Quality Assessment of Various Brands of Bottled Water Marketed in Port Harcourt

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Abstract---The quality of selected brands of bottled water in Port Harcourt metropolis was determined for potability. Physicochemical and microbiological parameters were determined using standard methods. The results showed mean values of pH 4.30±0.01 to 6.35±0.12, EC 10.1±0.2 to 147.8±15.2µS/cm, Turbidity 0.0±0 to 0.8±0.1NTU, Salinity 0.0±0.0 to 0.06±0.0‰, TDS 6.9±1.2 to 102.9±5.2mg/l, Cl⁻ 2.0±0.2 to 7.9±0.3mg/l, SO₄²⁻<1.0 to 1.6±0.2mg/l, PO₄³⁻<0.05 to 0.08±0.01mg/l, NO₃⁻ 1.0±0.01 to 2.57±0.05mg/l, Hardness 3.8±0.2 to 7.7±0.4mg/l, Alkalinity 4.0±0.1 to 6.0±0.2mg/l, Ca²⁺ 0.8±0.2 to 2.3±0.1mg/l, Mg^{2+} 0.5±0.1 to 1.4±0.1mg/l, $Mn^{2+}<0.001$ to 0.174±0.1mg/l, Fe²⁺<0.001mg/l, total heterotrophic bacteria 10±0.1cfu/ml, total and faecal coliforms 0.0MPN/100ml. All the results were below permissible limits for potable water recommended by SON, NAFDAC and WHO indicating the potability of the bottled waters. The pH and total heterotrophic bacterial levels portend heath concern. It was recommended that the pH needs to be raised and all the water should be properly treated.

Keywords: Bottled Water, Physicochemical parameters, Potable, Port Harcourt

I. INTRODUCTION

The importance of water to man cannot be overemphasized due to its essentiality in body metabolism and proper functioning of cells [1]. Water is considered absolutely essential to sustain life [2]. It is increasingly recognized that the provision of good quality water is central to any meaningful human development [3].

Drinking water is never pure. Water naturally contains minerals and microorganisms from the rocks, soil and air with which it comes in contact. Human activities can add many more substances to water, but drinking water does not need to be pure to be safe. In fact, some dissolved minerals in water can be beneficial to health. [4]. The National Research Council (National Academy of Science) states that drinking water containing dissolved calcium and magnesium generally contributes a small amount of calcium and magnesium human dietary needs. Majority of the population in developing countries are not adequately supplied with potable water and are thereby compelled to use water from sources like shallow wells, streams and boreholes that render the water unsafe for domestic and drinking purposes due to high possibilities of contamination [5], [6]. In 1997, World Health Organization (WHO) reported that Forty percent (40%) of deaths in developing nations occur due to infections from water related diseases [7]. Diseases contacted through drinking water kill about 5 million children annually and make one – sixth of the world population [8] and an estimated 500 million cases of diarrhorea occur every year in children below 5 years in parts of Asia, African and Latin American [6]. The chemical compositions of groundwater are influenced by many factors which include precipitation, mineralogy of water shed, aquifer, climate and topography.

Port Harcourt is the capital city of Rivers State and is highly industrialized with high influx of people due to petroleum and non petroleum based activities. Thus it is a centre for many brands of bottled water in Nigeria especially for the middle and high income social classes due to its relative high cost. The low-income class depended absolutely on untreated water sources for their drinking water supply.

In Nigeria, most people depended absolutely on shallow wells and surface water for their survival. Unfortunately, most of these wells and surface water are polluted and unfit for human consumption [9], [10], [11].

Many companies are into production of bottled water with different processes of treatment and packaging. The National Agency for Food and Drug Administration Agency Control (NAFDAC) has made it compulsory for companies to be registered with the Agency in order to ensure qualitative production of potable water for the populace. However, there are influxes of fake brands of bottled water into the markets, which poses threat to health. Despite the high cost of bottled water, the global bottled water market has grown since 2006 [12]. The study by [13] on the distribution of heavy metals in water and sediment along Abonnema shoreline, showed that the concentration of Zn in water were higher than the permissible limit, this implied that the water is polluted with zinc due to dumping of decaying roofing sheets and metal components containing zinc. Also that the water body surrounding Abonnema island is contaminated with heavy metals especially Zn, Cr, Cu, and Cd which can contaminate sea foods and hence humans. [14] in their studies on assessment of borehole water quality in Yola-Jimeta metropolis, Nigeria, revealed that chloride, Iron, nitrate, pH, sodium and total hardness exceeded the guideline values

provided by both WHO and SON and are the main sources of borehole water contamination in the study area; having health implications that include hypertension, heart and kidney diseases which are on the increase in the region. They also stated that poor sanitary condition and intensive use of inorganic fertilizer are implicated as sources of contaminants.

Water is bottled and packaged for the purpose of drinking by various accredited and unaccredited companies and private individuals. There has been recent out break of cholera, typhoid fever and other water-borne diseases in Rivers State in particular and Nigeria in general. This research work on bottled water is therefore very important since water from various sources (groundwater, spring, distilled and tap) is bottled, packaged and sold to the public. The aim of this study is to assess the potability of most popularly consumed brands of bottled water marketed in Port Harcourt with a view to create awareness among the inhabitants.

II. MATERIALS and METHODS

A. Sample Type, Collection and Preparation

Based on popularity and cost, two each of seven brands of bottled water namely: BWP, BWI, BWL, BWE, BWA, BWB and BWR were bought from outdoor markets in Port Harcourt and taken to the laboratory for analysis. A total of fourteen water samples were analyzed.

B. Analytical Methods

i) *Physicochemical Parameters*: Winkler solutions I and II were added to the water samples for Dissolved oxygen (DO) and kept under laboratory condition at 30°C. Conductivity and salinity were determined using Horiba water checker U-10. Turbidity was determined using Lamotte TC 3000wi, Trimeter 1969 – ISO while Extech Dissolved Oxygen meter (Water proof series) DO 700 was used to determine pH and Total Dissolved solids (TDS).

The chemical analysis was done using standard laboratory methods suggested by the American Public Health Association [15]. Nitrate was determined using the Brucine method, Sulphate was determined by Turbidimetric method, Phosphate was determined using stannous chloride method, Chloride was determined by Argentometric method, Total Alkalinity was determined by Acid-Base Titration method, Dissolved Oxygen was determined by the modified Azide or Winkler method, Calcium and Magnesium were determined by EDTA Titration method. Heavy metals (Fe and Mn) were analyzed using Atomic Absorption Spectrophotometer by GBC Avanta Version 2.02.

ii) *Microbiological Analysis*: Heterotrophic plate count was performed using pour plate method. Serial ten-fold dilutions of the samples were prepared using sterile normal saline as diluents. Nine milliliters of normal saline was dispensed into each tube and sterilized using autoclave. After cooling, one milliliter of the water sample was transferred with the aid of a sterile pipette into nine milliliters normal saline to obtain 10^{-1} dilution. This was well mixed manually using the same sterile pipette; 1ml of the mixture (10^{-1} dilution) was transferred into the second tube (10^{-2} dilution). The same procedure was repeated until 10^{-7} dilution was prepared.

An aliquot (0.1) of the suitable dilution 10^{-4} to 10^{-7} was aseptically transferred into sterile Petri dish and cooled sterile nutrient agar was added. The mixture was allowed to solidify and then incubated at 37°C for 48h. Bacterial colonies on each plate was counted and multiplied by the reciprocal of the appropriate dilution.

III. RESULTS AND DISCUSSIONS

The results of mean levels of the parameters measured in the different brands of bottled water are presented in Tables 1-3 and Figs. 1-5. The correlation matrix showing the relationship between the parameters is presented in Table 4.

A. *pH*

The mean pH of the bottled water from the study area varied from 4.30 ± 0.01 in BWR to 6.35 ± 0.1 in BWL. The pH values indicate that all the bottled water are acidic and below the permissible limit (6.5-8.5) set by WHO, SON and NAFDAC. BWR is very acidic while the others are slightly acidic. Low pH has implication on the solubility and thus the bioavailability of other substances especially the heavy metals which are deleterious to humans.

pH is an important parameter for determining the quality of drinking water. It indicates the balance between the acids and bases in water and is a measure of the hydrogen ion concentration in solution. As an index of hydrogen ion concentration, a value of 7 indicate a neutral condition; values less than 7 indicate acid condition and values greater than 7 indicate alkaline condition in water. All the bottled water were acidic (McNeely *et al*, 1979).

B. Electrical Conductivity (EC)

Electrical conductivity is the ability of an object to conduct electric current. It gives the total concentration of the electrolytes; it depends upon the presence of various ionic species. The mean electrical conductivity of the bottled water in this study ranged from $10.1\pm0.20\mu$ S/cm in BWA to $147.8\pm15.2\mu$ S/cm in BWL.

Table 3.4 shows high significant correlation between EC and salinity (r = 0.9979), TDS (r = 0.9999), Cl⁻ (r = 0.7750), hardness (r = 0.5507), alkalinity (r = 0.9714), Ca²⁺ (r = 0.9958), Mg²⁺ (r = 0.6107), Mn (r = 0.5023) and NO₃⁻ (r = 0.8238). Analysis of variance (ANOVA) between electrical conductivity and pH, total dissolved solids levels showed significant difference (P < 0.05). However while ANOVA between the various brands of bottled water showed no significant difference (P < 0.05) for electrical conductivity and pH, significant difference (P < 0.05) existed between them in the case of electrical conductivity and total dissolved solids.

C. Turbidity

The mean turbidity of all the bottled water varied between 0 ± 0.0 NTU in most bottled water and 0.8 ± 0.1 NTU in BWP. The turbidity levels were below 5.0 NTU permissible limit recommended by WHO, SON and NAFDAC. High turbidity adversely affects domestic, industrial and recreational uses of water. Also high turbidity may be associated with disease-causing microorganism such as viruses, bacteria and parasites [17]. However, no trace of coliform was found in any of the bottled water.

Turbidity is a measure of the suspended particles such as silt, clay, organic matter, plankton and microscopic organisms in water which are usually held in suspension by turbulent flow and Brownian movement [16]. Turbidity measures the relative clarity or cloudiness of water and an indication of effectiveness of filtration of water supply [18].

Correlation matrix (Table 3.4) shows no significant correlation between Turbidity and other parameters.

D. Salinity

The salinity values in the bottled water ranged between $0\pm0.0\%$ in BWA and BWB and $0.06\pm0.0\%$ in BWL and BWR. The EC of water is a useful and easy indicator of its salinity or total content. The salinity values are less than 1000mg/L set by the World Health Organization [19]. This implies that the water is within limit.

Salinity had significant correlation with TDS (r = 0.9976), Cl⁻ (r = 0.7982), Hardness (r = 0.5389), Mn⁺ (r = 0.5384), Mg²⁺ (r = 0.6013), and NO₃⁻ (r = 0.7990).

E. Temperature

In this study, the temperature of of the bottled water ranged from $29.3\pm0.1^{\circ}$ C in BWI to $29.7\pm0.1^{\circ}$ C in BWA. Public Drinking waters should be of a Temperature that is refreshing to the consumer.

Physical, biological and chemical processes in the aquatic environment are affected by temperature; for example increasing water temperature decreases the solubility of oxygen in water while increasing the oxygen demand of fish [16].

The temperature of surface water is a function of latitude, elevation, seasons, time of day, rate of flow, depth, etc. Surface water temperature varies from 0°C under ice cover to 40°C in hot springs [16].

Table 3.4 shows that temperature did not show significant correlation with other parameters.

F. Total Dissolved Solid (TDS)

The Total Dissolved Solids of the bottled water ranged between 6.9 ± 1.2 mg/l in BWA and 102.9 ± 5.2 mg/l in BWL.

All the samples were within the permissible limit prescribed by [5], [20] and [21].

Total Dissolved solids (TDS) are index of the amount of dissolved substances in the water [16]. In natural water dissolved solids are composed of carbonates, bicarbonates, chlorides, sodium, sulphate magnesium and phosphate. Concentrations of dissolved solids are important parameter in drinking water. The total dissolved solids (TDS) indicate the general nature of salinity of water [22]. High TDS could impact taste in drinking water while water of very low TDS may be unacceptable because of flat inspirable taste [23].

Salts of calcium, magnesium, sodium, potassium present in irrigation water may prove to be injurious to plants. When present in excessive quantities, they reduce the Osmotic activities of the plants and may prevent adequate aeration [24].

TDS showed significant correlation with Cl⁻ (r = 0.7695), Hardness (r = 0.5462), Mn^{2+} (r = 0.5068), Mg^{2+} (r = 0.6071) and NO₃⁻ (r = 0.8280).

G. Sulphate (SO_4^{2-})

Sulphate is the stable, highly oxidized form of sulphur. It can be produced by bacterial oxidation of reduced sulphur compounds, including metallic sulphides and organo-sulphur compounds; the sulphate ion is readily soluble in water [16]. However, the concentrations of Sulphate in all the bottled water in this study varied between <0.05mg/l in most of the bottled water and 1.6±0.2mg/l in BWB and are all below the permissible limit recommended by WHO (500mg/l), NAFDAC and SON (100mg/l). Sulphate values in these analyzed brands of bottled water were also low, and fell below the permissible sulphate limit of less than 250 mg L^{-1} in drinking water with BWB recording the highest value. Sulphate is one of the least toxic anions in water. However, high sulphate could contribute to undesirable taste in water [25]. According to [26], when sulphate concentration in drinking water exceeds 500 mg L⁻¹, urgent action must be taken by appropriate authorities as concentration between 800 mg L^{-1} and 1200 mg L^{-1} could result into health effect such as diarrhea [27]. Sulphate showed high significant correlation with only Ca^{2+} (r = 0.8948).

TABLE 1

Sample code	pН	Sal. ‰	SO4 ²⁻ mg/l	PO4 ³⁻ mg/l	NO ₃ ⁻ mg/l	Cl ⁻ mg/l	Hardness mg/l	Alk mg/l	Ca ²⁺ mg/l	$M g^{2+} mg/l$	$M n^{2+}$ mg/l	Fe ⁺ mg/l
BWA	5.66 ± 0.01	0.0 ± 0.0	<1.0	< 0.05	1.0 ± 0.01	2.0±0.2	3.8±0.2	4.0±0.1	0.8±0.2	0.5±0.1	< 0.001	< 0.001
BWB	5.62±0.03	0.0±0.02	1.6±0.2	0.05 ± 0.01	1.48 ± 0.10	4.4±0.2	7.7±0.3	4.0±0.2	2.3±0.1	0.5±0.1	< 0.001	< 0.001
BWE	5.92±0.10	$0.04{\pm}0.0$	<1.0	< 0.05	2.33±0.16	3.0±0.1	3.8±0.3	6.0±0.1	0.8±0.2	0.5±0.1	< 0.001	< 0.001
BWI	5.28±0.02	0.01±0.0	<1.0	0.06 ± 0.01	1.77±0.04	3.0±0.1	5.8±0.3	6.0±0.2	0.8 ± 0.1	0.9±0.1	< 0.001	< 0.001
BWL	6.35±0.12	0.06 ± 0.0	<1.0	0.08 ± 0.01	2.57±0.05	5.9±0.3	7.7±0.2	6.0±0.2	0.8±0.3	$1.4{\pm}0.1$	< 0.001	< 0.001
BWP	6.04±0.14	0.03±0.0	<1.0	0.05 ± 0.01	1.41±0.10	5.9±0.2	5.8±0.2	4.0±0.1	0.8±0.2	0.9±0.1	< 0.001	< 0.001
BWR	4.30±0.01	0.06 ± 0.0	<1.0	0.05 ± 0.01	1.97 ± 0.12	7.9±0.3	7.70±0.4	4.0±0.1	1.5 ± 0.2	0.9±0.1	0.174±0.1	< 0.001
WHO	6.5-8.5	-	500	-	50	250	500	100	-	20	0.4	0.3
SON	6.5-8.5	-	100	-	10	100	100	100	75	0.20	0.05	0.3
NAFDAC	6.5-8.5	-	100	-	10	100	100	100	75	20	2	0.3

Mean Chemical Composition of Various Brands of Bottled Water Marketed in Port Harcourt

TABLE 2

Mean Physical Properties of Various Brands of Bottled Water Marketed in Port Harcourt

Sample code	EC µS/cm	Turb. NTU	TDS mg/l	Temp. °C	
BWA	10.1±0.2	$0.0{\pm}0.0$	6.9±1.2	29.7±0.1	
BWB	58.1±0.2	0.0 ± 0.0	39.9±3.1	29.6±0.1	
BWE	99.8±2.4	$0.0{\pm}0.0$	69.9±3.7	29.4±0.1	
BWI	33.70.6	0.0±0.0	23.5±1.3	29.3±0.1	
BWL	147.8±15.2	$0.0{\pm}0.0$	102.9 ± 5.2	29.6±0.1	
BWP	72.8±4.1	0.8±0.1	49.4±2.6	29.6±0.1	
BWR	139.1±6.3	$0.0{\pm}0.0$	97.3±3.4	29.5±0.1	
WHO	1200	5.0	1000	-	
SON	100	5.0	500	-	
NAFDAC	100	5.0	500	-	

TABLE 3

Mean Microbiological composition of Brands of Bottled Water Marketed in Port Harcourt

Sample	THB	TCB	FCB
code	(cfu/ml)	(MPN/100ml)	(MPN/100ml)
BWA	20±0.1	0±0.0	0 ± 0.0
BWB	300 ± 10.1	0±0.0	$0{\pm}0.0$
BWE	1420+25.6	0±0.0	0 ± 0.0
BWI	20+0.1	0±0.0	$0{\pm}0.0$
вил	20±0.1	0±0.0	0±0.0
	10±0.1	0±0.0	$0{\pm}0.0$
BWP	40±0.4	0+0.0	0+0.0
BWR	300±8.3	0.10	0_0.0
WHO	<1000	0-10	0



FIG. 1 Levels of some Parameters Measured in various Brands of Bottled Water



FIG. 2 Levels of some Parameters Measured in various Brands of Bottled Water



FIG. 3 Concentrations of Cations Measured in Various Brands of Bottled Water



FIG. 4 Concentrations of Metals Measured in Various Brands of Bottled Water

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FIG. 5 Levels of Heterotrophic Bacteria Measured in Various Brands of Bottled Water

TABLE 4

Correlation Matrix of Physicochemical Parameters Measured in Bottled Water Marketed in Port Harcourt

	рН	EC	Turbidity	Salinity	Temp	TDS	SO_4^{2-}	PO4 ³⁻	NO ₃ ⁻	Cl	Hardness	Alkalinityl
рН	1											
EC	-0.06116	1										
Turbidity	0.294525	-0.06311	1									
Salinity	-0.09483	0.997899	-0.02692	1								
Temp	0.30111	-0.06703	0.228218	-0.06635	1							
TDS	-0.06814	0.999877	-0.07654	0.997595	-0.07427	1						
SO_4^{2-}	0.016099	-0.18846	-0.16667	-0.21535	0.228218	-0.19223	1					
PO ₄ ³⁻	0.430265	0.444298	-0.22222	0.403786	-0.01521	0.444297	-0.22222	1				
NO ₃ ⁻	0.141639	0.823787	-0.30615	0.798971	-0.43907	0.827971	-0.24975	0.623043	1			
Cl	-0.34821	0.775021	0.277401	0.798197	0.117257	0.769495	-0.0392	0.165837	0.349519	1		
Hardness	-0.25166	0.550739	-0.06112	0.53892	0.090591	0.546225	0.417083	0.396708	0.301555	0.764251	1	
Alkalinityl	0.357592	0.245423	-0.35355	0.209381	-0.6455	0.2518	-0.35355	0.628539	0.740593	-0.27717	-0.14746	1
Ca^{2+}	-0.37331	0.044571	-0.23718	0.034825	0.180099	0.04294	0.894804	-0.31624	-0.17667	0.27871	0.593534	-0.50313
$M g^{2+}$	0.160159	0.610699	0.132954	0.601272	-0.03641	0.607133	-0.39886	0.842042	0.563734	0.577276	0.562177	0.376051
Mn	-0.85895	0.502287	-0.16667	0.538382	-0.09129	0.50675	-0.16667	-0.22222	0.145019	0.699532	0.417083	-0.35355
Fe	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
THB	0.048771	0.233164	-0.22587	0.230054	-0.39582	0.239287	-0.00123	-0.33284	0.420155	-0.20802	-0.41629	0.333396
	Ca ²⁺	Mg^{2+}	Mn	Fe	THB							
Ca ²⁺	1											
Mg^{2+}	-0.3268	1										
Mn Fe	0.291081 #DIV/0!	0.132954 #DIV/0!	1 #DIV/0!	1								
тнв	-0.00176	-0.47261	-0.00123	#DIV/0!	1							

H. Phosphate (PO_4^{3-})

The permissible limit for phosphate found in literature ranged between 0.05 to 1.0 mg/l [28]. In this study mean phosphate level ranged between <0.05 in most of the samples and $0.08\pm0.01 \text{mg/l}$ in BWL. This indicates the acceptability of the water for drinking with respect to phosphate.

Phosphate showed significant correlate with NO₃²⁻ (r = 0.6230), Alkalinty (r = 0.6285) and Mg²⁺ (r = 0.8420).

I. Nitrate (NO_3^-)

The concentration of nitrate in the bottled water varied between 1.0±0.01mg/l in BWA and 2.57±0.05mg/l in BWL. Nitrate is the principal form of combined nitrogen found in natural waters. The highly soluble nitrate ion, which is the most stable form of combined nitrogen, results from the complete oxidation of nitrogen compounds. The consumption of waters with high nitrate concentrations decreases the oxygen-carrying capacity of the blood [16]. Nitrate values were generally low in all the brands of the bottled water and fell within WHO permissible standard of 50 mg L⁻¹ in drinking water [29]. Short-term exposure to nitrate in drinking water above the permissible standard could lead to health problems in infants below six months leading to a disease known as methemoglobinemia or baby-blue syndrome, which is characterized by cyanosis, bluish mucous membranes, digestive and respiratory problems. High methemoglobin levels may lead to anoxia, brain damage or death [30]. Nitrate in form of nitrogen-nitrate level between 19-26 mgL⁻¹ has been reported to cause a spontaneous abortion in women [31]. Nitrate showed significant correlation with Alkalinity (r =0.7406) and Mg^{2+} (r = 0.5637).

J. Chloride (Cl⁻)

Chloride ions are generally present in natural waters and its presence can be attributed to dissolution of salts. The concentration of chloride in the bottled water under study ranged from 2.0 ± 0.2 mg/l in BWA to 7.9 ± 0.3 mg/l in BWR. Chloride concentrations of the analyzed bottled waters were generally low and fell within WHO standard for chloride of 250 mg L⁻¹ in drinking water. In drinking water, sources of chloride could be from dissolving salt deposits, salting of highways to control ice and snow, effluents from chemical industries, oil well operations, sewage, irrigation drainage, refuse leachates, sea spray and seawater intrusion in coastal areas [32]. However, no health risk has been associated with high chloride concentration in water.

Significant correlation exist between Cl⁻ and Hardness (r = 0.7643), Mn^{2+} (r = 0.6995) and Mg^{2+} (r = 0.5773). Analysis of variance (ANOVA) between chloride, sulphate, phosphate, nitrate and salinity levels showed significant difference (P < 0.05) but no significant difference (P > 0.05) between the various brands of bottled water.

K. Total Hardness (TH)

Total Hardness in the bottled water varied from 3.8 ± 0.3 mg/l in BWA and BWE to 7.7 ± 0.4 mg/l in BWB, BWL and BWR and is attributed to high presence of calcium, magnesium, carbonate, and hydrogen-carbonate in the water. The hardness levels do not exceed guideline value of 500mg/l set by WHO.

Hard water results in the formation of scale on boilers and pipes and it adversely affects textiles, plating, and canning industries and also results in increased soap consumption, which affects both domestic and industrial cleaning and laundering activities [16]. Total hardness mean results in all the samples were below 70 mg L⁻¹ could be described as soft water except for sample A where hardness value is greater than 70 mg L⁻¹ but less than 120 mg L⁻¹ is moderately hard water [33]. Water supplies with hardness greater than 200 mg L⁻¹ are considered poor, but have been tolerated by consumers; those in excess of 500 mg L⁻¹ are unacceptable for most domestic purposes. Water hardness (very high value) may cause an and Mg²⁺ (r = 0.5622).

L. Alkalinity

Alkalinity is a measure of the capacity of water to neutralize a strong acid. It indicates the presence of carbonates, bicarbonates, and hydroxides, and less significantly, borates, silicates, phosphates, and organic substances. It is expressed as an equivalent of adverse health effect in humans [8]. Studies have shown weak correlations between cardiovascular health and water hardness [34]. Total hardness showed significant correlation with Ca²⁺ (r = 0.5935) calcium carbonate (CaCO₃). The species composition of alkalinity is affected by pH, mineral composition, temperature, and ionic strength; however, alkalinity is normally interpreted as a function of carbonates, bicarbonate, and hydroxides [16].

Mean total alkalinity in the bottled water was low, with mean values ranging between $4.0\pm0.1\text{mg/l}$ in BWA, BWB, BWP and BWR and $6.0\pm0.1\text{mg/l}$ in BWE and BWI. This is much below the standard value of 100mg/l set by [5]. When water with high alkalinity is boiled over an extended time period, either a deposit may be formed or an unpleasant taste is created depending upon the chemical reaction. However, total alkalinity in this study is low and can corrode pipes and plumping. No health implication has been identified with alkalinity. In natural water, high alkalinity values act as buffer against acid rain and other acid laden wastes that could cause a sudden change in water pH and thereby posing threats to aquatic life. Alkalinity showed significant but negative correlation with Ca²⁺ (r = -0.5031).

M. Calcium (Ca^{2+})

Calcium is one of the most abundant cations in surface and ground water and one of the alkaline earth metals. It is a major

constituent of most Igneous rock, metamorphic and sedimentary rocks. The principal sources of calcium in groundwater are some members of the silicate minerals such as pyroxenes, amphiboles among igneous and metamorphic rocks, and limestone, dolomite and gypsum among sedimentary rocks.

The mean concentrations of calcium in the bottled water varied between 0.8 ± 0.2 mg/l in BWA, BWE, BWI, BWL, BWR and 2.3 ± 0.1 mg/l in BWB. These concentrations are below the permissible limit of 75mg/l by SON and NAFDAC. The main source of calcium in natural water is leaching of rocks in the catchments [35].

N. $Magnesium (Mg^{2+})$

Magnesium, an alkaline-earth metal, is an abundant element and a common constituent of natural water. Natural sources clearly outweigh all cultural inputs of this constituent to the natural environment. Ferromagnesian minerals in igneous rock and dolomitic sedimentary rocks are the principal contributors of magnesium to water [16].

The magnesium values in the bottled water ranged from 0.5 ± 0.1 mg/l in BWA, BWB, BWE to 1.4 ± 0.1 mg/l in BWL. These are below the permissible limit of 20mg/l set by WHO and NAFDAC and 0.2mg/l by SON.

There was no correlation between Mg^{2+} and all other parameters in the bottled water.

The values of Ca hardness were generally higher than the values of Mg hardness. Acceptable range of calcium in water has been given as 25-100 mg L^{-1} [36], as all the observed mean values of Ca fell below this range. Therefore, the values of hardness in these brands of water samples may be due to Ca salts rather than Mg salts.

O. *Manganese* (Mn^{2+})

Manganese mean values in the bottled water ranged between <0.001 in most bottled water and 0.174 ± 0.1 mg/l in BWR. These are below the permissible limit of 0.4mg/l by [5] and 2.0mg/l by [21]. This is an indication of acceptability. Manganese is an essential element for the nutrition of both humans and animals. A manganese deficiency may inhibit growth, disrupt the nervous system, and interfere with reproductive function. It is an essential element for plant metabolism [16].

P. Iron (Fe)

Iron concentrations in all the bottled water were less than 0.001mg/l. The mean concentrations of Fe in all the bottled water brands were below the guideline (0.3mg/l) for Iron set by NAFDAC, SON and WHO.

In water, Iron can discolour cloths, plumbing fixtures, and cause scaling which encrusts pipes. Iron is highly objectionable for drinking water because of the stringent taste [37].

The values of iron concentration in all the bottled water fell below the WHO permissible limit that is based on taste and appearance rather than detrimental health effect [29]. Iron is not considered hazardous to health. In fact, instead it is an essential element for good health because it transports oxygen in the blood. Iron is considered a secondary or aesthetic contaminant [29]. [37] has established a maximum concentration for iron in drinking water of 1.0 mg L⁻¹. Iron in all the bottled water did not show any correlation with

other parameters.

Q Microbiological Content

The mean values of Total heterotrophic bacteria in the bottled water samples ranged from 10.0 ± 0.1 cfu/ml in BWL to 1420 ± 25.6 cfu/ml in BWE. Total and Fecal coliform bacteria were not present in all the bottled water investigated. All the water under study contained total heterotrophic bacteria with high values in BWE, BWB and BWR. The presence of this contamination could be attributed to inefficient sterilization processes at the production level; an indication of high health concern for consumers.

IV. CONCLUSION

The findings of this study showed that the various brands of bottled water marketed in Port Harcourt are acidic with BWR having the worst case. The levels of Total heterotrophic bacteria in BWB, BWE and BWR pose health concern for consumers. The bottled water investigated need further treatment(s) with either UV, Chlorination or Ozonation.

Based on the findings of this study, the following recommendations were made:

- The pH of all the bottled water should be raised.
- The water including many other brands in the market should be monitored regularly to avoid serious pollution problems (epidemics).
- Further study should be done using same brand of bottled water obtained from the production company or outfit and the open market.
- The Government Agencies should as a matter of urgency ensure adequate quality assurance and control measures by producers and create awareness on the quality of all bottled water and the presence of fake bottled water in the open markets and streets.

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