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Evaluating the Performance of Heavy Metals in Surface Ponds among Land-use using Z-score and Coefficient of Variation

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ABSTRACT
Heavy metals have high significance among the inorganic contaminants of surface water (e.g., ponds and streams) due to their non-degradable nature in heighten injurious biological effect. For this reason, therefore, this study examined the influence of the land-uses on the performance of the selected heavy metals using z-score and coefficient of variation. In order to achieve the aim of this study, thirty surface ponds water were sampled across four land uses in Akoko Northeast LGA of Ondo State, Nigeria. The sampled water were assessed for four heavy metals and evaluated using the Z-score and coefficient of variation. The heavy metals are zinc (Zn), iron (Fe), manganese (Mn) and copper (Cu) while the land uses comprise of built-up areas, cultivated lands, vegetation and crop plantation. Observed heavy metals results were converted to standardized Z-scores (z) to facilitate objective comparisons and enablement of performance among each parameter in the ponds across the land uses. The predefined water quality result variations were objectively subjected to coefficient of variation (CV) to confirm the level of parameters comparability. Thus, the z-score results of heavy metals identified strong remarkable spatial dependency when $p>0.01$ or weak remarkable spatial dependency when $p<0.01$ while performance denote homogeneous when $CV<50\%$ or heterogeneous when $CV>50\%$. In conclusion, the study exhibited spatial variation in concentrations of the four heavy metals as a result of different land uses characteristic.

Key words: Heavy metals, ponds, land uses, Z-score, coefficient of variation

INTRODUCTION
Foreign substances in form of organic, inorganic, bacteriological or radiological elements in water are dangerous and capable to vitiate the quality of water for domestic purposes (Salami, 2003) and water ecosystems (Tabatabaie *et al*., 2009; Ndome *et al*., 2011). Some of these foreign substances in particular, heavy metals may influence the levels of other parameters and possibly result into temporary or permanent impairments of water quality (Eletta, 2007). Presently, the increasing level of heavy metal pollution of surface water is one of the problems facing global water resources management and monitoring (Sekabira *et al*., 2010). This is a serious matter in developing countries such as Nigeria that lack sensitive tools and mechanisms to monitor water quality because of sources diversity. For example, the quality of surface waters may be influenced by the quantity and quality of underlying groundwater resulting from contaminated land and/or effluents from different land uses (Ellis *et al*., 2002; Ato *et al*., 2010) such as built-up (domestic

waste and sewage), agricultural (fertilizer and manure) and industrial waste (Linnik and Zubenko, 2000; Lwanga *et al*., 2003; Al-Momani, 2009; Pejman *et al*., 2009; Sekabira *et al*., 2010; Karami *et al*., 2011; Al-Farraj *et al*., 2012; Machiraju *et al*., 2012). This is because most surface waters used for domestic purposes and human activities are around human settlements and cut across different land uses (Ayeni *et al*., 2006, 2011). The use of such surface water may expose the user to heavy metal poisoning (Ochieng *et al*., 2008; Ayeni *et al*., 2011).

The spatial relationship between two parameters with respect to their sources may also lead to increase or decrease in their concentration. This relationship or association is usually established using widely accepted statistical techniques such as Analysis of Variance (ANOVA), principal component analysis, coefficient of variation and Z-score among others (Ogunkoya and Adejuwon, 1990; Ifabiyi, 1997; Jaji *et al*., 2007; Adekunle *et al*., 2007; Ato *et al*., 2010). The application of statistical techniques helps in the interpretation of complex data patterns and gives a better understanding of the relationship between water quality and ecological systems surrounding the water under scientific study (Pejman *et al*., 2009).

The above discussion provides the underlying rationale for this research, i.e., to evaluate the performance of heavy metals in pond waters across different land uses in Akoko Northeast LGA of Ondo State Nigeria. The study focuses on the influence of the land-uses on the performance of the selected heavy metals using Z-score and coefficient of variation. This is considered an objective means of assessing parameters performance and results comparability.

MATERIALS AND METHODS

Study area: This study was conducted in the Akoko Northeast LGA of Ondo State Nigeria. Geographically, the area lies between 5°38'N and 6°04'East of Greenwich Meridian and 7°26'N and 7°42'North of the Equator (Fig. 1, 2). The area is located on Basement Complex rock with its elevation ranging between 149 and 671 m above sea level. It has a sub-tropical climate that is attributed to high rainfall of over 1500 mm annum^{-1} with characteristic of warm temperatures ranging from 30 to 38°C.

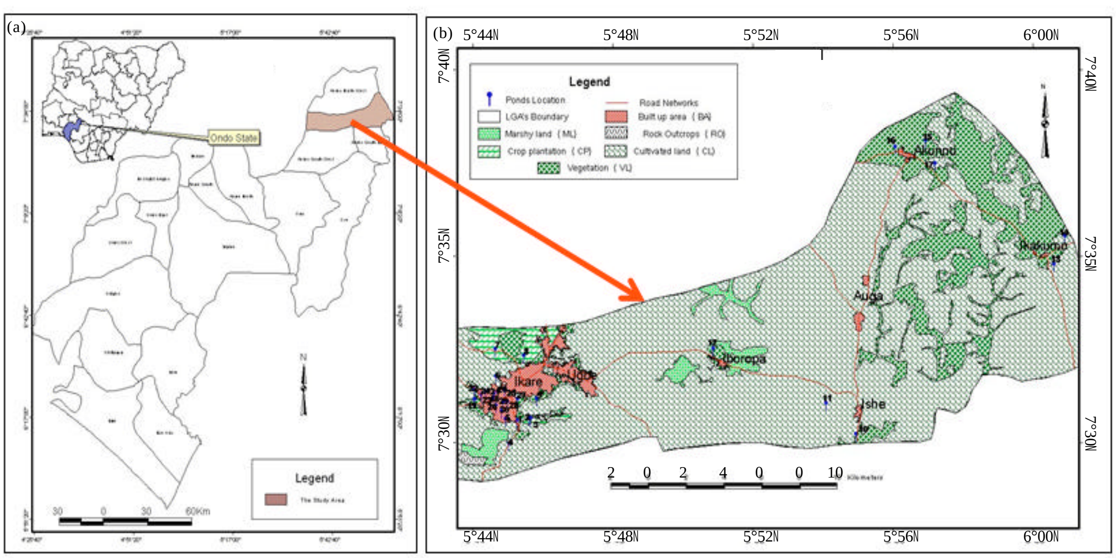


Fig. 1(a-b): The study area, (a) Akoko northeast in Ondo state, Nigeria and (b) Land uses

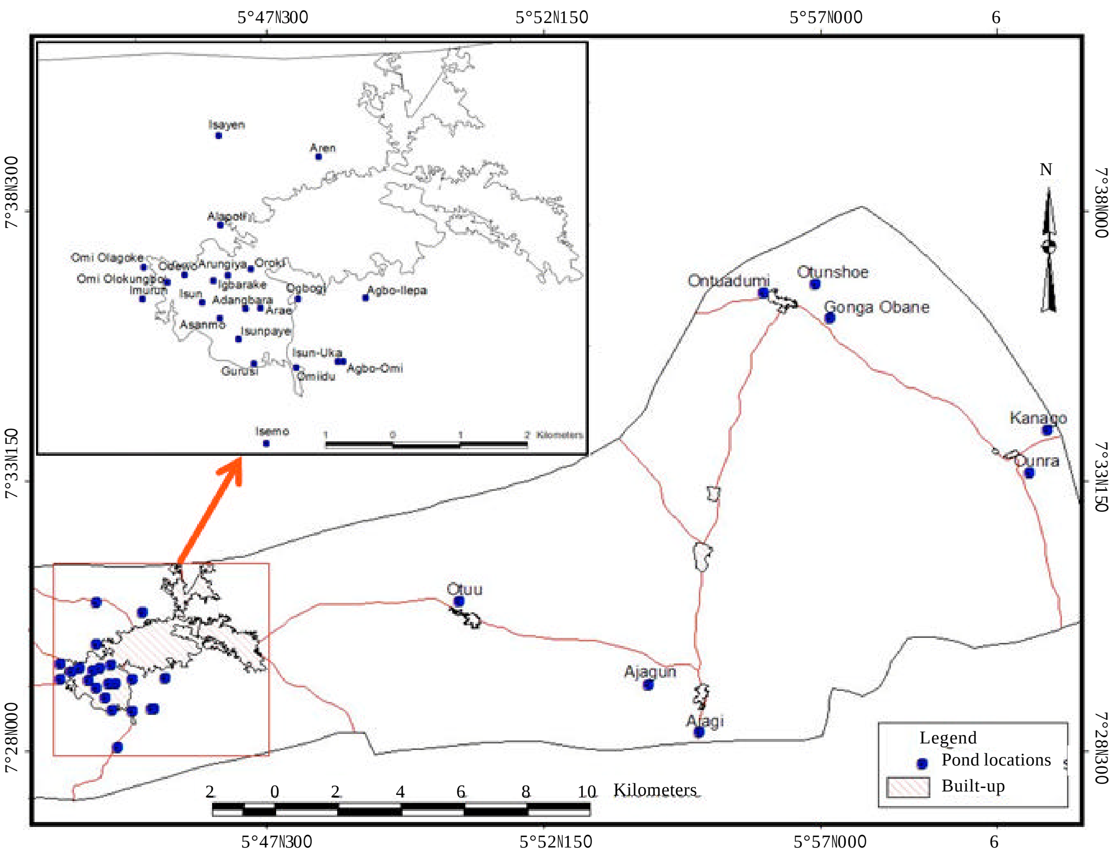


Fig. 2: Studied ponds in the selected area

Methods: Water samples were collected from 30 different ponds (Fig. 2) used for domestic purposes in the study area using new polyethylene plastic bottles. The bottles were rinsed many times with distilled water and finally rinsed with ultrapure water. The samples were collected by dipping the covered plastic bottle about 20-30 cm below the water surface; opened and filled up and covered with the cap before being taken out of the water. All water samples were given identification code to avoid error of handling and stored in insulated cooler containing ice and delivered on the same day to laboratory. Samples were kept at 4°C in the analytical laboratory until processing and analysis. The water samples were collected and analysed on monthly basis between December 2008 and December 2009. The results of the laboratory analysis were analysed for Z-score and coefficient of variation and then discussed.

Standard score (Z-score): Z-score is adopted in this study to facilitate comparisons of parameters' mean to enable the assessment of their performance among land-use types in the study area. Z-score is given by the formula:

$$Z_x = \frac{x - \mu_x}{\delta_x}$$

Where:
Z_x = Stand and score
x = Individual mean
$\mu_x = \Sigma(x)$ = The mean of the population
δ_x = The standard deviation of the probability distribution of x

Coefficient of variation (CV): CV is adopted in this study to determine and compare the spread of the parameters' mean and variation i.e., if either homogeneous or heterogeneous. It is given by the formula:

$$CV = \frac{\delta}{X} \times 100$$

Where:
CV = Coefficient of variation
δ = Standard deviation
X = Mean

RESULTS AND DISCUSSION

Landuse concept was used on the assumption that different types of land have different impact on water parameters. The Zn detected in sampled ponds ranges between 0.01 and 0.66 mg L^{-1} (Fig. 3), indicative of low Zn content when compared with WHO (2006) regulatory limit of 5.0 mg L^{-1} (Fig. 4). Iron (Fe) in all sampled ponds ranges between 0.4 and 4.7 mg L^{-1} (Fig. 3). On the average, the mean of Fe detected in all land uses are higher than the WHO (2006) and the SON (2007) regulatory limit of 0.3 mg L^{-1} (Fig. 4). Manganese (Mn) was detected in the 17 ponds with concentration values ranging between 0.01 and 1.15 mg L^{-1}. Of these 17 ponds, Mn contents

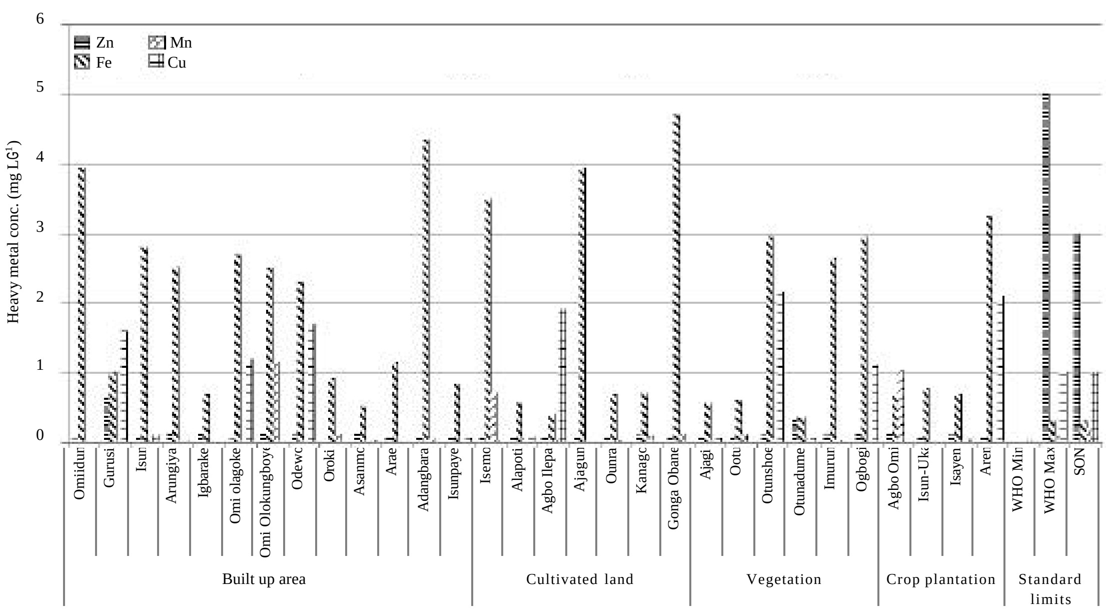
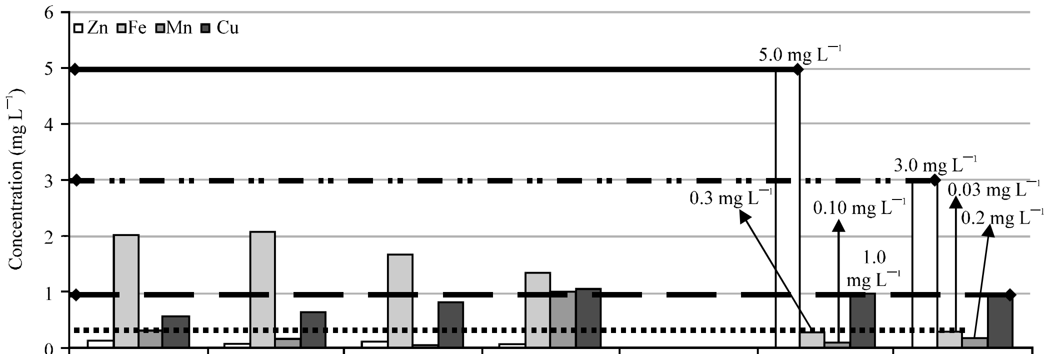


Fig. 3: Heavy metals concentrations in various ponds



	Built up area	Cultivated land	Vegetation	Crop plantation	WHO min	WHO max	SON
Zn	0.129	0.086	0.13	0.10	0.01	5.00	3.00
Fe	2.015	2.070	1.68	1.35		0.30	0.30
Mn	0.330	0.165	0.06	1.02	0.005	0.10	0.20
Cu	0.586	0.660	0.85	1.07	0.005	1.00	1.00

Fig. 4: Comparison of heavy metals concentrations mean with regulatory standards

in Omi-Olokungboye and Oroki (built-up); Isemo (cultivated land) and Agboomi (crop plantation) are higher than WHO (2006) limits of 0.05 and 0.1 mg L^{-1} and SON (2007) limit of 0.2 mg L^{-1} (Fig. 3, 4). Copper (Cu) in the sampled ponds ranges between 0.0 and 2.10 mg L^{-1}. From the findings, Cu contents in 7 ponds within three different land uses, e.g., built-up (Gurusi, Arae, Omi-Alagoke and Odewo), cultivated land (Agbo-Ilepa) and vegetation (Ogbogi and Otunshoe) are above both the WHO (2006) regulatory limit of 1.0 mg L^{-1} and SON (2007) regulatory limit of 0.1 mg L^{-1} (Fig. 3, 4). The mean values of Cu across the land uses shown that only crop plantation Cu found above the WHO (2006) and SON (2007) regulatory limits of 1.0 mg L^{-1} (Fig. 4).

The variation in the heavy metals, most especially in built-up area could be attributed to various urban activities (Ifabiyi, 1997; Obire and Aguda, 2006) while in cultivated land, it could be attributed to farming activities, the topography, rock composition, hydro-geological controls of the amplitude and the periodicity of water table fluctuations (Petrone *et al.*, 2005). The disparity in the vegetation land use could result from the nature of the vegetation (disturbed), human interference and geological composition of the area (Chudaeva, 1988; Ogunkoya and Adejuwon, 1990). Various crop farming activities such as seasonal clearing, types and quantity of insecticide and fertilizer applied and the topography of the area in which the ponds are located must have influenced the heavy metals contents in the crop plantation land use (Ifabiyi, 1997).

Evaluation of the mean across land uses: The mean of Zn among land uses is moderately homogeneous and comparable as indicated by a coefficient of variation of 16.73% (>10% and <50%). Observation made on Zn concentration in ponds across all the four land uses shows strong level of spatial dependency with a Z-score of 24.98 ($p>0.01$). The results suggest that Zn in the studied ponds are not randomly dispersed but instead are spatially correlated within the land uses. A comparison of the mean of Fe among land uses shows that Fe is homogeneous in its spread, hence comparable as demonstrated by a coefficient of variation of 23.23% (>10% and <50%). Fe in land uses ponds reveals a weak level of spatial dependency with a Z-score of -1.33 ($p<0.01$). The results indicate that Fe in the ponds water is not spatially correlated but dispersed randomly across the land uses. It also indicates no remarkable differences in the variability of Fe across land use.

The mean of Mn among land uses is spatially heterogeneous and highly comparable as demonstrated by a coefficient of variation of 109.72% (>100%). There are no remarkable difference in the variability of Mn across the land uses with a Z-score of -0.68 ($p<0.01$). The result suggests that Mn is highly dispersed but does not correlate with land uses, hence it posted a weak level of spatial dependency. Mean of Cu concentration among land uses is averagely homogeneous and comparable as indicated by a coefficient of variation of 29.03% (>10% and <50%). Slight differences are observed in Cu variability with a Z-score of 0.04 ($p>0.01$). The result suggests that Cu disperses consistently and slightly spatially correlates with land uses with a moderate level of spatial dependency.

The variability in the spatial dependency of the four studied heavy metals could result from different factors. For instance, Zn and Fe are commonly found in surface water like ponds and their occurrence could be natural (Ojosipe, 2007). Fe may result from dissolved rock and soil as well as anthropogenic sources such as leached corrosive iron materials in the urban environment and rural settlement (Jaji *et al*., 2007). The level and variation of Mn and Cu in the sampled ponds could be attributed to the geological composition of the parent rock on which the ponds are located (Chudaeva, 1988; Ogunkoya and Adejuwon, 1990; Biasioli *et al*., 2007). Cu occurrence in natural water could also be attributed to soluble copper salts or precipitated copper compounds of suspended solid (Ojosipe, 2007).

CONCLUSION

Spatial dependency was observed for Zn and Cu in their variability. Across the land uses, however, Zn has strong levels of correlation and homogeneity while Cu posts low correlation. Fe and Mn show weak and low level of spatial dependency as reflected in their Z-scores ($p<0.01$). In general, the four heavy metals assessed in the surface ponds show variation in concentrations as a result of different land uses and characteristic e.g., anthropogenic activities, effluent injections, parent rock chemistry.

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