

Analysis of Selected Heavy Metals in Surface Water and Sediments from Unreclaimed Mining Ponds Used for Irrigation Farming in Jos South, Nigeria

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ABSTRACT

The present study is aimed at examining the heavy metal contamination in surface water and sediments from selected unreclaimed mining ponds Bukuru and Rayfield towns, Jos south Local Government Area "L.G.A" Plateau State. Five representative unreclaimed ponds were purposively selected in each unreclaimed mine ponds of Bukuru and Rayfield. Water and sediment samples were collected from January to September, 2019, with January to March representing dry season and April to September as rainy season. A total of 22 water samples were collected for the study with 11 samples in each of the seasons. Samples collected for each of the seasons were analyzed for Cd, Mn, Hg, Cu, Ni, Pb, Ur and Zn, while a control point was selected in Riyom. In the exception of Cd, mean levels of sampled metals were within NESREA permissible limits in water samples for most locations, while Mn, Hg Cu were very high and above permissible limits. The result of a one-sample t-test showed that there is no significant difference between the observed mean levels and NESREA standard either in water at $p > 0.05$, $d = 0.0993$ or sediment at $p > 0.05$, $d = 0.209$. Mean levels of all heavy metals in both water and sediment samples were higher in the dry season when compared to the rainy season samples, although the difference was not statistically significant at $p > 0.05$, $d = 0.052$ for water, while the difference was found in sediment at $p > 0.05$, $d = 0.015$. The study found that concentration levels in sediment were significantly higher than levels in water at $p > 0.05$, $d = 0.006$. In terms of spatial variation, concentration levels differ significantly in sediment samples between Bukuru and Rayfield mine sites at $p > 0.05$, $d = 0.019$, while water samples did not show a statistical difference at $p > 0.05$, $d = 0.053$ between the two locations. Since the water in unreclaimed mining ponds are used for fish farming, irrigating and domestic purposes, it is of great concern that Cd is in high concentration because it is extremely toxic and carcinogenic.

Keyword: Unreclaimed mines, Heavy metal, surface water and sediment

INTRODUCTION

Mining on the Jos Plateau is dated back to 1902 with tin and columbite as the major targets (Federal Department of Museum and

Monuments, 1979). Mining played a major role in the economic development of the country from 1904 up to the late 1970s,

especially on the Jos plateau. Across the country, Wasiu *et al.*, (2016) reported that between 1933 and 1943, about 1.4 tonnes of gold metal was produced by the country. However, with the rapid expansion of mining activities on the Plateau especially in the 1940s, serious conflicts arose between the mining companies and the local population, the focus being the loss of agricultural land to mining activities. This led to the enactment of legislation mandating mining companies to pay compensation for crops damaged but not for the destruction of the land, a development that marked the beginning of abandoned mining pits (Alexander, 1985). According to Dabi, (1990), although these legislations were in existence, they were not appropriately implemented or enforced especially on the Jos Plateau given the level of unreclaimed mines. The promulgation of the Mineral Act in 1946 (now Nigeria Mineral Act 1999) in Nigeria for example, also paved the way for the reclamation of mined-out lands in the Jos Plateau as with some other parts of Nigeria. However, meaningful reclamation efforts did not begin until 1949 thereby leaving many unreclaimed mine dumps (Alexander, 1985). Over the years, these unreclaimed or abandoned mines have become permanent water bodies with high potential for irrigation, fisheries, water supply and recreation (Adeboye, 2012) as they are sometimes so deep that they are recharged by groundwater. Some of these unreclaimed mining ponds litter the towns of Bukuru and Rayfield. These mines, filled with water are generally referred to as mine ponds (Edun and Davou, 2013). More so, these unreclaimed mining ponds with their adjoining mine tailings are a potential source of heavy metals contamination. In Bukuru and Rayfield, relicts of unreclaimed or abandoned tin mines and tin ore processing sites are a common sight. Mine tailings from the processing of the tin ore often associated with heavy metals are disposed of indiscriminately. Studies have shown that mining is the major source of

heavy metal contaminations in the environment (Asklund *et al.*, 2005; Wang and Mulligan, 2005; Kusin *et al.*, 2012; 2014a & b; Lar *et al.*, 2014; Nyam and Ashano, 2017; Kumar, *et al.*, 2017; and Awuchi *et al.*, 2020).

Long-term exposure to heavy metals can be carcinogenic, affecting the central and peripheral nervous system and circulatory effects (Madzin *et al.*, 2015; Butu, *et al.*, 2019). Heavy metal contamination in water and sediments has received considerable attention worldwide due to the toxicity, persistence, abundance, and biomagnification of Heavy metals in the environment and their subsequent accumulation in aquatic habitats (Nghah *et al* 2007; Meng *et al.*, 2016). Because of this, research has shown that understanding the concentration, distribution and sources of heavy metals in aquatic environments is essential to provide a scientific reference for the protection of water resources and the control of water and soil pollution (Wei *et al.*, 2018). This present study is thus aimed at examining the heavy metal contamination in metals in surface water and sediments from selected unreclaimed mining ponds which are used by the communities for irrigation and fish farming and are known to provide a reasonable quantity of the fish and vegetable supply in Bukuru and Rayfield towns, Jos south L.G.A, Plateau State.

MATERIALS AND METHODS

Study Area

Bukuru and Rayfield are major towns in Jos South Local Government Area, Plateau State (Figure 1). Jos South is bordered in the north by Jos North and part of Bassa Local government Areas, Plateau State, in the east by Jos East and Barkin-Ladi Local Government Areas, in the south by Riyom Local Government Area and in the west by parts of Riyom and Bassa Local Government

Areas. Jos South L.G.A is located within latitude $9^{\circ} 54'N$ and longitude $08^{\circ} 52'E$ as shown in Figure 1. The study area is

accessible with a major road, minor and secondary roads.

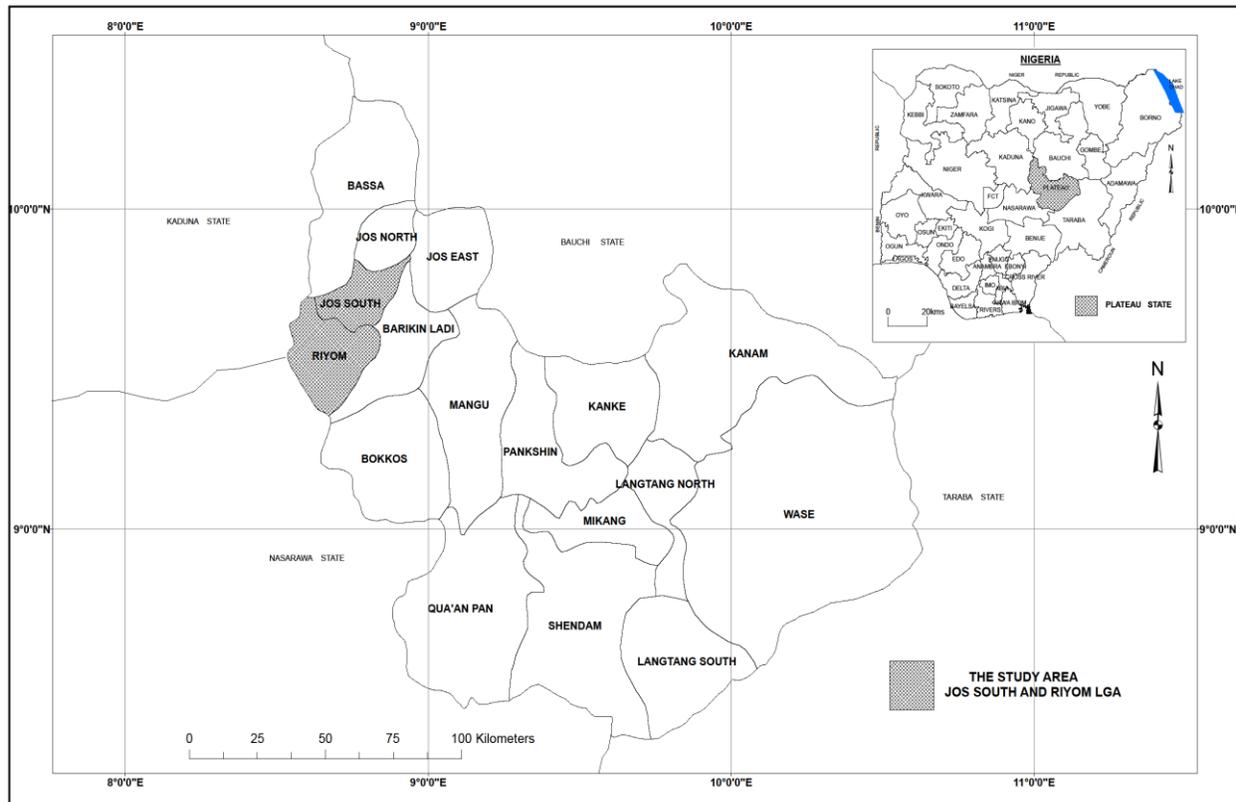


Figure 1.1: Jos South and Riyom Local Government Area. Source: Geography Department NDA Kaduna (2018).

The study area is characterized by two major seasons; wet and dry seasons. The wet (rainy) season usually starts from April and continues till mid or early October when the frequency and intensity would have drastically reduced. The rainy season is usually brought about by the South –Western Trade wind blowing from the Atlantic Ocean into the country. The dry season usually starts from November to March under the influence of the North-east Trade wind which blows from the Sahara Desert into the country. The effect of the harmattan wind is severely felt during December and January and is characterized by the very cold, dry and dusty wind. The mean monthly temperature of the area ranges between $19.93^{\circ}C$ to $27.4^{\circ}C$.

Geologically, the study area is overlain by the younger granite province in Jos-Bukuru ring complex. The younger granite province is a petrography province in Africa characterized by acid rocks that bear distinctive mineralization. This granite is associated with the biotite granite plutons especially the Jos-Bukuru complex which is the richest source of cassiterite and columbite, (Adiku-Brown, 2001). Soils are generally shallow, well-drained with sandy texture while some occurred at slopy areas and lesser slopes. Where the soils are moderately deep, they are well-drained to imperfectly drain and are either stony or concretionary and have surface horizon varying in texture between sandy loam, sandy clay loamy, sandy clay and

silt clay loam with concretionary or stony phase (Mankilik, 1995). The tributaries of the three major-river systems come together at a point near Rayfield, south of Jos. The study area is drained by the Delimi river basin which drains into the Gongola River in the northeast before entering the Benue River. Also draining from the Jos plateau are the Wase-Shemankar, Ankwe and Mada rivers. Discharge from these streams are highest in August and the lowest in March. In the dry season, many of the streams appear as a chain of water holes separated by alluvium and sand (Alford *et al*, 1997). These streams and mining ponds are sources of water for domestic and industrial/commercial uses. Farmers and fishermen also take advantage of the abandoned recharged mining ponds to practice irrigation farming and fish farming.

Data types and Collection

There are a total of twenty-four (24) unreclaimed mining ponds in Bukuru and Rayfield. Out of this, five (5) representative

unreclaimed ponds were purposively selected in each unreclaimed mine ponds of Bukuru and Rayfield, while a point was selected in Riyom, Riyom Local Government Area, to serve as the control. Samples of soil and water were taken in each of the five selected sampling points in Bukuru and Rayfield for analysis of heavy metals. The control point, Riyom is one of the Local Government Areas in Plateau State that has recorded the least mining activities (Stephen, 2007) and thus the choice as the control. The selected sampling points were chosen because they represented the best location for collecting water, and sediment samples in the mined-out areas and were also suitable for easy sampling of the current contamination status given their accessibility and geospatial spread. More so, these ponds were selected because these unreclaimed mine ponds are used for irrigation and fish farming among other uses. At each of the sampling points, a GPS was used in recording the geographical coordinates of the location Table 1.

Table 1: Geographical coordinates of sample locations

| Station | Location | Coordinate | Elevation | Altitude |
|---------|--|-----------------------------|-----------|----------|
| BKW I | ECWA farm, Bukuru | N09048.2991 E008053.2361 | 1288m: | A=8.7m |
| BKW II | Behind ECWA farm 1, Bukuru | N09048.334 E008052.685 | E=1268: | A=9.0m |
| BKW III | Behind ECWA farm 2, Bukuru | N09048.3421 E00852.688 | E=1266: | A=8.8m |
| BKW IV | Behind Yelwa club junction, Bukuru | N09048.010 E008052.452 | E=1271: | A=8.4 |
| BKW V | ECWA family church, Bukuru | N09048.975 E008054.219 | 1289: | A= 6.9m |
| RFW I | Chiroma farm, Rayfield | N09051.717 E008054.708 | E=1261: | A=6.4m |
| RFW II | Adjacent Chiroma farm, Rayfield | N09051.6941 E008054.5031 | E=1270: | A=7.2 |
| RFW III | Behind Rayfield resort (Du village), Rayfield | N09049.146 E008054.237 | E=1294: | A=7.9 |
| RFW IV | Behind Obedom Academy junction, Rayfield | N09050.090 E008054.037 | E=1281: | A=7.9 |
| RFW V | Rayfield Holiday Resort, Rayfield | N09052.374 E008052.631 | E=1293: | A=8.9 |

Source: Field work (2019)

Collection of water sample

The water samples were collected from January- September 2019 to account for rainy (April -September) and dry season (January - March), 2019. A total of twenty-two (22) water samples were collected for the study with eleven (11) samples in each of the seasons. Each of the 11 samples collected for each of the seasons was analyzed for eight (8) heavy metals which includes cadmium, manganese, mercury, copper, nickel, lead, uranium and zinc. These heavy metals are often associated with the Jos-Bukuru Younger granite which is a rich source of tin on the Plateau (Adiukwu-Brown, 2001). The sampling bottles were disinfected with methylated spirit and thoroughly rinsed with the sample water to ensure no contaminant is introduced into the sample as recommended by APHA (1995). The water samples were collected using the grab sampling method by dipping a 250 ml plastic bottle 30 cm below the water surface at each selected sampling point. The sample bottles were labelled with the appropriate source and date of collection before being transported to the laboratory of the Kaduna State Environmental Protection Agency (KEPA) where they were stored in the refrigerator for analysis.

Sediment Sample Collection

The sediment samples were collected for the same period as water samples (January - September 2019). A total of 22 soil samples were collected for the study with 11 samples in each of the seasons. Each of the 11 samples collected for each of the seasons was analyzed for eight (8) heavy metals which includes cadmium, manganese, mercury, copper, nickel, lead, uranium and zinc. The choice of sediments for this study is because sediments are also considered important indicators for environmental pollution. It is also known that heavy metals are more concentrated in the bottom sediments (Butu,

2011). The sediment samples were collected with the aid of a soil auger at depth of 0-15cm (top soil). This depth was chosen because they provide the bulk of plant nutrients and thus a good receptor of contaminants. The collected soil samples were carefully transferred into black high density polyethylene bags, properly labelled and transported to the laboratory unit of the Kaduna State Environmental Protection Agency (KEPA) for analysis.

Sample Preparation

Preparation of Water Sample: - Water samples were containerized and labelled before being taken to the laboratory for analysis. Fifty millimeter of water samples from each sampling point were thoroughly shaken using a water bath shaker (GYROMAX™ 939 and 939XL model) and then accurately measured into a beaker (representing one-third of the total weight) and digested with 5ml of concentrated HNO₃ for a few hours on a hot plate at 100° C until the solutions were reduced to less than 20 ml by volume. The solutions were then transferred into 100 ml plastic container and taken for heavy metals determination on Atomic Absorption Spectrometer (AAS), Agilent technologies model 200 series AA.

Preparation of sediment samples (Digestion): - The sediment samples were oven-dried (to avoid microbial effects), a temperature of 107°C till the moisture present was expelled and then passed through a 2 mm sieve before being subjected to laboratory analyses using standard procedures. About 2.0 g portion of dried sediment (representing one-third of the total weight) were digested in 15 cm³ of tri-acid mixture (HNO₃, HCl and H₂SO₄ at 5:1:1 ration) at 80°C until a transparent solution appeared. After cooling, the digested samples were filtered using what man No.41 filter paper and the filtrate was finally maintained at 50 cm³ distilled water. The clear solutions

were then poured into sample bottles for reading in the Atomic Absorption Spectrometer.

Preparation of Standard Curve

The standard curves for the heavy metals was prepared bearing in mind that these elements occur in trace concentration. Standard solutions was be prepared from 1000 parts per millions (ppm) stock solution. One milliliter of the 1000ppm stock solution was pipetted into a 100 ml volumetric flask and made up with distilled water. This solution was 10 ppm of the solution. From this solution, standard solutions of 0.2, 0.4, 0.6, 0.8 and 1ppm was be prepared by taken 0.2, 0.4, 0.6, 0.8 and 1ml portions into 10ml volumetric flasks and made to mark. These were then run in the Air Acetylene flame and standard curves for the various elements were obtained

Sample Analysis

All samples were analyzed for the selected heavy metal concentrations using a computer-controlled Atomic Absorption Spectrophotometer (Agilent technologies model 200 series AA). The AAS was calibrated with standard solution settings and operational conditions were done following the manufacturers' specifications and instructions. After calibration of the instrument, the samples were aspirated into the AAS instrument according to the standard method (APHA, 1995). Concentrations of heavy metals in the extracted water and sediment samples were estimated and analysed by using Atomic Absorption

Spectrophotometer. The samples were analysed in triplicates, and the blank determinations in triplicates were also run in the same manner during the analysis. This technique was used because of its affordability and reliability and also because, for the determination of most metals and metalloids, the technique offers sufficient sensitivity for many applications and is relatively interference-free. All samples were compared with the National Environmental Standards and Regulation Enforcement Agency (NESREA, 2011) of Nigeria and WHO (2011) permissible limits for drinking water.

Statistical Analysis

A one-sample t-test on the other hand was used to compare the level of significance between observed concentration levels and NESREA permissible limits. The equation is given as follows;

$$t = \frac{m - \mu}{s/\sqrt{n}}$$

Where

m is the observed mean

μ is the theoretical mean

S is the standard deviation

n number of observation

RESULTS AND DISCUSSION

The results of the heavy metal concentration in water samples in Bukuru and Rayfield with the control point in Riyom for rainy and dry seasons are shown in Tables 2-3.

Table 2: Concentration of heavy metals in water in Bukuru, (BSK), Rayfield (RFS) and the Control Point in Riyom in the rainy season.

| Samples | Cd(mg/l) | Mn(mg/l) | Hg(mg/l) | Cu(mg/l) | Ni(mg/l) | Pb(mg/l) | Ur(mg/l) | Zn(mg/l) |
|--------------------------|------------------------|-----------------------|-----------------------|------------------------|-----------------------|------------------------|----------|----------------------|
| BKW I | 0.0286 | 0.0333 | 0.0001 | 0.0178 | 0.0060 | 0.0016 | - | 0.2816 |
| BKW II | 0.0377 | 0.0279 | 0.0000 | 0.0267 | 0.0025 | 0.0181 | - | 0.1222 |
| BKW III | 0.0414 | 0.0401 | 0.0002 | 0.0638 | 0.0120 | 0.0200 | - | 0.0760 |
| BKW IV | 0.0500 | 0.0288 | 0.0021 | 0.0595 | 0.0253 | 0.0251 | - | 0.0588 |
| BKW V | 0.0540 | 0.0316 | 0.0021 | 0.0465 | 0.0165 | 0.0110 | - | 0.1604 |
| Mean ±SD | 0.04234 ± 0.009 | 0.03234 ±0.004 | 0.0009 ±0.0009 | 0.04286 ±0.0178 | 0.01246 ±0.008 | 0.01516 ±0.0081 | - | 0.1398 ±0.079 |
| S. Error | 0.004 | 0.02 | 0.001 | 0.001 | 0.003 | 0.003 | | 0.003 |
| RFW I | 0.0252 | 0.0625 | 0.0001 | 0.0168 | 0.0096 | 0.0016 | - | 0.1480 |
| RFW II | 0.0029 | 0.0060 | - | 0.0145 | 0.0018 | 0.0210 | - | 0.0799 |
| RFW III | 0.0117 | 0.0249 | - | 0.0210 | 0.0033 | 0.0030 | - | 0.9548 |
| RFW IV | 0.0047 | 0.0258 | - | 0.0140 | 0.0142 | 0.0110 | - | 0.0422 |
| RFW V | 0.0020 | 0.0266 | - | 0.0171 | 0.0137 | 0.0010 | - | 0.0781 |
| Mean ±SD | 0.0093 ±0.0096 | 0.02916± 0.021 | 0.0001±0.0001 | 0.01668± 0.0027 | 0.00852±0.0057 | 0.00752±0.0085 | - | 0.2606±0.389 |
| S. Error | 0.004 | 0.009 | 0.001 | 0.001 | 0.03 | 0.004 | | 0.17 |
| RIYOM (CONTROL) | 0.0100 | 0.0026 | 0.0000 | 0.0266 | 0.0000 | 0.0005 | - | 0.0028 |
| NESREA Standard, 2011 | 0.01 | 0.2 | 0.001 | 1.0 | 0.1 | 0.01 | 0.0013 | 3.0 |
| <i>p-value 0.05</i> | 0.008 | 0.367 | 0.076 | 0.019 | 0.107 | 0.061 | - | 0.280 |
| <i>T test</i> | | | | | | | | |

Source: Field-work, 2019

Table 3: Concentration of heavy metals in water in Bukuru, (BSK), Rayfield (RFS) and the Control Point in Riyom in the dry season.

| Samples | Cd(mg/l) | Mn(mg/l) | Hg(mg/l) | Cu(mg/l) | Ni(mg/l) | Pb(mg/l) | Ur(mg/l) | Zn(mg/l) |
|-------------------------|----------------------|----------------------|-----------------------|----------------------|-----------------------|------------------------|----------|-----------------------|
| BKW I | 0.0001 | 0.0714 | 0.0001 | 0.4761 | 0.0001 | 0.0100 | - | 0.0710 |
| BKW II | 0.0444 | 0.0412 | 0.0010 | 0.0280 | 0.0111 | 0.0026 | - | 0.1446 |
| BKW III | 0.0578 | 0.0614 | 0.0000 | 0.0317 | 0.0216 | 0.0112 | - | 1.0470 |
| BKW IV | 0.0628 | 0.0580 | 0.0001 | 0.0416 | 0.0024 | 0.0056 | - | 0.4776 |
| BKW V | 0.0388 | 0.0644 | 0.0001 | 0.0167 | 0.0160 | 0.0047 | - | 0.0482 |
| Mean ±SD | 0.04078±0.024 | 0.05928±0.011 | 0.00026±0.0004 | 0.11882±0.199 | 0.01024± 0.009 | 0.00682± 0.0036 | - | 0.35768±0.4222 |
| S. Error | 0.011 | 0.005 | 0.0001 | 0.089 | 0.004 | 0.002 | - | 0.188 |
| RFW I | 0.0001 | 0.0076 | 0.0013 | 0.0373 | 0.0040 | 0.0360 | - | 0.4301 |
| RFW II | 0.0678 | 0.0300 | 0.0020 | 0.2117 | 0.0282 | 0.0023 | - | 0.1917 |
| RFW III | 0.0400 | 0.0412 | 0.0041 | 0.2781 | 0.0280 | 0.0410 | - | 0.2011 |
| RFW IV | 0.0056 | 0.0389 | 0.0016 | 0.0978 | 0.0160 | 0.0078 | - | 0.1401 |
| RFW V | 0.0249 | 0.0401 | 0.0013 | 0.0138 | 0.0275 | 0.0044 | - | 0.1437 |
| Mean ±SD | 0.02768±0.027 | 0.03156±0.014 | 0.00206±0.0011 | 0.12774±0.113 | 0.02074± 0.010 | 0.0183±0.018 | - | 0.22134±0.119 |
| S. Error | 0.012 | 0.006 | 0.001 | 0.051 | 0.05 | 0.008 | - | 0.054 |
| RIYOM (Control) | 0.0099 | 0.0031 | 0.0000 | 0.0026 | 0.0013 | 0.0001 | - | 0.0294 |
| NESREA Standard 2011 | 0.01 | 0.2 | 0.001 | 1.0 | 0.1 | 0.01 | 0.0013 | 3.0 |
| <i>p-value 0.05</i> | 0.130 | 0.007 | 0.006 | 0.465 | 0.002 | 0.046 | - | 0.231 |
| <i>T test</i> | | | | | | | | |

Source: Field work, 2019

Cadmium levels in water for all the sampling points were generally high when compared with the NESREA standard of 0.001 mg/l including the control point except for RFW IV and RFW II. This was closely followed by Mn, Hg, Hi and Pb at some points across the study area, especially during the rainy season. In terms of differences in the concentration levels of individual parameters, between Bukuru and Rayfield for the rainy season, it can be seen that cadmium and copper differed significantly, while manganese, mercury, nickel, lead and zinc did not show significant differences (Table 2). In the dry season, concentration levels of cadmium, manganese, mercury and nickel differed significantly, while copper, lead and zinc concentration levels did not differ between Bukuru and Rayfield (Table 3). On the whole, the level of Cd in water samples was generally high, though slightly higher in the rainy season. Similar observations were reported by Wardhani *et al.*, (2021) in Saguling reservoir, West Java province. The study found an average concentration to be lower in the dry season than in the rainy season with a mean level of $11.12 \pm 2.16 \text{ mg.kg}^{-1}$ in the dry season, compared to an average value of $14.82 \pm 1.48 \text{ mg.kg}^{-1}$ in the rainy season. In another study, Chiba *et al.* (2011) observed an increase in levels of Zn, Cd, Fe and Mn in a sub-basin of São Carlos-SP, Southeast Brazil, during the rainy season, and attributed it to runoff from nearest agricultural land and diffuse pollution. Heavy metal levels in rivers are largely influenced in the wet season by storm water run-off from the surroundings on the river catchment and this usually leads to an increase in heavy metal concentration (Edokpayi *et al.*, 2017). Järup, (2003) also linked high contamination by cadmium, lead, copper and nickel during the rainy season and attributed it to the disposal of batteries in landfills located nearby bodies of water. According to the author, these metals are considered "industrial metals", as they are found in low concentrations in nature, but

used extensively in industrial processes. In the rainy season, there is high leaching of the surrounding bodies of water, which causes the carrying of large quantities of particles and pollutants into rivers and streams. Rietzler *et al.* (2001) related the elevated concentrations of metals recorded during the wet season to the landfill dump of the city and rain drainage.

On the average however, the dry season concentrations of heavy metals with the exception of Zn and Cu were higher than levels observed in the rainy season as well as exceeded both control limits and NESREA standard, in particular Mn, Hg and Pb (Fig 2). In a similar study, Islam *et al.* (2015), reported that heavy metals are expected to be low during wet season due to dilution effects of rainfall on heavy metal, but some site-specific activities and sources of metal contamination could lead to the exception to this general rule. According to Edokpayi *et al.*, (2016), there is a higher concentration of heavy metals in the dry season due to reduced water volume and flow and increased evaporation from water bodies. In another study carried out in Awash River, Ethiopia, Eliku and Leta (2017) found that mean concentrations of metals ranked (high to low): Fe>Cr>Cu>Zn>Pb>Cd>Ni during the dry season, whereas the concentration of heavy metals during the wet season was in the following order of decreasing magnitude Fe>Cu>Zn>Pb>Cr>Cd> Ni. The study attributed this pattern to a more gentle flow of the river during the dry season as well as the reduction in the volume of streamflow during the dry season, which makes the dissolved metals to be at higher concentration levels in the liquid phase. In Nigeria, Raji *et al.*, (2016) also found that heavy metal concentrations in Sokoto River were generally higher in the dry season than levels observed in the rainy season, and attributed the pattern to increased human activities during the dry season. Other studies which correlate with the observed pattern in the study area include the works of

Yao *et al.*, (2014) on seasonal and spatial variations of heavy metals in two typical Chinese Rivers, Concentrations, environmental risks, and possible sources, and Obasohan (2008) on the use of heavy metals load as an indicator of the suitability of the water and fish of Ibiekuma stream, in Ekpoma, Edo State, Nigeria, for domestic and consumption purposes.

For most sampling points, Mn levels in water samples were low for both locations when compared with the NESREA standard of 0.2 mg/l. Mn most points in Bukuru and Rayfield in the rainy season was low in contrast to the dry season. Mercury was low in all the sampling points in Bukuru and Rayfield water and the control when compared with the NESREA standard of 0.001 mg/l. The concentration of Hg in water samples was both low in the dry and rainy seasons (Table

2 &3). Cu level in water samples for all the sampling points in Bukuru, Rayfield and the control was low compared to the NESREA standard of 1.0 mg/l. Cu is an essential macronutrient that helps in the production of blood haemoglobin but in high concentration, it can cause anaemia, liver and kidney damage, stomach and intestinal irritation (Garba *et al.*, 2012). The concentration of Ni was low in all the sampling points when compared with the NESREA standard of 0.1 mg/l although slightly higher in the dry than level the rainy seasons. The concentration of Ur in water samples was also very low in all the sampling points when compared with the NESREA standard 0.0013 mg/l, irrespective of the season. Similarly, the Zn level in water samples is low in all the sampling points when compared with the NESREA standard 3.0 mg/l. The concentration of Zn was also both low in dry and rainy seasons.

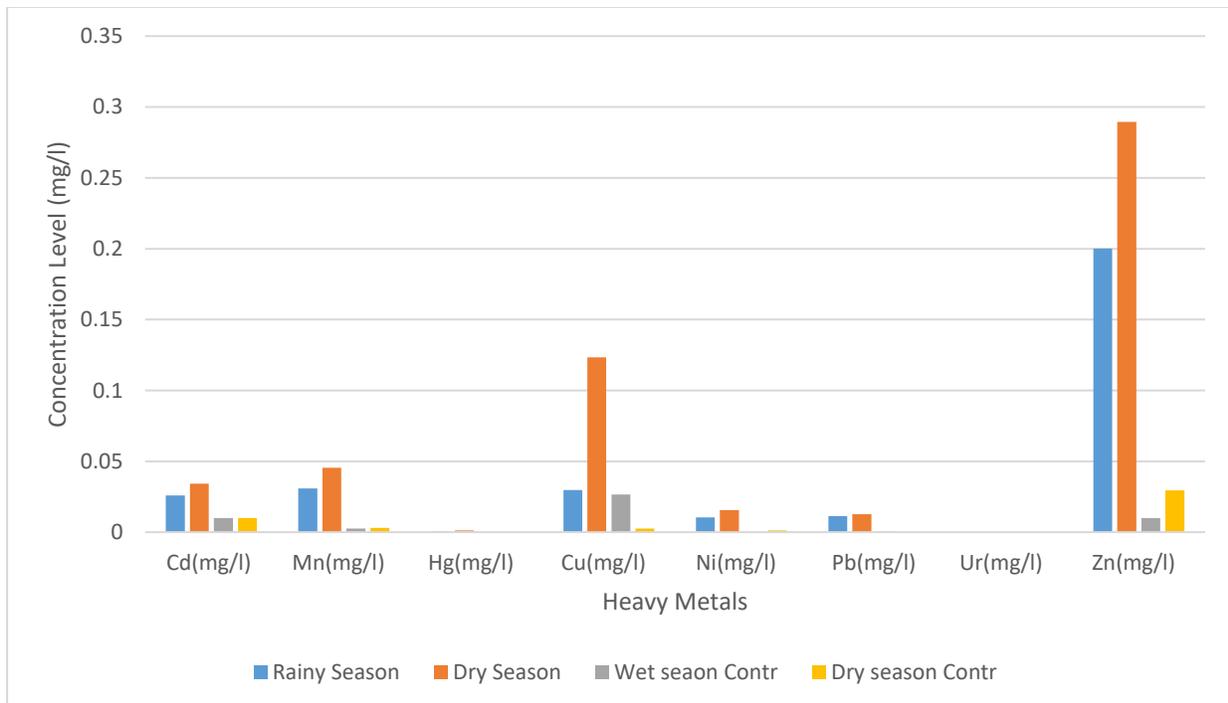


Fig. 2 Mean distribution of Heavy metals in water for rainy and dry seasons

Table 4: Concentration of heavy metals in soil in Bukuru (BSK), Rayfield (RFS) and the Control Point in Riyom in the rainy season.

| Samples | Cd(mg/l) | Mn(mg/l) | Hg(mg/l) | Cu(mg/l) | Ni(mg/l) | Pb(mg/l) | Ur(mg/l) | Zn(mg/l) |
|-------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| BKS I | 0.0916 | 0.8170 | 0.0610 | 1.6881 | 0.1426 | 0.0631 | 0.25 | 1.8760 |
| BKS II | 0.1236 | 1.7110 | 0.0173 | 2.0421 | 0.0857 | 0.0760 | 1.60 | 2.0111 |
| BKS III | 0.2160 | 1.4666 | 0.0167 | 1.8160 | 0.7000 | 0.0598 | 1.07 | 1.5023 |
| BKS IV | 0.1211 | 1.0310 | 0.0212 | 2.1134 | 1.3150 | 0.1636 | 0.45 | 2.251 |
| BKS V | 0.0819 | 0.9560 | 0.0130 | 1.5667 | 1.0244 | 0.1660 | 1.22 | 1.4284 |
| Mean ±SD | 0.12684±0.053 | 1.19632±0.376 | 0.02584±0.019 | 1.84526±0.231 | 0.65354±0.538 | 0.1057±0.054 | 0.918±0.557 | 1.81376±0.346 |
| S. Error | 0.024 | 0.168 | 0.009 | 0.103 | 0.241 | 0.024 | 0.249 | 0.155 |
| RFS I | 0.0395 | 0.4126 | 0.0010 | 1.4881 | 0.4210 | 0.0395 | 0.20 | 1.2061 |
| RFS II | 0.0038 | 0.2474 | 0.0023 | 0.3202 | 0.2378 | 0.0045 | 0.2947 | 0.3154 |
| RFS III | 0.520 | 1.0341 | 0.0001 | 0.1470 | 0.1470 | 0.0520 | 0.17 | 1.3276 |
| RFS IV | 0.0637 | 0.4719 | 0.0001 | 1.0811 | 1.0265 | 0.0637 | 1.01 | 1.0926 |
| RFS V | 0.0545 | 0.37000 | 0.0017 | 0.7401 | 0.0829 | 0.0545 | 0.40 | 1.1690 |
| Mean ±SD | 0.1363±0.215 | 0.5072±0.305 | 0.00104±0.009 | 0.7553±0.548 | 0.38304±0.382 | 0.04284±0.023 | 0.41494±0.344 | 1.02214±0.404 |
| S. Error | 0.096 | 0.137 | 0.0004 | 0.245 | 0.171 | 0.010 | 0.154 | 0.181 |
| RIYOM (CONTROL) | 0.0017 | 0.0070 | 0.0000 | 0.0040 | 0.0020 | 0.0001 | - | 0.0217 |
| NESREA Standard 2011 | 0.003 | 0.00001 | 0.0001 | 0.0001 | 0.59 | 0.0001 | 0.003 | 3.0 |
| <i>ρ-value 0.05</i> | <i>0.442</i> | <i>0.004</i> | <i>0.009</i> | <i>0.003</i> | <i>0.10</i> | <i>0.007</i> | <i>0.062</i> | <i>0.009</i> |
| <i>T test</i> | | | | | | | | |

Source: Field-work, (2019)

Table 5: Concentration of heavy metals in soil in Bukuru, (BSK), Rayfield (RFS) and the control point in Riyom in the dry season.

| Sample | Cd(mg/l) | Mn(mg/l) | Hg(mg/l) | Cu(mg/l) | Ni(mg/l) | Pb(mg/l) | Ur(mg/l) | Zn(mg/l) |
|-------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|--------------------|----------------------|
| BKS I | 0.0076 | 0.4594 | 0.0001 | 0.1072 | 0.0001 | 0.001 | - | 0.8172 |
| BKS II | 0.0876 | 1.3700 | 0.0120 | 2.1070 | 0.2160 | 0.0548 | 1.01 | 1.8116 |
| BKS III | 0.1026 | 1.4626 | 0.0176 | 2.7140 | 0.2461 | 0.0644 | 2.50 | 2.0781 |
| BKS IV | 0.1416 | 2.0717 | 0.0237 | 3.1701 | 1.1266 | 0.200 | 2.01 | 2.4187 |
| BKS V | 0.0950 | 1.9660 | 0.0237 | 3.1701 | 1.1266 | 0.200 | 2.01 | 2.4187 |
| Mean ±SD | 0.08688±0.048 | 1.46594±0.640 | 0.01542±0.009 | 2.25368±1.276 | 0.54308±0.541 | 0.10404±0.090 | 1.506±1.00 | 1.90886±0.661 |
| S. Error | 0.023 | 0.286 | 0.004 | 0.571 | 0.242 | 0.041 | 0.447 | 0.296 |
| RFS I | 0.0816 | 0.0412 | 0.0015 | 0.1410 | 0.0260 | 0.0777 | 1.3000 | 1.3911 |
| RFS II | 0.0166 | 1.0911 | 0.0101 | 1.4126 | 1.0489 | 0.0199 | 1.3000 | 1.3911 |
| RFS III | 0.0290 | 1.2706 | 0.0120 | 1.71200 | 0.8561 | 0.1025 | 1.0200 | 1.3720 |
| RFS IV | 0.0345 | 1.3131 | 0.0133 | 2.0167 | 1.2933 | 0.0989 | 1.2000 | 1.3750 |
| RFS V | 0.0799 | 1.2866 | 0.0114 | 2.1074 | 1.3166 | 0.1366 | - | 1.3119 |
| Mean ±SD | 0.04832±0.030 | 1.00052±0.543 | 0.00966±0.005 | 1.47794±0.795 | 0.90818±0.528 | 0.08712±0.043 | 0.964±0.551 | 1.36822±0.033 |
| S. Error | 0.014 | 0.243 | 0.002 | 0.355 | 0.236 | 0.019 | 0.246 | 0.015 |
| RIYOM (CONTROL) | 0.0775 | 0.0018 | 0.0001 | 0.0118 | 0.0110 | 0.0200 | - | 0.0674 |
| NESREA Standard 2011 | 0.003 | <01 | <0.0001 | <01 | <0.59 | <01 | <0.003 | 3.0 |
| <i>ρ-value 0.05</i> | <i>0.098</i> | <i>0.002</i> | <i>0.02</i> | <i>0.004</i> | <i>0.016</i> | <i>0.27</i> | <i>0.159</i> | <i>0.041</i> |
| <i>T test</i> | | | | | | | | |

Source: Field-work, (2019)

In Tables 4 & 5, the results of the heavy metal concentration in soil samples in Bukuru and Rayfield are presented. All the heavy metals except for Zn were high in both seasons as well as exceeded levels at control points and NESEA standards. In Table 4, it can be seen that there is no significant difference in concentration levels of cadmium, nickel and uranium between Bukuru, and Rayfield locations, however, manganese, mercury, copper and lead showed significant differences. Similarly, in the dry season, there was a significant difference in the individual concentration levels except for cadmium and uranium (Table 5). On average, the dry season concentrations were higher than levels in the rainy season (Fig. 3). This pattern correlates with the findings of Saeed *et al.*, (2014) which found that the amounts of heavy metals in sediment were highest in the dry season and attribute it to the turbulence created by an increase of flow as a result of which some sediments and heavy metals inside them are displaced and carried away from the river bed. As summer starts, the rise in temperature and evaporation and the end of the rain period cause the rise in heavy metals concentration in water and finally in sediments because metal ions transfer from water to sediment (Saeed *et al.* 2014). Hong *et al.*, (2021) in their study on Seasonal variation and ecological risk assessment of heavy metal in an Estuarine Mangrove Wetland in China, also found that the accumulation of metals was observed to be significantly higher in the dry season. The study found that Cr, Pb and Zn contents were significantly higher ($p < 0.01$) in the dry season than in the wet season. In another study, on the seasonal variation and effect of heavy metal pollution on microbial load of marine sediment, Rivers State Nigeria, Ebah *et al.*, (2016) recorded that the distribution of heavy metals demonstrated a unique seasonal pattern with the highest concentration being in the dry season and lowest during the wet season. The pattern observed for this study is also in agreement with the work of Mohiuddinni *et al.* (2011).

In Nairobi Dam, Kenya, Ndeda *et al.*, (2017) recorded higher concentration $Pb > Cd > Cu > Ni$ during the dry than during the wet season. Copper levels for example was significantly higher in the dry than wet season ($P < 0.001$). The authors attributed this to this is attributed to the concentration of metals on sediments arising from higher temperatures in the dry season. Lead on the other hand was also significantly higher in the dry than wet season ($P \leq 0.018$) and this was due to the settlement of metals concentrated sediments and higher temperatures in the dry season. A similar finding was shown by Kikuchi *et al.* (2009) on a study of characterization of heavy metal pollution in river sediment of Hanoi City and its downstream area. The study revealed concentrations of heavy metals (As, Cr, Cu, Mn, Ni and Zn) in the sediments of the Nhue River were higher in the dry season than in the rainy season. Another study by Mondol *et al.* (2011) on seasonal variation of heavy metals concentrations in water and plant samples around Tejgaon industrial area of Bangladesh showed that in the rainy season the pollution was lower because heavy rainfall was flushed out through the canal into the adjoining vast flood zone. As the rainy season receded the soils and water were enriched with the pollution load (Chamon *et al.*, 2009; Ullah *et al.*, 1999). Apart from reduction in the dilution effects of precipitation, high temperature in the dry season affects heavy metal accumulation in sediment through increased evaporation. Fritioff *et al.* (2005) reported an increase in metal bioaccumulation of zinc, lead, silver, chromium and cadmium except for iron and zinc in the shoots of aquatic plants with increasing temperature.

On location to location basis, Cd in sediment for both rainy and dry seasons was high for all the sampling points. A similar pattern was found for all the sampling points except the control point. The high levels of Cd may be attributed to its association with the bedrock

in the study area. Other sources of discharging Cd into the environment which include the usage of phosphate fertilizers, sewage sludge, industrial effluents from refined petroleum products (Vivian *et al.*, 2012) and household wastes can also say to be low in the study area. This is expected of the study area, as agricultural and residential land use activities are common around the study area. Mn level in sediment was also high in most sampling points in Bukuru except point BSK I. The high level of Mn in sediment may be attributed to the weathering of geological parent materials in the study area. Hg level in sediment was relatively high in all the sampling points in Bukuru and Rayfield soil except the control point when compared with the NESREA standard of 0.0001 mg/l. and this may be due to its release during the mining process since the ponds are abandoned mine sites. The most common natural forms of mercury found in the environment are metallic mercury, mercuric sulphide (cinnabar ore, mercuric chloride, and methyl mercury). Each of them has its profile of toxicity (Bernhoft, 2012). Methyl mercury is of particular concern because it can build up in certain edible freshwater and saltwater fish and marine mammals to levels that are many times greater than levels in the surrounding water. Metallic mercury is a liquid at room temperature, but some of the metal will evaporate into the air and can be carried long distances. In the air, the mercury vapour can be changed into other forms of mercury and can be further transported to water or soil in rain or snow (Bernhoft, 2012). Inorganic mercury may also enter water or soil from the weathering of rocks that contain mercury, from factories or water treatment facilities that release water contaminated with mercury, and from the incineration of municipal garbage that contains mercury (for example, in thermometers, electrical

switches, or batteries that have been thrown away (Lar et al., 2000). The copper level was also high in all the sampling points in Bukuru and Rayfield except Rayfield points II, III, V and the control when compared to the NESREA standard of <1.0 mg/l in the sediment samples. Nickel concentration in sediment was low except in Bukuru points III, IV, V and Rayfield point IV when compared with NESREA standard <0.59 mg/l (Table 4&5). The high concentration of Ni in sediment in these sampling points may be attributed to the nature of the underlying rocks, household wastes, sewage sludge and farm runoff. Ni can be carcinogenic and toxic in high concentrations. The concentration of Pb was low in all the sampling points except Bukuru points IV and V when compared with the NESREA standard of <1.0 mg/l. For most sampling points Pb was also low in both dry and rainy seasons were low. This may be as a result of the non-association of lead to the bedrock in Bukuru and Rayfield and lack of the presence of secondary sources of contaminants. Uranium concentration of Ur was very high in all the sampling points when compared with the NESREA standard of <0.003 mg/l. This shows that the concentration of Ur was high in both the dry and rainy seasons for all the sampled locations. This is in agreement with Adiukwu-Brown *et al* (2001) who reported the radio-active readings of some of the abandoned mines in Jos and environs are very high. Zn level in sediment was low in all the sampling points when compared with the NESREA standard 3.0 mg/l except in the control. The concentrations of Zn were low in both dry and rainy seasons in Bukuru and Rayfield. In Tables, 6 results of student T-test comparison of the mean concentration of heavy metals between soil and water samples, between seasons and locations are presented.

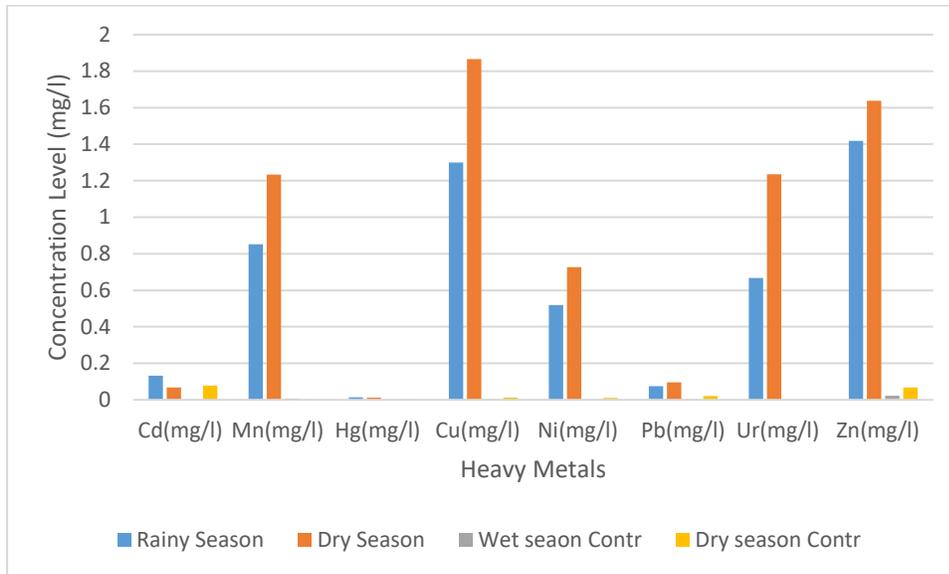


Fig. 3 Mean distribution of Heavy metals in sediment samples for rainy and dry seasons

Table 6: Student T-test comparison of mean in heavy metal levels between seasons, locations and contaminants indicators (water and sediment).

| Student's T-test comparison of mean concentration levels metals between soil and water in both sample locations | | | | | | | | | | |
|--|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------|---------|
| Sample | Cd (mg/l) | Mn (mg/l) | Hg (mg/l) | Cu (mg/l) | Ni (mg/l) | Pb (mg/l) | Ur (mg/l) | Zn (mg/l) | Mean | ρ-value |
| Water | 0.030 | 0.038 | 0.001 | 0.077 | 0.013 | 0.012 | - | 0.245 | 0.0067 | 0.006 |
| Soil | 0.100 | 1.042 | 0.013 | 1.583 | 0.622 | 0.085 | 0.951 | 1.528 | 0.4071 | |
| Student's T-test comparison of mean concentration levels of heavy metals in water samples between the rainy and dry season | | | | | | | | | | |
| Wet season | 0.026 | 0.031 | 0.000 | 0.030 | 0.010 | 0.011 | 0.000 | 0.200 | 0.0386 | 0.052 |
| Dry Season | 0.034 | 0.045 | 0.001 | 0.123 | 0.015 | 0.013 | 0.000 | 0.290 | 0.0065 | |
| Student's T-test comparison of mean concentration levels of heavy metals in soil samples between the rainy and dry season | | | | | | | | | | |
| Wet season | 0.132 | 0.852 | 0.013 | 1.300 | 0.518 | 0.074 | 0.666 | 1.418 | 0.622 | 0.015 |
| Dry Season | 0.068 | 1.233 | 0.013 | 1.866 | 0.726 | 0.096 | 1.235 | 1.639 | 0.859 | |
| Student's T-test comparison of mean levels of heavy metals in water samples between Bukuru and Rayfield | | | | | | | | | | |
| Bukuru pond | 0.042 | 0.046 | 0.001 | 0.081 | 0.011 | 0.011 | 0.000 | 0.249 | 0.055 | 0.053 |
| Rayfield pond | 0.018 | 0.030 | 0.001 | 0.072 | 0.015 | 0.013 | 0.000 | 0.241 | 0.049 | |
| Student's T-test comparison of mean levels of heavy metals in soil samples between Bukuru and Rayfield | | | | | | | | | | |
| Bukuru pond | 0.107 | 1.331 | 0.021 | 2.049 | 0.598 | 0.105 | 1.212 | 1.861 | 0.911 | 0.019 |
| Rayfield pond | 0.092 | 0.754 | 0.005 | 1.117 | 0.646 | 0.065 | 0.689 | 1.195 | 0.570 | |

Source: Fieldwork, 2019. Student's T-test tested at 0.05 statistical threshold

From table 6, there is a significant difference in the mean concentration of all heavy metals between soil and water samples in unreclaimed mining ponds of Bukuru and Rayfield irrespective of the season. On the

whole, mean levels of all the heavy metals were higher in the dry season when compared to the rainy season in sediment samples, while concentration levels in water samples did not show evidence of significant

differences. This is expected as the man-made pond retains water through the year though with little variation in reservoir volume within the year. The high concentrations of these heavy metals in the dry season may be attributed to the reduction in the dilution effect of rainfall. The mean concentration of cadmium (0.0676 mg/l) in the dry season was lower than the level observed in the rainy season (0.13157 mg/l). This may be attributed to other sources of pollution in the rainy season such as agricultural and industrial influents (Vivian *et al*, 2012). The statistically significant difference was not established in mean heavy metals levels in the water samples between Bukuru and Rayfield unreclaimed mining sites. However, variation

was observed for concentration levels in soils between the two locations.

In Tables 7 &8, the mean values of each of the heavy metals compared to the WHO/NESREA standard are presented. The mean values of the concentrations of each of the heavy metals were all low when compared with the WHO (2011)/NESREA standard except for Cadmium (Table 7). The high concentration of Cadmium in the soil and water samples above permissible limits may be attributed to its association with the bedrock in Bukuru and Rayfield and other sources of pollution such as agricultural and industrial effluents.

Table 7: Comparison of Observed Values of Levels of heavy metals in soil with WHO and NESREA Standards (One sample t-test)

| Parameters | Mean (mg/l) | WHO (mg/l) | NESREA (mg/l) |
|------------|-------------|------------|---------------|
| Cadmium | 0.099585 | 0.003 | 0.003 |
| Manganese | 0.999503 | 3 | 0.0001 |
| Mercury | 0.034323 | 0.05 | 0.0001 |
| Copper | 1.54498 | 2 | 0.0001 |
| Nickel | 0.621955 | 0.7 | 0.059 |
| Lead | 0.113855 | 0.4 | 0.0001 |
| Uranium | 0.950735 | 0.07 | 0.003 |
| Zinc | 1.478245 | 3 | 3 |

There is no significant difference in concentration levels between the observed mean values and NESREA standard ($p > 0.05$, $d = 0.209$)

Table 8: Comparison of Observed Values of Levels of the heavy metals in water with WHO and NESREA Standards (One sample t-test)

| Parameters | Mean (mg/l) | WHO (mg/l) | NESREA (mg/l) |
|------------|-------------|------------|---------------|
| Cadmium | 0.030025 | 0.003 | 0.001 |
| Manganese | 0.038085 | 0.04 | 0.2 |
| Mercury | 0.00081 | 0.05 | 0.001 |
| Copper | 0.076525 | 2 | 1 |
| Nickel | 0.01294 | 0.07 | 0.1 |
| Lead | 0.013105 | 0.01 | 0.01 |
| Uranium | 0.00097 | 0.0001 | 0.0013 |
| Zinc | 0.23789 | 3 | 3 |

There is no significant difference in concentration levels between the observed mean values and NESREA standard ($p > 0.05$, $d = 0.0999$)

Cadmium in high concentration is extremely toxic and carcinogenic (Butu *et al.*, 2019). Cadmium has no biological functions to humans, it has been linked to several health problems including renal tubular dysfunction, pulmonary emphysema and possibly Osteomalacia, a situation where the calcium in the bones is replaced by Cd in humans which results in cancer of the bones (Jarup and Jarup, 2003). Target organs include the liver, placenta, kidneys, lungs, brain and bones (Reilly, 2002). More so, the consumption of water with a high concentration of Cd can cause adverse health effects to end users especially since Cd is toxic to fish and other aquatic organisms. Cadmium is considered no-essential for living organisms and long term exposures to Cadmium also induce renal damage, cancer and increased blood pressure (Chaitali and Jayashree, 2013). The known fatal effects of heavy metal toxicity in drinking water include damaged or reduced mental and central nervous function and lower energy levels. They also cause irregularity in blood composition, badly affect vital organs such as kidneys and liver (Sher, *et al.*, 2011).

Mercury can enter and accumulate in the food chain and eventually be ingested by humans. Symptoms of mercury poisoning include permanent damage to the brain and kidneys, personality changes (irritability, shyness, and nervousness), tremors, changes in vision, deafness, muscle coordination, loss of sensation, and difficulties with memory (Garnier, 1981; Berlin *et al.*, 2007). In addition to the brain damage, metallic mercury is also deposited in the thyroid (Guzzi *et al.* 2006; Berlin *et al.*, 2007; breast (Crespo-Lopez *et al.*, 2009), myocardium (Frustaci *et al.*, 1999), muscles (Berlin *et al.*, 2007), adrenals (Berlin *et al.*, 2007), liver (Hahn *et al.*, 1989), kidneys (WHO, 1991), and prostate (Berlin *et al.*, 2007) and may be associated with dysfunction of those organs (Bernhoft, 2012).

When level Ni is high, it can be carcinogenic and toxic in high concentrations. The concentration of Pb in water samples was low for both low in dry and rainy seasons and all the sampling points when compared with the NESREA standard of 0.01 mg/l. Lead is a well-known neurotoxin. Impairment of neuro development in children is the most critical effect and the presence of Pb poses a high health risk of Pb poisoning as the element is known to be toxic even at low levels (Mwegoha and Kihampa, 2010). Other effects of Pb poisoning include deficiency in cognitive function due to destruction of the central nervous system, abdominal pain and discomfort, formation of weak bones as Pb replaces calcium and causes anaemia due to reduction of enzymes concerned with the synthesis of red blood cells (Lars, 2003). According to Rahman *et al.*, (2012). Prolonged exposure to Pb has been linked to mental retardation, coma and eventual death.

Ingestion of Cu and Zn have been reported to cause kidney problems such as nephritis and anuria (Rahman *et al.*, 2012; Adams *et al.*, 2014). Elevated levels on the other hand are known to cause sub-lethal effects (Nussey *et al.*, 2000). Other known health-related effects of Ni are skin allergies, lung fibrosis, variable degrees of kidney and cardiovascular system poisoning and stimulation of neoplastic transformation. Nickel sulphide fume and dust are believed to be carcinogenic, and various other Ni compounds may be as well (Kasprzak *et al.*, 2003). Since the water in unreclaimed mining ponds in Bukuru and Rayfield are used for fish farming, irrigating and domestic purposes, it is of great concern that Cd is in high a concentration because it is extremely toxic and carcinogenic.

CONCLUSION AND RECOMMENDATION

This present study found high levels of cadmium concentration in both water and soil samples for above permissible limits. There

is a significant difference in heavy metal levels between water and sediment samples. In terms of spatial significant difference in concentration levels, there was no significant difference in concentration levels in water samples between Bukuru and Rayfield sites. However, variation was observed for concentration levels in soils between the two locations. The concentration of heavy metals during the dry season was higher than the wet season in soil samples, although this variation was not statistically significant in water samples. In sediment, Mn, Hg Cu were very high and above permissible limits, especially in the dry season. Although most of the concentrations were within permissible limits in water, the intensive agricultural and residential land use activities around the study area make the area susceptible to further pollution. Since these unreclaimed mined-out sites are currently been used for fish farming and irrigation agriculture, there is a need to carry out further study on fish and vegetables harvested from these ponds to ascertain their bioaccumulation levels

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