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Assessment of Heavy Metal Levels in Water Samples Collected from Odugbo River, Benue State, Nigeria

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Abstract: Drinking water is essential for life worldwide and is used daily. However, the quality of this drinking water varies from one source to another. In this research, analysis of five heavy metals: Pb, Zn, Cu, Mn, and Cd was carried out using the AAS technique in four water samples:: upper river water (L1), middle river water (L2), lower river water (L3), and Bottled water. The results of the study showed that Pb was found in the range of 0.411±0.001 mg/L to 0.852±0.021 mg/L in all the water samples analysed which is above the permissible limits of USEPA (0.015 mg/L), WHO (0.01 mg/L), SON (0.01 mg/L), and NAFDAC (0.01 mg/L) indicating health risk. Report from the four samples indicated the concentrations of Zn to be in the range 0.140±0,003 mg/L to 0.171±0.003 mg/L, which is below the permissible limits of USEPA (5.0 mg/L), WHO (5 mg/L), NAFDAC (5 mg/L), and SON (3.0 mg/L), and hence, no possible health risk. The results of the findings showed that the concentration of Cu is within the range of 0.212±0.027 mg/L to 0.761±0.012 mg/L and is found to be lower when compared to WHO (2.0 mg/L), NAFDAC (1.5 mg/L), USEPA (1.3 mg/L), and SON (1.0 mg/L). Mn ranged from 0.140±0.002 mg/L to 0.162±0.002 mg/L, below the standard that all the regulatory agencies set. Cd was found in the range of 0.200±0.001 mg/L to 0.231±0.231 mg/L and was found to be above all the regulatory agencies. Therefore, there is a need to take proactive action following the results of this research, which showed that concentrations of Pb and Cd in all the water samples analysed were detected above the permissible limits of the regulatory bodies, which is a potential health risk, either short-term or long-term, to the human body. The study further reviewed the fact that the bottled water analysed is of no significant quality compared to the river water.

Keywords: AAS, Health Conscious, Heavy Metal, Water Contamination.

1 Introduction

Water is one of the most critical resources for sustaining all life forms. Food production, economic development, and general well-being depend on water availability [1][2]. Even though it is a renewable resource, several anthropogenic and natural activities can distort the quality of surface water, which could result in the outbreak of diseases such as cholera and amoebic dysentery, among others. Therefore, water pollution and its effects cannot be overemphasized because they significantly impact the survival and health of people who depend directly or indirectly on a water source, especially among people living in rural communities. It is therefore safe to say that water is essential for life, and without water, there would be no life [3][4]. In the absence of pipe-borne water, however, especially in rural communities, water from the streams has become readily available to meet the needs of people, even though there are cases of seasonal dryness in some areas, which could negatively impact the people's lives and activities.

Water means several things to several people around the world, and clean water is a key factor for economic growth because water is needed for basically everything, from life itself to economic production, industrial uses, agricultural purposes, and a variety of domestic or household functions [5][6][3]. Khatun stated that water pollution has become a significant issue worldwide, especially in developing countries like Nigeria [7]. This is because many people see water bodies as an easy means of disposing of household waste. They dump their refuse along waterways, which are washed down into surface water bodies in times of rain. It is therefore pertinent to understand that even though surface and ground water are limited in size and volume, they still receive a significant amount of the pollutants generated from anthropogenic forces [8][9].

Sewage disposal, oil spillage, industrial waste dumps, municipal or domestic waste are other popular sources of waste pollution [8][10][4][1]. These practices are still prevalent in countries with no proper legislation and enforcement of environmental laws. Introducing these pollutants into water bodies can change the water's taste, colour, acidity, alkalinity, and turbidity. The concentration of minerals in water also determines its use and function because hard water has limited uses, especially for industrial purposes [11][12][3]. Human activities could also increase the concentration of salt in water. Odugbo is a small community in the Apa Local Government Area of Benue State and a home for over 1,000 people. The primary economic activity in this place is farming. Water scarcity has persisted due to the limited availability of groundwater. Water scarcity is usually prevalent during the dry season. This has prompted the community's people to depend on the stream that flows through the community as the primary source of their drinking water, especially during the dry season.

The Odugbo neighbourhood offers several sources of drinkable water, including river water, well water, multiple bottled water brands, and packed or sachet water. Nevertheless, river water is the primary source. To assess the concentrations of heavy metals in the products, it is essential to analyse the heavy metal content of water samples collected from the river or sold daily in the market within these communities, as there is a lack of literature indicating the quality of this water. Metal contamination may arise during potable water manufacture or packaging if quality control measures are not strictly followed in those sectors. Consequently, the quality of drinkable water must be assessed regularly, since heavy metal pollution over a certain threshold may be poisonous or harmful to the body via acute or chronic poisoning. This analysis may be performed using Atomic Absorption Spectroscopy (AAS) for metal determination in specific water samples. Thus, this study was conducted to analyse water samples to assess the safety of the community's drinking water sources. The main aim of this study is to determine the safety of specific water samples for consumption by analyzing their heavy metal concentrations, including Lead (Pb), Cadmium (Cd), Copper (Cu), Manganese (Mn), and Zinc (Zn).

2 Materials and Methods

2.1. Sample Collection and Preservation

A total of 30 samples of water were collected at three different locations, and 10 samples each from a particular area were composited 1 leaving three composite samples each representing the upper river location (L1), the middle river location (L2), the lower river location (L_3), and a sample of Bottled water. Each sample was kept in a plastic bottle to avoid a reaction with the metals in the water sample that was to be investigated. Each sample bottle was rinsed three times—first with the respective water sample, then with deionised water, and finally with diluted HNO_3 [13]. To get appropriate results, it is essential to maintain the samples gathered. Thus, the likelihood of volatilisation or biodegradation between sampling and analysis may be minimised by producing a slurry of ice and water for cooling at 4°C [14]. Engwa et al. indicate that metal ions, such as aluminium, cadmium, chromium, copper, lead, silver, and zinc, are prone to loss via ion exchange with the walls of glass containers or by adsorption [15]. To diminish precipitation and adsorption, samples were acidified with ultrapure HNO_3 to a ph below 2.0 by incorporating 3 ml of HNO_3 into 1 litre of sample [16]. The samples were labelled as follows: L1 (upper river water), L2 (middle river water), and L3 (lower river water).

2.2. Sample Preparation for AAS Analysis

Sample preparation is a crucial stage in analytical chemistry that requires careful attention to prevent mistakes or oversight. The methodology used by Magaji et al. (2023) facilitates sample preparation via the digestion of water samples for metal ion determination by atomic absorption spectrophotometry. A 50 ml volume of the acid-preserved sample was measured into a beaker and homogenised. A limited amount of glass particles and 5 ml of concentrated HNO_3 were added. Subsequently, it was progressively cooked and evaporated on a hot plate until the volume diminished to 10-20 ml. The sample was not allowed to dry, and a little volume of concentrated HNO_3 (a few ml) was introduced until digestion was completed. The receptacle was rinsed three times with deionised water. It was then filtered and transferred to a 100 ml volumetric flask, which was carefully mixed to get a final volume of 100 ml.

2.3. Sample Analysis for the Determination of Heavy Metals

The digested samples were taken to the Central Research Laboratory at Umaru Musa Yar'adua University, Katsina, Katsina state, for AAS determination of heavy metals, including Cadmium, Manganese, Zinc, Lead, and Copper. Three replicates were determined for each metal analysis, and the instrument was used to quantify the concentration of each metal. After digestion, the AAS machine was used to determine the presence and concentration of the metal analyte in the sample. The digested sample is aspirated into an air-acetylene flame, causing evaporation of the solvent and vaporisation of free metal atoms. This method is called atomisation. A light source (hollow cathode lamp) operating in the UV-visible spectra region is used to cause electronic excitation of the metal, and the absorbance is measured with a conventional UV-visible dispersive spectrometer with a photomultiplier detector.

3 Results and Discussion

This section presents the concentrations of five heavy metals (Pb, Zn, Cu, Mn, and Cd) in the analyzed water samples (L1, L2, L3, and bottled water). The results are compared with permissible limits set by regulatory bodies such as the WHO, USEPA, SON, and NAFDAC, and their potential health impacts are discussed. Table 1 presents the mean amounts of lead in the water samples: L1, L2, L3, and bottled water, measured in mg/L. The table's findings indicated L1 (0.852±0.021 mg/L), L2 (0.561±0.002 mg/L), L3 (0.521±0.020 mg/L), and bottled water (0.411±0.001 mg/L). All these readings exceeded the local and international legal limits for drinking water established by United States Environmental Protection Agency (USEPA) (0.015 mg/L), WHO (0.01 mg/L), and Standards Organisation of Nigeria (SON) (0.01 mg/L), as seen in Fig. 1. The findings indicate a significant health risk in all water samples due to the harmful properties of lead on human health.

The average content of zinc (Zn) in the water samples, measured in mg/L, is shown in Table 2. The results indicated L1 at 0.158±0.003 mg/L, L2 at 0.140±0.003 mg/L, L3 at 0.140±0.003 mg/L, and bottled water at 0.171±0.003 mg/L. Upon comparison with Table 6 and Fig. 1, these findings were all determined to be below the regulatory standards established by governing organizations. Consequently, no potential health risks are associated with zinc in any of the examined water samples. Table 3 presents the mean copper (Cu) content in the four water samples, measured in mg/L. The findings indicated the copper concentrations in the samples as follows: L1 (0.751±0.023 mg/L), L2 (0.212±0.027 mg/L), L3 (0.212±0.027 mg/L), and bottled water (0.761±0.012 mg/L). In comparing the thresholds of local and international standards for drinking water quality, all values recorded in the four samples were below the established limits: WHO (2.0 mg/L), National Agency for Food and Drug Administration and Control (NAFDAC) (1.5 mg/L), USEPA (1.0 mg/L), and SON (1.0 mg/L), as seen in the figure. Consequently, copper in the examined water samples has no potential health risks.

Table 4 presents the mean manganese (Mn) values in the four water samples, measured in mg/L. The findings indicated the manganese contents in the samples as follows: L1 (0.141±0.003 mg/L), L2 (0.162±0.002 mg/L), L3 (0.141±0.003 mg/L), and bottled water (0.1400±0.002 mg/L). In comparing the thresholds of local and international standards for drinking water quality, all values recorded in the four samples were below the established limits, except for the results from WHO and NAFDAC, as shown in Table 6 and Fig. 1. The suitability of the samples for consumption concerning manganese remains uncertain.

The average concentration of cadmium (Cd) in mg/L in the water samples is shown in Table 5. The results indicated L1 (0.221±0.002 mg/L), L2 (0.230±0.003 mg/L), L3 (0.231±0.003 mg/L), and bottled water (0.200±0.001 mg/L). Upon comparison with Figure 1, these data were determined to exceed the standard limitations established by regulatory authorities. This level of contamination poses both short- and long-term health risks to the population. Table 6 delineates the permissible thresholds for the five heavy metals in the examined water samples, as USEPA, WHO, NAFDAC, and SON established. These values function as reference standards for comparison with the concentration observed in the samples examined. This table provides a straightforward means for comparison and facilitates the derivation of potential conclusions.

Table 1. The Mean Concentration of lead (Pb) in the Samples in mg/L

S/N	Samples	Concentration of Pb	SD	RSD %
1	L_1	0.852	0.021	2.47
2	L_2	0.561	0.022	3.87
3	L_3	0.521	0.020	3.80
4	Bottled water	0.411	0.001	0.26

Table 2. The concentration of Zinc (Zn) in the samples in mg/L

S/N	Samples	Concentration of Zn	SD	RSD %
1	L_1	0.158	0.003	1.53
2	L_2	0.140	0.003	1.96
3	L_3	0.140	0.003	1.96
4	Bottled water	0.171	0.003	1.77

Table 3. The mean concentration of copper (Cu) in mg/L

S/N	Samples	Concentration of Cu	SD	RSD %
1	L_1	0.751	0.023	2.47
2	L_2	0.212	0.027	3.87
3	L_3	0.212	0.027	3.80
4	Bottled water	0.761	0.012	0.67

Table 4. The mean concentrations of manganese in mg/L

S/N	Samples	Concentration of Mn	SD	RSD %
1	L_1	0.141	0.003	2.23
2	L_2	0.162	0.002	1.20
3	L_3	0.141	0.003	2.23
4	Bottled water	0.140	0.002	0.67

Table 5. The mean concentrations of cadmium (Cd) in the samples mg/L

S/N	Samples	Concentration of Cd	SD	RSD %
1	L_1	0.221	0.002	1.96
2	L_2	0.230	0.003	1.11
3	L_3	0.231	0.003	1.10
4	Bottled water	0.200	0.001	0.26

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Table 6. The Permissible limits of heavy metals in drinking water (mg/L) by some regulatory bodies [17][18][19]

METALS	USEPA	WHO	SON	NAFDAC
Pb	0.015	0.01	0.01	0.01
Zn	5.0	3.0	3.0	5
Cu	1.3	2.0	1.0	1.5
Mn	0.3	0.05	0.2	0.05
Cd	0.005	0.003	0.003	0.003

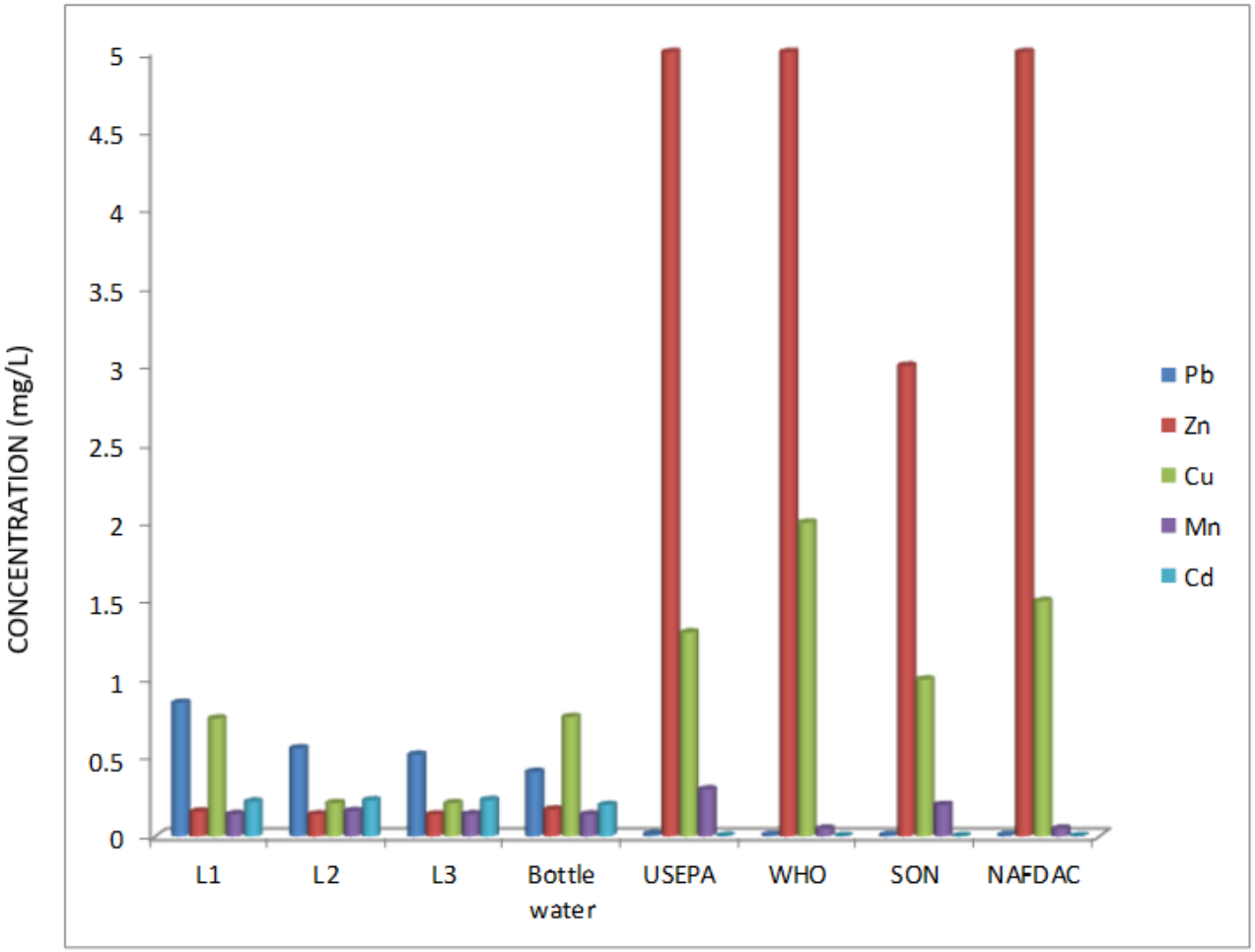

Fig. 1. Comparison of mean concentrations of Pb, Zn, Cu, Mn, and Cd in water samples against regulatory standards

The heavy metal analysis findings shown in Tables 1-5 illustrate the impact of the AAS approach on the examined water samples. The dispersion of individual data around the mean is characterised by the mean concentration of metals in mg/L, the standard deviation (SD), and the percentage relative standard deviation (RSD) shown in the tables. The actual mean lies within the range of $\boldsymbol{\mu = x + S.D}$

Therefore, the figures that fall beyond this range are probable errors. Any figure that lies beyond this range may be deemed a mistake. Subsequent statistical analyses lead to a decision to accept or reject these data at a designated confidence level, depending upon the degree of variance. The standard deviation is often expressed in the same unit as the mean. The relative standard deviation (RSD) is a specific version of the standard deviation (standard dev), according to Everitt et al. [20]. It is conventionally represented with two decimal places (e.g., 3.98 for an RSD of 3.9787878). The RSD consistently produces a positive number, as the denominator is the absolute value of the mean. The RSD compared the mean of the dataset to the standard deviation, irrespective of the quantity's size. For example, if the mean of an experiment is 0.141 and the standard deviation is 0.003. The RSD for this set of numbers is 2.13 %. The data is not markedly different from the mean. In contrast, a large proportion, such as 50%, would indicate that the identified data is more distributed. The RSD, sometimes used for convenience, suggests the accuracy of the experimental results. Consequently, the magnitude of RSD is inversely related to the dependability of the observed mean data. This indicates that the value's reliability diminishes as the RSD rises. The relative standard deviation (RSD) is typically expressed alongside the mean using a plus/minus format—for example, 0.141 ± 2.13%.

In some cases, the coefficient of variation and the relative standard deviation (RSD) are synonymous. The RSD cannot be negative, but the Coefficient of Variation may be positive or negative. This is attributable to the little differences between the two formulations. The RSD is calculated by dividing the standard deviation by the absolute value of the mean. In contrast, the Coefficient of Variation is derived by dividing the standard deviation by the mean. The relative standard deviation of a data collection may be represented as either a percentage or a numerical figure. The RSD Horwitch function stipulates that the maximum allowable relative standard deviation for concentrations 1000 mg/L or below is 10% [21]. The analysis exhibited satisfactory repeatable accuracy, with relative standard deviation values within the acceptable range, as shown by the standard deviations (% RSD) in Tables 1-5 below 10% [13].

4 Conclusions

The reports from this research showed that Pb was detected above the regulatory limits of USEPA, WHO, and SON, and in all three water samples from the three different river locations, including Bottled water. This discovery, which poses both short- and long-term risks to human health, should be a matter of concern to relevant bodies to identify the source of the pollutant and proffer solutions. A similar investigation had reviewed that the concentrations of Zn in all the samples of water verified had their levels below the permissible limits of drinking water set by USEPA and SON, as WHO set no value, and hence, no health risk is associated with the presence of Zn. The results of the detection of the amount of Cu present in the four samples of water showed that the concentrations were all below the drinking limits set by USEPA, WHO, and SON. Hence, this does not pose a health risk to the community, as was reported in Pb.

The study showed that the level of Mn detected in the water samples was below the limits set by USEPA and SON but above the limit of WHO for drinking water. This situation cannot tell whether or not the water is fit for drinking, considering the disagreement in the values by the regulatory bodies concerning Mn. Finally, the report from the study for the detection of Cd indicated that the concentration of Cd in the samples was all found above the limits set by USEPA, WHO, and SON, making the water unsafe for drinking. The study confirmed that Pb and Cd concentrations exceeded tolerable limits, hence the need for caution and action. This research has shown that the Bottled water was not significantly better than the river Odugbo, which serves as the primary source of drinking water during the dry season. Similar work carried out by Elsai *et al*. [22] in Ethiopia found that the levels of the heavy metals: Pb (1.92 mg/L), Zn (1.25 mg/L), Cu (0.40 mg/L), Mn (0.45 mg/L), and Cd (0.06 mg/L) in the drinking water analysed were found to be higher than the results obtained in this study except for Cd and Cu. The research found that Pb, Mn, and Cd concentrations were higher than the WHO standard for maximum tolerable limits.

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ETHICS STATEMENT

This study did not involve human or animal subjects and, therefore, did not require ethical approval.

STATEMENT OF CONFLICT OF INTERESTS

The authors declare no conflicts of interest related to this study.

LICENSING

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