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ASSESSMENT AND STATISTICAL ANALYSIS OF THE CONCENTRATIONS OF DISSOLVED METALS IONS IN SELECTED SURFACE WATER BODIES IN ZARIA

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ABSTRACT

The surface water bodies in Zaria, Kaduna State, Nigeria, are vital for supporting the local ecosystem and providing water resources for various human activities. However, increasing industrialisation and urbanisation in the region have raised concerns about the potential impact of metal pollution on these water bodies. This study investigates the composition of dissolved metals, including Pb, Cu, Co, Ni, and Cd, in three surface water bodies: Shika Dam, Gamma Dam, and ABU Dam. Atomic Absorption Spectroscopy (AAS) was utilised to detect the presence of these metals, followed by systematic calculations of correlation coefficients to simplify the interpretation of the data. The ANOVA conducted at a 95% confidence level indicated no significant differences in the analysed metal concentrations across all sampling points ($p > 0.05$), suggesting a common source of pollution. The concentrations of Pb, Cu, and Co were found to be below the detection limit. Correlational analysis revealed strong positive correlations between Pb and Cu ($r = 0.999, 0.998$) at sampling points 2 and 6, indicating a shared source of contamination, while negative correlations ($r = -0.998, -1$) at points 9 and 6 suggested indicate differing environmental conditions. Additionally, a perfect positive correlation ($r = 1$) between Cu and Co points to a single source, likely related to industrial activities. Similarly, there were strong correlations between Cd and Co, as well as between Cd and Cu. These findings show the complex interrelationships within aquatic ecosystems and highlight the need for holistic water quality management.

Keywords: Surface water, Water pollution, Dissolved metal ions, Statistical analysis, Atomic absorption spectroscopy

INTRODUCTION

Surface water bodies are crucial for urban development and human life (Gupta and Orbán, 2018), supporting both urban residents and agriculture (Khatri and Tyagi, 2015). However, their unsustainable use poses significant environmental risks, as these resources are not easily replenished (Abdulhamid, 2019). Heavy metals enter aquatic environments through natural and human-induced processes, with human activities becoming the dominant contributor over the past centuries. Water quality assessment is crucial (Smith and Brown, 2021), but monitoring all parameters regularly is challenging (Nyika and Dinka, 2023). Therefore, statistical correlation approaches have been developed to compare metal concentrations in surface water (Proshad *et al.*, 2021). Correlation studies reduce uncertainty in decision-making (Schroeder *et al.*, 1975), and ANOVA tests the significance of observed correlation coefficients. This research therefore provides crucial insights into the metal contamination levels in surface water bodies in Zaria, Kaduna State, Nigeria. By employing statistical methods such as correlation coefficients and ANOVA, the study reduces the complexity of large datasets and offers a clear understanding of water quality across various sampling points.

MATERIALS AND METHODS

Site Description

Shika Dam was constructed mainly for water supply and farming activities by people living around the dam; this has been substantial over the years. The dam is located on latitudes 11°07'45"E to 11°08'20"E and longitudes 07°46'N to 07°48'N (Tanko *et al.*, 2012). Galma Dam is located on latitudes 11˚07'45"E to 11˚08'20"E and longitudes 07˚46'N to 07˚48'N (Mohammed *et al.*, 2020). River Kubanni dam, which is prevalently called Ahmadu Bello University (ABU) dam, is located approximately within latitude 11°11'N and longitude 07°38'E; it is within the premises of the university's main campus (Sani *et al.*, 2024).

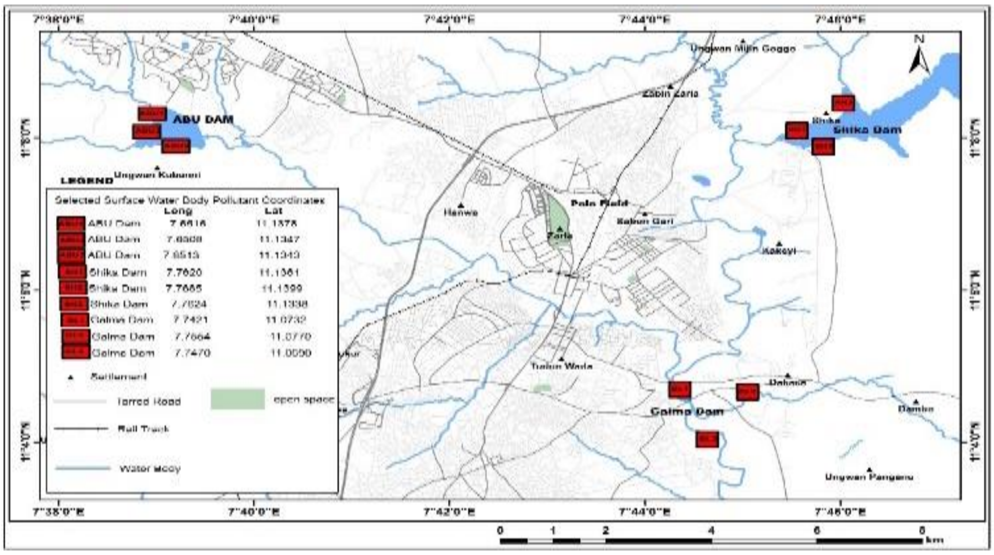

Figure 1: Map of Zaria Metropolis showing the points where the samples were collected

Sample Collection

Water samples were collected using the composite sampling method from three locations (Galma, Shika, and ABU Dam) with three sampling points at each location. Pre-soaked and rinsed 2L plastic bottles were used for collection. Before sampling, each bottle was rinsed three times with the water to be sampled and then carefully immersed to collect the sample. Samples were labelled and transported to the laboratory for analysis.

Quality Assurance

All reagents used are of analytical grade; distilled deionised water is being used. All the glassware, polythene bags, and sample bottles were washed with liquid soap, rinsed with distilled water, soaked in 10% HNO_3 for 24 hours, rinsed thoroughly with distilled deionised water, and thereafter dried (Worku and Destaw, 2006).

Classification of Sample Locations and Metal Identification

The study involves three primary locations: Shika, ABU Dam, and Gamma, each represented by a specific range of sample numbers:

i. Shika: Samples S1 to S3 are collected from this location. Consequently, any metal with these sample numbers (e.g., Pb 1 to 3) indicates that the sample is from Shika.
ii. ABU Dam: Samples S4 to S6 represent this location. Therefore, metals associated with these numbers (e.g., Pb 4 to 6) are indicative of ABU Dam.
iii. Gamma: Samples S7 to S9 correspond to this location. Metals assigned with these numbers (e.g., Pb 7 to 9) are representative of Gamma.

Determination of Metals in Water Samples

Determination of Pb, Cd, Cu, Fe and Ni was carried out in triplicate directly on each of the digested water samples using AAS machine (280FS AA) at the Multi- User Science Laboratory, Department of Chemistry, ABU- Zaria.

Statistical Treatment of Data

The statistical analysis has been performed using SPSS version 20 software. Statistical studies were carried out by calculating correlation coefficients between different pairs of metals and was used to test the significant differences in the levels of the physicochemical parameter studied (using ANOVA) across the sampling points at 95% ($p \leq 0.05$) confidence level. The correlation among the different parameters will be true when the value of correlation coefficient (r) is high and approaching to one (Schober et al., 2018).

Coefficient of correlation (r) = $\sqrt{\frac{\Sigma(x-\bar{x})(y-\bar{y})}{\Sigma(x-x)^2\Sigma(y-\bar{y})^2}}$

Where, x = Individual reading of 1st parameter, $\bar{x}$ =Mean of Σ x , y = Individual reading of 2nd parameter , $\bar{y}$ = Mean of Σ y

RESULTS AND DISCUSSION

The metal concentration results in the analysed water are revealed in Table 1. The variability in the concentration levels of lead (Pb), copper (Cu), cobalt (Co), nickel (Ni), and cadmium (Cd) in the sampled water from the study area can be attributed to multiple factors. These include natural processes and anthropogenic activities, such as industrial operations with inadequate wastewater treatment, as well as agricultural practices like farming, which is the predominant activity in the area. The range of concentrations, from below detection limit (BDL) to 0.049 ± 0.100 mg/L for Pb, BDL to 0.010 ± 0.003 mg/L for Cu, and BDL to 0.026 ± 0.002 mg/L for Co, underscores the complexity of metal distribution within the aquatic environment. These metals can originate from various sources, such as weathering of rocks and soil, as well as industrial discharge, urban runoff, and agricultural activities. The values obtained in this study are lower than those reported by Ngoubou *et al.* (2021) for the Djiri River in the Republic of Congo, where lead concentrations ranged from 0.53 to 1.28 mg/L. Agricultural activities, fertiliser and pesticide use near the sampling sites, and soil erosion may contribute to metal contamination. Runoff from domestic and industrial wastewater, as well as direct discharge from nearby industries, can also elevate metal concentrations, impacting water quality and ecosystem health.

The observed concentration ranges of BDL to 0.011 ± 0.002 mg/L for Ni and BDL to 0.001 ± 0.002 mg/L for Cd further underscore the potential impact of anthropogenic activities on metal levels in the sampled water. This finding aligns with Cobbina *et al*. (2015) in Northern Ghana. Despite low levels, nickel and cadmium still pose environmental and health risks due to their toxic properties.

Table 1: Mean concentration Heavy Metals Concentrations (mg/L) of heavy metals in selected surface water in Zaria.

Sampling point	Pb	Cu	Co	Ni	Cd
S1	BDL	0.002±0.004	0.020±0.010	BDL	BDL
S2	0.038±0.027	0.002±0.003	0.026±0.002	BDL	BDL
S3	0.003±0.014	BDL	BDL	BDL	BDL
S4	BDL	0.009±0.003	BDL	BDL	0.001±0.002
S5	BDL	0.004±0.002	BDL	BDL	BDL
S6	0.049±0.100	0.010±0.003	BDL	0.011±0.002	0.001±0.005
S7	0.030±0.009	0.006±0.003	0.002±0.011	BDL	BDL
S8	BDL	0.004±0.005	BDL	BDL	BDL
S9	BDL	0.005±0.002	BDL	BDL	0.001±0.007
WHO 2014	0.01	0.02	0.05	0.02	0.003

S1 to S3 is Shika, 4 to 6 ABU Dam and 7 to 9 is Gamma

Statistical Treatment of Data

Table 2: Analysis of Variance for the heavy metals across the sampling points

		Sum of Squares	Df	Mean Square	F	Sig.
Pb	Between Groups	.029	8	.004	1.812	.140
	Within Groups	.036	18	.002		
	Total	.065	26			
Cu	Between Groups	.000	8	.000	1.196	.355
	Within Groups	.000	18	.000		
	Total	.000	26			
Co	Between Groups	.002	8	.000	.602	.765
	Within Groups	.007	18	.000		
	Total	.008	26			
Ni	Between Groups	0.000	8	0.000		
	Within Groups	0.000	18	0.000		
	Total	0.000	26			
Cd	Between Groups	.000	8	.000	.747	.651
	Within Groups	.000	18	.000		
	Total	.000	26			

Table 3: Correlation Matrices for the Heavy Metals

Metal	Pb1	Pb2	Pb3	Pb6	Pb7	Pb9	Cu4	Cu5	Cu6	Cu7	Cu8	Cu9
Pb1	1											
Pb2	-.978	1										
Pb3	-.091	.296	1									
Pb6	.894	-.968	-.528	1								
Pb7	-.666	.497	-.682	-.261	1							
Pb9	.952	-.995	-.390	.988	-.408	1						
Cu4	-.629	.453	-.717	-.213	.999*	-.362	1					
Cu5	-.500	.309	-.817	-.058	.979	-.212	.988	1				
Cu6	.988	.999*	-.245	.953	-.542	.988	-.500	-.359	1			
Cu7	-.500	.669	.908	-.835	-.312	-.740	-.359	-.500	-.629	1		
Cu8	-.596	.750	.854	-.893	-.201	-.812	-.250	-.397	-.714	.993	1	
Cu9	-.866	.951	.577	.998*	.204	-.977	.156	0.000	-.933	.866	.918	1
Co1	.983	1.00*	-.273	.961	-.517	.992	-.474	-.331	1.000*	-.652	-.734	-.944
Co2	-.313	.504	.974	-.706	-.499	-.588	-.542	-.666	-.457	.979	.949	.746
Co3	-.500	.669	.908	-.835	-.312	-.740	-.359	-.500	-.629	1.00**	.993	.866
Co5	-.500	.669	.908	-.835	-.312	-.740	-.359	-.500	-.629	1.00**	.993	.866
Co6	1.00**	-.978	-.091	.894	-.666	.952	-.629	-.500	.988	-.500	-.596	-.866
Co7	0.00	-.208	-.996	.449	.746	.305	.778	.866	.156	-.866	-.803	-.500
Co8	-.500	.669	.908	-.835	-.312	-.740	-.359	-.500	-.629	1.00**	.993	.866
Co9	-.500	.669	.908	-.835	-.312	-.740	-.359	-.500	-.629	1.000**	.993	.866
Cd4	-.803	.661	-.521	-.450	.980	-.583	.968	.918	-.700	-.115	0.000	.397
Cd5	-.500	.669	.908	-.835	-.312	-.740	-.359	-.500	-.629	1.00**	.993	.866
Cd6	-.305	.101	-.921	.154	.913	-.001	.933	.977	-.154	-.672	-.583	-.212
Cd8	-.500	.669	.908	-.835	-.312	-.740	-.359	-.500	-.629	1.000**	.993	.866
Cd9	-.500	.309	-.817	-.058	.979	-.212	.988	1.000**	-.359	-.500	-.397	0.000

Table 2 shows the ANOVA results for heavy metals across the sampling points. However, the analysis indicated no statistically significant differences among the samples at a confidence level of 95%. This suggests that, based on this specific test, there were no notable variations, or the analytes share a common source of pollution.

The correlational relationships between heavy metals presented in Table 3 reveal significant insights. Strong positive correlations (r = 0.999, 0.998) between Pb and Cu at sampling points 2 and 6, as well as 9 and 6, suggest a common source of contamination, likely stemming from industrial activities. Conversely, strong negative correlations (r = -0.998, -1) between Cu and Pb at points 9 and 6, as well as Co and Pb at points 1 and 2, indicate differing environmental conditions or locations. A perfect positive correlation (r = 1) between Cu and Co suggests a single source, such as industrial activities or specific pesticides. Similarly, strong correlations between Cd and Co and between Cd and Cu indicate potential industrial sources like metal plating, battery manufacturing, and the nearby groundnut oil company, which is likely contributing to the contamination. These correlations highlight the complex interrelationships within aquatic ecosystems and emphasise the need for holistic water quality management. The correlation coefficient plays a crucial role in understanding patterns and trends in metal properties, which gives researchers the opportunity to identify key factors influencing metal behavior. Values close to 1 or -1 indicate stronger positive and negative correlations, respectively.

CONCLUSION

Metal concentrations in water samples reveal a complex interplay between natural and human-induced factors. Variable levels of Pb, Cu, Co, Ni, and Cd suggest diverse sources like industrial discharge, urban runoff, and agriculture. Correlations between metals indicate shared sources, with perfect correlations pointing to industrial contributions. Negative correlations between Cu-Pb and Co-Pb suggest environmental or location-specific differences. Comprehensive water quality management strategies are crucial, integrating regulation, sustainability, and ongoing monitoring.

RECOMMENDATIONS

It is recommended that educational programs, collaboration, and investment in advanced wastewater treatment infrastructure be implemented to address metal contamination. Further research and policy development promoting sustainable water use and management are also crucial to integrating environmental protection with economic development.

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