Potential Health Risks of Heavy Metal Contents in Bottled Water from Lagos State and Its Environs, Nigeria

Omeje Maxwell¹, Adewoyin Olusegun Oludegun .O¹, Joel Emmanuel S.¹, Okolie Soc'iis T.A.², Ayowe Omorotemu Efemena¹ Akinpelu Akinwumi¹, Arijaje Theophilus E.¹

¹Department of Physics, College of Science and Technology, Covenant University, P.M.B 1023, Ota, Ogun State, Nigeria
² Department of Mechanical Engineering, College of Engineering, Covenant University, Nigeria

maxwell.omeje@covenantuniversity.edu.ng

Abstract. The concentrations of lead (Pb), Cadmium (Cd), Chromium (Cr), Nickel (Ni), B and Fe in twenty (20) different brands of bottled water samples were investigated to ascertain the risk exposure to consumers using Atomic Absorption Spectrometry (AAS). The concentrations of the heavy metals analyzed varied from bottled water to bottled water samples. The BE bottled water sample was found to contain the least concentration of Pb with a value of 0.0232 mg/l. The risk of chronic daily intake (CDI) was determined based on the United State Environmental Protection Agency (USEPA) model for health risk. It was observed that Fe, Mg and Ca reported in all the bottled water samples. The estimated Chronic Daily Intake (CDI) of different metals from the water samples is found to be in order of magnitude of Pb>Fe>Cd>Ni. The highest CDI found in VA, SO, SO, LAT water samples are higher than the International Reference Dose Level according to WHO and USEPA respectively. This study suggest that some bottled water factories should be sited in zones that are safer from these heavy metals if Reverse Osmosis machine for proper removal of these trace elements from the raw water is not in use for water treatment.

Keywords: Water; AAS; Heavy Metals; Health Risk;

1. Introduction

Water is an indispensable part of the human environment and the source of portable water is an essential priority for the public health. Almost 70 % of the body system constitutes water which plays a vital role in biochemical processing. It will be difficult for human to survive without water.

Heavy metals are metals with high densities or high atomic weight such as Chromium (Cr), Cadmium (Cd) Arsenic (As), Mercury (Hg), Nickel (Ni), and Lead (Pb) are regarded as heavy metalsof health concern. This heavy metals pose health risk if found in water and lead to several health problems to the human populace. These heavy metals are known to be the elements with a special weight of about 4-5 times as much as that of water [1, 2]. These are metals with atomic weight of over 40 and do not break down easily once they are in the environment. Coal mining and smelting release arsenic, herbicides, pesticides, fungicides which contaminate both the surface and groundwater system.
in an environment[3,4]. If arsenic that if found in pesticide is washed from the surface to the plant by rainfall, it could be a source of contaminant to the stream, river and groundwater. The major source of arsenic exposure to human to Arsenic-containing water associate with diabetes, hepatitis, cancer, and cardiovascular disease in [5-8]. An ecologic standardized mortality ratio analysis showed that exposure to low-to-moderate levels of arsenic in drinking water was associated with increased mortality rates for CVD in both men and women [9]. High level of zinc in water may cause nausea, abdominal pain and vomiting [9]. In addition, it could lead to lethargy, anemia, and dizziness [9]. Lead in water according to studies shows those adverse effects on the functioning of the nervous system as well as hypertension, impaired thyroid function and preterm birth [9]. Presence of these heavy metals in bottled water, which is considered to be one of the purest forms of commercially sold water in Nigeria, would be hazardous to the health of the general public if found above the recommended level. This study is aimed at investigating the concentration of heavy metals and the potential chronic daily intake to the public that rely on the bottled water.

1.1 Geology of the Areas where the Water are Produced
1.1.1 Lagos.
Lagos State is situated in the south-western piece of the Nigerian Federation. On the North and East, it is limited by Ogun State. In the West it shares boundaries with the Republic of Benin. Behind its southern outskirts lies the Atlantic Ocean. Lagos is described by a wet tropical climate with mean yearly rainfall over 1800mm. There are two main seasons, specifically; the rainy season and dry season, which normally last from April to October and October to March separately. It experiences an average temperature of 270C. The vegetation cover is dominated by swamp forest, wetlands and tropical swamp forest. Water is the most significant topographical feature in Lagos State. Water and wetlands cover over 40% of the total land area that is within the state and an additional 12% is prone to seasonal flooding. The geology of Lagos State is majorly sedimentary of tertiary sediments and quaternary sediments. Where tertiary sediments are unconsolidated sandstones, grits with mudstone band and sand with layers of clay, and quaternary sediments are recent deltaic sands, mangrove swamps and alluvium near the coast. The state is located on sedimentary rock mainly of sand and alluvium.
2. Materials and Methods for Bottled Water Analysis of Heavy Metals

20 different brands of bottled water samples purchased in different shops in and around Lagos were analyzed for this present study. Each was put in 250 ml beaker for testing of pH, total dissolved solid (TDS) and conductivity. These parameters were measured directly before other analysis. The TDS, temperature and conductivity were analyzed using HACH Sension meter (TM5). The pH was analyzed using LAMOTTE Tracer Pochester meter. Also, heavy metal contents were measured in the water samples using Perkin Elmer A Analyst 600 Graphite Furnace Atomic Absorption Spectrometer (GF-AAS) instrument connected to the intuitive WinLab32 software system comprises of the tools to analyze, report as well as achieving the measured data.

2.1 Quality Control for the analysis of Heavy Metals in the Water Samples

The quality control for the measured water samples was carried out using GF-AAS (Perkin Elmer A Analyst 600) with a standard operation procedures suggested by the manufacturer. All other measurement meters such as TDS, pH and conductivity meters as well as the weigh balance were operated according the instructions of the SOPs to reduce analysis errors. All the equipment used in this study was calibrated before taken measurements. A calibration curve close to 1 was obtained for GF-AAS before the analysis was conducted on the bottled water samples so that the absorption of the atom of each element to be measured will be more accurate.

Where the Chronic Daily Intake of each heavy metal is measured with the formula below:

$$D = \frac{(C \times IR \times EF)}{BW} \text{ (1)}$$

Where

- $D$ = exposure dose (mg/kg/day)
- $C$ = contaminant concentration
- $IR$ = intake of contaminated water (L/day)
- $EF$ = exposure factor (unitless)
BW= body weight (kg)qw
Default Sinking Water Intake Rates
2 L/day – adult
Note: L/day – liters per day and BW (body weight) for Adults= 70kg

3. Results and Discussion

3.1. Water Quality Parameters

3.1.1. The pH Levels in All the Measured Water Samples
The pH values measured in this present study, which varies between 6.6 and 8.8 is in the range of acceptable value. Comparing this value with Turkish bottled water which ranges from 5.5 to 8.5, it can be observed that ours are within the range. The result was similar with the study by [11] in Lower Saxony, Germany who found that tap water was slightly basic and the mean pH value was 7.83. The standard pH for quality water made for drinking is between 7.2 to 8.5. All the water samples analyzed fall within this recommended level of quality water except VA water sample that is increasing to acidic range.

![Fig. 2. The Plot of pH in measured water samples against the Sample ID](image)

3.1.2 The Total Dissolved Solid (TDS) in the Measured Water Samples
The total dissolved solids (TDS) are shown in Fig. 2. The TDS which describes the inorganic salts and small amounts of organic matter present in solution in water. The more the TDS the less quality the water is whereas the less the TDS the purer the water is. It also indicates that the suspended solids that may enhance the pollution level in the water samples varies from 3 mgL\(^{-1}\) to 288 mgL\(^{-1}\). The highest value of 288 mgL\(^{-1}\) noted in BE water sample, whereas the lowest value of 3 mgL\(^{-1}\) was noted in MR water sample. According to NAFDAC, the recommended level of 100 mgL\(^{-1}\) is the safe level for our local community whereas 500 mgL\(^{-1}\) is the permissible level by WHO, 2006. TDS value values of the measured samples reported very low, as such, do not exceed the limit value [12] and far lower than the 1000 mgL\(^{-1}\) by [13]. Till date, no reliable data on possible health implication of TDS associated with drinking water [12]
3.2 Heavy Metal Analysis

Table 1 presents the variations in concentrations of the heavy metals in different brands of the bottled water samples. The details of individual metals were discussed and compared with the international reference levels recommended by the United States Environmental Protection Agency. The results are shown below.

Table 1. Concentrations of the Measured Heavy Metals in the Different Bottled Water Samples

| Bottled water samples | Units | Cd  | Cr  | Ca  | Mg  | Caco₃ | Pb  | Ar  | Ni  | Fe   |
|-----------------------|-------|-----|-----|-----|-----|-------|-----|-----|-----|------|
| PR                    | mg/l  | 0.0221 | 16.92 | 0.18 | 17.1 | 0     | 0   | 0   | 0   | 0.0003 |
| FU                    | mg/l  | 0.0332 | 34.08 | 0.12 | 34.2 | 0     | 0   | 0   | 0.0059 | 0.0213 |
| AQ                    | mg/l  | 0     | 16.97 | 0.13 | 17.1 | 0     | 0   | 0   | 0.0064 | 0.0182 |
| LAT                   | mg/l  | 0     | 16.98 | 0.17 | 17.1 | 0     | 0   | 0   | 0.0124 | 0.0226 |
| VA                    | mg/l  | 0     | 16.9 | 0.2   | 17.1 | 0.3481 | 0   | 0   | 0.0069 | 0.0046 |
| BE                    | mg/l  | 0.021 | 17.01 | 0.09 | 17.1 | 0     | 0   | 0   | 0.0073 | 0.0065 |
| EN                    | mg/l  | 0     | 0   | 0.0232 | 0     | 0   | 0   | 0   | 0   | 0.0082 |
| VES                   | mg/l  | 0     | 16.95 | 0.15 | 17.1 | 0     | 0   | 0   | 0   | 0.0022 | 0.0243 |
| LI                    | mg/l  | 0     | 34.02 | 0.18 | 34.2 | 0     | 0   | 0   | 0.0001 | 0.0158 |
| MR                    | mg/l  | 0     | 16.96 | 0.14 | 17.1 | 0.172 | 0   | 0   | 0   | 0.0105 |
| AQD                   | mg/l  | 0     | 16.92 | 0.18 | 17.1 | 0     | 0   | 0   | 0.0022 | 0.0243 |
| EV                    | mg/l  | 0     | 16.94 | 0.16 | 17.1 | 0     | 0   | 0   | 0.0004 | 0.0641 |
| UP                    | mg/l  | 0.0221 | 16.92 | 0.18 | 17.1 | 0     | 0   | 0   | 0.0003 | 0.0408 |
3.2.1 The Concentration of Lead (Pb) in the Water Samples

The concentrations of lead (Pb) measured in the selected bottled water samples show slight variations as presented in Figure 3. The highest value of 0.3481 mgL$^{-1}$ was found in VA and the lowest value of 0.0232 mgL$^{-1}$ was found in EN water sample. It can be observed that PR, FU, AQ, LAT, BE, VES, LI AQD, EV, UP, CW, NE, SO BI and AQF do not have any Pb contaminant. A slight relationship could be observed between pH and Pb in Figure 3 in VA water sample. It may be that the increase in the water acidity increases the concentration of Pb in water. The concentration of Pb reported in VA with the same sample recording more acidic value. Comparing the highest value of 0.3481 mgL$^{-1}$ obtained from this preset study with the value reported by [12] for treated sewage water in France, with a value of 0.034 mgL$^{-1}$, it can be observed that this present study is distinctly higher. Figure 4 shows the comparison of this present study with the International Standard.

![Graph showing concentration of Pb against Sample ID's](image_url)

**Fig. 4.** Concentration of highest values of Lead (Pb) against Sample ID in the Water Samples
3.2.2 The Concentration of Cadmium (Cd) in the Water Samples

The concentration of Cd in the water samples varies from 0.0021 to 0.072 mgL\(^{-1}\) with the highest value of 0.072 mgL\(^{-1}\) noted in SO water sample as presented in Figure 5. The lowest value of 0.0021 mgL\(^{-1}\) was found in AQF bottled water sample. It can be observed that there may be no relationship between the concentration of Cd and pH/TDS level in the water samples. Comparing the highest value of 0.072 mgL\(^{-1}\) obtained from this preset study with the value reported by [12] for treated sewage water in France, with a value of 0.011 mgL\(^{-1}\), it can be observed that this present study is slightly higher. Comparing the highest value of this present study with [12] standard of 0.003 and 0.005 mgL\(^{-1}\), this present study is distinctly higher. Figure 6 shows the comparison of this present study with the International Standard.

**Fig. 5:** Concentration of highest values of lead against international standards

**Fig. 6:** Concentration of Cadmium (Cd) against highest concentration of cadmium, comparing with the international standards.
3.2.3 The Concentration of Nickel (Ni) in the Water Samples

The concentration value noted for Ni all the samples ranges between 0.0003 mgL\(^{-1}\) (LI water sample) to 0.0124 mgL\(^{-1}\) (LAT bottled water sample) is presented in Figure 7. It can be observed that there is no relationship between the concentration of Ni and pH/TDS levels in the water samples. Comparing the highest value of 0.0124 mgL\(^{-1}\) from this present study with [12] standard of 0.02 mgL\(^{-1}\) (Provisional guideline value (this value is used for constituents for which there is some evidence of a potential hazard) and 0.1 mgL\(^{-1}\), this present study is slightly lower. Fig. 8 shows the comparison of this present study with the International Standard.

Fig. 7: Concentration of highest values of Cadmium (Cd) against Sample ID in the Water

Fig. 8: Concentration of Highest values of Nickel (Ni) against Sample ID in the Water
3.2.4 The Concentration of Iron (Fe) in the Water Samples

The results show that the concentration of Fe in the water samples varies from 0.0046 to 0.0715 mgL\(^{-1}\) with the highest value of 0.0715 mgL\(^{-1}\) found in SO water sample whereas the lowest value of 0.0065 mgL\(^{-1}\) was found in VA bottled water sample as presented in Figure 9. It can be observed that there may be no relationship between the concentration of Cd and pH/TDS level in the water samples.

Comparing the highest value of this present study with ref[12 & 13] standard of 0.3 mgL\(^{-1}\) (Secondary maximum contaminant level (SMCL, which are [not enforceable] guidelines established by the USEPA for use in evaluating esthetic properties in water), this present study is distinctly lower.

Figure 10 shows the comparison of this present study with the International Standard.

**Figure 9:** Concentration of Highest values of Nickel (Ni) against international standard.

**Figure 10:** Concentration of Highest values of Iron (Fe) against Sample ID in the Water.
Fig. 11: Concentration of Iron (Fe) against Sample ID with the highest concentration of Fe in the Water Samples and the international standards.

3.2.5. The Concentration of Calcium (Ca) in the Water Samples

The concentration of Ca in the water samples ranges from 16.9 to 51.1 mgL$^{-1}$ with the highest value of 51.1 mgL$^{-1}$ found in CV water sample whereas the lowest value of 16.9 mgL$^{-1}$ was found in VA bottled water sample as shown in Figure 12. It is noted that there is no relationship between the concentration of Ca and pH/TDS level in the water samples. Comparing the highest value obtained for this present study with the Turkish Legislation, 1979 for bottled water standard of 100 mgL$^{-1}$, this present study is distinctly lower by a factor of 1.9. Figure 13. shows the comparison of this present study with the International Standard.

Fig 12: Concentration of highest values of Calcium (Ca) against Sample ID in the Water Samples
3.2.6 The Concentration of Magnesium (Mg) in the Water Samples

The results show that the concentration of Mg in the water samples varies from 0.08 to 0.2 mgL$^{-1}$ with the highest value of 0.2mgL$^{-1}$ found in CV and VA and SO water samples respectively, whereas the lowest value of 0.08mgL$^{-1}$ was found in DE bottled water sample as presented in Figure 14. It can be observed that there may be no relationship between the concentration of Cd and pH/TDS level in the water samples. Comparing the highest value obtained for this present study with the Turkish Legislation, 1979 for bottled water standard of 50mgL$^{-1}$, this present study is far lower. Figure 15. shows the comparison of this present study with the International Standard.
3.3 RISK ANALYSIS OF HEAVY METALS IN THE BOTTLED WATER SAMPLES

3.3.1 Chronic Daily Intake of Heavy Metals in the Selected Bottled Water Sample

Table 2: Showing the CDI results of cadmium in the different bottle water samples.

| Dose Intake (L) | Body weight (kg) | Pb (mg/kg/d) | Cadmium (mg/kg/d) | Ni (mg/kg/d) | Fe (mg/kg/d) | Ca (mg/kg/d) | Cd (mg/kg/d) |
|----------------|-----------------|--------------|-------------------|--------------|--------------|--------------|--------------|
| 2              | 70              | 0            | 0.0009485         | 0            | 0.0003428    | 0.4885714    | 0            |
| 2              | 70              | 0            | 0.0001828         | 0            | 0.0003542    | 0.4851428    | 0.0048571    |
| 2              | 70              | 0            | 0.0001971         | 0            | 0.0002085    | 0.4828571    | 0.0057142    |
| 2              | 70              | 0.00099457   | 0                 | 0            | 0.0001314    | 0.486        | 0.0025714    |

Fig. 15: The Concentration of Magnesium (Mg) against Sample ID’s with the highest concentration of Mg in the Water Samples and international standard.
The chronic daily intake (CDI) of Cd between the ages of 1-12 and using the risk model suggested by [14], the Equation 1 used for this risk estimation is shown section 2.2. For the CDI estimated for adult in this present study, it varies from 0.000631 to 0.00206 mg/l. The highest value of 0.00206 mg/l reported in SO bottled water sample whereas the lowest value of 0.000631 noted in UP bottled water sample. It was observed that PR, AQ, LAT, VA, EN, VES, LI, MR, AQD, EV, CW, CV and NE Bottled water samples are free from Cd contamination.

The CDI due to lead (Pb) accumulation from different bottled water samples were calculated using USEPA risk model presented in Equation 1. The CDI varies from water sample to water sample with the highest value of 0.00995 mg/l recorded in VA bottled water sample and lower value of 0.000663 mg/l was found in EN bottled water sample.

The Nickel (Ni) risk exposure from the angle of CDI was calculated using the USEPA risk model published 1998 as presented in Equation 1. The Ni calculated varies from 0.0000857 to 0.000354 mg/l with the highest value recorded in LAT bottled water sample and the lowest value of 0.0000857 mg/l reported in UP bottled water sample.

The CDI calculated according to [14] for (Fe) indicates that the highest exposure from Iron (Fe) intake was higher in SO bottled water sample with a value of 0.00204 mg/l. The lowest value of 0.000186 mg/l was noted in BE bottled water sample.

The calcium (Ca) risk exposure from the angle of CDI was calculated using the USEPA risk model published 1998 as presented in Equation 2.1. The Ca calculated varied from 0.4834 to 0.9737 mg/l with the highest value recorded in FU bottled water sample and the lowest value of 0.4834 mg/l reported in BI, UP, AQD bottled water sample.

| Sample | Cd | Pb | Ni | Fe | Ca |
|--------|----|----|----|----|----|
| SO     | 0.00206 | 0.0000857 | 0.0000857 | 0.00204 | 0.4834 |
| UP     | 0.000631 | 0.0000857 | 0.0000857 | 0.00204 | 0.4834 |
| PR     | 0.000631 | 0.0000857 | 0.0000857 | 0.00204 | 0.4834 |
| AQ     | 0.000631 | 0.0000857 | 0.0000857 | 0.00204 | 0.4834 |
| LAT    | 0.000631 | 0.0000857 | 0.0000857 | 0.00204 | 0.4834 |
| VA     | 0.000631 | 0.0000857 | 0.0000857 | 0.00204 | 0.4834 |
| EN     | 0.000631 | 0.0000857 | 0.0000857 | 0.00204 | 0.4834 |
| VES    | 0.000631 | 0.0000857 | 0.0000857 | 0.00204 | 0.4834 |
| LI     | 0.000631 | 0.0000857 | 0.0000857 | 0.00204 | 0.4834 |
| MR     | 0.000631 | 0.0000857 | 0.0000857 | 0.00204 | 0.4834 |
| AQD    | 0.000631 | 0.0000857 | 0.0000857 | 0.00204 | 0.4834 |
| EV     | 0.000631 | 0.0000857 | 0.0000857 | 0.00204 | 0.4834 |
| CW     | 0.000631 | 0.0000857 | 0.0000857 | 0.00204 | 0.4834 |
| CV     | 0.000631 | 0.0000857 | 0.0000857 | 0.00204 | 0.4834 |
| NE     | 0.000631 | 0.0000857 | 0.0000857 | 0.00204 | 0.4834 |
The Magnesium (Mg) risk exposure from the angle of CDI was calculated using [14] as presented in Equation 1. The Mg calculated varied from 0.002571 to 0.005714 mg/l with the highest values recorded in SO, CV, VA bottled water sample and the lowest value of 0.002571 mg/l reported in BE, bottled water sample. All the samples are contaminated with Mg except PR and EN bottled water samples.

4.0 Conclusion
From the level of concentrations and the potential health risks of Pb>Fe>Cd>Ni from the bottled water samples measured has the mean values of 0.001022mg/kg/day for adult while Iron(Fe) has mean values of 0.0086051mg/kg/day for adults and Cadmium(Cd) has mean values of 0.0002508 mg/kg/day for adult while Ni has mean values of 5.9187E-05mg/kg/day for adults. This shows that the water samples from VA, SO, SO, LAT are considerably contaminated with these heavy metals. However, the pollution of these metals is in order of Pb>Fe>Cd>Ni respectively. Thus, these bottled water samples from VA, SO, SO and LAT were polluted significantly. The health risk due to chronic daily intake were found to be comparatively light in some bottled water samples such as EN, while some have shown to pose risks due to moderate level of heavy metals found in them. Within the scope of this study, a deep investigation of heavy metals as well as the health risks on the public is suggested as well as the bio-monitoring the level in blood and urine as a follow-up work.

Acknowledgment
The authors thank Covenant University for their financial support.

References
[1] Duruibe, J., Ogwuegbu, M., and Egwurugwu, J. “Heavy metal pollution and human biotoxic effects,”(2007).International Journal of Physical Sciences, 60 (2): 112-118.
[2] Raikwar, M. K., Kumar, P., Singh, M., and Singh, A. “Toxic effect of heavy metals in livestock health. Veterinary world,”(2008).1: 28-30.
[3] Dogaru, D., Zobrist, J., Balteanu, D., Popescu, C., Sima, M., Amini, M., and Yang, H. “Community perception of water quality in a mining-affected area: A case study for the Certej catchment in the Apuseni Mountains in Romania. Environmental management,”(2009).431131-1145.
[4] ATSDR. Toxicological profile for arsenic. 2007. Available online: http://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=22&tid=3 (2006).
[5] Hopenhayn, C. “Arsenic in drinking water: impact on human health. Elements”2006, 2, 103–107.
[6] Smith, A. H., Hopenhayn-Rich, C., Bates, M. N., et al “Cancers risks from arsenic in drinking water. Environmental Health Perspectives,”97: 259–267.
[7] Ferreccio, C., Gonzalez, C., Solari, J., et al. “Lung cancer and arsenic concentrations in drinking water in Chile. Epidemiology,”(2000). 11: 673–679.
[8] Rahman, M. M., Mordal, D. et al. “Status of groundwater arsenic contamination in all 17 blocks of Nadia district in the state of West Bengal, India,” a 23-year study report. Journal of Hydrology, (2014) 518: 363-372.
[9] Caussy, D. (2003). Lessons from case studies of metals: investigating exposure bioavailability, and risk. Ecotoxicology and Environmental Safety, 47 (2): 45-51.
[10] WHO (2011): Guide for drinking-water quality, fourth edition. World Health Organization, Geneva.
[11] World Health Organization, (1996). Guidelines for drinking-water quality. vol 2, health criteria and other supporting information. World Health Organization.
[12] WHO, (2006). Guidelines for drinking-water quality: First addendum to volume 1, Recommendations. World Health Organization.
[13] USEPA, (2012). Integrated Exposure Uptake Bio-Kinetic model for Lead in Children (IEUBK).
US Environmental Protection Agency.

[14] USEPA Environmental Protection Agency (EPA) (1999) Cancer risk coefficients for environmental exposure to radionuclides. United State Environmental Protection Agency. *Federal Guidance Report No* -13(EPA. 402 pp-99-101).