An Appraisal of Potable Water Quality in Calabar Metropolis (Calabar South and Municipality), Cross River State, Nigeria

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Abstract
The frequent consumption of bottled and sachet water and the adverse effect of impure water to human health prompted this study in 2018 and 2020. Eight randomly selected drinking water in Calabar Metropolis (Calabar South and Municipality), Cross River State, Nigeria were analysed and compared with World Health Organization standards. The physicochemical parameters evaluated included pH, temperature, DO, colour, odour, TDS, TSS, electrical conductivity, total hardness, BOD, COD, acidity, oil/grease, NH_4-N, PO_4-P, NO_3-N, SO_4; minerals (Cl, K, Mg, Ca, Na), heavy metals (Zn, Cu, Cr, Pb, Mn, Cd, Ni, Fe, Hg, As) and microbes (Escherichia coli, total coliform count and Salmonella) using the membrane filtration method. Results showed that most physico.chemical parameters and heavy metals analyzed did not conform to WHO threshold limits and were not consistent on yearly basis. However, the microbiological examination for all samples were in line with WHO standard. The was a significant ($p<.05$) difference between the analyzed samples and WHO standard, thus, making the selected drinking water produced and sold within the study location unsafe for human consumption despite their zero microbial load. The National surveillance agencies and WHO monitoring unit should be more proactive to avert such inconsistencies by regular re-evaluation of water quality.

***Keywords**: Potable water, physico.chemical, heavy metals, microbial*

Introduction

Water is one of the indispensable resources for the continued existence of all living things including man and adequate supply of fresh and clean drinking water is a basic need for all human beings (Edema, Atayese, & Bankole, 2011). An average man of body weight 53kg to 63kg, requires about 3 liters of water in liquid and food daily to keep healthy (Wardlaw, Hampl & Disilvestro, 2004). In nature, all water contains impurities; as water flows in streams, accumulates in lakes and filters through layers of soil and rock in the ground, it dissolves or absorbs substances it comes in contact with, which may be harmful or harmless (Ogamba, 2004). Water is said to be potable when its physical, chemical and microbiological qualities conform to specified standards. To achieve such standard, raw water is subjected to purification processes that range from simple to long term storage to enable sedimentation of some suspended solids through aeration, coagulation, filtration and disinfection among other treatments (Ajewole, 2005). The abundance of toxic chemicals in drinking water may cause adverse effects on human health such as cancer and chronic illness (AL-Saleh & Al-Doush, 1998) while toxic metals like Arsenic, Cadmium, mercury and lead when present in drinking water could cause acute or chronic poisoning known to be hazardous to health (Amoo, & Akinbode, 2005). Nearly 90% of diarrhea related cases and death have been attributed to unsafe or inadequate water supplies and sanitation conditions (WHO, 2006). Water that is meant for human consumption should be free of disease-causing germs and toxic chemicals that pose a threat to public human health (TWAS, 2005). Water consumers are frequently unaware of the potential health risks associated with exposure to water borne contaminants which have often led to diseases like diarrhea, cholera, dysentery, typhoid fever, legionnaire's disease and parasitic diseases (Omalu, *et al.*, 2011).

The continuous increase in the sale and indiscriminate consumption of packaged drinking water in Nigeria is of public health significance, as the prevalence of water related diseases in developing countries is determined by the quality of their drinking water (Ezeugwunne, Agbakoba, Nnamah, & Anhalu, 2009). Hygiene, purity, tastes, and, most importantly, safety is probably amongst various reasons for sachet water consumption. Unfortunately, the problems of its purity and health concerns have begun to manifest (Osibanjo, Ajayi, Adebiyi, & Akinyanju, 2000; Oladipo, Onyenike, & Adebiyi, 2009; Airaodion, et al., 2019).

Sachet water is not completely sterile; it may not be entirely free of all infectious microorganisms. The potential danger associated with sachet water is contamination, which is a factor of the source of the water itself, treatment, packaging materials, dispensing into packaging materials and closure (Omalu, et al., 2010).

The frequent consumption of unsafe bottled and sachet water and the resultant effect on human health prompted this study.

Materials and Methods

Location of the Research: Calabar Metropolis comprising Calabar south and Calabar Municipality, Cross River State, Nigeria located southern part of Nigeria, lying geographically on latitude $4^0$57’0” N and longitude $8^0$19’30” E (Figure 1). The areas have both urban features as well as rural settings. The area covers 406 KM square (157 sq mi) and a population of 371,022 at the 2006 census with population density of 910/km2 (2,400/sq mi). The postal code of the area is 540. Temperature in Calabar ranges from 21.5^{0}C to 33.5^{0}C while rainfall ranges from 42.0 to 1401.0 (mm/month) (Calabar - Wikipedia en.m.wikipedia.org).

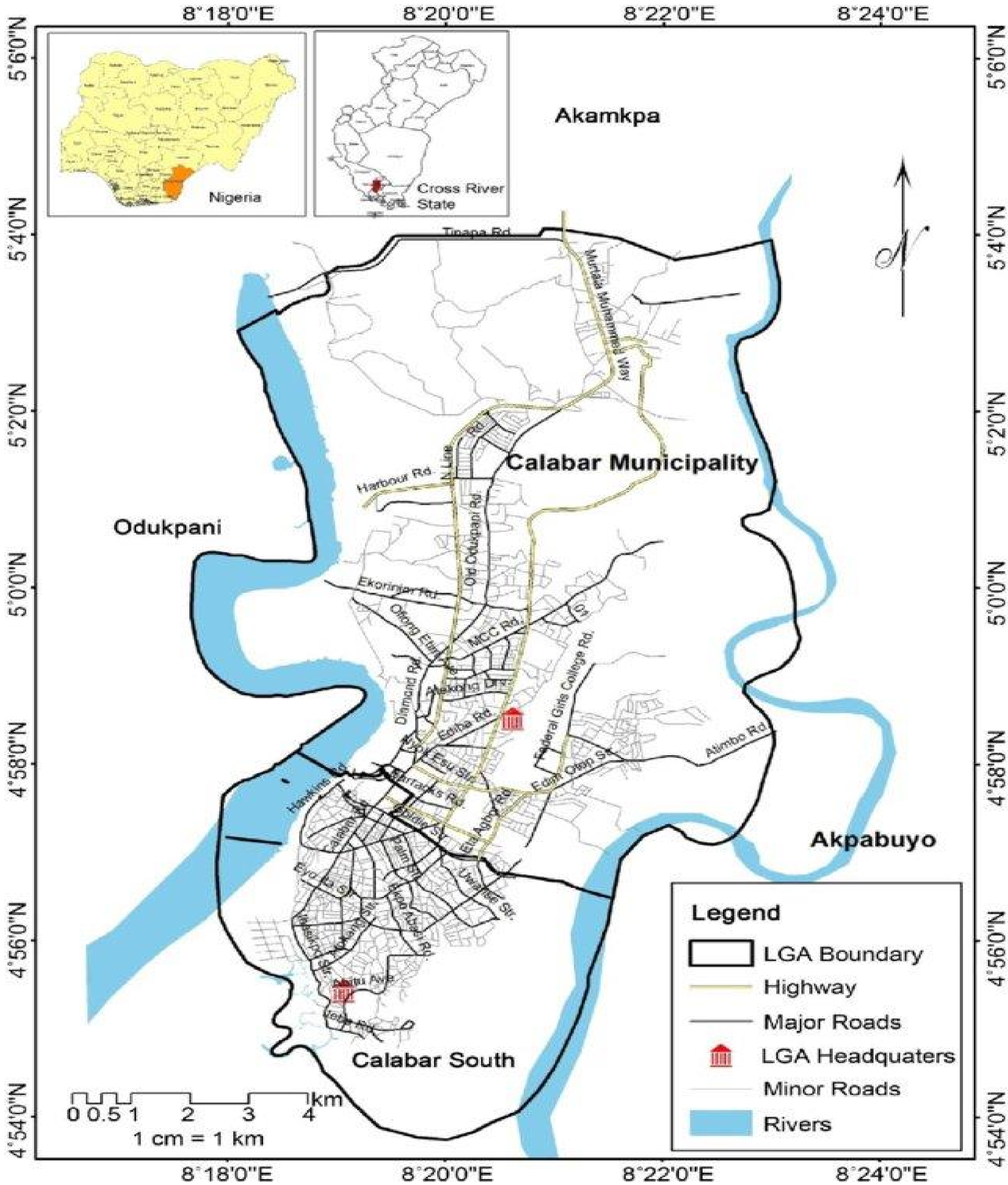

Fig.1. Map of Calabar Metropolis (Calabar south and municipality LGAs). Source: Office of the surveyor general, Cross River (OSG-CR), 2015.

Sample collection: 600ml samples of both bottled and sachet water mostly consider as safe for consumption by residence were collected randomly from the companies and kept in a clean sterile container to avoid contamination and re-labeled to bias by the analyzer. The samples collected were kept at room temperature on reaching the laboratory before the analysis was carried out at Projects Development Institute (PRODA), Federal Ministry of Science and Technology Enugu, Nigeria.

Total dissolved solid (TDS) was estimated by Gravimetric method. TDS was measured using conductivity/TDS meter. The pH of each water sample was determined immediately after receiving the sample at the laboratory using a calibrated pH meter. The color and turbidity of each sample was measured with a digital spectrophotometer. A thermometer was used to measure the water temperature. A calibrated conductivity meter was employed for the determination of the Conductivity of the water samples. Total hardness of the samples was determined by EDTA titrimetric method. Physico-chemical examination was by standard analytical methods. Microbiological examination was done using the Membrane Filtration method.

Results and Discussion

The results obtained were compared with the secondary data gotten from publication of the World Health Organization (2017) guidelines. The physico. chemical, heavy metals and microbiological parameters of the eight branded drinking water for 2018 and 2020 often consider by residence of Calabar Metropolis as the safest for human consumption are presented in Tables 1 and 2, respectively.

Though bottled waters had slightly better water quality than sachet water, there were not significantly ($p>0.05$) different from each other. 2018 and 2020 samples showed that color, odor, total hardness, electrical conductivity, TDS, TSS, turbidity, NO3, chloride and copper were all within the WHO (2017) permissible limits for drinking water for both years. Okwa and Gbadamosi (2017) observed that although the odour, colour and taste of all fifty sampled water in Lagos met WHO standard, only 58% was fit for drinking due to impurities and other parasitic organisms.

BOD and zinc were within the threshold limit in all but sample 4. Pb was higher in all but sample 4, Cr was higher in all except 1 &4, Zn in all was within the accepted limit except 4 while cadmium was only higher in sample 1. In 2020, temperatures for all samples analyzed were above the recommended standard of 25oC set by WHO (2017). Amoo, and Akinbode, (2005) had indicated that toxic metals like Arsenic, Cadmium, mercury and lead when present in drinking water could cause acute or chronic poisoning known to be hazardous to health. Though zinc in sample 4 in 2020 was higher than recommended, but zinc has no known health hazard (WHO, 2017) besides affecting older galvanized plumbing materials which may appear opalescent and develop greasy film on boiling.

The highest mean temperature of (28.67±0.2oC) was recorded in sample 2 while the lowest (26.00±00 oC) was recorded in sample 3. The increase in temperature may be as a result of the ambient temperature of the laboratory during the time of the analysis. Though the temperatures were above the required standards and should have caused increase in microbial load but this was not the case in all the samples that recorded zero microbe expected of good water quality due probably to such being the ambient temperatures obtainable then. More-so, the DO levels did not equally shoot up so high but within the standard limits of 5 mg/l. If the temperatures had shot up by a margin, the DO level would have reduced leading to stress on organisms and if DO is so high, supersaturation may occur and commensurate buildup of microbial load and enhanced corrosion of the pipeline but such wasn't the case. Evidence of the DO not being high is further exemplified by the non-acceleration of the copper level which for both years were within limits. However, the need for dissolved oxygen in water which occurs at ten molecules per millions of waters is inevitable being an important component of natural bodies critical for the maintenance of aquatic life and aesthetic quality of streams and lakes.

In 2018, only water sample two (2) had Alkaline as bicarbonate and temperature outside the expected. Alkaline as bicarbonate not only aid digestion but assist in acid base balance thus lowering the acidity, increases pH and assist in neutralizing bacterial metabolic acids.

In 2020, temp, COD, Arsenic, Lead and Chromium values all exceeding the WHO (2017) recommended standard while electrical conductivity, TSS, turbidity, SO4, No3, PO4, NH4, Mg, Na, K, Zn, Cu, Cr, Pb, Mn, Fe and Ni were all within the WHO (2017) standard. Okorafor, Agbo, Johnson, and Chiorlu, (2012) had the pH, electrical conductivity, calcium, magnesium, nitrate and ammonium of five streams and six borehole waters from Akamkpa and Calabar Municipality within WHO requirements. Chlorine and pH were only within the limit with sample 2 but the rest seven samples were above the set limit. However, WHO (2017) listed 'chlorine and pH among the naturally occurring chemicals for which guideline values are yet to be established since the occur in drinking water at concentrations well below those of health concern'. Onweluzo and Akuagbazie (2010) observed that all 17 branded bottled and sachet water from Nsukka Town in Anambra State, Nigeria were physically and chemically wholesome and met the WHO standards (also adopted by NAFDAC-The National Agency for Food, Drugs Administration and Control). Odiongenyi, Okon, and Enengedi (2015) opined that analytical results of five sachet and bottled water in Uyo, Nigeria when compared with permissible and desirable quality criteria found that all the water samples were fit for consumption if the concentration of ammonium, nitrate, conductivity and the bacteriological quality of the water is improved. This simply implies that they water weren't pure for drinking. Airaodion, et al., (2019) investigated 20 sachet water and five bottled water from Ibadan, Oyo State, Western Nigeria and found 90% meeting up WHO standard for drinking water in terms of physical, chemical and bacteriological parameters though the temperatures were higher than expected but did not promote increased microbial load. In the same vain, Yusuf, Jimoh, Onaolapo and Dabo (2015) got 75% compliance to standards in terms of physico. chemical and microbial burden amongst 21 sachet water from Zaria, Nigeria

Table 1. Result of physico.chemical, heavy metals and microbiological parameters for different bottled and sachet waters from Calabar Metropolis (Calabar, South and Calabar Municipality) in June 2018.

	Units	Sample 2	Sample 5	Sample 6	Sample 7	Sample 8	WHO 2017 standard
pH		6.67±0.01	6.03±0.02	5.89±0.001	5.46±0.2	5.72±0.003	6.5-8.5±0.01
EC	uS/cm	35±.45	76±2.11	82±.15	66±.4	57	900
Chlorine	mg/l	4.55±0.01	9.88±0.25	10.66±0.05	8.58±0.07	7.41±0.2	>0.2- <5
Alkalinity as Bicarbonate	mg/l	4.50±0.01	4.98±0.22	5.09±0.03	5.49±0.01	5.24±0.02	4-10
Total Suspended Solid	mg/l	<0.01±.01	<0.01±.02	<0.01±.02	<0.01±.01	<0.01±.05	<600
Total Dissolved Solid	mg/l	17.85±.55	38.76±.12	41.82±.15	33.66±.76	29.07±.05	5.0
Turbidity	NTU	<0.01±.01	<0.01±.03	<0.01±.05	<0.01±.01	<0.01±.05	< 1 NTU
Chemical oxygen demand	mg/l	7.35±.22	15.96±.11	17.22±.05	13.86±.07	11.97±.012	10
Sulphate	mg/l	0.22±.01	0.46±/05	0.73±.03	1.05±.10	0.66±.15	250
Nitrate	mg/l	0.04±0.05	0.07±0.01	0.13±0.05	0.04±0.05	0.33±0.11	50

Phosphate	mg/l	<0.01±.01	<0.01.02	<0.01.02	0.02±.05	<0.01±.04	5.0
Ammonium nitrogen	mg/l	<0.01±.01	<0.01±.06	<0.01±.03	<0.01±.05	<0.01±.011	35
Calcium	mg/l	0.15±.01	0.31±.05	0.44±.11	0.87±.05	0.19±.05	100-300
Magnesium	mg/l	0.31±0.6	0.66±.10	0.27±.05	0.73±.03	0.63±.05	<100-300
Sodium	mg/l	0.06±.05	0.11±.01	0.04±.01	0.03±.05	0.06±.02	50(200)
Potassium	mg/l	0.41±.11	0.65±.05	0.25±.01	0.18±.07	0.33.02	3000
Zinc	mg/l	<0.01±.05	<0.01±.01	<0.01±.06	<0.01±.01	<0.01±.05	0.1
Copper	mg/l	<0.01±.01	<0.01±.01	<0.01±.04	<0.01±.05	<0.01±.05	0.05-<5
Chromium	mg/l	<0.01±.05	<0.01±.01	<0.01±.05	<0.01±.01	<0.01±.05	0.05
Lead	mg/l	<0.01±.05	<0.01±.01	<0.01±.05	<0.01±.01	<0.01±.02	0.01
Manganese	mg/l	<0.01±.05	<0.01±.01	<0.01±.04	<0.01±.05	<0.01±.03	<0.1
Iron	mg/l	<0.01±.07	<0.01±.01	<0.01±.05	<0.01±.08	<0.01±.01	0.3
Nickel	mg/l	<0.01±.03	<0.01±.06	<0.01±.01	<0.01±/55	<0.01±.05	0.07
Coliform	cfu/ml	0	0	0	0	5	0
E. coli	cfu/ml	0	0	0	0	0	0

Table 2: Result of physico. chemical, heavy metals and microbial composition of different bottled and sachet waters analyze from Calabar Metropolis (Calabar South and Calabar Municipality) 7th August, 2020.

Parameters		**Sample 1**	**Sample 2**	**Sample 3**	**Sample 4**	**WHO 2017 Standard**
color	Pt/co	0.769±0.024	0.719±0.0029	0.778±0.00	0.765±0.0035	<15
Odour		unobjectionable	unobjectionable	unobjectionable	unobjectionable	Unobjection -able
Temperature	°C	27.83±0.20	28.67±0.20	26.00±00	26.67±0.20	25
TDS	Mg/L	10.081±0.074	39.987±0.145	40.086±0.347	20.274±0.365	<600
TSS	Mg/L	619.398±0.315	331.604±176.6	473.409±4.04	536.747±4.055	<600
Total solid	Mg/L	440.41±231.71	215.41±314.28	363.97±191.10	388.45±129	250
EC	µS/CM	63.46±o.563	167.12±1.735	150.77±1.432	22.18±0.471	900
Total hardness		48.004±0.024	100.078±0.077	260.073±136	48.005±	300-600
pH		4.640±0.001	3.892±0.00	6.311±2.323	4.360±0.001	6.5-8.5
COD	Mg/L	60.115±0.768	88.109±0.094	32.755±0.636	Nil	10
BOD	Mg/L	0.805±0.014	2.006±0.013	0.526±0.051	6.387±0.006	2.0-5.0
DO	Mg/L	8.119±0.249	10.965±0.697	7.082±0.049	4.204±0.006	5.0
Sulfate	Mg/L	36.123±0.20	53.142±0.03	55.761±0.72	35.371±0.25	250
Nitrate	Mg/L	0.559±0.09	0.523±0.06	0.541±0.02	0.554±0.10	50
Phosphate	Mg/L	1.981±0.11	2.999±0.07	1.237±0.38	0.961±0.02	5.0
Sodium	Mg/L	0.093±0.002	0.355±0.256	0.135±0.003	0.023±0.001	200
Acidity	Mg/L	1.217±0.03	2.479±0.13	2.001±002	5.013±0.02	
Chloride	Mg/L	22.746±0.66	39.353±0.23	32.692±0.33	14.681±0.16	250
Arsenic	mg/L	10.376±0.902	4.164±0.251	7.216±0.196	7.312±0.163	0.01
Lead	Mg/L	0.181±0.007	0.242±0.001	0.283±0.003	0.012±0.007	0.05
Chromium	Mg/L	0.042±0.015	0.111±0.071	0.153±0.024	0.017±0.028	0.05

Zinc	Mg/L	0.011	0.014±0.002	0.003±0.001	0.218±0.703	0.1
Copper	Mg/L	0.106±0.05	0.015±0.07	0.022±0.08	0.078±0.03	0.05-1.5
Iron	Mg/L	0.048±0.039	0.042±0.001	0.014±0.002	0.036±0.002	0.3
Cadmium	Mg/L	0.137±0.001	nil	Nil	Nil	0.01
Mercury	Mg/L	Nil	nil	Nil	Nil	0.001
Oil/grease	Mg/L	Nil	nil	Nil	0.629±0.004	
Salmonella		0	0	0	O	0
E. coli		0	0	0	0	0
Total coliform		0	0	0	0	0

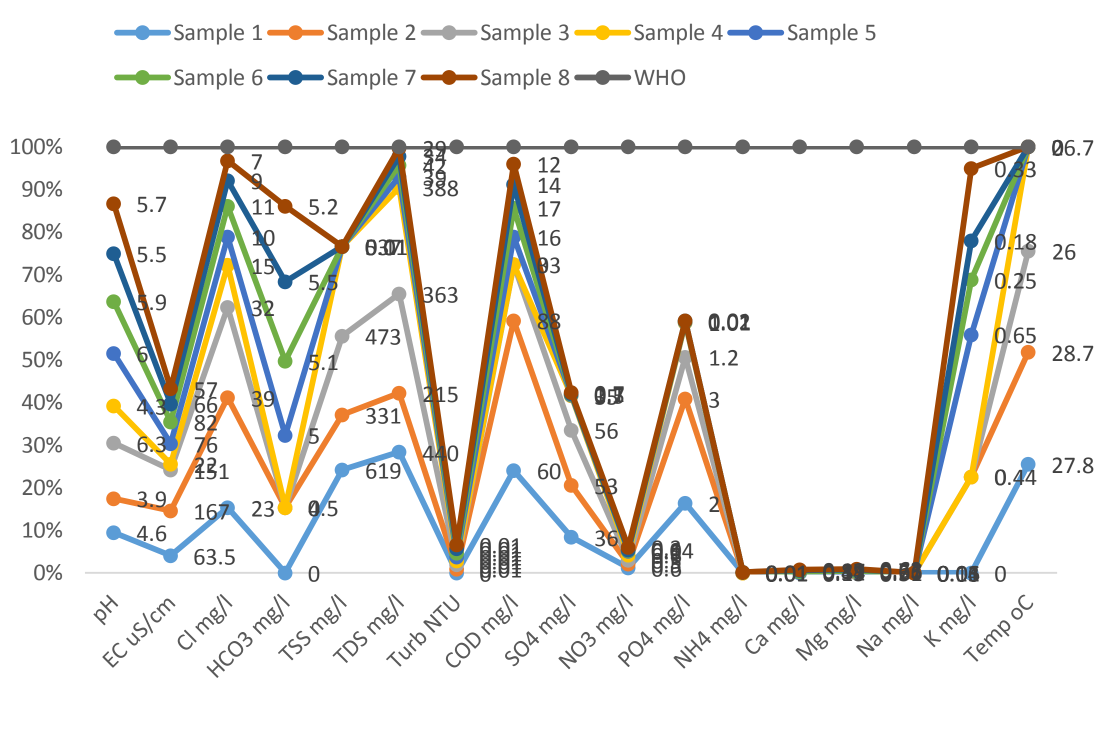

Figure 2. The comparative graph physico.chemical parameters and mineral composition of the eight water samples.

The chemical assessment shown in Tables 1 & 2 and Figure 2 revealed that the pH values of all but one sample (sample two) for both years were found below the recommended value of 6.5-8.5 for culture water. This general trend of low water pH tends towards acidity and are capable of causing gastro-intestinal irritation in sensitive individuals.

Chemical oxygen demand (COD), and dissolve oxygen (DO) for samples 1, 2 and 3 in 2020 were higher than the permissible limits of WHO (2017) while sample 4 had no trace of COD thus meeting the required standard. Similarly, the biological oxygen demand (BOD) for samples 1, 2 and 3 were equally within the threshold but sample 4 exceeded the limit. High BOD known to affect the amount of dissolved (DO) in rivers and streams could lead to stress, suffocation and eventual death. COD is the summation of organic and inorganic chemicals while BOD is the amount of oxygen used by aquatic microbes (aerobic bacteria) to oxidize organic matter. Sample 4 had no trace of COD, therefore falls within the acceptable limit. BOD for samples 1, 2 and 3 with exception of sample 4 with a value of 6.387±0.006, were within the WHO (2017) acceptable limit of 2 - 5 mg/l. Graphical presentation of pH, COD, BOD, and DO is illustrated in (fig. 2).

Nutrient elements such as sulfate, nitrate and phosphate were examined. Sulfate, Nitrate, and phosphate for all samples were within the approved limit of 250 mg/l for sulfate, 50 mg/l for nitrate, and 5.0 mg/l for phosphate. Figure 2 Shows the nutrients- sulfate, nitrate and phosphate compare to acceptable limit of WHO (2017).

Analysed values for all minerals (Sodium, calcium, magnesium, potassium and chloride) of selected bottled and sachet water, fell within the WHO (2017) required standard for drinking water for both years. Figure 2 also show the distribution of mineral elements present in the different water samples.

Heavy metals concentrations of the potable water were as illustrated in Tables 1 & 2. Metals concentrations in the water samples were found in the following order: As > Pb > Cr > Zn > Cu > Fe > Cd > Hg (Table 2) and showed statistically significant different at $P < 0.005$ level. The Hg, Fe, and Cd (fig. 8) levels were lower than/within the permissible limits (Table 2) as recommended by WHO, (1999). They were no trace of Hg in all samples. Cadmium (Cd) except for sample 1 with a value of 0.137±0.001 was also within the permissible limit. Levels of Cu and Zn (fig. 8) were also within the permissible limit recommended by WHO with exception of sample 4 for Zn that had a value of 0.218±0.703 against the 0.1mg/l recommendation by the WHO (2017). Arsenic (As) was relatively higher for all samples with the following values from samples 1 to 4 (10.376±0.902, 4.164±0.251, 7.216±0.196, and 7.312±0.163, respectively). Pb also had high levels in all samples with exception of sample 4 that fell within the approved limit of 0.05mg/l. Samples 2 and 3 have high levels of chromium. In general, the presence of heavy metals in bottled and sachet water samples as mentioned above can have casinogenic effect on consumers. The abundance of toxic chemicals in drinking water may cause adverse effects on human health such as Cancer and Chronic illness (AL-Saleh & Al-Doush, 1998). Chromium, particularly chromium (VI) has been found to be carcinogenic when inhaled. Upon breathing of dust or mists containing chromium (VI) compounds, ulceration and eventual perforation of cartilaginous portions of the nasal septum may ensues.

Microbiological Assessment

The results show that all eight samples analyzed for Salmonella, E. coli and total coli- form count met the WHO (2017) zero mg/l standard for drinking water. This implies that equipment such as filter systems used for water production processes were of good quality. Odiongenyi, Okon, and Enengedi, (2015) observed that all five sachets and bottled water from Uyo fell outside WHO standards in some physico.chemical and bacterial parameters thus making them unfit for drinking. Okorafor, Agbo, Johnson and Chiolu (2012) had only two out of five streams and six borehole waters from Akamkpa and Calabar Municipality's microbial load meeting the WHO standard. Whereas results of fifty samples of sachet water ('Pure water') analysed in Lagos (Okwa & Gbadamosi, 2017) showed that 58% was not pure due to contamination with impurities, parasites and coliforms such as cysts of Entamoeba histolytica (10%), Giardia lamblia (12%), eggs of Ascaris lunbricoides (16%) and Necator americanus (Hookworm) (4%). They concluded that what may be called pure water may end up not being pure. Edema, Atayese and Bankole (2011) while working on 108 sachet-packed water in South-western Nigeria, comprising six states Lagos, Ogun, Oyo, Osun, Ondo and Ekiti states, observed that 87% contained Salmonella and/or Escherichia coli, indicative of fecal contamination and inadequate water treatment or no treatment at all. In a recent study in Ghana looking at enteric pathogenic protozoan organisms in sachet water, 77% of the sample were found to contain infective stage of pathogenic parasitic organisms such as Microsporidia spp, Cryptosporidium parlum, Cyclosporalayetenesis, Sarcocystis spp, etc. (Kwakye-Nuako, et al., 2007). Onweluzo and Akuagbazie (2010) worked on 17 brands of bottled and sachet water from Nsukka town in Anambra State, Nigeria and found the physicochemical parameters within acceptable WHO limits but had 4 brands (24%) containing total viable count above the recommended 1000cfu/ml while 88% had coliform counts above the recommended zero cfu/ml.

Conclusion

This study was carried out to assess the physical, chemical, heavy metals and microbiological properties of bottled and sachet waters in Calabar Metropolis (Calabar South and Calabar Municipality) both of Cross River State, Nigeria. The results from the laboratory analysis showed that none of the eight water samples for both years met all the required standards for drinking water since most of the physical and chemical parameters and heavy metals did not conform to WHO standards.

Though all microbiological parameters were within the WHO standard for potable water, the physico.chemical parameters and heavy metal content were not implying that declaring drinking water pure should be holistic. There were differences in yearly water quality. Though bottled water was relatively safer than sachet water, there was no statistical difference between them. The overall results showed that both the bottled and sachet water produced and sold in the study areas were relatively unsafe for human consumption according to the World Health Organization standards for potable water even though some of the parameters conformed to the standard. No sample met all the requirements for potable drinking water. These findings align to those of the Institute of Public Health Analyst (IPAN) according to Osibanjo, Ajayi, Adebiyi, and Akinyanju (2000), that 50% of the "pure water" sold in the streets of Lagos are not fit for human consumption.

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