chromium

Exposure to Cr can be through inhalation, ingestion and skin contact. It is an essential nutrient for humans but shortages may cause heart conditions, disruptions of metabolisms and diabetes (ATSDR, 2008). However, uptake of excess Cr can cause health effects. Cr (VI) is the most

dangerous form of Cr and may cause health problems such as skin rashes, upset of stomach and ulcers, respiratory problems, weakened immune system, kidney and liver damage, alternation of genetic material and lungs cancer (Singh, *et al.*, Sneddon, 2012).

Cr in soils strongly attaches to soil particles, adsorb on sediment in water and become immobile; making it difficult for it to dissolve. Although Cr (III) is an essential element for organisms, high levels of Cr could be dangerous (Singh, *et al.*; Vincent, 2011).

2.9.1.4 Copper

Exposure to Cu is through inhalation, ingestion and dermal contact. Although Cu is a trace element that is essential for human health (Ferrante, *et al.*, 2013), excess uptake can be harmful. Long-term exposure can cause irritation of the nose, mouth and eyes, headaches, stomach aches, dizziness, vomiting and diarrhea.

High exposure of the metal may cause damage to the brain, liver and kidney, and even cause death (ATSDR, 2004).

Cu can be persistent in the environment and accumulate in plants and animals (ATSDR, 2004). It becomes strongly attached to organic matter and minerals in soil and cause diversity in farm products. Cu can interrupt the activities in soil, negatively influence the activities of microorganisms such as earthworms and eventually affect the decomposition of organic matter (Alloway, 2008).

2.9.1.5 Cadmium

Route of entry could be inhalation or ingestion. It can affect the liver and the kidney. It accumulates in the kidneys and causes the excretion of essential proteins and sugars from the body and further kidney damage (USEPA, 1999). Exposure to Cd can cause diarrhea, stomach

pains, psychological disorders, bone fracture, cancer, and damage to the lungs, central nervous system, immune system and DNA or death. Excretion of accumulated cadmium in kidneys takes time (Roberts, 1999).

Cd can be transported over great distances when it is absorbed by sludge (De Pieri, *et al.*, 2000); causing pollution to soil and surface water. It adsorbs to organic matter in soil which can be transport to plants; leading to an increase in the level of concentration in foods and eventually accumulate in the bodies of organisms that depend on these foods for survival. High Cd concentrations in soils can also influence soil processes of microorganisms and pose threat to the whole soil ecosystem. In aquatic ecosystems, Cd could bioaccumulate in mussels, oysters, shrimps, lobsters and fish. Animal exposure to cadmium could lead to high blood-pressures, liver disease, and nerve or brain damage (Kirkham, 2006).

2.9.1.6 Zinc

Zn is a trace element that is essential for human health. Zn deficiency has been associated with dermatitis, anorexia, growth retardation; poor wound healing, hypogonadism with impaired reproductive capacity, impaired immune function, and depressed mental function. Increased incidence of congenital malformations in infants has also been associated with zinc deficiency in the mothers (ATSDR, 2005).

Exposure to high level of Zn lead to loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores, stomach cramps, skin irritations, vomiting, nausea, anaemia, damage to the pancreas; and disturbs the protein metabolism and cause arteriosclerosis (Salgueiro *et al.*, 2000; Nriagu, 2007).

High levels of Zn concentration can accumulate in the bodies of fishes and magnify up the food chain. Water-soluble zinc in soils can contaminate groundwater and interrupt activities in soils; which can affect microorganisms and reduce the rate of decomposition of organic matter (Alloway, 2008).

2.9.1.7 Manganese

Although Mn is one of the essential trace elements (Keen *et al.*, 2000), excess exposure can cause damage to the respiratory tract, central nervous system and the brains (Crossgrove and Zheng, 2004). Symptoms of manganese poisoning are hallucinations, forgetfulness, nerve damage, languor, sleepiness, weakness, emotional disturbances, spastic gait, recurring leg cramps, and paralysis. Manganese can also cause Parkinson, lung embolism and bronchitis (Carl and Gallagher, 1994).

Mn compounds exist naturally in the environment as solids in soil, small particles in water, and present in dust particles in air. These Mn compounds eventually ends up in surface water, groundwater and sewage water. High concentrations of Mn in soils can cause swelling of cell walls, withering and brown spots on leaves. It can also cause lung, liver and vascular disturbances, decline in blood pressure, failure in development of animal fetuses and brain damage (ATSDR, 2012).

2.9.1.8 Vanadium

Mode of exposure could be ingestion or inhalation. V can have various effects on human health such as bronchitis, pneumonia, cardiovascular diseases, inflammation of the stomach and

intestines, damage to the nervous system, bleeding of livers and kidneys, skin rashes, paralyses, nose bleeding, throat pains, and dizziness (ATSDR, 2012).

V can bioaccumulate in fishes, algae, plants, invertebrates, mussels, crab etc. It causes the inhibition of certain enzyme in animals; which has several neurological effects that can cause breathing disorders, paralyses, and negative effects on the liver and kidneys. V can cause harm to the reproductive system in animals and DNA alteration (CSQG 1997).

2.9.1.9 Barium

The mode of exposure to Ba could be through inhalation, ingestion and possibly skin contact. Ba compounds that dissolve in water can be very harmful. Acute exposure can lead to breathing difficulties, increased blood pressures, heart rhythm changes, stomach irritation, muscle weakness, changes in nerve reflexes, swelling of brains and liver, kidney and heart damage. Chronic exposure of water-soluble Ba may cause paralyses and in some cases death (ATSDR, 2007). Ba is persistent in the environment; especially in soil surfaces. It can accumulate in the bodies of aquatic organisms due to its water-solubility (CSQG, 2013).

2.9.1.10 Arsenic

As is one of the most toxic elements (Roberts, 1999; Baby, *et al.*, 2010). Exposure to inorganic arsenic can cause various health effects such as irritation of the stomach and intestines, decreased production of red and white blood cells, skin changes, and lung irritation. Extremely high exposure to inorganic arsenic can cause infertility and miscarriages, declined resistance to infections, heart disruptions, brain and DNA damage. Organic Arsenic on the other hand may cause nerve injury and stomachaches (ATSDR, 2007).

High concentrations of the dangerous inorganic arsenic in surface waters enhance the chances of alteration of genetic materials in fishes (Baby, 2010), which is mainly caused by accumulation of arsenic in the bodies of plant-eating freshwater organisms. This As poisoning is transported through the food chain unto higher organisms.

2.9.1.11 Nickel

The exposure to Ni is through inhalation, ingestion and skin contact. Excess uptake may result in conditions such as pneumonitis, cancer (lung, nose, larynx and prostate cancer), sickness and dizziness, lung embolism, birth defects, asthma and chronic bronchitis, heart disorders and skin rashes (ATSDR, 2003).

Ni in acidic medium is bound to become more mobile and eventually end up in groundwater. The metal can cause various forms of cancer on different sites within the bodies of animals (Feder *et al.*, 1996; ATSDR, 2005).

2.9.2 Effects of BTEX and Derivatives

BTEX and derivatives are air, water and soil contaminants. Contamination of groundwater and subsurface soil can result in migration of these chemicals into basements as soil gas. Exposure to BTEX can occur by ingestion, inhalation or absorption through the skin, and each of them can produce neurological impairment (ATSDR, 2004). Benzene is carcinogenic and can cause various forms of cancer.

It is rapidly and efficiently absorbed and widely distributed throughout the body (ATSDR, 2007), and exposure to very high concentrations in air can cause death. Long-term exposure to benzene can cause cancer of blood forming organs (leukemia). Eating foods or drinking liquids

containing high levels of benzene can cause vomiting, irritation of the stomach, dizziness, sleepiness, convulsions, rapid heart rate, coma and death (IPCS, 1993; Leusch, 2010). Toluene is readily absorbed from the gastrointestinal tract after ingestion and is distributed preferentially in adipose tissue, then the kidneys, liver and brain. The main effect of toluene is on the brain and the nervous system, with fatigue and drowsiness being the most obvious symptoms (IPCS, 1985; ATSDR, 2000; Leusch, 2010).

Ethylbenzene is readily absorbed from the human gastrointestinal tract. Animal studies show it effects on the liver and kidney at high doses (IPCS, 1996; Leusch, 2010). Xylenes are readily absorbed after inhalation. Both short-term and long-term exposure to high concentrations of xylene can also cause a number of effects on the nervous system (IPCS, 1997; ATSDR 2007; Leusch, 2010).

2.9.3 Effects of Total Petroleum Hydrocarbons

The term Petroleum Hydrocarbon is used to describe a large family of several hundreds of chemical compounds that originally come from crude oil (ATSDR, 1999). Some chemicals that may be found in petroleum hydrocarbon are hexane, jet fuels, mineral oils, benzene, toluene, xylenes and naphthalene (ATSDR, 1999).

Petroleum hydrocarbon may be released directly into water through spills or leaks. Some fractions may float on the water and form surface films or sink to the bottom sediments. Bacteria and other microorganisms in the water may break down some of the petroleum hydrocarbon fractions competing with aquatic organisms for dissolved oxygen and as a result deprive them of the oxygen needed for their survival. Other petroleum hydrocarbon fractions can persist in soil and affect microbial activities (Alberta, 1993), which eventually affect plant

and animals. Others can affect the central nervous system, circulatory system, lungs, immune system, skin, eyes etc. (ATSDR, 1999).

2.9.4 Effects of Hydrogen Sulfide.

Exposure to low concentrations within the range of 30 ppb may cause eye, nose, and throat irritation, headaches and nausea (ATSDR, 1997 and 1999). It may also cause difficulty in breathing for some individuals with respiratory problems such as asthmatics (ATSDR, 1999). Acute exposures to high concentrations of hydrogen sulfide (greater than 500,000 ppb) can cause serious health effects including a loss of consciousness, poor attention span, memory and motor function. These effects may be long-term or even permanent (HSFS, 2004).

2.10 Generation and Environmental Impact of Used Motor Oil

2.10.1 Regular Vehicular Maintenance

Regular inspection of vehicles, immediate repair of parts showing signs of leakage, and daily checks on oil levels help reduce oil spill. Proper vehicle operation and continuous lubrication of engine parts reduce wear and tear (Aggeliki, 2011).

2.10. 2 Change of Oil and Filters

Regular changing of engine oil and filters reduce the levels of concentration of wear metals (ACS, 2004; Fitch, 1998), volatile aromatic hydrocarbons and toxic compounds from breakdown of additives, products of combustion, dirt and other contaminants in used motor oil.

One of the ways by which volatile aromatic hydrocarbons such as benzene accumulate in motor oil is through fuel contamination (Ronald, 2002); which are released into the environment

during engine operation. Excessive use of filters contributes to engine wear due to clogging (SAE, 1998; CIWMB, 2008; ACS, 2004). Dirt and other contaminants which can accumulate in oil over a period also increase engine wear as particles become grinding agents (Fitch, 1998). However, frequent change of these consumable can also lead to excessive generation of waste and impact negatively on the environment when discharged. It is therefore important to follow oil and filter change scheduled by experts. Oil and filter change by experts prevent/reduce oil spill.

2.10.3 Storage

Used motor oil must be stored in an environmentally safe manner to prevent leakage and spillage. The used oil must be carefully transferred with a funnel into a clean plastic container which has never held chemicals, food, or beverages with a tight lid. The container must be inspected to be sure it will not leak. It is important not to mix the oil with anything else (e.g. antifreeze, solvent, paint, water etc.) to avoid the formation of more toxic substances (USEPA, 2003). Oil filters contain oil, which must be drained to avoid spillage and environmental hazards such as fire. The oil must be stored in an area free from congestion and out of reach of children to avoid accidental spills.

There is the tendency to punch the storage container if the oil is stored over a long period (USEPA, 2003), and therefore it is necessary to carefully transport the used oil and filters to a service station or other location that collects used motor oil for recycling as soon as possible.

2.10.4 Recycling/re-use

Recycling used motor oil conserves natural resources (USEPA, 2003), and also prevents environmental pollution. Some of the re-use options include wood preservations, combustible material for burning rubbish, fuel oil for firing boilers in industries and other heating purposes, asphalt production, lubricating oil in corn mill operations etc. However, these uses pose danger to the Environment when the used motor oil is unrefined. Pollutants such as volatile organic compounds, heavy metals, oxides of sulfur, nitrogen, carbon and other products of combustion are released into the atmosphere (Rafael, 1988). Spilled oil also impact negatively on soil and water (Hopmans, 1974). It can seep underground and travel far distances to pollute underground water.



CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Sampling

Ten (10) used motor oil samples each were collected from private and commercial vehicles at

Silver Star Motors Ltd., Brians Toyota Motors Ltd. and One Touch Mechanical Shop in Tema in December, 2013. Fresh motor oil samples for petrol and diesel engines were also collected from Tema Lube Oil Company Limited. The used motor oil samples from private vehicles were motor oils for petrol engines while that of the commercial vehicles were for diesel engines. The oil samples were collected into 2 liters cleaned containers with tight lids to prevent spillage and release of volatile compounds into the atmosphere. The containers were washed and rinsed with deionised water and dried to get rid of the traces of water before sampling.

3.2 Determination of Physico-Chemical Parameters

3.2.1 Density/Specific Gravity

American Standard for Testing Measurement (ASTM) D 4052 Standard Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter was used.

Procedure

About 0.7 mL of the sample was introduced into the clean, dry sample tube of the instrument using a syringe. The external capillary tube was plug into the lower entry port of the sample tube and the other end of the tube immersed in the sample. Suction was applied to the upper entry port using vacuum line until the sample tube was properly filled. The illumination light was turned on and the sample tube was examined.

The reading was recorded after the instrument displayed steady readings to four significant figures for density and specific gravity concurrently, indicating that temperature equilibrium has been reached.

3.2.2 Viscosity

ASTM D 445 Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids was used.

Procedure

The viscometer bath was adjusted to the required test temperature range of 15 min to 100 °C with thermometer held in an upright position. A clean, dry, calibrated viscometer tube having a range covering the estimated kinematic viscosity of a flow time of not less than 200 s was selected and a drying tube fixed at the end to get rid of moist room air by applying vacuum. The viscometer was charged with the sample by inserting the tubes thinner area into the oil sample and suction applied through the thicker area with a vacuum machine. The sample was then drawn up to the upper timing work of the inverted viscometer and turned to its normal vertical position. The viscometer was placed into the holder and inserted into the constant temperature bath maintained at 40 °C. 10 min was allowed for the sample to come to equilibrium with the temperature and after 15 min it reached 100 °C. The efflux time was obtained by timing the flow of the fluid sample as it flowed freely from upper meniscus mark to the lower meniscus mark. The kinematics viscosity was calculated by multiplying the efflux time by the viscometer constant on a Viscometer Constant Table.

3.2.3 Flash Point

ASTM D 92 Standard Test Method for Flash and Fire Points by Cleveland Open Cup Tester was used.

Procedure

A clean Cleveland open cup tester was filled with the sample to the lower meniscus and positioned on the Bunsen burner with thermometer inserted vertically into the sample and held

with the thermometer holder. The test flame was lighted and the burner switched on. The flame was adjusted to a diameter of 3.2 to 4.8 mm. The temperature was increased rapidly at first and lowered to half the maximum value when the sample was approximately 56° below the anticipated flash point and then at a slower constant rate as the flash point approached. The test flame applicator was passed across the center of the cup with smooth continuous motion at specified intervals until the vapours of the test specimen ignited. The lowest temperature at which ignition occurred was recorded as the flash point of the sample.

3.2.4 Pour Point

ASTM D 97 Standard Test Method for Pour Point of Petroleum Products using GD-510D Petroleum Products Pour Point Tester.

Procedure

20 mL of the sample was poured into the test jar to the level mark and closed tightly with a cork carrying a pour thermometer. The test jar was then inserted into the jacket of the instrument. The appearance of the sample was examined when the temperature was around 9 °C above the expected pour point. The monitoring continued at subsequent 3 °C till the sample could not flow when the test jar was tilted. The temperature at which the sample freeze was recorded and 3 °C subtracted from the value to obtain the pour point.

3.2.5 Colour

ASTM D 1500 Standard Test Method for Colour of Petroleum Products (ASTM Colour Scale) using Lovibond Petroleum Oils Comparator AF 650.

Procedure

The standard glasses of the colorimeter were filled to a height of 50 mm with deionized water and placed in the left and right compartments. The sample was poured into the specimen glass and placed in the middle compartment. The container was covered to exclude all exterior light. The instrument was switched on and the knobs turned to compare the colour of the sample with that of the standard colored glass disks ranging in value from 0.5 to 8.0; with 8 being the maximum value of the equipment and the code for the darkest colour.

3.2.6 Water Content

ASTM D 6304 Standard Test Method for Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration was used.

Procedure

Karl Fischer solutions were added to the anode and cathode compartments of the titration vessel and brought to end-point conditions. The test specimen was added to the titration vessel using a clean, dry syringe. The syringe and content was weighed to the nearest 0.1 mg. The needle of the syringe was inserted through the inlet port septum, and the titration was started. With the tip of the needle just below the liquid surface, the test specimen was injected into the system. The syringe was withdrawn, cleaned with a paper tissue, and reweighed to the nearest 0.1 mg. After the end point was reached, the microgram of water titrated was recorded as the water content of the sample. The viscous sample was analyzed using water vaporizer accessory to heat the sample in the evaporation chamber, which carry the vaporized water into the Karl Fischer titration cell by a dry inert carrier gas.

3.2.7 Soot content

ASTM D 5967 Standard Test Method for Estimation of Soot Content in Engine Oil using Thermo Gravimetric Analysis (TGA).

Procedure

Tens (10) mg of sample was weighed and heated up to 650 °C in nitrogen environment to remove all the volatiles and other organic materials. The environment was changed to oxygen at 650 °C to burn off the soot. The soot content was determined by the difference observed in weight from oxygen switch over until stable weight residue or unchanged weight loss was observed for about 5 minutes.

3.2.8 Heavy metals

ASTM D 6595 Standard Test Method for Determination of Wear Metals and Contaminants in Used Lubricating Oils or Used Hydraulic Fluids by Rotating Disc Electrode Atomic Emission Spectrometry using Spectroil M

Procedure

The equipment was connected to a power source and switched on using the operate button on the operator's control panel to apply power to the electrode sharpener and exhaust fans. The sample stand exhaust system was checked and with the sample stand door open, a piece of tissue paper was held up to the exhaust filter. The paper was sucked up and held in place against the filter and then removed. A printer connected to the instrument was put on standby to print the results that will be displayed on the video monitor of the instrument. The samples were vigorously shaken. Series of burns were conducted using oil samples other than the test specimen to introduce light into the optics and to allow the electronics to become warm.

The analysis program screen was display on the video monitor of the equipment. A carbon disc was installed on the disc shaft using a clean laboratory grade tissue to avoid contact with fingers. The black plastic knob of the spring loaded rod electrode clamp was pressed inward to open the jaws of the clamp and a graphite rod electrode inserted until the tip of the carbon rod

was in contact with the disc electrode, and the knob released to secure the electrode in the clamp.

One (1) mL of the blank sample was poured into a test specimen holder and placed on the sample table and slid back to the end of the groove on the table. The sample table was raised using the sample table positioning lever to enable the sample fluid contact bottom of disc electrode. Function key according to sample identity was entered into the software of the equipment.

The sample stand door was then closed and the samples run using the start configuration. The results were displayed on the monitor after the burn was completed. The sample stand door was then opened and the rod electrode removed and set aside for subsequent re-sharpening before reuse.

The sample table was lowered and using a paper towel to protect fingers from the hot disc, it was removed and discarded together with the disc electrode. Using the same procedure, the standards and the used motor oil samples were analyzed. The equipment was cleaned after analyzing each sample to avoid cross contamination.

3.2.9 Volatile Aromatic Hydrocarbons (BTEX) and Hydrogen Sulfide

ASTM D 4490 Standard Practice for Measuring the Concentration of Toxic Gases or Vapors Using Detector Tubes - Dräger CMS (Chip Measuring System).

Procedure

Two Hundred (200) mL each of the samples were vapourized by boiling at a temperature of 250 °C, with the drager tube of the Drager CMS machine connected to it. The vapours were sucked through the tube unto the equipment which had an already calibrated chip of the parameter of interest inserted. The instrument automatically measured the concentration of the parameter whose chip were inserted into the equipment.

3.2.10 Total Petroleum Hydrocarbons (TPH)

ASTM D3921 Standard Test Method for Oil and Grease and Petroleum Hydrocarbons in Water by InfraCal TOG/TPH Analyzer was used.

Procedure

The model used for the analysis was CVH. The equipment was connected to power source and allowed to warm for at least one hour. Ten (10) mL quartz cuvette was filled with the sample to the lower meniscus and inserted into the sample stage, with the frosted side facing the front. The run button was pressed on and the result was displaced on the equipment.

3.3 Statistical tools for data analysis

The data obtained from the analysis were subjected to descriptive statistical analysis (Range, Mean and Standard Deviation).

CHAPTE R FOUR

4.0 RESULTS

Table 4.1 Physical Properties of the Used Motor Oil from Private and Commercial Vehicles (n=10).

Parameter	Used Motor Oil from Private Vehicles		Used Motor Oil from Commercial Vehicles		Fresh Motor Oil	
	Range	$\mu \pm \sigma$	Range	$\mu \pm \sigma$	Petrol	Diesel
Density at 15 °C (Kg/m ³)	878.8-882.1	880.5 \pm 1.2	891.3-899.2	895.3 \pm 5.6	888.2	850.7
Specific gravity (Kg/m ³)	879.7-882.8	881.3 \pm 2.2	899.9-900.1	900.0 \pm 0.1	889.1	851.50
Viscosity at 100 (cSt)	7.2-16.2	11.7 \pm 6.4	14.1-15.9	15.0 \pm 1.3	17.7	16.0
Water Content (%V)	0.1-0.2	0.2 \pm 0.1	0.5-1.2	0.9 \pm 0.5	BDL	BDL
Flash point (°C)	180.0-201.0	191.0 \pm 14.9	228.0-213.0	221.0 \pm 10.6	252.0	234.0
Pour point (°C)	(-18 .0)- (-21)	-19.5 \pm 2.1	(-3) - (-11)	-7.0 \pm 2.3	-24.0	-33.0
Soot (%Wt)	0.97 - 1.01	1.00 \pm 0.03	0.83-1.81	1.30 \pm 0.7	0.88	1.17
Colour (mg/L Pt)	>8	>8 \pm 0.0	>8	>8 \pm 0.0	3.5	3.5

* Colour: 8 is the maximum value on the scale of the comparator. Thus it cannot read beyond 8 mg/L Pt.

*BDL: Below Detection Limit.

4.1 Results of Physical Properties of the Used Motor Oil

4.1.1 Density

Table 4.1 shows that the mean densities detected for the used motor oil samples from private and commercial vehicles were $880.5 \pm 1.2 \text{ Kg/m}^3$ and $895.3 \pm 5.6 \text{ Kg/m}^3$ respectively. The mean density of the used motor oil from private vehicles was below the density of the fresh motor oil for petrol engines (888.2 Kg/m^3) while the value for commercial vehicles was above that of diesel engines oil (850.7 Kg/m^3).

4.1.2 Specific Gravity

$881.3 \pm 2.2 \text{ Kg/m}^3$ was the mean specific gravity measured for the used motor oil samples from private vehicles, which was below the specific gravity of the fresh motor oil for petrol engine (889.1 Kg/m^3) while that of commercial vehicles ($900.0 \pm 0.1 \text{ Kg/m}^3$) had its specific gravity above that of the fresh motor oil for diesel engines (851.5 Kg/m^3) as indicated in Table 4.1.

4.1.3 Viscosity

The mean kinematic viscosity for the used motor oil obtained from private vehicles was $11.7 \pm 6.4 \text{ cSt}$ while that of commercial vehicles was $15.0 \pm 1.3 \text{ cSt}$. These values were below that of the fresh motor oil for petrol engine (17.7 cSt) and diesel engine (16.0 cSt) respectively (Table 4.1). However, the value for commercial vehicles exceeded that of private vehicles.

4.1.4 Water Content

It could be realized from Table 4.1 that water was below detection in the fresh motor oil samples meanwhile mean levels of 0.2 ± 0.1 and 0.9 ± 0.5 %v were detected in the used motor oil samples from private and commercial vehicles respectively.

4.1.5 Flash Point

Used motor oil samples from private vehicles recorded a lower mean flash point (191.0 ± 14.9 °C) compared to the commercial vehicles (221.0 ± 10.6 °C). However, the flash points for the fresh motor oil for petrol (252 °C) and diesel engines (234 °C) were higher than those of the used motor oil samples respectively as presented in Table 4.1.

4.1.6 Pour Point

From Table 4.1, -19.5 ± 2.1 °C was detected as the mean pour point for the samples from private vehicles, which was higher than the pour point of the fresh motor oil for petrol engines (-24 °C). The mean value for commercial vehicles on the other hand was (-7.0 ± 2.3) , which was also higher than the pour point of the motor oil for diesel engines (-33 °C).

4.1.7 Soot Content

The mean soot content detected for samples from private vehicles was (1.00 ± 0.03 %wt), which was higher than that of the fresh motor oil for petrol engines (0.88 %wt). The value for commercial vehicles (1.30 ± 0.7 %wt) was also higher than that of the fresh motor oil for diesel engines (1.17).

4.1.8 Colour

The mean colour detected for each of the used motor oil samples categories was over the range (i.e. >8 mg/L Pt) set for the equipment as indicated in Table 4.1. Black colour was the code for the maximum value of the colour comparator, which was 8 mg/L Pt. However, the colour for the fresh motor oil samples was recorded as 3.5 mg/L Pt; signifying amber.

It was observed that the values detected for the used motor oil samples were high compared to the fresh motor oil samples. Also the mean values obtained for the used motor oil from commercial vehicles were higher than that of the private vehicles except colour where both recorded values above the maximum detecting limit of the colour comparator as shown in Table 4.1.

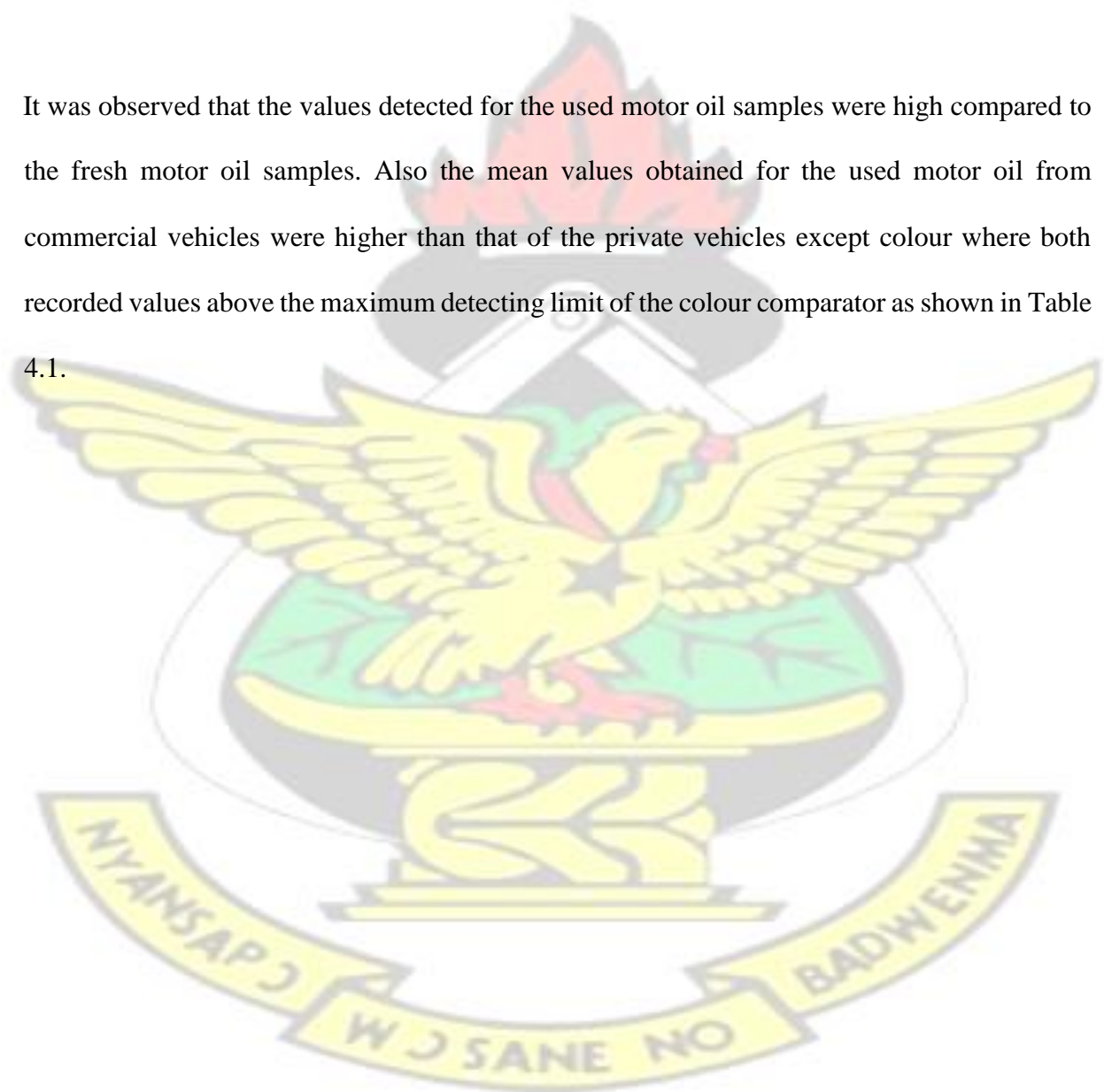


Table 4.2 Heavy Metal levels of Used Motor Oil from Private and Commercial Vehicles (n=10).

Parameter	Used Motor Oil from Private Vehicles		Used Motor Oil from Commercial Vehicles		Fresh Motor Oil		EPA STD
	Range	$\mu \pm \sigma$	Range	$\mu \pm \sigma$	Petrol	Diesel	
Pb (mg/L)	0.03-1.0	0.5 ± 0.7	0.08-28.0	14.0 ± 19.7	BDL	BDL	0.1
Fe (mg/L)	21.0-28.0	24.5 ± 4.9	186.0-480.0	333.0 ± 207.9	BDL	BDL	10
Cr (mg/L)	1.0-7.0	4.0 ± 4.2	110.0-200.0	155.0 ± 63.6	BDL	BDL	0.5
Cu (mg/L)	0.05-5.0	2.5 ± 3.5	0.28-23.0	11.6 ± 16.1	0.0014	BDL	5.0
Cd (mg/L)	0.0-0.01	0.1 ± 0.01	0.02-0.05	0.04 ± 0.02	BDL	0.0043	0.2
Zn (mg/L)	819.0-2580.0	1699.5 ± 1245.2	566-2800.0	1683.0 ± 1579.7	0.106	0.139	10
Mn (mg/L)	≤ 0.01 -3.0	3.0 ± 2.1	0.0-8.0	8.0 ± 5.7	BDL	BDL	0.2
V (mg/L)	BDL	BDL	BDL	BDL	BDL	BDL	1.0
Ba (mg/L)	0.0-1.0	1.0 ± 0.1	0.0-1.0	1.0 ± 0.7	BDL	BDL	0.7
As (mg/L)	1.0-2.0	1.5 ± 0.7	2.0-3.8	2.9 ± 1.3	BDL	BDL	0.5
Ni (mg/L)	1.0-13360.0	6680.5 ± 9446.2	2.0-14960.0	7481.0 ± 10576.9	BDL	BDL	0.5

***BDL: Below Detection Limit.**

4.2 Results of Heavy Metal levels of the Used Motor Oil

4.2.1 Lead

Table 4.2 shows that Pb was below detection in the fresh motor oil samples but present at a mean level of 0.5 ± 0.7 mg/L in the used motor oil samples from private vehicles which was lower than that of the commercial vehicles (14.0 ± 19.7 mg/L). However, these concentrations exceeded the EPA permissible limit of 0.1 mg/L.

4.2.2 Iron

Fe was below detection in the fresh motor oil samples. Mean Fe concentration in the used motor oil samples from private vehicles (24.5 ± 4.9 mg/L) and commercial vehicles (333.0 ± 207.9 mg/L) far exceeded the EPA permissible limit (10.0 mg/L) as indicated in Table 4.2. However, the mean concentration for commercial vehicles was extremely high compared to the private vehicles.

4.2.3 Chromium

Cr was not detected in the fresh motor oil samples meanwhile it was detected in the used motor oil samples with mean levels of 4.0 ± 4.2 mg/L and 155.0 ± 63.6 mg/L for private and commercial vehicles respectively. These were above the EPA permissible limit of 0.5 mg/L.

4.2.4 Copper

As shown in Table 4.2 above, the mean level of Cu for the used motor oil from private vehicles (2.5 ± 3.5 mg/L) was higher than the level in fresh oil for petrol engines (0.0014 mg/L) but lower than the EPA limit (5.0 mg/L).

Cu was not detected in the fresh motor oil for diesel engines, meanwhile a concentration of 11.6 ± 16.1 mg/L was detected in the used oil from commercial vehicles; which was also above the EPA guideline.

4.2.5 Cadmium

Table 4.2 shows that Cd was detected in the fresh motor oil for diesel engines at a concentration of 0.0043 mg/L while 0.04 ± 0.02 mg/L was found in the used motor oil from commercial vehicles. On the other hand, the metal was not detected in the fresh oil for petrol engines but a concentration of 0.1 ± 0.01 mg/L was detected in the used oil for private vehicles. These levels conformed to the EPA permissible limit of 0.2 mg/L.

4.2.6 Zinc

Zn was detected in the fresh motor oil for both petrol and diesel engines at low concentrations of 0.106 mg/L and 0.139 mg/L respectively. However, the mean levels for the used motor oil samples from private vehicles (1699.5 ± 1245.2 mg/L) and commercial vehicles (1683.0 ± 1579.7 mg/L) were extremely high compared to the EPA guideline (10.0 mg/L) as shown in Table 4.2.

4.2.7 Manganese

It could be observed from Table 4.2 that Mn was not detected in the fresh motor oil meanwhile mean levels of 3.0 ± 2.1 mg/L and 8.0 ± 5.7 mg/L were detected for the used oil from private and commercial vehicles respectively; which exceeded the EPA maximum permissible limit of 0.2 mg/L.

4.2.8 Barium

As indicated in Table 4.2, Ba was not detected in the fresh motor oil samples. However, mean concentration of 1.0 mg/L each were recorded for both used motor oil samples, which were above the EPA permissible limit of 0.7 mg/L.

4.2.9 Arsenic

Although As was not detected in the fresh motor oil samples, the mean levels for private and commercial vehicles were 1.5 ± 0.7 mg/L and 2.9 ± 1.3 mg/L respectively. These levels were high compared to the EPA guideline (0.5 mg/L) as shown in Table 4.2.

4.2.10 Vanadium

Vanadium was not detected in all the samples as shown in the above Table 4.2.

4.2.11 Nickel

From Table 4.2, it could be observed that Ni was not detected in the fresh motor oil samples. However, the mean levels obtained for private vehicles (6680.5 ± 9446.2 mg/L) and commercial vehicles (7481.0 ± 10576.9 mg/L) were far above the EPA permissible limit (0.5 mg/L).

Most of the levels detected were above the EPA permissible guidelines, and again the mean levels of heavy metals concentration in the used motor oils from commercial vehicles were higher than that of the private vehicles as shown in Table 4.2.

Table 4.3: Volatile Aromatic Hydrocarbons, Total Petroleum Hydrocarbons and Hydrogen Sulfide levels of Used Motor Oil from Private and Commercial Vehicles (n=10).

Parameter Vehicles	Used Motor Oil from Commercial Vehicles		Used Motor Oil from Private		Fresh Motor Oil	
	Range	$\mu \pm \delta$	Range	$\mu \pm \delta$	Petrol Engine	Diesel Engine
Benzene (mg/L)	5.2-6.1	5.7 ± 0.6	3.0-4.3	2.4 ± 0.9	<0.01	<0.01
Toluene (mg/L)	<0.01	$<0.01 \pm 0.0$	<0.01	$<0.01 \pm 0.0$	<0.01	<0.01
Xylene (mg/L)	<0.01	$<0.01 \pm 0.0$	<0.01	$<0.01 \pm 0.0$	<0.01	<0.01
Benzene derivatives (mg/L)	1.3-1.8	1.6 ± 0.4	1.8-2.1	2.0 ± 0.2	15.9	20.3
Toluene derivatives (mg/L)	17.9-21.5	19.7 ± 2.5	11.3-33.1	16.4 ± 15.4	12.6	14.6
Xylene derivatives (mg/L)	1.2-1.6	1.4 ± 0.3	1.1-1.5	1.3 ± 0.3	1.3	1.5
TPH (mg/L)	1190.0-2880.0	2035 ± 1195.0	242.0-414.0	328.0 ± 121.6	4.8	4.7
H₂S (mg/L)	180.0-201.0	191.0 ± 14.8	135.0 -190.0	163.0 ± 38.9	1.4	1.5

*<0.01: Below the minimum detection limit of the Drager CMS A analyzer.

4.3 Results of Volatile Aromatic Hydrocarbons, TPH and H₂S levels of Used Motor oil

4.3.1 Benzene

Table 4.3 shows that the level of benzene in the fresh motor oil samples for both categories of vehicles were below detection while mean levels of 5.7 ± 0.6 mg/L and 2.4 ± 0.9 mg/L were detected in the used motor oils from private and commercial vehicles respectively. The derivatives on the other hand, recorded 15.9 mg/L and 20.3 mg/L for fresh motor oil for petrol and diesel engines respectively, and that of the used motor oil were 1.6 ± 0.4 mg/L for private vehicles and 2.0 ± 0.2 mg/L for commercial vehicles. Therefore the concentration of benzene in the used motor oil was high while that of the derivatives were low compared to the concentrations in their respective fresh motor oil.

4.3.2 Toluene

Toluene concentration was below detection for both fresh and used motor oil. However, the levels detected for the toluene derivatives were 12.6 mg/L for fresh motor for petrol engines and 14.6 mg/L for diesel engines. The used motor oil had mean concentration of 19.7 ± 2.5 mg/L for private vehicles which was higher than that of the commercial vehicles of 16.4 ± 15.4 mg/L (Table 4.3). These values were higher than the concentrations in their respective fresh motor oils.

4.3.3 Xylene

The levels of Xylene in all the samples were below detection but the mean concentration of the derivatives in the used oil was 1.4 ± 0.3 mg/L for private vehicles which was higher than the concentration in fresh motor oil for petrol engines (1.3 mg/L).

The commercial vehicles also recorded mean value of 1.3 ± 0.3 mg/L which was lower than the value for diesel engines (1.5 mg/L) as shown in Table 4.3.

Table 4.3 shows that the mean values for the derivatives for samples from private vehicles were higher compared to commercial vehicles, except that of benzene.

4.3.4 Total Petroleum Hydrocarbons (TPH)

The fresh motor oil had TPH concentrations of 4.8 mg/L for petrol and 4.7 mg/L for diesel engines. The mean levels of TPH in the used motor oil samples from private vehicles and commercial vehicles were 2035.0 ± 1195.0 mg/L and 328.0 ± 1216 mg/L respectively (Table 4.3); which exceeded the concentrations of their respective fresh motor oils. However, the value for private vehicles was higher than that of the commercial vehicles.

4.3.5 Hydrogen Sulfide

The fresh motor oil for petrol engines had a concentration of 1.4 mg/L while that of diesel engines was 1.5 mg/L. Meanwhile the used motor oil recorded high mean concentrations of 191.0 ± 14.8 mg/L for private vehicles and 163.0 ± 38.9 mg/L for commercial vehicles as indicated in Table 4.3.

CHAPTER FIVE

5.0 DISCUSSION

The study shows that the physicochemical properties detected for the used motor oil exceeded that of the fresh motor oil (Table 4.1 and 4.3) as well as the EPA permissible limits (Table 4.2; Appendix 2), which is dangerous to the environment.

It was also observed that most of the mean levels detected for the used motor oil from commercial vehicles were higher than that of the private vehicles, as indicated in Fig. 4.1 and 4.2; which could be attributed to their respective workloads, vehicle maintenance, and perhaps attitude towards driving. Commercial vehicles tend to have more workloads in terms of distance driving or driving for several hours, and carrying passengers and goods heavier than their required capacities. They also have poor maintenance attitude due to their busy schedules, and cost savings on consumables such as oil and filters among others as commercial entities (ACS 2004; Aggeliki, 2011). Vehicles are not operated well and driven aggressively to catch up with the targeted sales for the day. These could increase engine wear and tear, accumulation of soot particles, dirt and other contaminants in the used motor oil and eventually pollute the environment when the oil is improperly discharged.

5.1 Density/specific gravity

Table 4.1 shows that the mean density/specific gravity detected for the used motor oil sampled from private vehicles was below the density/specific gravity for the fresh motor oil for petrol engines while that of the commercial vehicles was above fresh oil for diesel engines. However, the change in density/specific gravity was an indication of the presence of contaminants, and could be due to the presence of oxidation products and wear metals (Ihsan, *et al.*, 2013) which can impact negatively on the engine and the environment.

The used oil which has lost its lubricity due to contamination would not be able to perform its functions properly, causing more wear of engine parts. The oxidation products and metal oxides would be released into the atmosphere when the used oil is re-used as fuel oil for firing boilers and other heating purposes if not refined (Rafael, 1988). High specific gravity could cause the oil to form tar ball or interact with sediments in aquatic environment (Ihsan, *et al.*, 2013) which serves as food for bottom dwellers and be transported through the food chain unto higher organisms.

5.2 Kinematic Viscosity

Viscosity is the measure of a liquid's resistance to flow, and it can be used to determine the presence of contaminants in used motor oil. For instance, the oxidized and polymerized products dissolved and suspended in used motor oil as a result of base oil oxidation may cause increase in viscosity (Diaz, *et al.*, 1996). On the other hand, fuel has been identified by some researchers as one of the contaminants that could cause low viscosity of used motor oil (Diaz, *et al.*, 1996; Ashley, 2007). Other causes may include cross contamination with low viscosity oil, shear thinning of viscosity index improvers, and thermal cracking of oil molecules (Livingstone, *et al.*, 2006). Table 4.1 shows that the used motor oil samples had low viscosities compared to the fresh motor oil; which is an indication of the presence of contaminants. The low viscosity would cause spilled oil to spread; travel far distances to cause pollution. According to the US EPA, 1 gallon of used motor oil can contaminate 1 million gallons of fresh water (USEPA, 2003). In Ghana about 36 million liters of motor oil is produced per annum by the Tema Lube Oil Company, whose market share is about 80%; with the 20% imported by other companies and individuals which is about 9 million liters.

Therefore an estimated quantity of about 45 million liters of motor oil, which is equivalent to 11.89 million gallons could be used in Ghana every year; indicating the possible amount of

used motor oil that could be generated. Motor oil viscosity determines the temperature within which engine operates and therefore a change in viscosity affects engine performance. Viscosity index improvers in motor oil allow engine to operate within certain temperature ranges (SAE, 1999), and once they breakdown there is poor lubrication, especially at high temperatures; causing more wear.

5.3 Water Content

Motor oil does not contain water due to possible oxidation and the formation of free radicals in the presences of oxygen, heat, and metal catalysts that have the potential to cause damage to engine parts (Stern and Girdler, 2013). However, the analysis revealed that the used motor oil samples had some amount of water (Table 4.1). The contamination might have occurred during use (absorbing moisture directly from the air, condensation, heat exchanger, combustion, oxidation, neutralization of additives, and free water entry during oil changes) (Ihsan, *et al.*, 2013), or storage. Water has been known to cause certain oil additives to precipitate out (Stern and Girdler, 2013). This could reduce the efficiency of oil lubricity and cause more wear, and affect engine performance. The oxidation products and the free radicals that are formed would be released into the atmosphere, especially when the used motor oil is re-used as combustible material. These contaminants would eventually come down through rain and impact negatively on the aquatic and terrestrial ecosystems. Research has revealed that free radicals, especially those that are oxygen-centered play a central role in the pathogenesis of many pulmonary diseases (Val and Shi, 1997).

5.4 Flash Point

The flash point of motor oil is the lowest temperature to which the oil must be heated under specified conditions to give off sufficient vapour to form a mixture with air that can be ignited spontaneously by a specified flame (ASTM D92). Table 4.1 shows that the flash point detected for the used motor oil samples were lower than that of the fresh oil. The decrease in flash point was as a result of contamination with flammable material such as gasoline. Oxidation of motor oil leads to the formation of volatile components which can reduce flash point (Lenoir, 1975). These volatile compounds would escape into the atmosphere when the used motor oil is re-used for wood preservation, road dust suppression, asphaltting with asphalt containing oil or indiscriminate disposal (Rafael 1988). A low flash point would cause the used motor oil to ignite faster at low temperatures and therefore poses fire threat to human life and properties.

5.5 Pour Point

The pour point of motor oil is the lowest temperature at which it can be poured or be in the flowing state (ASTM D97). It could be realized from Table 4.1 that the pour points of the used oil samples were higher than that of the fresh oil, especially in the case of the samples from commercial vehicles. This high pour point could be attributed to the presence of contaminants such as product of combustion, wear metals, dirt and other impurities. Fig. 4.1b reveals that among the two used oil samples the one from commercial vehicles had a higher pour point, which shows that it contain higher amount of contaminants and therefore may pollute more than the used oil from private vehicles. The pour point of engine oil is an important variable, especially when starting the engine in cold weather. The oil must be able to flow into the oil pump and then be pumped to the various part of the engine, even at low temperatures (Riazi *et al.*, 1987).

However, this purpose would be defeated if the pour point is high; affecting engine performance, and causing more wear of engine parts into the motor oil; which would eventually end up in the environment.

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5.6 Soot Content

The soot levels detected for the used motor oil, as indicated in Table 4.1 were high. Soot is microscopic carbonaceous particle that is formed as a result of incomplete combustion of hydrocarbons and therefore the high soot content recorded is an indication of the presence of products of combustion such as carbon monoxide and polycyclic aromatic hydrocarbons (Green and Lewis, 2008). These are atmospheric pollutants and have various forms of health effects. Polycyclic aromatic hydrocarbons in soot are mutagens and are classified as human carcinogens (ATSDR, 1995; IARC, 2006). High soot in motor oil causes carbon deposit on engine parts and serves as abrasion, causing more wear. Excess soot leads to sludge formation and increase oil viscosity; which impedes oil flow and increase engine wear (Green and Lewis, 2008).

5.7 Colour

The level detected for both fresh motor oil samples was 3.5 mg/L Pt while that of the used motor oil was >8 mg/L Pt as presented in Table 4.1. These levels corresponded to amber and black colours respectively (Appendix, 3). The black colour of the used motor oil is an indication of the presence of contaminants such as soot, which is known to be harmful to human health and the environment (Green and Lewis, 2008).

5.8 Heavy metals

The presence of heavy metals in used motor oil originate from engine wear and tear, additives, and fuel (Rafael, 1988; MTS, 2011); and there are many of these metals. Some are known to be carcinogenic among other harmful effects they could cause to human health, ecosystem functions and biodiversity (Demayo, 1982; Roberts, 1999; Baby, *et al.*, 2010; Sneddon, 2012). However, those analyzed in this research were Pb, Fe, Cr, Cu, Zn, Mn, Ba, V, As, Ni and Cd.

Pb was not detected in the fresh motor oil. However, the highest mean level (14.0 ± 19.7 mg/L) detected in the used motor oil was above the EPA permissible limit of 0.1 mg/L as shown in Table 4.2. This could be attributed to engine wear and tear due to its use on surfaces such as bearings and seal gaskets of engines (MTS, 2011). Studies have shown that Pb is poisonous (Demayo, 1982) and has the ability to cause various forms of harmful effects to human health such as disruption of the biosynthesis of haemoglobin and anaemia, kidney damage (IOSH, 1999), behavioural disruptions of children (Roberts, 1999; Dietrich, 2004), damage to the nervous system and the brains of unborn babies (Jennings, *et al.*, 1996). when released into the environment, it can accumulate in the bodies of aquatic and soil organisms (Demayo, 1982; Baby, *et al.*, 2010) and impact negatively on them and other organisms that depend on these as food.

333 ± 207.9 mg/L was detected as the maximum mean concentration of Fe in the used motor oil; which exceeded the EPA maximum permissible limit of 10 mg/L (Table 4.2). Among the two categories of samples, the mean level for the one from commercial vehicles far exceeded that of the private vehicles as indicated in Fig.4.2b. Fe in used motor oil could be as a result of engine wear.

It is the main component of steel and it is usually found in cylinder liners, crankshaft journals, and engine block. Fe is responsible for oxygen transport in the body and very low concentration can cause anaemia. However, excess exposure can cause damage to the liver, cardiovascular system, kidneys, and various forms of cancer (Roberts, 1999).

Cr with maximum mean concentration of 155 ± 63.6 mg/L was detected in the used motor oil. This was above the EPA guideline of 0.5 mg/L (Table 4.2). The concentration for the samples from commercial vehicles far exceeded that of the private vehicles (Fig.4.2b). Cr is mostly associated with the piston rings and usually used as steel hardener (MTS, 2011). Some additives also contain Cr. Therefore the presence of the metal in the used oil could be due to engine wear and additives. Studies have shown that Cr is carcinogenic (Sneddon, 2012) among other harmful health effects it could cause. Therefore discharge of such contaminated used oil into the environment may cause Cr pollution and affect organisms living in the contaminated areas.

Cu is used as additive in motor oil for petrol engines at a very low concentration. However, the maximum mean level (11.6 ± 16.1 mg/L) detected in the used motor oil exceeded the concentration for the fresh motor oil as well as the EPA permissible limit (5.0 mg/L) as indicated in Table 4.2. Cu is also used in engines due to its high ductility and thermal conductivity (MTS, 2011), and therefore its presence in motor oil could be attributed to engine wear and tear as well as additives. Cu has the ability to cause harmful effects to the liver, kidney and other vital organs of the body (ATSDR, 2004); and also impact negatively on plant and animals (Alloway, 2008). Improper disposal of large quantities of used motor oil with high Cu content may pollute the environment and impact negatively on organisms including humans.

Cd is used as additive; and a concentration of 0.0043 mg/L was detected in the fresh motor oil for diesel engines; which was below the EPA limit of 0.2 mg/L as shown in Table 4.2. However, it was below detection in the used motor oil. Some additive can precipitate out, especially in the presence of water (Stern and Girdler, 2013). When this occur the efficiency of oil lubricity could be reduced; causing engine wear.

Zn is used as additive in fresh motor oil for both petrol and diesel engines at low concentrations. Table 4.2 shows 0.106 mg/L of Zn for fresh petrol and 0.139 mg/L for fresh diesel engines oils; meanwhile mean concentrations of 1699.5 ± 1245.2 mg/L and 1683.0 ± 1579.7 mg/L were detected in the used motor oil from private and commercial vehicles respectively. These exceeded the EPA permissible limit of 10 mg/L. The metal could be found in bearing alloys and therefore the high levels of concentration could be attributed to engine wear and tear. Although Zn is a trace element that is essential for human health (ATSDR, 2005), excess exposure to high levels could lead to stomach cramps, skin irritations, damage to the pancreas (Salgueiro *et al.*, 2000; Nriagu, 2007) etc. Zn can bioaccumulate in the bodies of fishes and magnify up the food chain. It can also interfere with soil mechanisms; reducing the rate of decomposition of organic matter and affect soil fertility (Alloway, 2008).

Mn is an additive in gasoline as an octane booster. The maximum mean level detected in the used motor oil (8.0 ± 8.7 mg/L) was above the EPA limit (0.2 mg/L). High level of Mn in the used oil may be due to leakages from fuel into the oil. Even though Manganese is one of the essential trace elements (Keen *et al.*, 2000), excess exposure could cause damage to the respiratory tract, central nervous system and the brain (Crossgrove and Zheng, 2004).

Mean level of 1.0 mg/L was detected for Ba in the used motor oil samples; which was above the EPA guideline (0.7 mg/L) as presented in Table 4.2. The metal is mostly present in motor

oil as additive (MTS, 2011). Acute exposure to Ba can lead to breathing difficulties, increased blood pressures, heart rhythm changes, stomach irritation, muscle weakness, changes in nerve reflexes, swelling of brains and liver, kidney and heart damage. Chronic exposure of water-soluble barium may cause paralyses and in some cases death (ATSDR, 2007). The metal is persistent in the environment; especially in soil surfaces. It can accumulate in the bodies of aquatic organisms due to its water-solubility (CSQG, 2013).

The maximum mean level of As detected in the used motor oil was 2.9 ± 1.3 mg/L. This was above the EPA permissible guideline (0.5 mg/L) (Table 4.2). The metal is used to harden Pb and Cu alloys (MTS, 2011) and could occur in used motor oil as wear metal. It is said to be the most toxic element ever found (Roberts, 1999; Baby *et al.*, 2010). Exposure to inorganic arsenic could cause irritation of the stomach and intestines, decreased production of red and white blood cells, lung irritation etc. Organic Arsenic on the other hand, may cause nerve injury and stomachaches (ATSDR, 2007). High concentrations of the dangerous inorganic arsenic in surface waters enhance the chances of alteration of genetic materials in fishes (Baby, *et al.*, 2010). This arsenic poisoning could be transported through the food chain unto higher organisms.

Ni was detected at maximum mean concentration of 7481.0 ± 10576.9 mg/L in the used motor oil; which was far above the EPA permissible limit of 0.5 mg/L as shown in Table 4.2. Nickel can be found in certain alloys of steel for internal engine parts and it is also used as a coat on bearings.

Therefore its presence in used motor oil is an indication of shaft, gear and bearing wear (MTS, 2011). The element is known to be carcinogenic to both humans and animals (ATSDR, 2005).

The metals with extremely high concentrations in the study were Ni, Zn, Fe and Cr as shown in Table 4.2. It could also be observed from Fig. 4.2 (a) and (b), that the levels of these metals in the used motor oil from commercial vehicles far exceeded that of the private vehicles.

Used motor oil is usually re-used as fuel oil for firing boilers and heaters in the industry as well as in other combustion processes. The presence of these heavy metals would lead to the emission of metal oxides into the atmosphere and affect the environment. Indiscriminate disposal of the used motor oil would release these metals into the soil and water bodies, especially underground water and pollute them.

5.9 Volatile Aromatic Hydrocarbons

These are volatile organic compounds and are very toxic (Zhao and Zhai, 2010). The volatile aromatic hydrocarbons considered in this research were benzene, toluene and xylene.

Although benzene was not present in the fresh motor oil, a maximum mean level of 5.7 mg/L was detected in the used motor oil. The levels of toluene and xylene in all the samples were below detectable limits (Table 4.3). Derivatives of benzene, toluene and xylene (Appendix, 2) were present in both the fresh and the used motor oil samples as shown in Table 4.3. The concentrations of benzene and xylene derivatives in the used motor oils were low compared to that of the fresh motor oil while that of toluene was high (Table 4.3).

However, Fig. 4.3 shows that the levels of toluene and xylene derivatives in the used oil sample from private vehicles were higher than that of commercial vehicles and vice versa for derivatives of benzene. Currently there is no EPA limit for benzene, toluene, and xylene; and

consultation with the agency revealed that no safe levels could be recommended due to their toxicity.

Studies have shown that benzene is carcinogenic to humans, and could cause even death (ATSDR, 2007). Excess exposure to toluene can affect the brain and the nervous system (IPCS 1985; ATSDR, 2000; Leusch, 2010); and long-term exposure to xylene can also have a number of effects on the nervous system (IPCS 1997; ATSDR, 2007; Leusch, 2010).

Volatile aromatic hydrocarbons such as BTEX or their derivatives could be present in motor oil as components of the formulation or as contaminants through fuel (Leusch, 2010). However, they are eventually released into air during engine operation, storage or re-use of used motor oil for other purposes (IPCS, 1985, 1993, 1996, 1997, and Leusch, 2010).

5.10 Total Petroleum Hydrocarbons (TPH)

The term Petroleum Hydrocarbon is used to describe a large family of several hundreds of chemical compounds that originally come from crude oil (ATSDR, 1999).

The highest mean level of petroleum hydrocarbons detected in the used motor oil was 2035.0 mg/L which was extremely high compared to that of the fresh motor oil (4.8 mg/L) as shown in table 4.3. According to the EPA there is no exposure limit for TPH in the environment due to the toxicity of the components.

Petroleum Hydrocarbons are present in motor oil as components of the formulation or as contaminants from petroleum products (ATSDR, 1999; Leusch, 2010). Some components of petroleum hydrocarbons such as benzene are carcinogenic (ATSDR, 2007). Others can affect the central nervous system, circulatory system, lungs, immune system, skin, eyes etc.

(ATSDR, 1999).

The volatile components of the petroleum hydrocarbons would escape into the atmosphere when the used motor oil is re-used for wood preservation, road dust suppression, asphaltting with asphalt containing oil or indiscriminate disposal (Rafael 1988). The heavier ends would be released as products of combustion such as dibenzodioxin compounds as well as oxides of carbon, sulphur, nitrogen, phosphorus, and halogens compounds (Mahaney, 1993) when the used oil is re-used as fuel oil for firing boilers and other heating purposes. Some fractions may float on water and form surface films or sink to the bottom sediments when the used oil is spilled into water. Microorganisms who feed on them may compete with aquatic organisms for dissolved oxygen and as a result deprive the fish of the oxygen needed for their survival (Alberta, 1993).

5.11 Hydrogen Sulfide

Hydrogen sulfide is very hazardous and the lowest concentration released into the environment can be very harmful. The highest mean level detected in the used motor oil was 191.0 mg/L as shown in Table 4.3. Exposure to low concentrations of 0.03 mg/L may cause eye, nose, and throat irritation, headaches and nausea (ATSDR, 1997; 1999). It may also cause difficulty in breathing for some individuals with respiratory problems such as asthmatics (ATSDR, 1999). Acute exposures to high concentration can cause serious health effects including a loss of consciousness, poor attention span, memory and motor function. These effects may be longterm or even permanent (HSFS, 2004).

Hydrogen sulfide is usually found in crude oil (Nicholson and Tim O'Brien, 2001), and therefore it could be present in motor oil as contaminant from fuel or as component of the base oil used in the formulations.

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CHAPTER SIX

6.0 CONCLUSION AND RECOMMENDATION

6.1 CONCLUSION

The research revealed that used motor oil could be harmful to the environment due to the high levels of the physicochemical properties detected.

High levels of heavy metals were detected which exceeded the maximum permissible limits of the Environmental Protection Agency for waste oil. The volatile aromatic hydrocarbons (benzene, toluene and xylene) and total petroleum hydrocarbons were also in significant concentrations in both types of used oil. The concentration of hydrogen sulfide detected was also above the EPA permissible guidelines. The presence of these contaminants in the used motor oil would impact negatively on the environment. The high heavy metals content of the used oil would lead to the emission of metal oxides and other contaminants into the atmosphere during combustion processes. Volatile aromatic hydrocarbons, H_2S and the volatile components of TPH can escape into air. Some of these contaminants could cause acid rain and impact negatively on aquatic and terrestrial ecosystems.

The low viscosity and flash point detected indicates that the used motor oil has high mobility and could spread to cause pollution and fire outbreaks. This shows that indiscriminate disposal of used motor oil could be dangerous to the environment. High quantities of motor oil (11.89 million gallons) are consumed in Ghana annually. As a result large quantities of used oil with high levels of volatile organics as well as heavy metals are discharged into the environment annually. These contaminants can seriously pollute the environment and impact negatively on human health.

It was also realized that the used motor oil samples from the commercial vehicles were highly contaminated as compared to that of the private vehicles.

Considering the high levels of contaminants in the used motor oil, it could be concluded that the impact of used motor oil could be highly significant when released into the environment without any treatment to reduce levels of these contaminants.

6.2 RECOMMENDATION

The following are some of the actions that can be considered to help eliminate/reduce the level of environmental pollution with regards to used motor oil:

- Automobile service stations should have oil spill contingency plan to deal with spillages.
- Mass transport system would help reduce the amount of used motor oil generated.
- Used motor oil must be treated before reuse or disposal.

APPENDICES

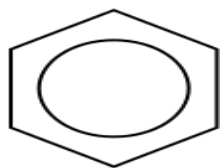
APPENDIX 1: EPA PERMISSIBLE GUIDELINES

Environmental Protection Agency (EPA) maximum permissible limits for lubricants and waste oil recycling and general guidelines were used as presented in the table below:

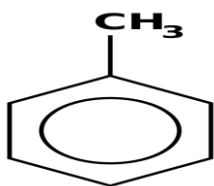
Table (Appendix 1): EPA Permissible Guidelines

Parameters	EPA Maximum Permissible Levels (Lubricants and Waste Oil Recycling).	EPA Permissible Levels (General)
Pb (mg/L)	0.1	0.1
Fe (mg/L)	10	2.0
Cr (mg/L)	N/A	0.5
Cu (mg/L)	5.0	5.0
Cd (mg/L)	0.2	0.2
Zn (mg/L)	10	10
Mn (mg/L)	N/A	0.2
V (mg/L)	N/A	0.1
Ba (mg/L)	N/A	0.7
As (mg/L)	N/A	0.5
Ni (mg/L)	N/A	0.5
Benzene (mg/L)	N/A	N/A
Toluene (mg/L)	N/A	N/A
Xylene (mg/L)	N/A	N/A
TPH (mg/L)	N/A	N/A

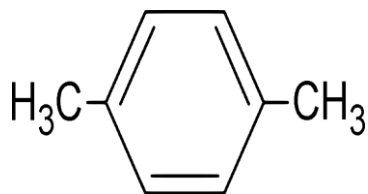
APPENDIX 2: STRUCTURE OF BENZENE AND ITS DERIVATIVES



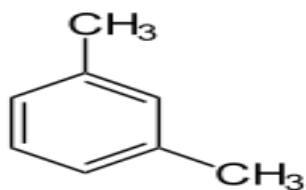
Benzene



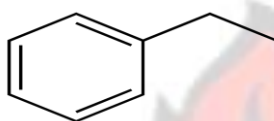
Toluene



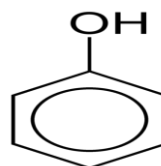
p-Xylene



m-Xylene



Ethylbenzene



Phenol

APPENDIX 3: EQUIPMENT USED, THEIR MANUFACTURERS AND COUNTRY OF ORIGIN

Equipment	Manufacturer	Country of Origin
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Density Meter DM 4500	Anton Paar	Europe
Cleveland Open Cap Flash Point Tester	Koehler Instruments Company	USA
Koehler Kinematic viscosity bath	Koehler Instruments Company	USA
Koehler Viscometer	Koehler Instruments Company	USA
GD-510D Petroleum Products Pour Point Tester	Chongqing Gold Mechanical & Electrical Equipment Co., Ltd.	China
Spectroil M	Spectroil Scientifics	USA
Coulometric Karl Fischer Titration Apparatus	Metrohm AG.	Europe
Lovibond Petroleum AF 650 colour indicator	The Tintometer Ltd.	Europe
Intracal TOG/TPH Analyzer.	Wilks Enterprise, Inc.	USA
Dragger CMS Machine	Dräger Safety AG. & Co. KGaA	Germany
Thermo gravimetric Analysis Apparatus	PerkinElmer	India

APPENDIX 4: PICTURES OF FRESH AND USED MOTOR OIL SAMPLES



APPENDIX 5: PICTURES OF EQUIPMENTS & EXPERIMENTAL SET-UPS USED FOR THE ANALYSIS

Equipment used for the Heavy Metals Analysis



Spectroil M

Equipment and Materials used for the analysis of Benzene, Toluene, Xylene and Hydrogen sulfide



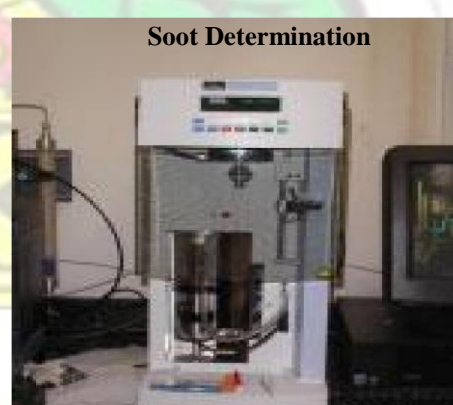
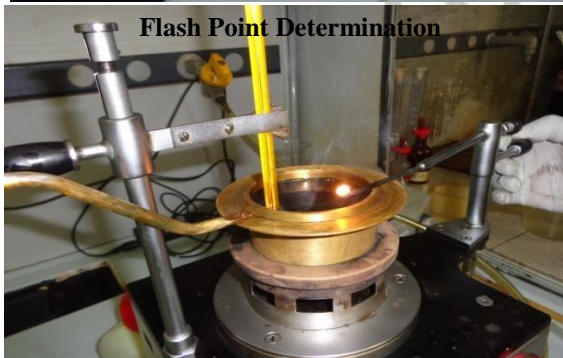
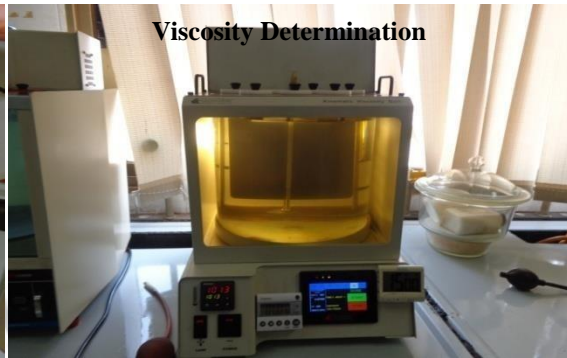
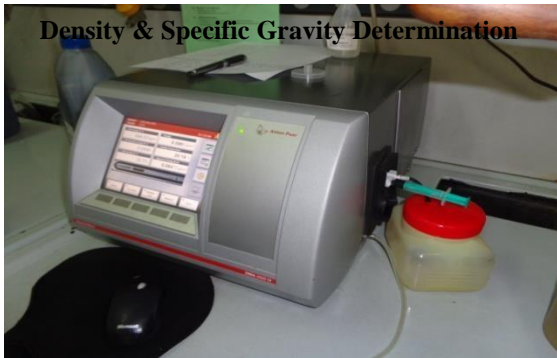
Dragger –Chip Mess System.

Equipment used for the Analysis Total Petroleum Hydrocarbons



InfraCal® TOG/TPH Analyzer

Equipment used for the Analysis of Physical Properties



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