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# Heavy Metals Speciation And Human Health Risk Assessment Of Soil Around Prism Steel Mill, Ikirun, Osun State, Nigeria

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## *Abstract*
This study determined the trace metal concentrations of soil around the study area and it also estimated the contamination indices of the soil around the factory and assessed the health risk and hazard index of the human population around the factory. Five perimeters at 100, 200, 300, 400 and 500m radii were mapped out around the factory. Within each perimeter, eight soil samples each were collected at random at 0 – 15 cm depth. The samples were added together to form a composite sample for each perimeter radius which gave a total of five composite samples. Similarly, one control sample, about 10 km away from the factory was collected from an undisturbed area. All samples were separately air-dried, sieved and pulverized to ensure homogeneity using standard methods before being kept in the polythene bags for speciation analysis. The worked up samples from above were taken to a standard laboratory for Atomic Absorption Spectroscopy (AAS) analysis of Fe, As, Cd, Cu, Co, Pb and Ni in the samples. From the result of the analysis, the Geo-accumulation (I-geo), the Mobility Factor, the Enrichment Factor and the Health Risk Index were estimated using standard formulae**.** The data obtained were subjected to appropriate descriptive and inferential statistical analyses. The results showed that the total heavy metal concentration in the soil decreased with distance from the factory. The concentration of the metals for all the distances were also significantly higher (at $p \leq 0.5$) than that of the control. The mean levels of metal concentration followed the order (in $\mu gg^{-1}$); Pb (395.05 - 500.52) > Co (318.32 - 447.45) > Cu (335.57 - 385.57) > Fe (253.75 - 443.25) > Ni (156.40 - 211.45) > As (147.85 - 170.85) > Cd (95.80 - 101.55). The study concluded that the concentrations of Fe and Pb at 100 m away from the factory were about four times and that of Cd Cu, As, Ni and Co were three times higher than the control. This calls for putting in place remediation steps that could prevent heavy metal-associated health effects to humans and the biota.

**Keyword:** Heavy Metals Speciation, Human Health, Risk Assessment, Soil, Prism Steel Mill, Ikirun, Osun State, Nigeria.

## *Introduction*
The presence of heavy metals in industrially polluted soils is of substantial interest because they are usually present at significant levels that if discharged into surface water could have severe effects on public health and the environment. Across the globe, there is an overwhelming concern about the dangers heavy metals pose to human health and the environment because of their strong retention and persistence in the environment (UNEP-GEF, 2002). The situation is even more alarming in developing countries like Nigeria where research efforts towards environmental monitoring is yet to be given the much desired attention

by the stakeholders.

Heavy metals are introduced into the soil environment either through natural or anthropogenic means. Natural pathways include phenomena such as weathering and volcanic eruptions while anthropogenic pathways encompass various human activities, such as construction works, mining, industrial and energy production, smelting, vehicle exhaust, waste disposal, as well as coal and fuel-oil combustion (Kabata-Pendias and Pendias, 2001). The concentration of soil's heavy metal may be influenced by the geology of parent materials among other factors, however, the elevation of the heavy metal content of soils above the tolerable levels is a strong indication of anthropogenic influence on the environment (Awotoye *et al.*, 2011). The general levels of heavy metals in any soil environment depend on the parent materials' background natural geological levels, input of metals as a result of diverse anthropogenic activities and the ability of soil particles to retain metals by adsorption, precipitation or chelation mechanisms (Oyekunle *et al.,* 2011). Heavy metals are known to concentrate through food chains and produce significant magnification of their original concentration because of their ability to resist biodegradation.

Heavy metals at elevated levels can affect the central nervous function leading to mental disorder, damage blood constituents and may also damage the lungs, liver, kidneys and other vital organs promoting several disease conditions while their long-term accumulation in the body system may result in slowing the progression of physical, muscular and neurological degenerative processes which can lead to diseases such as Parkinson's disease and Alzheimer's disease (Monisha *et al.,* 2104).

This study investigated the levels of heavy metals in surface soil samples around the sampling site with the intent to determining the levels of Fe, As, Cd, Cu, Co, Pb and Ni in the soil in terms of pollution index and their extent of bioavailability.

## MATERIALS AND METHOD

### Description of the Study Area

The study area, Prism Steel Mill (Figure 1), is located on the outskirt of Ikirun, along Osogbo/Ilorin Road. Ikirun is located on longitude $4^0$ 39.929' E and latitude $7.55^0$ 899' N. Established around 2009, the factory is located close to the main road. Ogunkunle *et al.*, (2016) described the vegetation of the area as lowland tropical rainforest, which has now turned to secondary forest and derived savannah. The climatic condition of the region is classified as humid tropical climate and controlled by the tropical maritime and tropical continental air masses. The dry season occurs between November to early March while the rainy season is between late March and early November (Tijani and Onodera, 2009). Annual rainfall in this region is 1335 mm (NIMET, 2014). Geologically, the region lies within the Pre-Cambrian basement complex of southwestern Nigeria, and it is a member of the Pan-African mobile belt east of West African craton. Migmatites and schists are the dominant basement rocks in the region and are associated with quartzite ridges forming the characteristic undulating terrain (Tijani and Onodera, 2009). In soil taxonomy, the soil of the area is classified as Iwo Association (Smyth and Montgomery, 1962; Tijani and Onodera, 2009), derived from coarse-grained granite and gneiss parent materials. Under the FAO classification system (FAO, 1990), the soil is termed ferric acrisol.

The factory's surrounding area is primarily rural with agricultural activities in both cash and subsistence crops practiced nearby. The surrounding has few residential houses, a cafeteria for those that normally bring the scrap iron, two petrol stations and a market some kilometers away.

The coordinates and sampling locations where sampled were taken are presented in Table 1 and Figure 1 respectively. The locations were mapped out using a Garmin 12 Channel GPS 310.

Table 1: Geographical locations of the sampling sites

| Sample code | Latitude (N) | Longitude (E) |
|---|---|---|
| **N1001 – N5002** | $07^0$ 52. 717' – $07^0$ 52. 991' | $004^0$ 39. 205' – $004^0$ 39. 392' |
| **E1001 – E5002** | $07^0$ 52. 163' – $07^0$ 52. 448' | $004^0$ 39. 210' – $004^0$ 39. 302' |
| **W1001 – W5002** | $07^0$ 52. 251' – $07^0$ 52. 891' | $004^0$ 38. 879' – $004^0$ 39. 159' |
| **S1001 – S5002** | $07^0$ 52. 234' - $07^0$ 52. 505' | $004^0$ 38. 974' – $004^0$ 39. 170' |
| **Control site** | $07^0$ 49. 593' | $004^0$ 35. 477' |

### Sampling and Pre-treatment

Sampling of the topsoils was carried out at 40 different locations around the perimeter fence of Prism Steel Mill at a depth of 0 – 15 cm. Within the 100 m radius, eight samples were taken, labelled N1001, N1002, E1001, E1002, W1001, W1002, S1001 and S1002, representing the directions of north, east, west and south. These eight samples were mixed together to form a composite sample PSM1. Likewise, in the 200 m radius, eight samples were taken – N2001, N2002, E2001, E2002, W2001, W2002, S2001 and S2002, to form composite sample PSM2. Same

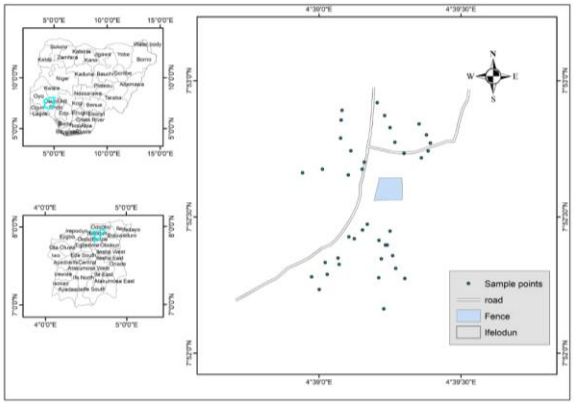



Figure 1: Map of study area showing sampling sites

was done in the 300 m radius; N3001, N3002, E3001, E3002, W3001, W3001, S3001 and W3002, to form composite sample PSM3. Also, in the 400 m radius, eight samples were taken – N4001, N4002, E4001, E4002, W4001, W4002, S4001 and S4002, mixed together to form PSM4. Lastly, from the 500 m radius; N5001, N5002, E5001, E5002, W5001, W5002, S5001 and W5002 were taken and pulled together to form the sample PSM5. Thus, five composite samples were generated and these were used for the study. A control sample was taken about 10 km away from the factory in an undisturbed area. The collected samples were placed in well-labelled self-sealing polythene bags. After air-drying for two weeks, the soil samples were sieved to remove large materials, ground with mortar and pestle into powdery form.

**Sterilization of Apparatus**

All glassware, polypropylene tubes and Teflon beakers were washed with soap, rinsed with distilled water. All were then soaked in 10% $HNO_3$ (v/v) for 48h, rewashed with soap and then rinsed thoroughly with doubly distilled water, following the process adopted by Ogunfowokan *et al.* (2009).

**Reagents used and their sources**

Reagents used include Nitric acid, $HNO_3$ (BDH Chemical Ltd, Poole, England); Hydrofluoric acid, HF (Riedel-deHaen, Germany); Acetic acid, $CH_3COOH$ (BDH Chemical Ltd, Poole, England); Ammonium acetate $CH_3COONH_4$ (M & B Ltd, Dagenham England); Hydrogen peroxide, $H_2O_2$ (BDH Chemical Ltd, Poole, England); Magnesium Nitrate, $MgCl_2$ (M & B Ltd, Dagenham, England); Sodium acetate $CH_3COONa$ (M & B Ltd, Dagenham England); Hydroxylamine hydrochloric, $NH_2OH.HCl$ (BDH Chemical Ltd, Poole. England); Perchloric acid, $HClO_4$ (Riedel-deHaen, Germany).

**Total Sample Digestion**

For the total sample digestion process, wet-acid digestion was carried out. 0.5 g of each soil samples was weighed into a well-washed dry beaker, 5 mL of concentrated $HNO_3$ was added and the beaker was covered with a watch glass. The sample was heated over a thermostated hot plate for two hours at a temperature of $150^0$C. Concentrated $HNO_3$ was used to replenish the mixture from time to time to prevent total dryness of the sample. The sample mixture was brought down and allowed to simmer and then 1 mL of concentrated $HclO_4$ was added and the sample was heated further for about 30 minutes. The mixture was brought down and allowed to simmer again before adding 1 mL of HF. Then, there was a further digestion of the sample for about 30 minutes, before it was brought down and allowed to simmer. Thereafter, the content of the beaker was quantitatively transferred into a 25 mL volumetric flask and made up to the mark with distilled water. The mixture was then transferred into a plastic bottle and kept prior to analysis determined by atomic absorption spectrophotometer using Perkin Elmer A Analyst 400 (S/N 201S12051104).

**Speciation Protocol**

The procedure of Tessier *et al.* (1979) was used for the study because it is well documented and adapted to the study of soils and dust (Clevenger, 1990). For each of the soil samples, 1 g was weighed into polyethylene tube

and extracted into six operationally defined geochemical fractions by addition of appropriate extractants in each step to ensure selective dissolution. The extraction process for each fraction is described below.

**Water soluble fraction (F1):** Water soluble fraction was extracted with 10.00 mL of distilled water by agitating continuously using mechanical shaker for 30 minutes.

**Exchangeable fraction (F2):** The residue from $F_1$ was leached at room temperature with 10.00 mL of 1.00 M $MgCl_2$ at pH 7 with continuous agitation for 30 minutes.

**Carbonate-bound fraction (F3):** Residue from $F_2$ was leached at room temperature with 10.00 mL 1.00 M solution of $CH_3COONa$ (at pH 5, adjusted with $CH_3COOH$) and continuously agitated for 5 hours.

**Fe-Mn oxides-bound fraction (F4):** The residue from $F_3$ was leached with 10.00 mL of 0.10 M solution of $NH_2OH.HCl$ (pH adjusted with 25% v/v $CH_3COOH$) at 96°C for 6 hours with occasional agitation.

**Organic matter-bound fraction (F5):** Accurately measured 3.00 mL of 0.02 M $HNO_3$ and 30% v/v $H_2O_2$ was added to the residue from $F_4$ and the mixture was heated to 85°C in water bath for 3 hours. After cooling, 5.00 mL of 1.00 M $CH_3COONa$ was used to extract with occasional agitations for 3 hours at 85°C.

**Residual fraction (F6):** The residue from $F_5$ was digested with mixtures of 8.00 mL 3:1 mixture of $HNO_3$ and $HclO_4$ in a Teflon beaker.

**POLLUTION INDEX MODELS**

**Geo-accumulation Index (Igeo)**

The geo-accumulation index (I-geo) values were calculated for the various metals using the formula proposed by Muller (1979), as follow:

$$\text{I-geo} = \log_2 (C_n / 1.5\, B_n)$$

where, Cn represents the measured concentration of the element of interest n. Bn is the background content of element n in abundance of chemical elements in the continental crust and the constant 1.5 enables us to analyze natural fluctuations in the content of a given substance in the environment and to detect very small lithogenic effects. Table 2 is the descriptive class of I-geo proposed by Huu *et al.* (2010) used for increasing I-geo values.

**Mobility Factor**

The formula used was modified from the relationship adopted by Olajire *et al.* (2003) was used to determine the mobility factor of the metals. This relationship is:

$$\text{MF} = \frac{F1+F2}{F1+F2+F3+F4+F5} \times 100$$

Table 2: Classes of Geo-accumulation index

| $I_{geo}$ | $I_{geo}$ class | Pollution intensity |
|---|---|---|
| <0 | 0 | unpolluted |
| 0-1 | 1 | unpolluted to moderately polluted |
| 1-2 | 2 | moderately polluted |
| 2-3 | 3 | moderately to strongly polluted |
| 3-4 | 4 | strongly polluted |
| 4-5 | 5 | strongly to very strongly polluted |
| 5-6 | 6 | very strongly polluted. |

Source: Huu *et al.* (2010)

**Enrichment Factor**

It is an effective tool for determining and differentiating heavy metals originating from anthropogenic activities from those originating from natural sources, so as assess the degree of anthropogenic influence on the environment. It can be calculated from the relationship:

$$\text{EF} = \frac{\left(C_x/C_{ref}\right)_{sample}}{\left(C_x/C_{ref}\right)_{background}}$$

where, Cx is the concentration of the element of interest. Cref is the concentration of adopted reference element. The background values were taken from average shale and Fe was selected as the reference metal because of all the seven metals investigated, it is the most abundant.

Values less than 5.0 are not considered significant, because such small enrichments may arise from differences in the composition of local soil material and reference soil used in the calculations. the Enrichment factor increases as the contributions of the anthropogenic origins increase. Five contamination categories are recognized on the basis of the enrichment factor as follows (Sutherland, 2000):

- EF < 2 is deficiency to minimal enrichment
- EF 2 – 5 is moderate enrichment
- EF 5 – 20 is significant enrichment
- EF 20 – 40 is very high enrichment
- EF > 40 is extremely high enrichment

**Health Risk Factor**

The health risk index (HRI) refers to the ratio of daily intake of metals to the oral reference dose ($RfD_o$). HRI of any metal that is greater than 1 means that the human population in the study area faces significant health risk.

**RESULTS AND DISCUSSION**

The reliability of the analytical procedure adopted in this study was tested in terms of sensitivity, precision, accuracy and recovery. Table 3 shows the result of percentage (%) recovery analysis conducted on soil samples for the heavy metals in order to verify the efficiency of sample treatment procedure. Recoveries of heavy metals for soils ranged from 81.84% for Pb to 88.60% for Cd and 85.72% for Ni to 86.56% for Cu respectively, indicating the efficiency of the procedures adopted for the analysis.

Table 3: Percentage Recovery (%R) for Soil Samples

| Heavy metals | Amount spiked (µg/g) | Amount recovered (µg/g) | % Recovery |
|---|---|---|---|
| **Pb** | 25 | 20.46 | 81.84 |
| **Cd** | 25 | 22.15 | 88.60 |
| **Ni** | 25 | 21.43 | 85.72 |
| **Cu** | 25 | 21.64 | 86.56 |

**Total Heavy Metals in the Soil Samples**

The concentration of the heavy metals in the soils at various distances to the factory is presented in Table 4. This result appears not significantly different (at $p \leq 0.05$) when compared to the mean total of the individual metals in different fractions of speciation presented in Table 5.

From Table 3, the average abundance of heavy metals in the soil around the factory was in the order: Pb > Co > Cu > Fe > Ni > As > Cd, indicating that of all seven heavy metals investigated in the study area, Pb had the highest concentration in the soil while Cd had the lowest concentration. Pb concentration ranged from 395.05 $\mu gg^{-1}$ to 500.52 $\mu gg^{-1}$ in all the distances investigated with an overall mean concentration of 440.36 $\mu gg^{-1}$ which is higher than 85 $\mu gg^{-1}$ set as maximum permissible level of Pb in soil (WHO, 1996; DPR, 2002). Its highest concentration, 500.52 $\mu gg^{-1}$, obtained at 100 m which is the closest point to the source of pollution from the factory was higher than the highest concentration of Pb obtained by Ogunkunle *et al.* (2016) in the same study site. Also, the mean concentration (440.36 $\mu gg^{-1}$) was higher than that obtained by Abidemi (2013) in the same study site and equally higher than the values obtained by Owoade *et al.* (2014) in soil in the vicinity of a scrap metal recycling factory in Southwestern Nigeria.

Table 4: Soil heavy metals (µg/g) concentration at different distances from Prism Steel Mill

| Distance (m) | Pb | Cd | Cu | As | Ni | Fe | Co |
|---|---|---|---|---|---|---|---|
| **100** | 500.52 ± 5.33 | 101.55 ± 1.88 | 375.73 ± 5.02 | 170.82 ± 2.24 | 211.45 ± 5.96 | 443.25 ± 5.69 | 402.13 ± 5.88 |
| **200** | 461.28 ± 4.47 | 101.25 ± 2.04 | 335.57 ± 4.78 | 166.40 ± 2.10 | 200.70 ± 4.73 | 429.50 ± 4.81 | 447.45 ± 4.77 |
| **300** | 430.78 ± 4.98 | 99.50 ± 2.02 | 385.62 ± 4.99 | 170.85 ± 3.12 | 176.95 ± 4.54 | 298.44 ± 3.86 | 404.15 ± 5.07 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **400** | 395.05 ± 4.02 | 95.80 ± 2.09 | 374.10 ± 3.16 | 151.02 ± 3.01 | 157.32 ± 3.44 | 391.32 ± 3.10 | 318.32 ± 4.56 |
| **500** | 414.15 ± 5.04 | 96.90 ± 2.11 | 346.50 ± 4.37 | 147.85 ± 3.78 | 156.40 ± 4.30 | 253.75 ± 3.26 | 378.15 ± 4.27 |
| **Control** | 142.90 | 39.75 | 122.25 | 54.62 | 84.05 | 114.12 | 137.27 |
| **Mean ± SD** | 440.36 ± 41.50 | 99.00 ± 2.57 | 363.50 ± 21.33 | 161.39 ± 11.12 | 180.56 ± 24.98 | 363.25 ± 83.32 | 390.04 ± 47.24 |

It can be inferred that the level of Pb in the surrounding soils of Prism Steel Mill has increased through years of intensive industrial activities. The concentration of Pb decreased with increasing distance from the factory, which suggests dispersion of pollutants from point of source to places of lower concentration. This finding is in agreement with the work of Oyeleke *et al.* (2016) on the surrounding soils of an automobile battery factory in Ibadan, Nigeria. The unexpected high Pb concentration at the 500 m distance more than the concentration at 400 m might be attributed to the proximity of the sampling points to the main road where high vehicular movement and tyre wares could also have contributed to the high level of Pb in the soil. Exposure to Pb has both physiological and neurological effects (Fuller, 1990), and can lead to decreased reaction time, weakness of the joints, nausea, insomnia and loss of memory (NSC, 2009). It can also cause serious injury to the central nervous system, kidneys, liver, reproductive system, basic cellular process and brain functions (Fatoki *et al.*, 2002).

The concentration of Cd in the study ranged from 95.80 $\mu gg^{-1}$ to 101.55 $\mu gg^{-1}$ while the mean concentration was 99.00 $\mu gg^{-1}$. The mean concentration was far higher than the WHO and DPR maximum permissible levels of 0.8 $\mu gg^{-1}$ (WHO, 1996; DPR, 2002). Similar to Pb, Cd concentration reduced as the distance from the factory is increased. Elevated concentration of Cd was recorded at 500 m distance of the factory which might be attributed to other anthropogenic activities in the area such as farming activities that involves the use of pesticides and other chemicals. The mean concentration of Cd in this work was higher than that recorded for the soil in the vicinity of a Korean mine in the study of Myung (2008). Renal damage which leads to proteinuria happens as a result of Cd adversely affecting the enzymes that are responsible for reabsorption of proteins in kidney tubules (Manahan, 2003). Elevated level of Cd in the environment can also lead to excessive salivation, nausea, vomiting, abdominal pain in the body system (Nordberg, 1972).

No definite patterns were observed in the concentration distribution of Cu, As and Co. Cu concentration in the soil samples ranged from 335.57 $\mu gg^{-1}$ in the 200 m to 385.62 $\mu gg^{-1}$ in the 300 m with a mean of 363.50 $\mu gg^{-1}$. The concentration at which Cu exist in the soil was far above the maximum permissible value of 36 $\mu gg^{-1}$ (WHO, 1996; DPR, 2002) for all the distances covered in this study. Mean concentration of Cu in this study was however lower than that recorded by Katana *et al.*, (2013) in the soils around open-air automobile mechanic workshop in Ngara area of Nairobi, Kenya. Cu is the third most used metal in the world and it is an essential micronutrient required in the growth of both plants and animals, it is not magnified, neither does it bioaccumulate in the food chain unlike some other man-made materials (VCI, 2011). Overdose of Cu can lead to anaemia, kidney and liver damage, and also irritation in the stomach and intestine (Martínez and Motto, 2000).

Concentration of As was from 147.85 $\mu gg^{-1}$ to 170.85 $\mu gg^{-1}$. Its mean concentration of 161.39 $\mu gg^{-1}$ was higher than the maximum permissible level of 20.00 $\mu gg^{-1}$ and 1.00 $\mu gg^{-1}$ of WHO and DPR respectively (WHO, 1996; DPR, 2002). The mean concentration and range of As in the present study was far lower than the values obtained by Liang *et al.*, (2017) in the vicinity soil of a tailing pond in Guangdong, China. Health problems as a result as a result of excessive exposure of humans to As include skin damage, increased risk of cancer and problems with circulatory system (Scragg, 2006). In soil, the mobility of As increases as the pH increases (Smith *et al.*, 1995).

Cobalt has its highest concentration at 200 m from the factory, while the lowest was obtained at 400 m distance. The concentration range is from 318.32 $\mu gg^{-1}$ to 447.45 $\mu gg^{-1}$ and the mean of the concentration was obtained as 390.04 $\mu gg^{-1}$ which was higher than 50 $\mu gg^{-1}$ and 20 $\mu gg^{-1}$ maximum permissible concentration of WHO and DPR respectively (WHO, 1996; DPR, 2002). The result of mean Co concentration in the study was higher compared to that recorded by Saraswathy *et al.*, (2010) in the polluted soils of Ranipet industrial area, India. Cobalt is beneficial to the body at low concentration as it is part of vitamin B12, which is essential to maintain human health but at abnormal exposure level, it causes difficulties in breathing and serious effects on the lungs including asthma, pneumonia and wheezing (ATSDR, 2004).

For Ni, its concentration gradually decreased as the distance from the factory is increased, such that its highest concentration was obtained at 100 m distance which is the closest sampling point to the factory and the lowest at 500 m distance away from the factory, suggesting the dispersion of pollutants from the point of source to locations

with lower concentration. The range of the concentration was from 156.40 $\mu gg^{-1}$ to 211.45 $\mu gg^{-1}$. The mean of the concentration was obtained as 180.56 $\mu gg^{-1}$ which appeared to be higher than the maximum permissible level of 35 $\mu gg^{-1}$ (WHO, 1996; DPR, 2002). Result of mean concentration of Ni was higher than the result obtained by Liang *et al.*, (2017) in the vicinity soil of a tailing pond in Guangdong, China. Short-term exposure to Ni by human being is not known to cause any health problems but long-term exposure can cause decreased body weight, heat, liver damage and skin irritation (Tiwana et al., 2005).

Unlike other metals investigated in this study, the mean Fe concentration of 363.25 $\mu gg^{-1}$ was very low compared to the WHO and DPR maximum permissible level of 50000.00 $\mu gg^{-1}$ and 38000.00 $\mu gg^{-1}$ respectively (WHO, 1996; DPR, 2002). The concentration of Fe in this study ranged from 253.75 $\mu gg^{-1}$ to 443.25 $\mu gg^{-1}$ and the concentration followed a gradual reduction as the distance from the factory was increased, except for the elevation at 400 m (391.32 $\mu gg^{-1}$) which was higher than the concentration at 300 m (298.44 $\mu gg^{-1}$). This could be as a result of uneven wind dispersion of the same pollutants in the area. The Fe levels (253.75 $\mu gg^{-1}$ - 443.25 $\mu gg^{-1}$) obtained in this study was lower than the levels (2312.50 $mgkg^{-1}$ - 3328.00 $mgkg^{-1}$) recorded in the study of metals in dumpsites in Sagamu, Nigeria by Ogunbanjo *et al.*, (2016) and significantly higher than the mean of 49.44 $mgkg^{-1}$ reported by Oyeleke *et al.*, (2016) in soil of an automobile battery factory in Ibadan, Nigeria. Fe is a vital micro-nutrient element required for physiological functioning of the body system, but excessive exposure to Fe could cause a wide range of free radicals that are believed to cause potential cellular damage, mutation and malignant transformations which in turn lead to an array of diseases (Grazuleviciene *et al.*, 2009).

**Heavy Metal levels in the various Soil fractions**

The level at which the metals exist in different soil fractions is presented in Table 5. The mean concentration of Pb in the various soil fractions of the soils ranged from 58.72±24.90 $\mu gg^{-1}$ to 87.01±21.72 $\mu gg^{-1}$. The presence of Pb in the soil samples could be as a result of anthropogenic inputs from the industrial process activities of Prism Steel Mill in which the raw materials are automobile parts, metals scraps, cans and metallic wires. The current concentration levels of Pb obtained in this study may pose serious environmental risk to humans, plants and animals around the study area since a larger proportion of the metal was associated with the non-residual fractions in all the samples analyzed. The high presence of Pb in water soluble fractions implies that, it could

Table 5: Metal level in various Soil fractions

| Metal | Distance (m) | F1 | F2 | F3 | F4 | F5 | F6 | TOTAL |
|---|---|---|---|---|---|---|---|---|
| Pb | 100 | 96.22±2.97 | 58.48±2.02 | 53.52±1.11 | 98.22±1.46 | 97.02±1.71 | 96.22±2.62 | 499.70±3.87 |
| | 200 | 98.25±1.66 | 81.07±1.87 | 71.30±3.00 | 73.48±1.69 | 70.78±2.03 | 68.80±1.87 | 463.68±4.04 |
| | 300 | 94.05±1.18 | 95.50±2.79 | 83.72±2.21 | 56.78±2.00 | 40.02±1.76 | 57.55±1.64 | 427.62±3.46 |
| | 400 | 48.28±3.13 | 86.00±2.63 | 83.72±2.05 | 81.78±3.16 | 40.02±1.09 | 57.55c±1.85 | 397.35±5.16 |
| | 500 | 98.25±3.37 | 81.07±1.60 | 46.30±1.96 | 73.48±0.85 | 45.78±0.89 | 68.80±2.14 | 413.68±4.21 |
| Cd | 100 | 15.55±1.18 | 18.25±2.30 | 16.35±1.37 | 15.50±1.38 | 18.78±1.54 | 18.75±0.88 | 103.18±1.89 |
| | 200 | 19.15±1.09 | 17.98±1.87 | 18.38±2.09 | 12.75±1.63 | 16.35±0.84 | 16.20±1.29 | 100.80±2.15 |
| | 300 | 19.20±1.44 | 14.58±1.52 | 18.00±1.65 | 17.22±1.47 | 17.05±0.58 | 14.20±1.50 | 100.25±2.03 |
| | 400 | 15.75±1.85 | 17.55±2.23 | 15.72±2.16 | 13.45±0.76 | 13.72±1.01 | 18.50±0.79 | 94.70±1.42 |
| | 500 | 18.48±2.04 | 18.50±1.42 | 15.72±1.87 | 13.45±0.82 | 13.72±1.86 | 18.50±0.90 | 98.38±0.68 |
| Cu | 100 | 65.00±0.96 | 63.50±2.03 | 62.50±1.69 | 59.75±1.48 | 65.00±2.02 | 62.00±1.96 | 377.75±4.24 |
| | 200 | 68.75±1.63 | 62.50±1.27 | 45.00±1.17 | 60.75±1.09 | 66.75 ±1.73 | 34.50±0.82 | 338.25±3.62 |
| | 300 | 89.25±1.90 | 61.50±0.98 | 69.25±1.72 | 60.75±0.60 | 67.25±2.00 | 34.00±0.87 | 382.00±3.81 |
| | 400 | 35.00±0.74 | 64.25±1.43 | 59.25±0.74 | 65.00±1.13 | 62.00±1.20 | 87.50±1.66 | 373.00±2.41 |
| | 500 | 48.00±0.55 | 65.00±0.77 | 69.25±1.17 | 60.75±1.62 | 67.25±1.33 | 36.50±0.95 | 346.75±2.76 |
| As | 100 | 30.70±1.01 | 30.78±0.85 | 28.70±0.40 | 29.30±3.19 | 31.00±1.57 | 18.80±0.48 | 169.28±3.90 |
| | 200 | 21.00±2.11 | 20.75±1.49 | 40.50±0.53 | 41.30±1.61 | 26.85±0.76 | 18.15±1.90 | 168.55±2.87 |
| | 300 | 30.85±0.92 | 32.85±2.63 | 20.80±1.67 | 20.72±1.50 | 33.20±1.08 | 33.60±0.36 | 172.02±4.15 |
| | 400 | 34.15±2.24 | 35.58±0.33 | 14.40±1.15 | 11.88±1.68 | 35.48±1.46 | 20.35±0.65 | 151.82±3.04 |
| | 500 | 10.80±0.55 | 30.40±0.46 | 20.80±0.82 | 20.72±0.93 | 33.20±2.06 | 33.60±1.31 | 149.52±1.36 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **Ni** | 100 | 36.75±0.40 | 35.15±0.42 | 37.65±1.11 | 37.72±0.32 | 30.22±0.24 | 37.70±1.01 | 215.20±0.74 |
| | 200 | 31.50±0.17 | 35.10±0.56 | 30.18±0.62 | 32.70±0.80 | 39.88±0.36 | 33.48±0.55 | 202.82±0.83 |
| | 300 | 38.05±1.32 | 33.60±0.14 | 26.40±1.28 | 28.62±1.23 | 25.92±1.04 | 26.58±0.27 | 179.18±2.17 |
| | 400 | 25.82±0.15 | 26.30±0.77 | 26.62±1.36 | 26.42±0.90 | 27.10±0.89 | 26.90±0.58 | 159.18±1.95 |
| | 500 | 26.02±0.68 | 26.12±2.06 | 26.38±0.09 | 28.70±2.15 | 25.98±1.74 | 26.70±1.15 | 159.90±0.36 |
| **Fe** | 100 | 45.00±0.60 | 52.50±0.26 | 15.00±0.44 | 57.50±0.73 | 142.50±1.09 | 137.50±0.50 | 450.00±1.21 |
| | 200 | 162.50±0.73 | 52.50±1.32 | 17.50±1.18 | 10.00±0.09 | 55.00±0.81 | 135.00±0.72 | 432.50±0.38 |
| | 300 | 35.00±1.28 | 55.00±0.20 | 10.00±0.78 | 10.00±0.58 | 55.00±0.92 | 135.00±1.25 | 300.00±1.04 |
| | 400 | 35.00±0.17 | 55.00±0.73 | 107.50±0.15 | 30.00±0.74 | 80.00±1.16 | 77.50±0.48 | 385.00±0.32 |
| | 500 | 35.00±0.11 | 30.00±1.17 | 10.00±0.07 | 35.00±1.63 | 80.00±0.46 | 60.00±0.60 | 250.00±1.65 |
| **Co** | 100 | 80.50±0.82 | 85.50±0.61 | 91.25±2.06 | 80.75±1.25 | 36.00±0.13 | 30.50±0.13 | 404.50±0.97 |
| | 200 | 83.00±1.05 | 83.00±0.08 | 87.50±0.85 | 83.42±0.20 | 60.50±0.52 | 50.62±0.58 | 448.05±1.61 |
| | 300 | 75.88±0.06 | 56.10±2.07 | 58.35±1.33 | 64.62±0.07 | 76.70±0.77 | 75.10±0.49 | 406.70±2.03 |
| | 400 | 52.45±0.28 | 27.40±1.64 | 32.88±0.77 | 52.20±1.59 | 76.10±052 | 75.72±1.12 | 316.75±1.63 |
| | 500 | 76.48±1.53 | 26.48±0.22 | 58.35±1.74 | 64.62±0.24 | 76.70±0.35 | 75.10±2.04 | 377.72±0.84 |

leach further down the soil, taken up by plants, as well as into the groundwater bed and can also be transferred to other area during wet season. Metals in these fractions would readily dissolve in surface waters, or percolate through ground waters in solubilized forms, making such metals bioavailable to plants.

Concentrations of Cd in the various fractions ranged from 14.47±1.85 $\mu gg^{-1}$ to 17.63±1.83 $\mu gg^{-1}$ in the soil samples. From the result, Cd concentration in the water soluble, exchangeable metal and the residual fractions were not significantly different from each other. The Fe-Mn oxide-bound fraction had the least concentration. High concentration in the water soluble and exchangeable metal fractions indicate its tendency to be relatively bioavailable for plants' uptake. However, its high occurrence in the residual fraction too reduces its associated hazards to plants and humans since metal concentration in this fraction are strongly bound and generally not bioavailable.

For Cu and As, their concentration in the soil fractions ranged from 50.90±23.58 $\mu gg^{-1}$ to 65.65±2.24 $\mu gg^{-1}$ and 24.90±7.98 $\mu gg^{-1}$ to 31.95±3.26 $\mu gg^{-1}$ respectively. Generally, Cu is known to easily complex with organic matters because of high formation of organic Cu compounds (Haung *et al.*, 2007). The result of sequential extraction shows that Cu and As are mostly abundant in the fraction bound to organics. Heavy metals that show high abundance in organic matter-bound fraction are more available than heavy metals in the residual fraction and can be mobilized under strong oxidizing conditions due to degradation of organic matters and when they are subjected to varying physicochemical weathering variabilities like elevated temperature, redox changes or pH.

The result of Ni and Co show similar pattern to that of As with the concentration in both residual and non-residual fractions being at par, implying that any fraction of these metals could contribute equally to the contamination of the soil. Among the non-residual fractions, water soluble fractions contained the highest concentration of both Ni and Co. The range of concentration was from 29.45±4.86 $\mu gg^{-1}$ to 31.63±5.76 $\mu gg^{-1}$ and 55.70±28.67 $\mu gg^{-1}$ to 73.66±12.21 $\mu gg^{-1}$ for Ni and Co respectively.

In the case of Fe, there was higher abundance in the residual fractions than in the non-residual fractions. This agrees with Ramirez *et al.* (2005), who reported that Fe was mostly associated with the residual phase. Concentrations of Fe in the fractions ranged from 28.50±19.80 $\mu gg^{-1}$ to 109.00±37.30 $\mu gg^{-1}$ in the samples. The residual fraction is considered as the most stable, less bioavailable and less reactive since it is absorbed within the crystal lattice layer of silicates and well crystallized oxide minerals, so, the occurrence of Fe in the residual fraction reduces its associated hazards to man and plants.

**Geo-accumulation Index (Igeo)**

The values of geo-accumulation index ($I_{geo}$) in the all the distances considered shows that the soil is extremely polluted in Cd and strongly polluted in Pb and As. Cu, Fe and Co show moderate pollution in the soil while the soil appears to be unpolluted in Ni. Also, the result as shown in Figure 2, suggests that the pollution of the soil in the metals might have been introduced through anthropogenic activities from the smelting processes. At the concentration these metals exist in the soil, they constitute potential toxicity to plants and for their consumers.

Presence of the metals in the food chain represents a geochemical risk because of their toxicity to human health, especially to the occurrence of bioaccumulation phenomena (Barbieri, 2016).

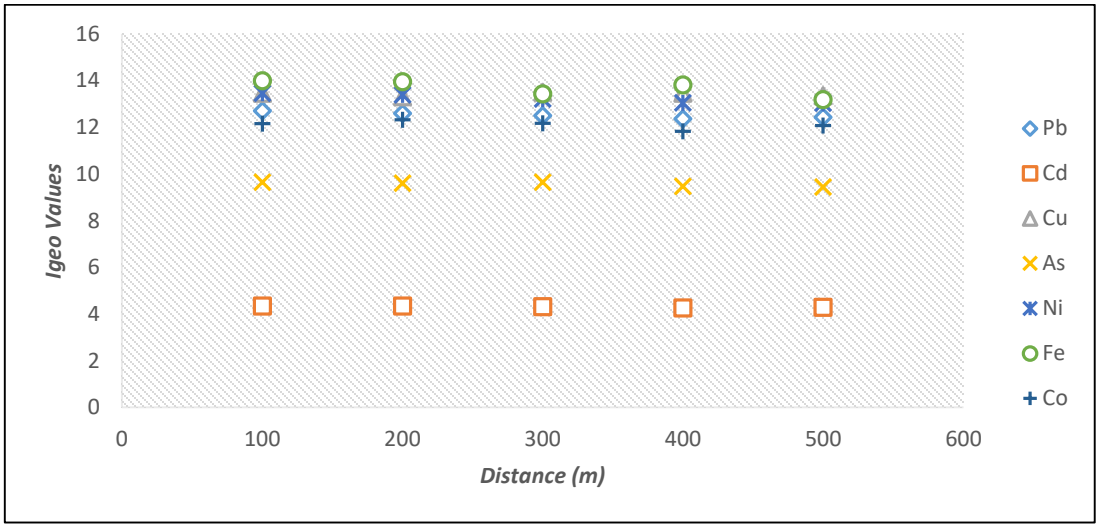



Figure 2: Geo-accumulation Index (Igeo) of metals

**Mobility Factor (MF)**

The mobility factor (MF) of metals in the sampling distances did not follow a definite pattern, with the highest value obtained at 300 m and the lowest value at 100 m. The low MF value at 100 m might be due to the dispersion of these metals from the immediate areas could be influenced through anthropogenic or natural activities such as wind, erosion and leaching processes. Pb, As and Cd are toxic metals even at low level of exposure as they pose serious health problems. Excessive exposure to Fe, Cu and Co can hinder the biological functioning of the body system (Badawy *et al.*, 2002). It was observed that Pb is the most bioavailable metal of all the metals studied at virtually all the sampling distances. This may be due to the porous nature of the sandy soil around this area. The order of MF reported in this study is Pb > Cd > As = Ni > Cu > Co > Fe.

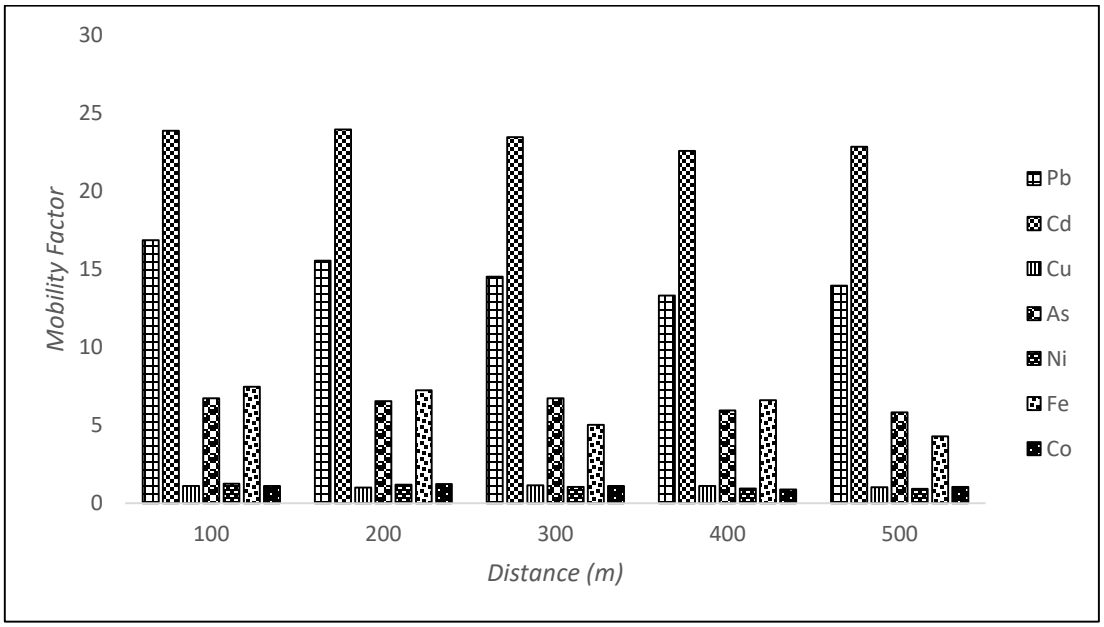



Figure 3: Mobility Factor (MF) of metals

**Enrichment Factor (EF)**

An increase in the values of enrichment factor (EF) is a clear indication that the metals are from anthropogenic sources (Sutherland, 2000). Zhang and Liu (2002) reported values between 0.5 to 1.5 means the metals are from crusted material or natural process, whereas EF values greater than 1.5 suggest the source of the metals may likely from anthropogenic activities. The EF of Cd, Pb and As were greater than 5, which follows that the soil is significantly enriched with Cd, Pb, As and the metals are likely from anthropogenic sources possibly from the milling activities, traffic emissions, tyre abrasion and fossil fuel combustion. Ni shows minimal enrichment in the soil while significant enrichment was discovered in Cu, Fe and Co. The soil is also very highly enriched in Pb and As. Extremely high enrichment appear in the case of Cd.

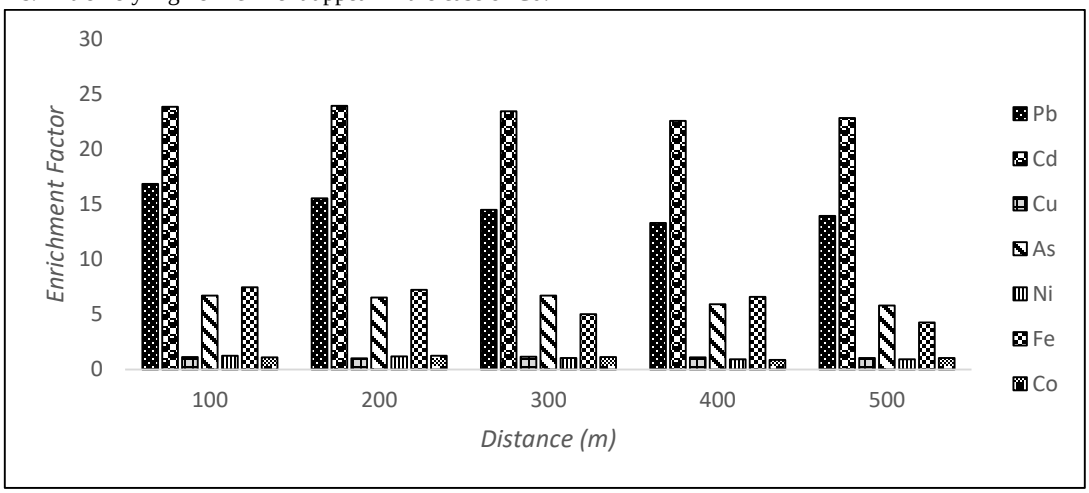



Figure 4: Enrichment Factor (EF) of metals

**Health Risk Index (HRI)**

The high values of health risk index (HRI) of the metals in this study might be linked to the iron milling activities and transportation of scrap metals materials from other places to the steel mill. The residents of the factory area are therefore at a great risk of these metals since their values are greater than 1. Except for Cu, Ni and Co, very high HRI values (1.02 – 67.08) were recorded for all the metals (Pb, Cd, As, Fe). Inhabitants of this area cannot be said to be at risk if the HRI of the metals were to be less than 1 (Sajjad *et al.*, 2009). The inhabitants and workers in this environment may experience health problems in the future as metals tend to accumulate over a period of time leading to biomagnifications of the metals in the body system.

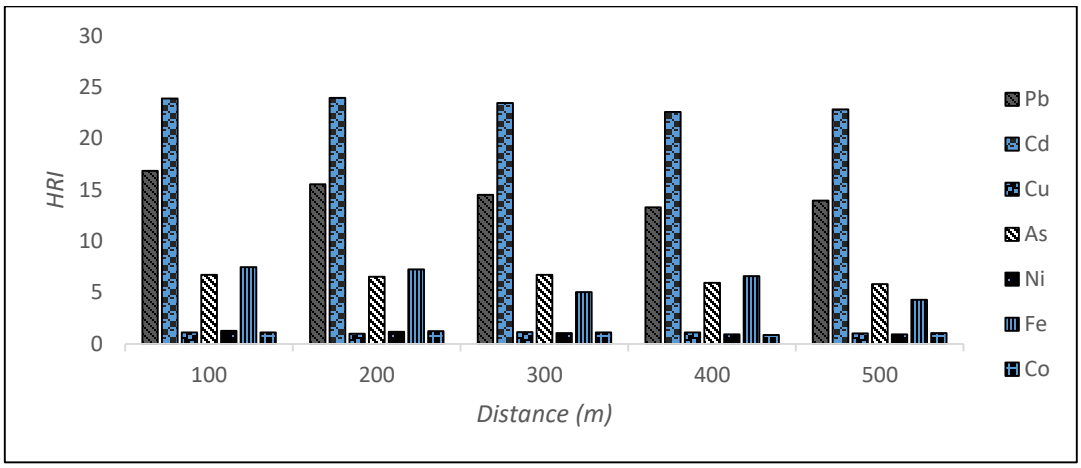



Figure 5: Health Risk Index (HRI) of metals

## CONCLUSION

The study examined the health risk of metals Pb, Cd, Cu, As, Ni, Fe and Co in the soil around Prism Steel Mill, Ikirun, Nigeria. A revised six-stage sequential extraction procedure by Tessier *et al*. (1979) was used to fractionate heavy metals in the soil samples.

The concentration of Pb was observed to be highest while Cd has the least concentration in the soil. The metals were found to be above the recommended limits with variance in terms of Fe falling below the permissible limit, a fact supported by the result of various pollution indices used in the study. Even though there was a gradual decrease in the concentration of metal pollution in the soil as we move away from the factory, the result of the study shows high level of pollution up to 500 m away from the factory, making the environment unsafe for agricultural practices and human habitation.

Speciation studies showed that a large percentage of these metals occur in the residual fractions of the soil which is less mobile in the environment and cannot be easily picked up by plants and animals. However, the concentration at which most of these metals exist in the soil, with the exception of Fe, may pose serious environmental risks to animals, plants and inhabitants of this area in the nearest future. This is a serious cause for concern as these metals accumulate to pollute the environment and thus, continuous monitoring of this area is necessary to ascertain long term effects of the industrial activities of this factory.

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