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# Determination of some heavy metals in water, soil and blood samples of workers at a quarry site in Kano

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**Abstract:** Substantial proportion of the total burden of diseases have been linked to environmental factors. Quarrying activity is associated with environmental and health consequences; the extraction processes cause the release of heavy metals into the air and groundwater of host communities. In this study, some heavy metals in pond and borehole water, top soil and blood samples of workers at Gerawa Quarry site in Kano were determined. Results: mean concentrations of elements in the blood samples: chromium (Cr), (0.304 mg/L), lead (Pb) (0.145 mg/L), cobalt (Co) (0.301 mg/L), manganese (Mn) (0.073mg/L) and Copper (Cu) (1.467mg/L). Nickel (Ni) was only detected in one sample with concentration of 0.471mg/L. Borehole water; Cr, Pb, Co, Mn, Cu have concentrations of 0.221, 0.295, 0.176, 0.039, and 0.014mg/L respectively. Ni could not be detected. Pond water; Cr, Pb, Co, Mn, have concentrations of 0.256, 0.063, 0.052, and 0.028mg/L, respectively, Cu and Ni could not be detected. Soil sample; Cr, Pb, Co, Mn, Cu, Ni have concentrations of 5.064, 1.260, 0.414, 4.194, 0.754, and 0.226mg/g, respectively. Conclusion: The mean blood concentrations of Cr, Co, Mn and Cu were above the permissible limit set by world health organization (WHO) and united states environmental protection agency (US EPA).

## 1. Introduction

Environmental pollutants that are widely distributed includes heavy metals, these results from several human activities including burning of fossils, industrial activities and several others (El

Hammari *et al*., 2022; Li *et al*., 2019). The environment is widely contaminated with heavy metals and exposure is long standing in occupational settings (Leelapongwattana and Bordeerat, 2020). This causes serious health problems and mutations in humans as well as animals and fish (Leelapongwattana and Bordeerat, 2020; Belbachir *et al.*, 2013). Fergusson (1990), defines heavy metals as metallic elements that have a relatively high density greater than 5g/cm$^3$ compared to water. A known characteristic shared by heavy metals found in the environment is accumulation in the body of living organisms when they are ingested resulting in elevation of their concentration in the blood (Moradi *et al*., 2016; Karim *et al.*, 2016). Environmental hazard is increased by activities of humans such as mining which is a vital source of heavy metals in areas where industries involved in such activities are domicile (Campos *et al*., 2021).

A well-known human activity that involves extracting rocks from the earth, crushed and screened to produce the required aggregate sizes is quarrying (Al-Otaibi *et al*., 2018). Some quarrying types prevail on mountainous or hilly terrains whereas in flat areas deep mining is applied to be able to reach the rocky surface. However, intermediate types of quarrying exist and are also applied occasionally. The characteristics of the quarried (metamorphic, igneous, or sedimentary) rocks plays important role in the decisions of the quarry industries (David, 2008). Quarrying provides a lot of benefit to the environment such as stones used in constructions, as well as hazardous wastes which pollute the environment causing a lot of illness to humans such as difficulty in breathing, coughing, sneezing, ophthalmic problems, skin irritations, among others (Al-Otaibi *et al*., 2018). The International Occupational Safety and Health Centre (1999) reported that heavy metal toxicity can result in irreversible changes in the brain or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs. It was also reported that long-term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis (Verma, 2017).

The heavy metals determined in this research includes; Lead (Pb), Copper (Cu), Chromium (Cr), Manganese (Mn), Nickel (Ni) and Cobalt (Co).

This study is aimed at determining the concentration of heavy metals in Water, Soil and Blood samples of workers at a quarry site in Kano State, Nigeria.

## 2. Materials and Methods

All chemicals used were of analytical grade purity. All glass wares and plastic containers were cleaned with detergent solution followed by 20% nitric acid and then rinsed with tap water and deionized water and then dried in an oven at 105$^{O}$C to eliminate contaminants. Blood, Water, and soil samples were obtained from Gerawa quarry site Kano.

### Blood sampling

Five milliliters of venous blood were collected from eleven Quarry workers of Gerawa Quarry site Kano using separate and disposable plastic syringes. Blood samples obtained were transferred into

EDTA sample bottles and were taken to the laboratory and kept in the refrigerator until needed for analysis. This was done with the assistance of laboratory technician in order to comply with ethics of blood sample collection procedure.

**Soil sampling**

The soil samples were collected from top soil at the depth of 15 cm using soil auger, leaves, roots and stones were removed manually to eliminate dirt. At site for sampling, five sub-sites were sampled for random sampling and five soil samples were collected randomly from each of the five sub-sites and pooled together to obtain a composite sample. Sample was transferred into polyethylene bag, labelled and transported to the laboratory.

**Water sampling**

Five (5) litre each of the two water samples (borehole water and pond water) were collected from the two water sources in the Gerawa quarry site using separate clean plastic containers and the samples were transported to the laboratory until needed for analysis.

**Soil Sample Treatment**

The soil sample was air – dried at ambient temperature for 3 days then pulverized with a mortar and pestle and sieved with a 2 mm mesh to remove pebbles and debris present. The air- dried sample (1g) was weighed using analytical balance and transferred in a 250cm$^3$ beaker and mixed with 24cm$^3$ of aqua regia (HCl: HNO3 3:1).

**Digestion of Blood samples**

Sample bottles containing the blood samples were shaken thoroughly. 2cm$^3$ of each of the blood samples were measured using 10cm$^3$ measuring cylinder and were transferred in to the digestion tubes, 6cm$^3$ of concentrated nitric acid (HNO3) and 4cm$^3$ of concentrated hydrochloric acid (HCl) were added and shaken. The mixture was heated from 30$^o$C to 200$^o$C using foss Tecator (2006 digestor) for 1hour. The digested samples were allowed to cool and 20cm$^3$ of deionized water was added to the samples and stirred, the samples were filtered using whatman No 2 filter paper, the filtrates were transferred to a 50cm$^3$ volumetric flask and make up to the mark with deionized water. The metals contents were determined using atomic absorption spectrometry (Yahaya *et al*., 2013).

**Digestion of Soil sample**

1 g of dried soil sample was weighed on a weighing balance and place in to a digestion vessel and mixed with 24cm$^3$ of aqua regia (HCl: HNO3 3:1) The solution was placed in a Digestor

(2006 Foss tecator) for 60 minutes at 120 $^{o}$ C and allowed to cool to room temperature. The digested solution was filtered using a Whatman No. 1 (110mm) filter paper and then diluted to 50cm$^3$ using deionized water. The resultant solution was stored in a sample bottle for AAS analysis (Orosun *et al*., 2020).

**Digestion of water samples**

Sample bottles containing the water samples were shaken thoroughly. 2cm$^3$ of each of the water samples were measured using 10cm$^3$ measuring cylinder and were transferred in to the digestion tubes, 6cm$^3$ of concentrated nitric acid (HNO3) and 4cm$^3$ of concentrated hydrochloric acid (HCl) were added and shaken. The mixture was heated from 30$^o$C to 200$^o$C using foss Tecator (2006 digestor) for 1hour. The digested samples were allowed to cool and 20cm$^3$ of deionized water was added to the samples and stirred, the samples were filtered using whatman No. 1 filter paper, the filtrates were transferred to a volumetric flask and make up to 50cm$^3$ mark with deionized water. The metals contents were determined using atomic absorption spectrometry (Nasiru *et al*., 2021).

**Statistical Analysis**

All data were subjected to statistical analysis. The values reported as mean ± standard deviation (SD) while One-way ANOVA was used to test for differences between the samples using statistical package for social sciences (SPSS) version 22. Post-Hoc analysis was performed using Turkey HSD. The results were considered significant at *P*-values of less than 0.05 that is at 95% confidence level ($P < 0.05$).

## 3. Results and discussion

The results of the blood, water and soil samples for the selected metals (Cu, Cr, Co, Ni, Mn and Pb) determinations are shown in figures 1- 15 and the results of some physical parameters of water tested are shown in tables 1 and 2. Figure 1 shows that; chromium (Cr), and lead (Pb) have the highest concentration with 0.303, and 0.122 mg/L respectively, while cobalt (Co), and manganese (Mn) 0.075 and 0.036mg/L respectively, have lower concentrations as compared to Cr and Pb, Copper and Nickel on the other hand were not detected.

Figure 2 is similar to what was found in the first donor, in that; chromium (Cr), and lead (Pb) have the highest concentration with 0.304, and 0.180 mg/L respectively, while cobalt (Co), and manganese (Mn) 0.077 and 0.031mg/L respectively, have lower concentrations as compared to Cr, and Pb. Copper and Nickel were not detected.

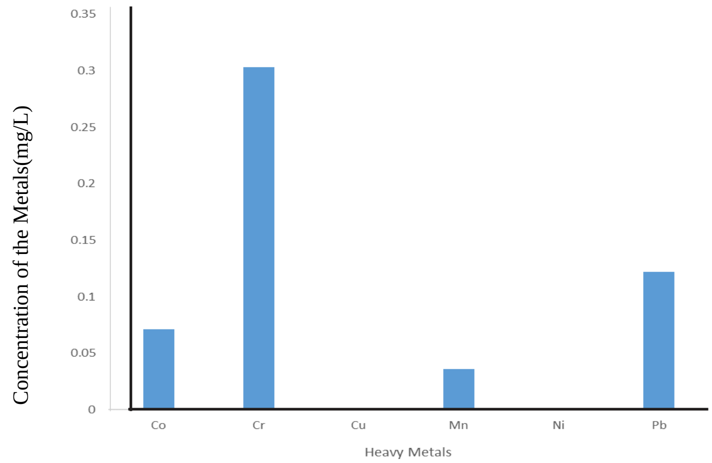


**Fig 1**: Concentrations of the Heavy Metals in the Blood sample of the first donor (mg/L).

Figure 3 is also similar to what was found in the previous donors; chromium (Cr), and lead (Pb) have the highest concentration with 0.315, and 0.172 mg/L respectively, while cobalt (Co), and manganese (Mn) with concentrations 0.083 and 0.037mg/L respectively, have lower concentration as compared to Cr, and Pb. Copper (Cu) and Nickel (Ni) were also not detected. Figure 4 is also similar to what was found in the previous donors. (Cr), and (Pb) have 0.316, and 0.150 mg/L respectively. while (Co), and (Mn) have concentrations of 0.089 and 0.033mg/L respectively.

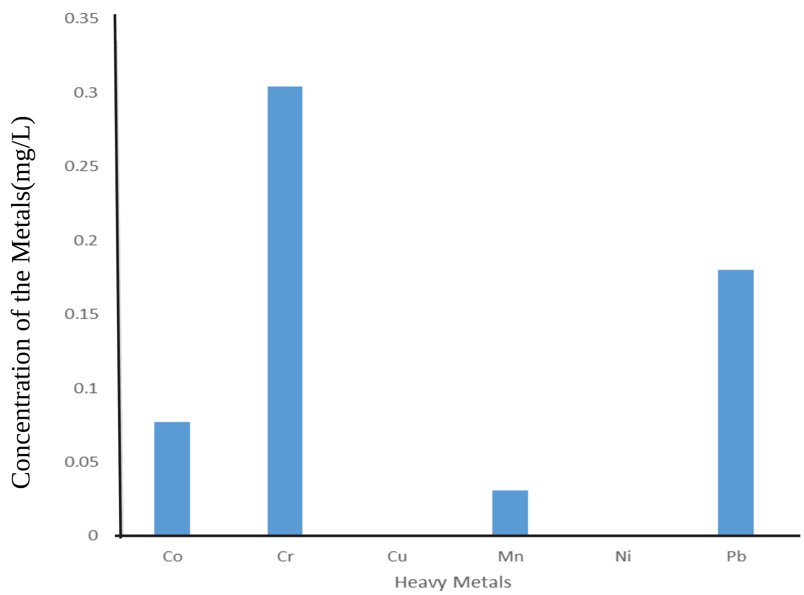


**Fig 2**: Concentrations of the Heavy Metals in the Blood sample of the second donor (mg/l)

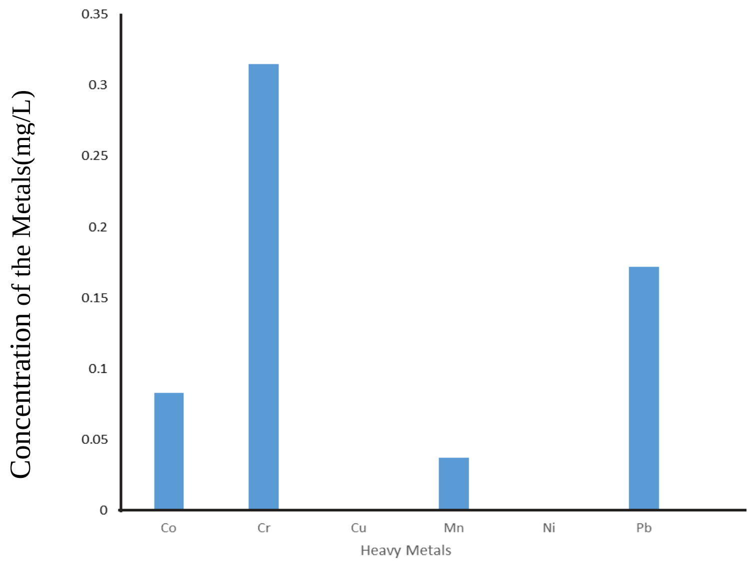


**Fig 3:** Concentrations of the Heavy Metals in the Blood sample of the third donor (mg/L).

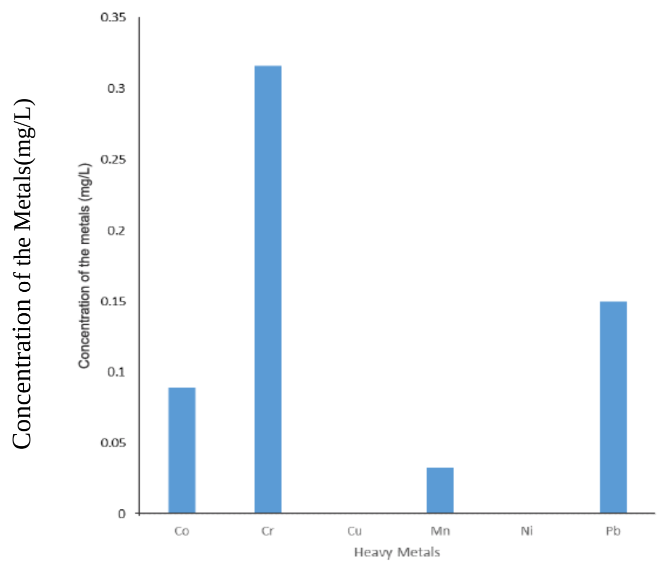


**Fig 4**: Concentrations of the Heavy Metals in the Blood sample of the fourth donor (mg/L)

Figure 5 shows the concentration of cobalt 0.518mg/L to be higher than those of other metals; Cr, Cu, Mn, and Pb which were 0.326, 0.274, 0.044, and 0.135mg/L respectively. This is the first donor in which copper is detected in his blood sample, which could be possibly because of the role he plays on the quarry site. Figure 6 shows that; chromium (Cr)> lead (Pb)> cobalt (Co)>> manganese (Mn) with concentrations 0.303, 0.123, 0.117, and 0.037mg/L respectively, while copper (Cu) and nickel (Ni) were not detected. figure 7 shows that; (Cr), and (Pb) have the highest concentrations with 0.279, and 0.145 mg/L respectively, while (Co), and (Mn) 0.108 and 0.047mg/L respectively, have lower concentrations. (Cu) and (Ni) on the other hand were not detected.

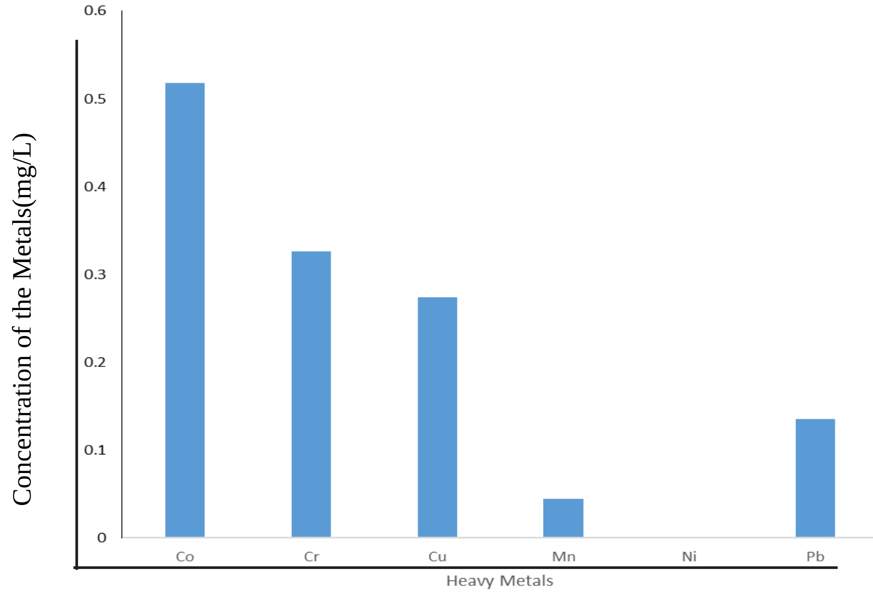


**Fig 5**: Concentrations of the Heavy Metals in the Blood sample of the fifth donor (mg/L)

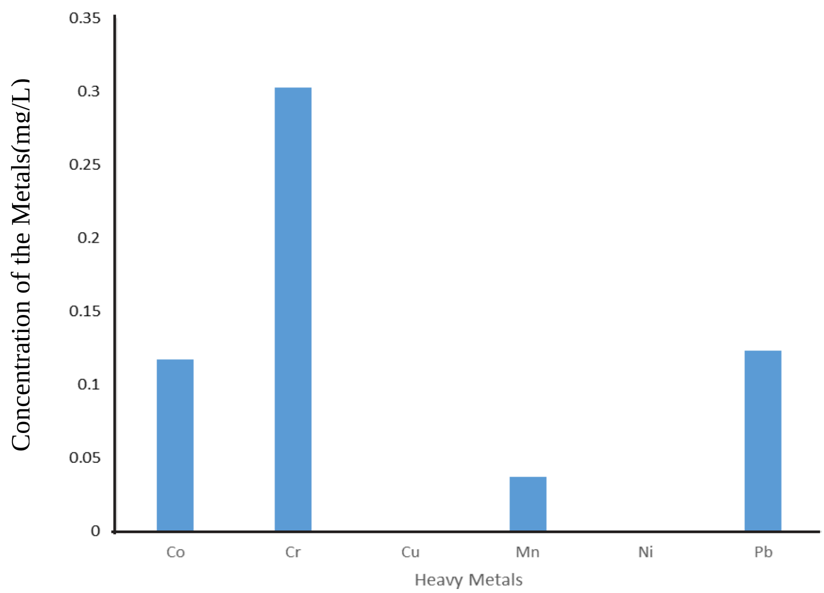


**Fig 6**: Concentrations of the Heavy Metals in the Blood sample of the sixth donor (mg/L)

Figure 8 shows that; chromium (Cr), and lead (Pb) have the highest concentrations with 0.322, and 0.140 mg/L respectively, while cobalt (Co), and manganese (Mn) 0.107, and 0.035mg/L respectively, have lower concentration. Copper (Cu) and Nickel were not detected.

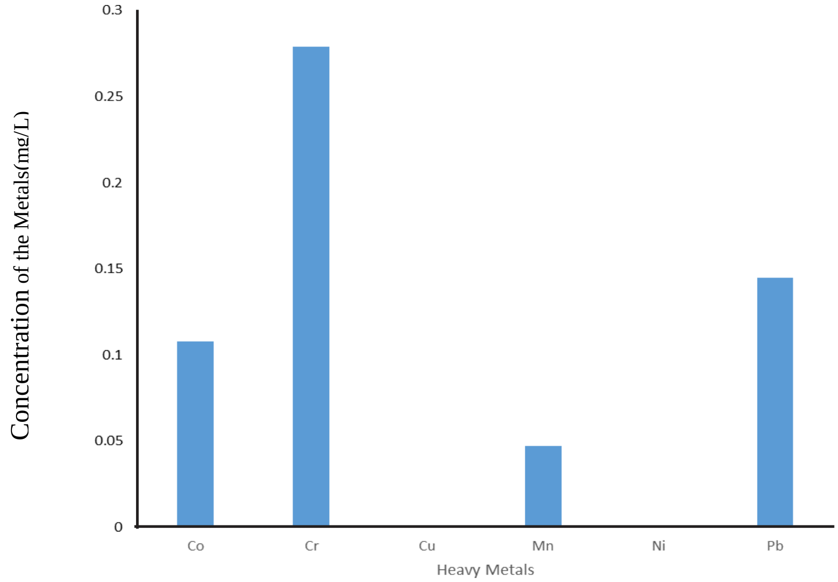


**Fig 7:** Concentrations of the Heavy Metals in the Blood

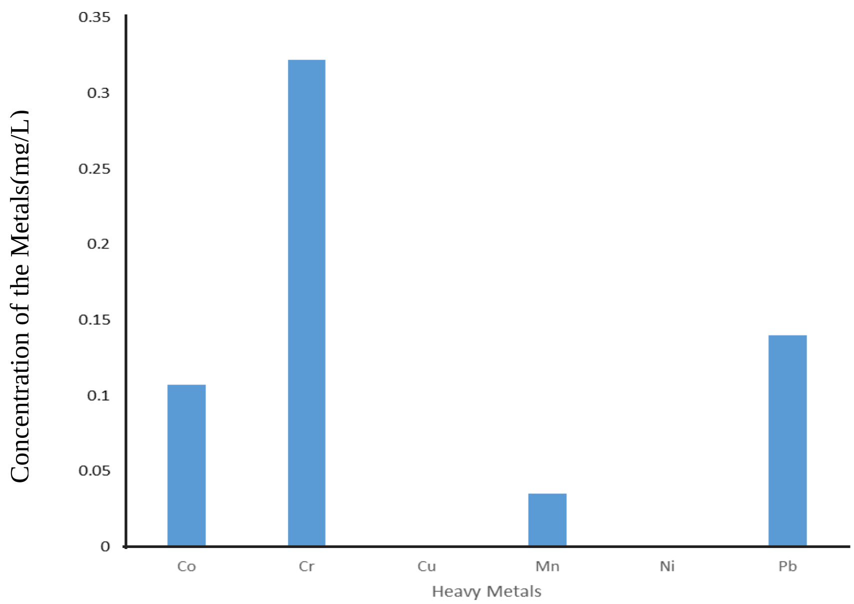


**Fig 8**: Concentrations of the Heavy Metals in the Blood sa

Figure 9 has similar blood heavy metals concentrations (mg/L), chromium (Cr), and lead (Pb) have the highest concentrations 0.290, and 0.130 mg/L respectively, while cobalt (Co), and manganese (Mn) have lower concentrations 0.120 and 0.042mg/L respectively. Copper (Cu) and nickel (Ni) were not detected. Figure 10 shows heavy metals concentrations for Cr, Pb, Co and Mn to be 0.322, 0.156, 0.139 and 0.040mg/L respectively. Copper (Cu) and Nickel (Ni) were not detected.

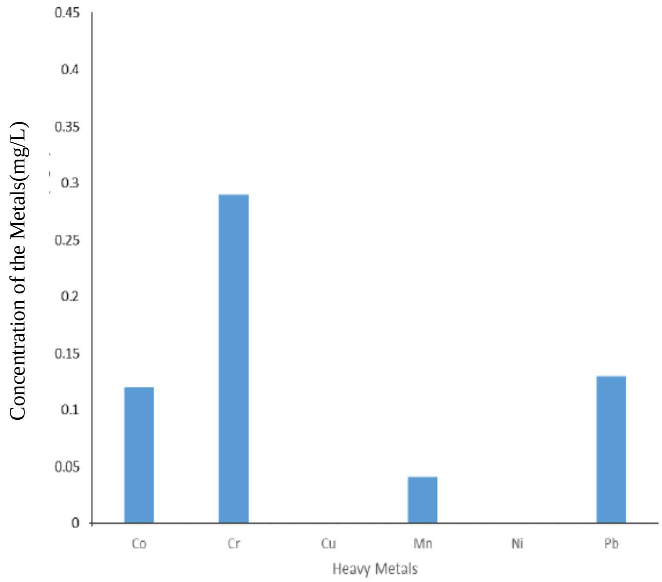


**Fig 9**: Concentrations of the Heavy Metals in the Blood sample of the ninth donor (mg/L)

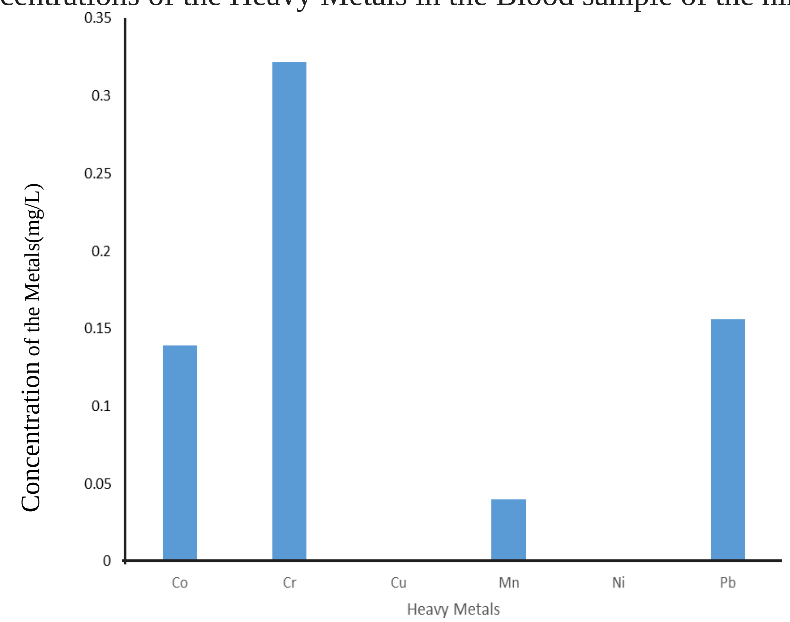


**Fig 10**: Concentrations of the Heavy Metals in the Blood sample of the tenth donor (mg/L)

Figure 11 shows the concentration of cobalt; 1.885mg/L, chromium (Cr); 0.264mg/L, lead (Pb); 0.144mgL, manganese (Mn); 0.039mg/L, Copper (Cu); 2.66mg/L and Nickel (Ni); 0.471. The concentrations of cobalt and copper in this donor are higher than those in all others. This is also the only donor in whose blood sample Ni was detected. Figure 12 The mean concentrations of the heavy metals in the blood samples of the donors (mg/L) shows that; chromium (Cr) has 0.304

mg/L, lead (Pb) has 0.145 mg/L, cobalt (Co) has 0.301 mg/L, manganese (Mn) has 0.073mg/L and Copper (Cu) has 1.467mg/L. Nickel (Ni) was only detected in one sample with concentration of 0.471mg/L.

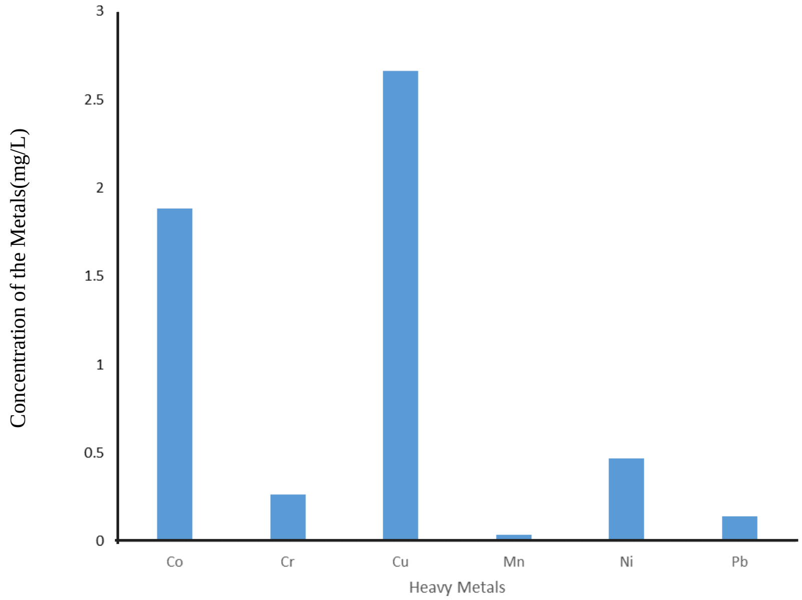


**Fig 11:** Concentrations of the Heavy Metals in the Blood sample of the eleventh donor (mg/L)

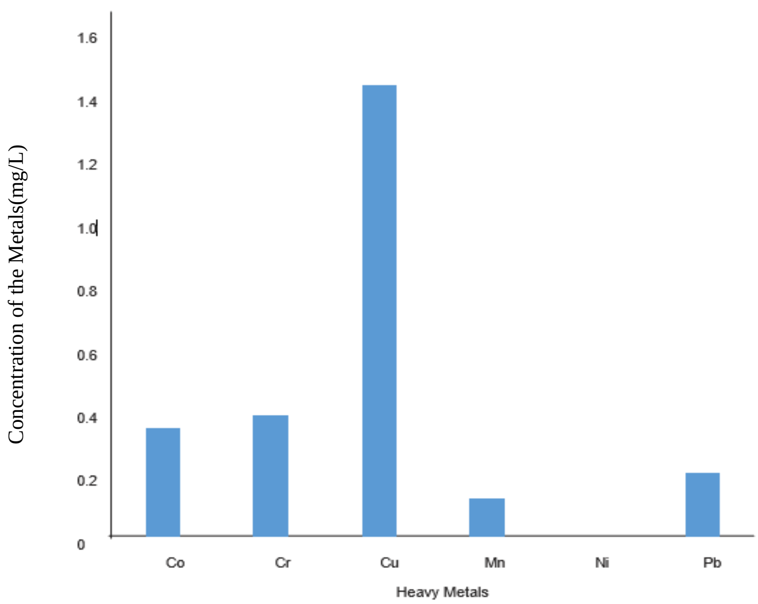


**Fig 12**: Mean concentrations of the Heavy Metals in the Blood samples of the donors (mg/L)

In this study, Cr has the mean concentrations which is higher than the healthy reference range of 0.7 to 28.0 µg/L (0.0007 to 0.028mg/L) used by many studies (Chen *et al*., 2022). In this study, its concentration ranges from 0.264 to 0.326mg/L in all the blood samples analyzed (Fig

1-11). Sample 5 (Fig 5) showed highest concentration of 0.326mg/L. This could be due to the direct exposure with earth and the elements in it by the quarry workers. Lawan *et al*., (2015) reported mean value of 24.78µg/l (0.02478mg/L) when studied blood samples in electricians in Kaduna metropolis, the value is not in accordance with the one reported in this study. Bolarin (2013), also found 0.9 µg/l and 0.43µg/l (0.0009, and 0.00043mg/l) for exposed and non-exposed population in German respectively. These values are not in accordance with the results from this study. Jantzen *et al.,* (2013) reported lower Cr concentrations which ranges between 1.3 and 2.2 µg/L (0.0013 to 0.0022mg/L) in blood and between 1.6 and 5.1 µg/L(0.0016 to 0.0051mg/L) in serum. This study was however carried out among individuals with metallic implant after hip replacement.

For lead (Pb), the mean concentration of lead found in this study is lower than WHO(1980) recommended blood level of 400µg/L (0.4mg/L) for males and females over the reproductive age and concentration of 300µg/L (0.3mg/L) for females of reproductive age (WHO, 1980). The results also indicated the concentration for the blood samples to range between 0.122mg/L to 0.180mg/L as shown in Fig 1-11, sample 2: (Fig 2) have the highest concentration of 0.180mg/L, Lawan *et al*., (2015), reported 29.33µg/dL (0.2933mg/L) for Pb among electronics repair technicians in Kaduna State, this value is in accordance with some of the findings from this study. Lukman (2015), also reported 45.43µg/dl (0.4543mg/L) for exposed workers and 12.08 µg/dl (0.1208mg/L) for non-exposed workers in Gwagwalada, the values were similar to the results of this research.

The mean concentration found in this study for cobalt is 0.301mg/L which is above the reference value of 0.45 µg/L (0.00045mg/L) (Nisse *et al*., 2017). In this work, the results for cobalt concentrations ranges from 0.071mg/L to 1.885mg/L as shown in (Fig 1-11) above. Sample 11 (Fig 11) recorded the highest concentration of 1.885mg/l while sample 1 (Fig 1) recorded the lowest concentration of 0.071).

The mean concentration of manganese is also greater than the WHO(1980) recommended safe concentration of not greater than 0.3µg/cm$^3$ (0.0003mg/L) (WHO, 1980). In this work, the result for manganese concentration ranges from 0.031 to 0.047mg/L as shown in Fig. 1-11 above. Bolarin (2013) reported 12µg/L(0.012mg/L) and 7.5µg/L(0.0075mg/L) of Mn in blood samples of exposed and non-exposed subjects in Germany respectively, the values were below the findings of this study. Hyuan *et al*., (2017) obtained 11.0µg/l (0.011mg/l) of manganese in the blood sample of healthy general Korean population, value was lower than the findings of this study. On contrary, Sani and Abdullahi (2017) reported range 0.0023mg/L – 0.0276mg/L concentration of manganese in blood of metal workers in Kano State, some of these values are in accordance with the results obtained in this study.

The mean concentration of copper is also higher than the recommended blood level of free serum copper of 1.6-2.4 µmol/L or 10-15µg/dL (0.2883 to 0.4324mg/L) by Longo *et al*., (2012) in a book of Harrison's principles of internal medicine. Its concentration in this work ranges from ND to 2.662mg/L (Fig 1- 11). Sample eleventh (Fig. 11) has the highest concentration. Hyuan *et al.*, (2017) reported 979.8µg/l (0.9798mg/l) of copper concentration among non- exposed Korean population, this value is similar to the findings of this study. Muhammad and Karman, (2002) reported higher concentration of 1.4mg/l in blood of non-exposed healthy subjects in Islamabad, Pakistan, this value is also similar to the results obtained in this study.

For nickel, the concentration was only found in one sample: eleventh sample with 0.471mg/L as shown in Fig 11. This element was also not detected in the water samples (Fig 13 and 14).

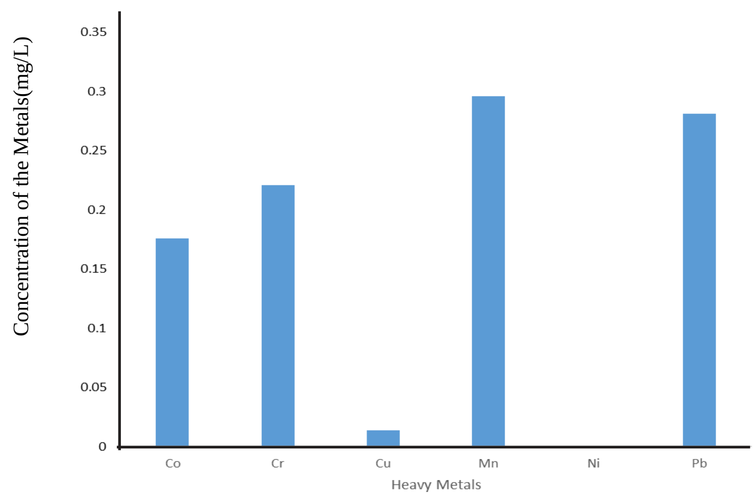


**Fig 13**: Concentrations of the Heavy Metals in the Borehole water sample of the quarry (mg/L)

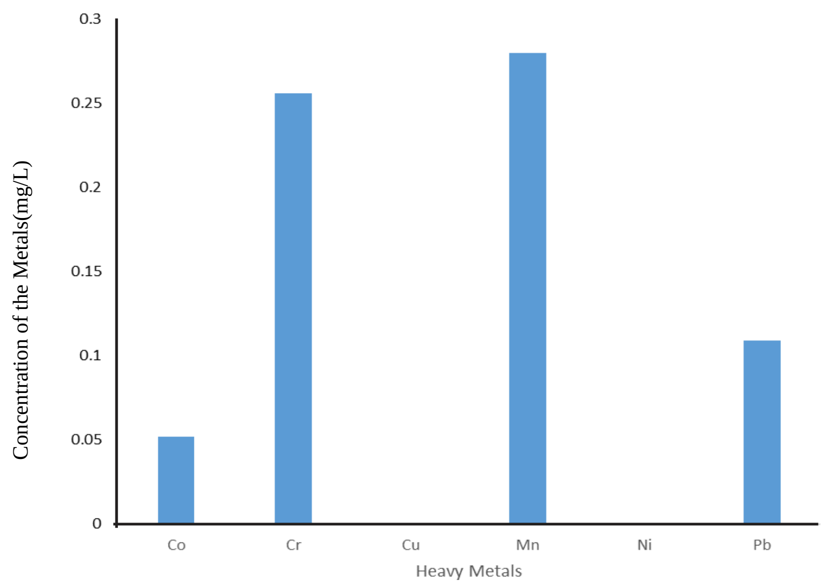


**Fig 14**: Concentrations of the Heavy Metals in the pond water sample of the quarry (mg/L)

Figure 13 shows that; chromium (Cr), lead (Pb), cobalt (Co), manganese (Mn), and copper (Cu), have concentrations (0.221, 0.295, 0.176, 0.039, and 0.014mg/L) respectively. Lead has the highest concentration, and nickel could not be detected as the concentration might be too small in the area. The concentration of Mn is below the limit of WHO (1996) standard of Mn (0.4mg/l) for drinkable water. However, the concentrations of Pb, is above the limit of WHO (1996) (0.01mg/l) (Kuwajima, 2007). Cr and Co concentrations were also above the permissible limit of WHO (2018) (0.05 and 0.01 mg/l) respectively and US EPA (2019) (0.05 mg/l) for Cr. Cu concentration is however below detectable limit by WHO (2018) (1.5 mg/l) and US EPA (2019) (1.3mg/l) (Ekramul *et al*., 2016). The result of this study is similar to what was found by Elinge *et al*., (2011) from some borehole waters in Kebbi state, Nigeria, where the concentration of Cu ranges (0.302 – 0.606mg/l) and Pb ranges (0.047 – 0.245mg/l). However, they found a slightly lower concentrations for Cr (0.052 – 0.121mg/l), lower concentrations for Co (0.03 – 0.07mg/l), and detected Ni (0.035 – 0.087mg/l). Similarly, Adumanya, (2013), found the concentrations of manganese (Mn) (mg/l) and lead in borehole waters in Imo state, Nigeria to range from 0.003mg/l to 0.023mg/l and from 0.024 to 0.072mg/l respectively. The result of the concentrations of manganese is similar to what was found in this study, but the concentration of lead in the quarry borehole water is higher. The difference in geographical location and activities at the quarry site may explain this difference.

Figure 14 shows that; chromium (Cr), lead (Pb), cobalt (Co), manganese (Mn), have concentrations (0.256, 0.063, 0.052, and 0.028mg/L,) respectively. Cr has the highest concentration, copper (Cu), and nickel (Ni), could not be detected. Akinola *et al*., (2015) in their study of heavy metals in the groundwater in Misau LGA of Bauchi state found the concentrations for lead to ranged (0.028 to 0.078 mg/L), Mn (0.452 to 1.021 mg/L), Cu (0.241 to 0.979 mg/L) and Ni (0.005 to 0.052 mg/L). The slight difference in the concentrations of some of the metals determined may be due to different geographical locations of the study areas. The study recommended an urgent need for remediation and regular monitoring of the groundwater in Misau. Figure 15 shows that; chromium (Cr), lead (Pb), cobalt (Co), manganese (Mn), copper (Cu), and nickel (Ni), have concentrations (5.064, 1.260, 0.414, 4.194, 0.754, and 0.226mg/g,) respectively. Chromium and manganese have the highest concentration while nickel has the least concentration. The higher concentration of chromium in the soil sample could explain the reason why the donors have high chromium concentration in their blood. These concentrations are also higher than the permissible standard limits recommended by the national environmental standard and regulation enforcement agency (NESREA, 2009), Cr(0.1mg/L), Co(0.05mg/L), Cu(0.1mg/L), Mn(0.164), Ni(0.05mg/L), Pb(0.05mg/). The result in this study for lead, chromium and copper are all higher than what Peter *et al*., (2016) found in the soil sample of the surrounding of an automobile factory in Ibadan, South west Nigeria, these are; Pb (0.005-0.182mg/g), Cr (ND-0.0087mg/g) and Cu (0.0005 – 0.0105mg/g). The difference in the compositions of the earth elements from the different regions and the difference in the activities of the industries could be the reason for the variation in the concentrations of these metals. Similarly, Isah *et al*., (2023) found the following result; Pb 0.00307mg/g, Mn 0.00124mg/g, and Cu, 0.00241mg/g in the soil sample of a mechanic workshop site in Azare Bauchi state, Nigeria.

**Table 1 Some Physical Parameters of the Borehole Water samples of the Quarry**

| | |
|---|---|
| Conductivity (mS/cm) | 0.24 x 1000 |
| Turbidity (NTU) | 0.00 |
| pH | 6.7 |

**Table 2 Some Physical Parameters of the Pond Water sample of the Quarry**

| | |
|---|---|
| Conductivity (mS/cm) | 0.3 x 1000 |
| Turbidity (NTU) | 8.9 |
| pH | 7.2 |

**Conclusion**

The results obtained from the analysis of water, soil and blood samples of workers at the quarry site using atomic absorption spectrometry showed that, the mean blood concentrations of Cr(0.304mg/l), Co(0.301mg/l), Mn (0.073) and Cu(1.467mg/l) were above the permissible limit set by world health organization (WHO) and united states environmental protection agency (US EPA) while the mean concentration of Pb(0.145mg/l) is below the limit. The concentrations of Pb(0.295mg/l), Cr(0.221mg/l) and Co(0.176mg/l) in the borehole water sample is above the permissible limit set by WHO whereas the concentration of Mn(0.039mg/l) is below the limit. In the soil sample, the concentrations of Cr(5.064mg/g), Co(0.414mg/g), Pb(1.260mg/g), Cu(0.754mg/g) and Mn(4.194mg/g) are all above the permissible limit set by WHO and NESREA. Only Ni (0.226) has a soil concentration within the WHO limit at the quarry site. It is concluded that most of the workers were less exposed to Cu and Ni as the concentrations were not detected in most of the samples, the concentrations of most of the heavy metals in the water, soil and blood sample of workers at the quarry site were above the permissible limit.

**Acknowledgement:** The technical inputs of the laboratory technicians of the Department of chemistry are acknowledged.

**Disclosure statement:** *Conflict of Interest:* The authors declare that there are no conflicts of interest.
*Compliance with Ethical Standards:* The authors ensured that all ethical considerations are duly followed and all safety guidelines are followed diligently.

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