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Abstract

Clean water is the most important inorganic substance for plants and animals, including humans, and the life of all living organisms depends on it. However, water is not naturally found pure, but always contains foreign components. In this study, seven commercial bottled water brands (ranging from 60 to 75 cL) were sampled across Awka city in Anambra State, Nigeria, to determine the concentration of six heavy metals (Manganese, Cadmium, Nickel, Chromium, Lead, Zinc) and evaluate their potential health risks to human consumption. The concentration ranges (in ppm or mg/L) for Mn, Cd, Ni, Cr, Pb and Zn were: 0.047 - 0.297, 0 – 0.024, 0.024 – 0.068, 0.012 – 0.056, 0.010 – 0.030 and 0.010 – 0.016 respectively. The heavy metals (HMs) concentration in this study was compared with other national and international studies on bottled water and other drinking water sources. Additionally, the results of non-carcinogenic health risk assessments using the Hazard Index (HI) and the Incremental Lifetime Cancer Risk (ILCR) indicated that the concentration of HMs in many of the samples pose adverse health effects (particularly in children than in the adults), especially as they bio-accumulate. This then suggests that the consumption of these bottled water brands may result to carcinogenic risks over a lifetime, particularly in children due to their lower body weight. Furthermore, this study contributes to the monitoring of SDG 6 (Clean Water and Sanitation) and SDG 3 (Good Health and Well-being) by identifying critical contamination pathways and evaluating the safety of commercial drinking water in urbanized African settings.

Keywords: Bottled water, Heavy metals, Health risk assessment, Carcinogenic, trace metals

1. Introduction

Water is a vital component in all organisms' life, and serves a crucial purpose in life sustenance on earth as well as supporting numerous vital functions, which includes production of food and energy, socioeconomic development, as well as the healthy ecosystems maintenance (Sanad et al. 2025). However, numerous undertakings of human beings lead to the degradation of the

environment (Okoye et al. 2025), including depletion of water quality sources. Such undertakings has led to the release of hazardous substances like heavy metals (HMs) into the environment.

HMs refers to metallic elements with high molecular weight and density in comparison to water (Piñeiro et al. 2021, Kinuthia et al. 2020). These metals exhibit poor solubility in water (Soliman et al. 2015, Algül and Beyhan 2020), and are naturally introduced into the environment through lithogenic processes and human activities (Rezapour et al. 2022). These metals in the natural environment are broadly considered as some of the most hazardous contaminants, due to their poisonousness, persistence, as well as accumulation tendency in living organisms (Bhuyan et al. 2023). Their poisonousness, bioaccumulation, non-biodegradability as well as cancer-causing nature, pose a noteworthy threat to the health of both humans and the aquatic ecosystem. These make their worldwide presence in water a chief environmental concern (Aziz et al. 2023). World Health Organization (WHO) opines that HMs are possibly cancer-causing and their potential exposure arises from ingestion or interaction with the residue of HM in water, animals and plants (Kawichai et al. 2023). Also United States Environmental Protection Agency (EPA) of the United States of America as well as the International Agency for Research on Cancer (IARC) opines that these HMs are also categorized as human cancer-causing agents that are “known” or “probable”, established on epidemiological as well as experimental surveys which reveals a relationship between cancer occurrence as well as exposure in human beings and animals (Tchounwou et al. 2012).

Among the most well-known HMs are arsenic (As), lead (Pb), mercury (Hg), cadmium (Cd), nickel (Ni) and chromium (Cr) (Qasem et al. 2021), of which As, Pb, Cd and Cr are not biodegradable (Sarker et al. 2022). These HMs are still hazardous even when detected in trace amounts (Qasem et al. 2021). Numerous severe as well as chronic poisonous effects of HMs affect different organs of the body. Disorders of the nervous system, Gastrointestinal as well as kidney dysfunction, vascular damage, skin lesions, dysfunction of the immune system, cancer as well as birth defects are instances of HMs toxic effects complications (Balali-Mood et al. 2021).

Recent studies (Alam, 2021; Olowoyo et al. 2022; Mirzaei et al. 2023; Ungureanu et al. 2022; Alhagri et al. 2024) have determined the heavy metals content in bottled water globally, however localized research in West African hubs remains largely limited. For instance, Nwasinobi et al. (2025) recently assessed heavy metals content in bottled drinking water sold in Awka metropolis: which only compared the physicochemical values gotten in the bottled water samples with standard level.

Consequently, a critical gap exists regarding comprehensive carcinogenic and non-carcinogenic health risk assessments. This lack of risk-based data is a significant oversight, as ensuring drinking water safety is fundamental to achieving United Nations Sustainable Development Goal (SDG) 6 (Clean Water and Sanitation). Furthermore, quantifying ingestion-based carcinogenic risks is essential for monitoring progress toward SDG target 3.9, which aims to reduce illnesses from hazardous chemical pollution.

This study, therefore, aims to bridge this gap by utilizing multivariate statistical modeling (PCA and HCA) to apportion sources of heavy metal contamination and determine the age-specific

health risks (adults vs. children) associated with commercial bottled water consumption in an urbanizing metropolitan hub of Awka city.

2. Materials and Methods

2.1. Study area, Sample collection, preparation and heavy metals analysis

Awka town is situated in the eastern part of Anambra State, in South-East Nigeria (Ezenwaji et al. 2017), and it's located between Longitude $7^0.04^1$E and $7^0.09^1$E and latitudes $6^0.11^1$ N and $6^0.15^1$N (Ezenwaji et al. 2017). One of the city's source of drinking water is bottled water, supplied from commercial dealers of bottled water, which situated their companies within and outside the city. Urban expansion has increased the potential for anthropogenic contaminants leaching into the water supply chain, necessitating a source apportionment approach to distinguish between these lithogenic and industrial inputs.

A total of 42 bottled water samples (60-75 cL volumes) from 7 different bottled water brands, namely: Aquafina water (AQ), Ivy water (IV), Nestle purelife water (NE), Eva water (EV) Lasena water (LA), Mangero water (MA) and Swam water (SW) were used for this study. Six samples for each brand, were randomly purchased from some local shops, stalls, and supermarket shops in Awka city. These samples were collected using a "market-basket" approach (which is to randomly purchase items from retail vendors without filtering for specific batch numbers or production dates). This pattern helps to represent the typical chemical exposure of the urban population in Awka, and to prioritize an assessment of the overall brand quality as encountered by the day-to-day consumer at the point of sale. They were then placed inside a container which contains ice blocks; and then taken to the lab for analysis. 50 mL of the 6 bottles of each brand were mixed into a composite form. This was done for the seven selected brands. Then 100 mL of the composite was taken out, placed in a 250 mL beaker and 1 mL of conc. nitric acid was added and heated to boil till the volume is reduced to about 15-20 mL. The mixture was cooled. The sample was aspirated into the oxidizing air-acetylene flame. When the aqueous sample is aspirated, the sensitivity for 1% absorption is observed. The metal analysis was conducted using Varian AA240 Atomic Absorption Spectrophotometer according to the method of APHA (1998). In addition, validation of the method such as the limit of quantification (LOQ) and limit of detection (LOD) were carried out, as seen in tables 1 and 2. Also, triplicate measurement (as seen in Supplementary Table ST6) for precision and accuracy were determined.

Table 1: limit of quantification (LOQ) and limit of detection (LOD) factors

Parameters	Detection limit (LOD)	Limit of Quantification (LOQ)
Mn	0.0001 ppm	0.0003
Cd	0.0003 ppm	0.0009
Ni	0.0001 ppm	0.0003
Cr	0.0002 ppm	0.0006
Pb	0.0001 ppm	0.0003
Zn	0.0002 ppm	0.0005

Table 2: Percentage recovery of the HMs from the bottled water samples

Samples	Mn ppm		Cd ppm		Ni ppm		Cr ppm		Pb ppm		Zn ppm	
	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd
Unspiked sample (ppm)	0.4	0.72	0.24	0.29	1.98	1.87	0.22	0.25	2.76	2.70	0.298	0.280
Original conc. Spiked (ppm)	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
% recovery	84.3	83.5	88.5	87.9	89.1	90.6	88.5	88.2	91.3	84.1	89.82	91.9

2.2. Heavy metal pollution/evaluation indices (HPI and HEI)

Heavy metal pollution and risk analysis was conducted to quantify contamination levels and evaluate potential non-carcinogenic health effects via water ingestion. Mathematical tools are effective for evaluating heavy metal pollution levels, with heavy metal pollution index (HPI) and the heavy metal evaluation index (HEI) being the most common methods globally (Dippong and Resz, 2024). HPI was proposed by Horton, which uses measured heavy metal levels in water samples to calculate the heavy metal pollution index, referencing regulatory guidelines for different water types and uses (Dippong et al. 2023).

$$HPI = \frac{\sum_{i=1}^{i=n}(Q_i \times W_i)}{\sum_{i=1}^{i=n} W_i} \quad (1)$$

$$\text{Where } Q_i = \sum_{i=1}^{n} 100 \times \frac{C_i - I_i}{G_i - I_i} \quad (2)$$

$$\text{Then } HEI = \sum_{i=1}^{n} \frac{C_i}{G_i} \quad (3)$$

Q_i = sub-index of the i^{th} heavy metal, W_i = the weight for each heavy metal, C_i = measured heavy metal, G_i = guideline value for the heavy metal, I_i = ideal value of heavy metal. From Preonty et al. (2025), HPI calculated values for the quality of drinkable water was classified as follows: HPI < 25 = excellence; 26–50 = good; 51–75 = poor; 76–100 = very poor; HPI > 100 = unsustainable for consumption. HEI calculated values are categorized as follows: HEI < 10 = low; 10 < HEI < 20 = medium; HEI > 20 = high.

2.3. Potential ecological risks (ERI and RI) assessment

The ecological risk (ERI) and potential ecological risks (RI) indices of HMs in the bottled water were calculated using the following equation:

$$ERI = \sum RI = \sum T_i \times PI = \sum T_i \times \frac{C_{HM}}{C_b} \quad (4)$$

Where Ti is the toxic-response factor of the PTE, C_{HM} is the concentration of heavy metals in the bottled water brand sample, PI is the pollution index, C_b is the background value. The values of Ti for the HMs are as follows: (5) Pb, (30) Cd, (5) Ni, (1) Zn (Onwordi et al. 2024, Hakanson 1980)

(1) Mn, (2) Cr (Kolawole et al. 2018) while the C_b are as follows: 0.3 for Cd, 20 for Pb, 90 for Cr, 68 for Ni, 95 for Zn and 850 for Mn (Turekian and Wedepohl 1961). RI has range and classification values as follows: <40 for Low, 40 ≤ RI < 80 for Moderate, 80 ≤ RI < 160 for Considerable, 160 ≤ RI < 320 for High, ≥320 for Very High. ERI's values for classification and range are as follows: ERI<150 for Low, 150 < ERI < 300 for Moderate, 300 < ERI < 600 for Considerable, >600 for Very High. (Onwordi et al. 2024)

2.4. Human health risk assessment

2.4.1. Hazard quotient

$$HQ = \frac{DDI}{RfD} \quad (5)$$

In equation (5): HQ = Hazard quotient, DDI = Daily dosage intake (mg/kg/day), RfD = Reference dose. HQ was used to determine the non-cancerous values. When HQ < 1, then the value represent an insignificant non-cancerous risk for the populace under study. But when HQ > 1, a significant health risk for the population (Mirzaei et al. 2023).

2.4.2. Daily dosage intake (DDI)

$$DDI = \frac{C \times IR \times EF \times ED}{BW \times AT} \quad (6)$$

In equation (6): C = metal concentration (for Pb, Mn, Cd, Cr, Zn and Ni metals) (mg/kg), IR = Daily ingestion rate (L/day), EF = Exposure frequency (day/year), ED = Exposure duration (years), BW = Body weight for children and adults, AT = Average exposure time (day)

2.4.3. Hazard index (HI)

$$HI = \sum_{k=1}^{n} HQ = HQ_{Pb} + HQ_{Mn} + HQ_{Zn} + HQ_{Cr} + HQ_{Cd} + HQ_{Ni} \quad (7)$$

In equation (7): HI = Hazard index (which shows the non-cancer effect of the HMs). If the amount of HI < 1 = no significant impact of non-cancerous disease. If HI > 1 = significant health impact of non-cancerous disease (Mirzaei et al. 2023).

2.4.4. Incremental lifetime cancer risk. ILCR

Furthermore, carcinogenic risk from equation (8), was stated as the ILCR, being the incremental lifetime cancer risk. ILCR is the probability of a person having cancer that may develop over a 70-year period/lifetime as a result of a 24-hour daily exposure to potential carcinogens. According to USEPA the least or tolerable carcinogenic risk for regulatory purposes to fall within the range of 1×10^{-6} to 1×10^{-4} (Ugwu et al. 2022).

$$ILCR = DDI \times CSF \quad (8)$$

In equation (8): ILCR = Incremental lifetime cancer Risk, CSF = cancer slope factor (mg/kg/day). The values of all the parameters are supplied in supplementary table ST1.

2.5. Statistical analysis

Multivariate source apportionment was conducted using IBM SPSS (v.20) via Principal Component Analysis (PCA) with Varimax rotation and Scree plots to identify latent metal sources. R (version 2026.01.0+392) Software was utilized for advanced visualizations, specifically generating Dendrogram for hierarchical clustering and Pheatmap to illustrate concentration gradients across brands. Quantitative toxicological and deterministic risk indices, including HPI, HEI, HQ, and HI, were systematically computed using Microsoft Excel. Probabilistic health implications for Incremental Lifetime Cancer Risk (ILCR) were modeled via Monte Carlo Simulation (MCS) in R to quantify uncertainty in carcinogenic exposure parameters. All statistical relationships were validated through these integrated platforms to provide a robust assessment of trace metal risks for the Awka urban population.

2.6.Use of AI-Assisted Technologies

During the preparation of this manuscript, Artificial Intelligence (AI) tool (Gemini AI from Google Chrome) was used to assist in drafting and refining the research topic, drafting portions of the abstract and methodology, and providing initial framework draft for the interpretation of results in the discussion, as well as the conclusions. Following this process, all generated content was manually reviewed, revised, and validated to ensure scientific accuracy. The authors take full responsibility for the final manuscript.

3. Results and Discussion

3.1. Concentrations of heavy metals in bottled water

Table 3: HMs concentrations in the bottled water brands (AQ, IV, NE, EV, LA, MA and SW) in mg/L

Bottled water Name	Sample ID	Mn	Cd	Ni	Cr	Pb	Zn
		mean ± SD	**mean ± SD**	**mean ± SD**	**mean ± SD**	**mean ± SD**	**mean ± SD**
Aquafina	**AQ**	0.138 ± 0.027	0.024 ± 0.004	0.024 ± 0.001	0.024 ± 0.001	0.023 ± 0.001	0.015 ± 0.002
Ivy	**IV**	0.297 ± 0.002	0.000 ± 0.000	0.063 ± 0.003	0.044 ± 0.001	0.015 ± 0.001	0.011 ± 0.001
Nestle pure life	**NE**	0.288 ± 0.009	0.000 ± 0.000	0.042 ± 0.004	0.013 ± 0.001	0.022 ± 0.001	0.010 ± 0.000
Eva	**EV**	0.047 ± 0.006	0.000 ± 0.000	0.062 ± 0.017	0.027 ± 0.001	0.010 ± 0.000	0.016 ± 0.001
Lasena	**LA**	0.247 ± 0.044	0.022 ± 0.009	0.053 ± 0.001	0.056 ± 0.002	0.017 ± 0.001	0.010 ± 0.001
Mangero	**MA**	0.167 ± 0.029	0.008 ± 0.001	0.061 ± 0.004	0.022 ± 0.001	0.030 ± 0.001	0.014 ± 0.001
Swan	**SW**	0.272 ± 0.018	0.006 ± 0.001	0.068 ± 0.005	0.012 ± 0.000	0.014 ± 0.001	0.014 ± 0.001
	Mean Range	0.047 - 0.297	0 – 0.024	0.024 – 0.068	0.012 – 0.056	0.010 – 0.030	0.010 – 0.016
	WHO(2022) limit	0.080	0.003	0.070	0.050	0.010	3.000

Table 3, Fig 1 describe the individual HM concentrations in the composite bottled water brands. Table 3 is calculated with the values from the supplementary table ST6 which shows the complete triplicate values of the heavy metal concentrations (mg/L) results from the selected bottled water brands. From Table 3, the concentration (mg/L) of the HMs in comparison with the WHO (2022) limit were stated. From the table, Manganese (Mn) metal was highest in bottled water brand IV but least in AQ. Six out of seven bottled water samples exceeded the WHO provisional health-

based standard/limit for Mn of 0.08 mg/L, in the following trend: IV > NE > SW > LA > MA > AQ > EV. Brands IV (0.297 mg/L) and NE (0.288 mg/L) had the highest values, showing concentrations nearly 4 times the WHO limit. However, Brand EV (0.047 mg/L) fell within the acceptable limit. The common nature of high Mn readings suggests that many producers may be sourcing water from groundwater sources with naturally high Mn levels without adequate treatment to reduce these concentrations. Also the water treatment method (by using $KMnO_4$) may also have contributed to the reason for the high amount of Mn in these bottled water brands. A study conducted by Umoafia et al. (2023) showed that increase of HMs was also as a result of the leaching of the metals into the PET (polyethylene terephthalate) bottles, which is brought about by exposing these bottles to sunlight. Mn can cause aesthetic problems which includes black-brown discolouration as well as unwanted taste plus odour (Pearl et al. 2025). Also, Mn being a well-known neurotoxin (Van-Wendel-De-Joode et al. 2016) can cause neurological issues in high amount in drinking water (Pearl et al. 2025).

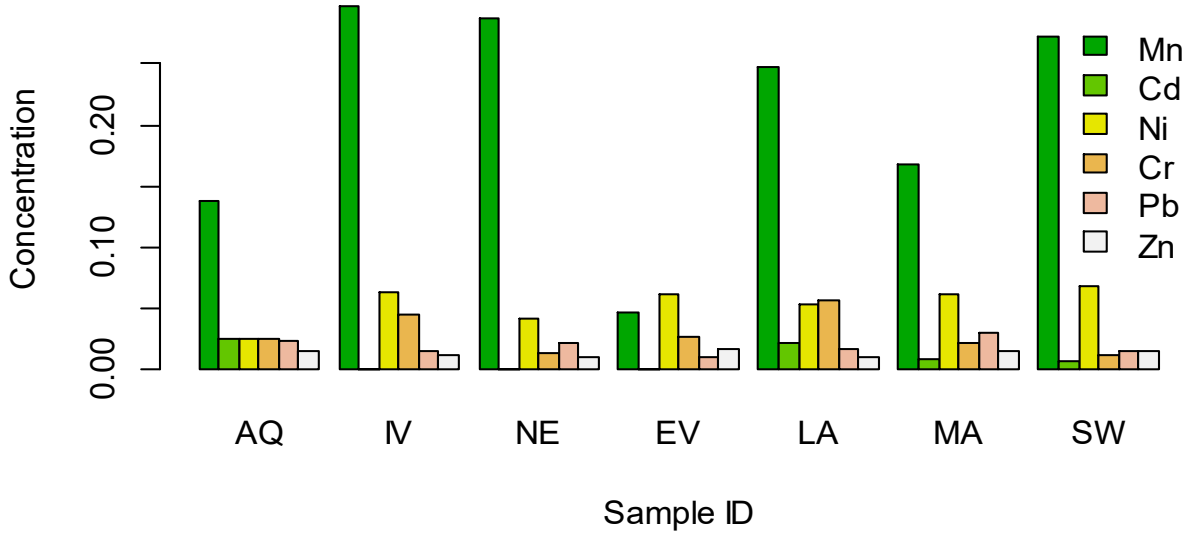

Fig 1: Individual Heavy Metal Concentrations (mg/L) per bottled water

Cadmium (Cd) metal has WHO guideline value of 0.003 mg/L. Four of the bottled water samples (AQ, LA, MA and SW) had concentrations of Cd above the acceptable limit. Brand AQ had the highest reading at 0.024 mg/L which is eight times the maximum acceptable concentration. IV, NE, and EV had zero Cd values. The possible reason for the significant level of the Cd could be traced to the fact that Cd being a pollutant can be introduced into the environment due to rapid industrial development as well as modern technologies (Genchi et al. 2020). Also pipeline corrosion as well as leaching from bottles can contribute to the presence or increase of the Cd Annibaldi et al. (2018). The following are cadmium induced cancer-causing mechanism: decreased capacity for DNA repair, reactive oxidative stress, epigenetics, apoptosis attenuation, DNA damage, gene expression alteration, abnormal DNA methylation, proliferation of cell as well as inflammatory process induction (Genchi et al. 2020). Also Cd exposure is linked to the following diseases, namely: Various cancers (like pancreatic, prostrate, bladder, breast as well as cancer of the kidney), chronic lung diseases and high blood pressure (Rasin et al. 2025).

Chromium (Cr) has WHO acceptable limit of 0.05 mg/L. All the samples have concentrations below the WHO limit, except LA (with value 0.056 mg/L). This suggests a possible quality control

issue for this specific brand regarding chromium levels: that is, the processes used to source, treat, or bottle LA specific brand might need review to ensure all batches comply with safety regulations. According to Monga et al. (2022), the toxicity of Cr in human beings differs contingent on the compound's chemical nature, the oxidation state as well as exposure route (Monga et al. 2022). In the environment, Cr exists in two stable oxidation states of Cr^{3+} and Cr^{6+}; with Cr^{3+} being less toxic than Cr^{6+}. In the course of industrial operations, the two ions can interconvert (Mitra et al. 2022). Owing to the Cr^{6+} high toxicity as well as carcinogenic properties, IARC (International Agency for Research on Cancer) has affirmed it as group 1 human carcinogen (Khan et al. 2024). Also Cr^{6+} is itemized in the Agency for Toxic Substances and Disease Registry (ATSDR) priority list of pollutants at seventeenth rank (Handa and Jindal, 2021). Cr exposure (mostly the Cr^{6+}) have been connected with liver, kidney, gastrointestinal tract, widespread dermatitis, respiratory tract cancer, cardiovascular disorder, and so on (Chakraborty et al. 2022).

The WHO guideline for Lead (Pb) is set at 0.01 mg/L, reflecting its status as a severe neurotoxin with no safe level of exposure. EV is at the WHO guideline limit. AQ, IV, NE, LA, MA, and SW all exceed the WHO limits. MA has the highest concentration at 0.030 mg/L, which is three times the WHO limit. A study carried out by Kusa and Joshua (2023) showed a mean range of Pb in 100 samples of 5 brands of sachet water to fall between 0 and 0.02 mg/L, which showed that (like this current study) Pb metal went above the standard limit in the water samples while some of the water samples had values lower than the WHO limit. Human beings ingest three thousand and sixty percent of lead (Raj and Das, 2023); and WHO (2024) postulated that exposure to Pb is not safe at any level (Gonzalez-Villalva et al. 2025). Drinking water is a source of Pb exposure in humans (Kumar et al. 2020), as one of the primary sources to Pb exposure is plumbing systems' aging, which then persist in polluting drinking water (Generalova et al. 2025). High blood pressure, gastric cancer, lung cancer, decreased intelligence quotient, anaemia, adults' as well as children's physical and mental retardation are the effects of Pb on the human heath (Eslami et al. 2022). Also, in males, Pb can cause low sperm count, affects the sperm's morphology as well as sperm's motility. Lead's high exposure in females, on the other hand, can result in preterm birth, miscarriage, low birth weight, fetus spontaneous abortion (Collin et al. 2022).

Nickel (Ni) element was another metal determined; which has a guideline value limit of 0.07 mg/L. From the result gotten, the seven brands had values that fell below the WHO acceptable limit. The highest reading was in SW (0.068 mg/L) while the lowest was in AQ (0.024 mg/L). When compared to other metals, Ni does not appear to be a major pollution concern in these specific brands. However, from Gates et al. (2023), Ni has the potential to leach from pipes, and when ingested, cause vomiting, abdominal pain, nausea and diarrhea. Chronic exposure can result to bronchitis, asthma as well as rhinitis. Even, there have been report of pulmonary as well as nasal cancer occurrences.

The WHO aesthetic guideline for Zinc (Zn) is 3 mg/L, because no health-based limit exists. All samples recorded very low, negligible levels of zinc (around 0.01−0.016 mg/L). Zinc levels in these brands are perfectly safe and well below the threshold for taste or appearance concerns. In the early 1960 zinc was known as an essential trace metal for human being, and the toxicity of zinc is rare (Huang et al. 2025). Toxicity of Zinc element hinges on method as well as amount of exposure. Major sources of Zn are mining and smelting. Mineral processing operations release

huge quantity of Zn into the environment, which subsequently impacts on both ecosystems and living organisms (Mitra et al. 2022).

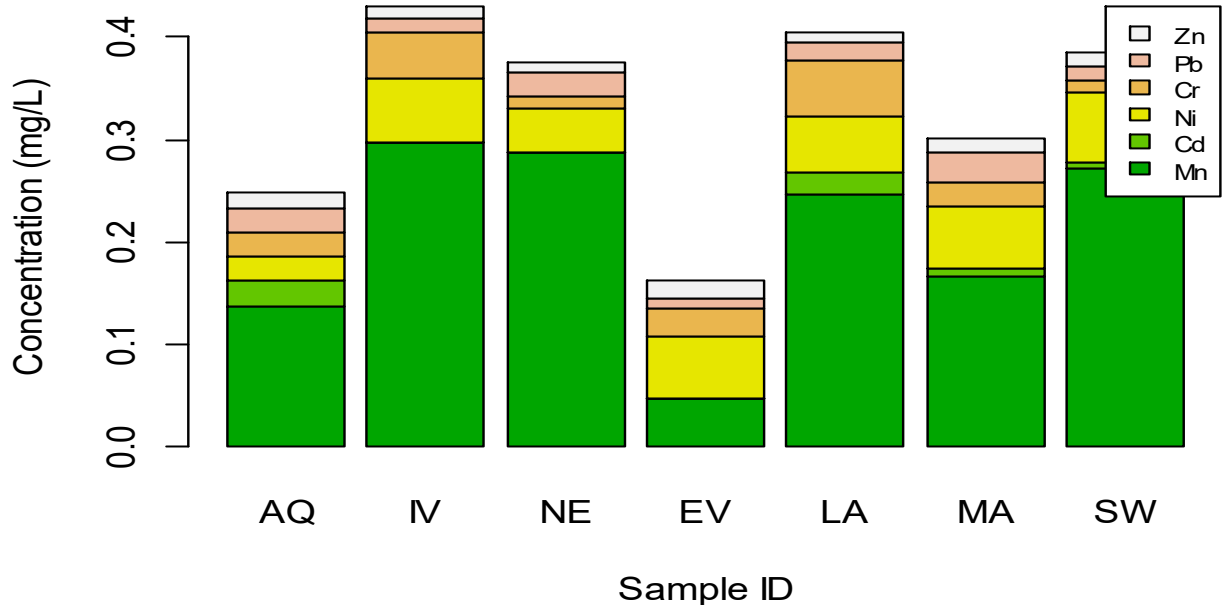

Fig 2: Stacked Bar Chart of the Total Cumulative HM Concentration for each bottled water brand

This stacked bar chart of Fig 2, generated in R, visually confirms that Mn is the primary trace metal contributor across all brands, particularly in Ivy (IV), Nestle (NE), and Swan (SW). That is, the stacked bar chart highlighted a dominant presence of Mn across the sampled brands, accounting for the largest share of the total trace metal concentration. While Eva (EV) maintained the lowest overall metal profile, brands such as Ivy (IV) and Lasena (LA) showed elevated levels of Ni and Cr. The persistent presence of Pb and Cd, though in smaller visual proportions, represents a significant toxicological concern given their low permissible safety thresholds

Table 4 shows similar research on heavy metal concentrations in portable water sources. The concentrations of Mn in the current study (0.047 – 0.297 mg/L) was higher than values on bottled water reported by Alam (2021) in Indonesia 0.0006 -0.0009 mg/L); but fell within the values of those determined by Hossain et al. (2025) in wells from Dhaka district, Bangladesh (0.203 mg/L) and Olowoyo et al. (2022) in Pretoria, South Africa (0.017 – 0.269 mg/L). Also for values for the current study went above the values of HMs in sachet water by Emenike et al. (2017) in Ogun, Nigeria, as well as those gotten by Liu et al. (2022) in Wuhan China, in surface and tap water respectively.

The Cd concentration values in the current study went above those gotten in bottled water by Olowoyo et al. (2022) in Pretoria, South Africa, Mirzaei et al. (2023) in Kashan, Iran. However the value of Cd in bottled water by Alam (2021) went below detectable limit. Cd concentration in the sachet water by Taiwo et al. (2023) in Ogun, Nigeria, Orisakwe et al. (2006) in Eastern Nigeria all fell within the value gotten in this study. However, Ugwu et al. (2022) in Anambra, Nigeria,

had Cd concentration in sachet water that went above those gotten in the current study. Russo et al. (2022) in Italy and Liu et al. (2022) in Wuhan, China, had Cd values in tap water that fell below those gotten in this study. Also, Liu et al. (2022) had Cd values that fell below the ones in this study. Values of Cd in borehole water, shallow well, harvested rain and stream water by Ugwu et al. (2022) in Anambra State and Latif et al. (2025) in his study of HMs in groundwater in Kasur, Pakistan both had values that went above the ones in this study. Hossain et al. (2025) in wells from Dhaka district, Bangladesh had Cd value that fell within the values of those determined.

Ni concentrations in different water sources by Mirzaei et al. (2023) in Iran, by Hossain et al. (2025) in wells in Bangladesh, Russo et al. (2022) in Italy, Liu et al. (2022) in China and Ghaderpoor et al. (2018) in Iran had concentrations that fell below those studied. However in the study of Ni concentrations in sachet water by Orisakwe et al. (2006) in Nigeria and in bottled water by Olowoyo et al. (2022) in South Africa, have values that respectively fell within and above the ones in this study.

For Cr, the concentration in this work was higher than those in bottled water samples which was reported by Mirzaei et al. (2023) in Iran. However the result of Cr in bottled water by Olowoyo et al. (2022) in South Africa had values higher than those reported in this study. Cr in bottled water by Alam (2021) was below detectable limit. Taiwo et al. (2023) and Emenike et al. (2017) in their research of Cr in sachet water had concentrations which fell within the concentration range of the ones gotten in this study. Russo et al. (2022) in Italy and Liu et al. (2022) in Wuhan, China, had Cr values in tap water that fell below those gotten in this study. Ghaderpoor et al. (2018) in Khorramabad, Iran and Liu et al. (2022), both had Cr values that fell below the ones in this study.

Pb levels in the current study was higher than the levels reported in the studies of Mirzaei et al. (2023) in Iran (in bottled water), Russo et al. (2022) in Italy (in tap water), Liu et al. (2022) in China (for tap and surface water), Ghaderpoor et al. (2018), in Iran (in City's water Distribution system). However, Pb level in our study has concentrations that fell within those reported by Olowoyo et al. 2022 in South Africa (for bottled water), Taiwo et al. (2023), Kusa and Joshua (2023) and Orisakwe et al. (2006) in Nigeria (for sachet water), Ugwu et al. (2022) in Nigeria (in borehole water, sachet water, harvested rain and stream water). The Pb level of this study was lower those reported by Hossain et al. (2025) in Bangladesh (in Hand tube-wells and electrically driven pumps), Ugwu et al. (2022) in Nigeria (in shallow well), Latif et al. (2025) in Pakistan (groundwater).

Zn concentrations in this study fell within those reported by Olowoyo et al. (2022) in Pretoria, South Africa (for bottled water), Emenike et al. (2017) in Ogun, Nigeria (for sachet water) and Ghaderpoor et al. (2018) in Khorramabad, Iran (for City's water Distribution system). However, the Zn concentration gotten by Hossain et al. (2025) in Dhaka district, Bangladesh (water from Hand tube-wells and electrically driven pumps) went above the values gotten in this study.

335 **Table 4: Comparison of approximated HMs in this study and other national and international studies.**

Country	Studied water source	Brands	No. of samples	Spec. type	Range of Heavy Metal (HM) concentrations (mg/L)						Ref.
					Mn	Cd	Ni	Cr	Pb	Zn	
Awka, Nigeria – This study	Bottled Water	7	42	AAS	0.047 -0.297	**< LOD** – 0.024	0.024 – 0.068	0.012 – 0.056	0.010 – 0.030	0.010 - 0.016	-
Pretoria, South Africa	Bottled Water	12	36	ICP-MS	0.017 - 0.269	0.0002 – 0.0007	0.075 - 0.089	0.143 - 0.190	0.006 – 0.123	0.011 – 2.978	Olowoyo et al. (2022)
Kashan, Iran	Bottled water	11	33	AAS	-	0.0015 – 0.007	0.002 – 0.029	0.005-0.034	0.001 – 0.007	-	Mirzaei et al. (2023)
Indonesia	Bottled water	4	4	ICP-MS	0.0006 –0.0009	< LOD	-	< LOD (Limit of Detection)	< LOD	-	Alam (2021)
Dhaka district, Bangladesh	Hand tube-wells and electrically driven pumps	-	60	ICP-MS	0.203 (mean)	0.002 (mean)	0.002 (mean)	0.002 (mean)	0.133 (mean)	0.068 (mean)	Hossain et al. (2025)
Italy	Tap water	-	40	AAS	-	0.0002 – 0.001	0.0002 – 0.001	0.0002 –0.001	0.0002 –0.0006	-	Russo et al. (2022)
Ogun, Nigeria	Sachet water	20	140	ICP-OES	-	0.001 - 0.0189	-	0.002 - 0.363	0.018 – 0.049	-	Taiwo et al. (2023)
Ogun, Nigeria	Sachet water	9	36	AAS	0.0053 – 0.019	-	-	0.020 – 0.105	-	0.0113 – 0.1238	Emenike et al. (2017)
Eastern Nigeria	Sachet water	41	41	AAS	-	**< LOD** – 0.036	0.003 – 0.045	-	0.002 – 0.036	-	Orisakwe et al. (2006)
Wukari, Nigeria	Sachet water	5	100	AAS	-	-	-	-	< LOD - 0.02	-	Kusa and Joshua (2023)
Wuhan, China	Tap water	158	158	ICP-MS	0.0002 - 0.0003	0.00003-0.00004	0.0012 - 0.0016	0.00016-0.00118	0.0008 - 0.0021	-	Liu et al. (2022)
	Surface water	9	9		0.0028 –0.0378	0.00002-0.00005	0.002-0.005	0.0008-0.0035	0.00004-0.0015	-	
Anambra, Nigeria	Borehole water	18	27	AAS	-	0.10 - 0 28	-	-	0 – 0.11	-	Ugwu et al. (2022)
	Sachet water	9	9		-	0.15 – 0.43	-	-	0 – 0.37	-	
	Shallow well	18	18		-	0.20 – 0.32	-	-	0.05 – 0.12	-	
	Harvested rain	27	27		-	0.14 – 0.35	-	-	0 – 0.34	-	
	Stream water	9	9		-	0.20 – 0.28	-	-	0 – 0.23		
Khorramabad, Iran	City's water Distribution system	45	45	ICP-OES	-	0.00002-0.00149	-	0.00039-0.01076	0.0004-0.0083	0.0074 – 0.1048	Ghaderpoor et al. (2018)
Kasur, Pakistan	Groundwater	25	25	AAS	-	0.15 -0.53	-	-	0.77 (max. conc.)	-	Latif et al. (2025)

336

337 *3.2.Heavy Metal Pollution Assessment (HPI and HEI)*

338 **Table 5: Approximated HPI and HEI values for the seven bottled water samples**

Bottled Water Sample	HPI Value	HPI Classification	HEI Value	HEI Classification
AQ	611	Unsustainable	13	Medium
IV	48	Good	7	Low
NE	59	Poor	7	Low
EV	27	Good	3	Low
LA	560	Unsustainable	14	Medium
MA	258	Unsustainable	9	Low
SW	182	Unsustainable	8	Low

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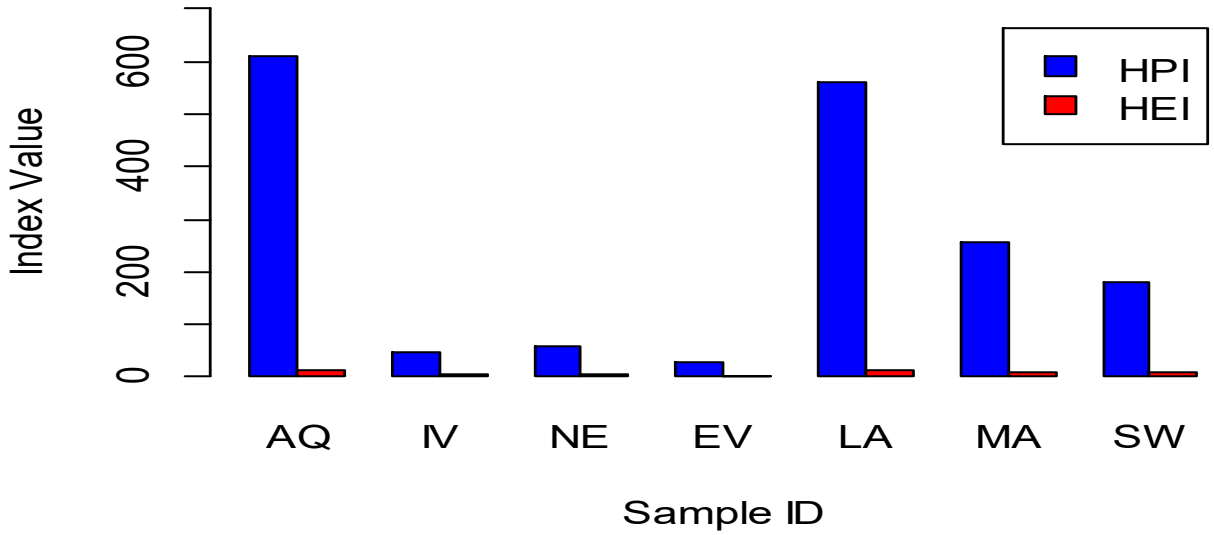


340
341 **Fig 3: Approximated HPI and HEI values for the seven bottled water samples**

342

343 Table 5, Fig 3, is the approximated HPI and HEI values for the seven bottled water samples. The
344 degree of heavy metal pollution was determined using the HPI and HEI indices. The HPI values
345 ranged between 27 and 611 while HEI values ranged between 3 and 14. HPI values were relatively
346 high for the HMs in the bottled water samples, especially in AQ (HPI = 611), LA (HPI = 560, MA
347 (HPI = 258) and SW (HPI = 182): which all went above 100 HPI threshold value, indicating that
348 these bottled water is "unsustainable for consumption" posing potential health risk. Also NE had
349 fell within "poor" threshold with HPI value of 59. The above values mean that the HMs quantity
350 in the water samples reduced the water quality, making them unsuitable for consumption. However
351 IV and EV had HPI values that fell within the "good" water quality threshold, making them
352 portable and safe for human consumption. The HEI provides a general overall water quality
353 assessment. From the HEI values of this study, IV (HEI = 7), NE (HEI = 7), EV (HEI = 3), MA
354 (HEI = 9) and SW (HEI = 8) all fell below the "low" pollution degree threshold, which then
355 indicate that the bottled water had low level of heavy metal pollution, making it generally safe
356 and suitable for drinking. However AQ (HEI = 13) and LA (HEI = 14) fell within 10 and 20 index
357 score, indicating a medium level of heavy metal pollution, making the bottled water samples
358 generally not very safe for human consumption. A study carried out by Khadija et al. (2021)

showed that 29 out of the 34 water samples had HPI and HEI that went beyond the critical point (100), which is similar to some of the results gotten in this current study. However, another study conducted by Badeenezhad et al. (2023) with 80 water samples, indicated that the HPI assessment value of the groundwater in all the sampling parts fell below 50 score safe limit: similar to some of the results gotten in this study: for IV and EV.

3.3. Potential ecological risks (ERI and RI) assessment

The potential ecological risk of the HMs across the bottled water brands was evaluated, as seen in Fig 4, using R software, with results, visualized on a log10 scale, were interpreted using the risk classification ranges from Onwordi et al. (2024), where an individual Risk Index (RI) < 40 and a cumulative Potential Ecological Risk Index (ERI) < 150 signify Low Ecological Risk.

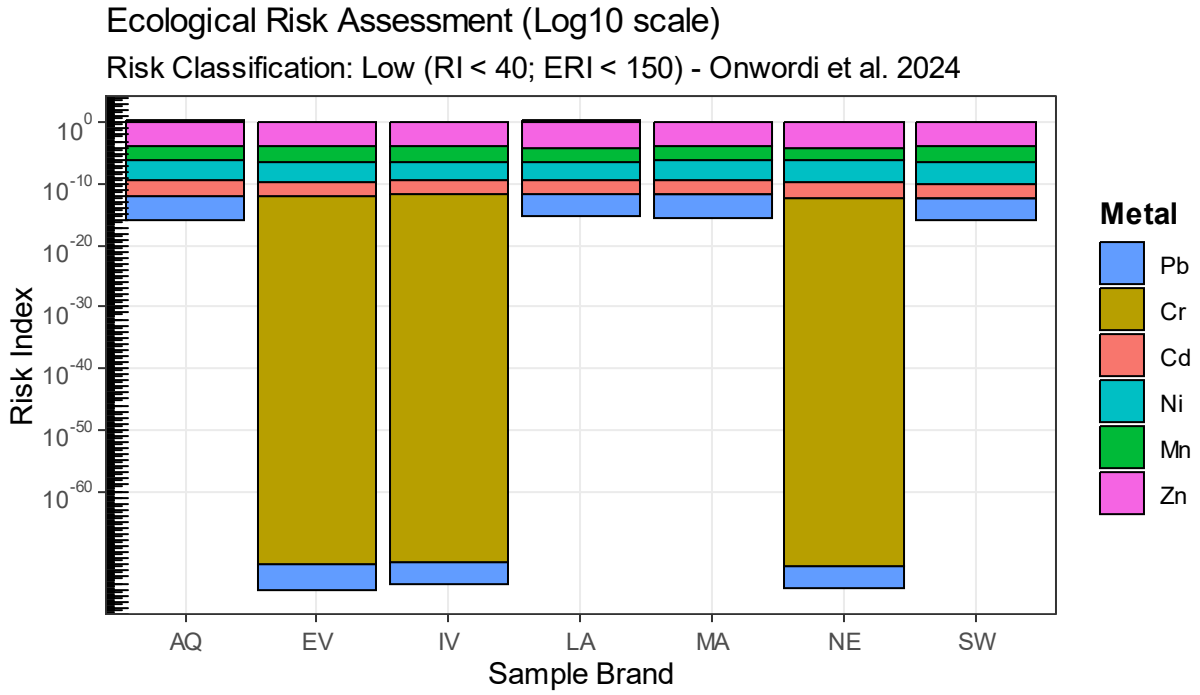


Fig 4: RI and ERI of the biscuit brands

According to the Onwordi et al. (2024) classification, all individual metals analyzed across the seven brands exhibited RI values significantly below the threshold of 40. RI for Chromium emerged as the primary driver of risk in brands AQ, LA, MA, and SW, where its RI values (ranging from 0.6000 to 2.4000) are several orders of magnitude higher than other metals, approaching 10^0 (a value of 1) on the logarithmic scale. Conversely, for brands IV, NE, and EV, the RI for Cr is visualized as a deep downward extension reaching a floor of 10^{-60}. This suggests that Chromium concentrations in these specific samples were 0.0000 or below the limit of detection (LOD). Because log10(0) is mathematically undefined, these "non-detects" are assigned a negligible baseline value to facilitate the visualization of the remaining detectable metals. The total cumulative risk for each brand, represented by the ERI, was assessed against the ERI < 150 "Low Risk" threshold. The ERI values ranged from a minimum of 0.0078825 of EV to a maximum of

2.408368 of AQ. Even in the Chromium-dominant brands, the total height of the stacked bars remains well below the $10^{2.17}$ level (corresponding to the 150 threshold). Thus, the combined heavy metal content in all sampled brands poses a Low Potential Ecological Risk. The risk distribution follows a distinct bimodal pattern. The group consisting of AQ, LA, MA, and SW shows a risk profile governed almost entirely by Chromium. In the group consisting of IV, NE, and EV, the total ERI is driven by the secondary contributions of Cd and Mn. Despite these fundamental differences in Cr levels, the RI for metals like Pb, Ni, and Zn remained remarkably consistent across all samples, typically clustering between 10^{-3} and 10^{-5}. This suggests a uniform background presence for most metals, while Chromium represents the significant source of variability between the brands. So, applying the Onwordi et al. (2024) standards confirms that both the individual metal risks (RI < 40) and the cumulative brand risks (ERI < 150) are categorized as Low Risk (as seen in Supplementary Table ST2). These findings indicate that the heavy metal concentrations in these products do not pose a significant threat to ecological systems, though the high relative concentration of the Cr metal in specific brands warrants further investigation into sourcing and manufacturing differences.

3.4.Human health risk assessment

3.4.1. *Daily dosage intake (DDI)*

Supplementary table ST3 displays the non-carcinogenic and carcinogenic daily dosage intake (DDI) of the metals in adults and children. From the non-carcinogenic DDI results, Mn has the highest intake (for non-carcinogenic) across all the sites with values as high as 1.980×10^{-2}mg/kg/day (in children) and 9.334×10^{-3} mg/kg/day (in adult) in bottled water IV. In fact the most contaminated brand is IV while the least contaminated is EV (3.13×10^{-3} and 1.477×10^{-3} mg/kg/day) in children and adult, respectively. The values for the children were higher due to the lower body weight of children compared to the adult. This then makes the consumption of these bottled water brands (especially IV; followed by NE and SW) impact more negatively on the health of the children than the adult, due to higher quantities of these metals. Brand EV, however, being the least contaminated, is free of Cd and has the lowest Pb and Mn metal levels, making the brand the safest bottled water for consumption. However, bioaccumulation of these metals still makes these water brands to not be completely safe for human (both adult and children). According to Nnaji et al. (2023), once metals are absorbed into the system of a living organism, they can accumulate to quantities sufficient enough to become toxic. The carcinogenic DDI results generally showed that SW brand had the highest metal contaminants while EV and NE showed the least overall risk. Cd in brands IV, NE and EV showed zero carcinogenic intake in these brands. Also brand NE and EV had the least Cr (for adults) and Pb (for adults and children) values respectively. Cr and Ni intake in SW (for adults) had high values of 3.771×10^{-3} and 2.137×10^{-3} mg/kg/day respectively. Also, from the Supplementary Table ST3, 4 of the 7 brands (IV, NE, EV, MA) showed that Ni had the highest carcinogenic dose (although AQ has the same values for Ni and Cr). When considering the combined load of all the four heavy metals:Cd, Ni, Cr, and Pb; brand EV emerges as the brand with the least carcinogenic contamination, while SW has the highest carcinogenic load of Cr and Ni metals. Summarily, from the Supplementary Table ST3 children were usually more vulnerable to non-carcinogenic toxicity, but for the carcinogenic DDI, adults had a higher intake of the metals than the children.

3.4.2. *Hazard Quotient (HQ) and Hazard Index (HI)*

Supplementary Table ST4 showed the HQ and HI for non-carcinogenic health risk assessment of the metals in the seven bottled water brands under study. HQ result (which measures the risk posed by the individual metals) showed, from this study, that Cd for adults in brands AQ and LA and for children in brands AQ, LA, and MA exceeded the health safety threshold of 1. However IV, NE and EV showed zero Cd values. HQ for Mn across all bottled water brands for both adults and children had values less than 1 (ranging from 0.037 to 0.495), making them pose no systemic risk to the study population. All the HQ values for Pb were all below the threshold health safety limit of 1. Ni, Cr and Zn metals all had HQ values below 1 across all the seven bottled water brands, making them to pose no visible risk in the water samples for both adults and children population.

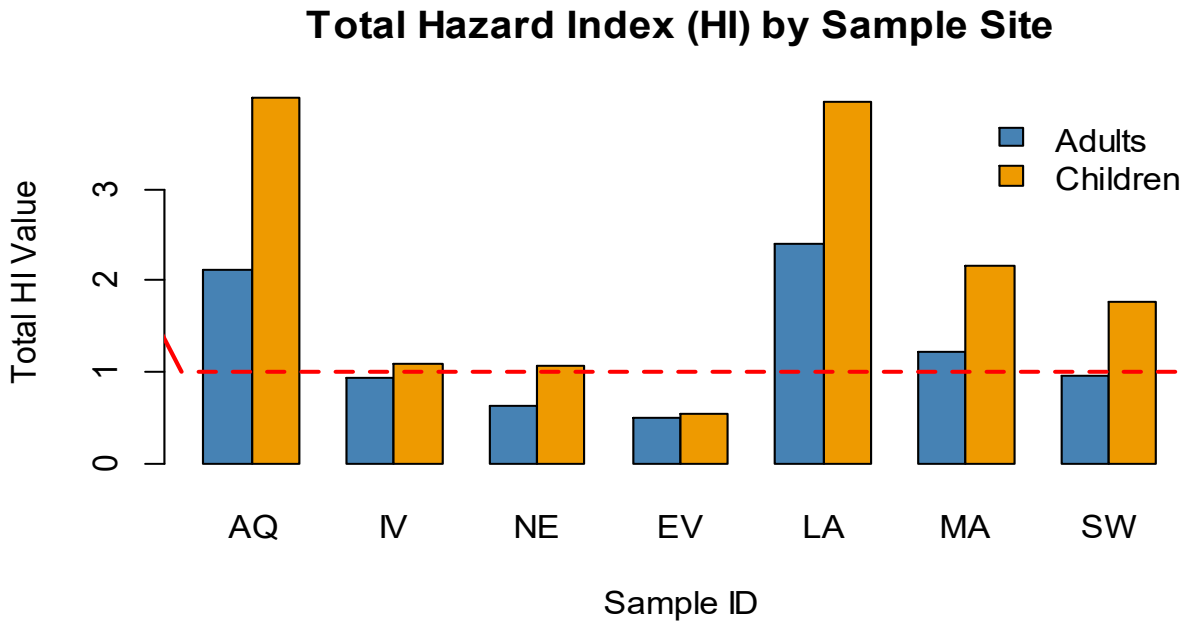


Fig 5: Hazard Index (bar chart) of the HMs in adults and children across the water brands

The HI (Fig 5-6 and Supplementary Table ST4) being the sum of the HQ for all the individual metals, showed that bottled water brands AQ, IV, NE, LA, MA and SW all had significant non-carcinogenic health risk for the children because the cumulative HI values across all the brands exceeded the health safety threshold of 1, while brand EV (0.534) fell within the health safety threshold. In fact AQ (HI = 3.993) and LA (HI = 3.963) both had HI values that were higher than the threshold. For the adult consumers, bottled water brands AQ (2.109), LA (2.396), and MA (1.224) also had HI values that exceeded the health safety threshold of 1. However, brand samples: IV (0.925), NE (0.622), EV (0.506) and SW (0.947) all fell within the health safety threshold. From the HI values, the children population had higher HI values than the adult, mainly due to the lower bodyweight of the children compared to the adult. Studies by Guerra et al. (2012) and Ugwu et al, (2022) also showed a higher HI for children than in adults, as seen in this study.

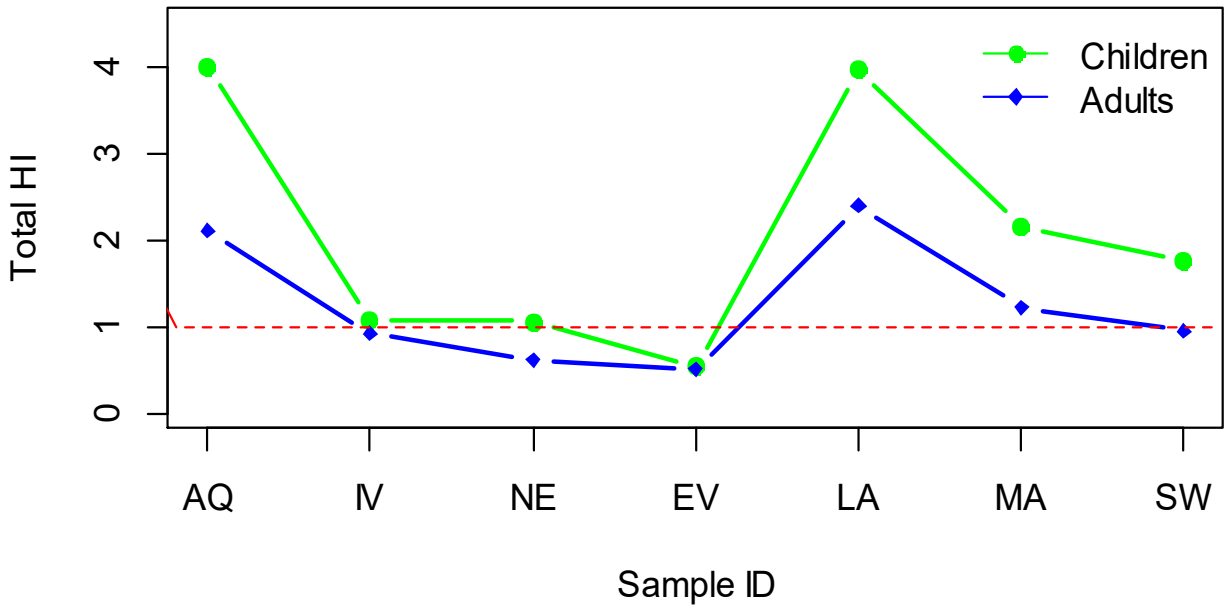


Fig 6: Hazard Index (line graph) of the HMs in adults and children across the water brands

Incremental Lifetime Cancer Risk Assessment (ILCR)

Supplementary table ST4 presents the ILCR for adult and children exposed to the HMs of Cd, Ni, Cr and Pb in the seven bottled water brands. Now, the acceptable 1LCR limit from USEPA ranges from 1.00×10^{-6} to 1.00×10^{-4} (Ugwu et al. 2022), where: (ILCR $< 1.00 \times 10^{-6}$) = negligible risk (less than 1 in a million), ILCR = 1.00×10^{-6} to 1.00×10^{-4}) = Acceptable or tolerable risk range; (ILCR $> 1.00 \times 10^{-4}$) = unacceptable, of potential health concern and action is usually recommended. In this study, Cd presents the most significant risk in your data. In adults, bottled water brands AQ, LA, MA, and SW show values above the 1.00×10^{-4} threshold, making these bottled water risky for adult consumption. From Rasin et al. (2025), lingering health concerns such as respiratory, cardiovascular, kidney diseases; bone disorder and increased cancer risk is due to the ability of the metal to accumulate over time in the body. Furthermore, cadmium can damage reproductive health, get the immune system compromised, as well as contribute to neurological disorders. In children, AQ and LA bottled water went above the 1.00×10^{-4} threshold, while MA and SW brands (5.976×10^{-5} and 4.482×10^{-5} respectively) had values exactly at 1.00×10^{-4} threshold. IV, NE and EV has zero values. Ni, on the other hand, had values that consistently exceeded the 1.00×10^{-4} threshold in all the bottled water brands for adult, but for the children, only EV (6.377×10^{-3}) and LA (5.451×10^{-4}) exceeded the 1.00×10^{-4} threshold. From Gates et al. (2023), abdominal pain, nausea, diarrhea and vomiting are associated with the ingestion of nickel salts. Also Ni and its compounds have been confirmed as a carcinogen (Guo et al. 2019). Cr risks are generally in the range of 2.0×10^{-4} and 9.0×10^{-4} (which is above the acceptable limit, posing a health concern) for adults; and 7.347×10^{-6} and 9.000×10^{-4} for children. However, for children at site EV (9.000×10^{-4}), the risk is exceptionally high indicating a severe brand hazard because it went above the 1.00×10^{-4} threshold, making these bottled water risky for children consumption. Cr exposure (mostly the Cr^{6+}) have been connected with liver, kidney, gastrointestinal tract,

widespread dermatitis, respiratory tract cancer, cardiovascular disorder, and so on (Chakraborty et al. 2022). Pb Lead shows the lowest ILCR values in this set, which ranged between 1.25×10^{-6} and 8.01×10^{-6} in adult, and 1.041×10^{-7} and 4.867×10^{-4} in children. The exception is site SW (4.867×10^{-4}) for children which hits the threshold of concern, making the SW brand risky for consumption. According to (Eslami et al. (2022), high blood pressure, gastric cancer, lung cancer, decreased intelligence quotient, anaemia, adults' well as children's physical and mental retardation are the effects of Pb on the human health.

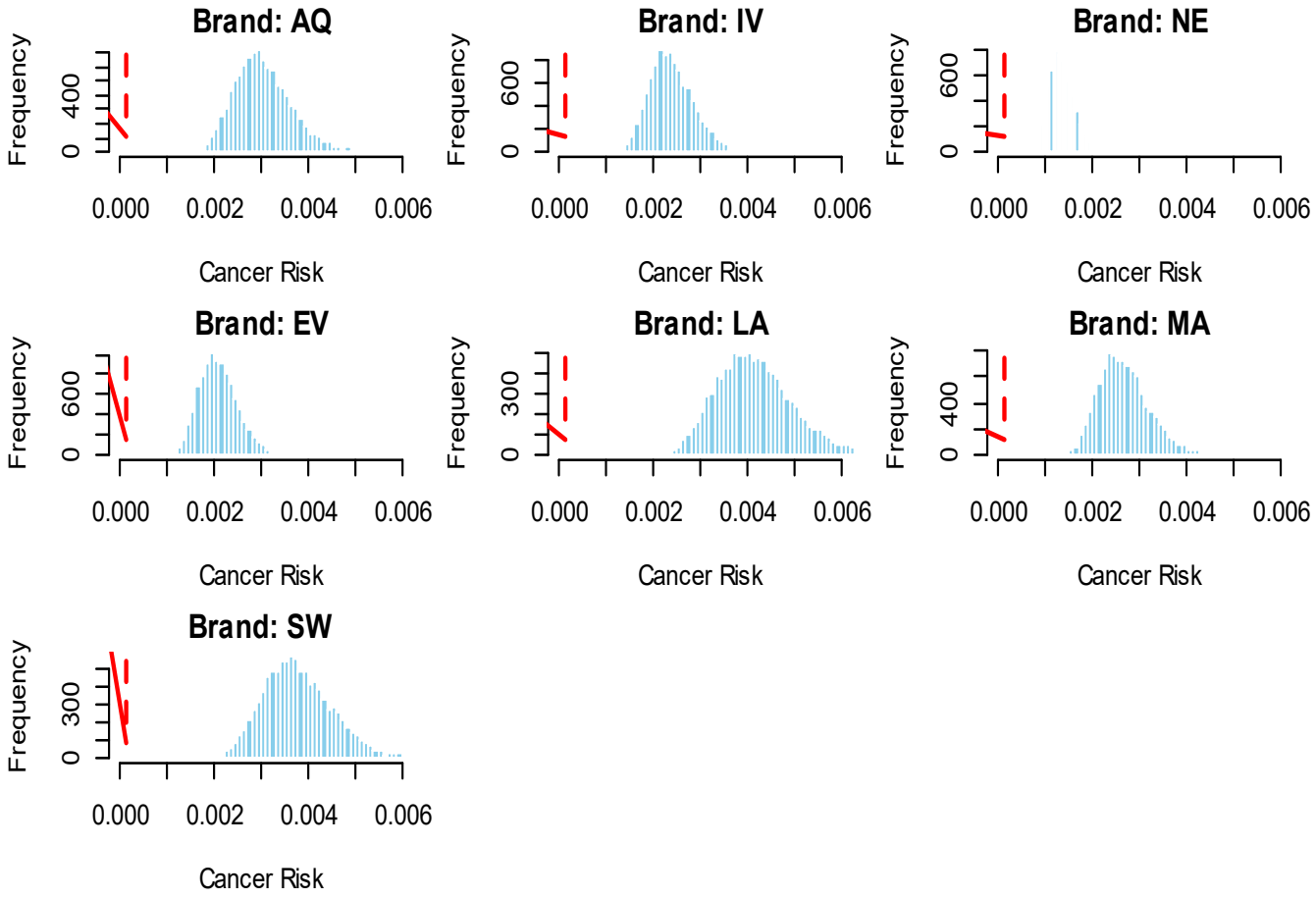


Fig 7: Monte Carlo simulation for ILCR of the bottled water brands in adult

Fig 7 displays the Monte Carlo simulation (MCS) results for the adults' Incremental Lifetime Cancer Risk (ILCR) of seven bottled water brands (AQ, IV, NE, EV, LA, MA, and SW). Each histogram represents 10,000 simulated iterations to account for uncertainty in exposure. The most critical finding is that the entire probability distribution for every single brand lies significantly to the right of the red dashed line, which represents the USEPA Limit (1×10^{-4}). This indicates a 100% probability that long-term adult consumption of any of these brands poses an unacceptable carcinogenic risk to adults. Brands LA and SW exhibit the highest risk profiles. Their distributions are shifted furthest to the right, with peaks (most likely risk) near 4.0×10^{-3}. This is 40 times higher than the USEPA safety threshold. Brands AQ, IV, EV, and MA show peak risks between 2.0×10^{-2} and 3.0×10^{-3}. Brand NE has the lowest risk profile. Its distribution is the

narrowest and closest to the safety limit, though it still remains entirely in the unacceptable zone. The "width" of the histograms (the spread of the blue bars) indicates the variability/uncertainty in the risk. For example, Brand LA shows a wider spread than Brand NE, suggesting its risk outcomes are more sensitive to fluctuations in metal concentration or intake rates. These results demonstrate a widespread public health concern. The consistent failure to meet USEPA standards across all sampled brands suggest potential systemic contamination issues, likely stemming from source water quality or industrial bottling processes.

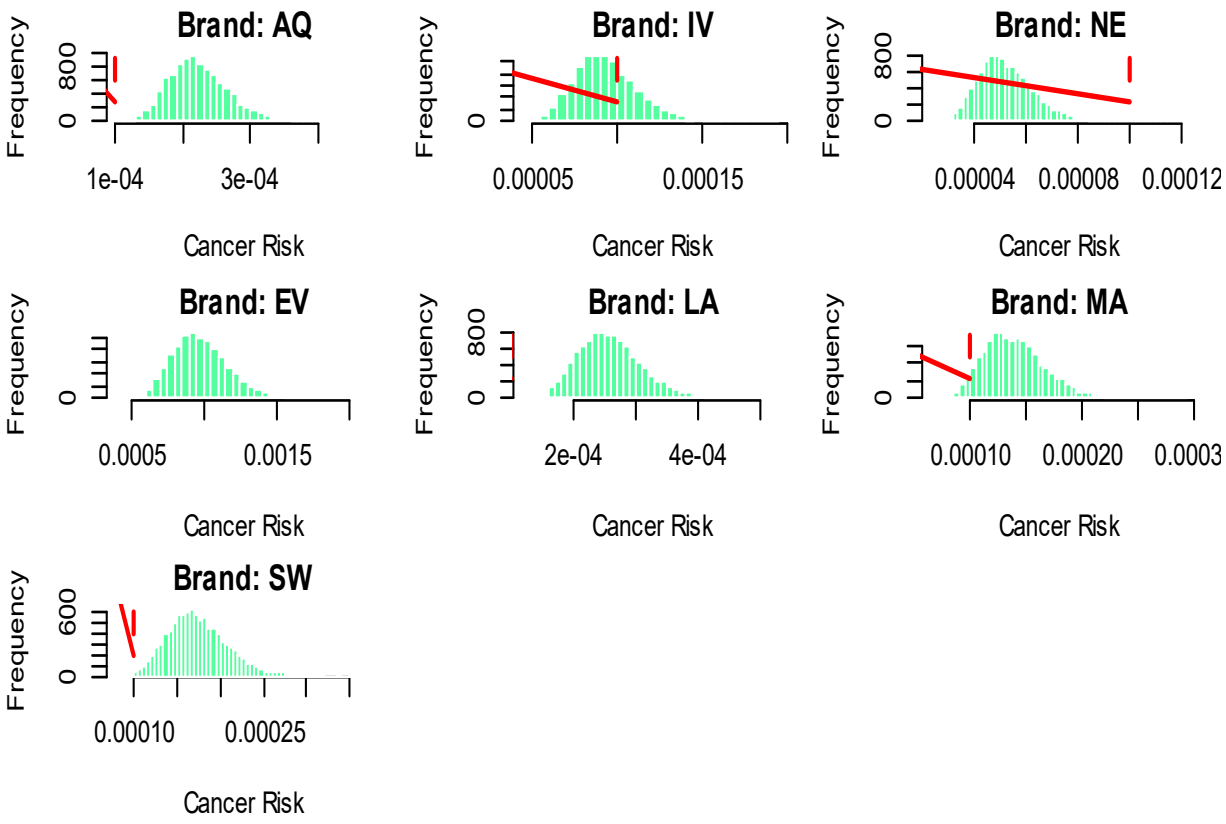


Fig 8: Monte Carlo simulation for ILCR of the bottled water brands in children

Fig 8 displays the Monte Carlo simulation results for children's Incremental Lifetime Cancer Risk (ILCR) across the seven bottled water brands (AQ, IV, NE, EV, LA, MA, and SW). By removing the fixed x-axis limits, all distributions are now clearly visible, providing a comprehensive view for your research. The histograms reveal significant differences in safety profiles between brands. The "width" of the green humps quantifies the uncertainty in the risk model. Brands with wider distributions, like EV, show a higher degree of variability in potential health outcomes compared to more tightly clustered brands like NE. For AQ, EV, LA, MA and SW brands, the majority of the probability distribution (green bars) sits to the right of the red dashed line, which represents the USEPA Limit (1.0×10^{-4}). This indicates that children consuming these brands are statistically

likely to face an unacceptable carcinogenic risk. Brand EV remains the most dangerous for children, with its entire risk distribution centered near 8.0×10^{-4}, nearly eight times the safety limit. For brand IV, the distribution is centered almost exactly on the USEPA limit. This brand is on the border of safety, with approximately 50% of simulated scenarios falling into the "unsafe" category. Brand NE is the only brand where the entire histogram lies to the left of the red line. So from this research, Brand NE is the only statistically safe choice for pediatric consumption among the brands tested.

The findings for children differ significantly from those for adults. While adults face unacceptable risks across all seven brands, the pediatric demographic has one relatively safe option (NE). However, the extreme outlier status of Brand EV highlights a critical public health concern that likely stems from high Nickel (Ni) levels, requiring urgent regulatory attention.

3.5. Source Apportionment using Principal Component Analysis (PCA) and Hierarchical cluster analysis (HCA)

Initial evaluation of heavy metal concentrations used the Pearson correlation matrix (Supplementary Table ST6) to determine inter-element relationships. The classification by Abdu-Raheem et al. (2024), states that: 0.9-1 (very high correlation), 0.7-0.9 (high correlation), 0.5-0.7 (moderate correlation), 0.3-0.5 (low correlation), < 0.3 (very low correlation). Also that elevated correlation coefficients indicate the existence of parallel geochemical developments, effects, and rejoinders, thus affecting the patterns of distributions of metals (Abdu-Raheem et al. 2024). From this study, the only "high correlation" was observed between Manganese and Zinc (r = -0.816), indicating they share a significant inverse relationship in the bottled water samples. The suitability of the data for PCA was assessed using the (Kaiser-Meyer-Olkin) KMO and Bartlett's tests (Supplementary Table ST7). The KMO value was 0.258, which is considered unacceptable for a robust factor analysis. However, while the KMO value was low, PCA was retained for exploratory visualization of variance distribution to complement the primary HCA results, which are more robust for this sample size. Bartlett's test of sphericity was also non-significant (χ^2 (15) = 10.114, p = 0.813) indicating that the correlation matrix was not significantly different from an identity matrix. These results collectively suggest that the heavy metals in this study tend to behave independently across the samples rather than forming strong, common source groupings. However, the PCA was conducted exploratorily to visualize variance distribution. The optimal number of components was determined using both Kaiser's criterion (Eigenvalues > 1) and the scree plot elbow criterion. As shown in Fig 10, the elbow in the plot occurs after the third component. The first three components have eigenvalues above 1.0 (1.998, 1.870, and 1.246, respectively), justifying their retention. These three components collectively explained 85.24% of the total variance in the heavy metal data.

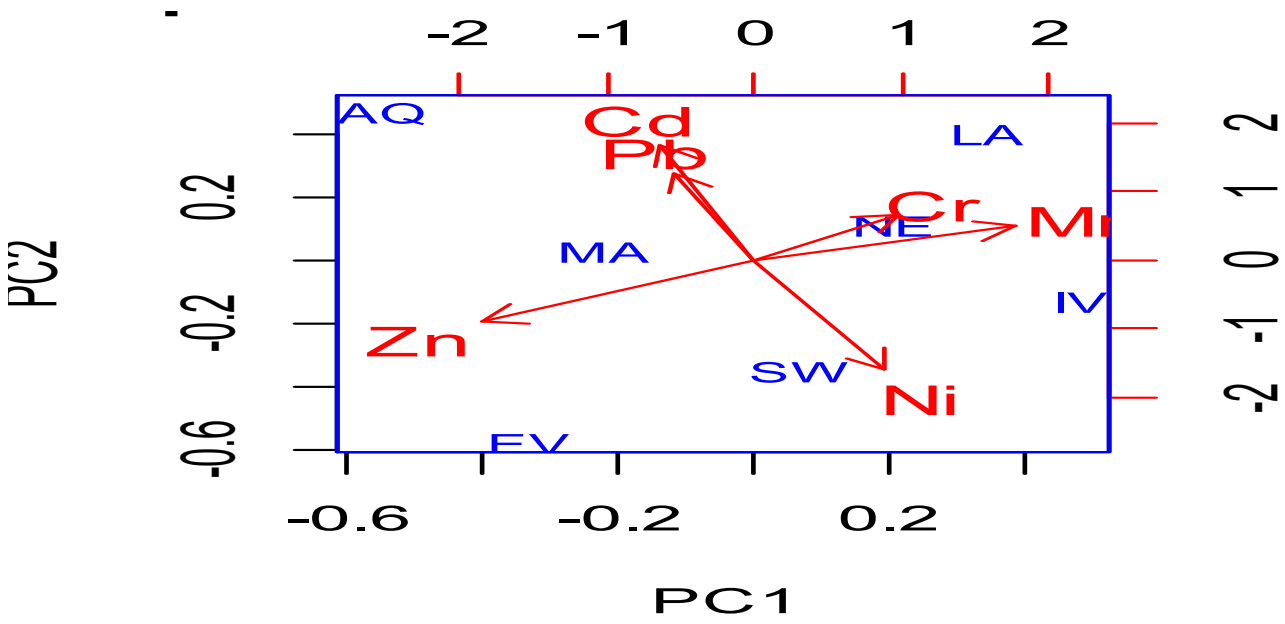


Fig 9: PCA Biplot of the HMs in the bottled water brands

This PCA biplot in Fig 9 illustrates the relationships between bottled water brands (blue labels) and their trace metal compositions (red vectors). The direction and length of the red vectors indicate how much a specific metal influences the brands. Cd and Pb vectors are nearly overlapping, indicating they are highly positively correlated in the samples. Brand AQ is positioned near these vectors, suggesting it has higher relative concentrations of these toxic metals. Ni vector is isolated from the others, pulling towards the bottom-right quadrant. Brand SW is positioned closest to this vector, indicating it is primarily characterized by its Nickel content. Zn vector points in the opposite direction of most other metals, suggesting it has a negative correlation with the others. Brand EV is most influenced by Zinc. LA, NE, and IV brands cluster together in the upper-right quadrant, influenced most by Chromium (Cr) and Manganese (Mn). MA brand (which is positioned near the center) likely has a more average profile with no single metal dominating its composition.

Table 6: The result of principal component analysis for HMs in bottled water brands (AQ to SW)

Heavy Metal	PC1	PC2	PC3
Manganese (Mn)	**0.945**	-0.081	-0.038
Zinc (Zn)	**-0.938**	-0.043	-0.246
Nickel (Ni)	0.077	**-0.862**	-0.002
Cadmium (Cd)	-0.142	**0.769**	0.507
Lead (Pb)	0.186	**0.730**	-0.418
Chromium (Cr)	0.214	-0.028	**0.930**

Extraction Method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization. Bold values indicate significant loadings (>0.7).

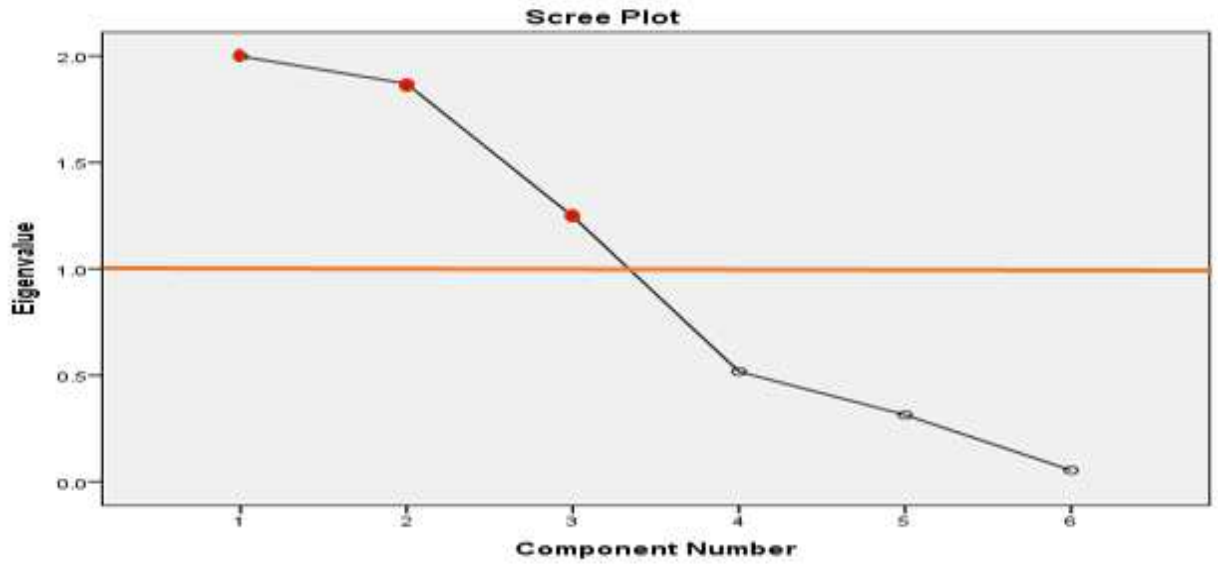
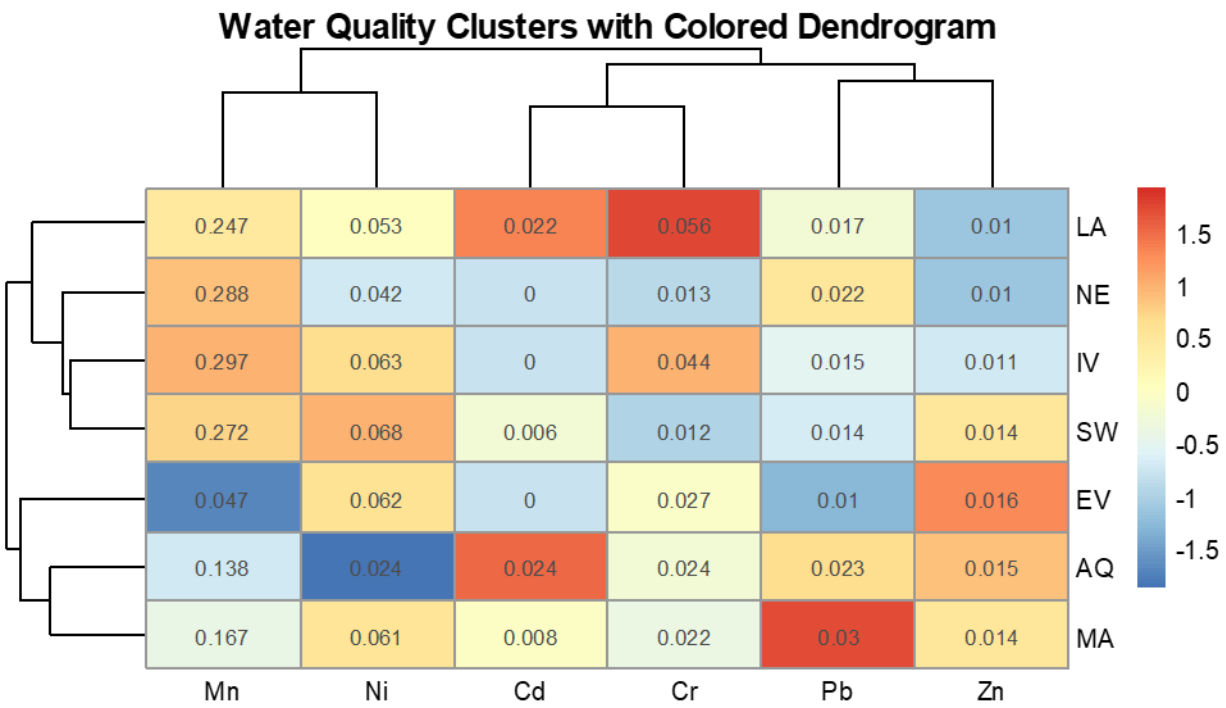


Fig 10: Scree plot of the HMs in the bottled water brands (AQ to SW)

Table 6 presents the Rotated Component Matrix, which is used to interpret the potential sources of the metals. The un-rotated matrix and further technical details are provided in Supplementary Table ST8. PC1 is strongly associated with Manganese (0.945) and Zinc (-0.938). Based on classification from Abdu-Raheem et al.'s (2024), these are "very high correlations" with the component. The inverse relationship suggests a specific geogenic process or a treatment stage during bottling where the concentration of one metal is reduced while the other is introduced. In PC2, Nickel (-0.862), Cadmium (0.769) and Lead (0.730) dominate this component. These are "high correlations" to the component. The co-occurrence of these metals in environmental monitoring studies is often linked to anthropogenic contamination, potentially related to plumbing corrosion, industrial activity, or certain material leaching. PC3 shows a very high correlation with Chromium (0.930) exclusively. This distinct loading suggests that the presence of Chromium is controlled by a specific source or mechanism separate from the other components, likely a highly localized source specific to certain brands or their supply chain. Applying the Abdu-Raheem et al. (2024) theory, the high correlation between Mn and Zn indicates the existence of parallel geochemical developments. Because these values are elevated, they suggest that the patterns of distribution for these specific metals are not random but are influenced by shared effects—likely related to the filtration processes, source water characteristics, or the bottling materials used across brands AQ to SW.



583

584 **Fig 11: Pheatmap Analysis of HMs in the bottled water brands**

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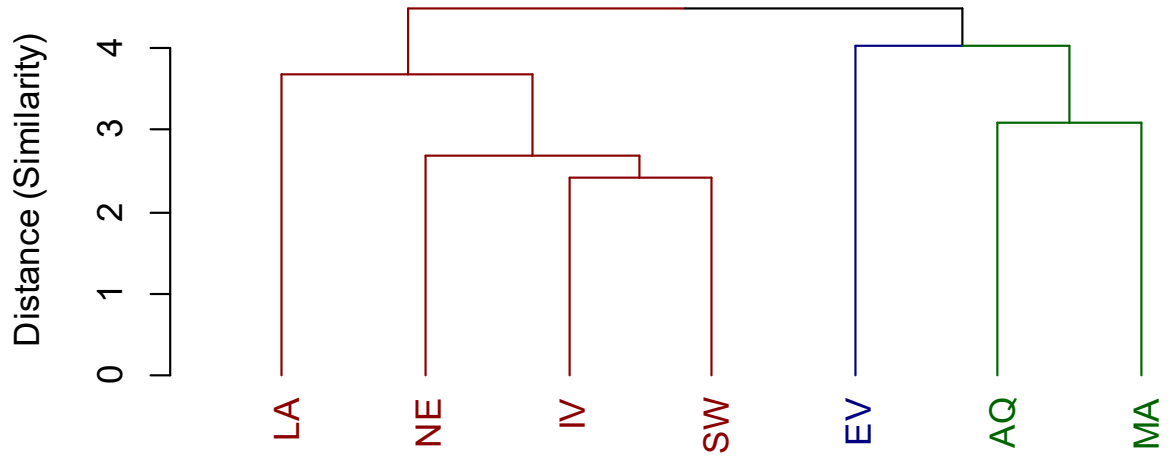
586



587

588 **Fig. 12: Hierarchical Cluster Analysis (HCA) on the HMs in the bottled water brands**

589 The integration of HCA and a pheatmap (Fig 11-12) provides a robust assessment of heavy metal
590 distribution across the seven bottled water brands. By visualizing the concentration data relative
591 to WHO (2022) guidelines, we can categorize the brands based on their chemical signatures and
592 safety profiles. The dendrogram (y-axis) identifies three distinct clusters based on Euclidean
593 distance, suggesting variations in sourcing or filtration efficiency. Cluster 1 comprise LA, NE, IV

and SW**.** These brands exhibit the highest similarity. The pheatmap reveals they are characterized by moderate-to-high concentrations of Mn. Specifically, IV and SW are the most closely related, indicating nearly identical mineral compositions. Cluster 2 comprises EV brand which acts as a geochemical outlier. Its distinct blue profile on the pheatmap indicates significantly lower concentrations across most tested metals compared to the other groups. Cluster 3 comprise AQ and MA**.** These brands form a separate group, defined primarily by elevated levels of **Pb** and **Cr**.

A critical evaluation of the pheatmap values against the provided WHO limits (0.080 for Mn, 0.003 for Cd, 0.070 for Ni, 0.050 for Cr, 0.010 for Pb and 3.00 for Zn) reveals the following: Pb metal Risk, because brand MA shows a concentration of 0.03, which is three times the WHO limit of 0.010 for Pb. This suggests a significant contamination risk or a failure in the purification process for this specific brand. For Cr, brand LA recorded a concentration of 0.056, slightly exceeding the WHO limit of 0.050. Other brands remain within the safe threshold, though AQ (0.024) is nearing the limit. Brand EV consistently shows the lowest concentrations (dark blue), staying well below all WHO thresholds, making it the most chemically "pure" in terms of heavy metal content among the samples.

The clustering of Mn and Ni in the top dendrogram suggests these metals may originate from a common geogenic source. In contrast, the isolation of Pb and Cr in the pheatmap for brands MA and LA highlights localized contamination. The use of this dual-visualization technique effectively proves that while most brands are within safe limits for Zn and Mn, specific brands (MA and LA) require stricter quality control to mitigate heavy metal toxicity.

4. Conclusion

From the results of this study on the analysis of heavy metals in seven bottled water brands, it was established that heavy metal concentrations in these brands were generally high when compared to the WHO (2022); and that due to their accumulation properties, they have the tendency to cause harm to the human system when consumed in these brands. The determined HM concentration in this study was compared with other national and international studies on bottled water and other drinking water sources. From Soliman et al. (2015), non-essential heavy metals, including Pb and Cd, usually exert significant toxicity even at relatively minimal concentrations. They bioaccumulate in tissues resulting in intoxication, manifesting as cellular and tissue damage, reduced fertility, multi-organ dysfunction, and eventual cell death. Regulatory bodies classify these elements as hazardous. The European Union regulates Pb and Cd specifically, while the United States Food and Drug Administration (USFDA) lists Cr and Ni among its hazardous metals (Soliman et al. 2015); and cumulative effects could result from concurrent exposure of two or more of the metals (Balali-Mood et al. 2021). This study showed that these metals are high in the majority of the water brands, making most of the brands generally unfit for consumption. Also our study showed the results of ILCR which demonstrate that for both adults and children, the total cancer risk at these sites are generally unacceptable by international safety standards and requires environmental intervention. The findings of this research provide a baseline for regulatory agencies like SON (standard organization of Nigeria) and NAFDAC (National Agency for Food and Drug Administration and Control) to implement stricter monitoring. Aligning local water safety standards with the targets of SDG 6 will be vital for protecting the health of vulnerable

populations, particularly children, from the long-term toxicological and carcinogenic risks identified in this study.

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Clinical Trial Number: Not applicable

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SDG Alignment: This research supports the implementation of Sustainable Development Goals 3 and 6 by providing empirical data on water safety and chemical risk in the Awka metropolitan area.

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