

Heavy metal levels in spent engine oils and fingernails of auto-mechanics

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Abstract. The levels of some heavy metals in spent engine oils and in the fingernails of auto-mechanics were studied. Engine oils and fingernails were collected from auto-mechanics who had practiced between ≤ 5 years, ≤ 10 years and ≤ 15 years in 3 auto-mechanic workshop clusters. Pb, Ni, V, Cd, and As levels were determined using Atomic Absorption Spectrophotometer. The mean levels of Pb, Ni, V and Cd in spent engine oils were 14.31, 2.25, 0.38 and 2.07 ppm respectively, and these far exceeded their permissible exposure limits. The mean levels of heavy metals in the fingernails of auto-mechanics who had practiced for ≤ 5 years, ≤ 10 years and ≤ 15 years were all considerably below their pathological thresholds. Thus, auto-mechanics in the study area are exposed to unsafe levels of Pb, Ni, V, and Cd, but no immediate threat of their toxicities in the study population exist. However, a progressive bioaccumulation of the heavy metals was observed with increase in years of practice.

Keywords: auto-mechanics; heavy metals; fingernails; spent engine oil; occupational exposure.

1. Introduction

Industrialization and economic growth have continued to create a growing need for the movement of people, goods and services from place to place [1-3]. This has contributed to the growing number of automobiles in use [4] as well as the number of auto-mechanics required to maintain them, such that the demand for auto-mechanics exceeds their supply [5-8]. However, in Nigeria, the supply of auto mechanics is believed to exceed their demand. The presence of Pb and other heavy metals in petrol, engine oil and car exhaust gases constitute some of the major sources of exposure of auto-mechanics to these heavy metals [9]. In mechanic workshops, heavy metal exposure occurs via nasal, oral and dermal routes [10]. Rising levels of these heavy metals in body tissues such as fingernail, blood and hair, of auto-mechanics may indicate their bioaccumulation from frequent occupational exposure [4], thus threatening the health and wellbeing of the limited number of people that constitute this peculiar workforce. Several studies have been carried out to determine the levels of heavy metals in auto-mechanic workshop soils [11-15], work clothes [4], engine oils [16], fingernail, hair [17, 18] and blood [19] as well as other samples linked with automechanics and several other populations exposed to heavy metals. All of such studies have reported varying levels of exposures that are mostly affected by a combination of factors peculiar to the study area, such as: the attitude of the study population to the use of protective gear, level of compliance with workplace safety precautions, level of existing awareness on ergonomic sources of exposure to heavy metals among others. For instance, Sani et al. [4] reported that in Africa, most auto-mechanics are not using the needed safety kits such as goggles, safety garb etc. In fact, automechanics use the same work-cloth for several months without washing. Also, as a result of inadequate equipment and working tools, mechanics often use their bare hands in most of their work resulting in adsorption of different contaminants into their skins. This is perhaps why it is important that, in order to actually ascertain the levels of exposure to heavy metals among auto-mechanics, such studies should be done in workshop clusters among auto-mechanics who operate under a similar set of conditions.

Although it is recognized that auto-mechanics are exposed to various types of hazardous substances, priority is often given to lead, nickel, vanadium, cadmium and arsenic because of the several sources of these heavy metals in automobile-workshops, ranging from spent engine oils, contaminated work clothes, contaminated workshop soils, materials used in the fabrication of auto-mobile parts, to the various petroleum products that are required for the smooth operation of vehicles [20, 21]. Spent engine oil refers to engine oil after it has been used for lubrication in vehicle engine. It has been reported that blood and other fluids present in the human body give transient concentrations of these analytes, this may be due to xenobiotic metabolism or their incorporation into bone tissue but human nails provide a continuous record of elemental exposure [22] as they provide a longer integration period for heavy metals. The use of nails as a biomarker of occupational exposure to heavy metals in the body is preferred also because, they are regarded as good bioindicators for several toxic elements to which workers had been exposed from all routes [23] for a duration of at least two to eighteen months [24]. Heavy metal accumulation in high amounts within the body can have severe health implications and may be lethal in severe

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cases [9, 10], as such, the exposure of auto mechanics to them must be determined as an empirical basis for the enforcement of safety protocols for use in such work environments. This study is one such study which seeks to determine, the concentrations of selected heavy metals in the spent engine oils which auto-mechanics routinely come into direct contact with, as well as the concentrations of same in their fingernails in order to ascertain the level of occupational exposure of these group of workers to heavy metals in their workplace.

2. Experimental

2.1. Materials

All reagents and standards used were of analytical grade and supplied by BDH, UK. Also, 1000 mg/L solution each of Pb, Ni, V, Cd, and As was used for the preparation of working standards. All glassware, porcelain and plastic wares were washed four times using deionized water, before soaking them in 20 % v/v HNO₃ for 24 h. Thereafter, the laboratory wares were rinsed four times in deionized water and oven-dried at 90 °C for 8 h.

2.2. Sample collection and pre-treatment

Three auto-mechanic workshop clusters in Makurdi (North-bank, New garage and Apir, coded as A, B and C respectively) located in Benue State, within the North-Central part of Nigeria were chosen for the study. Fifteen sampling stations were selected within each workshop cluster. In each of the auto-mechanic workshop clusters A, B and C, 5 mL each of spent and unspent engine oils were separately collected from 15 automobile workshops during routine automobile oil replacement. Pre-cleaned 5 mL syringes were used for the sample collection. Thereafter, each category of engine oil samples (spent and unspent) from a given cluster were composited into 3 groups of 25 mL sample triplicate and stored in prewashed glass bottles until needed for heavy metals analysis.

In each of the auto-mechanic workshop clusters A, B and C, fingernail samples were collected from all 10 fingers of each of the 30 auto-mechanics randomly selected per cluster by trimming with clean stainlesssteel nail-cutters. The fingernail samples were then composited in triplicates according to the durations of practice of the auto-mechanics, namely: short, medium and long terms (≤ 5 years, ≤ 10 years and ≤ 15 years respectively). The pre-digestion washing of the nail samples were done in a previously cleaned beaker for 15 minutes using 160 mL distilled acetone/hexane (3/5, v/v) for 24 h, before being washed repeatedly with deionized water and oven dried at 120 °C for 30 min. This was to remove external contaminants [4, 25, 26]. The oven-dried samples were pulverized into a fine powder using an acid-washed porcelain mortar before storing away in clean plastic containers until needed for heavy metals analysis.

2.3. Heavy metals analysis

The instrumental methods reported by Pam *et al.* [13] and Jacob *et al.* [27] were adapted for the determination of heavy metals in the engine oil samples in this study. Using a micropipette, 1 mL of each of the composite

engine oil samples were separately transferred into 25 mL acid washed, volumetric flasks, each containing 15 mL concentrated HNO₃ and slowly evaporated over a period of 9 h on a heating mantle. Each residue obtained was digested with 15 mL 3:1 v/v concentrated HNO₃ and HClO₄ mixture for 8 h at room temperature before heating intermittently on a heating mantle to ensure a steady temperature of 150 °C was maintained for over 6 h until the HClO₄ fumes were completely evaporated. Each mixture was separately allowed to cool to room temperature before filtering into a 50 mL volumetric flask using Whatman No. 1 filter paper and making up to the mark with deionized water, following quantitative rinsing of the reacting vessels. The solution of the sample filtrate was then stored in pre-cleaned amber bottles until instrumental analysis. Pb, Ni, V, Cd, and As levels in each sample diluent was determined in three repetitions for each sample using an Atomic absorption spectrophotometer (Phoenix-986, Biotech engineering, UK). The instrument was calibrated with analytical grade standard metal solutions (1 mg/dm³) and the instrument operated following the manufacturer's operational instructions. The mean levels of each heavy metal in the samples from each location were computed and statistically compared using One-way ANOVA for significant differences and thereafter, compared with set permissible exposure limits.

The instrumental methods reported by Mehra et al. [28] and Rashed et al. [17] were adapted for the determination of the heavy metals in fingernail samples in this study. 0.1 g amount of each category of the pulverised fingernail sample was digested in 5 mL concentrated HNO₃/HCl (3:1) acid mixture and allowed to stand at room temperature overnight before heating to near dryness on a heating mantle. Thereafter, 2 mL 19% HNO₃ was added to the sample digest and dissolved with deionised water and then made up to the mark in a 10 mL volumetric flask with more deionised water. The above procedure was repeated for the standard and reagent blank sample used to calibrate the equipment. Pb, Ni, V, Cd, and As concentrations were measured in the fingernail sample solutions by flame atomic absorption spectrophotometer (Phoenix-986, Biotech engineering, UK) following the instrument manufacturer's instruction. The mean level of the heavy metals determined in the fingernail samples were statistically compared according to clusters and by duration of practice for any significant difference using One-way ANOVA, and thereafter compared with set pathological limits established by regulatory bodies.

2.4. Statistical analysis

SPSS-statistics version 22.0 was used to calculate the mean \pm standard deviations of the concentrations of heavy metals determined in engine oil and fingernails samples as well as to compare them by location and duration of practice using One-way ANOVA.

3. Results and discussion

Table 1 shows the concentration of some heavy metals in spent and unspent engine oils in Makurdi metropolis, and it can be seen from it that, unspent engine oils have the lowest level of all the heavy metals in the study. This is an indication that, with usage in automobile engines, engine oils become laden with more heavy metals.

 Table 1. Heavy metal concentrations in spent and unspent engine oils in Makurdi Metropolis

SN	Type of engine oil and source	Pb (ppm)	Ni (ppm)	V (ppm)	Cd (ppm)	As (ppm)	
1	Spent engine	12.22 ^a	1.73 ^m	0.26 ^p	1.94 ^e	N. D.	
	oil – Cluster A	± 1.25	± 0.39	± 0.07	± 0.27	N.D.	
2	Spent engine	16.64 ^b	1.83 ^m	0.66 ^q	1.98 °	N. D.	
	oil - Cluster B	± 1.96	± 0.33	± 0.18	± 0.10	N. D.	
3	Spent engine	14.09 a	3.21 ⁿ	0.23 p	2.30 f	N. D.	
	oil - Cluster C	± 0.68	± 0.25	± 0.05	± 0.33	N. D.	
4	Unspent	8.07 ^d	1.35 ^p	0.14 ^r	1.16 ^e	N. D.	
	engine oil	± 0.13	± 0.03	± 0.00	± 0.03	N. D.	

Values are reported as mean \pm SD of four determinations.

Means with identical superscripts within a column are not significantly different at p = 0.05.

From Table 1 it can be seen that there is significant difference between the concentrations of heavy metals in spent engine oils across the 3 workshop clusters and there exists a significant high difference in the concentration of heavy metals present in spent engine oil compared with that in unspent engine oils regardless of the study location (cluster). This implies that the use of engine oils in vehicle engines lead to further accumulation of these heavy metals in spent engine oils, thus increasing the amount of these heavy metals that auto-mechanics are exposed to in the course of vehicle maintenance. Also, Table 1 shows that, whereas the highest concentrations of Pb, Ni, V and Cd, (16.64, 3.21, 0.66, and 2.30 ppm respectively), were recorded in spent engine oils, their lowest concentrations (8.07, 1.35, 0.14, and 1.16 ppm respectively) were recorded in unspent engine oil. This implies that the major determinant of exposure to heavy metals from engine oil is in the nature of the spent engine oils rather than in the nature of the cluster. Arsenic on the other hand was not detected in any of the samples. This implies that, auto mechanics are not at risk of As exposure both from spent and unspent engine oil sources.

 Table 2. Mean heavy metal concentration in spent engine oils in Makurdi and their exposure limits

SN	Heavy metal	Heavy metal concentration	Exposure limit (ppm) [29]			
		(ppm)	OSHA PEL	ACGIH TLV		
1	Pb	14.31 ± 2.21	0.01	0.01		
2	Ni	2.25 ± 0.82	0.21	0.62		
3	V	0.38 ± 0.24	0.02	0.02		
4	Cd	2.07 ± 0.19	0.02	0.02		
5	As	N. D.	-	-		

Values are reported as mean \pm SD of triplicate determinations. OSHA PEL – United States Occupational Safety and Health Administration Permissible Exposure Limit for an 8-hour time weighted average ACGIH TLV – American Conference of Governmental Industrial Hygienists Threshold limit value

Table 2 provides a comparison between the mean heavy metal concentration in spent engine oils and their exposure limits. The results demonstrate clearly that, the mean levels of these heavy metals in spent engine oils are higher than their exposure limits. Table 2 shows that, the mean levels of Pb, Ni, V, and Cd in spent engine oils are 14.31, 2.25, 0.38, and 2.07 ppm respectively. With the exception of As which was not detected, each of these concentrations far exceed both their permissible exposure limit and their threshold limit value. The implication is that auto-mechanics in all 3 workshop clusters are exposed to unsafe levels of Pb, Ni, V, and Cd. Hence, it is only a matter of time before heavy metal toxicities will begin to manifest from prolonged bioaccumulation of the heavy metals.

Table 3 shows the heavy metal concentrations in fingernails of auto-mechanics based on their duration of practice and demonstrates that there is increased heavy metal concentration in auto-mechanics who have practiced for a longer duration. Notably, the heavy metals concentrations are particularly higher in cluster B. Also, auto-mechanics who have practiced for ≤ 15 years, are seen to have the highest concentrations of the heavy metals. From Table 3, the concentration of the five heavy metals analysed is in the order; Pb > Ni > Cd > V > As and this is because of the use of Pb in higher quantities in the fabrication of automobile parts as well as lapses in the refining process of petroleum, resulting in its presence in fuels and lubricants. However, this result trend is in contrast with a study by Nada et al. [31] where Ni was highest in concentration and Cd was lowest. This is likely due to variation in the combination of heavy metals assessed in both studies. Also, the highest concentrations of all the heavy metals assessed were observed in the category of auto-mechanics who had practiced for a period of \leq 15 years and this is indicative of a greater bioaccumulation of heavy metals from longer duration of exposure on the job. Pb, Ni, Cd, and V were found in fingernail samples from all the study locations (clusters A, B and C) except arsenic, this implies that there is no potential for As toxicity among this category of workers. The peak concentration for the heavy metals present were mostly found in automechanics who had practiced for more than ten years in all three mechanic workshop clusters and particularly higher in auto-mechanics in cluster B. This may be due to the referral status of cluster B workshops and the associated high volume of maintenance work that is carried out there. The observed distribution trend in the heavy metal levels in the study locations is cluster B >cluster C > cluster A.

Table 3. Heavy metal concentration in fingernails of auto-mechanics by duration of practice

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XX7 la la	Pb (ppm)		Ni (ppm)		V (ppm)			Cd (ppm)		As (ppm)					
Workshop cluster	< 5	5-10	10-15	< 5	5-10	10-15	< 5	5-10	10-15	< 5	5-10	10-15	< 5	5-10	10-15
cluster	years	years	years	years	years	years									
	0.041 ^a	0.087 ^c	0.195 ^p	0.012 ^c	0.023 ^g	0.070 ^x	0.007^{B}	0.013 ^m	0.023 ^g	0.0 ¹ 11	0.016 ^a	0.026	N.D	N.D	N.D
A	±0.002	±0.004	±0.010	±0.003	±0.003	±0.001	±0.002	±0.001	±0.002	±0.002	±0.001	±0.002			
в	0.024 ^b	0.070 ^c	0.149 ^q	0.009°	0.018 ^k	0.053 ^y	0.007 ^e	0.011 ^b	0.018 ^g	0.007^{1}	0.011 ^b	0.040 ^k	N.D	N.D N.I	ND
D	±0.001	±0.001	±0.003	±0.001	±0.002	±0.002	±0.001	±0.001	±0.001	±0.001	±0.001	±0.004			N.D
С	$0.01^{p}\pm$	0.060 ^p	0.215 ^r	0.013°	0.022 ^k	0.041 ^z	N.D	0.011 ^m	0.020 ^g	0.012 ^r	0.019 ^a	0.029 ¹	N.D	N.D	N.D
	0.003	±0.003	±0.006	±0.001	±0.002	±0.002	IN.D	±0.001	±0.003	±0.001	±0.002	±0.001	IN.D	IN.D	IN.D

Values are means \pm SD of duplicate determinations.

Table 4. Mean levels of some heav	w metal in the fingernails of auto-n	nechanics and their reference /	pathological values

S/N	Heavy metal	\leq 5 years (ppm)	≤ 10 years (ppm)	≤ 15 years (ppm)	Reference values [30] (ppm)	Pathological values [30] (ppm)
1	Pb	$0.028^{a} \pm 0.012$	$0.072^{a} \pm 0.014$	$0.187^{b} \pm 0.034$	2.0	> 2.0
2	Ni	$0.011^{k} \pm 0.002$	$0.021^{k} \pm 0.003$	$0.055^{\rm i} \pm 0.015$	5.0	> 5.0
3	V	$0.005^{p} \pm 0.004$	$0.012^{p} \pm 0.001$	$0.020^{q} \pm 0.003$	0.01-0.21	> 0.21
4	Cd	$0.010^{\circ} \pm 0.003$	$0.015^{\circ} \pm 0.004$	$0.032^{\text{d}} \pm 0.007$	0.14	> 0.14
5	As	N. D.	N. D.	N. D.	< 0.87	> 0.87

Values are means \pm SD of triplicate determinations.

Means with identical superscripts within a column are not significantly different at p = 0.05.

Table 4 shows the mean levels of some heavy metals in the fingernails of auto-mechanics and their corresponding reference /pathological values. Table 4 shows that, As was not detected in all categories of automechanics, hence it fell below the reference and pathological values for As in humans. Pb, Ni and Cd in the fingernails of auto-mechanics were below their respective reference and pathological values in all categories of auto-mechanics assessed. However, V levels fell between the reference and pathological values for V. Table 4 shows that the mean concentrations of Pb in fingernails for auto-mechanics who have practiced for \leq 5 years, \leq 10 years and \leq 15 years (0.028 ppm, 0.072 ppm and 0.187 ppm respectively) fall below the pathological limit of 2.0 ppm as stipulated by Micro Trace Minerals (MTM) Germany [30] and Trace Minerals International (TMI) USA [30]. However, the World Health Organization provides a safe exposure limit of 0.2 ppm [32], and going by this limit, automechanics in Makurdi may soon be at risk of leadpoisoning. This is even more so with auto-mechanics who have practiced for ≤ 15 years as seen in Table 4. Ni, V, Cd and As levels in the fingernails, all fall below their pathological limits and there is no immediate risk of the toxicities of these metals in the auto-mechanics at the time of the study.

4. Conclusions

Auto-mechanics in Makurdi are occupationally exposed to unsafe levels of Pb, Ni, V and Cd but not so with As. However, there is no immediate threat of heavy metal poisoning in the study population with regards to these heavy metals, as their concentrations in the fingernails of the auto-mechanics assessed were still significantly below their pathological thresholds. However, there is a progressive bioaccumulation of the metals in fingernails of auto-mechanics as the number of years of practice on the profession increases. Arsenic posed the least threat to auto-mechanics as it was not detected in any of the samples.

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