ASSESSMENT OF HEAVY METAL LEVELS IN JUJI RIVER WATER AND CATCHMENT SOIL IN KADUNA CITY, NIGERIA

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Accepted:20/05/2016
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Abstract
The levels of cadmium (Cd), copper (Cu), lead (Pb), and chromium (Cr) in water from Juji River and its catchment soil (a valley popularly known for vegetable farming) in Kaduna City, Nigeria, were assessed. Water and soil samples were collected from four different points at two depths (0 – 15 cm; 15 – 30 cm), analyzed for routine attributes and metal concentrations using standard operating procedure. The results indicated that the ranges of metal concentrations in water (mg/L) were: Cr (213±0.867 to 0.098±0.001), Pb (0.092±0.023 to 0.101±0.064), Cu (0.015±0.007 to 0.013±0.005) mg/L. The concentration of Cd at all sampling points was below detection limit of 0.01 mg/L; while that of Pb exceeded the drinking water limit of 0.01 mg/L. Soil analysis indicated that metal concentrations (mg/kg) were highest at the top soil and decreased with depth. Pb had the highest concentration of (20.65±1.201); which did not exceed the maximum limit of 200 mg/kg for soils. Cr had maximum and minimum concentrations of (401.13±120.90) and (174.50±143.27) mg/kg, respectively, with most of samples exceeding the permissible limit of 200 mg/kg. The maximum and minimum concentrations of Cu were (19.056±2.881) and (4.514±1.712) mg/kg, respectively, lower than the permissible limit of 100 mg/kg. Cd concentrations at all sampling points were lower than the permissible concentration of 100 mg/kg in soils. The presence of heavy metals in the sampled soil and water portends their transfer to the food chain, especially as crop and vegetable cultivation in these valleys.

Keywords: Heavy metal, soil, water, Juji River, vegetable farming

Introduction
Pollution of the biosphere by toxic metals has accelerated severely since the beginning of the industrial revolution [1]. The primary sources of metal pollution include the burning of fossils fuels, mining and smelting of metal ores, municipal wastes, fertilizers, pesticides, and waste water irrigation. Contamination of groundwater and soil by heavy metals leads to major environmental and human health problems. Plant metabolism is also affected negatively by the heavy metals [2]. Although some of the heavy metals act as micronutrient at lower concentration, but at higher concentration these are harmful for the normal functioning of plants [2, 3]. Metals cannot be degraded to harmless products, such as carbon dioxide, but instead persist indefinitely in the environment, complicating their remediation. Occurrence of oxidative stress in plants could be the indirect consequence of heavy metal toxicity. [3,4]. Molecular oxygen can accumulate in the leaves of plants under heavy metal stress, as trace elements, some heavy metals e.g. copper, selenium and zinc are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning [5]. Prolonged exposure to heavy metals such as cadmium, copper, lead, nickel and zinc can cause deleterious health effects in humans [6]. Metal contamination of garden soils may be widespread in urban areas due to past industrial activity and the use of fossil fuels [7].

In Nigeria and particularly in Kaduna city, urban agriculture has been a normal practice along various river banks. These river/streams have been observed to be highly polluted by toxic chemicals from industries, car wash, mechanic workshops and farmlands which discharge untreated wastewater into receiving waters along the Juji River valley. The level of heavy metal pollution in soils and water in vegetable farms using irrigation water from the river is not adequately documented [8, 9, and 10]. This study is, therefore, aimed at determining the extent of heavy metal pollution in agricultural soils and water along river Juji and its valleys.

Materials and Methods
Description of the study area
This study was conducted along River Juji in Kaduna south northwest Nigeria located on Latitude 11°06′N and longitude 7° 18′E. The river receives tributaries that are loaded with effluent discharges from the Nigeria National Petroleum Corporation, several occupations in...
the area of car wash, steel welding, paints, abattoir, and electrical products respectively. 8, 11.

Sampling
A total of 4 water samples were collected from four (4) sampling points (Table 1) between July and September, 2014. These points are Juji behind Nigeria National Petroleum Corporation (SP-1), Sabo Tasha (SP-2), Ungwan-sauri (SP-3) and Karatudu (SP-4).

Table 1: Sampling protocol along Juji River in Kaduna city, Nigeria

<table>
<thead>
<tr>
<th>Sampling point/ location</th>
<th>Names of area</th>
<th>Sample collected</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Juji village</td>
<td>Soil and water</td>
</tr>
<tr>
<td>2</td>
<td>Sabo-tasha</td>
<td>Soil and water</td>
</tr>
<tr>
<td>3</td>
<td>Angwa-saure</td>
<td>Soil and water</td>
</tr>
<tr>
<td>4</td>
<td>Karatudu</td>
<td>Soil and water</td>
</tr>
</tbody>
</table>

Collection of water samples
Water samples were collected using 500 mL plastic bottles at a depth of 150cm. The sampling bottles for heavy metal determination were pre-soaked overnight with 10% HCl and rinsed with distilled water and rinsed using river water before sample collection. Sampling bottles for the determination of physicochemical parameters were cleaned and rinsed using distilled water only [12]. Preservation of water samples was done by adding 2 drops of concentrated HNO3 to each water sample before storage below 4°C until analyzed.

Collection of soil samples
A total of 8 soil samples were collected at depths of surface (0-15 cm) and sub surface (15-30 cm) from four sites, stored in plastic bags and transported to the laboratory for heavy metal extraction and analysis.

Soil sample preparation for heavy metal analysis
The soil samples were oven dried at 105°C for 24 hour, followed by grinding and sieving using 0.18 mm sieve. A 0.5 g of dry soil sample was poured into a graduated test tube and mixed with 2 mL of aqua regia 1:3 (1 conc. HCl; 3 conc. HNO3). The mixture was digested on a hot plate at 95 °C for 1 hour and allowed to cool to room temperature. The sample was then diluted to 10 ml using distilled water and left to settle overnight. The supernatant was filtered prior to analysis using AAS [6, 13].

Heavy metal analysis
Analysis of heavy metals in soil and water samples was done using Perking Elmer Analyst 100 Atomic Absorption Spectrophotometer equipped with Perking Elmer HGA 850 Graphite Furnace and Perking Elmer AS 800 Auto sampler with a computer interface for operation and readings display, Varian Spectra AAS with SpectrAA 55.

Quality control and statistical treatment of data
The data under different amendments were subjected to ANOVA test for assessing the significance of differences in heavy metal concentrations in agricultural soil and water. Furthermore, all the statistical tests were performed using SPSS software (SPSS Ins., version 12) [13]. Whereas precision and accuracy of analysis was assured through repeated analysis of samples against National Institute of water resources Kaduna, Nigeria Standard Reference Material (SRM 1410) for all the heavy metals. The results were found within ± 2 % of the certified value [8, 14] Quality control measures were taken to assess contamination and reliability of data. Blank and drift standards (Kaduna Environmental Protection Authority) were run after five determinations to calibrate the instrument. The coefficients of variation of replicate analysis were determined for different determinations for precision of analysis and variations were found to be less than 10 %.

Results and Discussion
Heavy metal concentrations in Juji River water
Result in Table 2 shows concentrations of heavy metals in water from various sampling locations. The highest concentration of Chromium (1.213±0.867) mg/L was detected at sampling point SP-1 Juji. As stated earlier, this point of the river receives effluent streams that are loaded with pollutants from the Nigerian National Petroleum Corporations, motor works and mechanic workshops which are known to contain chromium. The lowest concentration of (0.098±0.001) was detected at sampling point SP-4 located at Karatudu area, which receives streams from the Angwa-tanko abattoir and the old dump site with no known source of Cr contamination.

There was no substantial difference in the concentration of copper at various sampling points, ranging from (0.013±0.005) mg/L to (0.019±0.008) mg/L detected at sampling points SP-1 and SP-4. The concentration of lead in water throughout the river exceeded the specified level set by [15], drinking water limit of 0.01mg/L. The highest concentration of (0.101±0.064) mg/L was detected at sampling SP-4 where Drainages from abattoir and runoff from mechanical and motor workshops flows into the river at Karatudu River and the lowest concentration of (0.085±0.094) mg/L at sampling location SP-2.

Maximum concentrations of lead may be attributed to the inflowing channel from Angwa-saure which consists of various wastes from industrial and domestic effluents, including automobile garages and car wash, which discharge mixtures of oil and car washing into the stream leading to Juji River. Such activities may contribute much to lead contamination into Juji River. Cadmium concentration was below detection limit of 0.01 mg/L as indicated in Table 2. However, failure of
the AAS machine to detect Cadmium in water samples does not mean that it is meeting the recommended drinking water standard of 0.003 mg/L [11,16].

Table 2 Heavy metal concentration in Juji River water samples

<table>
<thead>
<tr>
<th>Sampling point</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP-1</td>
<td>bdl</td>
<td>1.213±0.867</td>
<td>0.015±0.007</td>
<td>0.092±0.023</td>
</tr>
<tr>
<td>SP-2</td>
<td>bdl</td>
<td>1.056±0.734</td>
<td>0.019±0.008</td>
<td>0.085±0.094</td>
</tr>
<tr>
<td>SP-3</td>
<td>bdl</td>
<td>0.654±0.845</td>
<td>0.017±0.005</td>
<td>0.094±0.092</td>
</tr>
<tr>
<td>SP-4</td>
<td>bdl</td>
<td>0.098±0.001</td>
<td>0.013±0.005</td>
<td>0.101±0.064</td>
</tr>
</tbody>
</table>

95% Confidence limit: (n=4), SP-1: Juji, SP-2: Sabo Tasha, SP-3: Angwa Saure, SP-4: Karatudu, SD: Standard deviation, bdl: below detection limit

Table 3 Heavy metal concentrations in catchment area soils of Juji River

<table>
<thead>
<tr>
<th>Sample Location</th>
<th>depth (cm)</th>
<th>Pb</th>
<th>Cr</th>
<th>Cu</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP-1</td>
<td>0-15</td>
<td>20.7±1.2</td>
<td>401.1±120.9</td>
<td>19.1±2.9</td>
<td>0.5±0.1</td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>14.6±4.2</td>
<td>330.8±132.8</td>
<td>12.4±2.5</td>
<td>0.3±0.1</td>
</tr>
<tr>
<td>SP-2</td>
<td>0-15</td>
<td>14.5±0.7</td>
<td>338.8±54.1</td>
<td>13.3±5.0</td>
<td>0.3±0.1</td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>11.5±2.2</td>
<td>198.3±19.6</td>
<td>10.3±6.0</td>
<td>0.2±0.0</td>
</tr>
<tr>
<td>SP-3</td>
<td>0-15</td>
<td>14.3±0.7</td>
<td>312.1±27.1</td>
<td>17.3±3.1</td>
<td>0.4±0.3</td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>17.7±0.9</td>
<td>205.8±112.0</td>
<td>12.8±3.0</td>
<td>0.4±0.3</td>
</tr>
<tr>
<td>SP-4</td>
<td>0-15</td>
<td>9.6±1.1</td>
<td>213.9±215.5</td>
<td>10.243±5.0</td>
<td>0.2±0.2</td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>12.9±0.9</td>
<td>174.5±143.3</td>
<td>4.5±1.7</td>
<td>0.16±0.1</td>
</tr>
</tbody>
</table>

95% CL: S1: Juji; S2: Sabo Tasha; S3: Angwa Saure; S4: Karatudu; SD: Standard deviation, dw: dry weight, n: sampling frequency, CL: Confidence interval.

Results indicate that for each sampling location, the concentrations are highest at the top soil and decreased with depth. The highest concentration of lead (20.65±1.201) mg/kg was obtained at sampling location SP-1 and a minimum of (9.623±1.086) mg/kg at sampling point SP-4. The highest concentration of lead at sampling point SP-1 may be attributed to the contribution of drainage from the NNPC effluent discharge and polluted channel from the Juji garage which utilizes river water for car washing and discharging effluents containing oil into the river. At this point there are also solid wastes dumped into the river which are likely to contain toxic materials including heavy metals. Nevertheless, concentrations of lead in soil at all sampling locations did not exceed the maximum limit of 200 mg/kg for soils, although may still pose risks to human being as well as the environment. The highest concentration of chromium (401.13±120.90) mg/kg for chromium was obtained at sampling point SP-1 and the lowest concentration was (174.505±143.27) mg/kg at sampling point SP-4, with most of samples exceeding the [18, 19] limit of 200 mg/kg. Higher concentrations of chromium at sampling point SP-1 may be contributed by Juji stream that receives effluent from the NNPC. Has reported massive heavy metal pollution. [20]. The maximum concentration of copper of (19.056±2.881) mg/kg was obtained at sampling location SP-1. This location features plumbing works and manufacture of electroplating materials. The lowest concentration of copper was (4.514±1.712) mg/kg at sampling location SP-4. Cadmium concentrations were consistently low at all sampling locations as compared to the rest heavy metals and lower than the recommended concentration of 100 mg/kg in soils [21]. The maximum concentration of cadmium was obtained at sampling location SP-1 with (0.543±0.123) mg/kg at a depth of 0-15 cm and minimum concentration at SP-4 with (0.155±0.143) mg/kg. Therefore, at low level, these heavy metals pose no significant threat to humans but at high level of contaminations, hence affect human metabolism and as such produced progressive toxicity which may leads to health disorder.
Conclusion
From the results obtained, water samples showed that the concentration of heavy metals in water and soil from the majority of sampling locations exceeded permissible limits for drinking water and soils, respectively. Variations in heavy metal concentrations in water and soil are a consequence of a wide range of human activities in the river valley. Much precaution has to be taken especially on the use of water from Juji River as may pose risks to the users. Juji River is mainly used as a major source water for wet and dry season farming, vegetable irrigation. Investigation on the implication of these high concentrations of heavy metals in water and soil on uptake by irrigated vegetables be highly needed.

Acknowledgement
Authors are thankful to the Kaduna Environmental Protection Authority for providing some facilities for this analysis.

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