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Assessment of heavy metal contaminants of used engine oil around automobile workshop in Nasarawa local Government area, Nasarawa state, Nigeria

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Abstract

The study was carried out on assessment of heavy metal contaminants of used engine oil around automobile workshops in Nasarawa Local Government Council**,** Nasarawa State, Nigeria. Samples of Soil, water, fluted pumpkin leaves, spinach and used engine oil were collected from selected mechanic workshops within the Nasarawa Local Government Area for both rainy and dry seasons were analyzed for heavy metal concentrations. These samples were subjected to analysis for eight elements; Co, Zn, Cd, Cu, Ni, Mn, Cr and Pb using Inductively Coupled Atomic Absorption Spectrophotometer. The results of the analysis carried out for both rainy and dry seasons showed clearly that there is more concentration of the heavy metals analyzed in the dry season than that of the rainy season. The result also shows that apart from the mechanic workshop, some of the metals have high concentrations in some control samples. The results of the analysis showed that most of the heavy metals examined in some samples were above the World Health Organization limit for human consumption.

Keywords: Heavy metals, used engine oil, automobile workshop, soil, water, Amaranthus Habridus

Introduction

The increase in population worldwide has led to a high level of industrialization and urbanization which in turn have led to environmental pollution arising from the indiscriminate discharge of industrial effluents. These effluents may contain most common heavy metals, such as Hg, Zn, Cu, Co, Pb, Cr (Madu *et al.*, 2007) [12]. It is known that pollution through heavy metal has become increasingly more in recent years, not only because people are more sensitive on this subject but also because the amount of pollution has increased markedly. There is need for research and public information on these metals, otherwise unknown dangers may create irreparable environmental damage. Since 1999, thousands of cars, Lorries, motor cycles are coming into Nigeria and the number of mechanic villages are increasing at a very high rate and consequently the amount of used automotive oil being disposed everyday has equally increased (Madu *et al.*,2007) [12].

Waste automotive oil can be defined as oil that has picked up foreign substances, or contaminants. This can occur before, during or after use (CCME, 2002). Waste automotive oils collect contaminant in many ways depending upon the original use of the oil. In general, waste automotive oils contain oxidation products, sediments, water and metallic particles resulting from machinery wear. In addition to these, waste automotive oil also contains gasoline fuels, organic and inorganic chemicals used in oil additives and metals which were present in gasoline and transferred to the crankcase during combustion (Adebayo *et al.*, 2004) [1]. Lead is the principal metallic contaminant found in waste automotive oils being present in amounts which sometimes exceed one percent by weight (Olonisakin *et al.*, 2005) [14].

Heavy metals are natural components of the earth crusts. They are stable and persistent environmental contaminants of coastal waters and sediments. Since they cannot be degraded or destroyed to a small extent, they enter our bodies via food chain, drinking water and air (Lawrence, 1990) [9]. Examples of heavy metals include mercury (Hg), cadmium (Cd) Arsenic (Ar) chromium (Cr) Lead (Pb) Nickel (Ni) Zinc (Zn), and Selenium (Se). Interest in metals like Zinc, Copper, Iron and Selenium which are required for metabolic activity in organisms lies in the narrow path between their essentiality and toxicity. Other heavy metals like lead, cadmium and mercury may exhibit extreme toxicity even at low levels under certain conditions, thus necessitating regular study, monitoring and assessment of heavy metal pollution of sensitive aquatic environment (Nriagu, 1996) [11].

Some of these heavy metals are important elements needed by both plants and animals in small quantity for their normal body development and physiological functions including effective immune system. They play regulatory function in the body tissues and are then discharged out of the body. Hence, their regular supply in the body is essential (Aremu *et al.*, 2008) [3]. However, the dietary concentration of one heavy metal can affect the availability of other heavy metals. Heavy metals reach the plants through the soil by direct application, direct deposition and from contaminated water by absorption process. The prolong usage and deposition of waste automotive oil has led to the accumulation of these heavy metals in agricultural soils (Aremu *et al.*, 2006) [2]. High intake of heavy metals by humans from diets can lead to fatal consequences to the liver and kidney, with copper causing hair damage, nickel causing increased incidence of cancer of the lungs and nasal passage and lead associated with hypertension (Lawrence, 1990) [9]. Heavy metals produce toxicity by forming complexes with organic compounds and active sites of enzymes (Nriagu, 1996) [11]. The aim of the research therefore, is to investigate the impact of discharged waste automotive oils from automobile workshops on heavy metal concentrations in soils, well water and selected vegetables in Nasarawa Local Government, Nasarawa State.

Materials and Methods

Sample Collection and Preparation

Sample Collection/ Preparation

Samples of water, Soil, Fluted pumpkin, Spinach and Used engine oil were collected at random from three (3) selected mechanic workshop (study area) within Nasarawa Local Government Area (Mararaba, Nasarawa and Shamage) between 28th August – 10th September, 2015 representing rainy. In addition, one (1) sample of unused engine oil (SAE40) was purchased from Total Filling Station to serve as control.

Soil Samples

Ten (10g) grams of soil sample was weighed and air-dried in the laboratory (NARICT ZARIA), pulverized with an agate mortar, and then sieved through a nylon sieve with a pore diameter of ≤0.149mm. The sieved soil sample (2g) was weighed into tetrafluoroethylene (PTEE) beaker, mixed with 6cm^3 of concentrated HNO^3, 3cm^3 concentrated HCl and 0.25cm^3 H_20_2 and then heated in microwave digestion system (GEM mars). The digested solution was then diluted to 50cm^3 with ultra-pure water and filtered through a 0.45µm micro porous membrane. The filtered solution (1cm^3) was measured and diluted to 10cm^3 for the analysis of Pb, Cd, Cu, Zn, Mn, Ni, Cr and Co by inductively coupled Atomic absorption spectrophotometer (AA-6800 SHIMADZU) as reported by Aloysius *et al*; 2013

Plant Samples

Plant samples were oven dried and pulverized with a pulverizer. Then, 2g of the sample was weighed into a digester and mixed with 1cm^3 of concentrated H_2SO_4, 8cm^3 concentrated HNO_3 and 1cm^3 concentrated $HClO_4$. The digester was covered with lid and heated in graphite furnace at low temperature between 30 - 40 ^{0}C. A black residue was formed. To the residue, 0.5cm^3 concentrated $HClO_4$ was added into the digester and then heated again. The process was repeated until the digested solution became clear. The digested solution was then filtered through a 0.45 µm microporous membrane filtered into a 100cm^3 volumetric flask and diluted to mark with deionized water for the analysis of Pb, Cd, Cu, Zn, Mn, Cr, Ni and Co by inductively coupled Atomic Absorption Spectrophotometer as specified by Adepoju *et al*; 2013 [4]

Water Samples

The water samples were collected from wells using a small plastic container within the study areas and stored in a 2 liter plastic containers for heavy metal determinations. 50cm^3 of the water samples was measured using a measuring cylinder into plastic containers and were digested with 6cm^3 of 1mol dm^{-3} HNO_3 for 24h to obtain a clear solution for heavy metal determination.

Used/Unused Engine Oil

Samples of used/unused engine oils were collected from the study area after being withdrawn from the vehicles during servicing using 500cm^3 plastic bottles. 5g of homogenized used/unused engine oils were weighed in a previously washed and dried silica crucibles. The crucibles were then kept on a hot plate at a temperature of 120 ^{0}C until the oils gets completely dried up. The crucibles were then transferred into a muffle furnaces set at a temperature of 450 ^{0}C for 4hrs and then at 750 ^{0}C for 2hrs to have complete ash content. The ash in the crucibles were kept in a dessicator for cooling. The content was then dissolved in 1.5cm^3 concentrated HCl. The solutions were then diluted to 100cm^3 by deionized water and stored in a plastic bottles. The diluted samples were then analyzed by Atomic Absorption Spectrophotometer as reported by Mohammed *et al;* 2014 [13].

Results and Discussion

Tables 1 – 5 show the mean result of heavy metal analysis in water, soil, used/unused engine oil and plant samples in Nasarawa Local Government Areas.

The result of the heavy metal concentrations in water sample was presented in Table 1 showing locations Mararaba, Nasarawa and Shamage respectively as follows:

Mn> Ni > Zn > pb > Cd > Cu. Metal such as Cobalt was not detected.

Mn> Pb > Zn > Cr > Cd > Cu. Cobalt and nickel were not detected.

Mn> Pb > Co > Ni > Cr > Zn > Cu > Cd.

Table 1: Rainy season Concentration (Mg/L) of Heavy Metals in well water from Auto mobile workshop in Nasarawa L.G.A.

Element	Mararaba Mean	SD	CV	Nasarawa Mean	SD	CV	Shamagye Mean	SD	CV
C0	0	0	0.00	0	0	0.00	26.61	2.29	8.61
Zn	20.02	1.67	8.34	48.43	3.98	8.22	2.72	0.28	10.29
Cd	1.68	0.11	6.55	2.84	0.29	10.21	1.91	0.26	13.61
Cu	1.64	0.17	10.37	1.65	0.17	10.30	2.45	0.29	11.84
Ni	50.72	4.16	8.20	0	0	0.00	14.12	1.16	8.22
Mn	140.28	9.82	7.00	224.52	18.06	8.04	142.57	11.42	8.01
Cr	11.81	0.97	8.21	14.42	1.29	8.95	7.21	0.67	9.29
Pb	5.22	0.49	9.39	68.81	4.87	7.08	53.21	4.37	8.21

The heavy metal concentration for all locations were within the WHO permissible limit of drinking water except locations such as shamage with high concentration of Cu (2.0mg/kg WHO, 2011) and lead (10mg/kg; WHO 2011). Similarly, Pb concentration was high compared to WHO at Nasarawa town. This observation was also reported by Hanuman *et al*, 2012 [8].

Table 2 shows the mean value of metal distribution for used oil in all the location as follows:
Cr > Pb > Co > Zn >Mn > Pb > Cu > Cd. Nickel was not detected at Nasarawa. However, the metal distribution for the control (SAE 40) show the following pattern -: Pb > Zn > Cr >Mn> Cu > Ni > Cd. Cobalt was not detected in the control sample.

Table 2: Rainy season Concentration (Mg/L) of Heavy Metals in used/unused oil from Auto mobile workshop in Nasarawa L.G.A.

Element	Mararaba Mean	SD	CV	Nasarawa Mean	SD	CV	SAE 40 (Control)		CV
							Mean	SD	
C0	13.31	1.18	8.87	85.72	6.9	8.05	0	0	0.00
Zn	6.21	0.67	10.79	22.33	2.04	9.14	15.69	1.33	8.48
Cd	2.91	0.22	7.56	1.52	0.12	7.89	1.37	0.15	10.95
Cu	1.61	0.16	9.94	2.02	0.24	11.88	2.51	0.29	11.55
Ni	0.81	0.17	20.99	0	0	0.00	1.92	0.26	13.54
Mn	5.15	0.47	9.13	15.71	1.45	9.23	6.62	0.59	8.91
Cr	20.91	1.9	9.09	26.12	2.15	8.23	8.56	0.83	9.70
Pb	18.83	1.74	9.24	13.52	0.91	6.73	57.32	4.67	8.15

The concentration of heavy metals in soil, as presented in Table 3, has the following distribution: Mn> Ni > Zn > Cr > Pb> Cu > Cd. Co was not detectable at AAS atMararaba. The following pattern was recorded at Nasarawa Mn> Pb > Zn > Cr > Cu while Ni and cobalt were below detectable limit of AAS. The results from shamage than the following metal distribution pattern.
Mn> Pb > Co > Ni > Zn > Cu > Cd. All metal were detected in all the location.

Table 3: Rainy season Concentration (Mg/L) of Heavy Metals in soil from Auto mobile workshop in Nasarawa L.G.A.

Element	Mararaba Mean	SD	CV	Nasarawa Mean	SD	CV	Shamagye Mean	SD	CV
C0	0	0	0.00	0	0	0.00	26.67	2.26	8.47
Zn	20.07	1.63	8.12	48.42	3.91	8.08	2.77	0.22	7.94
Cd	1.61	0.16	9.94	2.82	0.25	8.87	1.93	0.25	12.95
Cu	1.63	0.16	9.82	1.68	0.13	7.74	2.45	0.26	10.61
Ni	50.37	4.17	8.28	0	0	0.00	14.19	1.15	8.10
Mn	140.26	9.81	6.99	224.55	18.05	8.04	142.53	11.47	8.05
Cr	11.83	0.92	7.78	14.47	1.26	8.71	7.23	0.67	9.27
Pb	5.22	0.43	8.24	68.81	4.86	7.06	53.21	4.37	8.21

Cadmium concentration in soil sample were reported high (WHO (0.8mg/kg) 1996) for all the study areas. Ni Concentration was not at detectable limit at Nasarawa but with permissible limit shamage, while it was reported high at Mararaba (35.0mb/kg, WHO 1996). The concentration of all other elements were within the permissible limit.
This findings of elevated cadmium concentration is consistent with that of Luter *et al*, (2011) [10] who investigated heavy metals in soil of auto-mechanic shop add refuse dumps sites in other parts of Makurdi, Nigeria.
Table 4 indicates the heavy metal distribution in fluted pumpkin as follow:
Pb > Co > Cr > Zn >Mn> Cd. Metals such as Ni, Co and Pb were below the detectable limit. However, the metal distribution at shamage has pattern Co > Ni > Cr >Mn> Cd > Zn > Cu. Interestingly, metal such as Pb was below the detectable limit at the region.

Table 4: Rainy season Concentration (Mg/L) of Heavy Metals in fluted pumpkin from Auto mobile workshop in Nasarawa L.G.A.

Element	Mararaba Mean	SD	CV	Nasarawa Mean	SD	CV	Shamagye Mean	SD	CV
C0	89.42	7.24	8.10	0	0	0.00	27.81	1.76	6.33
Zn	5.62	0.46	8.19	2.72	0.26	9.56	1.64	0.17	10.37
Cd	2.23	0.26	11.66	1.76	0.18	10.23	2.74	0.28	10.22
Cu	0.53	0.07	13.21	0.91	0.17	18.68	1.04	0.17	16.35
Ni	0.81	0.16	19.75	0	0	0.00	23.71	1.46	6.16
Mn	5.32	0.44	8.27	20.52	1.44	7.02	5.32	0.45	8.46
Cr	13.13	0.91	6.93	10.51	0.86	8.18	21.67	1.53	7.06
Pb	93.81	6.64	7.08	0	0	0.00	0	0	0.00

Discussion on Plant

The plant samples understanding showed Cd & Zn metal distribution in all locations were higher than the WHO standard (0.02mg/kg, WHO 2006). The concentrations of Cu at all location were with the permissible limits (10mg/kg WHO std 2006). Cr distribution were high at all locations for the plant – fluted pumpkin while for spinach it was higher at Nasarawa &Shamage and not detected at Mararaba.

The concentration of Cd in the sample rage from 0.41 – 2.74 mean value. The maximum level of Cd allowable in leafy vegetables by the European economic commission is 0.2mg/kg. This high level of Cd reported in fluted pumpkin & spinach if consumed can result to chronic obstructive having diseases, renal diseases and fragile bones as reported by Adepoju *et al*, 2013 [4].

Finally, the metal concentration of spinach at Mararaba, Nasarawa and Shamage were presented in Table 5 as follows:

Co > Pb >Mn> Zn > Cu > Cd. Nickel and Chromium were not detected.

Pb >Mn> Cr > Zn > Cd > Co. Cobalt and Nickel were not found.

Pb > Ni > Cr > Co >Mn> Zn > Cd > Cu.

Table 5: Rainy season Concentration (Mg/L) of Heavy Metals in Spinach from Auto mobile workshop in Nasarawa L.G.A.

Element	Mararaba Mean	SD	CV	Nasarawa Mean	SD	CV	Shamagye Mean	SD	CV
C0	89.45	6.29	7.03	0	0	0.00	10.91	0.81	7.42
Zn	6.32	0.56	8.86	2.03	0.27	13.30	5.13	0.46	8.97
Cd	0.41	0.06	14.63	1.91	0.16	8.38	1.44	0.16	11.11
Cu	1.81	0.17	9.39	1.62	0.15	9.26	1.32	0.14	10.61
Ni	0	0	0.00	0	0	0.00	12.62	0.91	7.21
Mn	13.91	1.16	8.34	27.81	2.28	8.20	10.18	0.82	8.06
Cr	0	0	0.00	18.37	1.52	8.27	11.87	0.88	7.41
Pb	52.13	4.26	8.17	86.54	6.93	8.01	43.82	3.57	8.15

Conclusion/Recommendation

The study has presented data on the concentration of some heavy metal around Mech. workshop in Nasarawa L.G.A. The result of the analysis carried out for soil sample in all locations showed elevated values of Cd and Ni. Analysis of Cd, Zn, Cr, and Pd showed high levels of these heavy metals in plant samples; a commonly consumed vegetable poses potential health risk to consumers. Pollutants including heavy metals, oil and grease build up to very high concentration with time in the soil, and thereby seep or percolate into the ground water, and so poses great hazards to the people that consume the water. Based on the present study, it is recommended that strict compliance to regulatory limits in sludge to be released from the Mech. Workshop into the environment is recommended. In addition, people leaving around the Mech. Workshops should be discourage from eating large quantity of studied plants so as to avoid excess accumulation of these heavy metals in the body.

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