**Original Research Article**

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DETECTION OF OXIDATIVE STRESS BIOMARKERS AMONG ARTISANS EXPOSED TO HEAVY METALS IN JOS METROPOLIS, NIGERIABot Yakubu Sunday^{1*}, Nwanjo Harrison U², Nwosu Dennis C², Bot David Yakubu³

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ABSTRACT: Oxidative stress has been identified to play a role in the pathogenesis of heavy metals toxicity among artisans. However, there is paucity of information as to which of the artisan groups is more at risk of heavy metal toxicity in Nigeria. This study was designed to detect and estimate the serum levels of Heavy metals – Cadmium (Cd), Lead (Pb) and Chromium (Cr); and Oxidative stress biomarkers - Malondialdehyde (MDA), reduced Glutathione (GSH), and Superoxide Dismutase (SOD) in some artisans (welders, battery repairers, petrol hawkers, car painters and tin miners). Blood samples were collected from 400 artisans and 200 age-matched non-artisan control group. Levels of heavy metals, MDA, GSH and SOD were analyzed using standard methods. Data were analyzed using Statistical Package for Social Sciences (SPSS) version 23 and student t-test was used to compare mean values between the control and study groups. Statistically high levels of Serum Cd, Pb and Cr were detected among welders, car painters and petrol hawkers. Also serum of GSH and SOD were significantly lower ($p < 0.05$) among the tested population. However, MDA activity (24.98 ± 1.02 ; 21.23 ± 0.45 ; 19.28 ± 0.98 ; 23.07 ± 0.72 and 11.70 ± 0.39) were significantly higher ($p < 0.05$) across all the various artisans excluding tin miners when compared to the non-exposed (control). From the results of this study, we concluded that all artisans except tin miners are prone to oxidative stress due to heavy metal poisoning. Details of the empirical evidence on the existence of oxidative stress as a result of heavy metals exposure among five groups of artisans are discussed.

Keywords: Oxidative stress, Heavy metals, Artisans, MDA, SOD, GSH, Peroxidation.

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1. INTRODUCTION

Oxidative stress represents an imbalance between the production and manifestation of reactive oxygen species and a biological system's ability to readily detoxify the reactive intermediaries or to repair the resulting damage. Disturbances in the normal redox state of tissues such as the attraction of a free radical to another molecule can cause toxic effects through the production of peroxides and free radicals that damage some components of the cell, including proteins, lipid and DNA. Oxidative stress involves excess formation/insufficient removal of highly reactive molecules such as reactive oxygen species (ROS) and reactive nitrogen species (RNS) by antioxidants, such as glutathione etc. [1,2] Some basic properties which have a bearing on the expression of toxicity by metals include the fact that metals seldom interact with biological systems in the elemental form but are usually active in the ionic form [3]. Availability of metal ions to biological processes is often dependent on solubility. Soluble salts of metals readily dissociate in the aqueous environment of biological membranes, making transport into the body easy. On the other hand, insoluble salts are poorly absorbed. For instance, reduction of chromium (VI) to the less soluble chromium (III) will decrease its absorption [3]. Absorption of solutes may be modified by the formation of insoluble compounds in biological systems. A typical example is the reduction of lead absorbed by high dietary levels of phosphate, which leads to the formation of insoluble lead phosphate. Some metals produce alkyl compounds which are often lipid soluble and readily pass across the lipid membrane. Examples include methyl mercury and organo-tin compounds [4]. Strong attractions between metal ions and organic compounds will influence the deposition of metals and their rate of excretion. Most of the toxicologically important metals bind strongly to tissues, and are excreted slowly and therefore tend to accumulate on continued exposure. Affinities for different tissues vary significantly. Elements such as lead are bound in the bones while mercury and cadmium localize in the kidneys [5]. The use of Reduced Glutathione (GSH), Superoxide Dismutase (SOD) and Malondialdehyde (MDA) - a by-product of Lipid peroxidation; for evaluating Oxidative stress as biomarkers of heavy metal exposure help in establishing diagnosis in addition to initiating more suitable monitoring systems, making them very crucial for the protection of heavy metals exposed workers against their toxicity. In the city of Jos, the capital of Plateau State, Nigeria, just as it is with many cities in the country, there are several petrol hawkers, motor vehicle mechanics (involved in vehicles' repairs and painting activities), Lead/Cadmium battery repairers, welding workers and a host of other artisans whose activities may pose threats to their lives. Many of them are located in residential areas and there is non-conformity to international 'best practices' in such work places despite the dangers their activities pose to human health due to heavy metal toxicity. Heavy metals toxicity is unique in view of the fact that unlike organic contaminants, they neither get degraded further nor undergo complete decomposition into other chemicals [3]. Activities of these artisans result in the generation of gases, fumes and vapors of metals and metalloids of aerodynamic diameter that can

get into the system either via inhalation, ingestion or skin penetration [6,7&8], causing bioaccumulation in human system, ecosystem and agricultural products which may latter be consumed by either humans or animals alike. This entire process creates both environmental and health problems. Hence it's important to detect and assess the levels of heavy metals and oxidative stress markers among various artisans who are directly exposed to these pollutants as a result of the activities they are engaged in. This is necessary in order to create awareness on the inherent dangers involved and to reduce or prevent adverse health impact on them and the society.

2. MATERIALS AND METHODS

Study Area

The study was conducted among artisans doing business at building materials market Jos, Kuru Jenta in Jos South Local Government Area; and Dilimi and FarinGada areas of Jos North Local Government area of Plateau State, Nigeria. Jos has a land area of about 26, 899 square Kilometers (Km²). It is the most densely populated Local Government area in Plateau State with about 900,000 inhabitants[9]. It is located between Latitude 8° 24'North and Longitude 8° 32'and 10° 38' East. It lies on a Plateau with altitude that ranges from around 1,200 meters (about 4000 feet) to a peak of 1,829 meters above sea level.

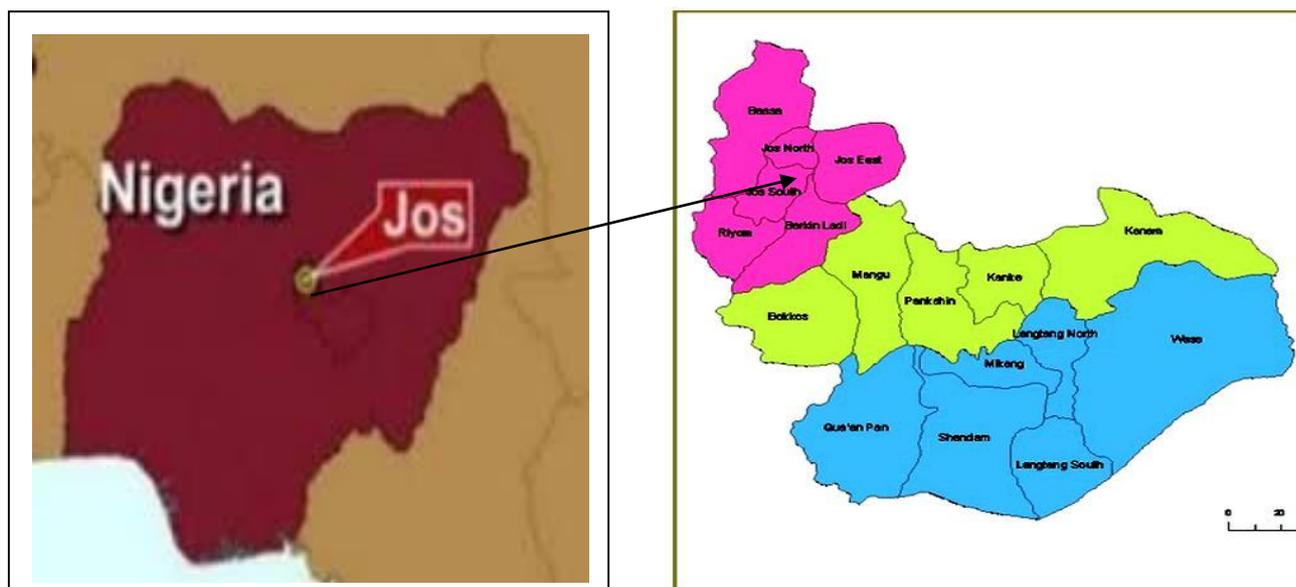


Fig 1: Map of Plateau State showing the Study area.

Source: [10]

Sample Size:

Stratified random sampling technique was adopted for the study. This was obtained using the Atchley's formular (Saunderet *al.*, 2009).

$$n = \frac{z^2 pq}{d^2}$$

Where n= the desired sample size (target population)

z=standard normal deviation at the required confidence level

p= proportion in the target population estimated to have the measured character.

$$q=1-p$$

d=the level of statistical significance set.

In this study, z=statistics was 1.96, and the desired accuracy was at 0.05 level.

$$\text{Hence, } n = \frac{(1.96)^2 \times (0.5) \times (0.5)}{(0.05)^2} = 384$$

Sample size =approximately 400.

Study Population

The study population was drawn from Building Materials market and Kuru-Jenta in Jos South LGA; Dilimi and Farin-Gada in Jos North LGA of Plateau State, Nigeria. All participants were artisans involved in welding, battery repairs, selling of petrol, Tin mining and car painting. Two hundred (200) control subjects were students from the University of Jos. All subjects recruited into the study were between the ages of 18 and 60 years. Hence, a total of 600 subjects were recruited. The study population which was stratified into welding, petrol hawkers, car painters, and Tin miners had eighty (80) each and a control of two hundred (200) individuals.

Inclusion and Exclusion Criteria

Participants who were between the ages of 18 and 60 years that consented to the study and have been on the job for a minimum of six (6) months and were apparently healthy, were included. On the other hand, smokers, persons with signs of one ailment or the other and those who refused consent, were excluded from the study.

Sample Collection

Blood samples were collected by veno-puncture using pyrogen-free sterile disposable syringes by a trained Phlebotomist according to the procedure described by Grassiet al[11]. Samples for evaluation of Heavy metals, and oxidative stress biomarkers were collected into plain tubes. They were allowed to clot and stand for 20 minutes after which they were centrifuged at 3000rpm for 20 minutes and the serum separated with sterile Pasteur Pipettes into cryo-vial containers. Samples were later stored

frozen at -20°C prior to analysis.

Laboratory Procedures

All reagents used were commercially purchased and the manufacturers' SOPs/instructions were followed strictly.

a. Determination of Heavy Metals (Cd, Pb and Cr)

To measure the serum levels of Cadmium (Cd), Lead (Pb) and Chromium (Cr), serum samples were thawed and directly diluted for the determination of the trace elements. Samples were diluted 1 in 50 in 0.1N Nitric acid. Levels of Cd, Pb and Cr were determined by Atomic Absorption Spectrophotometer (AAS-HITACHI 180-80 Polarised zee man model).

b. Estimation of Reduced Glutathione (GSH) Concentration

Reduced Glutathione (GSH) was estimated by its reaction with dithio-bis-2-nitrobenzoic acid (DTNB, which gives a yellow-colored complex with absorption maximum at 412 nm according to the method of Raja et al[12].

c. Malondialdehyde (MDA) Estimation of Lipid Peroxides

Lipid peroxidation in the supernatant fractions was determined spectrophotometrically by assessing the concentration of Thiobarbituric acid reactive substances (TBARS) according to the method of Ohkawa et al (1979) as described by Liu et al[13]. The results were expressed in Malondiadehyde (MDA) formed relative to an extinction coefficient of 1.56×10^6 mol/cm measured at 540nm).

d. Determination of Superoxide Dismutase (SOD) Enzyme

An ELISA OxiSelect™ Superoxide Dismutase Activity Assay Kit was used to quantitatively measure the SOD at 490nm as described by Marklund and Marklund [14].

e. Blood Pressure Measurements

Blood pressure measurement was measured two times on the left arm in each subject in supine position with a traditional sphygmomanometer and recorded as mmHg as described by Famodu et al[15].

Statistical Analysis

Data collected on questionnaires through interviews and Laboratory analyses were analyzed using Statistical Package for Social Sciences (SPSS) version 23. While the comparison between control and study groups was analyzed using Student t-test. The values were expressed as mean and standard deviation (\pm SD).

3. RESULTS AND DISCUSSION

Table 1: Mean Levels and Standard deviation of Heavy Metals (mg/L) in the study population

| Parameters | Cd | | Pb | | Cr | |
|--------------------------|-----------------------|-----------------------------|-----------------------|-----------------------------|-----------------------|-----------------------------|
| | Control Mean \pm SD | Total Mean \pm SD | Control Mean \pm SD | Total Mean \pm SD | Control Mean \pm SD | Total Mean \pm SD |
| Welders (n=80) | 0.21 \pm 0.02 | 1.81 \pm 0.08 P=0.000* | 0.07 \pm 0.00 | 0.06 \pm 0.00 P=0.068 | 0.07 \pm 0.00 | 0.11 \pm 0.02 P=0.000* |
| Battery repairers (n=80) | 0.21 \pm 0.02 | 0.24 \pm 0.03 P=0.389 | 0.07 \pm 0.00 | 0.08 \pm 0.01 P=0.036* | 0.07 \pm 0.00 | 0.06 \pm 0.00 P=0.059 |
| Petrol hawkers (n=80) | 0.21 \pm 0.02 | 0.23 \pm 0.03 P=0.519 | 0.07 \pm 0.02 | 0.80 \pm 0.03 P=0.000* | 0.07 \pm 0.00 | 0.06 \pm 0.00 P=0.074 |
| Car painters (n=80) | 0.21 \pm 0.02 | 0.34 \pm 0.00 P=0.000* | 0.07 \pm 0.00 | 0.16 \pm 0.03 P=0.000* | 0.07 \pm 0.00 | 0.06 \pm 0.00 P=0.068 |
| Tin Miners (n=80) | 0.21 \pm 0.02 | 0.20 \pm 0.02 0.575 | 0.07 \pm 0.00 | 0.06 \pm 0.00 P=0.081 | 0.07 \pm 0.00 | 0.06 \pm 0.00 P=0.055 |

Key: *Statistically Significant

Table 1 shows the mean levels of the Heavy metals Cadmium, Lead and Chromium. Data revealed that Welders had the highest level of Cd (1.81 \pm 0.08) and Cr (0.11 \pm 0.02) at $p < 0.05$; the highest level of Pb was seen among car painters (0.16 \pm 0.03) at $p < 0.05$; while Pb was detected in significantly high levels among battery repairers, petrol hawkers and car painters and Cd was detected among welders and car painters only. Cr was only detected among welders.

Table 2: Summary of Levels of Oxidative Stress Biomarkers in the various occupations

Key: *Statistically Significant

| Parameter | Control (n = 200) Mean±SD | Welders (n = 80) Mean±SD | Battery Repairers (n = 80) Mean±SD | Petrol hawkers (n = 80) Mean±SD | Car painters (n = 80) Mean±SD | Tin miners (n = 80) Mean±SD |
|-------------|---------------------------------|--------------------------------|---------------------------------------------|------------------------------------------|-------------------------------------|-----------------------------------|
| MDA(µmol/L) | 11.73±0.45 | 24.98±1.02 p = 0.000* | 21.23±0.45 p = 0.000* | 19.28±0.98 p = 0.000* | 23.07±0.72 p = 0.000* | 11.70±0.39 p = 0.612 |
| GSH (U/ml) | 13.64±0.40 | 9.68±0.44 p = 0.000* | 9.31±0.21 p = 0.000* | 9.54±0.65 p = 0.000* | 9.18±0.33 p = 0.000* | 13.45±0.39 p = 0.072 |
| SOD (U/ml) | 11.96±0.56 | 9.07±0.39 p = 0.000* | 9.23±0.67 p = 0.000* | 9.13±0.21 p = 0.000* | 9.02±0.51 p = 0.000* | 11.75±0.57 p = 0.065 |

Table 2.shows changes in the mean and standard deviation values of Oxidative stress markers of the study population. Superoxide Dismutase (SOD) and Glutathione (GSH) activities in Car painters, Iron welders, Petrol hawkers and Battery Repairers were significantly lower ($p < 0.05$) when compared to control subjects. Whereas the levels of Malondialdehyde (MDA) were significantly increased in all except among Tin miners, suggesting an elevated systemic oxidative stress among these artisan groups.

Table 3: Mean Levels and Standard Deviation of Cadmium (mg/L) in the study population according to duration of exposure in years.

| Study group | Control Mean±SD | 1-2 Mean±SD | 3-4 Mean±SD | 5-6 Mean±SD | 7-8 Mean±SD | Total Mean±SD |
|--------------------------------|--------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| Welders (n=80) | 0.21±0.02 | 1.80±0.08 P=0.000* | 1.81±0.08 P=0.000* | 1.82±0.07 P=0.000* | 1.81±0.08 P=0.000* | 1.81±0.08 P=0.000* |
| Battery repairers (n=80) | 0.21±0.02 | 0.23±0.02 P=0.214 | 0.23±0.02 P=0.372 | 0.24±0.03 P=0.365 | 0.25±0.03 P=0.531 | 0.24±0.03 P=0.389 |
| Petrol hawkers (n=80) | 0.21±0.02 | 0.22±0.02 P=0.347 | 0.22±0.02 P=0.721 | 0.23±0.03 P=0.486 | 0.23±0.03 P=0.502 | 0.23±0.03 P=0.519 |
| Car painters (n=80) | 0.21±0.02 | 0.03±0.00 P=0.000* | 0.03±0.00 P=0.000* | 0.03±0.00 P=0.000* | 0.05±0.00 P=0.001* | 0.04±0.00 P=0.000* |
| Tin Miners (n=80) | 0.21±0.02 | 0.20±0.02 P=0.438 | 0.20±0.02 P=0.476 | 0.19±0.02 P=0.724 | 0.21±0.00 P=0.078 | 0.20±0.02 0.575 |

Key: *Statistically Significant

Table 3 shows the mean and standard deviation data of Cadmium in the study population according to duration of exposure in years is shown in. Highest levels of Cadmium (1.82 ± 0.08 mg/L) were observed among welders who had 5 - 6 years exposure. All the measured values in the welders were significant higher ($p < 0.05$) when compared to the control using student t-test. Although the blood samples of the artisans expressed some level of significance for presence of Cd, such expressed values were lower when compared to the control.

Table 4: Mean Levels and standard deviation of Lead (mg/L) in the study population according to duration of exposure.

| Study group | Control Mean \pm SD | $\leq 1-2$ Mean \pm SD | 3-4 Mean \pm SD | 5-6 Mean \pm SD | 7-8 Mean \pm SD | Total Mean \pm SD |
|--------------------------------|--------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| Welders (n=80) | 0.07 \pm 0.00 | 0.05 \pm 0.00 P=0.179 | 0.06 \pm 0.00 P=0.072 | 0.07 \pm 0.00 P=0.043* | 0.06 \pm 0.00 P=0.047* | 0.06 \pm 0.00 P=0.068 |
| Battery repairers (n=80) | 0.07 \pm 0.00 | 0.07 \pm 0.00 P=0.007* | 0.09 \pm 0.00 P=0.048* | 0.08 \pm 0.01 P=0.029* | 0.08 \pm 0.00 P=0.035* | 0.08 \pm 0.01 P=0.036* |
| Petrol hawkers (n=80) | 0.07 \pm 0.02 | 0.14 \pm 0.03 P=0.000* | 0.18 \pm 0.03 P=0.001* | 0.17 \pm 0.04 P=0.000* | 0.15 \pm 0.03 P=0.000* | 0.16 \pm 0.03 P=0.000* |
| Car painters (n=80) | 0.07 \pm 0.00 | 0.70 \pm 0.04 P=0.000* | 0.80 \pm 0.03 P=0.000* | 0.80 \pm 0.04 P=0.000* | 0.90 \pm 0.05 P=0.000* | 0.80 \pm 0.04 P=0.000* |
| Tin Miners (n=80) | 0.07 \pm 0.00 | 0.06 \pm 0.00 P=0.096 | 0.05 \pm 0.00 P=0.104 | 0.07 \pm 0.00 P=0.154 | 0.06 \pm 0.00 P=0.063 | 0.06 \pm 0.00 P=0.081 |

Key: *Statistically Significant

Table 4 shows the data on Mean Levels and standard deviation of Lead (mg/L) in the study population according to duration of exposure are depicted in. We reported significantly elevated levels of Pb among Battery repairers (0.09 ± 0.00) with 3-4 years exposure. The lowest was recorded among welders (0.06 ± 0.00) with 7-8 years exposure.

Table 5: Mean Levels and standard deviation Chromium (mg/L) in the study population according to duration of exposure.

| Study group | Control Mean±SD | ≤1-2 Mean±SD | 3-4 Mean±SD | 5-6 Mean±SD | 7-8 Mean±SD | Total Mean±SD |
|--------------------------------|--------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| Welders (n=80) | 0.07±0.00 | 0.10±0.02 P=0.000* | 0.12±0.03 P=0.000* | 0.09±0.02 P=0.000* | 0.13±0.00 P=0.000* | 0.11±0.02 P=0.000* |
| Battery repairers (n=80) | 0.07±0.00 | 0.07±0.00 P=0.142 | 0.06±0.00 P=0.063 | 0.06±0.00 P=0.071 | 0.05±0.00 P=0.033* | 0.06±0.00 P=0.059 |
| Petrol hawkers (n=80) | 0.07±0.00 | 0.06±0.00 P=0.069 | 0.06±0.00 P=0.081 | 0.07±0.00 P=0.132 | 0.05±0.00 P=0.013* | 0.06±0.00 P=0.074 |
| Car painters (n=80) | 0.07±0.00 | 0.06±0.00 P=0.076 | 0.07±0.00 P=0.116 | 0.05±0.00 P=0.014* | 0.06±0.00 P=0.083 | 0.06±0.00 P=0.068 |
| Tin Miners (n=80) | 0.07±0.00 | 0.06±0.00 P=0.072 | 0.06±0.00 P=0.088 | 0.06±0.00 P=0.073 | 0.06±0.00 P=0.064 | 0.06±0.00 P=0.055 |

Key: *Statistically Significant

Table 5 shows the mean and standard deviation of Chromium in the study population according to duration of exposure in years. Individuals with 7-8 years exposure among welders had the highest levels of Chromium (0.13 ± 0.00) and all measured values in this group were statistically significant as compared to control.

Table 6: Mean and standard deviation values of Arterial Blood pressure (mmHg) and weights (kg) of the study population according to duration of exposure.

| Study group | Arterial BP Systolic | Diastolic | Weight |
|-----------------------------|----------------------------------|--------------------------------|---------------------------------|
| Welders (n=80) | 156 ± 6 t= 49.449 P=0.012* | 95 ± 5 t=26.013 P=0.028* | 68 ± 3 t=-25.190 P=0.049* |
| Battery repairers (n=80) | 132 ± 4 t=22.677 P=0.117 | 85 ± 2 t=18.898 P=0.313 | 82 ± 2 t=12.977 P=0.372 |
| Petrol hawkers (n=80) | 144 ± 4 t=45.355 P=0.043* | 89 ± 2 t=34.713 P=0.144 | 84 ± 3 t=15.118 P=0.118 |
| Car painters (n=80) | 152 ± 6 t=43.955 0.026* | 93 ± 3 t=35.713 P=0.36* | 66 ± 3 t=-30.230 P=0.044* |
| Tin Miners (n=80) | 125 ± 4 t=9.449 0.374 | 84 ± 3 t=10.988 P=0.255 | 76 ± 4 t=-4.040 P=0.617 |
| Control | 120 ± 4 | 80 ± 2 | 78 ± 3 |

Key: p<0.05 is significant,* implies significant

Table six shows the mean and standard deviation values of Arterial blood pressure and weights of the study population according to duration of exposure in years. The highest level of Arterial Blood Pressure among study group was measured in Welders (Systolic, 156 ± 6 and Diastolic 95 ± 5) while the least was seen among Tin miners (Systolic 125 ± 4 and Diastolic 84 ± 3). The control group had Systolic 120 ± 4 and Diastolic 80 ± 2. Comparison with the control group showed significant difference in Welders, Battery Repairers and Car painters. Car painters had the highest weight (88 ± 4 while Tin miners had the least (76±4). Significant difference was only observed only Car painters as compared to the control.

DISCUSION

The heavy metal data analysis in tables 1, 3, 4 and 5 clearly shows that Cd and Cr are found particularly in Welders, whereas Pb is implicated among battery repairers, petrol hawkers and car painters in Jos. This is in line with the observation of Johriet al[16], that heavy metals, particularly Cd and Pb are implicated as occupational and environmental toxicants. They major route of entry

into the human system is also well established. To a larger extent, either by inhalation, ingestion or both. In all of these, inhalation has been known to be the primary route of occupational exposure. The bioaccumulation of Cd in blood samples of welders and car painters in relation to the control group (table 1) reveals statistically increased levels ($p < 0.05$) which was far above the recommended reference ranges of 0.06 mg/L [17]. These results indicate that continues exposure to chemicals and substances in a work-related environment is capable of impacting negatively on the overall health status of practitioners. The increased levels of Cd, Pb and Cr found in the blood samples of welders, and car painters could be attributed to the fact that inhalation of an oxide of these metals might have resulted in increased metal uptake into their system. Such oxides of these metals are released in very large quantities into the environment continually through the activities of welding or car spraying in form of nanoparticles which is later inhaled as metal dust, paint dust or ingested due to poor hygiene habits by such workers [18]. Pb levels in the petrol hawkers who were exposed from 3-8 years was also higher than the permissible level of 0.1 mg/L [17], and all the observed values were significantly high < 0.05 when compared to the control (Table 4). Similar increase in Pb was also seen among Battery repairers and car painters. Therefore in this study, high level of Cd as observed among welders and battery repairers is in tandem with the findings of Abdull-Wahab [19], who reported that galvanized and ungalvanized iron pipe products used in mechanical industries and vehicle construction industries contain various types of metals like Cr, Pb, Zn, Cu, Mn and Ni. Welders, battery repairers and car paint workers were equally seen to have the highest levels of Arterial blood pressure (Table 6, which increased significantly ($p < 0.05$). This agrees with the report of Proctoret *et al* [20], which showed that toxic metal exposure can result to nephropathy (kidney damage), gastro intestinal disturbances, anaemia and neurological effect and such effects may be felt as weakness, fatigue, irritability, high blood pressure, mental deficiencies or even associated infertility in both sexes as well as fetal damages [21]. Harlan [22], has also reported that lead may elevate blood pressure in susceptible adults in United State population with blood lead levels as low as 14 $\mu\text{g}/\text{dl}$. Bener [23], also confirmed this hypothesis by finding a positive correlation between lead exposure and high blood pressure among lead exposed workers in United Arab Emirates. Similarly, high levels of Cd as observed in this study has been reported by Vallee [24], as a cause of Emphysema and proteinuria in occupationally exposed individuals. Chromium levels among the 5 study groups were higher only among welders in limits far beyond the permissible and acceptable level of 0.05 ppm [17]. However, in this study Tin, Arsenic and Mercury were not detected. From this study, serum levels of malondialdehyde (MDA) were significantly increased specifically among all the exposed workers except among tin miners. On the other hand, there was a significant reduction ($p < 0.05$) in Superoxide Dismutase (SOD) and Glutathione (GSH) activities suggesting an increase or an elevated systemic oxidative stress among them (table 2). Thus agreeing with previous and recent chemical and cellular studies which have hitherto showed that metal induced stress which is

a phenomenon associated with pathogenic mechanisms of several diseases such as cancer, diabetes mellitus, inflammatory diseases, parkinson's disease, arthrosclerosis, aging process and Alzheimer's disease; are due to accumulated ROS which can be heavy metal induced. Several researchers including Adedara et al [25], Achiparakiet al [26] have reported some of the implications of heavy metal toxicity to include:- ulceration, skin irritations, endocrine imbalance, kidney damage, liver damage as well as alterations in even normal biochemical processes which is likely to alter the synthesis of hemoglobin and affect the joints, reproductive system, the gastrointestinal tract, damage the nervous system, decrease body weight etc; and their environmental health impact becomes increasingly a threat due to their non-biodegradability. The studies of Szymańska-Chabowska et al [27], had also shown that ROS do play an important role in mediating metal induced cellular responses and carcinogenesis. Cells under oxidative stress display various dysfunctions due to distortions caused by ROS to lipids, proteins and DNA. And MDA concentration in a system has been used to correlate the oxidative state of that system in terms of ROS generation. Therefore the presence of heavy metals as demonstrated earlier on, particularly lead, and cadmium which have been known to cause increase in production of reactive O₂ species such as hydroxyl radicals (HO⁻), superoxide radicals (O₂⁻) or hydrogen peroxide (H₂O₂) are most likely to have enhanced generation of ROS among the studied artisans (exposed), leading to an overwhelmed cells' intrinsic oxidant defenses of these groups of workers resulting into oxidative stress. As observed from the result of this study (Table 2) a higher level of this marker (MDA) was recorded among welders (24.98±1.02) with reference to the control group (11.73±0.45), whereas the tin miners had statistically lower and the least. This marker which has been implicated in arterogenesis, hepato renal syndrome, rheumatoid arthritis, carcinogenesis as well as atherosclerosis indicates that welders, car painters, and petrol hawkers, may well be susceptible to suffering from these conditions due to chronic exposure to heavy metals toxicity. The presence of Cd, Cr and Pb were found in the blood samples of welders, car spray workers and petrol hawkers. This therefore means that all heavy metals probably influenced the concentrations of the oxidative stress biomarkers among these artisans; thereby eliciting high levels of MDA on one hand, but low levels of SOD and GSH on the other hand. The levels of SOD and MDA have been used as the indicators of disease status associated with oxidative injury. For example, levels of SOD and MDA are significantly changed in chronic hepatitis [28], Aluminium poisoning [29], cardiovascular diseases [30], Alzheimer's diseases [31]. However, some environmental or other factors such as acute exercises, smoking and aging could lead to a significant increase in lipid peroxidation (MDA as an indicator) and a significant decrease in antioxidant enzyme activity (SOD as an indicator) [32]. Therefore, a marked deduction of GSH and SOD activity with an increased MDA as shown in table 2 clearly suggest an elevated oxidative stress among the career welders, car painters and petrol hawkers. It is unclear though, whether the undue oxidative stress among these workers is due to Cd, Cr or Pb exposure only or Pb only, or due to a

combined effect of exposure to mixed metals in these exposed groups of workers. In this study also, it is apparent that serum levels of Cd, Cr, Pb were significantly higher ($p < 0.05$) in welders as against Pb in car painters and petrol hawkers. Earlier on, employees working in automobile workshops were reported to be affected by toxic chemicals like lead, fumes, carbon dioxide and benzene [33]. Abdulwahab [19], had also reported that Chromium, Lead and Zinc are components of spare parts used in vehicle construction industries which could contribute to the levels of metals in sera of professionals having contact with them just like Lockitch [34], reported elevated concentrations of hair Cr among tannery workers.

4. CONCLUSION

The above observations relating to blood levels of heavy metals and oxidative stress antioxidant parameters suggests that Cd, Pb and Cr may have induced oxidative damage to welders, car painters, petrol hawkers and battery repairers by generating free radicals and lipid peroxidation which impaired their enzymatic and non-enzymatic antioxidant defenses. This damage may have been increased as duration of exposure/work increased. Therefore, analyses of oxidative-stress and antioxidant-related parameters in heavy metal-exposed workers are important in evaluating the health effects and biomarkers of heavy metal exposure, thus establishing a better diagnosis and prevention standards. We recommend that routine Medical Laboratory tests of these Biomarkers should be carried out on these categories of artisans. The Government should show interest in the health and well-being of these artisans and assist in ensuring that these tests are done on the artisans at least once every year. People living in communities where such activities are carried out should also be encouraged to undergo Medical check-ups as they could be exposed to Heavy metal poisoning as well over time.

ETHICS APPROVAL AND CONSENT TO PARTICIPATE

Not applicable.

HUMAN AND ANIMAL RIGHTS

No Animals/Humans were used for studies that are base of this research.

CONSENT FOR PUBLICATION

Not applicable.

AVAILABILITY OF DATA AND MATERIALS

The authors confirm that the data supporting the findings of this research are available within the article.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

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