Pollution indices and health risk assessment of heavy metals in floodplain of urban catchment of Asa drainage systems, southwestern Nigeria

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Abstract. Urbanization and industrialization have significantly caused deterioration of surface waters. Since there is close association between river quality and its associated floodplain, the later could therefore provide a quality index of the former. This study examines heavy metal concentrations in floodplain sediment of urban catchment of Asa River and assessed associated risks. Samples were collected at 10 points but at interval of 5cm in vertical profile to a depth of 15cm. Atomic Absorption Spectrophotometer (AAS) analyses were done for Pb, Ni, Zn, Fe, Cu and Al. The following computational models were employed for risk analysis; Depth Ratio (DR), Contamination Factor (CF), Degree of Contamination (Cdeg), Geoaccumulation Index (Igeo), Pollution Load Index (PLI), Hazard Quotient (HQ), Hazard Index (HI) and Cancer Risk Index (CRI). Considerable degree of metal contamination was observed with various pollution levels from non-pollution with Ni, through moderate pollution with Pb, to a moderately strong pollution with Zn, Fe, Cu and Al. PLI revealed a baseline pollution level (PL ≈ 1) but contamination factor for each of Zn, Fe and Cu was considerable and may pose ecological threats and by extension, human health. Metal association reveals a positive correlation among all the metals evaluated (p < 0.05) which is suggestive of similar source. HQ via ingestion and dermal routes calculated were > 1 for both children and adult but < 1 via inhalation. CRI for lead shows that children are predisposed to cancer risks than adults. Hence, industrial activities in the urban catchment of Asa River must be monitored for environmental compliance.

Keywords: Asa Drainage Systems; Floodplain ; Sediment ; Heavy metals; Pollution; Health Risk

1. Introduction

Urbanization and industrialization undoubtedly play significant role in human and economic development, but these have not been without their attendant pollution impacts which largely result into the degradation of air, water and the general natural environment [1]. Water environment have continued to be of tremendous importance to man, they house living organisms that are food for man, their non-living resources and other aesthetic values are increasingly sort after by man. These environments are however threatened by various human activities [2]. Industry, large-scale agriculture, mining and run-offs from residential areas are major sources of pollution in surface waters and floodplain sediment, especially rivers that flow within the urban regiment [3].
Floodplain have long been known to be a repository of different pollutants including heavy metals, they retain overtime the suspended sediments and particles that had adsorbed heavy metals, which are transported by erosion from various sources and afterwards redistribute the pollutants into the nearby water bodies [4]. Heavy metals are important determining factor of health conditions of living organisms and humans because, once introduced to the natural environment, they undergo biological accumulation. Heavy metals pollution is a critical environmental issue in riverine systems of many developing countries like Nigeria. Rivers are perceived as best disposal means for liquid and solid wastes of domestic and industrial sources [5] even when the input wastes is beyond the natural self-purifying capacity of the rivers.

Asa River is the major river in Ilorin – the capital city of Kwara; it is of industrial, environmental, agricultural, economic and socio-cultural importance to the people of Ilorin and its environs. The study was carried out within the urban catchment of Asa River in Ilorin, Kwara State, North Central Nigeria (8°28’N, 4°38’E to 8°31’N, 4°40’E). The sampling area houses the major industries in the state. Sampling was done throughout the urban catchment of the river; Asa Dam (southern end) at the very upstream down north through Osere, OdoOkun, Saw Mill, Flamingo Stadium, Ejiba, Unity to New Yidi. The river and its floodplains have variously been reported of gross metal pollution due to discharge of complex mixtures of industrial effluents as well as domestic wastes [6, 7]. Amongst the industries located around the Asa River are Global Soap and Detergent Ltd, Unifoam Ltd, Nigeria Bottling Company Ltd and Tuyil Pharmaceuticals. The quality of the water, sediments and soil samples of this river determines utilization possibilities, so it is especially important to assess the level of the contaminants. This study thus examines the concentration of heavy metals in the floodplain sediment of the urban catchment of the Asa River.

2. Materials and Methods

2.1 Pedological Analysis

Floodplain sediment samples were collected in polythene bags at ten (10) different sampling points (P1, P2,P3, ..., P10) of the urban catchment of Asa River, at every 5cm in the vertical profile from the top sediment to a depth of 15cm (i.e. 0cm, 10cm and 15cm designated A1, A2 and A3 respectively). Collection was done in April just at the onset of raining season. In the laboratory, samples were homogenized and spread on a flat platform for 4 weeks to ensure proper air drying until uniform weight is achieved. Samples were sequentially sieved with different mesh sizes until the clay fraction (<63µm) was obtained. The choice of clay fraction is due to their non-participation in cation exchange processes due to their negative charge, and thus serves as a good metal accumulator. Acid digestion was done by adding to the clay fraction, freshly prepared mixture of HNO3/HCl (3:1) to each sample portion, stirred and covered to allow the initial effervescence to subside. Then, the reaction mixture was heated slowly with continuous stirring for 20 minutes in a fume cupboard. After digestion, samples were then allowed to cool, and then filtered through Whatman filter paper (No 42). Filtrate was diluted to 50ml by double distilled water. The heavy metals viz; Lead (Pb), Nickel (Ni), Zinc (Zn), Iron (Fe), Copper (Cu) and Aluminium (Al) were then analysed using Atomic Absorption Spectrophotometer (AAS) (AA-320N, Shanghai China). Analysis was done in triplicate. Instrumental detection limit (IDL) was done according to standard procedures; determined from analysis of seven replicates of calibration blanks which were digested in the same digestion procedure as the actual samples. IDL is calculated as the concentration equal to three times the standard deviation of the blank signal. The obtained data were statistically analysed using one way analysis of variance (ANOVA) followed by Duncan’s Multiple Range Test for comparison of means and Pearson Correlation was used for evaluating elemental association in the study area. Computations were done for various parameters as follows;

2.1.1 Depth Ratio (D_R)

Depth ratio was computed to understand variations in the concentrations of the heavy metal in relation to the depth. The depth ratio (top/bottom) would represent the present impacts in terms of anthropogenic inputs or erosion/run-off removal of heavy metals as well as subsurface vertical
transport of the heavy metals. Depth ratio is calculated with the assumption that the middle layer (A2) has concentration nearly equal to either layer i.e. top (A1) and bottom (A3) layers.

\[ D_R = \frac{A_{C1}}{A_{C3}} \]  

\( A_{C1} \) = Concentration of metal at the top layer  
\( A_{C3} \) = Concentration of metal at the bottom layer  
\( D_R \) = Depth ratio

2.1.2 Contamination Factor (CF)

Contamination factor (CF) is calculated as the ratio of the mean of metal concentration at a sampling point and the background value. As categorized by [8]; <1 = low contamination, 1-3 = moderate contamination, 3-6 = considerable contamination, and >6 = very high contamination.

\[ CF = \frac{C_m}{C_b} \]  

\( CF \) = Contamination factor of the metal of concern  
\( C_m \) = Concentration of the metal of concern in the sediment sample  
\( C_b \) = Background concentration of the metal of concern

2.1.3 Degree of Contamination (C_deg)

The degree of contamination is the summation of all contamination factors of all the considered metals in the sample. Four categories have been defined for the degree of contamination viz; <8 = low degree of contamination; 8-16 = moderate degree of contamination; 16-32 = considerable degree of contamination and; >32 = very high degree of contamination [8].

\[ C_{deg} = CF_1 + CF_2 + CF_3 + \ldots + CF_n \]  

\[ C_{deg} = \sum (C_{F_s}) \]  

2.1.4 Geoaccumulation Index (I_geo)

This parameter is used to evaluate the degree of metal pollution in different environments such as the floodplain sediment. According to [9], the following classification is given for geo-accumulation index: <0 = practically unpolluted, 0-1 = unpolluted to moderately polluted, 1-2 = moderately polluted, 2-3 = moderately to strongly polluted, 3-4 = strongly polluted, 4-5 = strongly to extremely polluted, and >5 = extremely polluted.

\[ I_{geo} = \log_2 \left( \frac{C_m}{C_b \times 1.5} \right) \]  

\( C_m \) = Concentration of the metal of concern in the sediment sample  
\( C_b \) = Background concentration of the metal of concern. 1.5 is a factor for possible variation in the background concentration due to lithological differences.

2.1.5 Pollution Load Index (PLI)

Pollution load index measures the extent of metal pollution in a given site/sample. [10] categorized PLI into three; <1 = perfection; 1 = baseline level of pollution and >1 = deterioration of site quality.

\[ PLI = (C_{F_1} \times C_{F_2} \times C_{F_3} \times \ldots \times C_{F_n})^{1/n} \]  

Where \( n \) is the number of metal studied and \( C_F \) is the contamination factor for each metal.

2.2 Health risk assessment

USEPA risk models was employed to assess carcinogenic and non-carcinogenic health risks associated with heavy metals in the floodplain sediments of urban catchment of Asa River. Mean values of quantified metals was computed for the risk estimation.

2.2.1 Non-carcinogenic health risk

Non-carcinogenic health risks associated with children and adults via ingestion, inhalation and dermal routes were estimated using the equations 7 and 8.

\[ HQ_{ingestion/inhalation/dermal} = \frac{CDI}{RFD} \]  

\[ HI = \sum HQ \]  

Where HQ = hazard quotient, CDI = chronic daily intake, RFD = reference dose and HI = hazard index.

However, CDI is dependent on exposure route using equation 9 to 11

\[ CDI_{ingestion} = \frac{CM \times logR \times EF \times ED}{BW \times AT} \]  

Where CM = concentration of metal in the sediment, logR = log of reference ingestion rate, EF = exposure frequency, ED = exposure duration, BW = body weight and AT = average time of exposure.
CDI_{inhalation} = \frac{CM \times InhR \times EF \times ED}{BW \times AT \times PEF} \quad (10)

CDI_{dermal} = \frac{CM \times SA \times WAF / SAF \times DAF \times EF \times ED}{BW \times AT} \quad (11)

CM is the concentration of heavy metal; \( \text{IngR} \) is the ingestion rate; \( \text{EF} \) is the exposure frequency; \( \text{ED} \) is the exposure duration; \( \text{BW} \) is the body weight; \( \text{AT} \) is the average time; \( \text{InhR} \) is the inhalation rate; \( \text{PEF} \) is the particulate emission factor; \( \text{SA} \) is the skin surface area; \( \text{WAF} \) is the water adherence factor; \( \text{SAF} \) is the sediment adherence factor and \( \text{DAF} \) is the dermal absorption factor.

HQ > 1 shows that the reference heavy metal would elicit non-carcinogenic health effect while HI > 1 revealed that the total metal at a site would cause adverse non-carcinogenic health effect.

2.2.2 Carcinogenic health risk
Cancer risk index (CRI) was evaluated using equation 12.

\[
\text{CRI}_{\text{ingestion/inhalation/dermal}} = \text{CDI}_{\text{ingestion/inhalation/dermal}} \times \text{SF} \quad (12)
\]

\( \text{CRI}_{\text{ingestion/inhalation/dermal}} \) = Cancer risk index via ingestion/inhalation/dermal route, \( \text{CDI}_{\text{ingestion/inhalation/dermal}} \) = chronic daily intake via ingestion/inhalation/dermal route and \( \text{SF} \) = slope factor for a heavy metal. Currently, the available SF is via ingestion route for only Pb among all the heavy metals analysed and it is 8.5E-3. Hence, carcinogenic risk was calculated for only Pb through oral route.

Acceptable value of cancer risk is \( 1 \times 10^{-6} \leq \text{CRI} \leq 1 \times 10^{-4} \).

\( \text{IngR} = 200\text{mg/day for child and 100mg/day for adult} \)
\( \text{EF} = 365\text{day/year} \)
\( \text{ED} = 6\text{ years for child and 70 years for adult} \)
\( \text{BW} = 15\text{ kg for child and 65 kg for adult} \)
\( \text{AT} = 2190\text{ days for child and 25550 days for adult} \)
\( \text{SA} = 2800\text{cm}^2\text{ for child and 17500cm}^2\text{ for adult} \)
\( \text{SAF} = 0.2\text{ mg/cm}^2\text{ for child and 0.07 mg/cm}^2\text{ for adult} \)
\( \text{DAF} = 0.001 \)
\( \text{InhR} = 8.6\text{m}^3/\text{day for child and 15.2 m}^3/\text{day for adult} \)
\( \text{PEF} = 1.32E9\text{m}^3/\text{kg for child and 6.79E8m}^3/\text{kg for adult} \)

3. Results and Discussion

3.1 Pedological Analysis
The total concentration of analyzed metals; Pb, Ni, Zn, Fe, Cu and Al revealed generally that there was no significant difference (p<0.005) in the levels of the metals across the sampling points of the urban catchment of the Asa River. Fe was found to be the most abundant metal in the study area (Table 1). The concentration (mg/kg) of heavy metals in the floodplain sediments of urban catchment of Asa River showed the range of Pb (0.60-4.20), Ni (ND-3.20), Zn (5.26-16.23), Fe (300.00-900.00), Cu (1.70-9.80) and Al (0.68-3.10). The dynamics of the heavy metals (figure 1) across the sampling points recorded that Zn increases from the upstream to the downstream. The instrumental detection limit was 0.005 ± 0.002 mg/L and this indicates good instrument sensitivity. As revealed in figure 2, except Fe, other metal concentrations increased with depth. In this study, all metals showed a depth ratio below 1 (<1) except Fe with depth ratio higher than 1 in all the sampling points (figure 3). While the contamination factors of Pb, Ni and Al were between the range of 1-3 (moderate contamination), the contamination factors of Zn, Fe and Cu revealed considerable contamination (figure 4). The degree of contamination obtained in this study was 18.67 which shown that there was a considerable degree of metal contamination.

The geoaccumulation indices calculated for the heavy metals in the floodplain sediment of the urban catchment of Asa River are plotted (figure 5). Except Ni that has I_{geo} less than 0, others are with values between the ranges of 0-3, depicting various pollution levels from moderate pollution to strong.
pollution level. PLI in this study is approximately 1 depicting a baseline level of pollution. The correlation coefficient matrix is shown in Table 2. The metal association showed a positive correlation among all the metals evaluated. There was widespread of heavy metals in the floodplain sediment of urban catchment of Asa River from the very southern upstream region to the northern downstream end was observed in this study. And the non-significance difference in their level across all the sampling points may be due to uniformity in distribution, removal or transportation mechanisms of heavy metals in the area studied. Elevated level of Fe in all the sampling points could be suggestive of very high industrial iron-containing wastes discharged from industrial activities along the urban catchment; a similar scenario where high level of metal in water sediment is attributed to industrial activities was reported by [11]. The surface layer depletion of Pb, Ni, Zn, Cu and Al observed in this study could be attributed to rainfall of the early period of the season which had probably washed the metals into the Asa River and/or caused vertical downward transport of the heavy metals, while the inverse association with depth observed with Fe had possibly been the result of the most latest atmospheric deposition or heavy industrial discharge of iron-containing waste/particles into the study area, a similar relationship reported by [12].

The metal contamination in the floodplain sediment was considerable and this could undoubtedly be due to various industrial, agricultural and other anthropogenic activities that are done in the area which had introduced the heavy metals to the environment. Only Ni has a geoaccumulation index less than zero (-1.57), Pb has an index of 0.92 while 2.14, 1.19, 2.81, 1.77 are indices of Zn, Fe, Cu and Al respectively. This implies that the study area is practically not polluted with respect to Ni but moderately to strongly polluted by Zn, Fe, Cu and Al based on Igeo [13, 14]. Though the PLI revealed that the pollution is still at baseline level but continuous waste input will deteriorate floodplain and the Asa River. Positive correlation was observed in all the metals i.e. they are all correlated with one another, this may implies that these metals emanates from similar anthropogenic or lithological sources [15, 16].

3.2 Health Risk Assessment

3.2.1 Hazard Quotient (HQ), Hazard Index (HI) and Cancer Risk Index (CRI)

The results of HQ, HI and CRI associated with heavy metals; lead (Pb), nickel (Ni), zinc (Zn), iron (Fe), copper (Cu) and aluminum (Al) in the floodplain sediments in the study area for both children and adults are presented in table 3. HQ from ingestion and dermal routes calculated for all the six heavy metals for both children and adult were > 1 while estimations for inhalation were < 1 for the two age groups. In addition, HQ values calculated for children were higher than those for adults in all the three exposure pathways. HI which signifies non-carcinogenic risk was well above 1 for both children and adult but for ingestion and dermal pathways. HI via ingestion were 7.3E4 and 8.4E3 for children and adult respectively; via inhalation were 2.3E-6 and 1.8E-6 for children and adult respectively and; via dermal route were 2.8E2 and 1.4E2 children and adult respectively. CRI calculated for Pb via ingestion route for both children and adult were 2.4E-1 and 2.7E-2 respectively which is outside acceptable cancer risk range.

The hazard quotient (HQ) and hazard index (HI) values for ingestion and dermal routes for all the metal analyzed both in children and adults suggested that the values are not within the acceptable level of non-carcinogenic adverse health risk which negates the report of [17] whose work was based on surface water. This could possibly be that floodplain sediments serve as repository for heavy metals and would therefore elicit more non-carcinogenic human health hazard upon exposure when compared to surface water. Conversely, the analysis of HQ and HI for both children and adult depicts that inhalation exposure route might not pose non-carcinogenic health risk to human. In addition, the results also showed that exposed children are at higher health risk when compared to adults. The estimated value of cancer risk index (CRI) for Pb via oral pathway for both children and adults revealed that the two age groups are predisposed to carcinogenesis with higher risk in children than in adults. Pb has been implicated to cause mental retardation in children [18]. This therefore calls for proper monitoring and regulatory enforcement that would abate pollution of Asa River.
| Sampling Points | Pb    | Ni    | Zn    | Fe (X10²) | Cu    | Al    |
|-----------------|-------|-------|-------|-----------|-------|-------|
| P₁              | 1.70±1.21a | 1.27±1.10a | 7.44±3.24a | 3.30±0.36ab | 4.17±3.2a | 1.29±0.57a |
| P₂              | 1.84±1.32a | 1.93±0.99a | 7.52±3.28a | 4.00±0.11ab | 4.53±3.01a | 1.37±0.59a |
| P₃              | 2.08±1.56a | 1.93±1.17a | 7.92±2.91a | 4.38±1.41ab | 4.70±3.18a | 1.50±0.69a |
| P₄              | 2.02±1.43a | 1.91±1.17a | 7.89±2.94a | 4.62±2.30b | 4.83±3.10a | 1.56±0.68a |
| P₅              | 2.15±1.65a | 1.89±1.39a | 8.20±3.52ab | 4.85±2.11b | 5.40±2.95a | 1.27±0.75a |
| P₆              | 2.23±1.76a | 1.72±1.56a | 8.32±3.43ab | 5.03±1.97b | 5.12±3.14a | 1.60±0.70a |
| P₇              | 2.10±1.52a | 1.75±1.58a | 9.79±4.00b | 4.93±1.97b | 5.57±2.40a | 1.96±1.03a |
| P₈              | 2.33±1.47a | 2.00±1.40a | 12.26±2.78b | 4.92±1.64b | 5.87±2.99a | 1.94±1.11a |
| P₉              | 2.30±1.61a | 2.07±1.33a | 12.27±2.75b | 5.43±2.31b | 5.97±3.43a | 1.89±0.90a |
| P₁₀             | 2.36±1.59a | 2.20±1.15a | 13.93±2.75ab | 5.97±2.62b | 5.93±3.16a | 2.00±1.00a |

*Mean in the same column with the same superscript are not significantly different (p<0.05)
Figure 1: Dynamics of heavy metals in floodplain sediment in the ten sampling points from the very upstream (P1) to the very downstream (P10) along the urban catchment of Asa River. Fe concentrations are divided by 100 to bring their value to scale.

Figure 2: Levels of Heavy Metals in Floodplain Sediment of the Urban Catchment of Asa River in relation to Depth.
4. Conclusion

The concentrations of Pb, Ni, Zn, Fe, Cu and Al of floodplain sediment in the urban catchment of Asa River were investigated, and elevated level of Fe was observed. An inverse relationship was noted in Fe concentration with depth as opposed to what was observed in Pb, Ni, Zn, Cu and Al concentrations with depth. Though the PLI revealed a baseline pollution level of the assessed metals altogether but the contamination factor of each of Zn, Fe and Cu in the study area was considerable and may be a threat to ecological health and by extension to human health. The health risk assessment indices like HQ and HI for the metals except Pb revealed non-carcinogenic adverse effects risk though greater in children than adults. However, the cancer risk index (CRI) for lead implicated the two age groups to be carcinogenic though greater in children than adults. Therefore the industrial and waste generated in the urban catchment of the Asa River must be monitored for adherence to environmental management and sustainability laws; and further research is needed to establish the dynamics and association between the heavy metal in the urban floodplain sediment of Asa River.
### Table 3: Reference dose, hazard quotient, hazard index and cancer risk for heavy metals of the floodplain sediments in the study area.

| Metal | RFD ingestion (mg/kg/day) | RFD inhalation (mg/kg/day) | RFD dermal (mg/kg/day) | HQ (ingestion) Child | HQ (inhalation) Child | HQ (dermal) Child | Cancer risk (Oral route) Child |
|-------|---------------------------|---------------------------|------------------------|---------------------|---------------------|-------------------|--------------------------|
| Pb    | 4.0E-3                    | 3.5E-3                    | 4.2E-4                 | 6.9E3               | 8.0E2               | 2.6E-7            | 2.4E-1                   |
| Ni    | 2.0E-2                    | 2.5E-2                    | 5.4E-3                 | 1.2E3               | 1.4E2               | 3.2E-8            | 2.7E-2                   |
| Zn    | 3.0E-1                    | 3.5E-1                    | 6.0E-2                 | 4.2E2               | 4.8E1               | 1.2E-8            | 3.0E0                    |
| Fe    | 7.0E-1                    | 8.0E-1                    | 4.5E-1                 | 8.9E3               | 1.0E3               | 2.5E-7            | 2.0E1                    |
| Cu    | 4.0E-2                    | 4.0E-2                    | 1.2E-2                 | 1.7E3               | 2.0E2               | 5.6E-8            | 8.1E0                    |
| Al    | 4.0E-4                    | 4.2E-4                    | 3.8E-3                 | 5.4E4               | 6.2E3               | 1.7E-6            | 8.0E0                    |
| HI    | -                         | -                         | -                      | 7.3E4               | 8.4E3               | 2.3E-6            | 1.4E2                    |

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